processes

MDPI

Article

Study of the Physical and Mechanical Properties of Thermoplastic Starch/Poly(Lactic Acid) Blends Modified with Acid Agents

Carolina Caicedo [1,]* and Heidy Lorena Calambás Pulgarin [2]

[1] Grupo de Investigación en Química y Biotecnología (QUIBIO), Facultad de Ciencias Básicas, Universidad Santiago de Cali, Pampalinda, Santiago de Cali 760035, Colombia
[2] Grupo de Investigación en Desarrollo de Materiales y Productos, Centro Nacional de Asistencia Técnica a la Industria (ASTIN), SENA, Cali 760003, Colombia; hlcalambas@misena.edu.co
* Correspondence: carolina.caicedo03@usc.edu.co

Abstract: In this work, we present a functionalization strategy of starch-poly(lactic acid) (PLA) blends with organic acids. Lactic and acetic acid were used as acid agents, and oleic acid was also included in the previous acids, with the aim of finding a synergy that thermodynamically benefits the products and provides hydrophobicity. The ratio of starch and sorbitol was 70:30, and the added acid agent replaced 6% of the plasticizer; meanwhile, the thermoplastic starch (TPS)–PLA blend proportion was 70:30 considering the modified TPS. The mixtures were obtained in a torque rheometer at 50 rpm for 10 min at 150 °C. The organic acids facilitated interactions between TPS and PLA. Although TPS and PLA are not miscible, PLA uniformly dispersed into the starch matrix. Furthermore, a reduction in the surface polarity was achieved, which enabled the wettability to reach values close to those of neat PLA (TPS–L-PLA increased by 55% compared to TPS–PLA). The rheological results showed a modulus similar to that of TPS. In general, there were transitions from elastic to viscous, in which the viscous phase predominated. The first and second-order thermal transitions did not show significant changes. The structural affinity of lactic acid with biopolymers (TPS–L-PLA) allowed a greater interaction and was corroborated with the mechanical properties, resulting in a greater resistance with respect to pure TPS and blended TPS–PLA (28.9%). These results are particularly relevant for the packaging industry.

Keywords: biopolymers; thermoplastic starch; organic acids; poly(lactic acid); rheology; surface wettability

check for updates

Citation: Caicedo, C.; Pulgarin, H.L.C. Study of the Physical and Mechanical Properties of Thermoplastic Starch/Poly(Lactic Acid) Blends Modified with Acid Agents. *Processes* **2021**, *9*, 578. https://doi.org/10.3390/pr9040578

Academic Editor: Katherine M. E. Stewart

Received: 17 February 2021
Accepted: 18 March 2021
Published: 26 March 2021

1. Introduction

The conformation and functionalization of biopolymers as potential substitutes for plastics derived from petroleum has recently gained momentum for a wide range of applications [1–3]. Important research and technological developments have been made in biopolymer blends as an alternative to plastics. TPS, PLA, poly(hydroxyalkanoates) and chitosan are among the most promising biopolymers for the packaging sector [4,5]. The efficiency of starch thermoplasticization stems from the capacity of hydrogen bonding and the mechanism of cleavage of the starch chain. In this sense, the crystallinity loss accounts for starch granule destructuring, thereby compromising material stability and physico-mechanical properties [6,7]. Compared to conventional polymers, neat TPS has shown disadvantages, especially when it comes to its high hydrophilicity and permeability to gases and even microorganisms. This disadvantage has been overcome by incorporating inorganic particles in the biopolymer matrix that offer better mechanical and barrier properties to the composite material [8–11] and by using natural fibers as reinforcement for TPS [8,12–14] and blends with different polymers such as polycaprolactone, polyvinyl alcohol and PLA [15]. Likewise, starch has been modified by oxidation, esterification and etherification processes [16,17]. Modification with low molecular weight organic and/or fatty acids (e.g., acetic acid, maleic anhydride, linoleic acid and oleic acid) creates a steric hindrance that prevents the formation of hydrogen bonds on the hydroxyl group of starch, which is protected because of the new interaction. This prevents—or makes starch less prone to—retrodegradation [18]. In the research conducted by Abdul Rasheed et al. [19], it is evident that the modification of cassava starch with acetic anhydride and citric acid reduces the water absorption capacity, thereby reducing its degradation rate without affecting film biodegradability. Other fatty acids have been used to modify starch, such as oleic acid, whose main effect is reflected in the decrease in the glass transition temperature [18,20]. A previous study demonstrated that the organic (lactic) acid content facilitates gelatinization, resulting in efficient plasticization; however, the decreased hydrophilicity was not noticeable [17]. PLA is compostable and has excellent optical, chemical, mechanical and barrier properties, but applications are largely limited due to its rigidity. To this end, research continues to investigate better conditions. The range of plasticizers that contribute to this problem continues to expand. The aforementioned characteristics enable TPS and PLA to be considered as candidates for developing new biopolymers from this blend [21,22]. However, these components show low compatibility due to the hydrophilic nature of starch and the hydrophobic nature of PLA. The results generated show that the blends are thermodynamically immiscible, with high brittleness, low resistance and toughness [18]. The compatibilization of polymeric materials from different sources has been attempted to achieve adequate synergy and guarantee the best properties in the product [23].

Yu et al. [24] studied the compatibilization effect of TPS and PLA blends by including methylenediphenyl diisocyanate (MDI). They found that, when it was previously distributed in PLA, the modulus, elastic limit and impact resistance increased. In 2013, Shirai et al. [25] concluded that the increase of adipate esters in these blends presents higher elongation at break (120–148%) with respect to citrate esters (72–103%), because their linear structure allows a better interaction and plasticization of PLA. Akrami et al. (2016) evaluated the compatibilization effect of grafted starch with polyethylene glycol and maleic anhydride in a mixture including 70% PLA that demonstrated a better interfacial adherence without affecting biodegradability. Recently, improvements in the barrier properties of TPS/PLA blends have been reported, resulting from additivation with epoxidized cardoon oil. This is due to the possible formation of a physical barrier that prevents the diffusion and solubilization of water and oxygen, in addition to producing a slightly improved miscibility between biopoymers that was evidenced by differential scanning calorimetry (DSC) [26]. Another development of mixtures involved citric acid and cassava pulp (CP) as reinforcing materials. The mechanical properties reflected an increase in strength and improved biocompatibility as the CP concentration increased. However, the elongation at break decreased [5]. The lack of miscibility between PLA and TPS is a great challenge for researchers in the field. In the present work, mixtures of plasticized achira starch and PLA were developed that incorporated organic acids through melt mixing in order to study the effect and synergy that saturated and unsaturated organic acids have on the thermal, rheological, mechanical, surface and morphological characteristics of the biopolymer blend. The results have been compared with neat biopolymers, which allowed us to determine the performance; these results constitute an important antecedent in the packaging sector.

