Effect of the processing method on the physicochemical and active properties of poly (vinyl alcohol) films incorporating phenolic acids

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Abstract

Poly (vinyl alcohol) films containing cinnamic acid (C) and ferulic acid (F) at 1 wt % and 2 wt % were successfully produced by solvent-casting the polymeric solution and melt blending and compression moulding. The effect of the processing method and the phenolic acid content on the microstructure, crystallinity and the optical, thermal, barrier and mechanical properties of partially hydrolysed poly (vinyl alcohol) based films have been analysed, as well as the antioxidant and antimicrobial properties of the films. The processing method influenced the microstructural arrangement of the matrix, leading to differences in the degree of crystallinity and in the tensile and barrier properties of the films. The incorporation of phenolic acids, especially ferulic acid, enhanced the barrier properties of the materials without affecting their thermal stability. The presence of phenolic acids in the films clearly induced the inhibition of *Listeria innocua* growth and had a positive antioxidant response, thus suggesting the great potential of these active materials for food packaging applications.

Keywords

Cinnamic acid; Ferulic acid; Active films; Cast-films; Thermoprocessed-films; Food packaging.

1. Introduction

Plastic packaging has become an essential part of the food supply chain due to its significant role in the preservation of the quality of the food product until its final consumption (Trabold & Babbitt, 2018). In fact, during the initial stages of the COVID-19 pandemic, consumer preference for packaged food has

skyrocketed, probably due to the increase in online ordering and food delivery, as packaging is a way of offering consumers reassurance (Kakadellis et al., 2021; Vanapalli et al., 2021). However, the increasing pressure on the generation of waste has brought plastic food packaging back into the spotlight amidst growing public concern about the environmental impact of plastic pollution (Kakadellis et al., 2021).

A great deal of research has successfully reported the development of biodegradable polymer-based materials that constitute an alternative for the progressive replacement of synthetic plastics (Brockhaus et al., 2016; RameshKumar et al., 2020). Pol (vinyl alcohol) (PVA) is a semi-crystalline, water-soluble and biodegradable polymer that has a high degree of biocompatibility, while being capable of self-crosslinking due to the high density of hydroxyl groups located on its side chains (Havstad, 2020). PVA is easily produced by the saponification of poly (vinyl acetate), a process that allows the molecular weight and the degree of hydrolysis to be controlled and, consequently, permits the development of materials with differing degrees of crystallinity, solubility in water and tensile, barrier and thermal properties (Andrade et al., 2020b). The molecular characteristics provide PVA with a marked affinity for several active compounds (Andrade et al., 2020b; Cano et al., 2015), which, when effectively incorporated into the polymeric matrix, could enable the development of active packaging materials. Active packaging systems are characterised by interacting dynamically with the target intrinsic and/or extrinsic factors of the packaged product, whose action enhances the protective function of the package (Lim, 2015). Additionally, the partially hydrolysed PVA could be thermo-processed due to the thermo-protective action of the residual acetate groups in the polymer chain, providing flexibility in the type of processing used for the development of PVA-based materials (Andrade et al., 2020b).

The processing conditions may result in modifications of the structural arrangement, especially of the crystalline fraction of semi-crystalline polymers, which are relevant in view of their effect on the density and the mechanical and optical performance of the final product, as well as, to a lesser extent, on its physical aging and long-term stability (Mileva et al., 2018). The processing factors that are the major influencers on the characteristics of the material are the thermal history, pressure and flow phenomena. Depending on the polymer structure

(molecular weight and polydispersity), the effect of the processing conditions, such as the increase in cooling rate, can range from simple reductions in crystallinity to the formation of a completely amorphous structure, nearly always involving changes in tensile and optical properties. The effects of flow and pressure, especially important in the injection moulding process, generally modify nucleation, crystal growth and orientation, with a clear correlation with stiffness and elongation at break, the effect of which is dominated by the stress applied to the material (Mileva et al., 2013). Thus, the different processing methods and their inherent conditions lead to the development of materials with specific final characteristics, which could determine their application. These changes that films may undergo could also affect their functionality when incorporating active agents, especially when using phenolic compounds, such as phenolic acids (PA), capable of interacting with the hydroxyl and acetate groups of the PVA matrix (Lan et al., 2019). Of the phenolic acids, cinnamic and ferulic acids are of increasing potential interest because of their proven antioxidant and antimicrobial properties (Lima et al., 2019; Mathew & Abraham, 2008; Olszewska et al., 2020).

This study aims to evaluate the impact of two types of film processing, casting and thermo-processing (melt blending and compression moulding), on the crystallinity and the mechanical and barrier characteristics of partially hydrolysed PVA films, containing or not cinnamic and ferulic acids as active agents. To our knowledge, these analyses have not yet been addressed and are of great interest due to the importance of developing new biodegradable active materials for safe and sustainable food packaging.

2. Materials and methods

2.1. Materials

Partially hydrolysed poly (vinyl alcohol) (P) (Mw 13,000–23,000; 87–89% hydrolysed), glycerol as plasticizer and phenolic acids (PA), cinnamic (C) and ferulic (F) acid, were purchased from Sigma-Aldrich (Steinheim, Germany). Magnesium nitrate ($Mg(NO_3)_2$), phosphorus pentoxide (P_2O_5) salts, UV-grade methanol and UV-grade ethanol were supplied by Panreac Química S.A. (Barcelona, Spain).

2.2. Preparation of films

Two processing methods, casting (C) of the polymeric aqueous solutions and melt blending and compression moulding (T), were used to obtain the poly (vinyl alcohol) films.

To cast films, glycerol (10% wt. with respect to the polymer) and phenolic acids (1% or 2% wt. with respect to the polymer) were added to distilled water previously heated to 100 °C. After the dissolution of the acids, the polymer (10% wt.) was incorporated by stirring (1,200 rpm) and heating (100 °C) for 3 h, until polymer solutions were obtained. Subsequently, all the formulations were degassed by using a vacuum pump and the solution (equivalent amount to 2 g of polymer per plate) was subsequently spread evenly onto Teflon plates (150 mm in diameter). The films were then obtained by drying at controlled temperature (25 ± 2 °C) and relative humidity (55 ± 2%) for 48 h.

Thermoprocessed-films were obtained by the compression-moulding of pellets using a hot plate-press (Model LP20, Labtech Engineering, Thailand). Pellets were obtained by melt blending the different components by using an internal mixer (HAAKE™ PolyLab™ QC, Thermo Fisher Scientific, Germany) at 160 °C and 50 rpm, for 10 min. In every case, 10 wt% of glycerol was used with respect to PVA and the PA was added to the mixture at 1 or 2 g/100 g polymer. The pellets were cold-milled in a Universal Mill (IKA, model M20, Germany) and the preconditioned particles (at 53% RH and 25ºC) were compression moulded with a preheating step for 3 min at 160 °C, followed by 3 min thermocompression at 100 bars. Thereafter, a 3 min cooling cycle was applied. Plasticised films without PA were used as controls. The different film formulations and the mass ratio of the respective components are shown in **Table 1**.

Cast and thermoprocessed films were conditioned for one week at 25ºC and 53% relative humidity (RH) by using $Mg(NO_3)_2$ over-saturated solution before the characterisation of their functional properties. Films were conditioned at 0% RH, using P_2O_5, for the analyses of the final PA content in the film, water solubility, microstructure and thermal behaviour.

2.3. Characterisation of the active PVA films

2.3.1. Final content of phenolic acids, moisture content and water solubility of the

films

The final content of the phenolic acids (PA) was determined by solvent extraction and spectrophotometric quantification. The PA extraction was carried out by immersing dry samples (25 mg) in 10 mL of a 50% methanol aqueous solution under stirring at 300 rpm for 48 h. The absorbance (*A*) of the solutions was measured at wavelengths of 320 nm for ferulic acid (F) and 270 nm for cinnamic acid (C), using a spectrophotometer (Evolution 201 UV–Vis, Thermo Fisher Scientific, USA). The PA concentration (C_{PA}) was obtained using the calibration curve of each acid: ferulic acid ($C_{PA} = (A - 0.005)/0.0852, R^2 = 0.995$) and cinnamic acid ($C_{PA} = (A - 0.02)/0.1372\,, R^2 = 0.992$). The corresponding extracts from the PA-free films were used as backgrounds. The mass of extracted PA (mg) was compared to the corresponding mass of initially incorporated PA and the percentage of retention was determined. The measurements were taken in triplicate.

The moisture content of the previously conditioned films (53% RH; 25 °C) was analysed gravimetrically. Four weighed samples per treatment were dried in a convection oven (JP Selecta S.A., Barcelona, Spain) at 60 °C for 24 h; subsequently, these were equilibrated (0% RH;25 °C) until constant weight.

