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Physico-Chemical, Mechanical and Morphological Properties of Biodegradable Films Based on Arrowroot Starch and Poly(vinyl alcohol)

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ABSTRACT

Biodegradable polymeric blends have been widely studied due to their potential of reducing pollution caused by non-biodegradable materials. The research described here describes a polymer blend that benefits both from the abundance of arrowroot starch (AS) and the good mechanical properties of poly(vinyl alcohol) (PVA). Glycerol (GLY) was used in different proportions as a plasticizer. The addition of GLY improved the mechanical properties of the blends, increasing the elongation at break up to 667%. On the other hand, the GLY addition adversely affected other properties, increasing the water vapor permeability (WVP), solubility and hydrophilic characteristics and reducing the thermal stability and the crystallinity index. The AS/PVA blend without GLY addition showed better physical-chemical properties, having strong chemical interaction between the two kinds of polymeric chains (according FTIR analysis) and a homogeneous morphology (SEM morphological analysis). In general, decreasing the AS content improved the mechanical and WVP properties, the film becoming less hydrophilic. In conclusion, the AS/PVA blends cast films, with or without GLY, are biodegradable materials suitable for packaging applications.

1. Introduction

There is a growing search for the development of packaging using biodegradable natural polymers with the objective of minimizing the impacts caused to the environment by plastics, mainly derived from petroleum products.[1,2] Among the biodegradable polymers with potential for packaging production, especially in the food area, arrowroot starch (AS) stands out due to its low cost and high abundance in nature.[3] Due to its rhizomes with high starch content, arrowroot (*Maranta arundinaceae* L.) has been

widely used for industrial starch production. The plant originates from South America, ranging from the northeast to the south of Brazil, and is currently cultivated on a larger scale in Jamaica, São Vicente, Australia, Southeast Asia, and South and East Africa.[3–5]

However, films produced exclusively from AS are not suitable for application on a commercial scale as they suffer from poor mechanical and thermal properties and have relatively low water barrier capacity [6]. Thus, in order to improve these properties, it is necessary to produce blends with other biodegradable polymers, such as poly(vinyl alcohol) (PVA).[7,8] PVA is a synthetic polymer with excellent mechanical properties, in addition to being nontoxic, biocompatible and hydrosoluble.[9] Blends formed with PVA and starch are stable due to hydrogen bonding interactions between the hydroxy groups present in the two types of polymeric chains.[10–12] However, the flexibility of the AS/PVA blend films often needs to be improved, according to its desired application, which can be done with the addition of plasticizers.[13] Polyols, such as glycerol, are frequently used as plasticizers, improving the mechanical properties and processability of the starch films.[14,15]

Polymeric blends between PVA and starch have been explored with starch from various sources, such as cassava,[9,11,16] corn,[12,17,18] potato,[19] peas[20] and wheat;[21] however, regarding PVA and arrowroot starch there is no publication. Nevertheless, few studies reporting edible films with blackberry pulp and arrowroot starch,[22] and with glycerol and arrowroot starch,[23] have been found. Therefore, this work proposes a methodology to obtain a new, biodegradable material based on starch from arrowroot and PVA with suitable properties for application in food packaging. Additionally, the effect of glycerol, as a plasticizer, was evaluated.

2. Material and methods

2.1. Materials

Commercial AS was purchased from a local market (Jitaúna, BA, Brazil). Poly(vinyl alcohol) (PVA, with a degree of hydrolysis of 87.7% and molecular weight of 104,500 g.mol^{-1}), was obtained from Neon Co. Ltd., Brazil. Glycerol (GLY) was acquired from Vetec Quimica Fina Ltd., Brazil. All reagents were used as-received. All solutions were prepared in ultrapure water.

2.2. Preparation of the polymeric blends by casting

The film blends were prepared by casting, maintaining the total mass of the solution at 60 g and 3.0% (w/w) of polymeric concentration (Table 1). For samples with added (GLY), the added GLY mass corresponded to 20% (w/w) of the polymeric concentration. For the AS film, one sample with GLY at 30% (w/w) was also prepared.

The basic process consisted of adding the correspondent mass of PVA to 50 mL of ultrapure water under magnetic stirring for 60 minutes at 85 °C. Then, the corresponding masses of AS and/or GLY were added and homogenized for 2 minutes. The system was then submitted to mechanical stirring (Fisatom Equipamentos Científicos Ltd., Brazil, model 715) for starch gelatinization at 1,000 rpm under heating in a water bath at 90 °C for 10 minutes. Finally, the solution was poured into a Petri dish (diameter

Table 1. Compositions of the blend polymeric films based on PVA and arrowroot starch, with glycerol at 3.0% (w/w) of the solution.

Samples*	PVA (g)	AS (g)	Glycerol (g)	Water (g)
PVA	1.80	–	–	58.20
PVA75/AS25	1.35	0.45	–	58.20
PVA75/AS25/GLY	1.35	0.45	0.36	57.84
PVA50/AS50	0.90	0.90	–	58.20
PVA50/AS50/GLY	0.90	0.90	0.36	57.84
PVA25/AS75	0.45	1.35	–	58.20
PVA25/AS75/GLY	0.45	1.35	0.36	57.84
AS/GLY20	–	1.80	0.36	57.84
AS/GLY30	–	1.80	0.54	57.66

*The numbers correspond to the respective percent mass proportion (w/w) of solid in each solution, except for the sample named PVA, which corresponded to 100% PVA polymer.

15 cm), leaving it in an oven with air circulation at 45 °C for 24 hours. It is noted that, although this film preparation process would not be used commercially, based on the results presented we intend to investigate extrusion of the blends on an industrial scale.

2.3. Characterization of the polymeric films

2.3.1. Thickness
Film thickness was measured by means of a micrometer model 103–137 (Mitutoyo Sul Americana Ltd., Brazil) with accuracy of 0.01 mm, taking the average at three different points of the film.

2.3.2. Water vapor permeability (WVP)
The WVP was determined according to the standard method, ASTM E96-95.[24] The films were cut, fixed on the opening of a weighing-flask containing anhydrous calcium chloride as desiccant (0% RH), and placed in a sealed vessel in which the relative humidity and temperature were maintained at 75% and 25 °C. The changes in the mass of the weighing-flask were recorded periodically and the WVP was calculated according to Equation (1):

$$\mathbf{WVP} = \frac{\mathbf{\Delta m}}{\mathbf{A} \ \mathbf{\Delta t}} \frac{\mathbf{X}}{\mathbf{\Delta P}} \qquad (1)$$

in which Δm is the mass increment (g) of the flask, Δt is the time (s), X is the average film thickness (mm), A is the permeation area (m^2), and ΔP is the water vapor pressure difference between the two sides of the sample (Pa).

2.3.3. Solubility in water
Water solubility was determined according to the method proposed by Gontard et al. [25] with modifications. Film samples were cut into rectangular pieces of 1.5 cm x 4.0 cm, dried at 100 °C for 24 h and weighed. The dehydrated samples were then immersed in 50 mL of deionized water and stayed at rest for 24 h at 25 ± 2 °C. After this period of time the sample was taken out, dried (105 °C for 24 h) and the non-solubilized mass was determined. The solubility (S) was expressed according to Equation (2):

$$S(\%) = \frac{m_i - m_f}{m_i} \times 100 \tag{2}$$

in which m_i is the initial dry mass and m_f is the final, non-solubilized dry mass. The experiments were carried out in triplicate.

2.3.4. Mechanical properties

The mechanical properties of the films were studied by characterizing the tensile strength and elongation at break according to the standard method ASTM D882-02[26] in a Universal Testing Machine model DL-1000MF (EMIC Equipamentos e Sistemas de Ensaios Ltd., Brazil). Test conditions were the following: crosshead speed of $1\,mm.s^{-1}$, cell load of $100\,kN$, distance between the grips of $40\,mm$, and sample dimensions of $25 \times 75\,mm$. The tests were carried out with 9 repetitions for each sample, with the averages shown.

2.3.5. Thermogravimetry analysis (TGA)

Thermogravimetric analyses were carried out in a TGA 2 Star System thermal analyzer (Mettler-Toledo International Inc., USA). The samples (about $5\,mg$) were heated from $30\,°C$ to $600\,°C$ at a heating rate of $10\,°C\ min^{-1}$ under a $50\,mL\ min^{-1}$ N_2 flow.

The TGA data were submitted to the mathematical approach proposed by Broido[27] in order to determine the kinetic parameters, such as the activation energy. According to this dynamic method, the activation energy (E_a) is given by Equation (3):

$$\ln\left[\ln\left(\frac{1}{1-\alpha}\right)\right] = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + K \tag{3}$$

in which R is the gas constant ($8.314\ 10^{-3}$ J mol^{-1} K^{-1}), T is the temperature (K) and α is the extent of conversion, given by $\alpha = W_e/W_0$, in which W_e is the mass of polymer evolved as volatile fragments and W_0 is the initial mass. E_a (kJ mol^{-1}) is found by plotting $\ln[\ln[1/(1-\alpha)]]$ versus $1/T$.

2.3.6 X-Ray diffraction (XRD)

X-ray diffractometry was carried out in reflection mode in the angular range $2\theta = 5–75°$ at room temperature with a model D8 Advance Davinci diffractometer (Bruker Corp., USA). The copper anode was adjusted to $40\,kV$ and $45\,mA$. The measurements were performed at a scanning speed of $2°min^{-1}$. The crystallinity index (CI) was determined by resolution of the crystalline and amorphous scattering integration of these areas under the curve,[21] and estimated using Equation (4):

$$CI(\%) = \frac{A_c}{A_c + A_a} 100 \tag{4}$$

in which A_c is the area of the crystalline peaks and A_a the area of the amorphous scattering, with the areas being those of both PVA and AS in the blends.

2.3.7. Contact angle

Contact angles were determined using an Attension Theta goniometer (Biolin Scientific – Surface Science Instruments, Sweden). A drop of deionized water ($10 \, \mu L$) was placed on the sample surface, and pictures of the drop were taken for 30 s with 14 FPS (photos per second). Each contact angle was the average of three measurements taken at different positions on the film, and considering both sides of the sample.

2.3.8. Fourier transform infrared spectroscopy (FTIR)

FTIR spectra of the films were recorded on an IR Tracer 100 spectrometer (Shimadzu Corp., Japan) with a resolution of $4 \, cm^{-1}$, using the Attenuated Total Reflectance (ATR) accessory. Each spectrum shown was the average of 45 scans in the $4000–400 \, cm^{-1}$ spectral range.

From the obtained infrared spectra, a Principal Component Analysis (PCA) was carried out with the program Unscrambler 9.7 (CAMO Analytics – An Aspen Technology Company, Norway). The spectra of the films without GLY were pretreated with a Savitzky-Golay (13-point window) filter, first derivative and second-order polynomial, while the films containing GLY were pretreated by average normalization. The spectra of 5 films were considered for each formulation.