2. Materials and Methods

Achira starch was supplied by Surtialmidon (Huila, Colombia) with a density of 1.59 g/mL. The plasticizer was obtained from Sigma Aldrich, sorbitol with a density of 1.28 g/mL (purity: 99.5%) and acetic acid (purity: 99.7%). Oleic acid was obtained from Quimifast Ltd.a., and lactic acid was supplied by Mol Labs (purity: 85%), the density of which was 1.21 g/mL. Ingeo 2003-D polylactic acid (PLA) from Nature Works Company (Lancaster, PA, USA) with a density of 1.24 g/cm^3 and MFI (210 °C/2.16 kg) of 6.0 g/10 min.

2.1. Preparation of Blends TPS

The samples of TPS and TPS/PLA modified with organic acids were prepared using a torque rheometer (Thermo Scientific HAAKE Rheomix). The rotors were of the roller type and worked at a speed of 50 rpm at 150 °C for 10 min. The amounts of achira starch, plasticizer agent, PLA and organic acids (lactic (L), acetic (A) and oleic (O)) are specified in Table 1. For this experiment, the materials were obtained in duplicate.

Table 1. Proportions of starch, plasticizing, acid agent and poly(lactic acid) (PLA) used for the preparation of the thermoplastic starch. TPS: thermoplastic starch.

Sample	Starch (wt.%)	Sorbitol (wt.%)	Acid Agent (wt.%)			PLA (wt.%)
			Lactic Acid	Acetic Acid	Oleic Acid	
TPS	70	30	-	-	-	-
TPS-L	70	24	6	-	-	-
TPS-A	70	24	-	6	-	-
PLA	-	-	-	-	-	100
TPS-PLA	49	21				30
TPS-L-PLA	47.5	18.5	4	-	-	30
TPS-A-PLA	47.5	18.5	-	4	-	30
TPS-L-PLA-O	47.5	14.5	4	-	4	30
TPS-A-PLA-O	47.5	14.5	-	4	4	30

2.2. Rheological Analysis

We used a rotational rheometer DHR-2, TA Instruments to study the material rheological behavior. This study was conducted at a strain of 0.1% at 160 °C with controlled stress and a cone-plate configuration using the equilibrium flow test with a gap of 145 µm, a diameter of 25 mm and an angle of 5753°. The shear varied between 0.1 and 100 s^{-1}.

2.3. Fourier Transformed Infrared Spectroscopy (FTIR)

An FTIR analysis of sheets was carried out in ATR mode with a Shimadzu IR Affinity-1. Once the dry film was formed, it was analyzed using 16 scans, a wave number range between 600 and 4000 cm^{-1} and a resolution of 4 cm^{-1}.

2.4. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)

We carried out a thermogravimetric analysis (TGA) to assess the thermal stability of TPS and TPS/PLA. To this end, we used a TGA/DSC 2 STAR System thermogravimetric analyzer, Mettler Toledo, USA. We employed a heating rate 20 °C min^{-1} from 25 °C until 600 °C, using a nitrogen purge at a flow rate of 60 mL/min. This analysis was performed using a nitrogen purge and 10 ± 0.5 mg of TPS.

Differential scanning calorimetry (DSC) analysis was carried out to identify the sample's thermal transitions using TA Q-2000 equipment at a heating rate of 10 °C min^{-1} in a temperature range between 25 and 200 °C and a nitrogen purge. An amount of 10 mg of the TPS and TPS/PLA samples was used for this analysis. The samples were subjected to heating–cooling–heating cycles. We used the results of the second heating run to evaluated the thermal properties because of the elimination of the thermal history of the test specimens.

2.5. Scanning Electron Microscopy Analysis

The surfaces of cryofractured TPS, and TPS/PLA were examined and the micrographs were digitally captured using a scanning electron microscope (SEM) JEOL, JCM 50,000 (Tokyo, Japan). A voltage of 10 kV was applied. The samples were coated with a thin layer of gold. Magnifications of 1500× and 500× of the fracture surface were taken.

2.6. Contact Angle Analysis

Measurements of the contact angle with water were carried out using a Ramé-Hart Model 250 goniometer at room temperature. A 20 µL drop of distilled water was placed on the surface of the TPS and TPS/PLA samples. After stabilization (60 s), the image was recorded and the contact angle was measured by ImageJ software. The average of the three measurements was taken and subjected to an analysis of variance (ANOVA). Tukey's test was applied at the 0.05 level of significance, which allowed the measurements of each group (TPS and TPS-PLA) to be compared in order to determine that they were significantly different. All statistical analyzes were performed with IBM SPSS Statistics 25.

2.7. Tensile Test

The samples had a length and width of 100 mm and 25 mm, respectively, and had a variable thickness. The specimens were conditioned at 23 °C for 2 days. The tensile test took place in a universal testing machine INSTRON model EMIC 23–50 equipped with a 50 kN load cell. The tests were performed at 23 °C using a constant rate of 10 mm/min. The results were taken as the average of six samples and submitted to the statistical analysis indicated in Section 2.7.

3. Results

3.1. Rheological Analysis

Figures 1 and 2 present the curves corresponding to the modulus (storage G′ and loss G″) for the TPS/PLA blends. The modulus values increased proportionally to the angular frequency. This behavior is typical in thermoplastics, because an energy input is required to increase the mobility of polymeric chains. The TPS and TPS-L samples showed two transitions in the range studies. The first transition was from a viscous to an elastic phase at 0.3 Hz, with a modulus of 6.3 and 18.4 kPa, respectively. The second transition was from an elastic to viscous phase for TPS at 34.1 Hz and 10.3 kPa, while for TPS-L, there was a coincidence with the first phase for TPS-A at 6.2 Hz with a modulus of ~30 kPa. The addition of acidic agents generated a premature transition (shorten the solid phase). This result matches the data derived by previous studies [17,27]. Conversely, the PLA content in the different samples of TPS with acidic agents did not alter the behavior described; i.e., the rheological nature of the prevailing TPS. It was observed that acetic acid in starch notably increased the elastic component, facilitating the gelatinization process with a modulus close to 6 kPa. Finally, the incorporation of oleic acid in the modified TPS/PLA blends showed a slight increase in modulus and decreased the elastic component, allowing more to flow.

