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Study of the Mechanical and Biodegradable Properties of Cassava Starch/Chitosan/PVA Blends

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Summary: Natural and synthetic polymers have been widely used for preparation of biodegradable materials. In this work, three different blends containing starch/chitosan/PVA were prepared by varying the contents of cassava starch (MS blend), chitosan (CH blend) and PVA (PVA blend). The films were characterized through tensile/strength tests, infrared spectroscopy and biodegradation tests in soil. The PVA blends showed higher values of extension at break and lower loads, leading to more flexible materials when compared to MS and CH blends. The infrared spectra of all blends showed new bands that can be assigned to the carbonyl group (1716–1732 cm^{-1}). Besides, changes in the intensity of other characteristic bands indicate that there are significant physical/chemical interactions among the components of the blends. All samples were shown to be biodegradable, leading to weight losses above 50% after 18 days of biodegradation in soil.

Keywords: biodegradation; cassava starch; chitosan; polymeric blends

Introduction

The study of potentially biodegradable materials has grown significantly in the last decade as an attempt to reduce the impact caused by waste dumping and aiming at the reduction of the overall volume of discarded materials. Microbiological polymer degradation is usually caused by microorganisms that use polymer materials as sources of nutrients under normal conditions of humidity, temperature and pressure. Such materials are almost always hydrolysable to CO_2 and H_2O or CH_4.[1] The use of biodegradable polymers can be particularly important for applications in agriculture and production of lightweight containers, irrigation pipes and coverage films (greenhouses, low tunnels, mulching, etc.).[2]

Starch is one of the alternative sources of raw materials for production of biodegradable plastics because of its film formation properties and natural abundance. For this reason, blends of starches and synthetic polymers have been extensively studied in the literature.[3] However, films containing 100% of starch are fragile and brittle, being necessary to use additives. Water, oligosaccharides, polyols and lipids are widely used as additives to overcome some of these problems.[4,5] Poly(vinyl alcohol) (PVA) also finds widespread use as additive in blends due to its excellent mechanical properties and biodegradable properties.[6,7] The stereochemical and physicochemical properties of PVA are highly dependent on the preparation method. For instance, the solubility of PVA in water depends on the degree of hydrolysis. Usually, PVA with high degree of hydrolysis (above 90%) can be dissolved in water at 70 °C.[6] Chitosan has also been used frequently as additive in blends with starch or PVA due to its polyelectrolyte nature, high capacity to absorb water, biocompatibility, biodegradability and non-toxicity.[8]

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Blends of starch and chitosan have been reported as potentially useful materials for development of food packaging, especially as edible films and coatings.[9] Chitosan can also be blended with synthetic polymers to yield products for therapeutic applications.[10]

Based on the previous discussion, the main objective of the present study was the preparation of blends containing starch, chitosan and PVA and the study of the blend degradation in soil, aiming at the posterior preparation of biodegradable films for use in agriculture (mulchings), medicine (membranes) and food packaging.

Experimental Part

Raw Material

The unfermented cassava starch (*Manihot esculenta Crantz*) was obtained from the fresh roots of cassava, purchased in the local supermarkets. Chitosan (degree of deacetylation of 82% and M_w of 1×10^5 g/mol) was provided by Polymar (Ceará, Brazil). PVA(degree of hydrolysis of 86.5–89.5% and molar mass of 100.000 g/mol) was provided by Vetec (Rio de Janeiro, Brazil).

Blend Preparation

Blends were prepared by casting specified contents of cassava starch (MS), chitosan (CH) and PVA, as described in Table 1. Starch suspensions (1.5% w/v) were initially treated at 95 °C for 1 hour. Then chitosan (1% w/v in acetic acid) and PVA (1% w/v) solutions were added. The suspensions were mixed at 70 °C and stirred for 1 hour until. The final homogeneous solutions were cast on acrylic plates. Specimens were dried for 3 h at 60 °C in a recirculating air oven. Obtained films were peeled off the plates, labeled and stored for posterior analysis.

Film Thickness

Film thickness was measured with a digital micrometer (Mitutoyo, ±0.001 mm) at 12 different points. Averages were saved for quantitative analyses.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

An IR Prestige–21 FTIR (Shimadzu, Japan) spectrometer equipped with an attenuated total reflectance (ATR) probe was used for infrared analyses of the films. Films were placed directly on the ZnSe crystal, with refraction index of 2.4 and angle of incidence of 45°. All spectra were recorded at ambient temperature and averages of 16 scans were saved for quantitative analyses. The resolution was equal to 4 cm^{-1} in the range of 4000–400 cm^{-1}.