2.3.9. Scanning electron microscopy (SEM)

The cross-section morphologies of the films were observed with a MIRA3 microscope (Tescan Orsay Holding, Czech Republic). The films were cryofractured by immersion in liquid nitrogen, mounted on the stubs perpendicularly to their fracture surface, and gold coated prior to imaging.

2.4. Statistical analysis

The data were submitted to statistical analysis by Analysis of Variance (ANOVA), using the Statistica® software, version 8.0 (StatSoft Enterprise, Brazil). Duncan's test was used to determine differences at a level of significance of 5% ($p \leq 0.05$).

3. Results and discussion

3.1. Thickness and water vapor permeability (WVP)

The formation of the polymeric blends based on different proportions of AS and PVA without GLY did not influence the thickness (Table 2). The thickness values were very similar for all the films, irrespective of the proportion, in comparison with the parent PVA polymer.[11,28] However, the thickness of the films increased significantly with the addition of glycerol in the filmogenic solution, except for the sample PVA25/AS75/GLY (Table 2). This occurs because the glycerol, which was an added component, increased the total amount of material in the preparation solution and remained between the polymeric chains, increasing the total volume. This prevents gel shrinkage and increases the thickness of the films.[29] In agreement, such effects have also been reported for other biodegradable films, such as starch/chitosan,[30] cassava starch/PVA,[11] and

Table 2. Thickness (mm) and Water Vapor Permeability (10^{-8} g.[h m Pa]$^{-1}$) values for blend polymeric films based on PVA, arrowroot starch and glycerol.

Samples*	Thickness	WVP
PVA	0.102 ± 0.013^a	1.69 ± 0.26^a
PVA75/AS25	$0.120 \pm 0.001^{a,b}$	2.25 ± 0.40^a
PVA75/AS25/GLY	0.154 ± 0.017^c	10.24 ± 2.06^b
PVA50/AS50	0.100 ± 0.008^a	$3.73 \pm 0.72^{a,c}$
PVA50/AS50/GLY	0.144 ± 0.012^c	$8.65 \pm 2.68^{b,c}$
PVA25/AS75	$0.108 \pm 0.003^{a,b}$	6.33 ± 1.13^c
PVA25/AS75/GLY	0.122 ± 0.001^b	$7.88 \pm 0.77^{b,c}$
AS/GLY20	0.123 ± 0.006^b	14.21 ± 2.07^d
AS/GLY30	$0.120 \pm 0.013^{a,b}$	13.63 ± 2.88^d

*Values followed by different superscript letters, in the same column, differed significantly by Duncan's test ($p \leq 0.05$), wheress those with the same letter are statistically identical for all. Values presented are mean values $\pm$ standard deviation (n = 3).

cassava starch plasticized with GLY.[31] It is noted that it was not possible to prepare pure AS films by casting.

Regarding the WVP, it was observed that the higher the AS proportion without GLY, the higher the WVP values (Table 2). In fact, the PVA film showed the lowest WVP value. This indicates that the presence of AS in the blend increased its hydrophilic character, facilitating water vapor diffusion.[32] This may be due to the presence of many hydroxy groups in the starch polymeric chains, which favors the diffusion of water molecules instead of hydrophobic gases, such as CO_2 and O_2.[33] The molecular structure of the PVA matrix was relatively more compact due to the intermolecular forces (hydrogen bonds) that arise between hydroxy groups.

As previously mentioned, the presence of GLY in the polymeric blend also favored a significant increase in the WVP value (Table 2), although it decreased with increasing AS relative to PVA. This occurs because the GLY increased the distance between the chains in both the AS and PVA polymeric domains, facilitating the diffusion of water molecules through the film.[34] For films made only with AS, the addition of GLY resulted in the highest observed WVP values, but was lower for the larger amount of GLY.

3.2. Solubility in water

The solubility in water of the polymeric blend films without glycerol increased with the increasing amount of PVA (Figure 1). This performance may be associated with the hydrophilic character of PVA, which results in a high-water absorption capacity and solubility.[35,36] Chiellini et al.[37] studied blends of PVA and gelatin, which also verified this effect. This outcome results in rapid film disintegration in water for films with high PVA concentration.

For the blends plasticized with GLY, it is seen in Fig. 1 that the solubility increased with the presence of GLY, in comparison to that of the corresponding blend without GLY, as also shown by Damian et al.[38] GLY is a small molecule and would be washed away as it is soluble in water. However, the mass loss as soluble material was greater than the 20% initially added GLY mass. Therefore, the glycerol was probably influencing the starch chains intermolecular interactions and chain conformations, facilitating its hydration and solubilization.[29,39–41] The results also confirm the low solubility of the
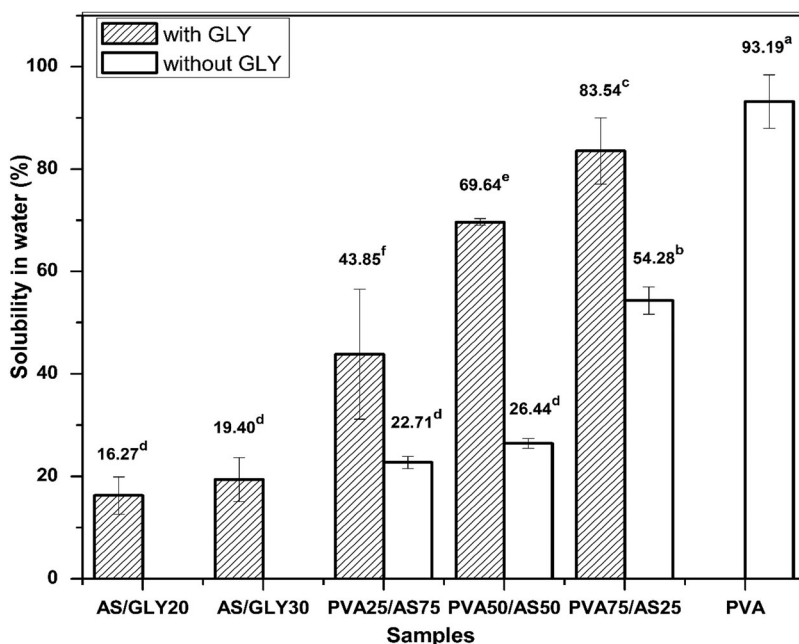
Figure 1. Influence of GLY addition on the solubility of PVA and AS polymeric blends. Values presented are mean values ± standard deviation (n = 3). Values followed by different letters differ significantly by Duncan's test (p ≤ 0.05), while those with the same letter were within the same confidence interval.

arrowroot starch in comparison with PVA. The films based only on AS/GLY showed the lowest solubility, nearly 70% lower than that of the PVA film.

The solubilities found for the AS/PVA films were close to values reported in the literature. For instance, in a study of cassava starch and PVA blends, the solubility ranged between 60 and 70% according to the different proportions.[42]

3.3. Mechanical Properties

The stress-strain curves obtained in the mechanical analysis experiments showed that the tensile strengths for the PVA based films were much higher than for the AS/GLY containing films (Figure 2a). This is in accordance with published results in which the PVA film features good mechanical properties, showing more resistance to breaking in comparison with starch films plasticized with glycerol [8,29,43,44] Increasing the PVA proportion in the blends without GLY, however, did not improve the mechanical properties. The film with the lowest PVA proportion (PVA25/AS75) exhibited the highest tensile strength. The reason for this is not clear yet, but this indicates clearly that interactions between the PVA and AS polymeric chains were taking place.

Addition of GLY resulted in a decrease of the tensile strength, although, for the PVA/AS/GLY films the tensile strength increased with increasing PVA (Figure 2a). As discussed above, the glycerol molecules increase the distance between the AS and PVA chains and, consequently, decrease the effect of the PVA-AS intermolecular forces. This
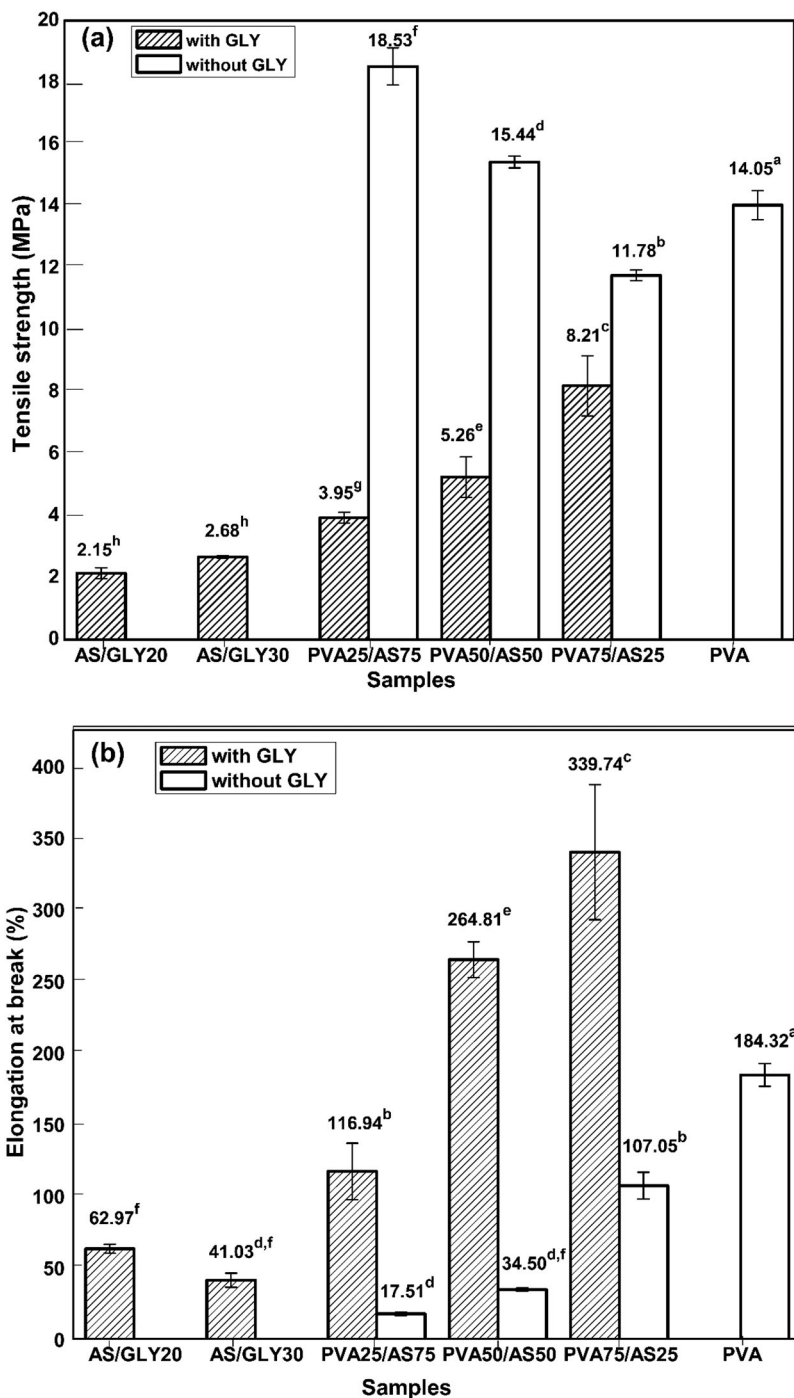
Figure 2. Tensile stress (**a**) and elongation at break (**b**) according to the stress-strain curves obtained for the polymeric blend films based on PVA and AS with or without GLY. Values presented are mean values $\pm$ standard deviation (n $=$ 9). Values followed by different letters differ significantly by Duncan's test (p $\leq$ 0.05).

