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ORIGINAL PAPER

High moisture strength of cassava starch/polyvinyl alcohol-compatible blends for the packaging and agricultural sectors

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Abstract This study aimed to evaluate the thermal, mechanical, physical, structural and morphological properties of new polymeric mixtures based on cassava starch (CMS) and polyvinyl alcohol (PVA) in the proportions of 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 using the casting method. The polymer concentrations and choice of plasticizer were defined after preliminary tests. Mechanical tests revealed that blends became more flexible and ductile with increasing the PVA proportion. The spectroscopy analysis showed significant alterations on the positions and intensity of the bands in 2920, 1415, 1150, 1077, 927 and 848 cm^{-1}, thus indicating a good compatibility among the polymers. Increase of the CMS proportion was reduced until reaching 45 % of the values of water vapor permeability (WVP) in relation to PVA biofilm. Any of the combinations was enough to make the blend less permeable than the CMS biofilm. After increasing the CMS proportions, all blends were more soluble in water compared to PVA biofilm. The exception was the 20P80A blend. Besides representing a tendency of higher opacity, all blends with elevated CMS proportions were more thermally stable when compared to those with the same proportions of PVA. Results showed the potential of such blends for applications on sectors of plastic and agricultural packages.

Keywords Biodegradable polymers · Blends · Plastic packages · Agricultural sector

Introduction

Nowadays, the interest in developing biodegradable materials in substitution to conventional synthetic materials, e.g., polyolefins, is increasing [1, 2]. This has been occurring due to the great environmental impact caused by the inadequate discard of these polymers in the environment. More sustainable raw materials have attracted great attention for engineering of materials due to the new potential applications in several sectors, like packaging and agriculture purposes.

Products of agricultural origin, like polysaccharides and proteins constitute a good alternative for the development of such materials. In this sense, starch rises as the main product to be explored as a cheap and abundant raw material. The two main components of starch are amylose and amylopectin. Amylose is formed by units of anhydroglucose joined through α bonds (1→4) under an helical form, while amylopectin is compounded by thousands of anhydroglucose residues joined by α bonds (1→4) forming the linear part and α bonds (1→6) forming thousands of points of the molecule branching [3, 4].

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Several authors [5–7], have demonstrated the possibility to convert native starch on thermoplastic material by means of the rupture of the granular structure in the presence of plasticizers by application of thermo-mechanical energy. However application of these materials produced only with this polysaccharide are still limited due to the hydrophilic character of the resulting products, which is the main cause of alteration on mechanical and barrier properties, as well as water absorption in different conditions of humidity [8, 9]. Several strategies have been applied to improve the performance of such materials, among them: the addition of plasticizers [10], chemical modifications [11], reticulation [12], radiation [13], reinforcement with natural fibers [14–16] and blendings [17–22].

The development of new polymers to obtain materials with differentiated properties that attend specific conditions of application is a slow and expensive process that demands much investigation. In this context, polymeric blends have been a very attractive alternative for the development of materials with different characteristics, once the physical and chemical properties may be altered by the blend composition.

The obtainment of new products from the mixture of starch with other polymers has been studied as an attractive alternative to obtain materials more stable to environmental variations and with lower hydrophilicity. In this sense, starch has been inserted in blends with different polymers, such as polylactic acid (PLA) [23], polyethylene adipate-co-butylene terephthalate (PBTA) [24], polyethylene succinate co-butylene adipate (PBSA) [25], polyhydroxybutyrate-co-hydroxyvalerate (PHB-HV) [26], polyhydroxybutyrate (PHB) [27], polycaprolactone (PCL) [28] and polyvinyl alcohol (PVA) [29, 30]. The addition of starch on polar synthetic polymers, as in the case of PVA, has demonstrated improvements on physic-chemical properties of the resulting products [31], thus increasing its potential use in the market of biodegradable films for agriculture and food packaging [32, 33]. Another advantage of using PVA in blends with starch is that the new materials obtained become biodegradable, which does not occur with most synthetic polymers.

It is important to highlight that the mixture of polymers does not guarantee the formation of a blend with desirable final properties. Compatibility is an important characteristic that must be considered in order to provide good interaction among the components [34]. Kalambur & Rizvi [35] commented that many degradable polymers are hydrophobic and thermodynamically immiscible with starch, which is an highly hydrophilic polymer. Among the several possible systems, we still must consider the lack of information about many properties of compatible cassava starch and PVA blends. Therefore, the objective of the present work was to evaluate the effect of different proportions of modified cassava starch and PVA on physical, mechanical, morphological, thermal and structural properties of biodegradable blends obtained through the technique of solvent evaporation (casting).

Material and methods

Materials

Modified cassava starch (CMS) produced by Cargill lot 1209035, type A, esterified, crystallinity index (CI) of 44.8 % and amylopectin of 85 %. Polyvinyl alcohol (PVA): molecular weight (Mw)=130.000 g/mol, 99 % hydrolyzate, lot MKBK3473V, Sigma-Aldrich. The plasticizer agents used were liquid glycerol (Mw=92.09 g/mol, ≥ 99 %, density=1.26 g/mL) and sorbitol powder (Mw= 182.17 g/mol, ≥ 98 %), both of which were provided by Sigma-Aldrich.

Preparation and choice of biofilms

The CMS and PVA biofilms were produced combining several varying concentrations of polymers and plasticizers (glycerol and sorbitol). The choice was made as a function of the results of mechanical, physical and morphological properties. The arrays with 3 % of CMS (m/m) and 12 % of glycerol (m/m), and with 4 % of PVA (m/m) and 25 % of glycerol (m/m) were selected for biofilms of CMS and PVA, respectively. The plasticizers were used in relation to the dry basis of polymers. In order to rehydrate them, both polymers remained immersed for 24 h in distilled water under constant agitation at 100 rpm at room temperature. Then, glycerol was added and both solutions (CMS and PVA) were submitted to magnetic agitation at 500 rpm at 80 and 90 °C, respectively, until the complete disintegration of both polymers. The mixture was then agitated for an additional 20 min. The solutions were cooled and sonified. After the correction of concentrations, the solutions were shed in acrylic plexiglass plates (40 g) with a diameter of 15 cm and conditioned in acclimation rooms [20±3 °C and 60-% relative humidity (RH)] during 10 days for drying and stabilization of the humidity variation. The thickness was controlled through the mass of samples. The structures of amylose and amylopectin, as well as the chemical structure of PVA are shown in Figs. 1a-e.

Preparing biodegradable blends

The mass proportions of PVA and CMS solutions on the blends were fixed at 100 % (pure PVA), 80/20 (80P20A), 60/40 (60P40A), 50/50 (50P50A), 40/60 (40P60A), 20/80 (20P80A) and 100 % (pure CMS), which were submitted to mechanical agitation at 750 rpm and 50 °C for 10 min. The solutions obtained were homogenized at 15,000 rpm during 5 min followed by sonication (450 W) at 25 % of the amplitude during 1 h in ice bath. The energy generated during cavitation was approximately 1.7 KJ/mL, and the individual

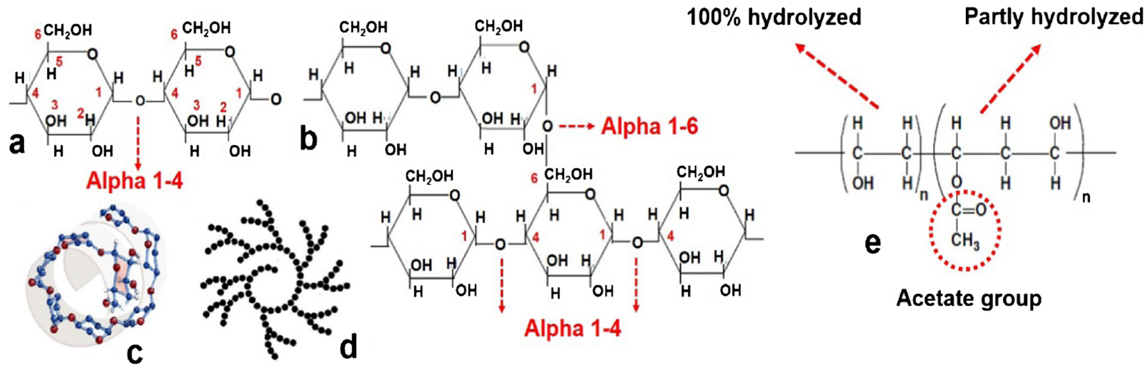


Fig. 1 Structure of amylose and amylopectin: **a**) interrelation of anhydroglucose molecules forming amylose through glycosidic bonds α (1→4); **b**) interrelation of anhydroglucose molecules forming linear glycosidic bonds α (1→4) and branchings α (1→6); **c**) helical conformation of amylose; **d**) branching conformation of amylopectin; e) chemical structure of PVA representing the 100-% hydrolised polymer, without an acetate group, and with hydrolysis lower than 100 % depending on the amount of acetate group on the polymer. Adapted from [4], [36] and [37]

volume of each solution was around 240 mL. Solutions were sonicated in order to eliminate bubbles and then were shed on acrylic plexiglass plates (40 g) with a 15-cm diameter. Drying and stabilization of the humidity variation occurred in an acclimation room (20±3 °C and 60-% RH) for 10 days. Thickness was controlled through the mass of the shed sample. Forty-two samples were obtained for preparing the specimens, including the individual samples of starch and PVA standards (100-% CMS and 100-% PVA). Figure 2 shows the PVA (Fig. 2a) and CMS biofilms (Fig. 2c) and the biodegradable 50/50 blend (Fig. 2b).