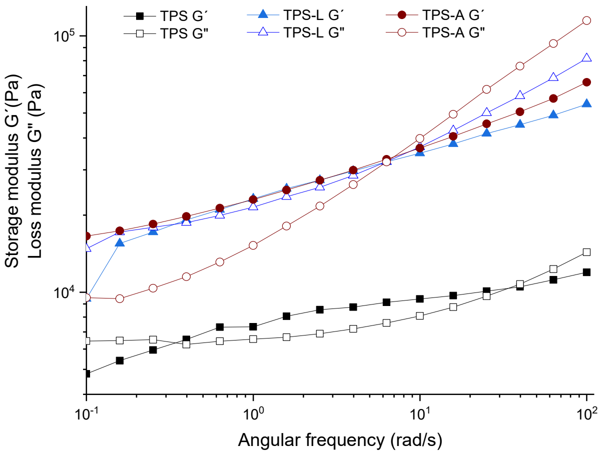


Figure 1. Dynamic rheological properties of TPS samples.

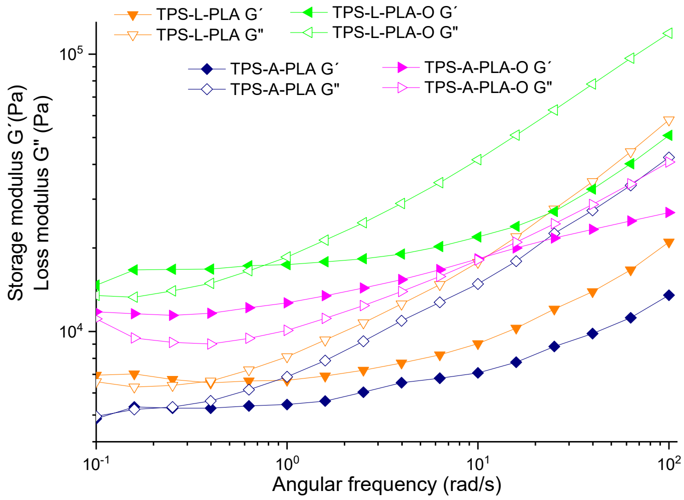


Figure 2. Dynamic rheological properties of TPS and PLA samples.

The curves that show complex viscosity with respect to the angular frequency (Figure 3a) depend on the acid content in the different TPS and TPS/PLA samples. In general, lower values for acetic acid relative to lactic acid were shown in all samples analyzed. The incorporation of oleic acid in TPS/PLA samples increased the viscosity in a similar way to that when added to the TPS-L and TPS-A samples (~170 kPa). The TPS-L-PLA and TPS-A-PLA samples did not change from TPS (~70 kPa). Polymers became very thin as the shear increased, following a linear drop by two orders of magnitude. It should be mentioned that, in the range studied, no possible esterification or crosslinking reactions were shown, as had been observed for TPS samples. In this way, the curves obtained in the Cole–Cole diagram (Figure 3b) that relate the imaginary viscosity component (η″) to the real viscosity component (η′) increased the viscosity in TPS-A samples and shortened the relaxation times with respect to those of lactic acid. According to the previous results, it is possible to observe a smooth behavior in all samples. The absence of a multiphase system condition allowed the material's mechanical properties to be predicted well.

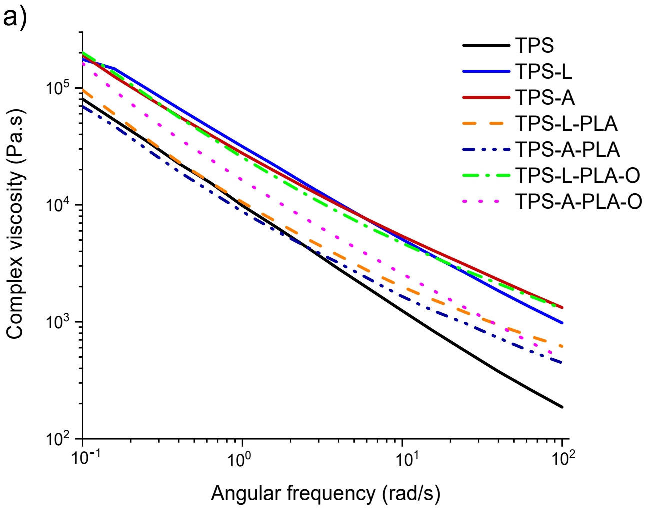


Figure 3. *Cont.*

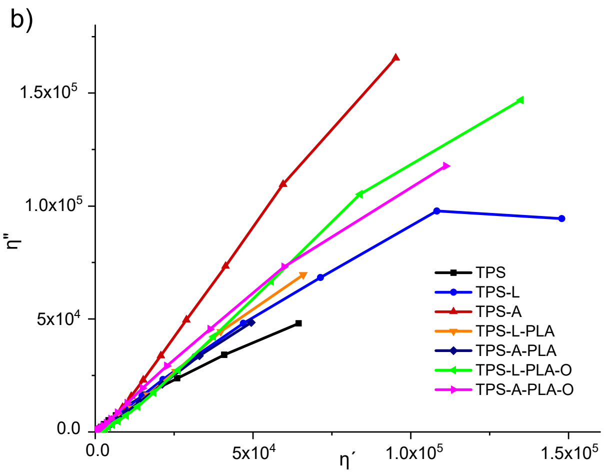


Figure 3. Rheological characteristics: (**a**) complex viscosity and (**b**) Cole–Cole diagrams of TPS blends.

3.2. IR Analysis

The IR spectrum allowed us to observe the characteristic bands of TPS and TPS/PLA and their interactions with functionalizing acids (Figure 4). At a wavelength of 2921 cm^{-1}, one of the characteristic absorption bands of the C-H groups of CH_2 occurred in the C6 glucose unit. The 1645 cm^{-1} band belonged to the bending vibration of O-H attributed to the absorption of hydroxyl groups in starch [17,28]. For TPS and TPS-A, the vibrations corresponding to the stretching of the C-O bond of the C-O-C group [2,26] appeared at 995 cm^{-1}, while for TPS-L, these appeared at 999 cm^{-1}. In the same way, the band at 1012 cm^{-1} in TPS and TPS-A showed a shift for TPS-L and appeared at 1017 cm^{-1}. This demonstrated that the incorporation of lactic acid helped form more stable hydrogen bonds than those obtained with acetic acid or only the plasticizer. The TPS-L mixture demonstrated a characteristic band at 1721 cm^{-1}, revealing an efficient acetylation process that occurred between the hydroxyl group in starch and lactic acid.

