

Article



Barrier, Mechanical, Thermal, and Rheological Properties of Plasticized Biopolymeric Films Manufactured by Co-Extrusion

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Abstract: The thermal, rheological, mechanical, and barrier properties of flat biopolymeric films processed by extrusion with different proportions of plasticizer and surfactant were evaluated. In the first stage, pellets were developed through twin-screw extrusion using a temperature profile in the ascending step process. These samples were analyzed using rotational rheology analysis to understand the viscoelastic transitions through the behavior of the storage and loss modulus, as well as the incidence of complex viscosity concerning concentration. The interaction among the components was analyzed under infrared spectroscopy after the two processing stages, revealing the miscibility of the mixture due to the action of the surfactant. The degradation temperatures increased by more than 20 °C, generating thermal stability, and the temperatures related to polymer transitions were determined. In the second stage, co-extrusion was carried out using pellets from the blend with a melt flow index (MFI) suitable for this process. The samples TPS50-PLA50-T5 and TPS75-PLA25-T5-A10 presented MFI values of 2.27 and 1.72 g/10 min, respectively. These samples were co-extruded for the production of films, impacting the physical properties. The resistance to traction, Young's modulus, and elongation showed limited effectiveness of plasticizer and surfactant, with high resistance and elongation values (4.276 MPa and 2.63%) in the TPS50-PLA50-T5 film. Additionally, morphological analysis showed the detailed action of the plasticizer on the regular shapes of threads as a product of deformation during material processing. The barrel properties exhibited limited biopolymer-plastic-tensile miscibility, resulting in different water vapor permeability for the TPS75-PLA25-T5-A10 film on each side (a difference of two orders of magnitude). The contact angle corroborated the effect, with values in each case ranging from 103.7° to 30.3° . In conclusion, we assert that biopolymeric films, when modified with plasticizers and surfactants, can be tailored for various applications within the packaging sector while maintaining control over each film.

Keywords: starch; Tween 20; twin-screw extruder; water vapor permeability; acetyltributyl citrate

1. Introduction

Our society today, driven by environmental awareness, demands alternative materials in the packaging sector, particularly in the realm of biodegradable single-use packaging. Single-use packaging serves various functions: it facilitates storage and transportation, contributes to mitigating product and environmental contamination, acts as an insulator for humidity or temperature, and communicates information about the product through ink adhesion [1]. All these aspects collectively make it an essential element for maintaining or enhancing the useful life and preserving the nutritional value of food or the quality of products [2,3]. Over the last 20 years, research has intensified, focusing on several aspects of these materials, including type, concentration, design, process, and control of variables (such as speed, temperature, and pressure, among others) regarding the performance of



Citation: Calambás Pulgarin, H.L.; Caicedo, C. Barrier, Mechanical, Thermal, and Rheological Properties of Plasticized Biopolymeric Films Manufactured by Co-Extrusion. *Processes* 2024, *12*, 524. https:// doi.org/10.3390/pr12030524

Academic Editors: Xingyuan Huang, Mengshan Li and Shiyu Jiang

Received: 9 January 2024 Revised: 7 February 2024 Accepted: 9 February 2024 Published: 6 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). physical properties. Critical variables include mechanical resistance, thermal degradation, state transitions, water absorption, barrier properties to water, oxygen, or other gases, and optical properties (transparency, adhesion capacity) [4]. In the case of mixtures involving biopolymers and composite derivatives with reinforcements, there has been an exponential trend in the last 10 years. According to Scopus, using the search equation "packaging and biopolymers", 37 original documents were published in 2013. In contrast, a total of 312 were published in 2023, indicating a substantial increase. During this period, a total of 1683 original documents were published in areas such as materials science, chemistry, agricultural and biological sciences, chemical engineering, engineering, and environmental science.