Characterization of biodegradable blends

Fourier transform infrared (FT-IR) analysis

Samples were characterized by absorption spectroscopy on the region of infrared using a Shimadzu Prestige-21 FT-IR instrument, with an attenuated reflex accessory, ATR-301, for observing the evolution of chemical modifications of the polymer. Spectra were recorded from 400 to 4000 cm^{-1} with 32 scans and a resolution of 2 cm^{-1}. The test was conducted at !~20±3 °C.

Morphology

Scanning electron microscopy (SEM): A Phillips XL-20 scanner operating in high vacuum was used to analyze blends and biofilms. The secondary electron (SE) detector was used to capture the images. Samples were gold (Au)-coated using vapor deposition. The acceleration voltage used was 15 Kv.

Mechanical properties

The maximum tensile strength (TS), elongation at break (TB) and tensile modulus (TM) of blends and biofilms were measured in an universal testing machine (INSTRON 5966–E2) operating with an 1-kN load cell at a 50 mm/min displacement, and with an initial distance among clamping jaws of 50 mm. The tensile properties of the samples were determined based on ASTM D 882–00 standard [38]. Specimens with a 15-mm width and 100-mm length were evaluated and the TM was calculated from the tangent of the initial linear function of the stress-strain curve, considered as an elastic behavior. The test was conducted at 23±2 °C. Five repetitions were used for each combination of CMS and PVA blends, with a total of 45 repetitions, including the CMS and PVA biofilms. A digital micrometer (0–30 mm) was used to take 20 random

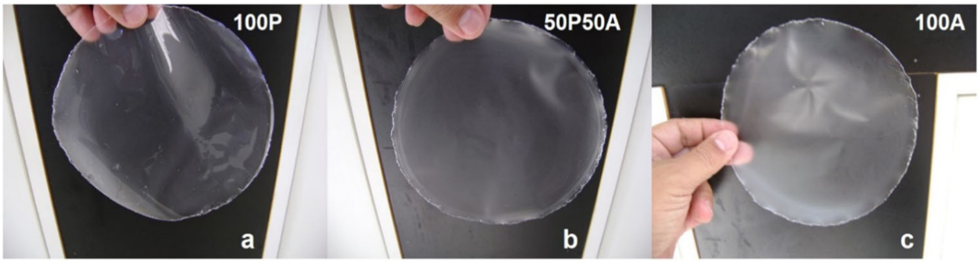


Fig. 2 Biofilms and biodegradable blends produced by the technique of solvent evaporation (casting) - **a**) biofilm of PVA (4 % m/m) with 25 % of glycerol (m/m); **b**) biodegradable blend 50/50 (50 % aqueous solution of PVA and 50 % aqueous solution of CMS); **c**) biofilm of CMS (3 % m/m) with 12-% glycerol (m/m). All samples present a 15-cm diameter

measurements of the thickness per specimen, with a resolution of 0.001 mm [39].

Thermogravimetric analysis

A Shimadzu DTG 60H was used for TGA. Samples of approximately 3 mg were placed on platinum crucibles and submitted to a temperature gradient of 25 to 700 °C at a heating rate of 10 °C/min using a flow rate of 50 mL/min in a nitrogen atmosphere. The test was conducted at around 20±3 °C. The initial and final temperatures of degradation (T_{onset} and T_{endset}) were obtained from the initial and final points of the TG curve, being represented by the intersections of extrapolation lines in the beginning and end of the thermal event, with the curve tangent in these same events. Using the first derivative of the TG curve, which establishes the mass loss as a function of temperature, it was possible to identify characteristic peaks of thermal degradation of the samples.

Physical properties

Optical transmittance – Tr The light transmission throughout samples was measured in a Shimadzu ultraviolet-visible light (UV–Vis) 1601 spectrophotometer, using a dual beam with a tungsten lamp, an accuracy of 0.5 nm and spectral band of 2 nm. This technique allows evaluating the total percentage of incident light that is transmitted through the biofilms and blends. The scan occurred from 400 to 800 nm and the transmission was determined according to Kampeerapappun et al. [40], Chen et al. [21] and Bibao-Sainz et al. [41]. Before evaluating the samples in relation to transparency, their thicknesses were determined according to the technique described in section "Fourier transform infrared (FT-IR) analysis". Samples were cut into rectangles (10×50 mm) and adhered to the internal wall of the spectrophotometer quartz cuvette [42]. Three repetitions were made for each combination of CMS and PVA for the formation of blends, with a total of 21 repetitions, including biofilms. The empty quartz cuvette was used for comparisons. The apparatus was programed to present the transmittance value (%) to the passage of light through the samples. The test was conducted at around 20±3 °C.

Water vapor permeability (WVP) The water vapor transmission rate (WVTR) of the blends was determined by gravimetry using ASTM E 96–00 standard. The test specimens were cut with a radius of 5.25 mm and applied to holes in amber glass with ¾ of its volume containing $CaCl_2$(desiccant) previously dried for 24 h at 150 °C. A sample was placed between the glass and the cap of each glass with silicone sealant. The glass had a 10-mm diameter, a 58-mm length and a 26-mm base diameter. The caps, which had a height and diameter of 18 and 20 mm, respectively, were perforated on the superior portion with the diameter of the permeation area of the glass. This system sets the water activity to 0 (zero) in the atmosphere in contact with the specimen's lower face. The amber glass vessels were placed in hermetic desiccators at 18.5±2 °C in which a volume of water sets the water activity. This system sets a water activity of 0.1 in the atmosphere in contact with the specimen's upper face. Weight gain measurements were taken by weighing the test glass to the nearest 0.001 g with an electronic scale every day such that the of amber glass water uptake was measured each 24 h for 240 h (10 days). A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady-state amount of water vapor diffusing through the specimen per unit time (g/h). The WVTR was expressed in gram units per square meter per day. Steady state over time (slope) yielded a regression coefficient of 0.98 or greater. Three repetitions were performed for each percentage of nanofibrils added to the blends, yielding a total of 27 repetitions including the blend. Specimen WVPs were calculated by multiplying the steady WVTR by the specimen thickness (mm) and dividing that by the water vapor pressure difference (Δp em KPa) across the specimen [43]. Δp is the ambient vapor pressure difference containing silica gel (zero) and pure water (2.1297 KPa at 18.5 °C*). Figures 3a-d show the preparation steps of the permeability cell. *Calculated using the Tetens equation [44].

Solubility in water Solubility in water was determined using circular test specimens of 3.14 cm^2. The initial dry mass was obtained using an analytical balance after drying at 55±2 °C for 24 h. The test specimens were immersed in a vessel containing 30 mL of distilled water and shaken at 50 rpm (dubnoff) for 24 h at room temperature (at around 20±3 °C). The resultant suspensions were filtered, and the residues were dried at 105 °C for 24 h. After weighing, the amount of non-solubilized drought material was determined. Solubility of the blends was expressed in percentage of specimen mass solubilized in relation to the initial mass [45].

Statistical analysis

Sisvar 5.0 was used for carrying out statistical analyses of the data through comparison of the means. Fisher's least significant difference and a Scott-Knott test were used at the 95 % confidence level for mechanical and physicals tests of WVP and solubility, respectively.