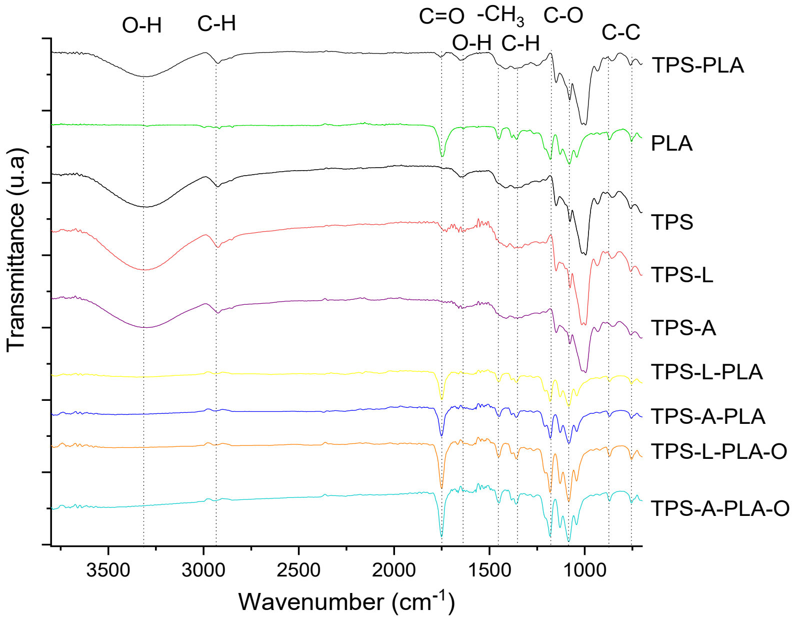


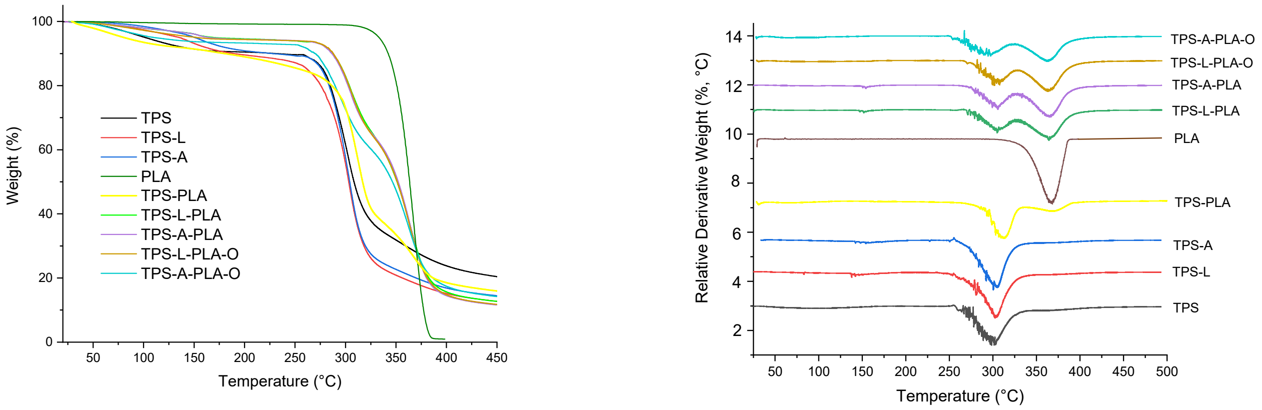
Figure 4. Fourier Transformed Infrared Spectroscopy (FTIR) spectra of the TPS and TPS/PLA samples.

The FTIR spectra of the TPS-PLA blends showed the characteristic band at 1750 cm^{-1} corresponding to the carbonyl stretching [29]. This showed an increase in intensity for the TPS-L-PLA-O and TPS-A-PLA samples due to interactions with the oleic acid present.

A band at 1455 cm^{-1} was also shown for the -CH_3 group. The typical band of the asymmetric stretching of C-O in the ester group appeared at 1182 cm^{-1}, and in the TPS and PLA blends presented a greater intensity for samples containing oleic acid [29]. Ultimately, in the fingerprint region, two bands at 868 and 755 cm^{-1} were related to the C-C stretch vibration that corresponded to the amorphous and crystalline phase of PLA, respectively [21].

3.3. Thermal Analysis—TGA, DSC

Figure 5a presents the curves of the TGA thermogram, where it is clear that the first mass losses were due to the detachment of weakly (between 25 and 70 °C) and strongly (between 70 and 180 °C) bound water [30]. The highest value was related to the evaporation of the plasticizer (sorbitol). A loss of mass due to starch degradation occurred at 300 °C, whereas for the samples containing PLA, this degradation was observed at around 360 °C [7,13]. When comparing the systems based on TPS/PLA (derivative thermogravimetry (DTG) curves (Figure 5b)), we observed that they presented two separate weight loss drops. This phase separation was due to the nature of the polymer [7]. Specifically, the TPS-PLA blend presented two peaks: the maximum degradation occurred at 312 °C and the minimum at 368 °C. This result was reversed when acids were incorporated into the different mixtures. Likewise, the addition of organic acids allowed a better thermal stabilization of the TPS that was observed in the TGA curve; the TPS and TPS-PLA samples presented a greater slope, indicating water loss. From the above, it can be inferred that these samples are more hydrophilic. Therefore, it is necessary to continue studying systems that allow a better coupling and/or thermal stabilization that facilitates the processing of the mixtures.



(**a**) (**b**)

Figure 5. Thermogravimetric analysis (TGA) (**a**) and derivative thermogravimetry (DTG) (**b**) curves for TPS samples.

Figure 6 shows the second heating curve of TPS samples and TPS/PLA blends after cooling at a heating rate of 10 °C/min. Starch is less sensitive to thermal transitions than PLA; in TPS, only a second-order transition was observed around 57 °C. The enthalpy values for TPS with acidic agents were clearly reduced by the molecular disorganization caused by gelatinization [17]. Neat PLA showed a glass transition at ~60 °C and two transitions for both crystallization (112 °C) and melting (148 °C and 156 °C). In general, the TPS/PLA samples and their respective blends with acidic agents did not significantly change in the glass and melt transitions with respect to the neat polymers or TPS-PLA. However, for crystallization, both temperatures and enthalpies depend on the type of acidic agent. Acetic acid achieved a decrease ($\leq$2 °C) in crystallization temperatures and a greater degree of disorder with lower enthalpies, while lactic acid at increased temperatures (2 to 4 °C) also caused a greater disorder of the structure. This behavior resembles that obtained by Yu et al. [31]. The above allows us to conclude that TPS acts as a nucleating agent in PLA and that organic acids increase the crystallization speed.