The water solubility was evaluated by a modification of the method described by Talón, Vargas, Chiralt, & González-Martínez (2019). Dry film samples (2 cm x 2 cm) inside a mesh, were weighed and placed in a crucible with 10 mL of distilled water for 24 h at 25 °C. The meshes with the remaining film sample were dried in an oven (J.P. Selecta, S.A., Barcelona, Spain) at 60 °C for 72 h and, subsequently, were transferred to a desiccator with P_2O_5 until reaching constant weight. The assay was performed in triplicate and the results were expressed as g of solubilised film/100 g initial film.

2.3.2. Microstructure and X-ray diffraction analysis

The microstructure of the cross-section films was observed using a Field Emission Scanning Electron Microscope (FESEM) (ZEISS®, model ULTRA 55, Germany), at an acceleration voltage of 2 kV. Previously, the film samples were cryofractured by immersion in liquid nitrogen and platinum coated.

The degree of crystallinity was analysed through the X-ray diffraction spectra of the films by means of a D8 Advance X-ray diffractometer (Bruker AXS, Karlsruhe, Germany). The range 2θ of evaluation was from 10° to 50°, with a step size of 0.05, using KαCu radiation (λ: 1.542 Å), 40 kV and 40.mA. The diffraction curves were deconvoluted by using the Lorentz model with the OriginPro 2021 software to define the crystalline and amorphous regions. The ratio of the crystalline peak area and the total area of the diffractograms defined the degree of crystallinity of the samples.

2.3.3. Optical properties

The optical properties were determined by measuring the reflectance spectra of the samples from 400 to 700 nm of wavelength using a spectrocolorimeter (CM-3600d Minolta CO., Tokyo, Japan), using both black and white backgrounds, following the method reported by (Sapper et al., 2018). The transparency was measured through the internal transmittance (Ti), applying the Kubelka-Munk theory for multiple scattering. CIE L*a*b* colour coordinates and chromatic parameters (chroma and hue) were obtained from the reflectance of an infinitely thick layer of the material by considering D65 illuminant and 10º observer, according to Hutchings (1999). Three measurements were taken from each film and three films were considered per formulation.

2.3.4. FTIR characterisation

The attenuated total reflection Fourier transformed infrared spectra (ATR-FTIR) (BRUKE, VERTEX 80, Germany), over the range 4000-600cm^{-1}, were analysed for the different samples. These analyses were carried out in triplicate and at three different locations in each sample.

2.3.5. Tensile properties and barrier properties

The tensile properties of the films were measured using a Universal Machine (Stable Micro Systems, TA.XT plus, Haslemere, England). Equilibrated test specimens (25 mm x 100 mm) were mounted in the film extension grips with an initial separation of 50 mm and stretched at 50 $mm.min^{-1}$ until break, following the standard method ASTM D882-02 (ASTM, 2002). Elastic modulus (EM),

tensile strength (TS), and elongation at break point (E) were determined from the tensile stress (σ) vs. Hencky strain (εH) curves. The measurements were taken in eight samples of each treatment.

The water vapour permeability (WVP) was analysed in triplicate following a standard method, E96/E95M-05 (E. ASTM, 2003). In order to obtain a RH gradient of 53 to 100%, the samples were placed on Payne permeability cups (3.5 cm in diameter) (Elcometer SPRL, Hermelle/s Argentau, Belgium) containing 5 mL of distilled water, which were placed inside a desiccator at 25 °C with an oversaturated $Mg(NO_3)_2$ solution. The cups were weighed periodically every 1.5 h for 24 h using an analytical balance (0.00001 g). The slopes of the weight loss *vs.* time during the steady state period were determined by linear regression to calculate the water vapour transmission rate (WVTR). WVP was calculated as described by Cano, Jiménez, Cháfer, Gónzalez, & Chiralt (2014).

The oxygen permeability (OP) in film samples (50 cm^2) was analysed in triplicate using an Ox-Tran system (Mocon, Minneapolis, US) at 23 °C and 53% RH, following a standard method, F1927-07 (F.-07 ASTM, 2004). The OP was calculated from the oxygen transmission rate multiplied by the average film thickness and divided by the partial pressure of oxygen. The film thickness was measured with a digital electronic micrometer (Palmer, COMECTA, Barcelona, Spain) to the nearest 0.001 mm at six random positions.

2.3.6. Thermal behaviour

The thermal behaviour of the films was assessed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). For DSC measurements, the sample was inserted into a hermetically-closed aluminium pan and placed in a differential scanning calorimeter (DSC 1 stareSystem, Mettler Toledo, Schwarzenbach, Switzerland), with an empty aluminium pan used as a reference. The temperature scanning profile was a first heating step from -25 °C to 250 °C, holding this temperature for 2 min, followed by a cooling to -25 °C, holding this temperature for 2 min and a second heating step to 250 °C; all of the scans were run at 10 C/min. For TGA analysis purposes, the samples were heated in alumina crucibles from 25 °C to 700 °C at 10 °C /min, by using a thermogravimetric analyser (TGA/SDTA 851e, Mettler Toledo, Schwarzenbach,

Switzerland). All of the measurements were taken in triplicate using nitrogen (10 mL/min) as purge gas.

2.3.7. Antioxidant activity

The antioxidant capacity of the PVA films was evaluated in terms of the radical scavenging capacity of the ferulic and cinnamic acids released from the films into different food simulants. The simulants used were ethanol at 50% (v / v) in water, as a food simulant of an alcoholic beverage or o/w emulsions, and ethanol at 95% (v / v), as a simulant of more fatty foods. The DPPH method was used, as proposed by Aragón-Gutiérrez et al. (2021), with some modifications. A film sample of each formulation (50 mg) was immersed in 10 mL of the simulant and kept under constant stirring (300 rpm) at 20 ° C, for 48 h. Afterwards, filtered aliquots of 500 µL of each extract were mixed with 2 mL of a 0.06 mM DPPH solution in methanol (Abs 515nm = 0.7 ± 0.2) in a closed cuvette, which was kept in the dark at room temperature for 60 min. The absorbance was measured at 515 nm by using a spectrophotometer (Evolution 201 UV-Vis, Thermo Fisher Scientific, USA). The ethanolic extracts of the films without phenolic acids were used as a control. All of the tests were carried out in triplicate and the DPPH radical scavenging activity was expressed as % according to Equation (1)

$$Scavenging\ of\ DPPH\ (\%) = \frac{A_C - A_S}{A_C} x100 \quad (1)$$

Where A_C and A_S are the absorbance of the black control and the tested sample, respectively.

2.3.8. Antimicrobial activity

The antimicrobial activity of the active PVA films was evaluated by means of the agar diffusion method with slight modifications (Brito et al., 2021) against *Escherichia coli* (CECT 515), Gram (+), and *Listeria innocua* (CECT 910), Gram (−), obtained from Spanish Type Culture Collection (CECT, Burjassot, Spain). The bacterial strains, stored under protective conditions (glycerol 30%) at -25 °C, were regenerated as described by Valencia-Sullca et al. (2016), by incubating

them at 37 °C for 24 h in tryptic soy broth (TSB) (Scharlab, S.L., Barcelona, Spain) and harvested in their exponential growth phase. The active cultures were properly diluted in tryptone phosphate water (Sharlab S.A., Barcelona, Spain) to obtain a target inoculum of 10^5 colony-forming units (CFU)/ml.

The films were cut into discs (10 mm in diameter) and sterilised under UV light before the antimicrobial tests. Circular samples were carefully placed on the inoculated plates with 1 mL inoculum. Culture media in the plates were 10 mL of violet red bile agar (VRBA) (Scharlab, S.L., Barcelona, Spain) for *E. coli* and palcam agar base (PAB) (Scharlab, S.L., Barcelona, Spain), enriched with palcam selective supplement, for *L. innocua* (Scharlab, S.L., Barcelona, Spain). The petri dishes were then incubated at 10 °C for 7 days in the incubation chamber. The plates were examined to measure the halo of inhibition of the film discs. Five replicates were carried out for each film.

