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Sericin as compatibilizer in starch/ polyester blown films

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Abstract

This study investigated the effects of low concentrations of sericin (≤ 1.5 wt%) in starch- poly(butylene-adipate-co-terephthalate) (PBAT) films. The films were produced by blown extrusion and mechanical, barrier and structural properties were determined. Films containing 1.0 and 1.5 wt% sericin showed higher tensile strength (6.41 and 6.59 MPa) and Young's modulus (90.88 and 132.71 MPa) compared with film without sericin (4.76 MPa and 18.64 MPa). When 0.5 wt% of sericin was used, the elongation was reduced by 62%. The addition of sericin in a concentration of 1.5% (w/w) decreased the water vapor permeability of films from 7.55 to 5.94 g (m s Pa)⁻¹, likely due to the formation of a more homogeneous and compact matrix. Based on these results, a mechanism of action is proposed, whereby sericin acts at the interface of the polymers (starch and PBAT), reducing the interfacial tension and enhancing compatibility.

Keywords: *biodegradable packaging, compatibilization, extrusion, poly(butylene- adipate-co-terephthalate).*

1. Introduction

The blending of starch with biodegradable polyesters is a well-known strategy to improve the mechanical and/or barrier properties of starch-based packaging materials. Thus, mixtures with poly(butylene adipate co-terephthalate) (PBAT)^[1-4], polylactic acid (PLA)^[5,6], and poly(vinyl) alcohol (PVOH)^[7], among others, have been studied. Due to the differences in polarity between starch (hydrophilic) and polyesters (hydrophobic), the use of a compatibilizer has been shown to be necessary. Compatibilizers act by reducing interfacial tension caused by differences in polarity, thereby improving the polymer compatibility. Consequently, barrier and/or mechanical properties of the materials are improved^[1-3,8-11].

In previous studies, proteins have been added to starch for the manufacturing of packaging materials^[12-15]. In these works, proteins were generally included at levels ranging from 10 to 50 wt%, as part of the polymer matrix. The impact of these additions on the mechanical properties of the materials can be positive or negative, depending on the protein structure, concentration in the blend and processing conditions.

To the best of our knowledge, there are no studies on the use of protein at low concentrations (≤ 1.5 wt%) as an additive in starch/polyester blends. However, in preliminary tests, we observed that sericin (a silk protein) seems to present compatibilizer action in blends of starch/PBAT processed by extrusion. During processing, the denaturation of sericin

should occur, which unfolds its chains and improves its interaction with both starch and PBAT.

Sericin is a protein extracted from the *Bombyx mori* silkworm. Sericin acts as a natural glue that fixes silk fibers (fibroin) together. During silk production, fibroin is recovered and sericin removed and discharged as a waste. The molecular weight of sericin ranges from 24 to 400 kDa^[16], and the predominant amino acids are serine (40%), glycine (16%), glutamic acid, aspartic acid, threonine, and tyrosine^[17]. While fibroin is being studied as an interesting biocompatible material for tissue engineering, sericin is generally neglected^[18]. However, sericin could be used as an additive or adjuvant in polymer blends, thereby adding value and promoting a positive impact on the environment. Thus, the objective of this work was to evaluate the role played by small amounts of sericin (≤ 1.5 wt%) in blown films of starch-PBAT and to propose a mechanism of action.

2. Materials and Methods

2.1 Materials

The films were manufactured with cassava starch (23 wt% amylose and 13.3 wt% moisture), provided by Indemil (Paranavaí, Brazil); poly(butylene-adipate-co-terephthalate) - PBAT (Ecoflex® S BX 7025, Basf, Ludwigshafen, Germany); glycerol (Dinamica, Diadema, Brazil), and sericin (extracted

from silkworm cocoons (*Bombyx mori*), according with the methodology employed by Turbiani et al.^[18].