Results and discussion

FT-IR

Figures 4a-e present spectra on the infrared region for CMS and PVA biofilms and blends. The IR spectrum profile of the

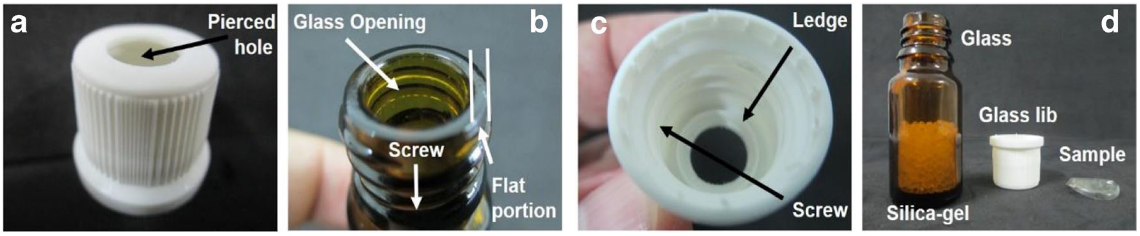
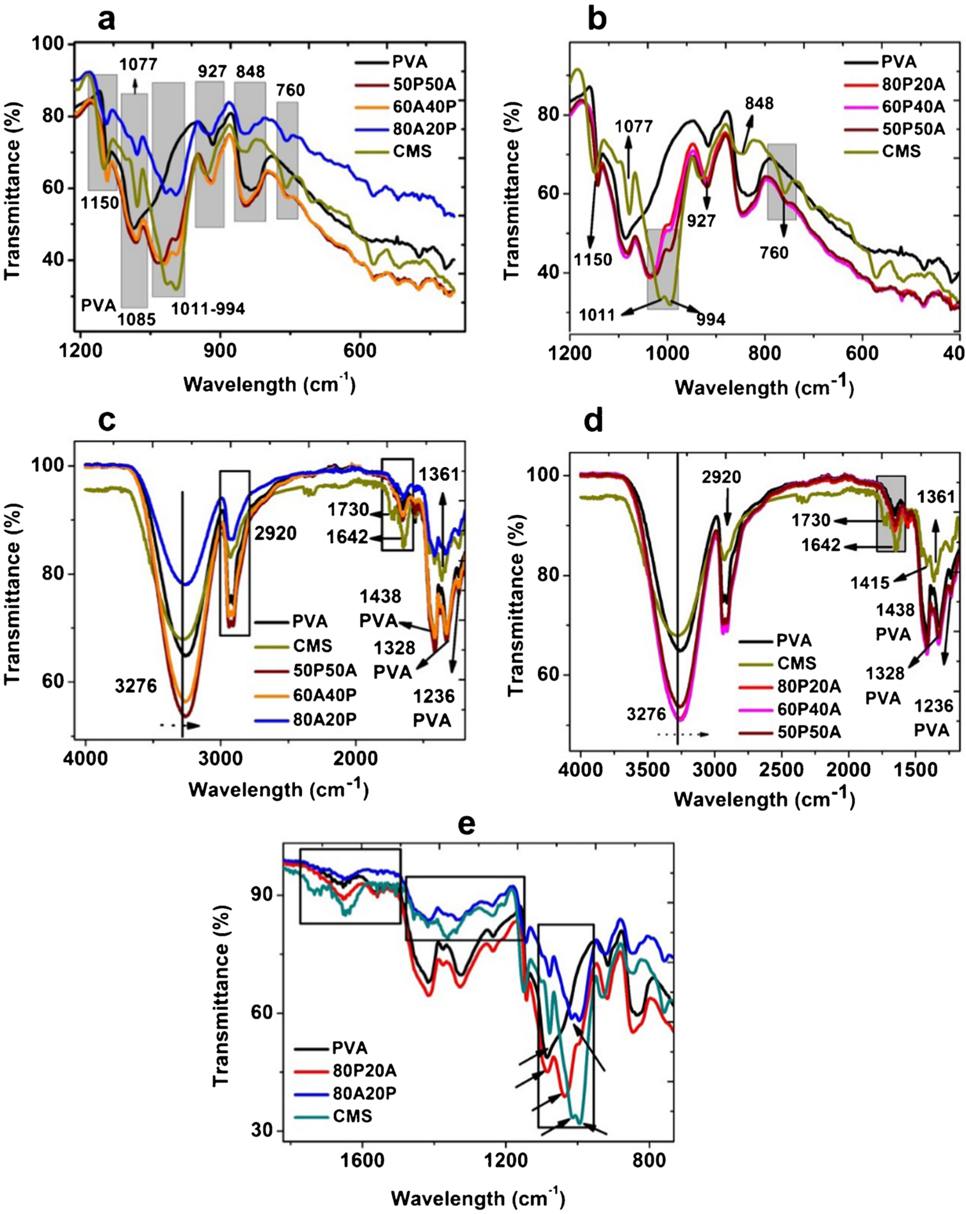


Fig. 3 Preparing the cell of water vapor permeability. **a**) Hole pierced on the cap for diffusion of water molecules in the sample; **b**) Flat portion where the cap ledge rests to avoid interferences between the pressures created. The screw aides sample fixation; **c**) Ledge to press the sample in the flat portion of the glass; and **d**) Parts that compose the cell

CMS biofilm is typical of polysaccharide biofilms, and the main observed absorptions were on 3276 cm^{-1} bands, attributed to the stretch of the free O-H group, and it was associated to inter- and intramolecular hydrogen bonds. Bands in the region between 3000 a 2800 cm^{-1} were attributed to C-H stretching; the band at 1642 cm^{-1} was attributed to the angular deformation of water; the region between 1410 and 1361 cm^{-1} was attributed to two bands of angular deformation of CH$_2$

Fig. 4 FT-IR spectra of CMS and PVA biofilms and CMS/PVA blends: (**a** and **d**) biofilms and blends with elevations on the proportions of CMS (50, 60 and 80 %) on the ranges from 1181 cm^{-1} to 302 cm^{-1} and 4079 cm^{-1} to 1193 cm^{-1}, respectively; (**b** and **c**) with elevated proportions of PVA (50, 60 and 80 %) on the range from 1184 cm^{-1} to 386 cm^{-1} and 4079 cm^{-1} to 1193 cm^{-1}, respectively, and (**e**) biofilms and blends 80P/20A and 80A/20P in the range from 1821 cm^{-1} to 733 cm^{-1}



and CH groups; the region between 1200 and 1100 cm^{-1} was attributed to stretches of C-O and C-OH. Bands between 1101 and 994 cm^{-1} may be attributed to angular deformations of C-OH and CH_2 groups. Bands at approximately 927 and 760 cm^{-1} are attributed, respectively, to stretching of the glycosidic bond α-1,4 and vibrations of glycosidic ring. A band at 848 cm^{-1} was attributed to the C-O-C bond of the glicopiranase ring [46, 47]. Similar results were found by Zullo & Iannance [48] and Fang et al. [49]. A band was observed at 1730 cm^{-1} and also a discrete band at 1205 cm^{-1} related to the carbonyl group that does not exist on the native starch. The existence of these bands is due to esterification of the CMS.

The main absorptions observed on the spectra of PVA biofilm are the bands 3698–3000 cm^{-1}, stretching of the group O-H, 2990–2800 cm^{-1}, stretching of the C-H group; 1438 and 1236 cm^{-1}, angular deformation of CH_2; 1328 cm^{-1}, angular deformation of C-H; 1141 cm^{-1}, stretching of the C-O-C group of the saccharide structure β (1–4); and 1085 cm^{-1}, stretching of the C-O group (Fig. 4a-e). The lack of peaks at 1733 and 1713 cm^{-1} (Fig. 4c-d) proves the high level of hydrolysis of the polymer, once these bands are attributed to the residual acetate group [50]. According to Chen et al. [29], maintenance of the peak at 760 cm^{-1} in the blends (characteristic vibration of starch) indicates successful blending with PVA (Fig. 4a-b).

The displacement of peaks at 1011 and 994 cm^{-1} for superior positions in different intensities clearly indicate compatibility among the polymers, thus suggesting the existence of specific interactions between the chains (Fig. 4a-b).

The wide band at 3276 cm^{-1} is due to the O-H groups that form hydrogen bonds. This band is greatly important because it indicates the presence of hydrogen bonds in the polymer [51]. A displacement was observed for the lower frequencies of this band (3276 cm^{-1}) for all the blends, and for bands with higher intensity for those containing larger amounts of CMS (Figs. 4c-d). This may mean the formation of bonds among the O-H groups of CMS and PVA [52, 53]. For this same band, a decrease in the transmittance value was observed, indicating an increase of hydroxyl groups bonded to the polymeric chain. This decrease becomes more pronounced with an increase of PVA content on the blend (Fig. 4d), which is what was expected since a high degree of polymer hydrolysis increases the number of hydrogen bonds [54]. The decrease of the band intensity at 1642 cm^{-1} (angular deformation of the water) after the formation of blends (Fig. 4c-d) suggests a decrease in the amount of water molecules absorbed by the matrices due to the strong hydrogen bonds caused by the increase of PVA content with high degree of hydrolysis and also by the chemical modification that occurred on the starch (esterification) [49].

When comparing the spectrum of obtained blends and the spectrum of pure polymers, specially for CMS, some displacements are observed in relation to PVA (1415, 848, 927 and 1150 cm^{-1}), variations of intensity (848, 1415, 927, 1077, 1150 and 2920 cm^{-1}), shape (848 cm^{-1}) and enlargement (1077 cm^{-1}), which suggests partial miscibility and, in certain conditions, favors the blend compatibility, depending on the proportion among the polymers applied on the mixture [55, 56]. The region between 1150 and 400 cm^{-1} overlaps several absorption bands of PVA and CMS due to the angular deformation of C-H and O-H bonds, among others. In this interval, a strong and distinct interaction of peaks is noted due to the stretching of the C-OH bond, which may indicate the compatibility of CMS and PVA (Fig. 4a-b). Short position displacements may indicate, as already proposed, the existence of local interactions among functional groups of the same nature. The intensity and number of intermolecular interactions between two polymers may be a positive factor for the compatibility of this system [57–60]. The region between 1200 and 900 cm^{-1} presents a significant change in relation to the pure polymers (Fig. 4a-b). A decrease in peak intensity was observed, of undefined peaks, and this may be attributed to the weakening of C-O bond deformations due to increasing forces of O-H interactions [57].