Mechanical Properties

Films were characterized through tensile tests using a universal testing machine (Instron, model 4333), according to standard D882-97.[11]

Table 1.
Composition (w/w) of MS/CH/PVA blends.

Blend 1[a]				Blend 2[b]				Blend 3[c]			
Samples	MS (%)	CH (%)	PVA (%)	Samples	CH (%)	MS (%)	PVA (%)	Samples	PVA (%)	MS (%)	CH (%)
MS100	100	0	0	CH100	100	0	0	PVA100	100	0	0
MS 80	80	10	10	CH80	80	10	10	PVA80	80	10	10
MS 60	60	20	20	CH60	60	20	20	PVA60	60	20	20
MS 40	40	30	30	CH40	40	30	30	PVA40	40	30	30
MS 20	20	40	40	CH20	20	40	40	PVA20	20	40	40
MS0	0	50	50	CH0	0	50	50	PVA0	0	50	50

[a]Blend 1 = variation in cassava starch (MS) content; [b]Blend 2 = variation in CH content [c]Blend 3 = variation in PVA content

Soil Preparation

300 m^2 of a sandy-loamy field located near the Department of Agronomy of the Federal University of Ceará (UFC) (Brazil) was used for soil experiments. The field was 30 cm deep and was cleaned and sifted for proper homogenization prior to use. Weight losses were analyzed after 12, 14, 16 and 18 days of biodegradation in soil, with the exception of samples MS100 and MS80, which were analyzed after 9 days of biodegradation in soil.

Biodegradation Rate (Weight Loss)

The rate of biodegradation was determined through gravimetric analysis, as described by Rutiaga et al.[12] Samples with average thickness of 0.05 mm were initially weighed (*Wi*) and then deposited under the soil for the specified period of time. After that, samples were removed and cleaned with a brush in order to remove the excess of sand from the surface of the film. Finally, films were weighed (*Wf*) and the rate of biodegradation was calculated as:

$$\text{Biodegradation rate} = \frac{Wi\text{-}Wf}{Wi} \times 100 \qquad (1)$$

Result and Discussion

Infrared Spectroscopy (FTIR-ATR)

The infrared spectra of prepared films are shown in Figure 1. Peak assignments are presented in Table 2. Bands at 1236–

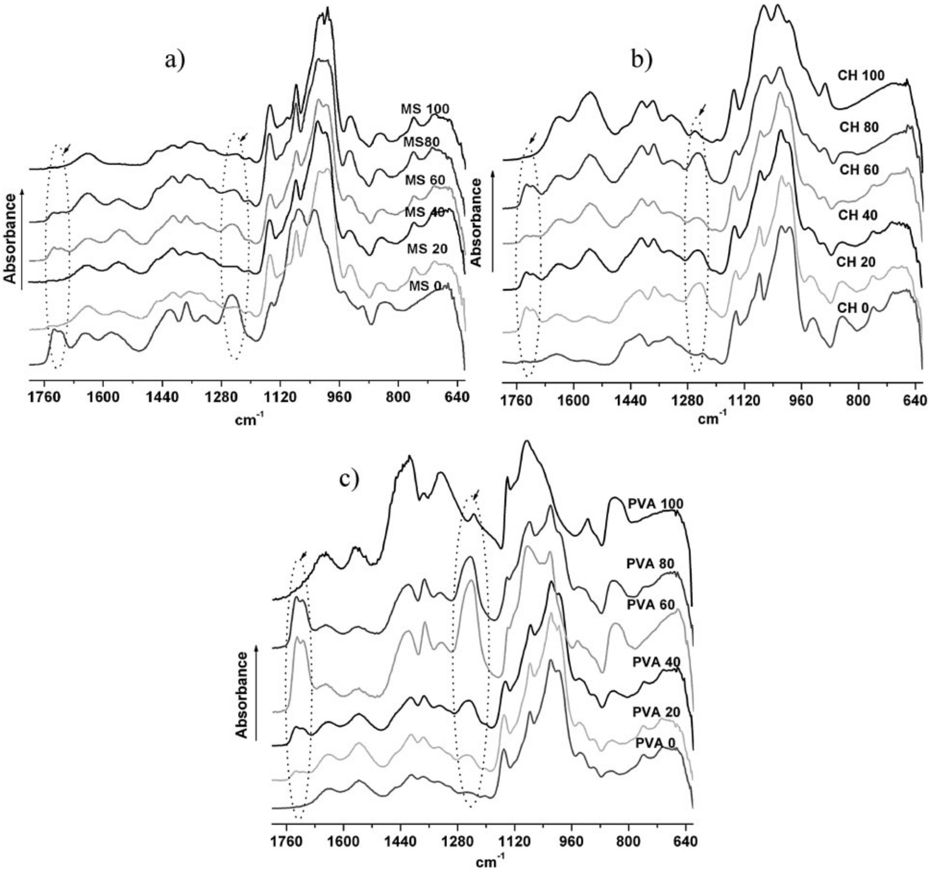

Figure 1.