behavior agrees with other studies in which plasticizers were added to biopolymer films.[1,11,14,18,29,32,43,45,46]

Contrary to the trend for tensile strength, the elongation at break increased with the increase in PVA percentage in the PVA/AS polymeric blends without GLY, although the elongation at break of all of the AS only containing samples were lower than that of PVA (Figure 2b). However, as a general rule for polysaccharides, the tensile stress, as here, is inversely proportional to the maximum elongation.[31,35,39,47] Thus, a brittle material is resistant to the stress but presents poor elongation (flexibility). In this way, it is clear that the polysaccharide (AS) addition made the material (AS/PVA) more brittle and less flexible.

On the other hand, addition of glycerol caused a remarkable change in the elongation behavior. Particularly for the AS/PVA blends, the elongation increased significantly compared to the parent materials PVA and PVA/AS. For the PVA50/AS50, for instance, the presence of glycerol increased the elongation by 667%, confirming that the GLY plasticizer acted by increasing the molecular mobility of the polymer chains.[1,48]

3.4 X-ray diffraction (XRD)

The diffractogram of the PVA film (Figure 3a) showed three characteristics peaks. The most intense peak, centered at $2\theta \approx 20°$, corresponds to the [101] planes, while the broad, less intense peak at $2\theta \approx 41°$ corresponds to the [200] planes and one weak peak, at $\approx 11°$, is assigned to the [100] crystallographic planes.[19,49,50] PVA present a semicrystalline structure mainly due to high physical intermolecular interactions by hydrogen bonding.

The diffractogram for the AS/GLY30 and AS/GLY20 films indicates a predominantly amorphous structure (Figure 3b). Such behavior was fully documented in the literature, showing that the starch granule lost its crystallinity after processes such as gelatinization and casting film with glycerol,[43] or acid hydrolyzes treatment.[35] However, some low intensity peaks can be seen at $\approx 9°$ and $17°$ for the AS/GLY30. According to the literature, the arrowroot starch exhibits a pattern that can be referred to as type C that is a mixture of polymorphs type A (cereal) and B (tuber).[23,35]

For all the PVA/AS blends without glycerol addition the characteristic PVA diffraction peak at $2\theta \approx 20°$ is seen (Figure 3a). Such pattern suggests that the crystalline structure of PVA was not affected by the presence of AS, in accordance with what has been described before.[43,51] Further, the absence of the AS characteristic peak at $17°$ in the PVA75/AS25 and PVA50/AS50 samples is attributed to the disorganization of the crystalline structure of the starch granules as a result of gelatinization during the process of preparing the film.[21,31,35,43,44,49,52] However, for the high starch content sample (PVA25/AS75), this AS characteristic peak was seen at $2\theta \approx 17°$, although with very low intensity. This indicates that a low fraction of the starch crystalline structure was preserved in this sample. Kahvand and Fasihi,[53] observed that in films based on corn starch and PVA, with the PVA being in low concentrations, the PVA had an anti-plasticizer effect due to possible strong interactions between the polymers PVA and corn starch. This effect was confirmed by the CI, in which the PVA25/AS75 blend presented a higher value when compared to the PVA50/AS50 film (Figure 4).

The diffractograms of the blends with GLY addition showed some differences in comparison with the blends without GLY addition (Figure 3b). First, the characteristic
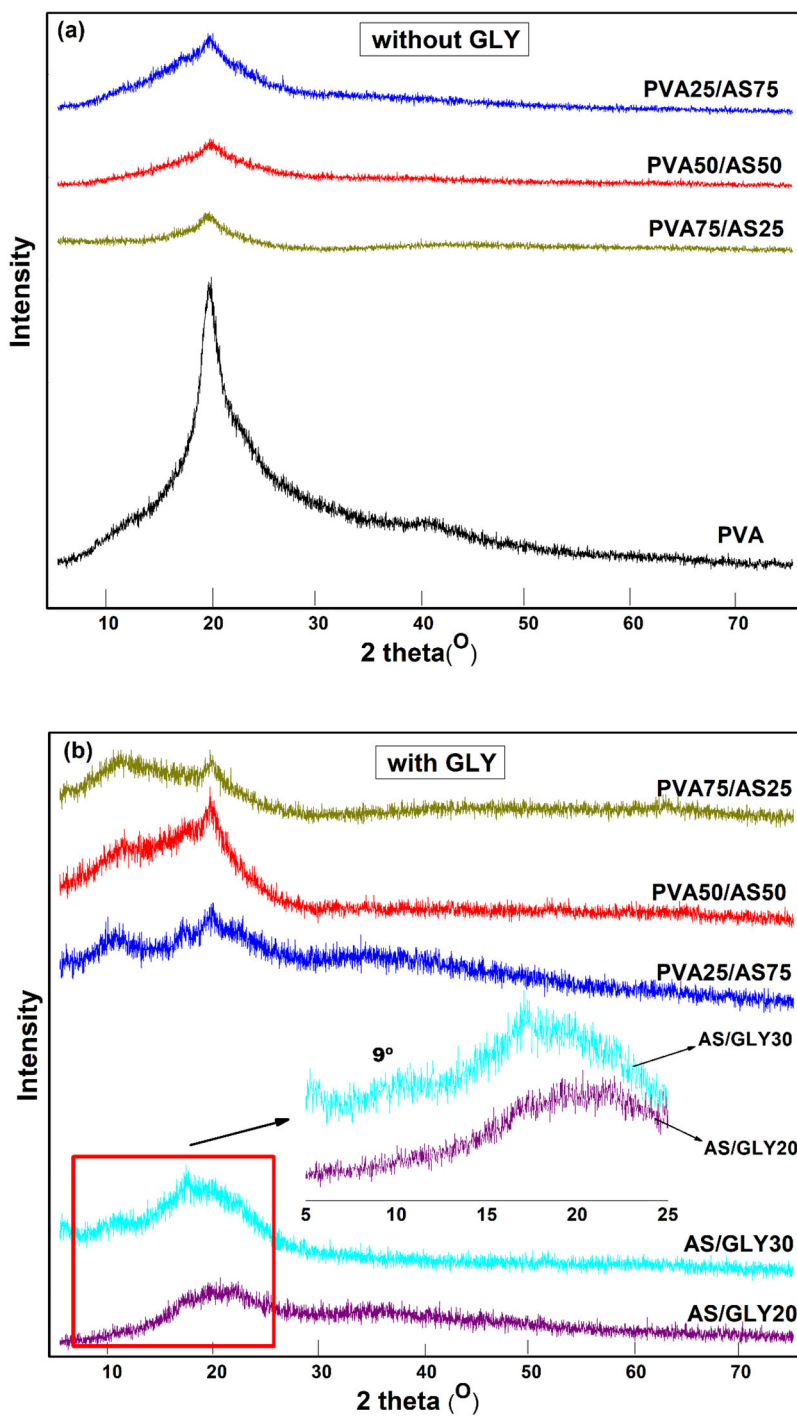
Figure 3. Diffractograms of the polymeric blends based on PVA/AS without GLY (**a**) and with addition of the plasticizer glycerol (**b**).
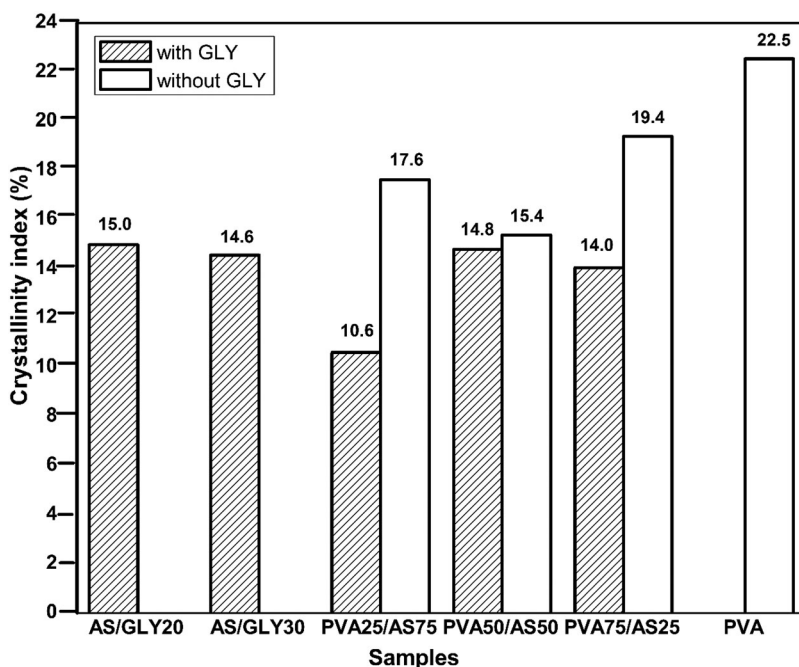
Figure 4. Crystallinity index of the polymeric blends based on PVA and AS with and without GLY.

PVA peak at $2\theta \approx 20°$ decreased in intensity in comparison with the sample without GLY addition. This is an indicative that the GLY addition can affect the PVA crystalline phase in the blend or even to improve the interaction between PVA and AS, decreasing the crystalline extension of the former. Second, characteristics starch patterns at $2\theta = 9°$ and $17°$ are more evident for blends with GLY addition in comparison with the patterns exhibit by blends without GLY addition. This is particularly evident for sample PVA25/AS75 that has a high AS content. In this way, some arrowroot starch crystalline phase was more preserved for blends with GLY addition.