Morphology

SEM was used to obtain structural information of samples, such as homogeneity, the presence of delamination, disruptions or flaws. The presence of flaws may affect mechanical properties and barrier properties of the material. Analyses were performed on the surface of the biofilms and blends, showing a cohesive structure on most of the researched combinations. Figures 5a-b and c-d show the SEM micrographs of PVA and CMS biofilms, respectively, while Figs. 5e-h and 6a-g present the micrographs of the CMS and PVA blends.

PVA biofilms (Figs. 5a and b) presented a more compact, continuous, cohesive surface, and without formation of bubbles and cracks. Biofilms of CMS (Figs. 5c and d) presented cracks and fractures on the surface. Figure 5d shows more details on the fractures with a magnification of 2000x. The low quantity of the plasticizer (12 % in relation to the dry mass of CMS) also may have contributed to the development of the fractures, thus making the biofilms more rigid and brittle.

The 80P20A (Figs. 5e-f) and 20P80A blends (Figs. 6e-f) were more compact, continuous and cohesive when compared to other blends. Fractures, cracks, roughness and erupted bubbles were not observed on the surface of these blends. The separation of phases or delamination was not observed among the polymers. The structure obtained, which was more uniform, may indicate the existence of a higher compatibility, and this is an important aspect when considering mechanical and barrier properties. The matrix

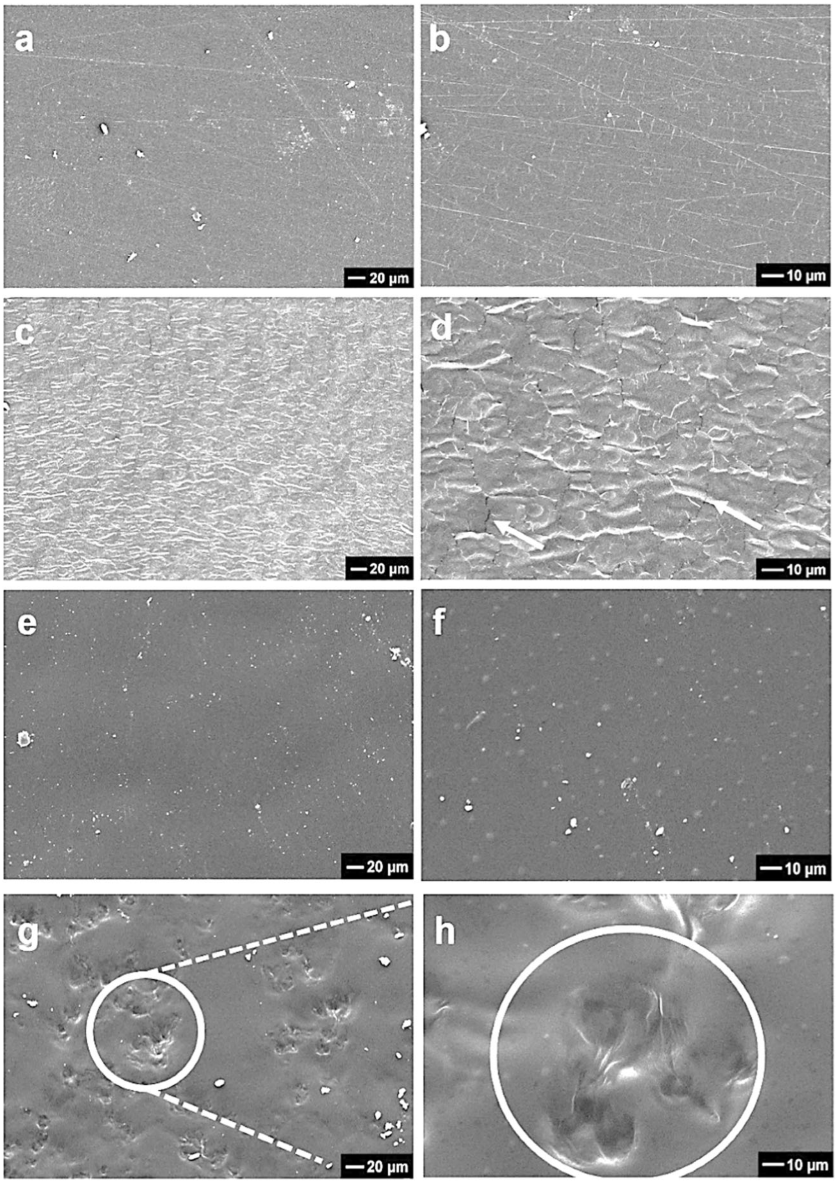


Fig. 5 SEM micrographs of the surface of CMS and PVA biofilms and CMS/PVA blends with magnification of 500x (scale of 20 μm) and 2000x. (**a**, **b**) biofilms of PVA; (**c**, **d**) biofilms of CMS; (**e**, **f**) 80P20A and (**g**, **h**) 60P40A. Arrows indicate small cracks and circles indicate the imperfections on the surface (roughness/ depressions)

homogeneity of a film is a good indicator of the structure integrity, as well of its mechanical properties. Mechanical tests performed with the blends showed a high value of elasticity and TS for samples containing 80 and 20 % of PVA, respectively, as presented in the next section. 50P50A, 40P60A and 60P40A blends (Figs. 6a-f) showed some discontinuities and cracks on the surface. Some incompatibility among the blend components was observed, which culminated in the difficulty of polymers to mix. The obtained morphological structure show the existence of a lower compatibility for these three proportions of PVA/CMS, as was proved by the poor values of mechanical properties obtained for these blends. Results of morphological analyses were consistent with results observed for mechanical tests, FT-IR, transmittance and WVP.

Mechanical properties

Mechanical properties of highest interest on flexible blends are those related to the TS. Such properties include the maximum TS, TB and TM. These properties are directly related to the nature of the material used and with the cohesion of the polymeric matrix. The preferred scenario is to present a high TS, while the value of elongation depends on the type of application of the film.

The effect of different proportions of CMS and PVA on the mechanical properties of the blends obtained was evaluated until the rupture of biofilms. Figures 7a-c show the TS, TB and TM for the blends according to the values obtained from typical stress/strain curves of these biofilms.

The mean TS, TM and TB values of the PVA biofilms were 40.3 MPa, 119 MPa and 391 %, respectively; for the CMS