2.2 Production of films

The components of each formulation were manually mixed and extruded through a die with six 2-mm diameter holes in a laboratory twin-screw extruder (D-20, BGM, Taboão da Serra, Brazil) in order to obtain the pellets. The screws had a 20 mm diameter (D) and L/D=35. The screw speed was 100 rpm and the temperature profile was 90/120/120/120/120 °C at the five heating zones. Then, the pellets were again extruded using a mono-screw extruder (EL-25, BGM, Taboão da Serra, Brazil) to obtain the blown films. The screw had D=25 mm and D/L=26. The temperature profile was 90/120/120/130 °C at the four heating zones and 130 °C at the 50-mm film- blowing die, and the screw speed was 40 rpm. The control formulation (without sericin) contained 61, 26 and 13 (wt %) manioc starch, PBAT and glycerol, respectively. Preliminary tests suggested that sericin has a plasticizing effect. Additionally, these tests showed that sericin contents higher than 2 (wt%) may compromise the production and the properties of the films. Therefore, three other formulations were tested containing 0.5, 1.0 and 1.5 sericin (wt%). These concentrations were deducted from those of glycerol to keep the concentration of plasticizer constant. The samples were coded as 0S, 0.5S, 1.0S and 1.5S, with the numbers representing the sericin concentration (wt%). The thickness of the films was determined as the average of five random measurements of each sample, using a digital micrometer (Mitutoyo, Illinois, USA).

2.3 Scanning Electron Microscopy (SEM)

The fractured surfaces of the films were assessed using an FEI Quanta 200 scanning electron microscope (FEI Company, Tokyo, Japan), which was operated at an acceleration voltage of 20 kV. The samples were cooled in liquid nitrogen and then broken (cryogenic fracture). Before coating with a gold layer, the samples were stored at 25±2 °C in a desiccator with anhydrous CaCl₂ (~0% RH) for 2 days. Images were taken at a magnification of 1600x.

2.4 Mechanical properties

The tensile properties were determined using the texture analyzer model TATX2i (Stable MicroSystems, Surrey, England), according to the ASTM-D882-02 method^[19]. The samples, previously conditioned at 53±2% RU (Mg(NO₃)₂ saturated solution) and 25±2 °C for 48 h, were cut (50 mm x 20 mm) along the longitudinal direction. The crosshead speed was set at 0.83 mm.s⁻¹ (load cell of 50 kg), and the initial distance between the grips was 30 mm. Five replicates were evaluated.

2.5 Water Vapor Permeability (WVP)

The ASTM E-96-00 method^[20], modified as described in our previous work^[1], was used. Tests were conducted in triplicate.

2.6 Fourier transformed infrared spectroscopy (FT-IR)

Previously cut films were dried for one week in a desiccator containing anhydrous CaCl₂ (~0% RH). FT-IR spectra were obtained with an FT-IR spectrophotometer 640-IR model (Varian, São Paulo, Brazil) provided with a module of Attenuated Total Reflectance (ATR). The analyses covered the wave numbers from 4000 to 400 cm⁻¹ with a resolution spectrum of 4 cm⁻¹. Twelve scans were performed on each sample.

2.7 Dynamic Mechanical Analysis (DMA)

A Dynamical Mechanical Analyzer (DMA - model Q800, TA Instruments, New Castle, USA) was used. The samples (previously conditioned at 53% RH for 7 days) were scanned from - 90 °C to 100 °C with heating rate of 3 °C /min and fixed frequency of 1 Hz. Glass transition temperatures (T_g) were obtained as the temperatures of the tan δ peaks.

2.8 Statistical analysis

The data were analyzed using STATISTICA 7.0 software (StatSoft, Oklahoma) with analysis of variance (ANOVA) and Tukey test at a 5% significance level.

3. Results and Discussion

All the films, both with and without sericin, presented good handleability, processability, flexibility and uniformity with smooth surfaces. The mean thickness ranged from 180.4 to 247.7 µm.

3.1 Films morphology-scanning electron microscopy (SEM)

As observed on the micrographs of film fracture (Figure 1), the absence of starch granules demonstrates the process was adequate, promoting the desired disruption of the granular structure. This disruption is essential to enable better starch interaction with glycerol and PBAT.