In general, the most studied biopolymers include polyesters, polylactic acid (PLA), polybutylene succinate, and polyhydroxyalkanoate; and polysaccharides, starch, chitosan, and cellulose [5]. Some studies present preliminary results on the mixtures of PLA and tapioca starch (TS), resulting in a fragile and brittle material [6,7]. To address this, strategies are sought to improve the synergy between these biopolymers within a mixture and achieve substantial improvements in physical properties, overcoming the challenge of miscibility and compatibility [8,9]. An improved strategy involves the development of PLA/TPS bilayer films with a 50:50 ratio. The interaction process between the two layers is studied and evaluated through physical properties [10]. Last year, Yoksan and Dang investigated the effect of the surfactant Tween 60 (TW) on the compatibility and performance of thermoplastic starch/poly(lactic acid) (PLA)/poly(butylene succinate-co-butylene adipate) blends (TPS/PLA/PBSA) in a proportion of 40:30:30, respectively. The mixtures were prepared using a twin-screw extruder, and then a blown film was obtained. In their study, they reported increases in tensile strength (50%), elongation at break (130%), and impact resistance (63%) when using contents of 2 and 2.5% Tween 60. The presence of Tween 60 improved the thermal stability, oxygen, and water vapor barrier properties of the TPS/PLA/PBSA blend [11]. In contrast, the mixture of poly(butylene adipate-co-terephthalate) (PBAT) with TPS studied by Ivanič, Kováčová, and Chodak showed dependence on urea as a plasticizer. The 50:50 ratio between these biopolymers exhibits a significant increase in tensile strength [12]. Glycerol, as a plasticizer, and citric acid and Tween 80 as compatibilizers, had no positive effects on the mechanical properties. Other binary and ternary mixtures, prepared by fusion of poly(lactic acid) (PLA), poly(butylene succinate) (PBS), and thermoplastic starch (TPS), showed improved mechanical properties by presenting core-shell structures of TPS-PBS, and the adhesion was evaluated by molecular dynamics, explaining the model of shells that allows high energy absorption against impact [13]. In the case of ternary mixtures, the influence of a multifunctional agent, such as citric acid, has also been studied to allow for greater compatibility [14].

Current research involves complex mixtures that include three components for the biopolymeric matrix (PLA, PBS, starch) and the incorporation of fibers as reinforcement. The values of physicomechanical properties align with the predicted values of the theoretical models, showing increases in elastic modulus (EM), elongation at break (EB), impact strength (IS), and equilibrium moisture content (EMC) by 80.8 MPa, 11.4%, 2 kJ/m², and 4.1%, respectively. In addition, the biodegradability rate in the fifth month is 71.1% [15]. In contrast, traditional mixtures, such as polylactic acid (PLA) and thermoplastic and halloysite nanotubes (HNT) or bleached Kraft hardwood fibers, do not allow an understanding of the miscibility process between biopolymers [16,17]. Knowledge is also advancing through the understanding of mixtures involving biopolymers and plasticizing agents to promote ductility in PLA and ensure low permeability in food packaging [18]. In a previous study on the development of PLA/TPS blends, surfactant Tween 20 and poloxamer (F127) were used to evaluate the compatibility of the mixtures [8,19]. However, the impact of plasticizers has not been studied, and in complex mixtures, it is necessary to consider their presence due to the low ductility of PLA [20].

On the other hand, scaling up conventional and nonconventional processes continues to be a challenge for obtaining biopolymers, ensuring quality, and promoting sustainability through eco-design and the recyclability or biodegradability of materials [21]. Currently, the extrusion process has shown significant improvements compared to other techniques because it enables layered design in materials, thereby enhancing the performance of physical properties. Specifically, for films intended for primary packaging where barrier properties are crucial, co-extrusion technology offers an excellent cost–benefit ratio compared to other conventional manufacturing techniques [22,23].

The objective of this work is to evaluate the synergistic effect of the Tween 20 compatibilizer and acetyltributyl citrate (ATBC) plasticizer on TPS/PLA mixtures at different concentrations using co-extrusion technology. The mechanical, morphological, thermal, rheological, and surface results will provide a deeper understanding of the structural interaction phenomenon, contributing to the precise formulation of a biodegradable polymeric matrix with improved properties suitable for application in the packaging sector.

2. Materials and Methods

2.1. Materials and Sample Preparation

In this study, the following materials were utilized: Achira starch with a density of 1.59 g/mL, sourced from Surtialmidon (Huila, Colombia), and polylactic acid (PLA) obtained as Bio-Flex FX 1130 with a density of 1.39 g/mL and a melt flow index of 3 g/10 min. Sorbitol served as the plasticizer (procured from Sigma Aldrich Chemicals, Saint Louis, MO, USA) with a purity of \geq 98%. Lactic acid, supplied by Chemi SpA (Milan, Italy), had a density of 1.21 g/mL and a purity of 85%. Tween 20 surfactants, with 100% purity and a density of 1.09 g/mL, were obtained from Sigma Aldrich. Acetyltributyl citrate (ATBC or A), of commercial quality with a density of 1.05 g/mL and a purity of 99%, was purchased from SUCROAL S.A. (Cali, Colombia).

Mixtures were developed according to the compositions described in Table 1. The development process employed the Thermo Scientific HAAKE Rheomix brand torque rheometer, operating at 160 °C and 50 rpm. Thermoplastic Starch (TPS) was obtained using 57% starch and 40% glycerol (Gly), with 3% lactic acid [16]. Additionally, Tween 20 was used as a surfactant (T) in variable proportions of 5% and 10%. Furthermore, the ATBC content varied between 0% and 10%, serving as a substitute for the plasticizer. These percentages have been tested in previous works [8,20].