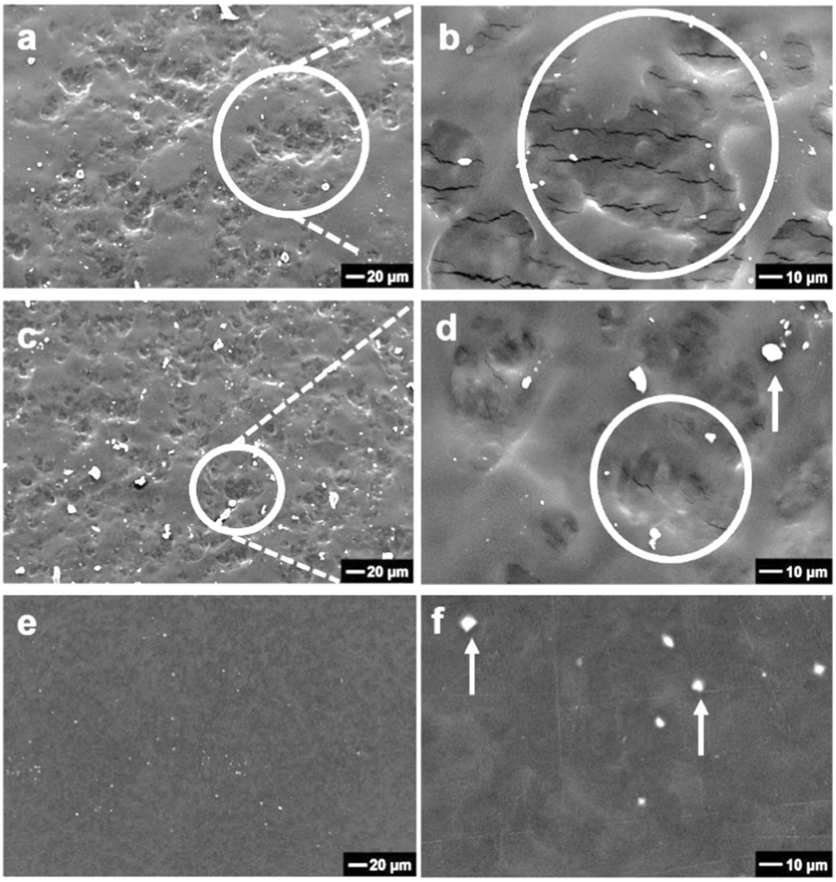
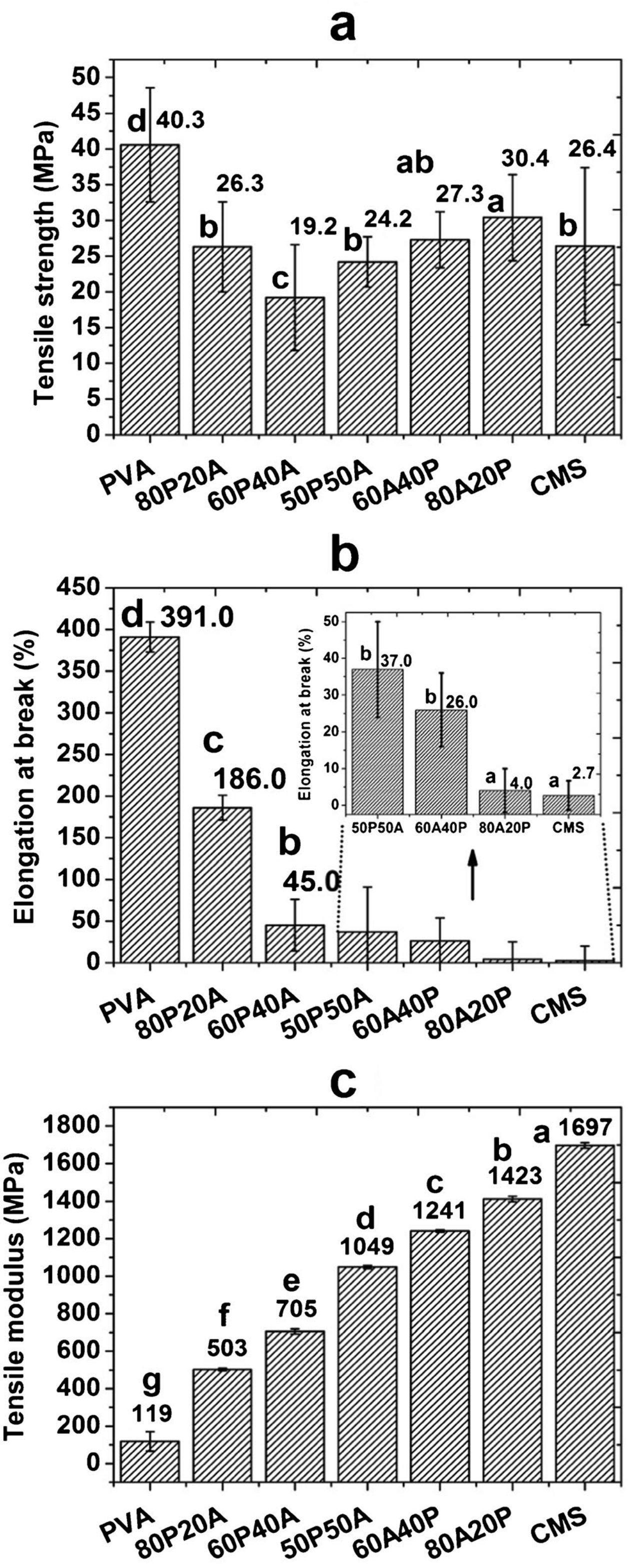


Fig. 6 SEM micrographs of the surface of CMS and PVA biofilms and CMS/PVA blends with magnification of 500x (scale of 20 μm) and 2000x. (**a**, **b**) 50P50A; (**c**, **d**) 40P60A; and (**e**, **f**) 20P80A. *Circles* indicate the imperfections on the surface (roughness/depressions). *Arrows* indicate eventual impurities

biofilms, the mean values found were 26.4 MPa, 1697 MPa and 2.7 %, respectively. All blends presented values significantly lower ($p \geq 0.05$) than to the TS of the PVA biofilm (40.3 Mpa), and samples with 80 and 60 % of PVA presented the lowest values (Fig. 7a). In relation to the CMS biofilm, the blend containing 80 % of CMS presented higher TS values, differing statistically from the others, improving by 15 % its mechanical property of TS in relation to the pure biofilm of CMS. The blends containing 50 and 80 % of PVA were not significantly different at 5 %, compared to modified starch film.

In relation to TB and TM, it was noted that the higher contents of CMS on blends make them less flexible, as can be observed in Fig. 7b-c. There is no significant difference at 5 % using Fisher's least significant difference test between the blends containing 40, 50 and 60 % of CMS. Results showed significant improvements ($p \geq 0{,}05$) of these properties when PVA was added to the blends, becoming more resistant and more flexible when compared to the CMS biofilm. The 80P20A blend kept the strength of CMS biofilm, acquiring the elasticity of the PVA biofilm, thus becoming more tenacious and developing a more ductile behavior. These results suggest that the blends became miscible, presenting partial compatibility, as observed for those with higher proportions of PVA, when strength decreased. Such results were corroborated by the FT-IR and SEM observations of the previous sections. Several works found in the literature also presented similar results [29, 61–65]

The lowest synergism caused by the higher proportion of PVA on the blend may have been one of the factors responsible for the partial compatibility among the polymers, which was confirmed by some authors [29], who stated that high contents of PVA on the blends with starch causes a lower compatibility, with decrease of TS. Chen et al. [29] showed that the addition of starch to the PVA biofilms did not improve TS due to the excellent individual mechanical properties presented by PVA. Those authors also mention the low compatibility among these polymers as the probable cause for this behavior. According to Lawton [66], the amount of amylose present on starch interferes on the compatibility of this polysaccharide with PVA during the formation of blends. Higher concentrations of amylose present better mechanical properties in relation to structure with a high content of amylopectin, comments the author, which still asserts a more practical and economic use of a blend with higher amount of starch. In this sense, Sin et al. [67] showed through FT-IR analysis that the hydrogen bonds between PVA and starch are stable, and the high concentration of PVA in relation to starch makes the system more stable and compatible. The mechanical behavior, analyzed as a whole considering the TB, showed that the blend 80P20A presented the best result once the elongation



◀ **Fig. 7** Average and standard deviation (SD) values of tensile properties: (**a**) maximum TS; (**b**) TB; (**c**) TM of biofilms and blends with different proportions of CMS and PVA. Average values refer to five determinations. *Bars* indicate the values of standard deviation. The *letters* "A" and "P" refer to CMS and PVA, respectively, while the *numbers* before the *letters* are related to the proportions of each polymer on the blend. a, b, c, d, e, f, g: means the different letters represent significantly different values at ($p \leq 0.05$) using Fisher's least significant difference test

increased without significant reduction of strength. There was a large increase in the elongation of this blend in relation to the others and to the CMS biofilm. Follain et al. [68] and Azahari et al. [69] found a similar behavior.

Analyses have showed (Fig. 7b) that the increase of the proportion of CMS in the blends caused a reduction of TB values, making them brittle and stiff, with high values of elasticity modulus (Fig. 7c) as a consequence of the high content of crossed bonds [70]. According to some authors, the absence of a coupling agent is another factor that may have contributed to low performance [66, 69, 71].

Blends containing high contents of CMS became stronger than those with higher proportion of PVA. More intra- and intermolecular interactions between PVA and CMS by means of hydrogen bonds contributed to this behavior. However, the increase on the proportion of CMS in the blends decreased the TB values (Fig. 7b), becoming brittle and stiffer, with high TM values (Fig. 7c), which is a consequence of a high content of cross-linking bonds [68].

The 80P20A blend was the most efficient and presented the best mechanical properties, once it could absorb a great amount of energy without breaking due to its ductile behavior with an intermediate TS value (26.3 MPa) and an elevated value of elongation (186 %). This TS value is lower than the value presented by linear low-density polyethylene (LLDPE, 37 MPa), polypropylene (PP, 35 MPa), and higher than values presented by low density polyethylene (LDPE, 6.9-16 MPa), polyesteramide (PEA, 17 MPa) and highly branched LDPE (8.5-10.5 MPa), which are polymers frequently used in the production of flexible packages for the food industry and agricultural sector [72, 73]. However when compared to this 80P20A blend, those polymers presented higher TB values : 100 % for PP, 3-6 % for polylactic acid (PLA), 2-20 % for polyglycolic acid (PGA), 630 % for LLDPE, 100-800 % for LDPE and 500 % for highly-branched LDPE [72]. In this context, except for LLDPE, the blend was more resistant and less flexible if compared to films produced by LDPE polymers and highly-branched LDPE, and more flexible compared to films produced by PP, PLA and PGA, but was totally biodegradable.

It is essential that the blend retain its integrity under the normal stress applied during transport and handling. Blends with adequate barrier properties may be inefficient if mechanical properties do not allow fopr maintenance of the integrity of the material formed during handling, packaging and transport. It is essential that the blend retain its integrity under the normal stress applied during transport and handling. Blends with adequate barrier properties may be inefficient if mechanical properties do not allow maintenance of integrity of the material formed during handling, packaging and transport.