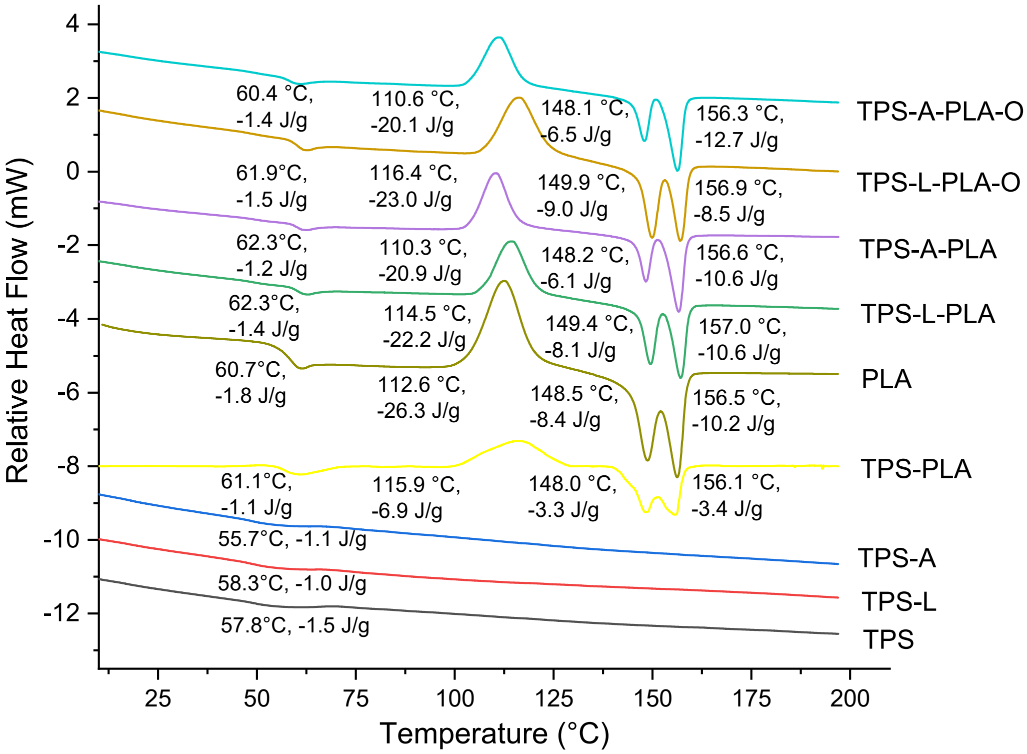


Figure 6. The differential scanning calorimetry (DSC) thermogram for TPS samples.

We performed an SEM analysis to investigate the microstructure of the TPS and TPS/PLA. Figure 7 shows the SEM cross-sectional morphology of the samples. The TPS sample shows a low level of starch destructuring. TPS functionalized with lactic acid and acetic acid, namely TPS-L and TPS-A, allowed us to obtain a more compact and homogeneous material, with the presence of a small amount of non-gelatinized starch [17]. Specifically, TPS-L presented a smoother and more compact surface, with a small number of pores, while TPS-A presented greater roughness. For TPS/PLA blends functionalized with organic acids, the low miscibility between the hydrophobic PLA and the hydrophilic TPS can be observed through the phase separation between the TPS matrix and the PLA [32]. It is important to note that acetic acid promoted PLA dispersion in the matrix. The blends incorporating oleic acid were more homogeneous, which was confirmed by the lack of a clearly defined interface. The PLA filaments and particles were almost covered by the TPS matrix. Furthermore, it is clear that the size of the dispersed phase was significantly reduced in the presence of oleic acid, especially in the TPS-A-PLA-O. However, there was an increased number of pores.

3.4. Contact Angle Analysis

The results of the contact angle are presented in Figure 8. Derived from this analysis, it can be observed in a general way that the contact angle values increased with respect to the pure plasticized starch matrix by 11% and 20% for TPS-L and TPS-A. These results may be associated with hydrogen bonds promoted by the hydroxyl group leaving fewer groups available on the surface that allowed interaction with water [17,26]. This suggests greater protection from acetic acid, which presented less steric hindrance. The blends of TPS with PLA showed a decrease in wettability, reaching values in the contact angle similar to those of neat PLA (70.1°); the increase for TPS-L-PLA was 55% and TPS-A-PLA of 38%, compared to TPS-PLA. The additional presence of oleic acid did not show a significant hydrophobic effect. In contrast, hydrophobicity slightly reduced in the TPS-L-PLA-O sample. This can be attributed to the porous microstructure (observed in SEM), as well as the low dispersion of the components.