All samples showed fibrillar structure, with oriented grips indicating the chain orientation promoted by the process. The addition of sericin at 1.0 and 1.5 (wt %) levels formed films with slightly more homogenous and compact structures, suggesting the matrices were more cohesive.

3.2 Mechanical properties

The values of tensile strength, elongation at break and Young's modulus are shown in Table 1. Increasing sericin concentration up to 1.0 (wt%) (1.0S) significantly (p ≤ 0.05) increased the tensile strength of the films. A further increase was not observed when sericin was added at the 1.5 (wt %) level (1.5S). The maximum value obtained (6.59 ± 0.28 MPa) was 36% greater than that of the film without sericin (4.76 ± 0.16 MPa).

On the other hand, the elongation was reduced by 62% with the inclusion of the lower level of sericin (sample 0.5S). Indeed, the elongation decreased even further with the increase of sericin concentration up to the maximum concentration tested. These effects also impacted the Young's modulus, which increased with the increasing protein

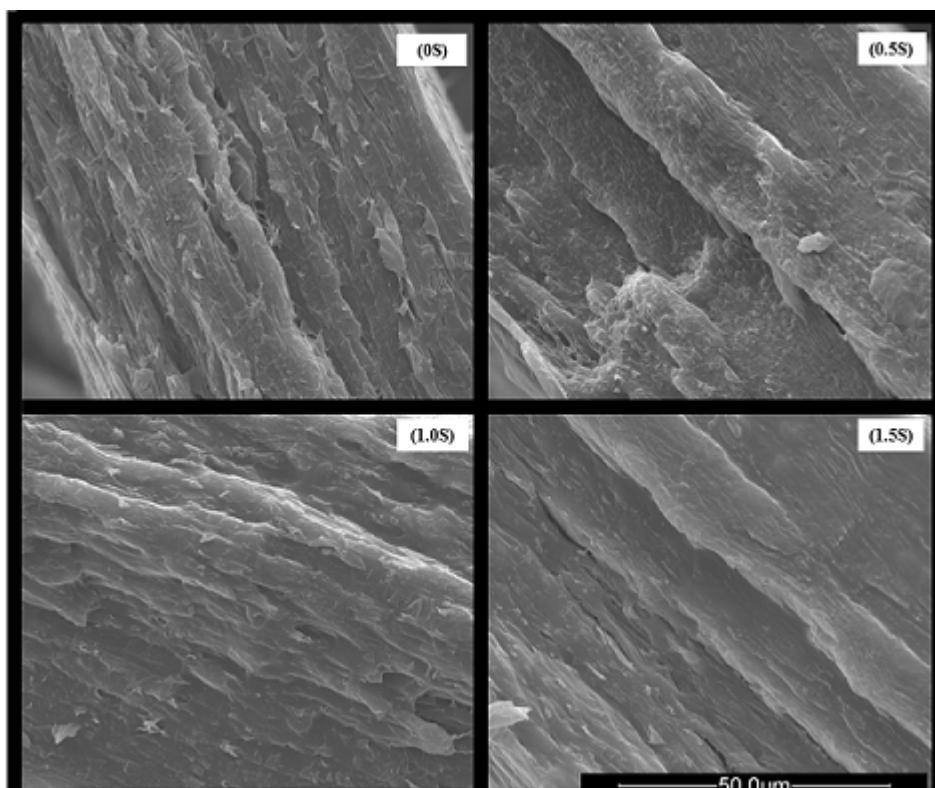


Figure 1. Electron micrographs of films (fractures) containing different levels of sericin.

Table 1. Mechanical properties and water vapor permeability of the films.