The mean thickness found at 15 random points on each specimen using PVA/CMS in different proportions, including biofilms of PVA and CMS, ranged between 0.047 and 0.112 mm. The value found for the blend P80A20 ranged from 0.064 to 0.093 mm. The biofilms of CMS and PVA presented the lowest and the highest mean thickness, respectively.

This variation of thickness may be explained through structural changes caused by the swelling of the matrix during the preparation, thus affecting the structure of films and forming different re-arrays for each formulation. Difficulties in controlling the mass/area ratio, problems in controlling the relative humidity of the air and variations in the solution viscosity of the film also may have influenced the thickness values [74].

Thermogravimetric analysis (TGA)

Figure 8a-d show the curves of TG and DTG, while Table 1 presents data obtained from these curves for the biofilms of PVA and CMS, as their blends. The CMS biofilm presented initial temperature of decomposition (T_{onset}; 320 °C) superior to those presented by the PVA biofilm (248 °C; Table 1). The same happened with the maximum temperature of degradation (T_{max}315 °C) for the CMS biofilm, which was superior to those found for the PVA biofilm (Table 1). The CMS biofilm was more thermodynamically stable due to a higher initial stability. The increase of molecular mass caused by the high concentration of amylopectin, as well as the covalent bonds formed by the acylation of these groups, may have contributed to this higher thermal stability [75, 76]. According to these authors, lower amounts of hydroxyl groups for the formation of decomposition reactions may have contributed to this higher thermal stability, since the same significantly reduce the mass loss of the samples. In this stage, dehydration of hydroxyl groups of neighboring glucose chains also may have occurred, resulting in the formation of C-C bonds or in the disruption of the glucose rings, which, in this case, may have collaborated for the formation of aldehyde groups. Several works reported the improved thermal stability of acetylated starch in relation to the native one [77, 78].

The mechanism of thermal decomposition of the starch biofilm may be divided in three stages: the first phase (at around 100 °C) is the physical dehydration, which depends on the amount of water absorbed and accumulated on the biofilm. The second phase is the chemical dehydration and thermal decomposition in which the reactions start at about 300 °C with the thermal condensation of the hydroxyl groups in the starch chains, thus forming segments of ether, releasing water and other species of small molecules. The last stage of thermal degradation is carbonization at higher temperatures (>500 °C), whose relative intensity of aromatic carbon resonances increases over the intensity of aliphatic carbons. This may explain the larger amount of residuals on the pyrolysis obtained by the CMS biofilm (Table 1).

Incorporation in the same proportion of both PVA and CMS to the blends changed the value of T_{max} for higher values of temperature, also increasing the value of T_{onset} in relation to the values presented by pure biofilms of PVA and CMS. This

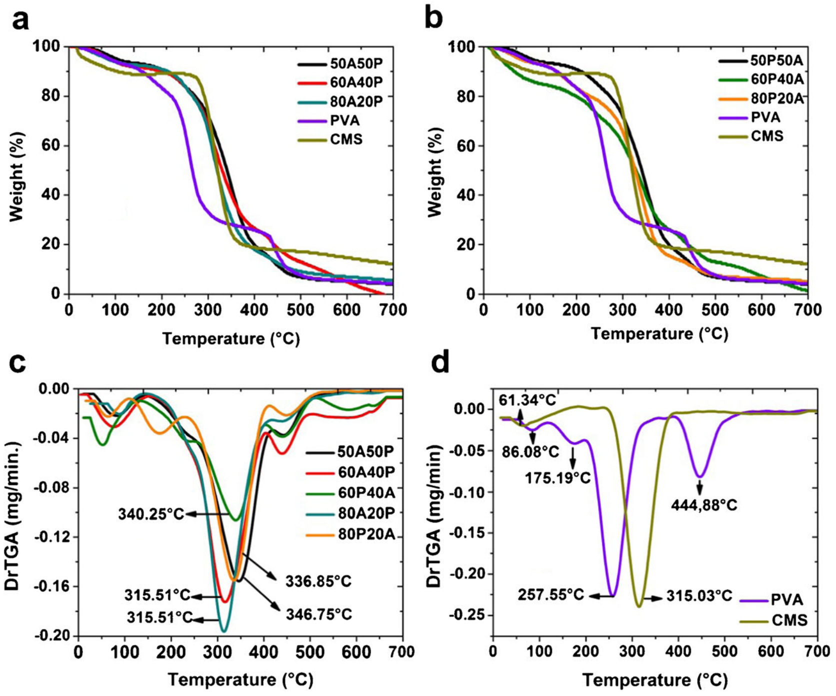


Fig. 8 **a** TG curves of PVA, CMS and blends of PVA/CMS with elevation on the proportions of CMS (50, 60 and 80 %); **b** TG curve for PVA, CMS and blends of PVA/CMS with elevation on the proportions of PVA (50, 60 and 80 %); **c** first derivative of the TG curve (DTG) for all the obtained blends; and **d** DTG for the PVA and CMS biofilms

Table 1 Data obtained through the TG and DTG curves of pure biofilms and of the mass composition of the PVA/CMS blend

Parameters	PVA	80P20A	60P40A	50P50A	40P60A	20P80A	CMS
T_{onset}[1]	248	286	289	276	271	278	320
T_{endset}[2]	309	383	409	400	411	365	346
P_{M2}[3]	66	77	55	75	66	75	79
T_{max}[4]	258	337	340	347	316	316	315
P_{M300}[5]	67	34	37	28	30	33	25
R_{final}[6]	4.4	6.4	2.7	5.8	1.5	6.9	11.2

[1] Initial temperature of decomposition (T_{onset}) in °C; [2] final temperature of decomposition (T_{endse}t) in °C; [3] mass loss of the second stage of decomposition (T_{M2}) in %; [4] maximum temperature of decomposition (T_{max}) in °C; [5] mass loss at 300 °C (T_{M300}) in %; and [6] final residues (R_{final}) in % for PVA and CMS biofilms and blends of PVA/CMS

demonstrated an improvement in the thermal stability of the blends (Tab. 5.8). Better results were achieved when 50, 60 and 80 % of PVA were added to the mixtures, probably due to the greater compatibility and homogeneity presented by them. It was also observed that blends with higher proportions of PVA were more thermally stable in relation to the blends with the same proportions of CMS. The biofilm of CMS presented two degradation stages, while the biofilm of PVA presented three stages. The blends presented three degradation stages, indicating a good synergy among polymers [79, 80], which corroborated with results found by the SEM and FT-IR analyses.

The behavior of the mass loss curves was similar for both blends with higher proportions of CMS (Fig. 8a) and higher proportions of PVA (Fig. 8b). The mass loss between 35 and 150 °C occurred, in general, because of the loss of volatile compounds (water, glycerol, urea, etc.). The second stage of thermal degradation (~150-500 °C) was predominantly due to the degradation of hydroxyl groups and subsequent formation of species of unsaturated and aliphatic carbon of low molecular weight [30]. The final stage (above 500 °C) was caused by carbonization [81].

The PVA/CMS blends showed lower values of mass loss until 300 °C when compared to the PVA biofilm (Table 1). This occurred partially due to the mixture of PVA and CMS being synergistically compatible [30], while the PVA biofilm lost 67 % of its mass at 300 °C, the CMS biofilm lost just 25 %. Liu et al. [82] explained that this behavior may be related to the fact that CMS presents a cyclic hemiacetal group in its structure. Similar results were found elsewhere [80, 30, 82].

Biofilms with higher proportions of PVA lost more mass at around 300 °C when compared to blends with higher proportions of CMS. The 60P40A blend presented a higher loss which may be related to the low compatibility among these mixtures for higher amounts of PVA, and this loss was predominantly related to the PVA decomposition (Figs. 8a-b). Similar results were found by Gaspar et al. [83].

After 600 °C, it was observed that the concentration of ashes for the PVA biofilm and all the blends was lower than for the CMS biofilm (Figs. 8a-b). This may be associated with the chemical structure of starch, which forms a species layer of thermal resistance and, consequently, produces an elevated degree of residual carbon within these ranges of temperature ranges [80]. The results were consistent with the literature [80, 30].

Physical properties

Optical transmittance - Tr

The optical properties of package biofilms may influence the appearance of the packaged product. Many times, a transparent package is desirable, which allows visualization of the product [84]. The brightness and transparency of some plastic packages constitute a tool for good visual presentation of the product, however, protection against light incidence is necessary, as in the case of products sensitive to reactions of deterioration catalyzed by light [85], such as some "*much-films*" and covers for greenhouses used in the agricultural sector. These characteristics are consequence of the morphology or chemical structure related to the molar mass of the components used [86].

Figures 9a-b show the Tr curves for the obtained biofilms, in which those produced with PVA became more transparent and those produce with CMS were more opaque. The curves were displaced for regions of lower transparency according to the increase of CMS proportion in the blends. Mali et al. [87] also verified that for films of yam starch, the opacity increased with increasing starch concentration. Chandra & Rustgi [88] also observed an increase of opacity when improving the concentration of starch on films of LDPE and maize starch. The same occurred with Ortega-Toro et al. [89] when studying the influence of incorporating hydroxypropyl methylcellulose (HPMC) and citric acid in the formation of thermoplastic biofilms of starch. The increase of HPMC in the starch matrix increased the opacity.