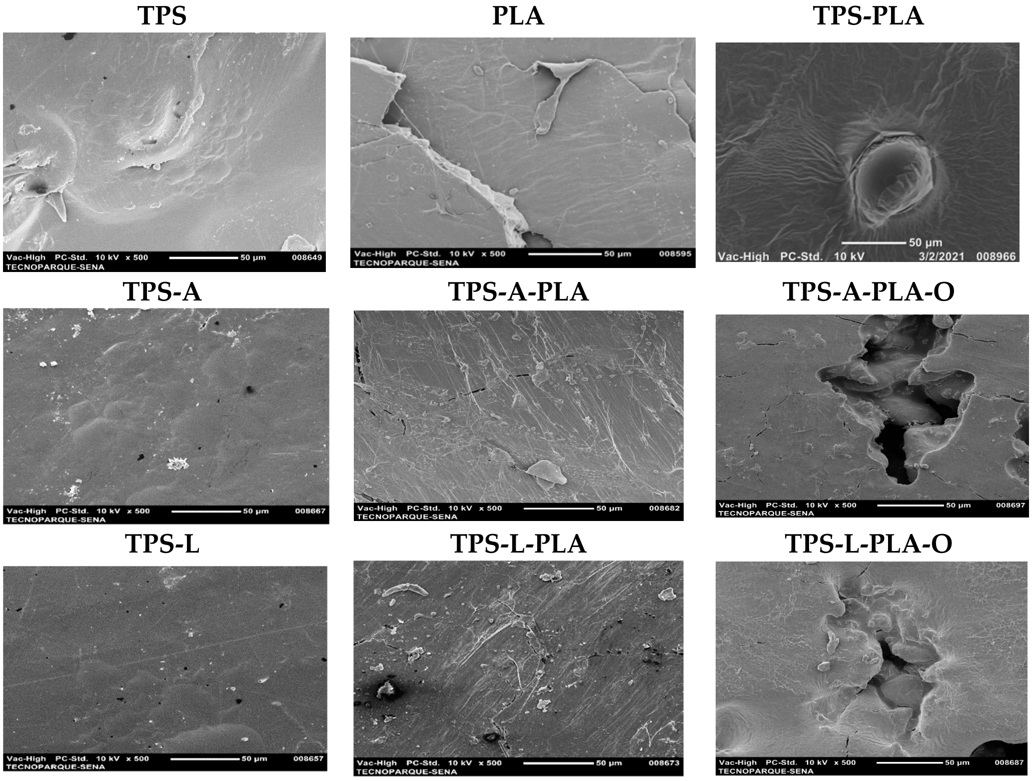


Figure 7. Micrographs obtained by scanning electron microscopy (SEM) with magnifications of 500X for blends of TPS and TPS/PLA.

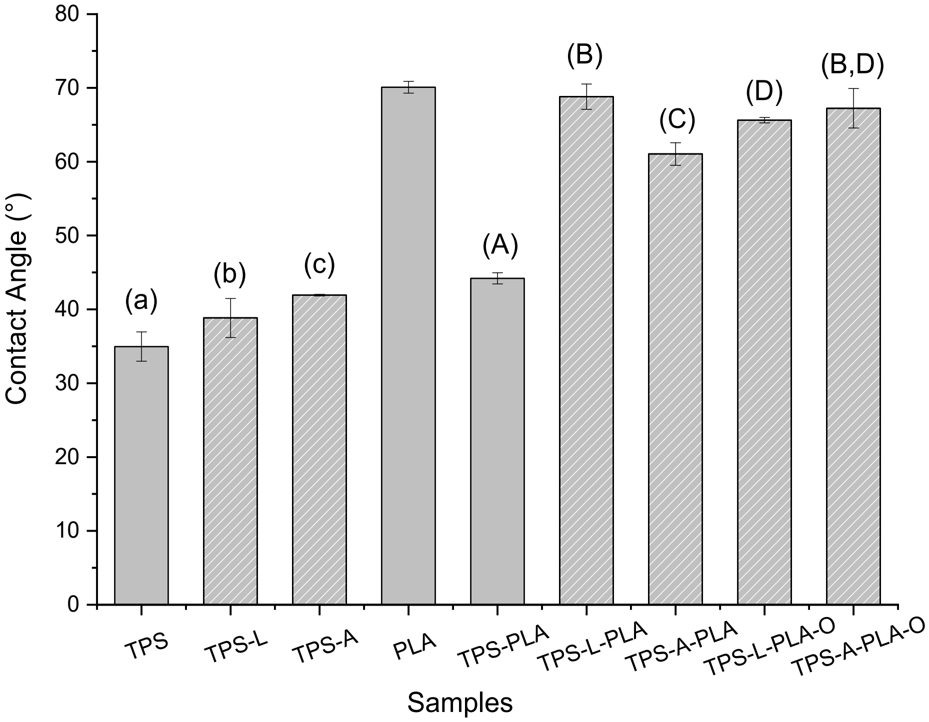


Figure 8. Average contact angle values and their respective standard deviations for modified TPS and blends of TPS/PLA. a–c; A–D: Different letters in the same column indicate significative differences from a set of means of each reprocessing group ($p < 0.05$).

3.5. Tensile Test

The tensile properties of the samples are presented in Table 2. The data analysis results show that the functionalization of TPS with acidic agents TPS-L and TPS-A slightly increased the value of the tensile strength by 13.1% and 6.5%, respectively; additionally, the Young's modulus increased. However, the plasticity of the material diminished with low elongations. In this way, an increase was observed in the mixtures of TPS and PLA with lactic acid (28.9%) and acetic acid (15.9%) with respect to the blank (TPS-PLA). These results contrast with the other physical properties previously discussed, where the formation of more stable hydrogen bonds was evidenced in this type of system [17]. In contrast, it was observed that there was no synergistic effect with oleic acid; despite being hydrophobic, its dispersion on the matrix was inefficient, causing a possible emulsion in the molten state, and when the material solidified, a porous appearance was observed as in the case of the TPS-L-PLA-O and TPS-L-PLA-O samples. Therefore, a detriment to the mechanical properties was obtained, which did not follow the "rule of mixtures" due to the immiscibility between the components; weak macromolecule interactions allowed them to easily move when subjected to an external force [26]. In general, the nature of a flexible polymer such as TPS with a rigid polymer such as PLA significantly increases the Young's modulus and considerably reduces the deformation at break for all mixtures with respect to homologues with organic acids.

Table 2. Tensile properties in the TPS, PLA and the blends of TPS-PLA.

Sample	Tensile Strength (MPa) *	Young Modulus (MPa) *	Deformation at Break (%) *
TPS	5.40 ± 0.86^{a}	77.00 ± 15.00^{a}	51.00 ± 3.00^{a}
TPS-L	6.10 ± 0.62^{a}	509.12 ± 24.09^{b}	7.49 ± 0.81^{b}
TPS-A	5.75 ± 0.59^{a}	498.06 ± 30.21^{b}	4.49 ± 0.59^{c}
PLA	64.00 ± 2.70	3198.00 ± 132.00	2.50 ± 0.10
TPS-PLA	5.60 ± 0.90^{A}	135.71 ± 14.08^{A}	2.62 ± 0.59^{A}
TPS-L-PLA	7.23 ± 1.40^{B}	1801.81 ± 22.15^{B}	2.70 ± 0.11^{A}
TPS-A-PLA	$6.49 \pm 0.60^{A,B}$	1456.55 ± 41.81^{C}	2.81 ± 0.27^{A}
TPS-L-PLA-O	3.68 ± 0.69^{D}	1502.32 ± 40.24^{D}	0.59 ± 0.17^{B}
TPS-A-PLA-O	2.92 ± 0.25^{D}	1114.27 ± 52.57^{E}	0.55 ± 0.17^{B}

$^{a\text{–}c}$; $^{A\text{–}E}$ Different letters in the same column indicate significative differences from a set of means of each reprocessing group ($p < 0.05$). * Mean of six replications ± standard deviation.