Comula	Starch (%)	Plasticizers			
Sample		Gly (%)	Tween 20 (%)	ATBC (%)	rla (%)
TPSS75-PLA25-T10	45	27	3	0	25
TPS75-PLA25-T10-A10	45	25.5	3	1.5	25
TPS75-PLA25-T5	45	28.5	1,5	0	25
TPS75-PLA25-T5-A10	45	27	1.5	1.5	25
TPS50-PLA50-T10	30	17	3	0	50
TPS50-PLA50-T10-A10	30	15.5	3	1.5	50
TPS50-PLA50-T5	30	18.5	1.5	0	50
TPS50-PLA50-T5-A10	30	17	1.5	1.5	50
TPSS75-PLA25-T10	45	27	3	0	25
TPS75-PLA25-T10-A10	45	25.5	3	1.5	25

Table 1. Composition of plasticized biopolymeric blends based on TPS and PLA.

2.2. Extrusion of Biopolymeric Blends to Obtain Pellets

For the development of pellets by extrusion, the mixtures TPS75-PLA25-T5-A10 and TPSS50-PLA50-T5 were utilized due to their fluidity index of 1.72 and 2.27 g/10 min, respectively, according to ISO 1133, method A (cutting off and weighing method) [18,19,24].

A Haake twin-screw extruder was employed, operating at a speed of 80 rpm with the following temperature profile in screw transport zones 1 to 10: 115 °C, 117 °C, 120 °C, 125 °C, 130 °C, 135 °C, 137 °C, 140 °C, 143 °C and 145 °C. After the process, the extruded biopolymer filament was cooled with air and pelletized, as illustrated in Figure 1.



Figure 1. Reliable image of the extrusion process carried out to obtain pellets.

2.3. Obtaining Flat Film

A COLLIN®E20Tx25L/D multilayer co-extruder equipped with a Teach Line®Chill Roll CR 72 T 5-layer flat film head was utilized. The system temperature was set at 145 °C, operating at a speed of 15 rpm with a pull ratio R/H = 6. For this process, two samples with ideal rheological and thermal characteristics were carefully chosen. The resulting films had an average thickness of 1.2 mm, as depicted in Figure 2.



Figure 2. Reliable image of the co-extrusion process carried out to obtain flat polymeric films.

2.4. Characterization

2.4.1. Fourier Transformed Infrared Spectroscopy (FTIR)

The FTIR analysis was conducted on the films in attenuated total reflection (ATR) mode. An IR Affinity-1 spectrometer (Shimadzu Corporation, Kyoto, Japan) was employed for the analysis, utilizing 16 scans. The analysis covered a wavenumber range between 600 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹. This technique offers insights into the functional groups through the vibration of bonds and interactions between the atoms comprising the molecules.

2.4.2. Rheological Analysis

Viscosity was determined using a rotational rheometer (DHR-2, TA Instruments, New Castle, DE, USA) with a parallel plate configuration. The rheological measurements were conducted at 170 °C with a gap of 145 μ m, a diameter of 25 mm, and an angle of 5.753°, using a strain of 10% and a frequency range of 0.01 to 1000 rad/s to determine the storage modulus and the loss modulus. Rheology studies the resistance to flow and deformation of matter in a molten state under dynamic and static conditions to understand viscoelastic behavior.

The melt flow index of the samples was determined using MFI2 Melt Flow Indexers (extrusion plastometer, Atlas Electric Devices Company, Chicago, IL, USA), following ASTM D1238 standards. It was determined according to the results of the fusion of the material in the DSC analysis. The measurement was conducted at 170 °C under a load of 2.16 kg. Five repetitions were performed for each sample, and the results are presented as an average (n = 5) [25].

2.4.3. Thermal Properties

Thermal characteristics were studied using DSC and TGA. A TGA/DSC 2 STAR System thermogravimetric analyzer from Mettler Toledo (Schwerzenbach, Switzerland), was employed. Thermal analysis facilitates the determination of degradation temperatures, stability, and transitions concerning temperature. The operating conditions were as follows: a heating rate of 10 °C/min from 25 °C to 600 °C, and a nitrogen purge at a flow rate of 60 mL/min into 10 \pm 0.5 mg of material. Differential scanning calorimetry (DSC) analysis was conducted to identify the thermal transitions of the sample using a TA Q-2000 instrument at a heating rate of 10 °C/min within a temperature range of 30 to 200 °C, accompanied by a nitrogen purge. Approximately ~10 mg of the samples were utilized for this analysis.

2.4.4. Mechanical Properties

The Instron 5586 Universal tensile testing machine was utilized for tensile strength testing, following the thin film testing procedure outlined in ASTM D882. This machine was equipped with a 500 N load cell. The tests were conducted at a rate of 5 mm/min in both longitudinal and transverse modes, employing a consistent speed of 10 mm/min until failure. This analysis aims to ascertain the tensile strength, percentage of elongation, and Young's modulus.