The higher amount of CMS in the blend may have favored dispersion of light, causing a reduction in their transparence.

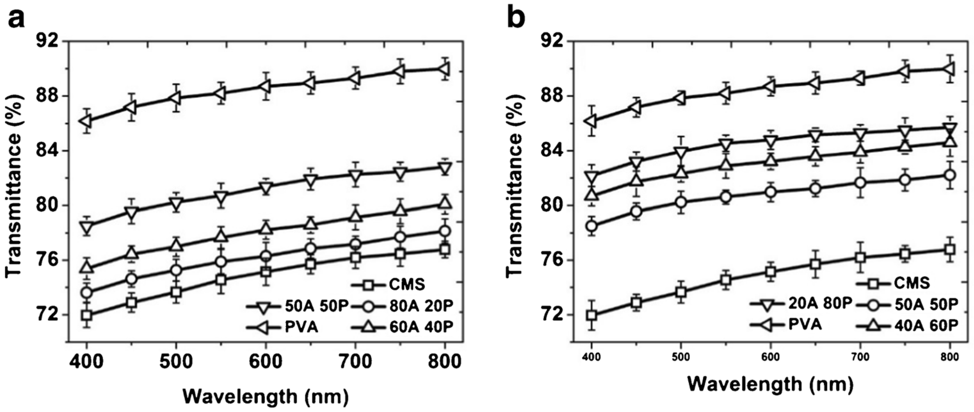


Fig. 9 Mean values and SD of transmittance obtained for biofilms and blends of CMS/PVA in the range from 400 to 800 nm; (**a**) higher proportions of CMS; and (**b**) higher proportions of PVA on the blends

The great amount of amylopectin present in the cassava starch [90] may have contributed to increased opacity of the obtained blends, once it is formed by branching chains that may have contributed to the formation of crossed bonds and then increase the degree of chain entanglement [87]. The interactions and alignment among chains of amylopectin and amylose also comprise a factor to be considered, because these interactions may lead to the formation of cross-linking bonds, which may deviate or absorb the passage of light through the blends.

The external roughness is another parameter that may influence opacity. Morphological analysis revealed some samples containing roughness and depressions (Figs. 5g-h, 6a-b and c-d), which may have deviated the light over the blends, making them more opaque.

The opposite was observed when higher proportions of PVA were added to the blends, i.e., curves were displaced for regions of higher transparency. Results were similar to the literature [91]. Limpan et al. [91], studied the influence of the degree of polymerization and molecular weight of PVA on the properties of blends formed with myofibrilar proteins of fish, and observed that the formed blends presented poor barrier properties against visible light, and these properties were directly influenced by the concentration and degree of polymerization of PVA. Results showed that an increased concentration and/or degree of polymerization of PVA in the blends caused the decrease of the optical barrier, thus allowing the passage of more light through the blend. It suggests that incorporation of PVA in the blends contributes to an increased transparency of the resultant blends.

Furthermore, the opacity tends to increase linearly with the thickness. Similar results were found by Cuq et al. [92], studying the opacity of biofilms of protein on Nile tilapia and beef. According to the authors, the opacity was not influenced by the thickness of biofilms between 0.010 mm and 0.053 mm.

Figures 10a-i show the transparency of the biofilms. It is observed that biofilms with higher contents of PVA presented higher transparency than blends with higher contents of CMS, repeating the same behavior of transmittance curves plotted in Figs. 9a-b. More opaque biofilms and blends are adequate for products more sensible to light, but on the other hand, the transparency may influence a consumer's choice for the packaged product.

Water vapor permeability (WVP)

The migration of water vapor is one of the main factors altering the sensory quality and stability of food storage, and it also may interfere mechanical properties and promote the dimensional instability of the obtained blends [45, 87]. WVP is defined by the ASTM E96-00 [93] as the rate of transmission of water per unit of area through the film of known thickness induced by a gradient of pressure between two specific surfaces of specific temperature and relative humidity. The coefficient of permeability is not a function of just the chemical structure of the polymer, but it also depends on factors like density, crystallinity, polymer cross-linking, plasticizer, sensitivity to humidity and temperature. The mean WVTR and WVP values of the blends are presented in Table 2.

Since the beginning of the evaluation, a linear behavior was observed for all the samples when the permeability cell mass was increased, as the amount of absorbed water molecules in one side of the blends was desorbed for the opposite side. All the linear expressions presented a coefficient of correlation R^2 between 0.97 and 0.99. The less permeable and statistically different ($p\geq0,05$) blends were those formed by 60 and 80 % of CMS, while there was not a significant difference ($p\leq0.05$) between blends more permeable with 80 and 60 % of PVA compared to the PVA film. Increasing the PVA content in the blends caused an elevation of both WVTR and WVP for all the obtained blends, while the opposite occurred when FMM was added to the blends (Table 2). These results were not expected because PVA content is in a higher degree of hydrolysis and should have caused the decrease of WVP, since the strong hydrogen bonds among the molecules allowed the formation of more cohesive and dense structures. It seems that PVA acted as a facilitator of water transport through the blend due to the nature of its chemical structure in which several hydroxyl groups are present [94–96]. The great amount of

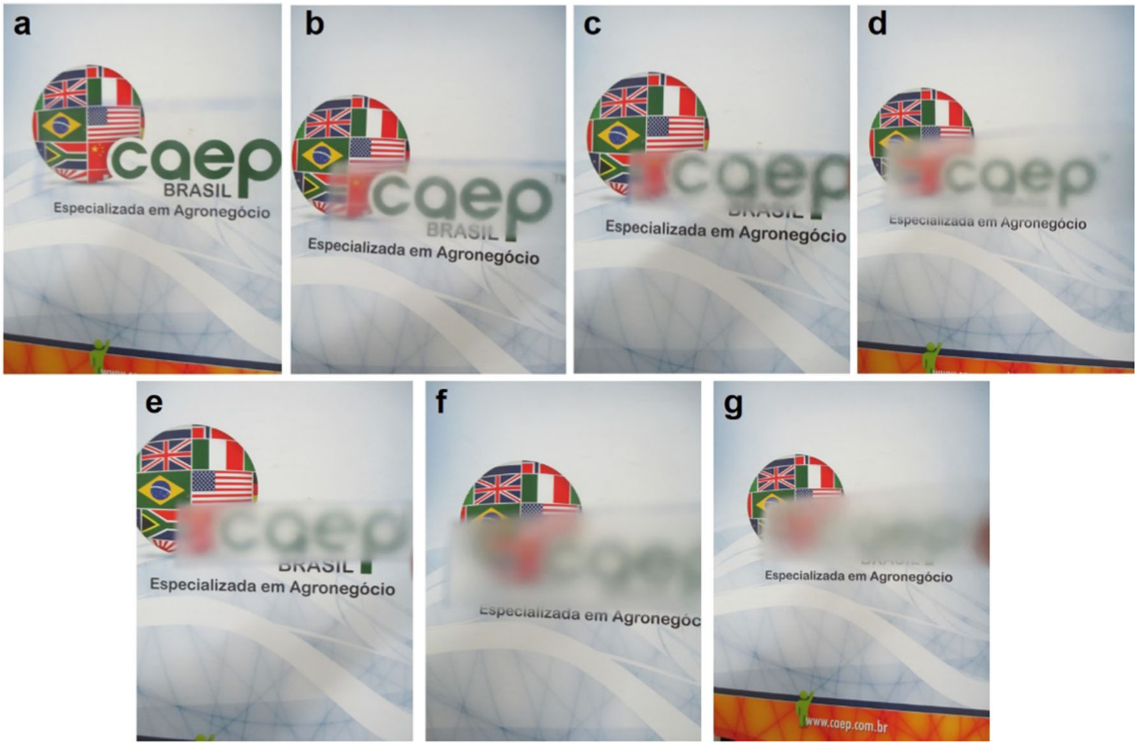


Fig. 10 Visual aspect of (**a**) PVA films; (**b**–**f**) blends obtained with different proportions of CMS and PVA; and (**g**) CMS biofilm

plasticizer (glycerol) inserted is a factor to be considered, once the same is favorable to the adsorption and absorption of water molecules by the biofilm [97]. Glycerol improves the mobility of chains with a plasticizing effect, thus increasing the free volume of the sample (more empty spaces in the structure). The insertion of the ester group between to the amylose and/or amylopectin chains that compose the cassava starch is also a possibility, since these bonds make difficult the alignment among these chains. According to Brandelero [98], the hydrophilic character of the blend increases the amount of water absorbed from the biofilm matrix. These results corroborate with the mechanical and thermal analyses. All the found values, for both WTVR and WVP, remained within the range of values mentioned for biofilms of pure CMS and PVA, i.e., values between 0.4 and 1.2 %.