4. Conclusions

The addition of acids to TPS and blending with modified starch PLA can effectively improve the material's processability according to the rheological results obtained. There is an optimal component dispersion in the system. Despite having slightly higher modulus, the components demonstrate a transition in which the viscous behavior prevails for a high rate of shear. DSC and DTG analyses show that TPS and PLA compounds are incompatible. The addition of acetic acid promotes the phase changes (crystallization) of PLA and increases its thermal stability. Lactic acid delays crystallization; however, it maintains good stability. The contact angle and the nature of organic acid favor the dispersion of PLA and hydrophobic systems such as oleic acid. This interaction was confirmed in the infrared spectra. The tensile properties showed a non-synergistic process between acidic agents (lactic/oleic and acetic/oleic) that was corroborated by thermal analysis results. It should be noted that the TPS-L-PLA sample demonstrated greater resistance to tension compared to that of neat TPS, in which the structural affinity of lactic acid with the macromolecules allowed better interactions.

The TPS/PLA blends present a good interaction due to the inclusion of functionalizing acids that allow the improvement of component affinity. However, it is necessary to incorporate surface-active agents that increase the interactions in these hydrophilic–hydrophobic systems during the mixing process. This should improve dispersion and reduce porosity.

These results allow us to continue studying biopolymeric blends for use in both flexible and rigid single-use packaging.

Author Contributions: C.C. and H.L.C.P. participated in the analysis of the images and contributed to the writing; all authors participated in the corrections. Conceptualization, C.C. methodology, C.C., H.L.C.P.; investigation, C.C., H.L.C.P.; writing—original draft preparation, writing—review and editing, C.C., H.L.C.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This research has been funded by Dirección General de Investigaciones (DGI) of Universidad Santiago de Cali under call No. 01-2021. C.C. acknowledge financial support from DGI of Universidad Santiago de Cali under project No. 939-621120-2148. H.L.C.P. acknowledge the ASTIN SENA (Cali-Colombia) for its technical support through manufacturing and rheological measurements.

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

Abbreviations

A	Acid acetic
C	Carbon
CP	Cassava pulp
DSC	Differential scanning calorimetry
DTG	Derivative thermogravimetric
ECO	Epoxidized cardoon oil
FTIR	Fourier Transformed Infrared Spectroscopy
G′	Modulus storage
G″	Modulus loss
H	Hydrogen
L	Acid lactic
MDI	Methylenediphenyl diisocyanate
O	Acid oleic
O	Oxygen
PLA	Poly(lactic acid)
SEM	Scanning electron microscope
TGA	Thermogravimetric analysis
TPS	Thermoplastic starch
TPS/PLA	Thermoplastic starch/poly(lactic acid)
η'	Real viscosity component
η''	Imaginary viscosity component

References

1. Siracusa, V.; Blanco, I. Bio-Polyethylene (Bio-PE), Bio-Polypropylene (Bio-PP) and Bio-Poly(Ethylene Terephthalate) (Bio-PET): Recent Developments in Bio-Based Polymers Analogous to Petroleum-Derived Ones for Packaging and Engineering Applications. *Polymers* **2020**, *12*, 1641. [CrossRef] [PubMed]
2. Palai, B.; Biswal, M.; Mohanty, S.; Nayak, S.K. In Situ Reactive Compatibilization of Polylactic Acid (PLA) and Thermoplastic Starch (TPS) Blends; Synthesis and Evaluation of Extrusion Blown Films Thereof. *Ind. Crop. Prod.* **2019**, *141*, 111748. [CrossRef]
3. Przybytek, A.; Sienkiewicz, M.; Kucińska-Lipka, J.; Janik, H. Preparation and Characterization of Biodegradable and Compostable PLA/TPS/ESO Compositions. *Ind. Crop. Prod.* **2018**, *122*, 375–383. [CrossRef]
4. Pierre Sarazin, M.; Baszil, D.F. Polymer Blends Comprising Phase-Encapsulated Thermoplastic Starch and Process for Making the Same. U.S. Patent Application 13/464,209, 8 November 2012.
5. Andreae, J.; Eric, M.; Arthur, A.; Zweed, K.; Gordon, S. Capsule and Device for Preparing Beverages and Method for Producing Capsules. U.S. Patent Application 15/101,068, 12 January 2017.
6. Ranganathan, S.; Dutta, S.; Moses, J.A.; Anandharamakrishnan, C. Utilization of Food Waste Streams for the Production of Biopolymers. *Heliyon* **2020**, *6*, e04891. [CrossRef]