3. Results and Discussion

3.1. Phenolic acid and moisture content in the films, and their water solubility

The final phenolic acid content (PA) in the films is shown in Table 1. In every case, the remaining amount of PA was lower than that initially incorporated. The retention percentage ranged between 90-77% for cast films and 72-20% for thermoprocessed samples. The losses were higher for films containing ferulic acid, especially in thermoprocessed films. Therefore, the losses of active compound depended on the type of phenolic acid and the type of film processing. The combined effect of high temperature, shearing stress and pressure conditions given in thermo-processing provoked significantly greater reductions in the final PA concentration of the thermoprocessed films than those obtained in cast-films. Cinnamic acid (C) has greater thermal stability than ferulic acid (F), which could explain its greater retention in the films. However, the onset temperature of degradation (230 °C for cinnamic acid and 210 °C for ferulic acid) of both acids is higher than that applied during melt blending (160 °C) or compression moulding. Therefore, the losses could not be principally attributed to compound degradation brought about by thermal effect, but rather to the fact that their antioxidant nature causes oxidative degradation, under the process

conditions. In fact, the UV spectra of the compounds extracted from films for their spectrophotometric analyses revealed changes in the UV spectral pattern with respect to the standard compounds in the case of ferulic acid (**Annex 1**) that had a greater antioxidant capacity (Li et al., 2021). These changes must be associated with the presence of modified molecular structures produced by the partial oxidation of the active. (Aragón-Gutiérrez et al., 2021) also reported 30% losses of ferulic acid in EVOH films obtained by melt extrusion at 190 °C, but with a shorter residence time (3 min). Oxidative processes will also be affected by the exposure time of the material to the processing conditions. A reduction of 40% in the case of ferulic acid and 5% in that of cinnamic acid were also observed for in starch films obtained by thermo-processing at 130 °C (Ordoñez et al., 2021).

Table 1. Nominal mass fraction of the film components and final content of cinnamic (C) or ferulic (F) acids at 1 or 2%. The ratio between the determined final content and the incorporated amount of phenolic acid (% retention), the equilibrium moisture content and the water solubility (% of solubilised solids) were also shown for films obtained by casting (C subscript) and thermo-processing (T subscript). Mean values and standard deviation in brackets.

Sample	X_{PVA}	X_{GLy}	X_{PA}	Final PA content in the films		Equilibrium Moisture Content (%)	Water solubility (%)
				mg PA/g PVA	Retention (%)		
P_C	0.91	0.09	0	-	-	6.0 (0.1) ^{d,2}	80 (6) ^{a,2}
$PC1_C$	0.9	0.09	0.01	9.1 (0.16)	90.8 (0.6) ^{c,2}	5.7 (0.2) ^{bc,2}	75 (3) ^{a,1}
$PC2_C$	0.89	0.09	0.02	17.2 (0.8)	86.0 (4.0) ^{b,2}	5.5 (0.2) ^{ab,2}	82 (5) ^{ab,1}
$PF1_C$	0.9	0.09	0.01	7.8 (0.3)	78.0 (3.0) ^{a,2}	5.5 (0.1) ^{a,1}	74 (1) ^{a,1}
$PF2_C$	0.89	0.09	0.02	15.4 (0.1)	77.0 (0.3) ^{a,2}	5.9 (0.1) ^{cd,2}	90 (1) ^{b,1}
P_T	0.91	0.09	0	-	-	5.8 (0.5) ^{b,1}	68 (3) ^{a,1}
$PC1_T$	0.9	0.09	0.01	8.32 (0,03)	83.0 (0,3) ^{d,1}	5.3 (0,0) ^{a,1}	72 (3) ^{ab,1}
$PC2_T$	0.89	0.09	0.02	14,4 (0,5)	72.0 (3.0) ^{c,1}	5.2 (0.1) ^{a,1}	85 (1) ^{c,1}
$PF1_T$	0.9	0.09	0.01	1,99 (0,04)	19.9 (0.4) ^{a,1}	5.4 (0.0) ^{a,1}	83 (7) ^{c,1}
$PF2_T$	0.89	0.09	0.02	5,5 (0,2)	27.0 (1.0) ^{b,1}	5.3 (0.0) ^{a,1}	81 (9) ^{bc,1}

Different superscript letters indicate significant differences between formulations within the same processing method, while different numbers indicate significant differences between formulations with equivalent mass fractions but processed by different methods ($p < 0.05$).

*(Single 2-columns)

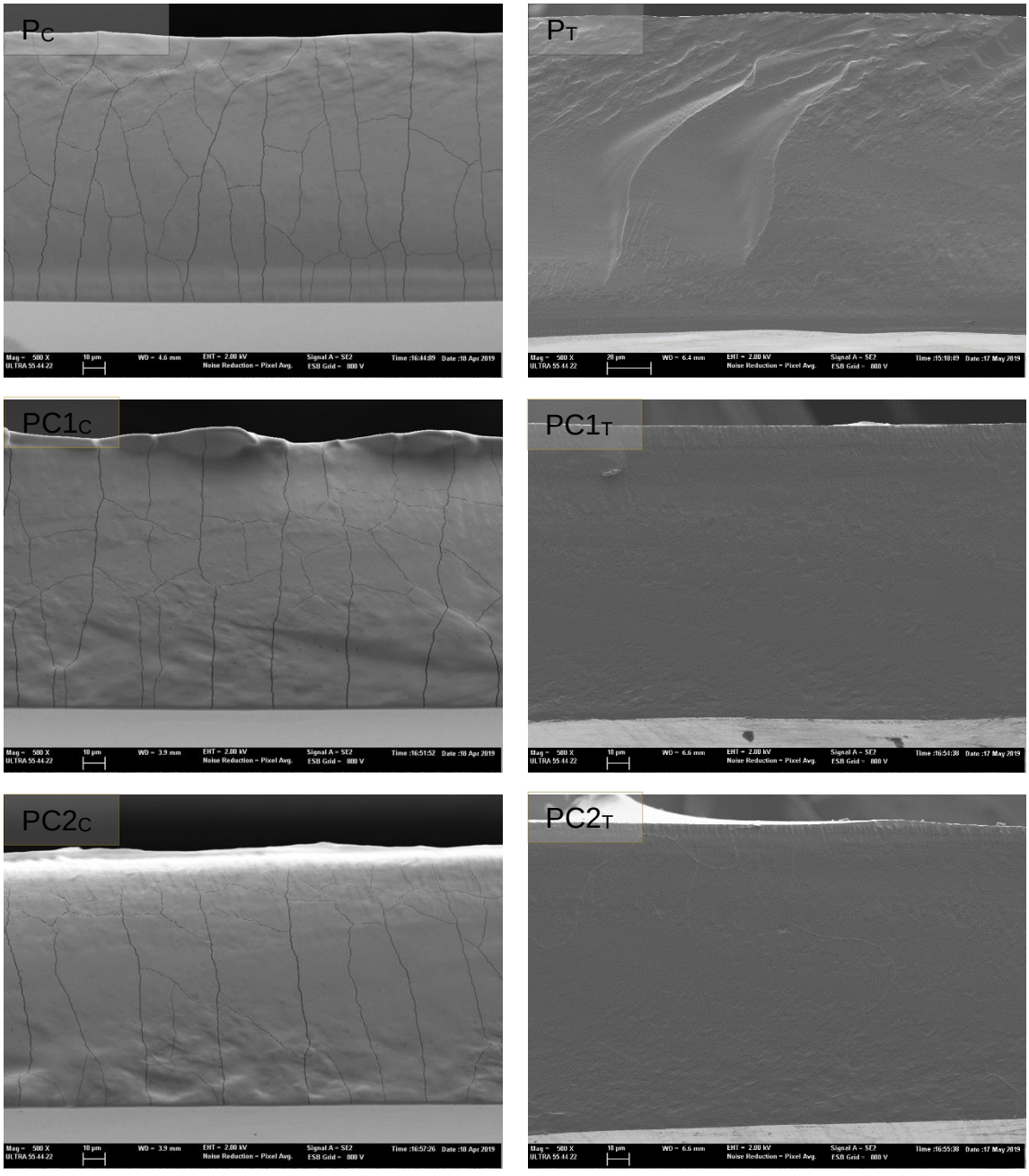
The equilibrium moisture of PVA films was affected by the PA incorporation, which reduced the water sorption capacity in both cast and thermoprocessed films. This may be due to the formation of hydrogen bonds between the OH groups of the polymer chains and the carboxyl or phenolic groups of PA, which should reduce the number of active points of the PVA chains for bonding water molecules (Hernández-García et al., 2021). In general, thermoprocessed films exhibited slightly lower values of moisture content than cast films, which could be attributed to the different chain rearrangement obtained in each case and the different interchain bond established, which can modify the active points of the matrix to bond water molecules.

As regards the water solubility values, films without phenolic acids obtained by casting (Pc) presented significantly higher solubility values (80%) than thermoprocessed films (Pt) (68%). However, the incorporation of phenolic acids promoted changes in the water solubility of the films, but these were only significant in thermoprocessed films. This could be due to the partial hydrolysis induced in the polymer chains by phenolic acids at the high processing temperature.