2.4.5. Morphological Analysis

Scanning electron microscopy analysis was conducted on the surface of the samples using the JEOL JCM 50.000 equipment from Tokyo, Japan. The equipment was operated at a voltage of 10 kV to obtain images at magnifications of $100 \times$ and $200 \times$. The samples were coated with a layer of gold. Morphological analysis enables the identification of elements in the microstructure, involving qualitative analysis to recognize granules, cavities, and phase changes.

2.4.6. Contact Angle (CA) Analysis

The sessile drop analysis method was applied using distilled water as a solvent to study the hydrophilicity of the materials. Contact angle measurements were conducted using a goniometer (Ramé-Hart Instrument Co., Ltd., model 250, Succasunna, NJ, USA), with the addition of 20 μ L of water at 25 °C. A 20 μ L drop of distilled water was placed on the surface of the polymer samples. After a 60 s stabilization period, the image was recorded, and the contact angle was measured using the free software ImageJ version 5.0.3. The results were obtained by averaging at least three measurements.

2.4.7. Water Vapor Transmission Rate (WVTR) and Water Vapor Permeability (WVP)

The water vapor transmission rate (WVTR) analysis was conducted on the flat films A50-PLA50-T5 and A75-PLA25-T5-10 using a Permatran-W®3/33 apparatus (Mocon Inc., Minneapolis, MN, USA). The test conditions included a 5 cm² film sample area, 37.8 °C, 90% relative humidity, and a partial pressure of oxygen set at 760 mmHg for 10 measurement cycles. To determine the WVP, the WVTR was normalized to the film thickness (1.2 mm). The mean value was calculated from three replicates for each film formulation.

3. Results

3.1. Rheological Analysis

Figure 3 presents the results of the rheological study conducted with the blends, in general, indicating a pseudoplastic behavior where the complex viscosity decreases as the shear stress values increase. The viscosity is influenced by the content of the Tween surfactant, which delays the cross-linking reaction occurring in the target blend (TPS75-PLA25) at around 250 rad/s. Additionally, the presence of the ATBC plasticizer exhibits optimal interaction between the components, reflected in higher viscosity values. In the studied range, no cross-linking reactions were observed. Cross-linking is induced by the mechanical energy imparted to the system as the shear increases. Figure 4 depicts values of the storage modulus (G') and the loss modulus (G'') representing the elastic and viscous components, respectively, in the polymeric material. In TPS75-PLA25 blends, the storage modulus shows characteristics of pure mixtures and interactions with the polymer surfactant, resulting in moderate interactions that tend to stiffen the system with the presence of the plasticizer. This behavior resembles a network with greater structural stability, similar to hydrogels. Values reported in samples TPS75-PLA25, TPS75-PLA25-T10, and TPS75-PLA25-T10-A10 support the behavior of nonlinear polymers with G' > G''. Conversely, samples TPS75-PLA25-T5 and TPS75-PLA25-T5-A10, with lower Tween content, exhibit G'' > G', indicating a tendency for linear polymers or those with weak interactions between chains. Additionally, the internal structure shows a predominantly liquid and viscoelastic behavior at high shear rates (600 rad/s) in TPS75-PLA25-T5-A10. On the other hand, TPS50-PLA50 mixtures with higher PLA content alter the trends discussed above. The presence of the plasticizer ATBC, which demonstrates a greater structural affinity for PLA at ~150 rad/s, shows cross-linking reactions according to dynamic viscosity analysis. Generally, the behavior of these modified mixtures is viscoelastic with G'' > G'. The unmodified TPS50-PLA50 mixture is the only one displaying a viscous behavior. For the processability of polymers through conventional techniques, a fundamental criterion is to maintain a high rate of chain mobility, ensuring viscoelasticity without loss of structural stability under shear conditions [26,27].



(a)

(b)

Figure 3. (a) Log–log plots of complex viscosity (η^*) versus angular frequency obtained from flow measurements conducted on TPS75-PLA25 blends. (b) Rheological data from oscillatory measurements are plotted as elastic and viscous modulus (G' and G'') versus oscillatory frequency.



Figure 4. (a) Log–log plots of complex viscosity (η^*) versus angular frequency obtained from flow measurements carried out on blends prepared TPS50-PLA50. (b) Rheological data from oscillatory measurements plotted as elastic and viscous modulus (G' and G'') versus oscillatory frequency.