From the diffractograms, the crystallinity index, CI, was calculated according to Equation 4. The results showed that the films plasticized with GLY had lower CI than those without GLY (Figure 4). This is an expected behavior, since the low molecular weight GLY plasticizer disrupts the PVA intermolecular interactions, decreasing its crystallinity.[10,43,49] In fact, even the water, acting as a plasticizer, can decrease the PVA crystallinity, as observed previously.[21] Accordingly, the powder PVA was more crystalline than the cast film.

For the blends without GLY, the CI decreased by increasing the AS amount in comparison with the parent PVA film (Figure 4). It is not clear if its CI decreasing was exclusively due to physical interaction between the PVA and AS chains, or if the interstitial H_2O could act as a plasticizer, interfering in the PVA crystalline pattern.[21] It may be a combination of effects.

3.5. Contact angle

The contact angle measurements showed that the addition of AS to the PVA lowered the contact angle, signifying an increase in the wettability (Figure 5). The sample with
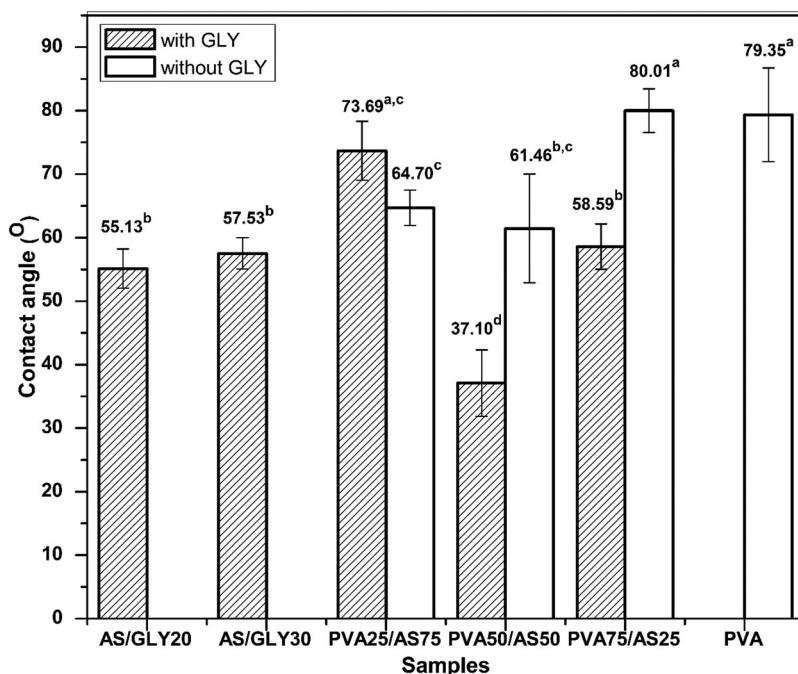
Figure 5. Contact angle values for the polymeric blends based on PVA and AS with or without GLY. Values presented are mean values ± standard deviation (n = 3). Values followed by different letters differ significantly by Duncan's test (p ≤ 0.05), whereas those with the same letter are statistically identical for all.

the highest content of PVA (PVA75/AS25) showed a high contact angle value, similar to the pure PVA film, whereas samples with high content of AS showed lower contact angle values. The number density of hydroxy groups in AS is higher than those of the PVA, resulting in a more hydrophilic material.[12] On the other hand, the gelatinization process leads to the breakdown of intramolecular hydrogen bonds in starch,[12,52,54] which increases the number of free hydroxyl groups, thus favoring hydrophilicity and decreasing the contact angle.[55]

The addition of glycerol resulted in a sharp decrease of the contact angle, as seen, for example, for the PVA50/AS50 and PVA75/AS25 films, each with a decrease of near 65% (Figure 5). In general, addition of glycerol would be expected to favor wettability, leading to films with a more hydrophilic surface and a lower contact angle due to the hygroscopic nature of glycerol.[56,57] However, contact angle is a surface property liable to phenomena like rearrangement of hydrophilic or hydrophobic moieties toward or away from the surface and difference in surface roughness.[21] An exception was the sample PVA25/AS75/GLY, which showed a high contact angle value when compared with the plasticized blends with a higher PVA concentration and with itself without GLY. However, the results showed no significant range (p > 0.05) when compared to the PVA25/AS75 film. That can be related to the anti-plasticizing effect associated with low PVA concentrations in starch films, which can be attributed to the formation of the strong complex between PVA and AS,[53] as discussed above for our XRD results.

3.6. Thermogravimetric analysis (TGA)

The thermal degradation profile of the PVA film was characterized by three stages (Figures 6a and b).[44,58] The first stage (I), ranging from room temperature to 200 °C,
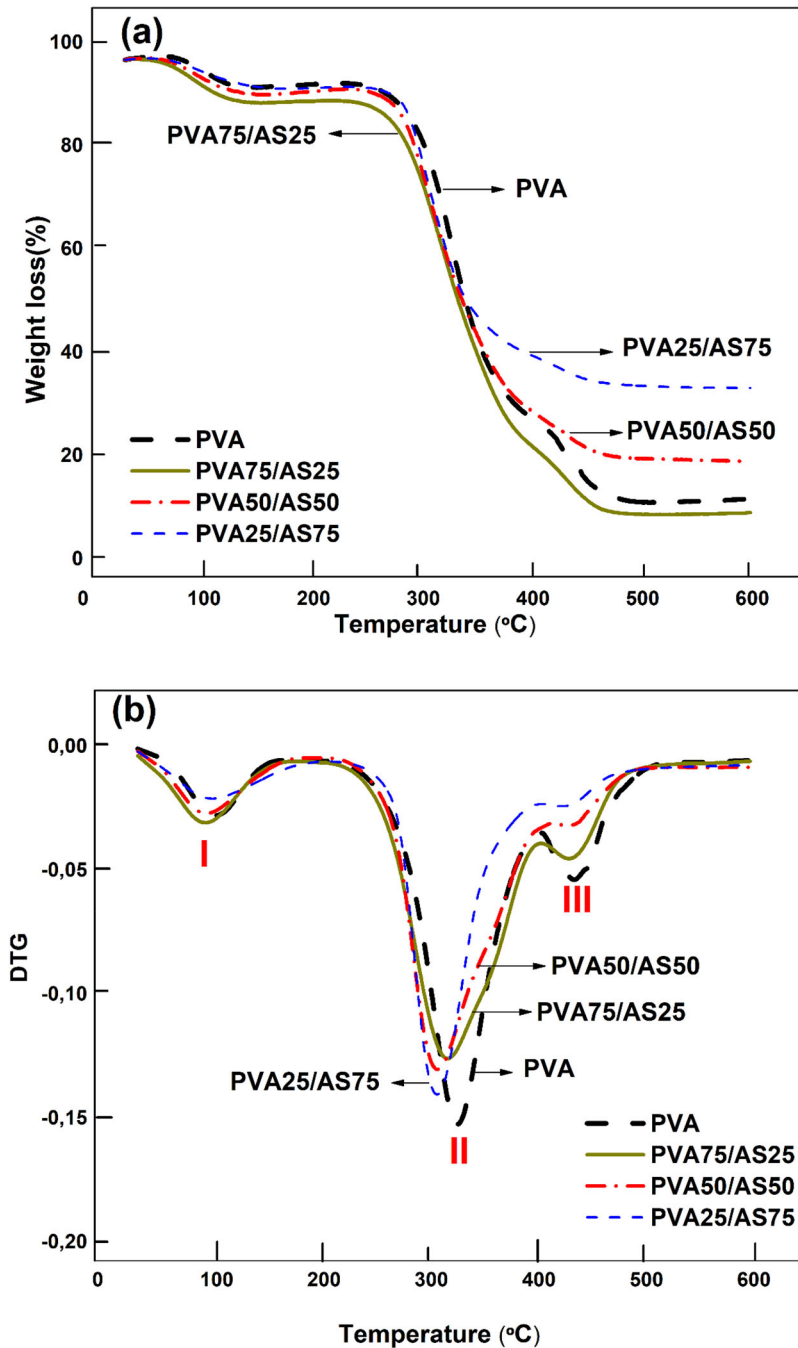

Figure 6. Thermogravimetric curves of the polymeric blends based on (**a**) PVA and arrowroot starch and (**b**) are the respective DTGA curves.

Table 3. Apparent activation energy (E_a, kJ/mol) and maximum degradation temperature (T_{max}, °C) relative to the second thermal degradation stage (200 °C to 400 °C) of PVA, blends PVA/AS films and AS/GLY mixtures and third degradation stage for the PVA/AS/GLY films.

Samples	Thermal degradation parameters	
	E_a	T_{max}
PVA	114	329
PVA75/AS25	82	320
PVA50/AS50	86	308
PVA25/AS75	118	309
PVA75/AS25/GLY	61	320
PVA50/AS50/GLY	68	308
PVA25/AS75/GLY	98	308
AS/GLY20	140	316
AS/GLY30	100	315

was related to the loss of weakly physiosorbed water.[9,17,20,59] In the second stage (II), from 200 °C to 400 °C, decomposition of the PVA occurred, predominantly due to dehydration of the hydroxyl groups followed by scission and main-chain decomposition.[9,59] The third stage, (III), from 400 °C to 500 °C, is due to the by-products generated by the PVA during the reactions in the stage II, undergoing thermal degradation, as carbonaceous materials, resulting in release of CO_2 and CO.[7,9]

After the PVA/AS blend preparation, two main changes occurred in the TGA curve (Figures 6a and b). The first one is related with the amount of physiosorbed water, stage I, that were lower for the samples with the higher starch contents, indicating that the water affinity was higher for PVA than for AS. The second change was in the decomposition temperature, T_{max}, of the stage II that decreased in the samples with lower PVA content (Table 3). This change, related to the blends, was a superposition of the PVA decomposition (side chains) and starch decomposition (cleavage of glycosidic bonds and formation of small, volatile compounds).[59,60] This was clearly evidenced previously,[59] where the native starch showed a narrow decomposition pattern, with the onset temperature at 279 °C and the endset temperature at 310 °C, while the PVA exhibited a broad one, with the onset temperature around 200 °C and the endset temperature near 360 °C.