3.2. Microstructure and crystallinity of the films.

The PVA films obtained both by casting and by thermo-processing presented a smooth and homogeneous appearance, as observed in **Figure 1**. The incorporation of PA did not generate marked modifications in the structure of the film matrix, which suggests that the acids presented a chemical affinity with the polymeric matrix. Nevertheless, at higher magnification, different structural features could be observed for films with phenolic acids, as shown in **Figure 1** for ferulic acid. Thermoprocessed films exhibited some domains with a rubbery cryofracture (image of higher magnification in Figure 1), which suggests the presence of highly plasticised regions in the film. Likewise, few dispersed acid particles of approximately 200 nm were observed in all the cast films (image of higher magnification in Figure 1). This could be attributed to the local aggregation/precipitation of PA molecules during film drying, caused by oversaturation in the polymeric solution in line with water loss. This local oversaturation of acids at high temperatures (thermoprocessing) could promote

partial hydrolyses at some points of the PVA matrix, thus provoking local plasticised regions with the observed rubbery fracture.



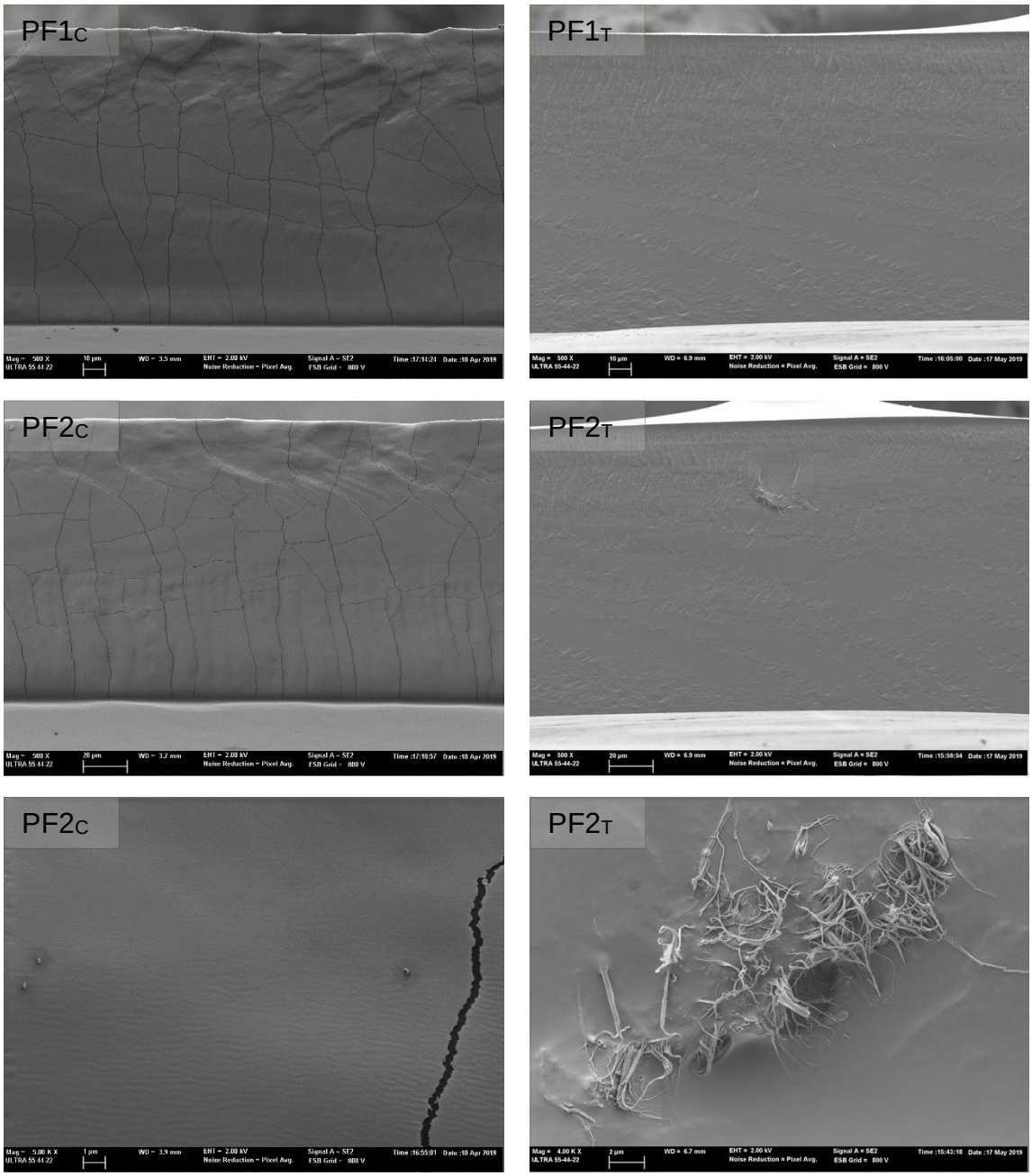


Figure 1. Field Emission Scanning Electron Microscope (FESEM) micrographs of the cross-section of the PVA (P) films with cinnamic (C) or ferulic (F) acid (1 or 2 g/100 g PVA) obtained by casting (C) or thermo-processing (T) (500X). Micrographs at higher magnification (4k-5k X) were included for films with 2% ferulic acid.

Figure 2 shows the XRD pattern and the degree of crystallinity of the PVA samples. As can be observed, the thermoprocessed and cast films presented differentiated patterns, both corresponding to the characteristic XRD pattern of

the PVA monoclinic cell. The diffraction peaks of the thermoprocessed films were sharper, allowing for the identification of a greater number of peaks: the two main peaks (a doublet at 2θ = 19.5°/20° and the second at 40.4°) and other peaks with less intensity at 11.5 ° and 32.8 °, as well as a shoulder that protrudes from the main peak at 22.8 °. In contrast, only two main peaks were observed (at 2θ 20° and 40.4°) in the diffraction trace of the cast films. Therefore, the degree of crystallinity of the active-free PVA films obtained by thermoprocessing was greater (35%) than that obtained by casting (26%). These results are coherent with what was reported by Di Vona (2015), who stated that the processing conditions of semicrystalline polymers affect the crystal structure, the degree of crystallinity, the perfection of the crystals and the orientation of both the crystalline and amorphous phases in the films. Assender & Windle (1998) also claimed that the intensity of the peaks depends on the orientation of the hydrogen bonds, both intermolecular and intramolecular, found within a crystalline lattice. Therefore, it can be concluded that the PVA film processing method influenced the orientation of the hydrogen bonds in the crystalline unit cell, giving rise to different diffraction traces of the films and crystallinity.

The incorporation of phenolic acids also promoted some changes in the XRD patterns and in the degree of crystallinity of the films. Whereas this incorporation, enhanced the film crystallinity in cast films, this did not occur in thermoprocessed films. For both kinds of films, the addition of ferulic acid implied greater crystallinity than that of cinnamic acid. In thermoprocessed films, the incorporation of ferulic acid enhanced the sharpness of the diffraction peaks, which is mainly visible in the 19.5°/ 20° doublet; in cast films, however, the highest concentration of ferulic acid gave rise to an additional peak at 17.2°, also reported as characteristic of PVA crystallisation. The p-hydroxyl group in ferulic acid could promote the interchain bonds, affecting the orientation of the hydrogen bonds inside the unit cell.

Therefore, thermoprocessing and the incorporation of ferulic acid promoted the crystallisation of PVA; thermal treatment in the presence of phenolic acids, however, generally implied a reduction in crystallinity, probably due to the occurrence of partial hydrolyses in the PVA chains that affect the overall chain interactions in the matrix and the plasticisation of local regions where acids could become oversaturated, as observed in FESEM images.

