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Processability Study of Thermoplastic Starch/ Poly(Butylene Succinate Adipate) Blends in a Reactive Extrusion

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Processability Study of Thermoplastic Starch/ Poly(Butylene Succinate Adipate) Blends in a Reactive Extrusion

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Abstract: Growing concerns about ocean contamination from fossil fuel based polymers have created a demand for biodegradable alternatives, particularly for packaging applications. Thermoplastic starch (TPS) is a promising, eco-friendly biopolymer but has poor mechanical properties and high hydrophilicity. To address these issues, this article explores modifying starches through reactive extrusion and blending them with other biodegradable polymers. The study evaluates blends of native or acetylated starch with poly(butylene succinate) adipate (PBSA), using glycerol as a plasticizer and tartaric acid as a reactive agent. Films were processed using an internal mixer and compression molding. Results show tartaric acid improves processability and slightly enhances mechanical properties such as ductility and tensile strength, though limitations persist due to morphological and thermal stability issues. Despite these challenges, reactive extrusion with tartaric acid offers a promising approach for developing new packaging materials.

Keywords: Thermoplastic Starch, BioPBSA, Polymer Blend, Processability, Hydrophilicity

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Introduction

The global production of fossil-based polymers for industrial sectors has been steadily increasing annually due to high demand since its creation. In 2020, its global production reached around 400 MT/year, with 44% from the packaging sector [1]. These polymers are difficult to recycle due to global economics and the physical impossibility of its degradation [2]. Consequently, polymers are often landfilled, incinerated, exported, or released into water sources and soil [3], particularly from the packaging industry. By 2030, an estimated 90 MT/year of these materials will be in the ocean [4], which threatens biodiversity, drinking water, and sustainable fishing. Biodegradable and compostable biopolymers are proposed as alternatives [5,6] to improve the management of single-use plastic pollution in the ocean.

Starch is a promising biopolymer due to its renewability, low cost, thermoplastic behavior, biodegradability, and compostability [7,8]. However, it faces issues such as difficult processability, fragility, and high hydrophilicity. Plasticizers are added to improve its behavior [7], creating thermoplastic starch (TPS). TPS is a low-density and cost-effective biopolymer, with limited stability due to its water absorption, and inferior mechanical properties [9]. To improve these issues, polymers blends are used. Several polymers have been tested [10,11], but degradability remains an issue when using fossil-based polymers for the blends. However, adding inherently biodegradable biopolymers to the blend can create materials that biodegrade quickly into non-toxic compounds.

Polybutylene succinate adipate (PBSA) is an aliphatic polyester biopolymer that degrades completely in water or soil over time. It also has good ductility, making it suitable for extrusion and injection molding [12]. Given these properties, blending TPS and PBSA is a potential solution to the problem. However, this blend has immiscibility issues due to the hydrophilic nature of starch and the hydrophobic nature of PBSA [13]. To overcome this, one strategy is to decrease the hydrophilic nature of the starch by replacing hydroxyl groups with carboxyl groups, via an esterification reaction. This article uses acetylated starch and reactive extrusion with tartaric acid to increase the substitution degree, by esterification, of modified and native starch in the blends with PBSA. This is expected to enhance mechanical properties, alter FTIR absorption wavelengths, and improve the microscopic structure observed in SEM images.

Materials and Methods

Materials

Native and acetylated modified corn starch was supplied by Ecobioplastic, Colombia. Glycerol (99%) and tartaric acid L(+) from Panreac AppliChem, USA was used as a plasticizer and esterification agent. Poly(butylene succinate adipate) (PBSA) pellets were supplied by Mitsubishi Chemical Performance Polymers, USA.

Blend and Films Preparation

To begin, the experimental design consists of 3 factors: type of starch (native and acetylated), proportion of TPS/TPSA and PBSA (60:40 and 70:30), and tartaric acid concentration (1, 2, and 3% wt. of starch weight). To plasticize the starch, glycerol was used in a 30% concentration based on TPS/TPSA weight. TPS refers to thermoplastic native starch, and TPSA refers to thermoplastic acetylated starch.

For the process, the raw materials were dried overnight at 80°C. Each material was then added to an internal mixer: PBSA was added first, followed by starch, tartaric acid, and glycerol. This was processed at 60 rpm and 150°C until the torque stabilized (10 min). The obtained blends were cut into pieces and placed in a molding press to form films of 0.3 mm thickness. Finally, the obtained films were die-cut into type V samples according to ASTM D638 and kept in a controlled environment to avoid moisture absorption.