Table 2 Mean values and standard deviations (SDs) of water vapor transmission rate (WVTP) and water vapor permeability (WVP) of the PVA/CMS blends

PVA/CMS Blends [1]	Thickness[2] (mm)	WVTR[3] (gH_2O/m^2 day)	WVP[3] (g mm/KPa day m^2)
100/0	0.063±0.03	31.3±0.9	1.1±0.06 e
80/20	0.077±0.02	29.1±0.8	1.2±0.01 e
60/40	0.053±0.06	28.8±0.8	1.1±0.03 e
50/50	0.049±0.09	27.9±1.0	1.0±0.02 d
40/60	0.047±0.03	25.5±1,1	0.8±0.01 c
20/80	0.043±0.08	23.8±0.9	0.6±0.03 b
0/100	0.047±0.05	17.2±1.0	0.4±0,05 a

[1] blend produced from polyvinyl alcohol (PVA) and modified cassava starch (CMS; %); [2] mean of ten measurements followed by the SD; [3] mean of three measurements followed by the SD. a, b, c, d, e: reported values correspond to the mean±SDn. Values within each column followed by different letters indicate significant differences ($p \leq 0.05$) using the Scott-Knott test

The lower content of PVA in the blends may have reduced the diffusion of water through the matrix, thus decreasing the permeability of the mixtures [99]. The use of the lowest content of PVA may have induced a stronger interaction between PVA and CMS, thus resulting in lower values of permeability to water steam. A similar process occurred in studies performed by Limpan et al. [91], who suggested as a cause the increase of the disturbance degree of the amorphous region caused by the elevation of PVA contents, which, according to the researcher, could have caused the increase of free volume among the molecules of the blend components. According to Park & Chinnan [100] and Muller et al. [8], the reasons for this behavior are connected to structural changes of the formed biofilm matrix. In this sense, Schwartzberg [101] affirmed that the transmission of water through hydrophilic materials is much more complex due to the non-linearity of their sorption isotherms.

Except for the blends containing 50 and 60 % of CMS, which presented small cracks, morphological analysis indicated a lack of fissures or pores that may cause an increase in WVP. FT-IR results (Figs. 4a-e) showed that good interactions occurred among the polymers for the obtained blends. Results for mechanical and transmittance properties are in accordance to those measured for WVP, once blends with higher contents of PVA were more flexible and transparent as a function of a probable disorder in the amorphous region, as previously discussed. Similar results were found in the literature [43, 102, 29, 103].

Moreira [104] found for the blend of starch/pectin (1:1), WVTR with a value of 76.2±2.28 g/m^2.day (23 °C, 75 % RH). Averous & Boquillon [105] found for the poly(butylene succinate co-adipate) (PBAT), mean WVTR values of about 330 g/m^2.day in an atmosphere of 75 % at 22 °C. By analyzing the effect of plasticizers in WVP from hydroxypropylmethyl cellulose (HPMC)-coated films, Laboufie et al. [106] obtained a value of 1.7 g.mm/m^2.day.Kpa (40 °C, 75 % RH), much higher than to those found for the blends obtained in this work. LDPE polymer, often used in the production of plastic bags and in the agricultural sector, presents a WVP of only 0.11 g.mm/m^2.day.Kpa (40 °C, 75 % RH), but exhibits low barrier properties to oxygen and to solvents, apart from not being biodegradable and showing reduced mechanical strength [106]. PLA, a biodegradable polymer with similar properties to polystyrene, could be used in the field of plastic bags and agricultural sector, if it does not exhibit a low TB and high cost compared to the polymers employed for this purpose. PLA presents a WVTR of 12.6 g/m^2.day (23 °C, 50 % RH) [107]. This value is lower than that observed for the blends of this work with a high proportion of starch.

Solubility in water (SOL)

The solubility of the specimens by the direct contact with water is an important property for biodegradable films; for several applications, it is necessary to know the resistance of the material to water, as well as a possible interference on mechanical properties. All resulting blends after remaining immersed in water during 24 h under agitation were apparently integer in relation to the form, well flexible and folding on handling. However, the visual aspect of the samples became opaque. This indicates that the intra- and/or intermolecular chain entanglements formed by PVA and CMS remained intact [108].

The insertion of more PVA to the blends make the materials produced less resistant to water absorption in relation to blends containing the same concentrations of CMS (Tab.5.10). It was observed that results were very similar. Blends containing 20 and 40 % of FMM did not differ statistically at 5 %, as determined by the mean of the of Scott-Knott test. The same behavior was observed for the samples with 50 and 60 % CMS. The values of thickness of specimens were very similar, indicating homogeneity among them.

Indeed, these essays presented the same behavior of the previous essay regarding permeability to water steam, meaning the solubility of blends was reduced as a function of elevating the CMS content. The low solubility of CMS may have contributed to the reduced permeability of the blend, because the solubility of the components has a direct relation with structural components of the biofilm and it will interfere with the barrier property (to water steam). It is probable that the increase of solubility and permeability to water steam for higher contents of PVA is related to the increase of hydrophilic portions of the blend, as already commented. The statement that PVA molecules with a high degree of hydrolysis could interact among themselves through hydrogen bonds, thus increasing their resistance to water, was verified in this study, as shown by Table 3. The same behavior was expected for the blends, which did not occur as a function of modifying the blend structure after the union of CMS and PVA biofilms.

This higher solubility can be related to increases in the amount of hydroxyl groups in the polymer matrix with increased formation of hydrogen bonds with water resulting in blends being more soluble [109, 110]. The explanation by some authors, e.g., Chiumarelli & Hubinger [111] and Mehyar & Han [112], after to find similar results, is based on water penetration in the blend occasioned by a possible disruption of intermolecular interactions. According to these authors, this behavior may have caused higher water diffusion followed by an increase in solubility.

The blends with a high proportion of PVA were more permeable to water steam and more soluble in water, which makes possible their application on products that need previous hydration, as in the case of fertilizers of slow nitrogen release, which need a high solubilization in order to be released. The coverage of agricultural seeds that need a rapid absorption of water to germinate in the field, bagging of fruits

Table 3 Mean values and SDs of the SOL of PVA/CMS blends

Blends ^{1} PVA/CMS	Thickness^2 (mm)	SOL^3 (%)
100/0	0.062±0.002	21.1±2.11 a
80/20	0.068±0.004	25.4±4,58 b
60/40	0.062±0.001	25.0±3.22 b
50/50	0.058±0.003	23.3±2.16 c
40/60	0.057±0.001	22.8±2.08 c
20/80	0.064±0.002	20.2±3.11 d
0/100	0.056±0.001	18.6±4.23 e

^{1} blend produced from polyvinyl alcohol (PVA) and modified cassava starch (CMS; %); ^{2} mean of ten measurements followed by the SD; ^{3} mean of three measurements followed by the SD. a, b, c, d, e: reported values correspond to the mean±standard deviation. Values within each column followed by different letters indicate significant differences ($p \leq 0.05$) using the Scott-Knott test on pre-harvest and bags for seedlings are other applications for the blends with higher proportions of PVA.

Blends with a high content of CMS, contrarily, may be used on packages of meat, cheeses, fruits and some fresh vegetables, thus avoiding humidity loss, however, there must be a balance between O_2 and CO_2 [113]. In this sense, blends formed by starch and PVA guarantee this balance. The cassava starch presents values of permeability to O_2 similar to cellophane, which is very much required for packages of food [112]. Packages containing starch are very selective to gas permeability, in which the permeability to O_2 is much lower than to CO_2 [114]. Its use as film to cover soils (*much film*) is recommended, because it reduces the humidity losses by evaporation, thus increasing the efficiency of water use [107]. In this case, the use of UV light stabilizers will be necessary due to their oxidation. Studies regarding the utilization of blends with modified starch and polyesters in the production and use of these products in the agricultural sector were found in the literature [115–117]. According to the authors, the results were similar to those found with polyethylene films, but with the advantage of biodegradability of theses blends. Products that are susceptible to deterioration due to the gain of humidity as dehydrated food and mixtures of powder that harden or agglomerate also are indicated to be packaged by these blends, which present low WVP and SOL [118].

Conclusions

Morphological, TG and IR spectroscopic analyses confirmed the compatibility among the polymers forming the blends for most of proportions. SEM and FT-IR analyses confirmed the effective interaction among the polymers used. The increase in the proportion of CMS led to the formation of blends more rigid, brittle, thermally stable, opaque and less permeable (to water vapor), while the addition of a higher amount (60 and 80 %) of PVA originated blends more flexible and ductile, less stable to temperature, more transparent and more soluble (in water). Blends of CMS with proportions of 60 and 80 % were more thermally stable (up to 300 °C) in relation to the blends with the same proportions of PVA. Blends produced with PVA and CMS are cheaper alternatives for the production of more sustainable biodegradable films to attend to the demands of the plastic packaging and agricultural sectors.

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