FTIR spectra of the MS/CH/PVA blends. (a) variation of starch content, (b) variation of chitosan content, (c) variation of PVA content.

Table 2.
Assignments of the meaning bands of the infrared spectrum of the MS, CH and PVA blends.

Assignments[a]	MS100	MS Blend	PVA100	PVA Blend	CH100	CH Blend
ν C=O	–	1738[b]	–	1732	–	1734
ν C=O	–	1714[b]	–	1715	–	1716
δ OH, ν C=O	1643	1645	1651	1645	1641	1644
δ NH	–	1563	1568	1557	1556	1562
δ CH_2	1456	1456	–	–	1446	–
δ CH_2	1413	1412	1416	1411	1409	1415
δ CH_2	1366	1373	1377	1375	1379	1370
δ CH_2	1335	1332	1328	1333	1327	–
ω CH_2	1239	1242	1236	1250	1261	1247
ν C–O; ν CH	1078	1075	1085	1080	1066	1073
ν C–O/C–C	1014	1017	–	1020	1028	1018
δ C-OH	993	993	–	999	997	995
ρ CH_2; ν_a C–O–C	851	847	840	843	–	844

[a] ν_a = asymmetric stretching ν_s = symmetric stretching δ = bending (ω = *wagging;* ρ = *rocking*) [b] present only in the MS80 and MS60 blends.

1261 cm^{-1} can be attributed to bending of CH_2 and are weak in samples MS100, CH100, PVA100, PVA0 and CH0 and stronger in MS, CH and PVA blends, suggesting that the increase in intensity is related to interactions of starch with PVA and CH. Bands at 1732 cm^{-1} and 1716 cm^{-1} can be assigned to stretching of the carbonyl group and are only significant in the blends that contain the three components (MS/CH/PVA) and in sample MS0. This indicates the interaction among the blend components, probably through formation of hydrogen bonds. Several authors have studied PVA and chitosan blends and demonstrated the good compatibility between these two polymers.[13,14]. Mya et al.[15] suggested that the increase of compatibility could be due to the formation of hydrogen bonds between the hydroxyl groups of PVA and the hydroxyl or amino groups of chitosan. Mansur[16] explained the appearance of carbonyl bands in PVA hydrogels, after crosslinking with glutaraldehyde (GA), in terms of the incomplete reaction of GA with the OH groups of PVA during the formation of crosslinks.

Mechanical Properties

The variation in tensile strength and elongation at break of MS/CH/PVA blends are shown in Figure 2. The tensile strength in MS blends (Figure 2a) decreased as the starch content was reduced, resulting in greater values for the MS0 blend (50/50 w/w%, chitosan/PVA). This indicates that the films became more fragile and brittle with the increase of the starch content. On the other hand, the tensile strength values of CS blends increased with the CS content, while in PVA blends these values were always lower.

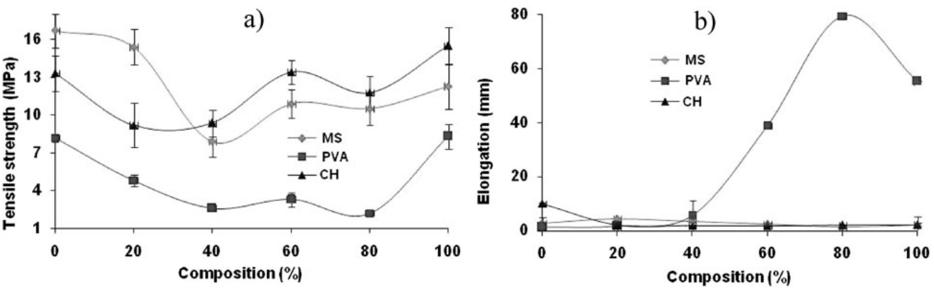

Figure 2.
Tensile strength (a) and elongation at break (b) of the MS/CH/PVA blends.