The main change observed for the thermogravimetric curves for PVA/AS/GLY blends and AS/GLY sample is related to an additional thermal event centered at 200 °C, which is attributed to the glycerol volatilization (Figure 7b). Although the boiling point of pure glycerol is 290 °C, when in a blend its temperature of maximum vaporization is lower. This is characteristic of low molecular weight components present in materials subjected to thermogravimetry in which diffusional property and heating rate greatly influence the temperature of maximum vaporization. This phenomenon also occurred for the physiosorbed water (stage I), whose temperature of maximum vaporization was shifted to below 100 °C. Regarding the thermal events II and III (Figure 6b), the GLY addition did not impart any significant change (Figure 7b). Also, the T_{max} found in DTGA did not show any difference between the blends with GLY and without GLY (Table 3). Finally, the thermal degradation curves for AS/GLY20 and AS/GLY30 were typical of glycoside polysaccharides, showing a narrow profile with a $T_{max} = 315$ °C (Table 3), as discussed above. Such a thermal event is exclusive to the arrowroot starch decomposition.[59]
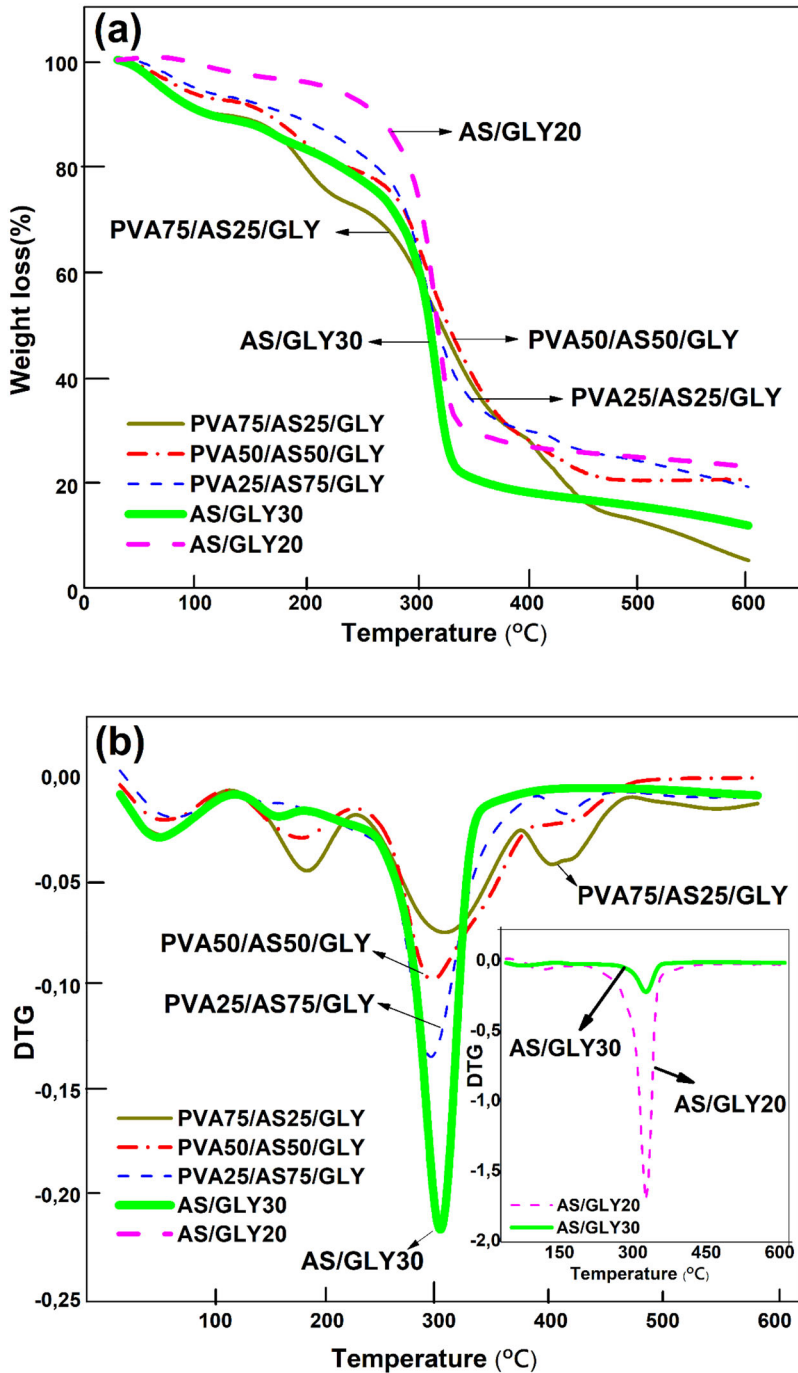
Figure 7. Thermogravimetric curves of the polymeric blends based on (**a**) PVA and arrowroot starch with addition of the plasticizer glycerol and (**b**) are the respective DTGA curves.

Applying the mathematical approach proposed by Broido (Equation 3), it was possible to determine the apparent activation energies associated with the main thermal degradation event in the range $200 - 400\,°C$ (Table 3). The E_a found for PVA ($114\,kJ$

mol^{-1}) was somewhat lower than that reported in the literature (133 kJ mol^{-1}).[60] Generally, the E$_a$ analysis is useful to compare similar materials as, for example, different proportions between two materials[59] or small chemical modification in the structure.[61] Very different materials can adopt distinct temperature rate constant and reaction models, preventing any comparison between them. In this way, comparing the E$_a$, according the Broido method, for the polymeric blends PVA75/AS25, PVA50/AS50 and PVA25/AS75 it was seen that by increasing the AS content in the blend, the E$_a$ value increased accordingly (Table 3). This indicates that the blends with high AS content should be more stable than those with lower AS content. This may be attributed to the cyclic hemiacetal structures present in starch that confer greater thermal stability to the blends. [9] There is little information about the E$_a$ variation as a function of the PVA: starch ratio, but a previous work showed that the E$_a$, according to the Broido approach, decreased slightly for a sample with high starch content (PVA40/Starch60) in comparison with a sample with a low starch content (PVA50/Starch50/glycerol).[62] However, a difference in the composition of the parent materials, components proportion and preparation procedure may influence the Ea value.

In agreement with the E$_a$ found for PVA/AS, the E$_\mathbf{a}$ calculated for the PVA/AS/GLY samples followed the same trend (Table 3). The E$_\mathbf{a}$ increased proportionally in accordance with the increasing amount of AS in the blend. However, the absolute E$_a$ value found for samples with GLY was inferior in comparison with that found for samples without GLY counterpart. This is a clear indication that the GLY addition lowered the thermal stability of the PVA/AS blend.

Finally, the sample with the lowest amount of GLY (AS/GLY20) showed the highest E$_a$ values in comparison with the sample with the highest amount of GLY (AS/GLY30). Once more, the results confirmed the influence of the glycerol in reducing the thermal stability regarding the E$_a$.

3.7. Fourier transform infrared spectroscopy (FTIR)

The FTIR analysis (Figure 8) showed a common broad band centered at 3290 cm^{-1} that corresponds to the O-H stretching vibrations present in PVA, starch and GLY (peak A). The absorbed water also contributes to this band.[35] The common band at 2932/2910 cm^{-1} results from the methylene (–CH$_2$–) stretching vibrations (peak B).[42,43] The band centered at 1718 cm^{-1} particularly for the PVA film (peak C) corresponds to the C$=$O stretching vibrations from residual acetate groups after the partial hydrolysis of the poly(vinyl acetate),[21,43] while the band resulting from absorbed water that is seen at 1647 cm^{-1} (peak D) is due to hydroxy bending vibrations.[19,21] The peak E, centered at 1240 cm^{-1}, corresponds to PVA –CH$_2$OH (side chain related mode vibrations).[43] The spectral analysis of AS showed a strong, characteristic band centered at 1012 cm^{-1} (peak F) corresponding to the glycoside linkage C-O-C.[42,43]

One important feature about the hydroxy stretching vibrations in PVA and the AS/GLY20 films, at 1656 and 1643 cm^{-1} (peak D), respectively, is that they shifted to lower wavenumbers with the decrease in the concentration of PVA (Table 4). Such behavior confirms the formation of intermolecular hydrogen bonds between PVA and AS. Likewise, for the peak at 1012 cm^{-1} (peak F), attributed to the stretching vibrations of
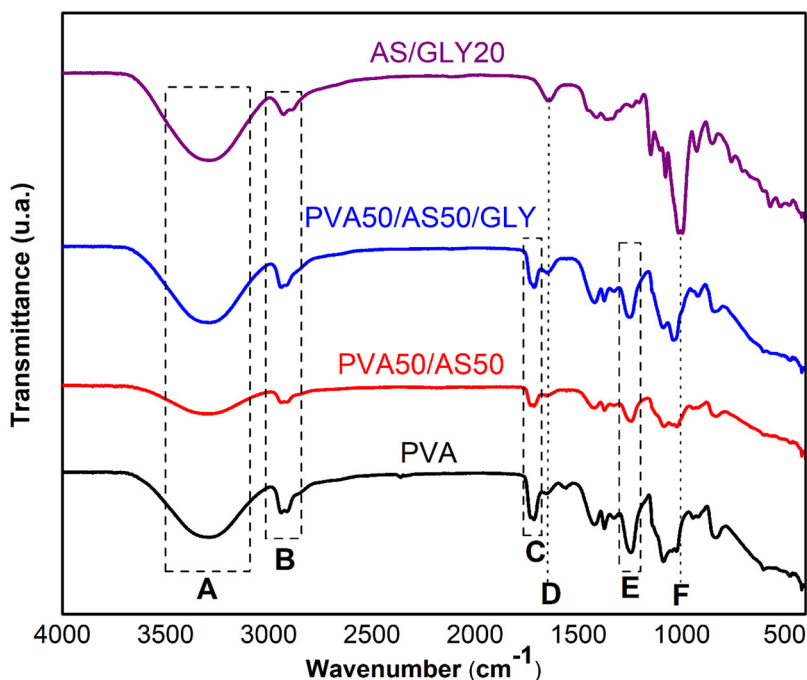
Figure 8. ATR-FTIR spectra of PVA, AS/GLY20 and PVA/AS blends films.

Table 4. Peak assignments in the FTIR spectra of pure PVA, AS/GLY20 and PVA/AS blends films for the two peaks the greatest wavenumber shifts.

	Peak assignment	
Samples	−OH bending (cm^{-1})	−C−O−C stretching (cm^{-1})
PVA	1656	−
PVA75/AS25/GLY	1652	1035
PVA75/AS25	1648	1022
PVA50/AS50/GLY	1649	1033
PVA50/AS50	1643	1020
PVA25/AS75/GLY	1647	1012
PVA25/AS75	1643	1020
AS/GLY20	1643	1012

the starch glycosidic bonds, there was a shifting to higher wavenumber values according to the decreasing in the amount of AS. These observations were similar to those reported by CANO et al.[28] indicating good miscibility between the components.