Sample	σ (MPa)	ε (%)	E_0 (MPa)	WVP ($\times 10^{-11}$ g (m s Pa) $^{-1}$)
0S	4.76 ± 0.16^c	252.22 ± 18.13^a	18.64 ± 2.44^d	7.55 ± 0.72^a
0.5S	5.75 ± 0.16^b	95.49 ± 16.24^b	66.33 ± 4.54^c	$6.80 \pm 0.56^{a,b}$
1.0S	6.41 ± 0.31^a	83.05 ± 29.95^b	90.88 ± 10.58^b	$6.91 \pm 0.67^{a,b}$
1.5S	6.59 ± 0.28^a	45.79 ± 16.02^c	132.71 ± 12.97^a	5.94 ± 0.21^b

σ : tensile strength; ε : elongation at break; E_0 : Young's modulus; and WVP: water vapor permeability. Results expressed in (mean \pm standard deviation). ^{a,b} Different letters in the same column indicate significant differences ($p \leq 0.05$) according to the Tukey's test.

concentration, ultimately reaching a value 700% greater than 0S when 1.5 wt% sericin was added. Both results, decreased elongation and increased rigidity, indicated the molecular mobility of the starch and PBAT chains was reduced by the presence of sericin. Initially, one can understand this effect as similar to that produced when the plasticizer is reduced. Sericin levels were substituted at similar levels to glycerol; thus, if the plasticizing action of sericin was null or lower than that of glycerol, there would be a decrease in plasticizer level. However, this cannot be the only reason for the increase in stiffness of the films, as the reduction in glycerol was very small to justify this behavior.

Several authors have employed proteins in blends with starch for the manufacturing of films^[12,13,15,21,22]. However, in these works, protein was incorporated at higher concentrations (10 to 50 wt%), thereby configuring the protein as another constituent of the polymer matrix. In these cases, the effects of the proteins on the mechanical properties of the films varied as a function of the structural configuration of the protein and of the characteristics of the starch; however,

the tensile strength predominantly decreased, while the elongation of the starch films increased.

These results are contrary to those observed in our work, which show that sericin may be considered as an additive due to the low amounts used. Thus, we propose another mechanism of action by which the sericin, due to its amphoteric character, acts similarly to a surfactant agent. Thus, the side chains of amino acid residues with hydrophobic character (such as glycine) and hydrophilic character (such as serine, aspartate, and asparagine) interact with PBAT and starch, respectively. Then, once located in the interface between these polymers (Figure 2), sericin establishes molecular interactions with them, making the material more resistant and less flexible. In addition to being a plasticizer, sericin could act as a compatibilizer, contributing to greater dispersion and interaction between the starch-PBAT phases. This proposed mechanism explains the more homogenous and compact morphology (shown in Figure 1) and the higher values of tensile strength and Young's modulus observed in samples 1.0S and 1.5S (Table 1).

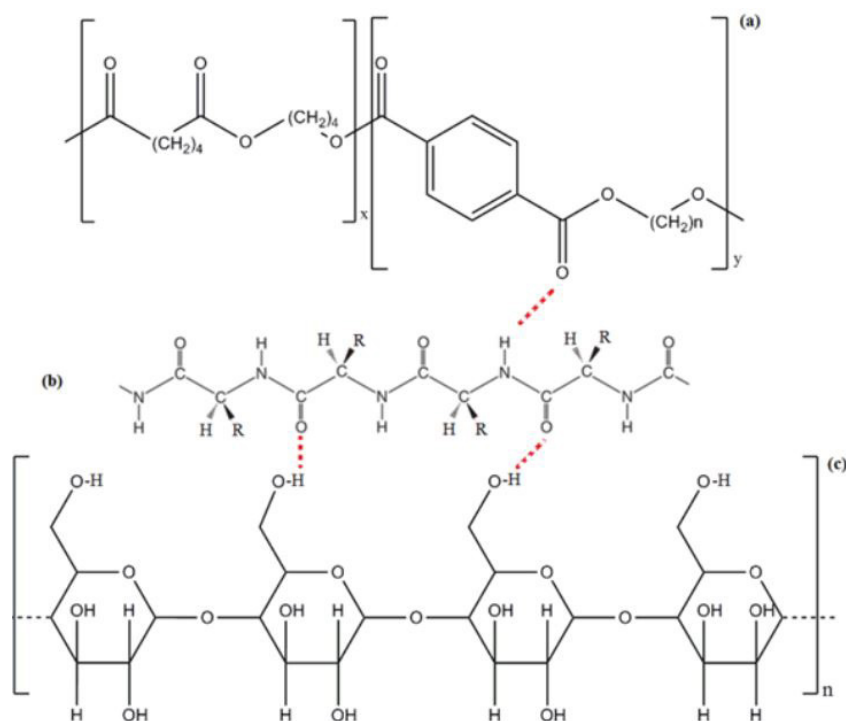


Figure 2. Scheme representing interactions between fragments of: (a) PBAT, (b) protein and (c) starch. R=side chains of amino acids residues.