Characterization of Blends

Chemical Analysis – FTIR Test

Films of raw materials and blends were used to analyze molecular interactions. A Thermo Scientific Nicolet iS50 spectrophometer was used, with a spectral range of 4000 to 400 cm^{-1} and 32 scans. No replicates were performed for this test. All spectra were baseline corrected and normalized.

Mechanical Analysis – Tensile Test

Type V samples were tested using a Universal Testing Machine INSTRON 3367 following ASTM D882 standards. Testing was performed at room temperature with a strain rate of 12.5 mm/min. At least eight specimens were tested for each sample, and the average and standard deviation results were reported.

Morphological Analysis – SEM Images

Films of raw materials and blends underwent cryogenic fracturing to expose the transversal plane. These fragments were gold metallized to ensure conductivity to the test. Subsequently, these samples were observed in the LYRA3 TESCAN machine with a magnification of ×3000. No replicates were conducted for this test.

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Results and Discussion

Chemical Analysis – FTIR Test

To confirm the hypothesis that reactive extrusion increases the substitution degree of starch by replacing hydroxyl groups with carboxyl groups, FTIR analyses were conducted. This was assessed by the increase in carboxyl groups at the 1750 cm^{-1} wavelength and a decrease of hydroxyl groups at the 3250 cm^{-1} wavelength [14].

The IR spectra of TPS, PBSA, and their blends are shown in Figure 1. For the blends, no chemical interaction between raw materials is noted as no new peaks appeared. However, some absorbances changes were noted. For the 60:40 TPS and PBSA blends, contrary to expectations, the 3250 cm^{-1} peak increased with more tartaric acid and the 1750 cm^{-1} peak showed no clear trend. The same observations were made for the 70:30 TPS and PBSA blends. These results indicate that the esterification of native starch with tartaric acid did not occur. According to literature, starch tends to not esterify in the presence of glycerol and under thermal conditions. It needs an external catalytic agent to facilitate the reaction. In this case, the short mixing time was not enough to provide a self-catalytic reaction [15].

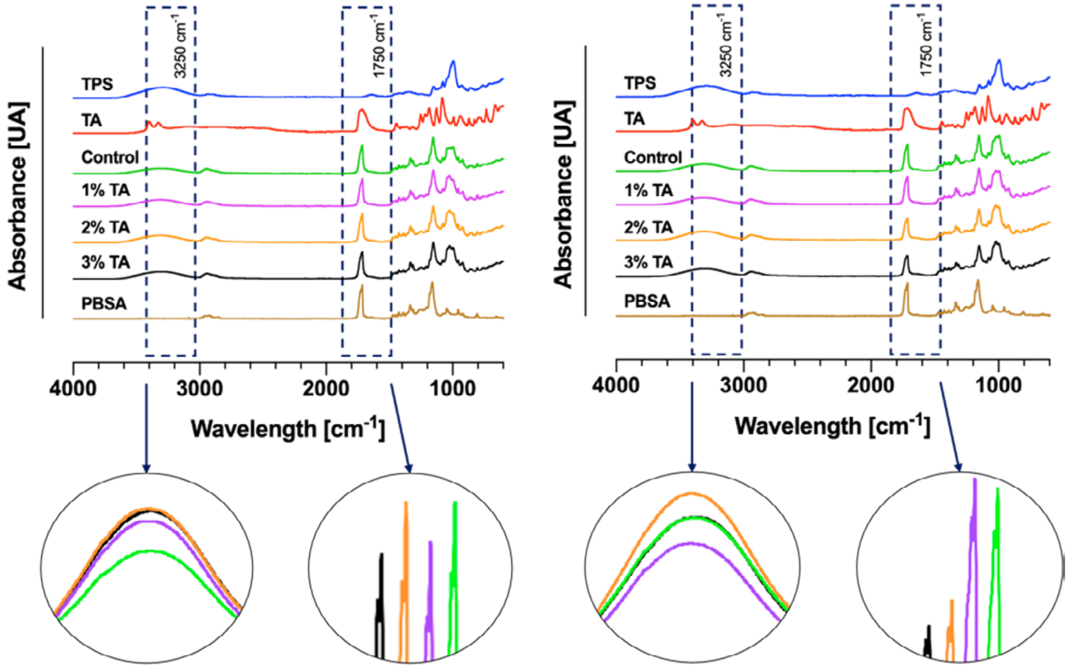

Figure 1. Comparative FTIR between the raw materials and the blends of TPS and PBSA (60:40 – left, 70:30 – right) with addition of tartaric acid (TA). The studied signals are shown in the graphs.