7. Jullanun, P.; Yoksan, R. Morphological Characteristics and Properties of TPS/PLA/Cassava Pulp Biocomposites. *Polym. Test.* **2020**, *88*, 106522. [CrossRef]
8. Müller, C.M.O.; Laurindo, J.B.; Yamashita, F. Composites of Thermoplastic Starch and Nanoclays Produced by Extrusion and Thermopressing. *Carbohydr. Polym.* **2012**, *89*, 504–510. [CrossRef] [PubMed]
9. Castillo, L.A.; López, O.V.; García, M.A.; Barbosa, S.E.; Villar, M.A. Crystalline Morphology of Thermoplastic Starch/Talc Nanocomposites Induced by Thermal Processing. *Heliyon* **2019**, *5*, e01877. [CrossRef] [PubMed]
10. Ayana, B.; Suin, S.; Khatua, B.B. Highly Exfoliated Eco-Friendly Thermoplastic Starch (TPS)/Poly (Lactic Acid)(PLA)/Clay Nanocomposites Using Unmodified Nanoclay. *Carbohydr. Polym.* **2014**, *110*, 430–439. [CrossRef]
11. Amin, M.R.; Chowdhury, M.A.; Kowser, M.A. Characterization and Performance Analysis of Composite Bioplastics Synthesized Using Titanium Dioxide Nanoparticles with Corn Starch. *Heliyon* **2019**, *5*, e02009. [CrossRef] [PubMed]
12. Collazo-Bigliardi, S.; Ortega-Toro, R.; Chiralt, A. Improving Properties of Thermoplastic Starch Films by Incorporating Active Extracts and Cellulose Fibres Isolated from Rice or Coffee Husk. *Food Packag. Shelf Life* **2019**, *22*, 100383. [CrossRef]
13. Ji, M.; Li, F.; Li, J.; Li, J.; Zhang, C.; Sun, K.; Guo, Z. Enhanced Mechanical Properties, Water Resistance, Thermal Stability, and Biodegradation of the Starch-Sisal Fibre Composites with Various Fillers. *Mater. Des.* **2021**, *198*, 109373. [CrossRef]
14. Wu, N.N.; Qiao, C.C.; Tian, X.H.; Tan, B.; Fang, Y. Retrogradation Inhibition of Rice Starch with Dietary Fiber from Extruded and Unextruded Rice Bran. *Food Hydrocoll.* **2020**, *113*, 106488. [CrossRef]
15. Kahvand, F.; Fasihi, M. Plasticizing and Anti-Plasticizing Effects of Polyvinyl Alcohol in Blend with Thermoplastic Starch. *Int. J. Biol. Macromol.* **2019**, *140*, 775–781. [CrossRef] [PubMed]
16. Cummings, S.; Zhang, Y.; Smeets, N.; Cunningham, M.; Dub, M.A. On the Use of Starch in Emulsion Polymerizations. *Processes* **2019**, *7*, 140. [CrossRef]
17. Caicedo, C.; Aguirre Loredo, R.Y.; Fonseca García, A.; Ossa, O.H.; Vázquez Arce, A.; Calambás Pulgarin, H.L.; Ávila Torres, Y. Properties of Thermoplastic Achira Starch Modified with Lactic Acid and Oleic Acid. *Molecules* **2019**, *24*, 4433. [CrossRef] [PubMed]
18. Ačkar, D.; Babić, J.; Jozinović, A.; Miličević, B.; Jokić, S.; Miličević, R.; Rajič, M.; Šubarić, D. Starch Modification by Organic Acids and Their Derivatives: A Review. *Molecules* **2015**, *20*, 19554–19570. [CrossRef] [PubMed]
19. Tawakaltu, A.-A.; Egwim, E.C.; Ochigbo, S.S.; Ossai, P.C. Effect of Acetic Acid and Citric Acid Modification on Biodegradability of Cassava starch Nanocomposite Films. *J. Mater. Sci. Eng. B* **2015**, *5*, 372–379. [CrossRef]
20. Boruczkowska, H.; Boruczkowski, T.; Leszczyński, W.; Tomaszewska-Ciosk, E.; Miedzianka, J.; Drozdz, W.; Regiec, P. The Obtaining of Starch—and Oleic Acid—Based Ester and Its Properties. *Nauka Technol.* **2012**, *4*, 98–107.
21. Gálvez, J.; Correa Aguirre, J.P.; Hidalgo Salazar, M.A.; Mondragón, B.V.; Wagner, E.; Caicedo, C. Effect of Extrusion Screw Speed and Plasticizer Proportions on the Rheological, Thermal, Mechanical, Morphological and Superficial Properties of PLA. *Polymers* **2020**, *12*, 2111. [CrossRef]
22. Tokiwa, Y.; Calabia, B.P.; Ugwu, C.U.; Aiba, S. Biodegradability of Plastics. *Int. J. Mol. Sci.* **2009**, *10*, 3722–3742. [CrossRef]
23. Kakoli, M.; Davarpanah, A.; Ahmadi, A.; Jahangiri, M.M. Recommendations for Compatibility of Different Types of Polymers with Potassium/Sodium Formate-Based Fluids for Drilling Operations: An Experimental Comparative Analysis. *J. Mater. Sci. Eng.* **2016**, *5*, 1–6. [CrossRef]
24. Yu, L.; Petinakis, E.; Dean, K.; Liu, H.; Yuan, Q. Enhancing Compatibilizer Function by Controlled Distribution in Hydrophobic Polylactic Acid/Hydrophilic Starch Blends. *J. Appl. Polym. Sci.* **2011**, *119*, 2189–2195. [CrossRef]
25. Shirai, M.A.; Grossmann, M.V.E.; Mali, S.; Yamashita, F.; Garcia, P.S.; Müller, C.M.O. Development of Biodegradable Flexible Films of Starch and Poly(Lactic Acid) Plasticized with Adipate or Citrate Esters. *Carbohydr. Polym.* **2013**, *92*, 19–22. [CrossRef]
26. Turco, R.; Ortega-Toro, R.; Tesser, R.; Mallardo, S.; Collazo-Bigliardi, S.; Boix, A.C.; Malinconico, M.; Rippa, M.; Di Serio, M.; Santagata, G. Poly (Lactic Acid)/Thermoplastic Starch Films: Effect of Cardoon Seed Epoxidized Oil on Their Chemicophysical, Mechanical, and Barrier Properties. *Coatings* **2019**, *9*, 574. [CrossRef]
27. Fourati, Y.; Tarrés, Q.; Mutjé, P.; Boufi, S. PBAT/Thermoplastic Starch Blends: Effect of Compatibilizers on the Rheological, Mechanical and Morphological Properties. *Carbohydr. Polym.* **2018**, *199*, 51–57. [CrossRef] [PubMed]
28. Salazar-Sánchez, M.; Campo-Erazo, S.D.; Villada-Castillo, H.S.; Solanilla-Duque, J.F. Structural Changes of Cassava Starch and Polylactic Acid Films Submitted to Biodegradation Process. *Int. J. Biol. Macromol.* **2019**, *129*, 442–447. [CrossRef]
29. Ortega-Toro, R.; Alex, L. Epoxidised Sesame Oil as a Biobased Coupling Agent and Plasticiser in Polylactic Acid/Thermoplastic Yam Starch Blends. *Heliyon* **2021**, *7*, 1–8. [CrossRef]
30. Yi, T.; Qi, M.; Mo, Q.; Huang, L.; Zhao, H.; Liu, D.; Xu, H. Ecofriendly Preparation and Characterization of a Cassava Starch/Polybutylene Adipate. *Processes* **2020**, *8*, 329. [CrossRef]
31. Yu, M.; Zheng, Y.; Tian, J. Study on the Biodegradability of Modified Starch/Polylactic Acid (PLA) Composite Materials. *RSC Adv.* **2020**, *10*, 26298–26307. [CrossRef]
32. Ibrahim, N.; Wahab, M.K.A.; Uylan, D.N.; Ismail, H. Physical and Degradation Properties of Polylactic Acid and Thermoplastic Starch Blends—Effect of Citric Acid Treatment on Starch Structures. *BioResources* **2017**, *12*, 3076–3087. [CrossRef]