3.2. FTIR Analysis

The infrared spectrum (Figure 5a,b) illustrates the characteristic bands of functional groups and bonds contained in the polymer chains of the mixed compounds. In the highest energy zone, O–H hydroxyls appear around 3280 cm⁻¹, related to carbohydrates (amylose and amylopectin), the foundational structures of starch [28]. At 2920 cm^{-1} and 2840 cm⁻¹, asymmetric and symmetric stretching of C–H is observed. The carbonyl vibration (C=O) corresponding to the structure of PLA and ATBC is recognized at 1720 cm⁻¹ [20]. Likewise, at 1736 cm⁻¹, the carbonyl of the ester in the Tween structure, related to the unsaturated chain (hydrophobic part of the amphiphilic molecule), is identified. A band at 1640 cm⁻¹ corresponds to absorbed water. In the ether zone, at 1375 cm⁻¹, 1398 cm⁻¹, and 1404 cm⁻¹, the positions of the O–C–O symmetric stretching modes are exhibited [29]. Subsequently, dialkyl ethers of the glucopyranose ring (C–O–C) and C–O are found at 1150 cm^{-1} and 1018 cm^{-1} , respectively. In the lower-energy zone (Figure 5c,d), vibration bands for amorphous and crystalline PLA microstructures are found at 875 cm^{-1} and 752 cm⁻¹, corresponding to out-of-plane bending vibrations of the γ C=O bond [30]. In the latter, the band of the crystalline phase decreases significantly in the different mixtures functionalized by the plasticizer and surfactants, disrupting the crystalline structure of neat PLA. Other bands between 920 cm⁻¹ and 960 cm⁻¹ also indicate rearrangement due to the interaction of PLA with other components, revealing the rocking vibration modes of -CH₃ [31]. Mixtures containing the plasticizer show a decrease in the OH band compared to the corresponding blanks TPS75-PLA25 and TPS50-PLA50. In previous works, strong interaction with Tween has been discussed; however, the presence of ATBC in high concentrations (TPS75-PLA25-T10-A10) shows an adverse effect on the interaction by exhibiting greater freedom of the hydroxyl bond (OH) at 3280 cm^{-1} . The limitations observed in mixtures where starch predominates (TPS75-PLA25) result from the limited movement of -OH due to interactions promoted between the components in mixtures with equal concentrations of these biopolymers. The area related to glycosidic linkage varies notably in the spectrum between ~1480 cm⁻¹ and ~1330 cm⁻¹, widening due to multiple interactions connected by hydrogen bonds (C-O $\bullet \bullet H$) with the hydroxyls of the other components. In general, the TPS-PLA blends, plasticized and homogenized with Tween and ATBC, show an additional band at 1585 cm^{-1} corresponding to the carbonyl group, a product of the formation of new esters, differentiable from the reagents or starting compounds. According to reports by some authors, ester derivatives can exhibit diverse chemical environments



that dramatically modify the displacement of the carbonyl group. In this case, the systems are favored by showing bands at lower wave numbers. The ether zone corroborates these changes by displaying greater intensity in the bands between 1150 cm^{-1} and 1018 cm^{-1} .

Figure 5. FTIR spectra of the polymeric blends of starch and polylactic acid from 4000 to 400 cm⁻¹ of (a) 75:25 and (b) 50:50. Amplification of the FTIR spectrum from 1000 to 900 cm⁻¹ to analyze the PLA crystallinity in the measurements (c) 75:25 and (d) 50:50.

3.3. Thermal Analysis

Figure 6a,b show the curves derived from the thermogravimetric analysis (DTG) of the modified TPS–PLA mixtures. The thermograms display curves with two significant weight loss stages proportional to the biopolymer content in the mixture. Additionally, minor variations of less than 10% weight loss, related to the partial evaporation of plasticizers (water and glycerol), were identified in the temperature range between 50 °C and 180 °C. It is observed that another portion of plasticizers is released after the degradation of starch, due to stronger interactions that have managed to encapsulate or form crystallization waters. The permanence of involved solvents (plasticizers and surfactants) is of great importance in homogenizing the mixture. This behavior has also been observed by other authors [19,32,33].



Figure 6. Derivative thermogravimetric (DTG) of the polymeric blends of starch and polylactic acid (**a**) 75:25 and (**b**) 50:50 with different proportions of the Tween surfactant and ATBC plasticizer.

According to the temperatures reported in Table 2, higher values can be observed for the modified mixtures compared to the blanks. The increase in thermal stability is due to the effect of the surfactant, which is more noticeable in the TPS50-PLA50 mixtures compared to TPS75-PLA25. In this sense, a higher PLA content allows greater utilization of the interaction between the molecules, stabilizing the mixture. It was observed that in mixtures with 50% starch with the addition of the plasticizer ATBC, the gap between the degradation of the biopolymers decreases. It increases by ~3 °C in the degradation temperature of starch (Td1), while the degradation temperature of PLA (Td2) decreases by ~5 °C. This approach between the two degradation temperatures demonstrates the plasticizer's capacity to promote interaction between TPS and PLA.