Mariani et al.^[23] added soy protein isolate (SPI) in blends of poly (3-caprolactone) and corn starch and observed an increase in tensile strength and elongation with 3.5 wt% SPI. However, when 11 wt% of SPI was added, no effect was observed. These results indicate that low concentrations of proteins could act as compatibilizers, although the authors did not explore this possibility.

3.3 Water Vapor Permeability (WVP)

The films containing the highest level of sericin (1.5S) showed significantly lower WVP ($5.94 \times 10^{-11} \text{ g (m s Pa)}^{-1}$) than the film without sericin ($7.55 \times 10^{-11} \text{ g (m s Pa)}^{-1}$), as shown in Table 1. The more compact structure observed in the 1.5S sample (Figure 1) may have reduced the WVP. The amphiphilic composition of sericin may have contributed to a better interaction with starch and PBAT, forming a more tight material, which restricted the water diffusion. Other authors^[1-3,11] have shown that when compatibilizers are used in starch/polyester blends the result is always a more homogeneous and denser matrix due to improvement in the interfacial adhesion.

3.4 Fourier Transform Infrared Spectroscopy (FTIR)

ATR-FTIR spectra of starch- PBAT- sericin films are shown in Figure 3. Characteristic bands previously observed by other researchers^[1,2] in starch/PBAT blends are present in all samples, such as those at 3000-3500, 2800-2930 and 1715 cm^{-1} , which is attributed to the OH- stretching, CH- stretching and absorption of carbonyl groups of esters, respectively. The broadband at 3000-3500 cm^{-1} could also represent N-H stretching from sericin in samples containing this protein.^[24,25]

As the concentration of sericin increased from 0 to 1.5 (wt%), a progressive reduction in the intensity of the absorption band at 3000- 3500 cm^{-1} was observed, indicating a hydrogen bonding interaction between sericin and starch and/or PBAT chains. This increase in hydrogen bonding could explain the action of sericin, which strengthens the material structure and thus explains the results of tensile strength and modulus. At the same time, the hydroxyl groups of starch and carbonyl groups of PBAT, involved in the interactions with sericin, become unavailable to form hydrogen bonds with water, thereby explaining the decrease in WVP.

In the samples 0.5S, 1.0S, and 1.5S, the characteristic bands of random coil structure of sericin at approximately 1650 cm^{-1} (C=O stretching, amide I) and 1520 cm^{-1} (N-H deformation, amide II)^[26] were marginally observed, likely due to its low concentration.

The absorption band at 1715 cm^{-1} in the film without sericin (0S) is attributed to the stretching of the C=O groups^[25] present in the PBAT structure. The progressive increase in the protein concentration in samples 0.5S, 1.0S, and 1.5S caused an increase in the number of amide bonds ($\text{-NH}_2\text{C=O}$), which justifies the increases in the relative intensities of the absorption bands in this region. Additionally, the residues of the amino acids aspartate and asparagine, constituents of sericin, have carbonyl groups in the side chain, which could also contribute to the increase in absorption in the region 1700 -1750 cm^{-1} .

The bands at 1025, 1110 and 1270 cm^{-1} are assigned to the stretching of the C-O bonds^[1,25] present in starch, glycerol, PBAT and sericin. The intensity of the last two bands increased as more sericin was added to the films.