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Figure 2 shows the IR spectra of TPSA, PBSA and their blends. With more tartaric acid, the 60:40 TPSA and PBSA blends shows the expected decrease in the hydroxyl peak (O – H) and increase in the carbonyl ester peak (C = O), indicating higher substitution degrees, similar to findings in other esterification studies [14]. For the 70:30 TPSA and PBSA blends, there is the expected change compared to the control. However, there are inconsistencies in the trend of the carbonyl ester peak and the hydroxyl peak, related with the change of tartaric acid. These changes can be related with the substitution degree of the starch, which will prove the initial hypothesis.

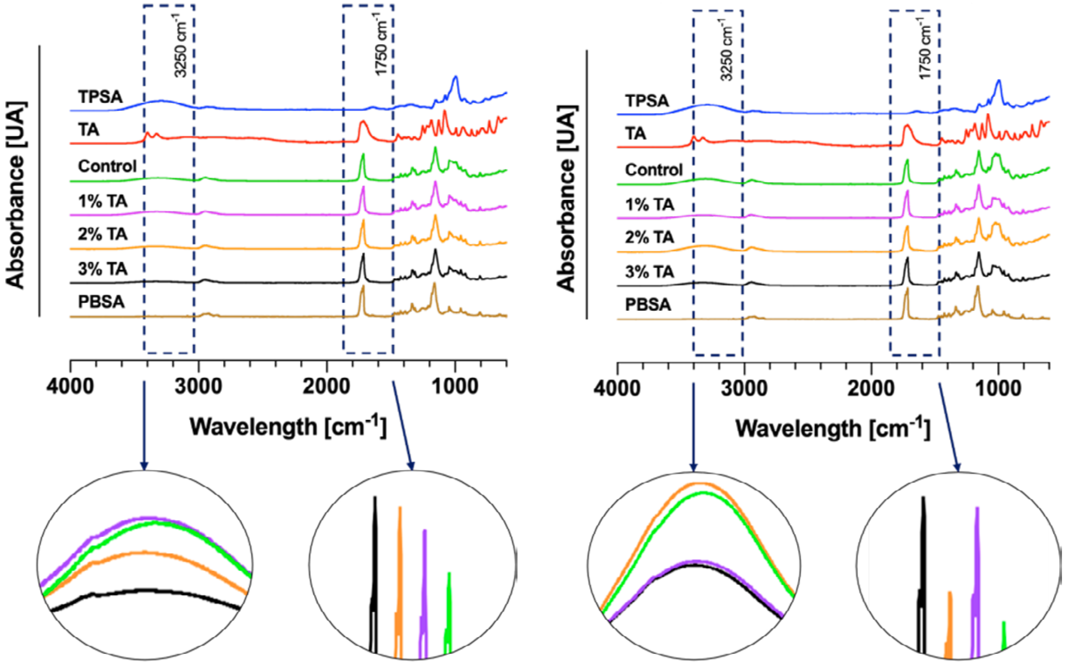

Figure 2. Comparative FTIR between the raw materials and the blends for TPSA and PBSA (60:40 – left, 70:30 – right) with addition of tartaric acid (TA). The studied signals are shown in the graphs.

Mechanical Analysis – Tensile Test

Tensile tests were performed to observe the consequences of a change in the substitution degree of the starch in the blends. For this study, the tensile strength and ductility were evaluated.

The tensile strength of the studied blends is shown in Figure 3. For blends with TPS, increasing tartaric acid results in a collective decrease in tensile strength, with a significant drop compared to the control. For blends with TPSA, the 60:40 blends show no significant change compared to the control, while the 70:30 blends show a slight decrease. All blend values fall between those of the raw materials. Comparing the controls for the blends with TPS and TPSA, there is a significant change where the higher value is for the TPSA blends. This result is expected as the acetylated starch has fewer hydroxyl groups, which makes it more hydrophobic. The change in the chemical nature of the starch gives a better miscibility with the PBSA.