The values of elongation at break of the MS and CH blends were similar, ranging from 1.4 mm to 4.3 mm and 1.7 mm to 10 mm, respectively (Figure 2b). PVA blends showed an increase in elongation at break as the PVA content was increased (40-80% w/w). The reduction in elongation of the PVA100 samples shows that PVA presents good compatibility with starch and chitosan.

Biodegradation Rate

The rates of biodegradation rate of the MS/CH/PVA blends are shown in Table 3. The MS100 and MS80 films degraded completely in a short period of time (9 days), meaning that reported rates of biodegradation are lower limits. The degradation process may have been accelerated by soil conditions, as high humidity, which may have favored the metabolism of microorganisms. Fast degradation can be useful in applications in agriculture (mulchings) and for production of disposable packaging. As shown in Figure 3, most MS blends were intact after 12 days, although these samples became darker than the others after 16 days of degradation, especially when the starch content was high (60 and 40%). The rate of biodegradation of all samples increased as the biodegradation time and starch content was increased, indicating the existence of an inhibitory or activation period.

Films containing 100 to 40% of PVA could not be analyzed properly, as the surfaces of these samples were always impregnated with large amounts of sand, especially after very long degradation time. Most blends containing 20% and 0% of PVA presented low biodegradation rates after 12 days, although they were almost completely degraded after 18 days (Table 3 and Figure 3). The highest rates of biodegradation were obtained for the blend containing 50% starch/chitosan (PVA0).

Several factors can affect the rate of degradation of polymeric materials, including the characteristics of the polymer materials (structure and chain length), the soil conditions (moisture and pH), the thickness of the films and the presence of microorganisms in the soil. The water solubility of PVA is strongly influenced by the degree of hydrolysis; thus, the higher the degree of hydrolysis, the greater the resistance to moisture.[6] The CH and PVA films showed high rates of biodegradation after 18 days in soil, which can be attributed to the particular PVA properties (low degree of hydrolysis) and soil conditions.

Table 3.
Biodegradation rate of the blends with variation of starch, chitosan and PVA subjected to degradation by 12 to 18 days.

Biodegradation Rate (%)					
Days	MS80	MS60	MS40	MS20	MS0
12	a	17.21	9.56	6.16	0.89
14	a	37.78	36.84	12.61	22.80
16	a	56.20	36.45	16.64	47.52
18	a	96.25	64.81	49.86	81.71
Days	CH80	CH60	CH40	CH20	CH0
12	11.66	8.81	14.60	4.60	15.42
14	34.53	22.60	10.88	27.30	40.20
16	97.45	94.81	89.40	70.60	50.62
18	100.00	100.00	100.00	100.00	50.64
Days	PVA80	PVA60	PVA40	PVA20	PVA0
12	b	b	b	12.60	20.54
14	b	b	b	43.71	83.60
16	b	b	b	60.11	98.63
18	b	b	b	100.00	100.00

[a] not determined, samples totally degraded; [b] not determined, samples very impregnated of sand.