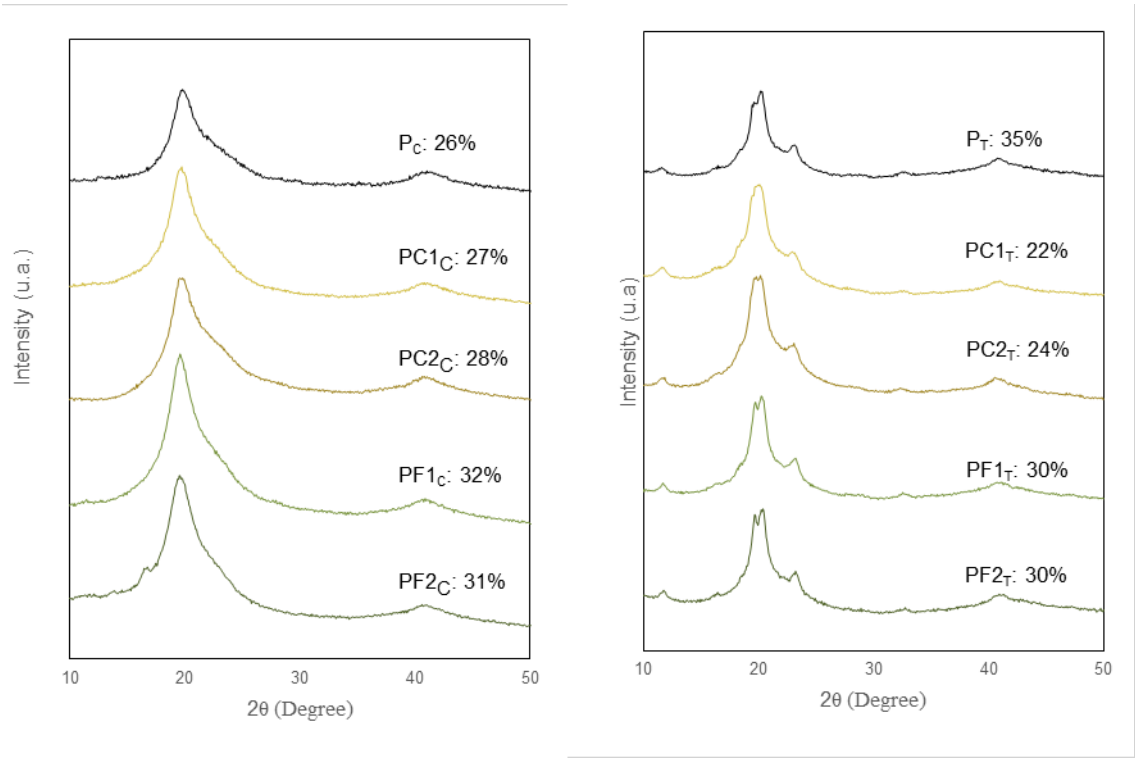


Figure 2. X-Ray diffraction spectra and percentage of crystallinity (%) of the cast (left) and thermo-processed (right) films with and without cinnamic (C) or ferulic (F) acid at different concentrations (1 or 2 g/100 g PVA).

*(Single column/Colour should be used)

3.3. FTIR characterisation

The FTIR spectra of the active-free PVA films and those containing phenolic acids are shown in **Annex 2**. The spectra of the films show the typical PVA bands, without being affected by the type of processing; a broad peak at 3270 cm^{-1} associated with intermolecular hydrogen bonding and hydroxyl stretching vibration (O-H) and consecutive peaks at 2930 cm^{-1} and 2900 cm^{-1} due to asymmetric and symmetric stretching vibrations. Peaks at 1410 cm^{-1}, 1310 cm^{-1}, 1080 cm^{-1} and 825 cm^{-1} are related to CH_2 bending, carbon skeleton movement (C-H), C-O and C-C stretching, respectively. The presence of residual acetate groups in the polymer chain is represented by peaks at 1737 cm^{-1}, 1706 cm^{-1}, 1365 cm^{-1} and 1250 cm^{-1} associated with the stretching vibration bands of the carbonyl and acetyl groups. The typical peaks of cinnamic acid (Chandran et al., 2006; Nolasco et al., 2009) and ferulic acid (Aarabi et al., 2016) were not detected

in the FTIR spectra of the films containing these compounds, probably due to their low concentration in the matrices and the overlapping with the PVA peaks. Similar results were found by (Aragón-Gutiérrez et al., 2021) for EVOH films incorporating 0.25 and 1% (w/w) of ferulic acid.

3.4. Tensile properties

The thickness values and tensile and barrier properties of the films are shown in **Table 2**. The compression-moulded films were significantly thicker ($p<0.05$) than the cast films due to the higher surface solid density (2 and 4 g polymer per film, respectively, for cast and thermoprocessed films). The incorporation of PA reduced the film thickness in thermoprocessed samples, which may be attributed to the higher degree of flowability of the material during the thermocompression. This increase in the flowability might be due to the partial hydrolyses in PVA chains and the subsequent local plasticisation, as commented on in FESEM analyses. The tensile strength and elongation at break and stiffness of the PVA films were also influenced ($p<0.05$) by the method used to process the material. Thus, thermoprocessing generated 30% stiffer films, whereas the solvent-casting process promulgated the development of materials that were highly stretchable (E) and resistant to break (TS), and whose values almost doubled those obtained by their thermoprocessed peers. The greater stiffness of thermoprocessed films is coherent with their greater degree of crystallinity. In contrast, in the cast films, the polymer chains can unfold and orient themselves throughout the drying step, thus giving rise to a network with more oriented chains, which enhanced chain slippage during film stretching, favouring the film extensibility and, subsequently, the resistance to break. During melt blending and compression moulding, the greater viscosity of the melt limited the opportunities for the polymer chain orientation, thus promoting the development of less stretchable, more brittle matrices. So, the two film-processing methods generated materials with different molecular arrangements and degrees of crystallinity that would present different degrees of impediment in the sliding of the molecular chains, giving rise to materials of varying stiffness, elongation and resistance. Moreover, differences in the thickness and moisture contents of the films will also affect their tensile behaviour.

453 The incorporation of PA did not significantly affect ($p>0.05$) the elongation at
454 break of the films. However, changes in the stiffness and mechanical resistance
455 were observed, depending on the processing method. In cast films, PA increased
456 stiffness and strength of the films, while the opposite behaviour was observed in
457 thermoprocessed films probably due to the above-mentioned effect of
458 hydrolyses. The established polymer-PA interactions (interchain bonds through
459 the chain hydroxyls and carboxyl and phenol groups) seem to enhance the load
460 mechanical parameters (TA, EM) in cast films, although this effect overlapped
461 with the potential effect of hydrolyses in thermoprocessed films, giving rise to
462 weakened matrices. In every case, ferulic acid promoted the film elastic modulus
463 and resistance to break to a greater extent, regardless of its concentration, while
464 cinnamic acid only provoked a significant effect when incorporated at the highest
465 concentration. This greater effect of ferulic could be attributed to its specific
466 molecular structure, with a p-hydroxyl group, that better allows for interchain
467 bonds and the crosslinking effect.
468
469 **Table 2.** Thickness, tensile strength (TS), elongation at break (E%) and elastic
470 modulus (EM), water vapour permeability (WVP) and oxygen permeability (OP)
471 of the PVA (P) films without and with cinnamic C and ferulic F acids (1 or 2 g/100
472 g PVA) obtained by casting (C) or thermo-processing (T). Mean values and
473 standard deviation.

Sample	Thickness (μm)	Tensile strength TS (MPa)	Elongation E (%)	Elastic modulus (MPa)	WVP (g mm/m^2.h. kPa) ·	OP (cm^3/m.h. kPa) · 10^8
P_C	104 (7) ^{a,1}	47 (9) ^{a,2}	111 (9) ^{a,2}	49 (3) ^{a,1}	8.2 (0.7) ^{b,1}	13.0 (2.0) ^{b,1}
$PC1_C$	118 (6) ^{b,1}	47 (12) ^{a,2}	107 (8) ^{a,2}	52 (3) ^{ab,1}	7.0 (.02) ^{ab,1}	12.0 (1.0) ^{ab,1}
$PC2_C$	124 (4) ^{b,1}	44 (10) ^{a,2}	107 (8) ^{a,2}	53 (4) ^{bc,1}	8.0 (0.5) ^{b,1}	11.8 (0.4) ^{ab,1}
$PF1_C$	105 (8) ^{a,1}	53 (6) ^{ab,2}	111 (4) ^{a,2}	56 (5) ^{c,1}	6.5 (0.5) ^{ab,1}	10.0 (0.9) ^{a,1}
$PF2_C$	103 (11) ^{a,1}	58 (6) ^{b,2}	109 (6) ^{a,2}	57 (4) ^{c,1}	6.5 (0.2) ^{a,1}	11.3 (1.1) ^{ab,1}
P_T	204 (17) ^{b,2}	25 (2) ^{b,1}	58 (7) ^{ab,1}	68 (4) ^{c,2}	11.4 (0.8) ^{b,2}	30 (4) ^{c,2}
$PC1_T$	189 (14) ^{ab,2}	23 (3) ^{ab,1}	55 (11) ^{a,1}	63 (2) ^{b,2}	10.5 (0.3) ^{ab,2}	24 (1) ^{b,2}
$PC2_T$	186 (8) ^{a,2}	20 (2) ^{a,1}	57 (4) ^{ab,1}	55 (7) ^{a,1}	9.1 (0.5) ^{a,2}	20 (2) ^{ab,2}
$PF1_T$	183 (12) ^{a,2}	22 (3) ^{a,1}	64 (7) ^{ab,1}	52 (2) ^{a,1}	10.2 (0.9) $^{ab.2}$	17 (2) ^{a,2}
$PF2_T$	182 (13) ^{a,2}	23 (3) ^{a,1}	66 (5) ^{b,1}	53 (6) ^{a,1}	9.6 (1.4) ^{a,2}	17 (2) ^{a,2}

Different superscript letters indicate significant differences between formulations within the same processing method, while different numbers indicate significant differences between formulations with equivalent mass fractions but processed by another method ($p < 0.05$).