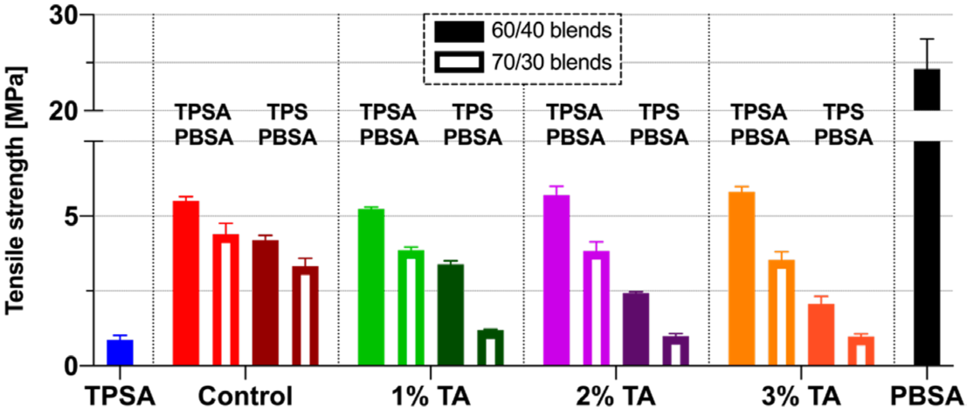

Figure 3. Comparative tensile strength between the raw materials and the blends between TPS/TPSA and PBSA (60:40, 70:30) with addition of tartaric acid (TA).

Subsequently, Figure 4 shows the ductility of the studied blends. For blends with TPS, increasing tartaric acid decreases ductility in the 60:40 blends, with no significant change in the 70:30 blends compared to the control. Using TPSA increases ductility compared to the control, more prominently in the 70:30 blends. All blend values fall between those of the raw materials.

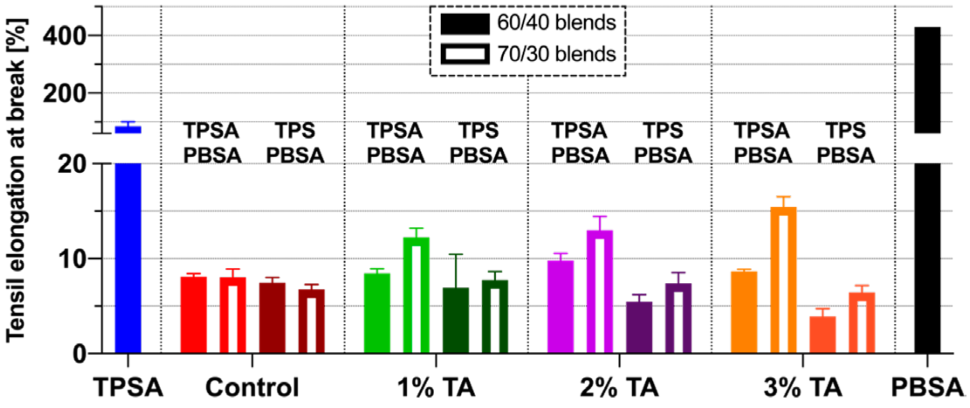

Figure 4. Comparative ductility between the raw materials and the blends between TPS/TPSA and PBSA (60:40, 70:30) with addition of tartaric acid (TA).

According to the FTIR analysis, the TPSA blends, especially those with 3% tartaric acid, showed changes in wavelengths related to starch esterification. These same blends did not show a significant change in tensile strength but had the highest increase in ductility. The tensile strength of polymers is linked to chain entanglement and organization, which suggest that the addition of tartaric acid had little effect on these factors [16]. For ductility, fewer matrix imperfections, such as cavities, pores, and fractures, facilitate elongation of the films which is related to a better interfacial adherence [17]. With the obtained results, it is expected to see less of these features in SEM images for the mentioned blends.

Morphological Analysis – SEM Images

A SEM analysis was performed to observe the direct consequences of a change in the substitution degree of the starch in the blends, related to an improvement in the ductility of the film and its relationship with the microstructure of the transversal section of the film.