Sample	T ₁₀ (°C)	Τ _{d1} (°C)	T _{d2} (°C)
PLA		367.7	
TPS	97.0	300.1	
TPS75-PLA25	58.2	304.0	363.4
TPS75-PLA25-T5	69.6	318.2	402.3
TPS75-PLA25-T10	92.1	326.4	395.9
TPS75-PLA25-T5-A10	125.3	325.7	399.8
TPS75-PLA25-T10-A10	69.5	322.4	401.1
TPS50-PLA50	51.9	306.2	366.7
TPS50-PLA50-T5	143.1	312.7	405.8
TPS50-PLA50-T10	82.6	309.4	404.6

85.1

128.6

299.8

297.7

407.3

406.1

Table 2. Degradation temperatures of starch, PLA, surfactant, and ATBC mixtures.

TPS50-PLA50-T5-A10

TPS50-PLA50-T10-A10

Figure 7 presents the results of differential scanning calorimetry (DSC) for the mixtures, showing two second-order transitions in the temperature range of 50 °C to 70 °C, which can be corroborated in the starting compounds. In the case of starch, a gelatinization temperature (Tgel) is observed once it is mixed with the plasticizers (water and glycerol), and for PLA, the glass transition temperature (Tg) is 64 °C. It is important to mention that the widened band due to Tgel overlaps with the Tg of PLA, limiting the comparative analysis between the samples that consider this parameter. The first-order transitions occur around 120 °C and 160 °C due to the fusion of TPS and PLA, respectively. The 75:25 and 50:50 TPS–PLA blends proportionally show the intensity in the absorption endotherm of the second-order transition. Once the plasticizers are incorporated, a significant increase in peak temperature between 15 °C and 20 °C is observed. The presence of ATBC radically



modifies the molecular structure, imprinting a greater degree of disorder that is evidenced by the decrease in intensity of the melting point of PLA.

Figure 7. The curve of the first heating of the polymeric blends of starch and polylactic acid (**a**) 75:25 and (**b**) 50:50 with different proportions of the Tween surfactant and ATBC plasticizer.

3.4. Melt Flow Index (MFI)

The melt flow index tests were conducted to guide the transformation process, as a critical parameter widely used in the plastics industry (applied to extrusion, injection, thermoforming, and blowing processes). Table 3 presents the results obtained from the melt flow index, considering that the samples with a high content of Tween 20 (TPS50-PLA50-T10, TPS50-PLA50-T10-A10, TPS75-PLA25-T10, TPS75-PLA25-T10-A10) did not flow under the conditions required to continue in the flat film co-extrusion processes. Samples with values between 1 and 5 g/10 min were selected based on the recommendation of the extrusion equipment supplier to proceed with the development of films and subsequent physical analyses (mechanical resistance and water vapor permeability) [26,34]. In general, samples with high melt flow index values allowed for the analysis of their rheological properties. Regarding complex viscosity, samples with low MFI values exhibited high viscosity. The resistance to flow is influenced by the entanglement of polymer chains through strong intermolecular interactions. The ability of some biopolymeric blends to facilitate mobility through greater interaction with plasticizers and the opening of the surfactant, generating a free volume through which chains of the other polymer can enter, makes fluidity possible under adequate temperature and shear conditions. Therefore, samples TPS50-PLA50-T5 and TPS75-PLA25-T5-A10 continue in the scaling stage intending to produce flat films by co-extrusion, as they presented values of 2.27 g/10 min and 1.72 g/10 min, respectively.

Table 3. MFI results were obtained from the TPS-PLA blends.

Sample	MFI (g/10 min)	Sample	MFI (g/10 min)
PLA	3.00 ± 0.21	TPS	0.48 ± 0.03
TPS75-PLA25-T10 *	0	TPS75-PLA25-T10-A10 *	0
TPS75-PLA25-T5	0.63 ± 0.04	TPS75-PLA25-T5-A10	1.72 ± 0.11
TPS50-PLA50-T10 *	0	TPS50-PLA50-T10-A10 *	0
TPS 50-PLA50-T5	2.27 ± 0.13	TPS50-PLA50-T5-A10	6.61 ± 0.31

* For the analysis conditions, the materials did not flow in the plastometer.

3.5. FTIR Analysis for Films

The infrared analysis of the films, selected based on the extrusion processing parameters, allowed for the evaluation of interaction and stability between the components during two thermomechanical processes. In the case of films, infrared analysis was conducted on each side of the film, identified as F1 and F2 (see Figure 8). This sampling approach was maintained for other physical analyses, such as water vapor permeability and contact angle. The F1 and F2 spectra of the TPS50-PLA50-T5 film exhibited minimal differences, with an increase in the band corresponding to C–O around 1100 cm⁻¹ for F2. This increase in intensity is attributed to the greater presence of Tween. However, the polymers remain in a mixture. For TPS75-PLA25-T5-A10, F1 displayed pronounced PLA bands, while F2 predominantly showed the TPS bands discussed in Section 3.2.