*(2-columns)

3.5. Barrier properties

PVA films present good barrier capacity against oxygen due to its polar nature and the low oxygen solubility in the matrix, which limits permeability. The highly cohesive nature of the polymer matrix due to the interchain hydrogen bonds also contributes to a reduction in the oxygen permeability through the limitation of molecular mobility and diffusion. In contrast, given the high degree of polarity of the polymer, the water molecules in the matrix are highly soluble, which favours their permeation through the matrix.

As expected, the values of OP (13.10^8 cm^3 / mhKPa) and WVP (8.2 g mm / $m^2 \cdot$h.KPa) of the phenolic-free, glycerol-plasticised PVA cast films (Pc) were higher than those reported for non-plasticised cast films (Andrade et al., 2020b). This is coherent with the plasticising effect of glycerol in the polymer matrix which leads to weaker interactions between the chains and, therefore, to greater molecular mobility and free volume in the polymer system (Hedenqvist, 2012).

As can be observed in **Table 2**, thermoprocessed PVA films exhibited significantly worse barrier properties ($p<0.05$) than cast films despite their higher crystallinity values, which could be explained by the better packing of oriented chains in cast films, which inhibited molecular diffusion. Similar results were found by (Moreno et al., 2017) for starch-gelatine films obtained by both casting and by compression moulding.

Although the barrier properties of the films were only slightly improved by the incorporation of PA, this effect was more marked in thermoprocessed films, where WPV was reduced by up to about 10% and OP by up to 43%, when ferulic acid was incorporated. The hydrogen bonds and Lewis adducts established between PA and the PVA chains may contribute to a reduction in molecular mobility, thus reducing the rate of molecule transport throughout the matrix. In addition, the antioxidant nature of phenolic acids could also contribute to the reduction in oxygen molecule transport, improving the barrier capacity of the material. Ferulic acid was more effective than cinnamic acid at improving the

barrier properties of the PVA films, especially the oxygen barrier capacity. Its molecular structure (with a p-hydroxyl group), which allows for interchain bonds, the promotion of crystallinity and a higher antioxidant capacity than cinnamic acid (Li et al., 2021), better contributes to an enhancement in the oxygen barrier properties of the films than cinnamic acid. This trend has also been reported for EVOH films with 0.25% and 0.5% of ferulic acid, which caused a decrease (25% and 28%, respectively) in the values of the oxygen transmission rate of the films (Aragón-Gutiérrez et al., 2021).

3.6. Optical properties of the films

The colour parameters (lightness (L*), Chroma (Cab*) and hue (hab*)), and internal transmittance pattern, used as a transparency indicator, of the different samples are shown in **Table 3** and **Figure 3**, respectively.

The incorporation of phenolic acids, especially ferulic, significantly reduced the hue values and increased the chrome, leading the film towards a more saturated yellowish appearance, regardless of the processing method. Nevertheless, thermoprocessed films incorporating PA were more saturated in colour and darker than cast films, which could be derived from the partial oxidation of acids under the thermal processing conditions. This also affected the loss of transparency (mainly at low wavelengths: 400 and 500 nm) of the films with ferulic acid, especially in the case of 2% ferulic, thermoprocessed films.

Table 3. Lightness (L*), chrome (Cab*), hue (hab*) and internal transmittance values at 460 nm (Ti) of the cast and thermoprocessed films of partially hydrolysed (P) PVA films.

Sample	L*	Cab*	hab*	Ti (460 nm)
P_C	90 (1) ^{a,1}	3.0 (0.1) ^{a,1}	102 (1) ^{c,1}	0.86 (0.01) ^{c,1}
$PC1_C$	90 (1) ^{a,1}	3.0 (0.1) ^{a,1}	102 (1) ^{c,1}	0.86 (0.01) ^{c,1}
$PC2_C$	90 (2) ^{a,1}	2.9 (0.1) ^{a,1}	102 (2) ^{c,1}	0.86 (0.01) ^{c,1}
$PF1_C$	89 (2) ^{a,1}	5.9 (0.4) ^{b,1}	99 (1) ^{b,2}	0.84 (0.01) ^{b,2}
$PF2_C$	89 (1) ^{a,2}	5.6 (0.6) ^{b,1}	97 (1) ^{a,1}	0.83 (0.01) ^{a,2}
P_T	90 (1) ^{c,1}	3.0 (0.1) ^{a,1}	102 (1) ^{d,1}	0.86 (0.01) ^{c,1}
$PC1_T$	90 (1) ^{c,1}	4.6 (0.3) ^{b,2}	102 (1) ^{cd,1}	0.86 (0.01) ^{c,1}

$PC2_T$	89 (1) ^{c,1}	4.5 (0.3) ^{b,2}	101 (1) ^{c,1}	0.86 (0.01) ^{c,1}
$PF1_T$	88 (1) ^{b,1}	10 (1) ^{c,2}	97 (1) ^{b,1}	0.80 (0.01) ^{b,1}
$PF2_T$	86 (1) ^{a,1}	19 (2) ^{d,2}	96 (1) ^{a,1}	0.74 (0.01) ^{a,1}

Different superscript letters indicate significant differences among formulations within the same processing method, while different numbers indicate significant differences between formulations with equivalent mass fractions but processed by another method ($p < 0.05$).

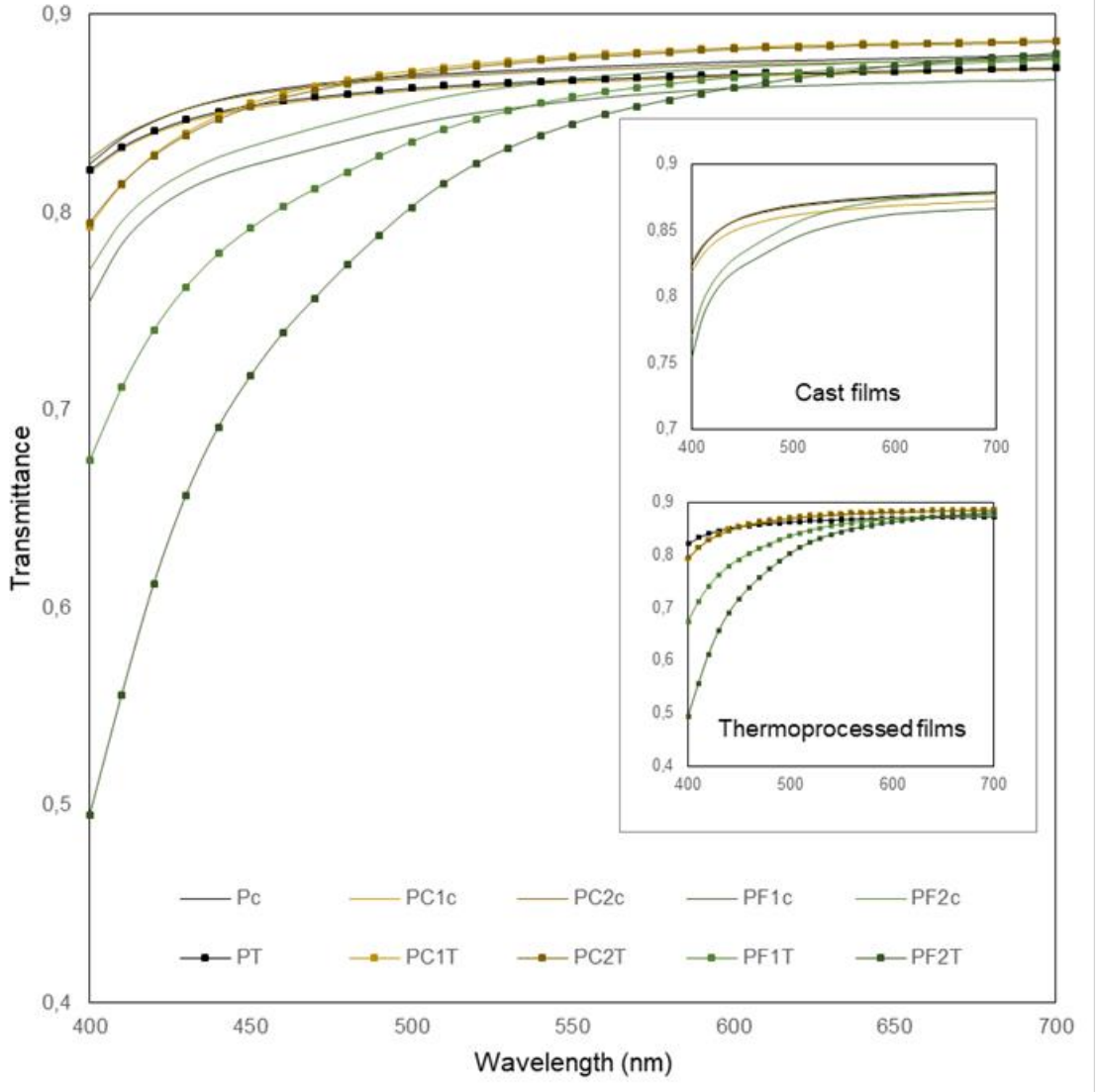


Figure 3. Internal transmittance pattern of cast (C) and thermoprocessed (T) films of partially hydrolysed (P) PVA films with the incorporation of cinnamic (C) and ferulic (F) acid (1 or 2 g/100 g PVA).