Figure 5 shows the microstructure of films made by TPS. Arrows in the pictures shows different features that indicates a poor interfacial adherence: cavities, pores, edges, cracks, and granules [17]. With the addition of tartaric acid there is a slight increase in cracks, which can explain the collective decrease of ductility for these blends, especially for the 60:40 blends.

Subsequently, the images for the blends with TPSA are shown in Figure 6. Unlike the TPS results, increasing tartaric acid in these blends results in progressively fewer granules, pores, and cracks. The surface shows small particles, likely from starch granule breakdown, compared to the control. These findings align with previous sections, where starch esterification indicated an increase in ductility and unchanged tensile strength, especially in the 3% tartaric acid blends. In this case, the images that show a better microstructure, related with the features mentioned before, are the ones with 3% tartaric acid, even more in the case of the 70:30 blend.

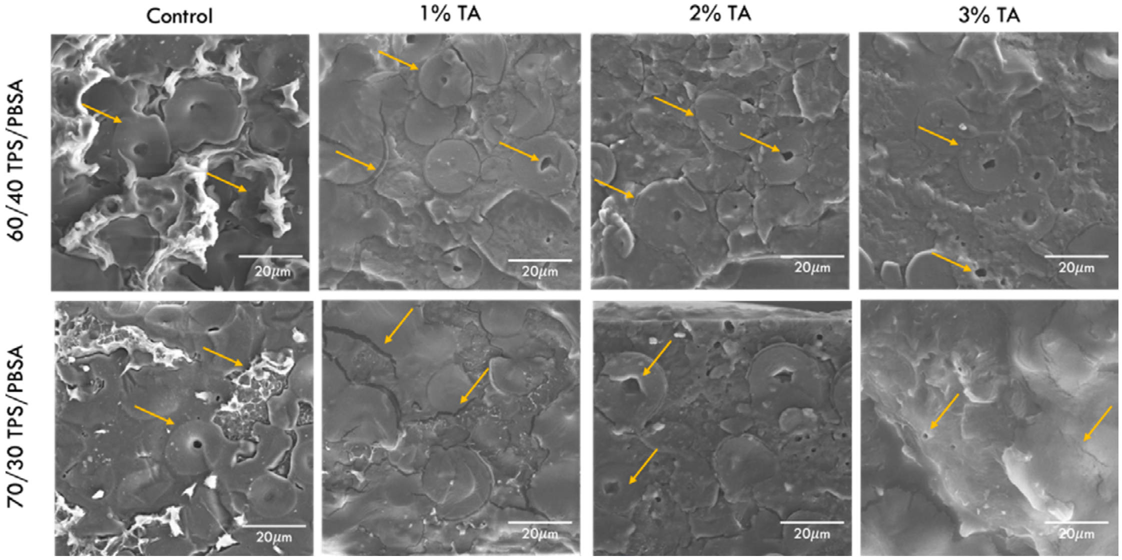

Figure 5. Comparative SEM images (×3000) between control and blends of TPS and PBSA (60:40, 70:30) with addition of tartaric acid (TA). Arrows indicate the important features of the microstructures.

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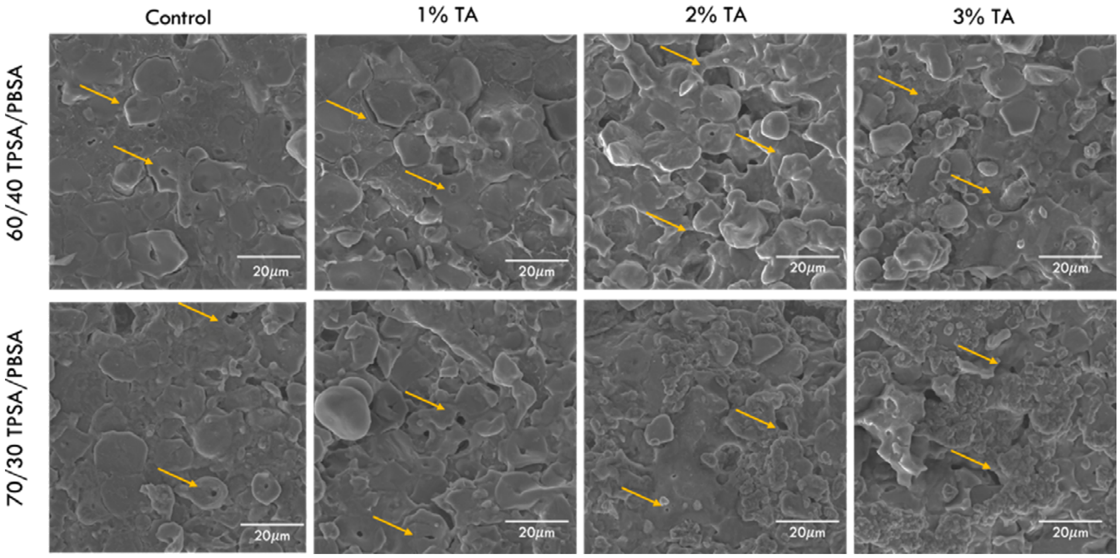