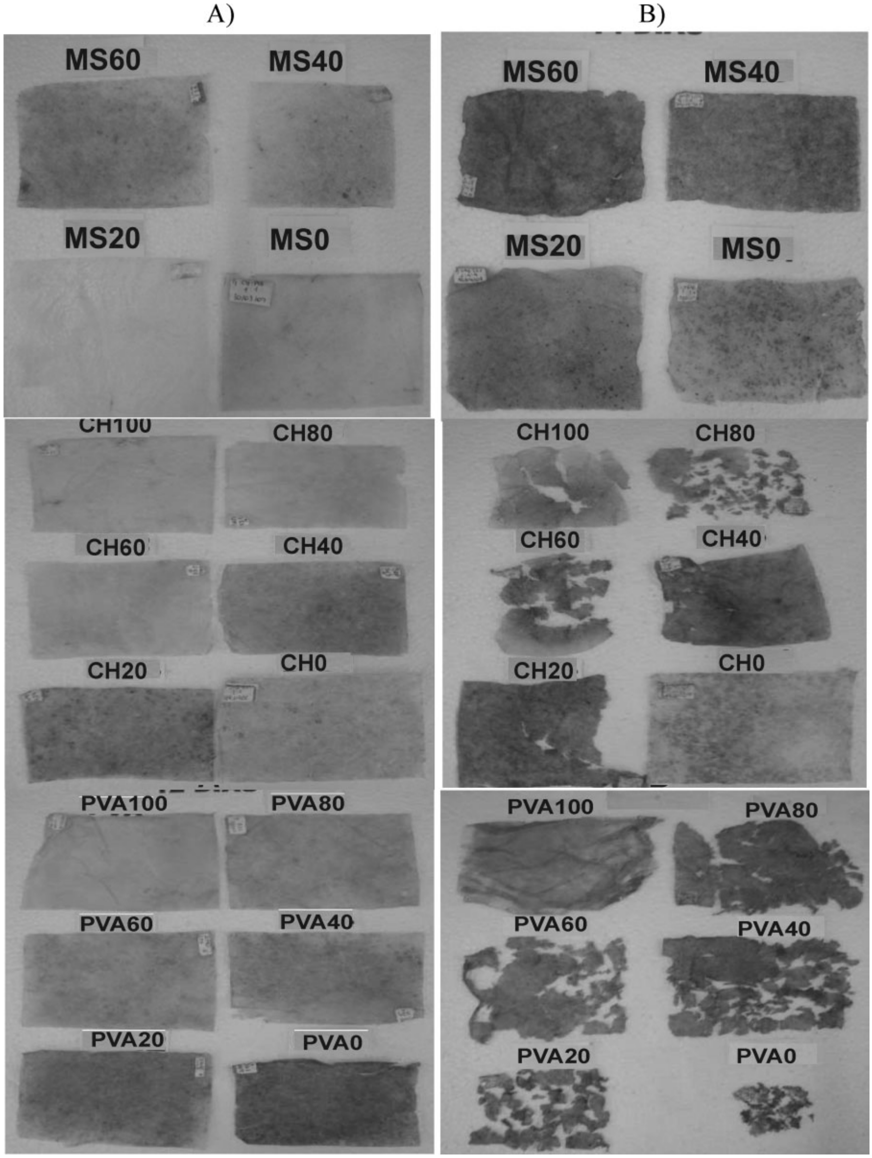

Figure 3.
MS/CH/PVA blends with variation of starch, chitosan and PVA content subjected to degradation by 12 (A) and 16 days (B).

Conclusion

Blends containing different amounts of starch, chitosan and PVA were prepared and characterized. Obtained results showed the good compatibility among the three components, as confirmed by the appearance of the carbonyl band at 1732 cm^{-1} and by the changes of the intensity of other characteristic infrared bands. Addition of PVA led to increase of film flexibility, as characterized through mechanical tests. All prepared blends were degraded in soil and presented weight losses of at least 50% after 18 days of degradation.

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[1] S. L. T. Lima, *Rev. Científica do IMAPES* **2004**, 28.
[2] D. Briassoulis, D. Waaijenberg, J. Gratraud, B. Von Elsner, *J. Agricultural Eng. Res.* **1997**, *67*, 81.
[3] I. Arvanitoyannis, C. G. Biliadois, H. Ogawa, N. Kawasaki, *Carbohydr. Polym.* **1998**, *36*, 89–104.
[4] N. Gontard, S. Guilbert, J. L. Cuq, *J. Food Sci.* **1993**, *58*, 206.
[5] B. Cuq, N. Gontard, S. Guilbert, *Cereal Chem.* **1998**, *75*(1), 1–9.
[6] T. Wang, M. Turhan, S. Gunasekaran, *Polym. Int.* **2004**, *53*, 911.
[7] J. V. Cauich-Rodriguez, S. Deb, R. Smith, *J. Appl. Polym. Sci.* **2001**, *82*(14), 3578.
[8] R. Signini, S. P. C. Filho, *Polímeros: Ciência e Tecnologia* **2001**, *11*, 50.
[9] M. A. García, M. N. Martino, N. E. Zaritzky, *Starch/Stärke* **2000**, *52*(4), 118–124.
[10] R. A. A. Muzzarelli, *Carbohydr. Polym.* **1983**, *3*, 53.
[11] ASTM method D882-97, **1997**, 159.
[12] M. O. Rutiaga, L. J. Galan, L. H. Morales, S. H. Gordon, M. S. H. Ima, W. J. Orts, G. M. Glenn, K. A. Niño, *J. Polym. Environ.* **2005**, *13*, 185.
[13] S. H. Imam, P. Cinelli, S. H. Gordon, E. Chiellini, *J. Polym. Environ.* **2005**, *13*, 47.
[14] S. D. Yoon, S. H. Chough, H. R. Park, *J. Appl. Polym. Sci.* **2006**, *100*, 2554.
[15] M. Mya, R. Iwamoto, S. Mima, *J. Polym. Sci. Polym. Phys Ed.* **1984**, *22*, 1149.
[16] H. S. Mansur, *Mat. Sci. Eng. C* **2008**, *28*, 539.