*(2-columns/Colour should be used)

3.7. Thermal behaviour

The first and first and second order thermal transitions, associated with semi-crystalline materials, were analysed from the second heating scan of the DSC analyses, as shown in **Figure 4**. The values of glass transition temperature, melting temperature and melting enthalpy are shown in **Table 4**.

The thermal properties of the films were affected by the incorporation of glycerol in the polymeric matrix, which produces significantly lower Tg and Tm values than those reported for non-plasticised films, (Tg: 56ºC, Tm: 168ºC). This effect is coherent with the plasticising effect of glycerol in the amorphous fraction and the formation of smaller crystals, due to the interference of glycerol in the crystallisation of the polymer (Andrade et al., 2020a). In general, the processing method did not generate significant effects on the melting behaviour of the materials. Nevertheless, the phenolic-free films obtained by thermo-processing (P_T) presented higher enthalpy values than films obtained by casting (P_C), in line with their higher crystallinity, as deduced from DRX spectra.

No remarkable changes were observed in the Tg, Tm or ΔH values of the films when incorporating PA. Nevertheless, the glass transition temperature (Tg) in both cast and thermoprocessed films decreased ($p<0.05$) when using the highest concentration of ferulic acid. This suggests a certain plasticising effect on the amorphous fraction of the material, as previously reported for EVOH films incorporating different concentrations of ferulic acid and in thermoprocessed starch films with PA (Aragón-Gutiérrez et al., 2021). The partial hydrolysis caused by acids under the process conditions could explain this mild plasticising effect.

Table 4. Glass transition (Tg), melting temperature (Tm) and enthalpy (ΔH) of the PVA films (P) without and with phenolic acids (1 or 2 g/100 g PVA). Mean values and standard deviation in brackets.

Sample	Second heating scan		
	Tg (ºC)	Tm (ºC)	ΔH (J/g PVA)
P_C	37 (3) ^{b,1}	154 (3) ^{a,1}	24 (1) ^{a,1}
$PC1_C$	37 (2) ^{b,1}	157 (1) ^{b,1}	21 (3) ^{a,1}
$PC2_C$	35 (1) ^{ab,1}	157 (1) ^{ab,1}	24 (3) ^{a,1}
$PF1_C$	38 (1) ^{b,1}	156 (1) ^{ab,1}	23 (3) ^{a,1}
$PF2_C$	33 (2) ^{a,1}	156 (1) ^{ab,1}	21 (1) ^{a,1}
P_T	37 (1) ^{bc,1}	158 (1) ^{a,1}	27 (2) ^{b,2}

$PC1_T$	39 (1) ^{cd,1}	158 (1) ^{a,1}	22 (1) ^{a,1}
$PC2_T$	36 (1) ^{ab,1}	161 (2) ^{a,2}	25 (2) ^{ab,1}
$PF1_T$	39 (1) ^{d,1}	159 (1) ^{a,2}	28 (1) ^{b,2}
$PF2_T$	35 (1) ^{a,1}	158 (2) ^{a,1}	24 (4) ^{ab,1}

Different superscript letters indicate significant differences among formulations within the same processing method, while different numbers indicate significant differences between formulations with equivalent mass fractions but processed by another method ($p < 0.05$).

*(Single column)

3.7.1. Thermal degradation

The thermal degradation of the samples was analysed using the curves of the thermogravimetric analysis (TGA) and its derivative (DTG), shown in **Figure 4**. The thermal degradation pattern, observed in the DTG curves, comprises multiple consecutive peaks corresponding to the degradation of the components in the polymeric matrix. The first stage corresponds to the vaporisation of the bonded water, which appeared at 62 °C and 82 °C in the casting (1.8% mass loss) and thermoprocessed (0.8% mass loss) films, respectively. The partial release of glycerol represents the second peak that occurred in the cast films (4% mass loss) at 160 °C and the thermoprocessed films (2.5% mass loss) at 167 °C. The thermo-released glycerol was less than 10% wt., concentration initially incorporated, which suggests that a fraction of the plasticiser remained closely bonded to the polymer chains due to its high affinity. The polymer degradation occurred in several stages; the first stage was associated with the detachment of side groups (hydroxyl and acetyl) from the chains, giving rise to by-products, such as acetaldehyde, acetic acid and water (Perilla, 2007). In the cast films, the main polymer degradation peak occurred at 274 °C, while in thermoprocessed films this peak moved towards higher temperatures, reaching 285 °C. This behaviour coincides with that previously reported by other authors for other matrices, such as starch-gelatine and PLA (Moreno et al., 2017; Rhim et al., 2006), indicating the early formation of degradation compounds during thermoprocessing, which may be responsible for the colour changes of these films, as previously commented on. This also points to the different chemical composition of the materials after being partially hydrolysed and/or degraded during the thermal process. Two subsequent peaks of polymer degradation were observed between 350 °C and 650 °C, which were related to the degradation of low molecular weight

products from the polymer backbone break, or of heavier structures formed in previous stages of degradation (Holland & Hay, 2001; Perilla, 2007).

The thermal degradation of pure phenolic acids, between 230 °C and 280 °C (peak: 267 °C) for cinnamic acid and between 210 °C and 270 °C (peak: 250°C) for ferulic acid, was not appreciated in the thermograms of the films, due to their low mass fraction and the fact that they overlapped with the polymer degradation events.

The incorporation of PA only affected the thermal degradation pattern of films with ferulic acid obtained by casting, regardless of its concentration. In these films, a 10 °C increment in the temperature of the main degradation peak of PVA was observed. This indicates that this phenolic acid interfered with the thermal stability of the polymer, probably due to the interaction between its carboxyl and phenolic hydroxyl group with the hydroxyl/acetyl groups of PVA chains, giving rise to more thermally stable cross-linked films with a larger crystalline fraction, as deduced from the XRD analysis. This effect was also reported in EVOH films incorporating ferulic acid in different proportions (Aragón-Gutiérrez et al., 2021) and in PVA films with tannic acid and quercetin (Luzi et al., 2019). These acids acted as natural stabilisers against polymer degradation, in response to their characteristic chemical structure with several phenolic rings with hydroxyl groups (Luzi et al., 2019).

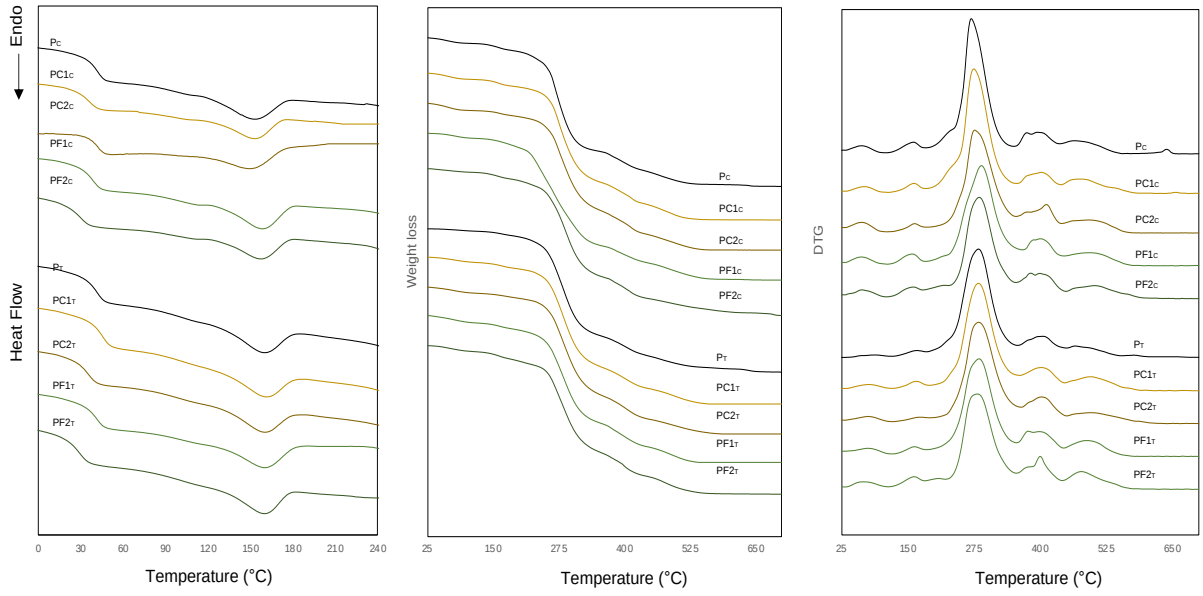


Figure 4. DSC (second heating scan) (left), thermogravimetric analysis (TGA) (middle) and DTGA (right) curves of the partially hydrolysed PVA films (P) without and with cinnamic (C) or ferulic (F) acid (1 or 2 g/100 g PVA).