For complementing the FTIR results, a statistical pattern recognition tool was employed. The Principal Component Analysis (PCA) converts a complex, multivariate data into a collection of data whose interpretation is easier, without losing relevant information.[63] The aim of the principal components analysis is to explain the variations in the results based on similarities and differences among the samples and verify whether or not they are correlated. The PCA was applied to the infrared intensity and peak position data to check if there were significant variations of the bond vibrations of the pure film constituents (PVA and AS) when they were compared to the blends.
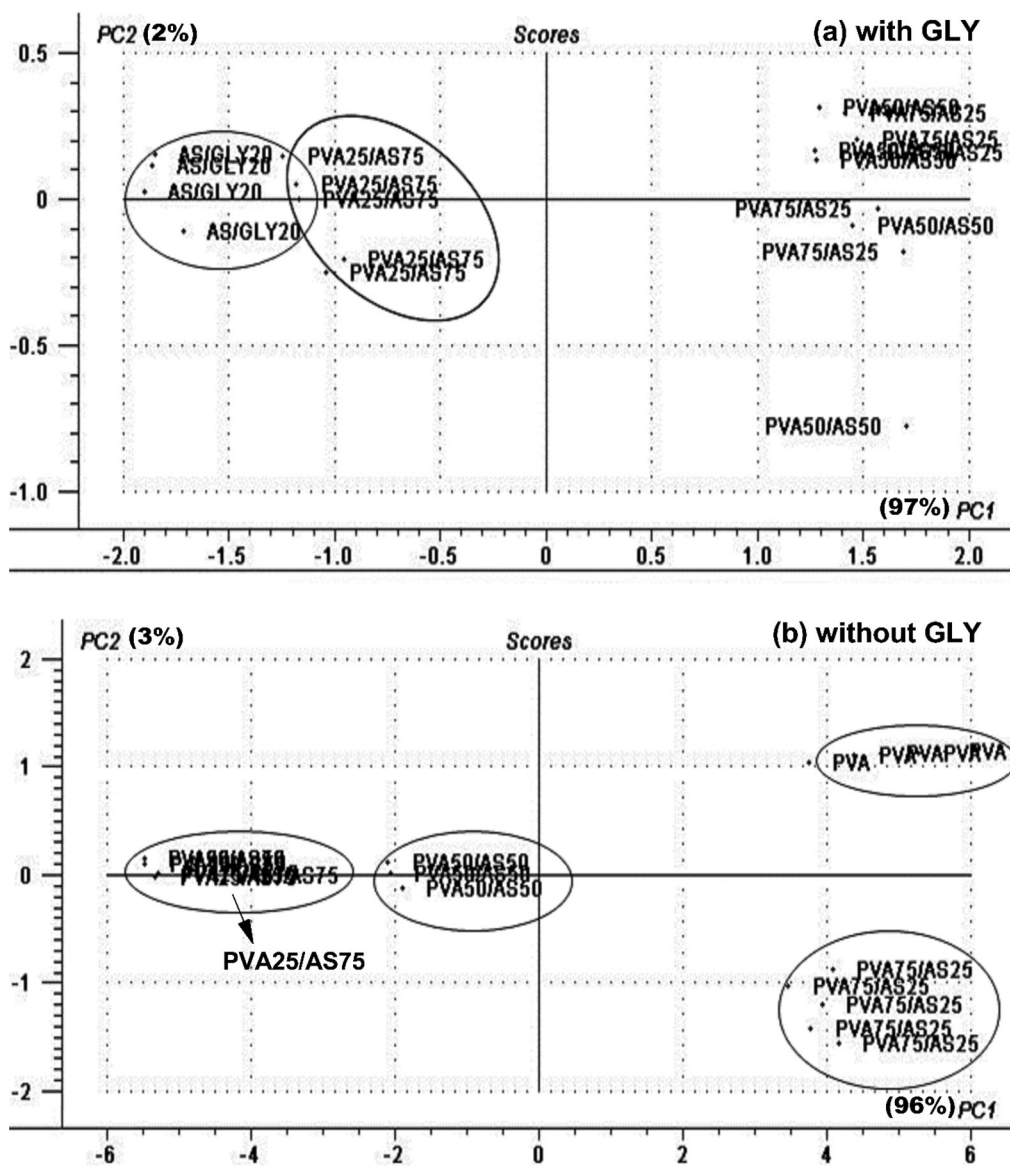
Figure 9. Scores plots for PC1 x PC2 of PVA and AS films with GLY (**a**) and without GLY (**b**).

From the plots of the scores, shown in Fig. 9, it can be seen that the two principal components (PCs) can distinguish the compositions.

For the films in which GLY was added (Figure 9a), principal component 1 (PC1) accounts for 97% of the sample variability and principal component 2 (PC2) accounts for another 2%. Three distinct groupings can be observed: PVA75/AS25 and PVA50/AS50 in one group, and AS/GLY20 and PVA25/AS75 in the other two groups. As the PVA concentration increased, a greater separation from AS/GLY20 occurred. This is due to a better differentiation between the vibrations of the polymers. Complete
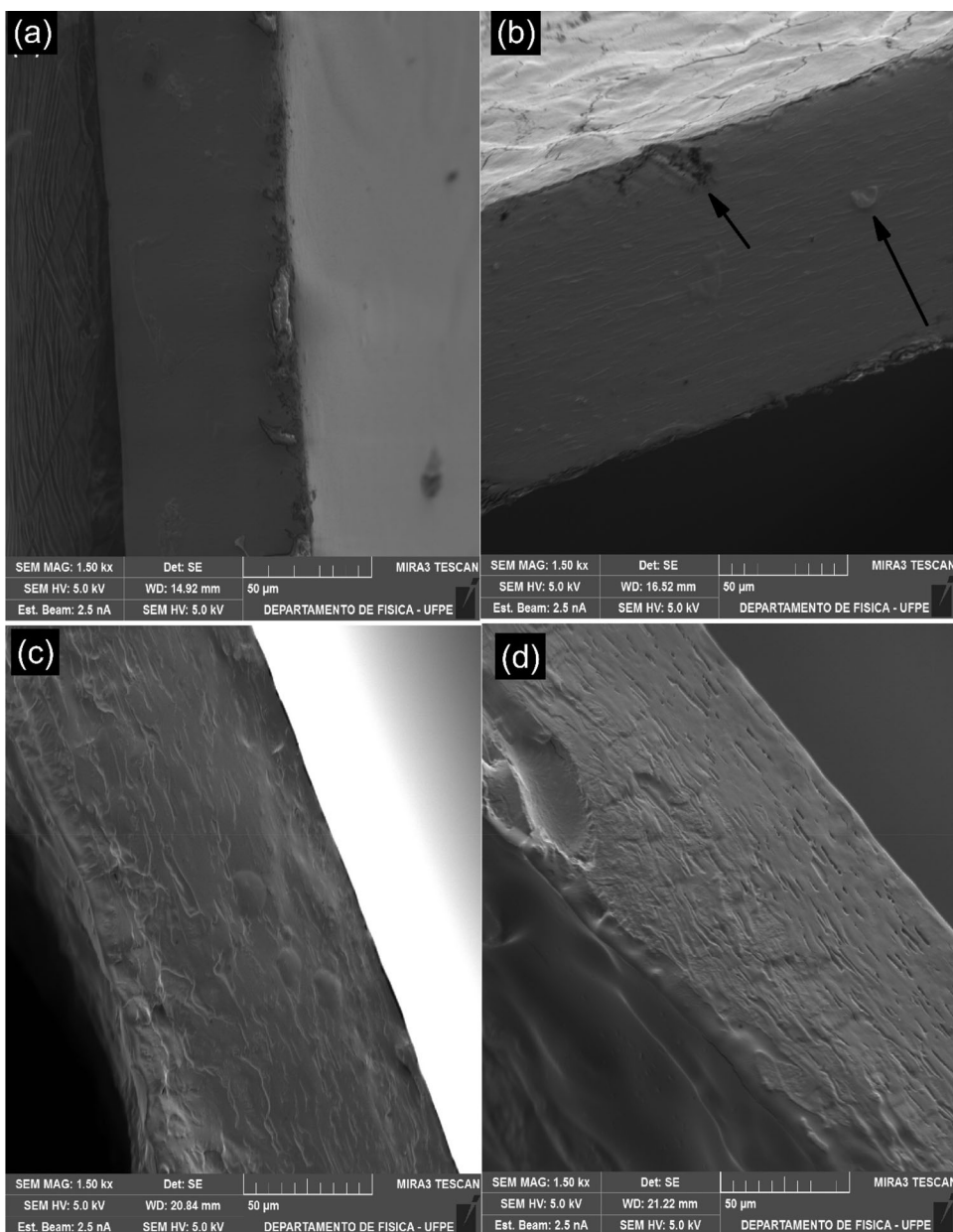
Figure 10. SEM images of the cryofractured films: PVA (**a**), AS/GLY20 (**b**), PVA25/AS75/GLY (**c**) and PVA25/AS75 (**d**).

separation of the groups PVA50/AS50 and PVA75/AS25 could not be achieved, possibly due to the high concentration of PVA in these films.

In the case of the pure PVA and the blends films without GLY, it was possible to group all the blend compositions into 4 groups (Figure 9b). PC1 (parallel to the x axis) has a tendency to separate the groupings of PVA25/AS75 and PVA50/AS50 from the other formulations, while PC2 (parallel to the y-axis) was necessary to observe the

separation between the pure PVA and PVA75/AS25 films. The percentages of variance explained by PC1 and PC2 were 96% and 3% respectively. As for Fig. 9b, the samples without GLY showed a distant relation to the pure PVA film, showing the differentiation between the formulations of the films. The separation into groups indicates chemical differentiation and possible interactions between the polymers according to each composition. Therefore, the PCA agreed well with the FTIR results discussed above.

3.8. Scanning electron microscopy

The SEM morphological analysis of the blend films (Figures 10 b-d) showed that, in general, the fracture surfaces of the polymeric blends PVA/AS, with and without GLY, were relatively smooth, compact and homogeneous, without discernible pores, discontinuities, cracks, bubbles or agglomerates (arrows, in Figure 10b, show a few). This indicated chemical compatibility and good miscibility of the components, as pointed out for similar samples before. [11,28]

The fracture micrograph of the PVA film (Figure 10a) also showed a homogeneous, smooth and compact morphology. For the AS/GLY20 film (Figure 10b), the presence of a few, small aggregates was observed. We suggest they should be attributed to small granules of AS that were not fully gelatinized during the film formation process.

The blends with higher AS content, as shown in Fig. 10c and d for the blends with 75% AS with and without glycerol, respectively, did not show significant differences in their morphologies, but had relatively rough fracture surface. That is, the micrographs of the blends indicated that there was a good interaction between the components.[43] Besides, it can also be concluded that the addition of GLY, as a plasticizer, favored homogeneous morphologies (with low roughness), with improved compatibility. This agrees with the improvement observed in the mechanical properties (increase in the elongation at break) of the blends containing glycerol.