Figure 8. FTIR spectra for each face (F1 and F2) of the flat films were obtained by extrusion.

3.6. Contact Angle Analysis

Figure 9 displays the contact angle values represented in bar graphs obtained from the wettability analysis. This characterization was conducted on both sides of the film to assess the surface behavior of the polymer mixture concerning humidity. The TPS75-PLA25-T5-A10 F1 sample exhibited limited hydrophilicity with an average value of 89.1°, while the opposite face (F2) presented a value of 29.9°, making this surface highly hydrophilic. This allowed water interaction with the material through hydrogen bonds with starch hydroxyls. This observation aligns with the infrared analysis, indicating a distribution of components between F1 and F2, identifying PLA and TPS, respectively. The flat film extrusion process resulted in the orientation of PLA polymer chains towards F1 and TPS towards F2. Although evident in slower processes like solvent casting (taking minutes), faster processes such as molding, extrusion, or injection (taking seconds) might limit molecular mobility [35], forcing interactions before the initial mixing. For the TPS50-PLA50-T5 film, no significant difference in humidity behavior was observed on different sides of the film, with angles of 83.5° and 82.2° for F1 and F2, respectively. This result aligns with the infrared analysis, indicating a combination of TPS and PLA polymers. The stability of the mixture, facilitated by the presence of the surfactant and polymer proportions, supports a homogeneous system. The orientation of starch and PLA caused by the surfactant is evident in the film conformation, with one surface appearing darker (starch) and the other white (PLA), as observed in photographs taken on both surfaces of the films (Figure 9).



Figure 9. The contact angle was measured by both surfaces of the developed films.

3.7. Water Vapor Permeability

Table 4 presents the results of water vapor transmission rate (WVTR) and water vapor permeability (WVP) for TPS75-PLA25-T5-A10 and TPS50-PLA50-T5 films on both sides of the samples. Generally, the behavior related to the composition was maintained. In the case of TPS50-PLA50-T5, there are values close to each other (9.0×10^{-4} and 7.5×10^{-4}), indicating strong cohesion between the polymer chains and the positive effect of the surfactant in achieving optimal miscibility and homogeneity in the material. Very high values of WVTR (20.2–35.4 g/m²·d) have been reported in similar blends (starch with other polyesters) [36]. These values demonstrate a high barrier capacity against the studied gas (water vapor), even surpassing samples containing nanoparticles [37,38]. The TPS75-PLA25-T5-A10 polymer matrix, in the presence of plasticizer and surfactant, did not exhibit a significant difference between one side of the film and the other. It is noteworthy that low values were obtained. The permeability results are promising for the use of this film in humid environments, presenting low permeability values compared to those reported in other studies on biological-based films [39,40]. A higher PLA content presents values of up to two orders of magnitude lower permeability, allowing a greater presence of crystalline domains that hinder the water solubility of the polymer. This effect has been explained in models representing a tortuous path for the gas to pass through the PLA spherulites [41–44].

Sample	WVTR g·mm/(m ² -Day)	WVP g/(m ² -Day)
TPS75-PLA25-T5-A10-F1	0.00572	0.00505
TPS 75-PLA25-T5-A10-F2	0.02157	0.02208
TPS 50-PLA50-T5-F1	0.00072	0.00090
TPS 50-PLA50-T5-F2	0.00063	0.00075

Table 4. Water vapor transmission rate (WVTR) and water vapor permeability (WVP) of starch-PLA films.

3.8. Mechanical Analysis

The results of the tensile tests conducted on the A75-PLA25-T5-10 and A50-PLA50-T5 films performed both transversely and longitudinally are presented in Table 5. According to previous studies [20], TPS films formed by hot compression exhibit a tensile strength of 5.40 ± 0.8 MPa, whereas in the case of PLA, it is 64.00 ± 2.70 MPa. As shown in Table 4,

films obtained by extrusion show low mechanical properties compared to their precursors. This is attributed to the low miscibility of the TPS and PLA blend [20,45]. The interactions observed by FTIR, indicating an increase in hydrogen bond formation, result in a brittle material due to the weak nature of this type of bond. Additionally, DSC and TGA reveal the reaction temperatures of the precursors, highlighting the low interaction between TPS and PLA, which is also reflected in the films' low elongation capacity. The mechanical variables measured for the A75-PLA25-T5-10 film (Table 5) exhibit similar behavior in both longitudinal and transverse directions. However, the A50-PLA50-T5 film in the longitudinal direction shows higher tensile strength and elongation percentage. The difference of 1 MPa and 0.6%, though present, does not significantly impact its final behavior. On the other hand, the longitudinally measured Young's modulus indicates greater stiffness in this direction, as it has a higher value compared to the transverse direction.