*(2-columns/Colour should be used)

3.8. Antioxidant and antimicrobial capacity of the films

The antioxidant capacity of the active films was evaluated through the inhibition power of the DPPH radical of the active compounds delivered from the films into food simulants: ethanol 50% (v/v) as a simulant of O/W emulsified foods and ethanol 95% (v/v), as a simulant of lipophilic foods. No significant radical scavenging activity was observed for the films with cinnamic acid; the inhibition values ranged between 0.5 and 2%. In contrast, the inhibition capacity of ferulic acid was very high, ranging between 32% and 81% as can be observed in **Figure 5**, depending on the film processing method and food simulant. This difference is directly related to the molecular structure, depending on the number and position of the hydroxyl groups on the benzene ring (Li et al., 2021). Thus, ferulic acid is an o-hydroxycinnamic acid with a methoxy group in the ortho position with respect to the hydroxyl in the benzene ring, a structural factor that greatly improves the hydrogen donation capacity of the phenol. The absence of a phenolic hydroxyl in the cinnamic acid structure reduces its antioxidant capacity (Li et al., 2021). Ferulic acid incorporated into EVOH films has also been proven to be highly effective at scavenging a DPPH radical (Aragón-Gutiérrez et al., 2021)

The inhibition values obtained for films containing ferulic acid are shown in **Figure 5**. These values will be related to the total amount of compound released from the films into the food simulant. This release depends on the solubility of the compound in the simulant and their relative chemical affinity with both the polymer matrix and the solvent, according to the corresponding partition coefficient, as well as on the relaxation of the polymer in contact with the solvent, which promotes the release rate. As can be observed in **Figure 5**, the antioxidant capacity of the films was affected by the film processing method and the food simulant. Thus, the thermoprocessed films presented a lower radical scavenging capacity than the cast films, this being about 35% and 65% for films with 1% and 2% ferulic acid, respectively. This can be attributed to the partial oxidation of the

compound during the thermal treatment, as commented on above, which reduced the radical inhibition capacity of the films. In cast films, the inhibition of DPPH was about 80 % in every case, except in the least polar simulant (ethanol 95%) when the films contain 1% of compound, where an inhibition of only about 56% was observed, probably due to the smaller amount of ferulic acid released.

Finally, the greatest antioxidant capacity was found in the most polar simulant (ethanol 50%) due to the greater affinity with the PVA matrix, which favoured its swelling, thus enhancing the release of phenolic acids available to inhibit the free radicals.

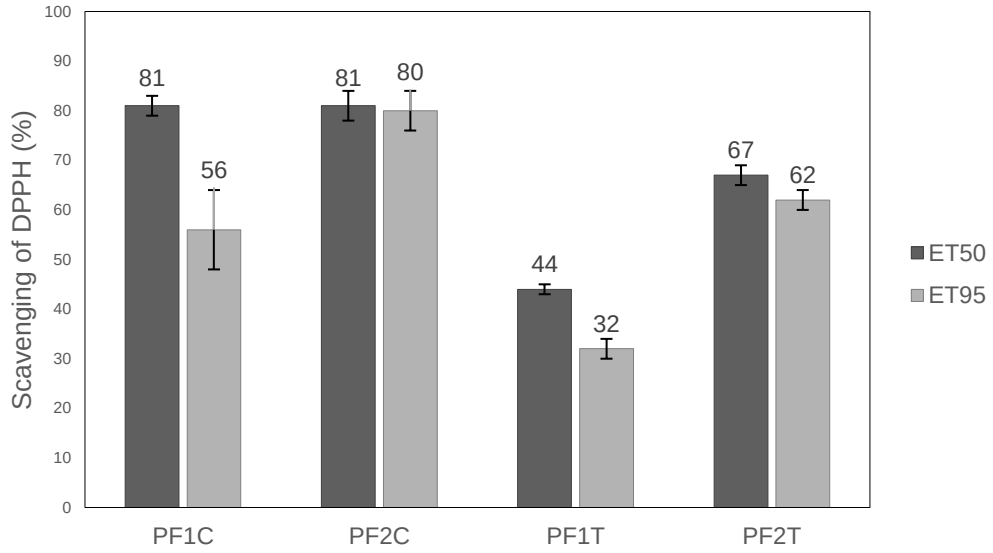


Figura 5. Antioxidant activity measured through the scavenging capacity of DPPH of two food simulants (50 and 95 % ethanol in water) in contact (48 h) with PVA films containing ferulic acid (F) at 1 or 2 %, obtained by casting (C) or thermoprocessing (T).

The antimicrobial activity was only evaluated in the films with the greatest PA content (2%) by means of the disk difussion method. The diameter of the inhibition halo of each film disk are shown in **Table 5**, for *Escherichia coli* Gram (-) and *Listeria innocua* Gram (+), as the diameter of the growth inhibition zone around the film disk. This method reflects the diffusion capacity of phenolic acids from the polymeric matrix and the sensitivity of each bacteria to compounds diffused into the agar.

The antibacterial activity of the films depended on the processing method, the type of PA incorporated and the bacteria. Thus, *L. innocua*, with inhibition halos of between 26 and 30 mm, was more sensitive to the antimicrobial effect of the active films than *E.coli,* which exhibited smaller inhibition diameters. Ordoñez et al., (2021) also reported this trend, when studying thermo-processed cassava starch films incorporating C and F acids, coherent with the higher MICs of phenolic acids of *E. Coli*.

As regards the film processing method, the cast films seemed to be more effective at controlling the microbial growth than the thermoprocessed ($p<0.05$); this difference was only significant ($p<0.05$) when using C acid. So, in general, the greatest antibacterial activity was found for cast films, regardless of the PA incorporated. In thermoprocessed films, those with ferulic acid exhibited greater inhibition halos ($p<0.05$) than those with cinnamic acid, despite the higher degree of oxidation of ferulic acid in the films and the lower MIC of cinnamic acid for both bacteria (Ordoñez et al., 2021). This suggests that the oxidated compounds of ferulic acid could also exhibit an antimicrobial effect (Aljawish et al., 2014)

Table 5. Diameters of inhibition halos (mm) of bacterial growth obtained in the agar difussion test for film disks containing ferulic (F) or cinnamic (C) acid of cast (C) and thermoprocessed (T) films.

Sample	Inhibition halo	
	***L. Innocua* (mm)**	***E. coli* (mm)**
$PC2_C$	29 (2) ^{a,2}	15 (3) ^{a,2}
$PF2_C$	30 (2) ^{a,1}	13 (2) ^{a,1}
$PC2_T$	26 (1) ^{a,1}	6 (2) ^{a,1}
$PF2_T$	29 (2) ^{b,1}	10 (2) ^{b,1}

Different superscript letters indicate significant differences among formulations within the same processing method, while different numbers indicate significant differences between formulations with equivalent mass fractions but processed by different methods ($p<0.05$).

4. Conclusion

The incorporation of cinnamic and ferulic acids into the PVA films significantly modified the physicochemical and functional properties of the films. These

changes were affected by the processing method (casting or thermoprocessing) and the type and concentration of phenolic acid. Thus, the addition of these active compounds improved the barrier properties of the films, especially when incorporating ferulic acid, which favours a greater degree of crosslinking in the matrix and polymer crystallinity. As concerns the processing method, cast films were more extensible and resistant to break, although thermoprocessed films were stiffer with a lower barrier capacity against water vapour and oxygen. In none of the cases was the thermal stability of the material compromised, while ferulic acid enhanced the thermal stability of the polymer in cast films. The PVA films with ferulic acid exhibited a remarkable antioxidant capacity and films with both ferulic and cinnamic acids had antilisteria properties. These results indicate that PVA films with ferulic or cinnamic acid, with modulated mechanical, barrier and antioxidant and antibacterial properties can be obtained by using casting or thermoprocessing, depending on the target application. Therefore, these are of great potential in the development of different materials for active food packaging purposes, such as coatings or films.

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