4. Conclusions

The physical-chemical changes observed for polymeric blends based on PVA and AS were related to the percent proportion of each. In general, the AS imparted a more hydrophilic character to the blends, as shown by WVP and contact angle tests. Despite this, the solubility in water was lower for samples with high AS content. We suggested this was associated with other physical-chemistry parameters peculiar to PVA, that possesses high-water absorption capacity and solubility. This greater interaction was confirmed by means of the TGA, in which the films with a greater amount of AS had higher activation energy values. The fracture surfaces of the PVA and AS films, observed under SEM, exhibited homogeneous surfaces, indicating good miscibility of the components.

The glycerol addition increased the flexibility of the polymeric blends, increasing its elongation at break by up to 667%, but decreased its tensile failure strain and the degree of crystallinity. Also, it contributed significantly to increasing the hydrophilic character of the material (with an increase of about 65%).

FTIR analysis confirmed the presence of the AS, PVA and GLY in the films, indicating possible intermolecular bonds which could improve the miscibility between these components.

The PVA presence greatly improved the mechanical properties of the blend relative to AS/GLY blends. Further, the polymeric blends exhibited good mechanical, thermal and morphological aspects. We suggest the blends, with or without GLY, would be suitable for film packaging designated as biodegradable materials.

Acknowledgement

References

[1] Mali, S.; Sakanaka, L. S.; Yamashita, F.; Grossman, M. V. E. Water Sorption and Mechanical Properties of Cassava Starch Films and Their Relation to Plasticing Effect. *Carbohydr. Polym.* **2005**, *60*, 283–289. DOI: 10.1016/j.carbpol.2005.01.003.

[2] Dufresne, A.; Castaño, J. Polysaccharide Nanomaterial Reinforced Starch Nanocomposites: A Review. *Starch-Starke* **2016**, *68*, 1–19. DOI: 10.1002/star.201500307.

[3] Cereda, L. M.; Sarmento, M. P.; Arrowroot, S. B. S. (Maranta arundinacea) as a Possible Raw Material for Starch Industries. *Braz. J. Food. Technol.* **2002**, *5*, 151–155.

[4] Neves, M. C. P.; Coelho, I. S.; Almeida, D. L. Arrowroot: Rescue of a Traditional Cultivation. *Embrapa Comunicado Técnico* **2005**, *79*, 1–4. https://ainfo.cnptia.embrapa.br/digital/bitstream/CNPAB-2010/33053/1/cot079.pdf. (accessed Oct 02, 2020).

[5] Charles, A. L.; Cato, K.; Huang, T. C.; Chang, Y. H.; Ciou, J. Y.; Chang, J. S.; Lin, H. H. Functional Properties of Arrowroot Starch in Cassava and Sweet Potato Composite Starches. *Food Hydrocoll.* **2016**, *53*, 187–191. DOI: 10.1016/j.foodhyd.2015.01.024.

[6] Olivato, J. B.; Müller, C. M. O.; Yamashita, F.; Grossmann, M. V. E.; Nobrega, M. M. Study of the Compatibilizer Effect in the Properties of Starch/Polyester Blends. *Polímeros* **2013**, *23*, 346–351. DOI: 10.4322/polimeros.2013.014.

[7] Bonilla, J.; Fortunati, E.; Atarés, L.; Chiralt, A.; Kenny, J. M. Physical, Structural and Antimicrobial Properties of Poly Vinyl Alcohol-Chitosan Biodegradable Films. *Food Hydrocoll.* **2014**, *35*, 463–470. DOI: 10.1016/j.foodhyd.2013.07.002.

[8] Abdullah, Z. W.; Dong, Y. Biodegradable and Water Resistant Poly(Vinyl) Alcohol (PVA)/Starch (ST)/Glycerol (GL)/Halloysite Nanotube (HNT) Nanocomposite Films for Sustainable Food Packaging. *Front. Mater.* **2019**, *6*, 58. DOI: 10.3389/fmats.2019.00058.

[9] Rahman, W. A. W. A.; Sin, L. T.; Rahmat, A. R.; Samad, A. A. Thermal Behaviour and Interactions of Cassava Starch Filled with Glycerol Plasticized Polyvinyl Alcohol Blends. *Carbohydr. Polym.* **2010**, *81*, 805–810. DOI: 10.1016/j.carbpol.2010.03.052.

[10] Jiang, X.; Luo, Y.; Hou, L.; Zhao, Y. The Effect of Glycerol on the Crystalline, Thermal, and Tensile Properties of $CaCl_2$-Doped Starch/PVA Films. *Polym. Compos.* **2016**, *37*, 3191–3199. DOI: 10.1002/pc.23517.

[11] Faria, F. O.; Vercelheze, A. E. S.; Mali, S. Physical Properties of Biodegradable Films Based on Cassava Starch, Polyvinyl Alcohol and Montmorillonite. *Quím. Nova* **2012**, *35*, 487–492. DOI: 10.1590/S0100-40422012000300009.

[12] Shi, R.; Zhu, A.; Chen, D.; Jiang, X.; Xu, X.; Zhang, L.; Tian, W. In Vitro Degradation of Starch/PVA Films and Biocompatibility Evaluation. *J. Appl. Polym. Sci.* **2010**, *115*, 346–357. DOI: 10.1002/app.31136.

[13] Tang, X.; Alavi, S. Recent Advances in Starch, Polyvinyl Alcohol Based Polymer Blends, Nanocomposites and Their Biodegradability. *Carbohydr. Polym.* **2011**, *85*, 7–16. DOI: 10.1016/j.carbpol.2011.01.030.

[14] Shimazu, A. A.; Mali, S.; Grossmann, M. V. E. Plasticizing and Antiplasticizing Effects of Glycerol and Sorbitol on Biodegradable Cassava Starch Films. *Cienc. Agrar.* **2007**, *8*, 79–88.

[15] Mali, S.; Grossmann, M. V. E.; Yamashita, F. Starch Films: production, Properties and Potential of Utilization. *Sem. Ci. Agr.* **2010**, *31*, 137–156. DOI: 10.5433/1679-0359.2010v31n1p137.

[16] Guimarães, M.; Botaro, V. R.; Novack, K. M.; Teixeira, F. G.; Tonoli, G. H. D. Starch/PVA-Based Nanocomposites Reinforced with Bamboo Nanofibrils. *Ind. Crop. Prod.* **2015**, *70*, 72–83. DOI: 10.1016/j.indcrop.2015.03.014.

[17] Luo, X.; Li, J.; Lin, X. Effect of Gelatinization and Additives on Morphology and Thermal Behavior of Corn Starch/PVA Blend Films. Carbohydr. Polym. **2012**, *90*, 1595–1600. DOI: 10.1016/j.carbpol.2012.07.036.

[18] Yun, Y. H.; Na, Y. H.; Yoon, S. D. Mechanical Properties with the Functional Group of Additives for Starch/PVA Blend Film. *J. Polym. Environ.* **2006**, *14*, 71–78. DOI: 10.1007/s10924-005-8709-8.

[19] Popescu, M. C.; Dogaru, B. I.; Goanta, M.; Timpu, D. Structural and Morphological Evaluation of CNC Reinforced PVA/Starch Biodegradable Films. Int. J. Biol. Macromol. **2018**, *116*, 385–393. DOI: 10.1016/j.ijbiomac.2018.05.036.

[20] Cano, A.; Cháfer, M.; Chiralt, A.; González-Martínez, C. Development and Characterization of Active Films Based on starch-PVA, Containing Silver Nanoparticles. *Food Packag. Shelf Life* **2016**, *10*, 16–24. DOI: 10.1016/j.fpsl.2016.07.002.

[21] Jayasekara, R.; Harding, I.; Bowater, I.; Christie, G. B. Y.; Lonergan, G. T. Preparation, Surface Modification and Characterization of Solution Cast Starch PVA Blended Films. *Polym. Test* **2004**, *23*, 17–27. DOI: 10.1016/S0142-9418(03)00049-7.

[22] Nogueira, G. F.; Soares, C. T.; Cavasini, R.; Fakhouri, F. M.; Oliveira, R. A. Bioactive Films of Arrowroot Starch and Blackberry Pulp: Physical, Mechanical and Barrier Properties and Stability to pH and Sterilization. *Food Chem.* **2019**, *275*, 417–425. DOI: 10.1016/j.foodchem.2018.09.054.

[23] Nogueira, G. F.; Fakhouri, F. M.; Oliveira, R. A. Extraction and Characterization of Arrowroot (*Maranta Arundinaceae L.*) Starch and Its Application in Edible Films. Carbohydr. Polym. **2018**, *186*, 64–72. DOI: 10.1016/j.carbpol.2018.01.024.

[24] ASTM - American Society for Testing and Materials. E96-95: Standard Test Methods for Water Vapor Transmission of Materials. ASTM Standards. **2014**, 1–13.

[25] Gontard, N.; Guilbert, S.; Cuq, J. L. Edible Wheat Gluten Films: influence of the Main Process Variables on Film Properties Using Response Surface Methodology. J. Food *Sci.* **1992**, *57*, 190–195. DOI: 10.1111/j.1365-2621.1992.tb05453.x.

[26] ASTM - American Society for Testing and Materials. D882-12: Standard Test Method for Tensile Properties of Thin Plastic Sheeting. In: Annual Book of ASTM Standards, Philadelphia, **2012**.

[27] Broido, A. A Simple, Sensitive Graphical Method of Treating Thermogravimetric Analysis Data. *J. Polym. Sci. A-2 Polym. Phys.* **1969**, *7*, 1761–1773. DOI: 10.1002/pol.1969.160071012.

[28] Cano, A.; Fortunati, E.; Cháfer, M.; Kenny, J. M.; Chiralt, A.; González-Martínez, C. Properties and Ageing Behaviour of Pea Starch Films as Affected by Blend with Poly(Vinyl Alcohol). *Food Hydrocoll.* **2015**, *48*, 84–93. DOI: 10.1016/j.foodhyd.2015.01.008.

[29] Zhang, Y.; Han, J. H. Mechanical and Thermal Characteristics of Pea Starch Films Plasticized with Monosaccharides and Polyols. *J. Food Sci.* **2006**, *71*, E109–E118. DOI: 10.1111/j.1365-2621.2006.tb08891.x.

[30] Thakur, R.; Saberi, B.; Pristijono, P.; Stathopoulos, C. E.; Golding, J. B.; Scarlett, C. J.; Bowyer, M.; Vuong, Q. V. Use of Response Surface Methodology (RSM) to Optimize Pea Starch-Chitosan Novel Edible Film Formulation. *J. Food Sci. Technol.* **2017**, *54*, 2270–2778. DOI: 10.1007/s13197-017-2664-y.

[31] Machado, B. A. S.; Reis, J. H. O.; Silva, J. B.; Cruz, L. S.; Nunes, I. L.; Pereira, F. V.; Druzian, J. I. Obtaining Nanocellulose from Green Coconut Fibers and Incorporation in Biodegradable Films of Starch Plasticized with Glycerol. *Quim. Nova* **2014**, *37*, 1275–1282. DOI: 10.5935/0100-4042.20140220.