Table 5. MFI results	from the	TPS-P	LA films
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Sample	Meaning of the Test	Tensile Strength (MPa)	Strain at Break (%)	Young's Modulus (MPa)
TPS75-PLA25-T5-A10	Lengthwise Cross	$\begin{array}{c} 3.603 \pm 0.495 \\ 3.490 \pm 0.321 \end{array}$	$\begin{array}{c} 2.59 \pm 0.36 \\ 2.56 \pm 0.33 \end{array}$	$\begin{array}{c} 436.54 \pm 46.28 \\ 436.72 \pm 46.17 \end{array}$
TPS50-PLA50-T5	Lengthwise Cross	$\begin{array}{c} 4.276 \pm 1.035 \\ 3.308 \pm 0.919 \end{array}$	$\begin{array}{c} 2.63 \pm 0.13 \\ 1.98 \pm 0.65 \end{array}$	$\begin{array}{c} 329.96 \pm 52.93 \\ 245.61 \pm 42.43 \end{array}$

3.9. Scanning Electron Microscopy (SEM)

Figure 10 shows SEM images of the fracture surfaces of the TPS75-PLA25-T5-A10 and TPS50-PLA50-T5 films obtained by extrusion. Through these micrographs, a surface with low deformation characteristics of semirigid materials is observed. Likewise, compact materials are seen, without the formation of pores, along with the presence of a single phase (homogeneous material). Sample TPS75-PLA25-T5-A10 presents short, wavy threads on the surface, with a narrow size distribution. This sample presents greater deformation (Figure 10b, right side), due to the effect of the plasticizer that appears well dispersed [38].



Figure 10. Cross-section micrographs (mag. 100×) of samples: (**a**) TPS50-PLA50-T5 and (**b**) TPS75-PLA25-T5-A10.

4. Conclusions

The study of mixtures between the biopolymers starch and PLA is dependent on the process conditions, the proportion between the components, and the presence of plasticizing agents and surfactants, generating significant changes in the final material. The samples were structurally analyzed by infrared spectroscopy, and the presence of bands corresponding to TPS and PLA, as well as the interactions that occur between them as an effect of the addition of surfactant and the plasticizer ATBC, were evident. Regarding the rheological properties, greater integration of the components in the mixtures is achieved with the presence that leads to an increase in viscosity, evidencing that the ATBC favors the plasticization of the samples, with a viscous to elastic transition, around 100 rad/s. On the other hand, the rheological study allowed us to discard mixtures with 75% starch without ATBC because the material does not plasticize. In the thermal properties, it was observed that the surfactant and the plasticizer generate a closer relationship between the degradation temperature of the TPS and the PLA, evidencing a greater interaction between the compounds in the mixture. Additionally, the glass transition temperature is reduced in PLA/TPS mixtures concerning PLA, due to a plasticizing effect of the ATBC and the interactions promoted by the surfactant. Finally, the determination of the fluidity index allows for defining the mixtures that plasticize and that may present suitable conditions for their possible application in plastic transformation processes, where the extrusion of flat film or blown film represents an alternative for obtaining a product. Through the work conducted, it was possible to obtain characterization, where it was evident through the degradation temperatures that the TPS-PLA mixture continues to present a certain immiscibility, which is also evidenced by the orientation of the polar and nonpolar groups on the surfaces, generating visual differences on the two sides of the film. On the other hand, the low mechanical characteristics obtained limit the stress to which these films can be subjected, which is in accordance with what has been presented in different research and development of biobased films that have low mechanical properties. Finally, the results obtained regarding contact angle and water vapor permeability indicate that the developed film supports humid environments better than other biobased films that have been developed in another research.

Author Contributions: Conceptualization, C.C. and H.L.C.P.; methodology, C.C.; software, C.C.; validation, C.C. and H.L.C.P.; formal analysis, C.C. and H.L.C.P.; investigation, C.C. and H.L.C.P.; resources, C.C. and H.L.C.P.; data curation, C.C. and H.L.C.P.; writing—original draft preparation, C.C.; writing—review and editing, C.C. and H.L.C.P.; visualization, C.C.; supervision, C.C. and H.L.C.P.; project administration, H.L.C.P.; funding acquisition, C.C. and H.L.C.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Vicerrectoria de Investigaciones of Unidad Central del Valle del Cauca under project No. PI-1300-50.2-2023-27.

Data Availability Statement: Data are contained within the article.

Acknowledgments: Carolina Caicedo (C.C.) acknowledges financial support from the Vicerrectoria de Investigaciones of Unidad Central del Valle del Cauca under project No. PI-1300-50.2-2023-27.

Conflicts of Interest: The authors declare no conflicts of interest.

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