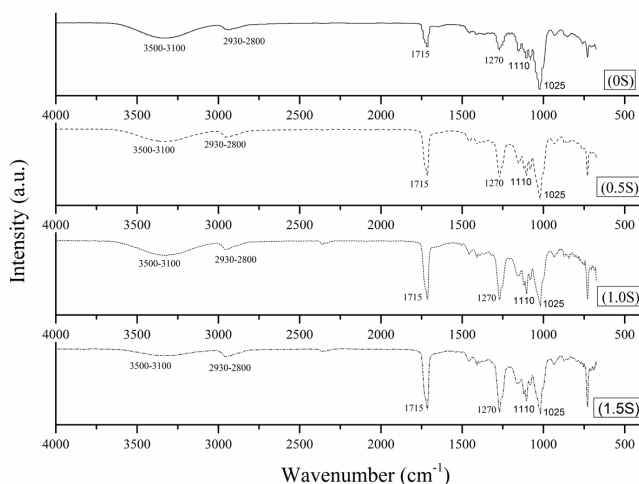


Figure 3. FT-IR spectra of the films with different sericin concentrations.

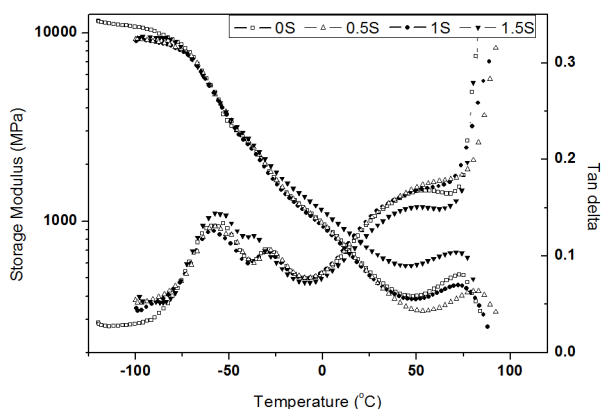


Figure 4. Storage modulus and $\tan \delta$ as a function of temperature.

3.5 Dynamic Mechanical Properties (DMA)

The results of storage modulus (E') and $\tan \delta$ are shown in Figure 4. The E' values of samples decreased with the increase of temperature. Similar values of E' were observed for all the samples at temperatures lower than -35°C . Further increases in temperature showed higher storage moduli of the sample 1.5S compared with those of the other samples indicating lower chain mobility. Additionally, at temperatures higher than approximately 50°C the E' values of samples 0.5S and 1.0S were lower than the observed for 0S.

The $\tan \delta$ curves showed three relaxations in all samples, indicating the presence of three partially miscible phases. In the control sample (0S), these relaxations are located at -58°C , -29°C and 54°C . According to Olivato et al.^[27], these peaks represent the glass transition temperatures (T_g) of the glycerol, PBAT and starch-riches phases, respectively.

Samples containing sericin showed different behaviors depending on its concentration. While in 0.5S films the T_g s were similar to those of the control, in the 1.0S sample the T_g of the starch-rich phase was shifted to a higher temperature (63°C). This result indicated the molecular mobility of the starch chains was reduced by the presence of sericin and

could explain the increase in stiffness observed in Table 1. Differently, the highest content of sericin (1.5S) shifted the $\tan \delta$ peaks of the PBAT and starch-rich phases to lower temperatures (-35°C and 50°C , respectively), indicating a plasticizing effect. The wide range of chain lengths and chain branching of starch (indicated by the relatively broad $\tan \delta$ peak) associated with the wide molar mass distribution of sericin can help to explain these results. The short chain segments of sericin could act as plasticizers improving the mobility of the polymer short chain segments, while the larger sericin segments could act as compatibilizers between polymers, increasing stiffness.

4. Conclusions

The mechanical and barrier properties of blown films manufactured with blends of starch and PBAT were improved when low (≤ 1.5 wt%) concentrations of sericin were added. These effects, together with the formation of a more homogeneous and compact microstructure of films, allows one to hypothesize that sericin may have a compatibilizing action. Due its amphoteric character, sericin could be located at the interface between starch and PBAT,

reducing the interfacial tension and enhancing compatibility. Further studies should be performed with other proteins to extend the applicability of these conclusions.

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