[32] Mali, S.; Grossmann, M. V. E.; Garcı́a, M. A.; Martino, M. N.; Zaritzky, N. E. Barrier, Mechanical and Optical Properties of Plasticized Yam Starch Films. *Carbohydr. Polym.* **2004**, *56*, 129–135. DOI: 10.1016/j.carbpol.2004.01.004.

[33] Cuq, B.; Gontard, N.; Guilbert, S. Protein as Agricultural Polymers for Packaging Production. *Cereal Chem.* **1998**, *75*, 1–9. DOI: 10.1094/CCHEM.1998.75.1.1.

[34] Bertuzzi, M. A.; Armada, M.; Gottifredi, J. C. Physicochemical Characterization of Starch Based Films. *J. Food Eng.* **2007**, *82*, 17–25. DOI: 10.1016/j.jfoodeng.2006.12.016.

[35] Chen, Y.; Cao, X.; Chang, P. R.; Huneault, M. A. Comparative Study on the Films of Poly(Vinyl Alcohol)/Pea Starch Nanocrystals and Poly(Vinyl Alcohol)/Native Pea Starch. *Carbohydr. Polym.* **2008**, *73*, 8–17. DOI: 10.1016/j.carbpol.2007.10.015.

[36] Silva, G. G. D.; Sobral, P. J. A.; Carvalho, R. A.; Bergo, P. V. A.; Mendieta-Taboada, O.; Habitante, A. M. Q. B. Biodegradable Films Based on Blends of Gelatin and Poly (Vinyl Alcohol): Effect of PVA Type or Concentration on Some Physical Properties of Films. J. Polym. Environ. **2008**, *16*, 276–285. DOI: 10.1007/s10924-008-0112-9.

[37] Chiellini, E.; Cinelli, P.; Fernandes, E. G.; Kenawy, E. R. S.; Lazzeri, A. Gelatin-Based Blends and Composites. Morphological and Thermal Mechanical Characterization. *Biomacromolecules* **2001**, *2*, 806–811. DOI: 10.1021/bm015519h.

[38] Damian, C. M.; Ott, C.; Stan, R.; Hanganu, A.; Trusca, R.; Balanuca, B. Harnessing a Byproduct from Wastewater Treatment to Obtain Improved Starch/Poly(Vinyl Alcohol) Composites. Carbohydr. Polym. **2020**, *238*, 115777. DOI: 10.1016/j.carbpol.2019.115777.

[39] Pelissari, F. M.; Andrade-Mahecha, M. M.; Sobral, P. J. A.; Menegalli, F. C. Nanocomposites Based on Banana Starch Reinforced with Cellulose Nanofibers Isolated from Banana peels. J. Colloid *Interface Sci.* **2017**, *505*, 154–167. DOI: 10.1016/j.jcis.2017.05.106.

[40] Mehyar, G. F.; Han, J. H. Physical and Mechanical Properties of High-Amylose Rice and Pea Starch Films as Affected by Relative Humidity and Plasticizer. *J. Food Sci.* **2006**, *69*, E449–E454. DOI: 10.1111/j.1365-2621.2004.tb09929.x.

[41] Lum, Y. H.; Shaaban, A.; Mitan, N. M. M.; Dimin, M. F.; Mohamad, N.; Hamid, N.; Se, S. M. Characterization of Urea Encapsulated by Biodegradable starch-PVA-Glycerol. J. Polym. Environ. **2013**, *21*, 1083–1087. DOI: 10.1007/s10924-012-0552-0.

[42] Junlapong, K.; Boonsuk, P.; Chaibundit, C.; Chantarak, S. Highly Water Resistant Cassava Starch/Poly(Vinyl Alcohol) Films. Int. J. Biol. Macromol. **2019**, *137*, 521–527. DOI: 10.1016/j.ijbiomac.2019.06.223.

[43] Boonsuk, P.; Sukolrat, A.; Kaewtatip, K.; Chantarak, S.; Kelarakis, A.; Chaibundit, C. Modified Cassava Starch/Poly(Vinyl Alcohol) Blend Films Plasticized by Glycerol: Structure and Properties. J. Appl. Polym. Sci. **2020**, *137*, 48848. DOI: 10.1002/app.48848.

[44] Sreekumar, P. A.; Al-Harthi, M. A.; De, S. Studies on Compatibility of Biodegradable Starch/Polyvinyl Alcohol Blends. Polym. Eng. Sci. **2012**, *52*, 2167–2172. DOI: 10.1002/pen.23178.

[45] Cervera, M. F.; Heinämäki, J.; Krogars, K.; Jörgensen, A. C.; Karjalainen, M.; Colarte, A. I.; Yliruusi, J. Solid-State and Mechanical Properties of Aqueous Chitosan-Amylose Starch Films Plasticized with Polyols. *A. A. P. S. PharmSciTech* **2001**, *5*, 1–6. DOI: 10.1208/pt050115.

[46] Chang, Y. P.; Karim, A. A.; Seow, C. C. Interactive Plasticizing Antiplasticizing Effects of Water and Glycerol on the Tensile Properties of Tapioca Starch Films. *Food Hydrocoll.* **2006**, *20*, 1–8. DOI: 10.1016/j.foodhyd.2005.02.004.

[47] Britto, D.; Assis, O. B. G. Synthesis and Mechanical Properties of Quaternary Salts of Chitosan-Based Films for Food Application. *Int. J. Biol. Macromol.* **2007**, *41*, 198–203. DOI: 10.1016/j.ijbiomac.2007.02.005.

[48] Orue, A.; Corcuera, M. A.; Peña, C.; Eceiza, A.; Arbelaiz, A. Bionanocomposites Based on Thermoplastic Starch and Cellulose Nanofibers. *J. Thermoplast. Compos. Mater.* **2016**, *29*, 817–832. DOI: 10.1177/0892705714536424.

[49] Tian, Y. J.; Zhang, H.; Xiang, Y. A. Effect of Urea and Formamide Plasticizers on Starch/ PVA Bioblend Sheets. *J. Appl. Polym. Sci.* **2015**, *132*, 42311. DOI: 10.1002/app.42311.

[50] Abral, H.; Hartono, A.; Hafizulhaq, F.; Handayani, D.; Sugiarti, E.; Pradipta, O. Characterization of PVA/Cassava Starch Biocomposites Fabricated with and without Sonication Using Bacterial Cellulose Fiber Loadings. Carbohydr. Polym. **2019**, *206*, 593–601. DOI: 10.1016/j.carbpol.2018.11.054.

[51] Siddaramaiah; Raj, B.; Somashekar, R. Structure–Property Relation in Polyvinyl Alcohol/ Starch Composites. *J. Appl. Polym. Sci.* **2004**, *91*, 630–635. DOI: 10.1002/app.13194.

[52] Chen, P.; Yu, L.; Simon, G. P.; Liu, X. X.; Dean, K.; Chen, L. Internal Structures and Phase-Transitions of Starch Granules during Gelatinization. *Carbohydr. Polym.* **2011**, *83*, 1975–1983. DOI: 10.1016/j.carbpol.2010.11.001.

[53] Kahvand, F.; Fasihi, M. Plasticizing and anti-Plasticizing Effects of Polyvinyl Alcohol in Blend with Thermoplastic Starch. Int. J. Biol. Macromol. **2019**, *140*, 775–781. DOI: 10.1016/j.ijbiomac.2019.08.185.

[54] Paes, S. S.; Yakimets, I.; Mitchell, J. R. Influence of Gelatinization Process on Functional Properties of Cassava Starch Films. *Food Hydrocoll* **2008**, *22*, 788–797. DOI: 10.1016/j.foodhyd.2007.03.008.

[55] Sarazin, P.; Li, G.; Orts, W. J.; Favis, B. P. Binary and Ternary Blends of Polylactide, Polycaprolactone and Thermoplastic Starch. *Polymer* **2008**, *49*, 599–609. DOI: 10.1016/j.polymer.2007.11.029.

[56] Forato, L. A.; Britto, D. D.; Scramin, J. A.; Colnago, L. A.; Assis, O. B. Mechanical and Wetting Properties of Zein Films Extracted from from Corn Gluten Meal. *Polímeros* **2012**, *23*, 42–48. DOI: 10.1590/S0104-14282012005000075.

[57] Britto, D.; Rizzo, J. S.; Assis, O. B. G. Effect of Carboxymethylcellulose and Plasticizer Concentration on Wetting and Mechanical Properties of Cashew Tree Gum Based Films. *Int. J. Polym. Anal. Charact.* **2012**, *17*, 302–311. DOI: 10.1080/1023666X.2012.668449.

[58] Othman, N.; Azahari, N. A.; Ismail, H. Thermal Properties of Polyvinyl Alcohol (PVOH)/ Corn Starch Blend Film. *Malaysian Polym. J.* **2011**, *6*, 147–154.

[59] Sreedhar, B.; Sairam, M.; Chattopadhyay, D. K.; Rathnam, P. A. S.; Rao, D. V. M. Thermal, Mechanical, and Surface Characterization of Starch–Poly(Vinyl Alcohol) Blends and Borax-Crosslinked Films. *J. Appl. Polym. Sci.* **2005**, *96*, 1313–1322. DOI: 10.1002/app.21439.

[60] Ünlu, C. H.; Turutoğlu, S. I.; Atici, O. G.; Ece, O. I.; Güngör, N. PVA Nanocomposites of Organoclays Obtained Using Different Cationic Surfactants. *J. Turkish Chem. Soc. Section A Chem* **2018**, *5*, 415–432. DOI: 10.18596/jotcsa.307602.

[61] Britto, D.; Campana Filho, S. P. Kinetics of the Thermal Degradation of Chitosan. *Thermochim. Acta* **2007**, *465*, 73–82. DOI: 10.1016/j.tca.2007.09.008.

[62] Ray, D.; Roy, P.; Sengupta, S.; Sengupta, S. P.; Mohanty, A. K.; Misra, M. A Study of Dynamic Mechanical and Thermal Behavior of Starch/Poly (Vinylalcohol) Based Films. J. Polym. Environ. **2009**, *17*, 49–55. DOI: 10.1007/s10924-009-0116-0.

[63] Pořízka, P.; Klus, J.; Képeš, E.; Prochazka, D.; Hahn, D. W.; Kaiser, J. On the Utilization of Principal Component Analysis in Laser-Induced Breakdown Spectroscopy Data Analysis, a Review. *Spectrochim. Acta Part B* **2018**, *148*, 65–82. DOI: 10.1016/j.sab.2018.05.030.