Figure 6. Comparative SEM images (×3000) between control and blends of TPSA and PBSA (60:40, 70:30) with addition of tartaric acid (TA). Arrows indicate the important features of the microstructures.

Conclusion

The use of tartaric acid as an esterification agent in TPS and PBSA blends did not present an improvement in the properties. On the contrary, it shown a greater incompatibility between the raw materials with a lower tensile strength and ductility and no change at the FTIR and SEM images. This decrease in compatibility was not the expected result, which provides the opportunity to conduct more tests and analyses to provide a possible response to the problem.

However, adding tartaric acid in TPSA and PBSA blends presented the expected changes in the FTIR analyses. The tensile strength did not significantly change, probably related to an unchanged structural organization of the chains. Ductility exhibited an improvement with the increase in tartaric acid, which is explained at the SEM images where a better microstructure is shown with the same trend. Nevertheless, the change in ductility is not enough for a flexible packaging application, which is why a new approach is needed.

References

1. Plastics Europe, "Plastics – The Facts 2023," 2023.
2. J. Ackerman and D. B. Levin, "Rethinking plastic recycling: A comparison between North America and Europe", *Journal of Environmental Management*, vol. 340, p. 117-859, Aug. 2023, https://doi.org/10.1016/j.jenvman.2023.117859

3. E. M. Foundation, “The new plastics economy: Rethinking the future of plastics”, Ellen MacArthur Foundation. [Online]. Available in: https://ellenmacarthurfoundation.org/the-new-plastics-economy-rethinking-the-future-of-plastics
4. S. B. Borrelle et al., “Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution”, *Science*, vol. 369, no. 6510, pp. 1515-1518, Sep. 2020, https://doi.org/10.1126/science.aba3656
5. Acoplásticos, “ABC: Ley 2232 de 2022 ‘Plásticos de un solo uso’”, Colombia, Review, 2022. [Online]. Available in: https://www.acoplasticos.org/index.php/mnu-noti/412-boletines-2022-abc-ley-de-plasticos-hd-pdf
6. T. M. Letcher, *Plastic Waste and Recycling: Environmental Impact, Societal Issues, Prevention, and Solutions*. Academic Press, 2020.
7. Z. N. Diyana et al., “Physical Properties of Thermoplastic Starch Derived from Natural Resources and Its Blends: A Review”, *Polymers*, vol. 13, no. 9, p. 1396, Apr. 2021, https://doi.org/10.3390/polym13091396
8. D. Plackett and V. Katiyar, “Biopolymers—New Materials for Sustainable Films and Coatings”, 2011, pp. 301-315. https://doi.org/10.1002/9781119994312.ch14
9. S. P. Bangar, W. S. Whiteside, A. O. Ashogbon, and M. Kumar, “Recent advances in thermoplastic starches for food packaging: A review”, *Food Packaging and Shelf Life*, vol. 30, pp. 100-743, Dec. 2021, https://doi.org/10.1016/j.fpsl.2021.100743
10. S. Jayarathna, M. Andersson, and R. Andersson, “Recent Advances in Starch-Based Blends and Composites for Bioplastics Applications,” *Polymers*, vol. 14, no. 21, 4557, Oct. 2022, https://doi.org/10.3390/POLYM14214557
11. A. Surendren, A. K. Mohanty, Q. Liu, and M. Misra, “A review of biodegradable thermoplastic starches, their blends and composites: recent developments and opportunities for single-use plastic packaging alternatives,” *Green Chemistry*, vol. 24, no. 22, pp. 8606–8636, Nov. 2022, https://doi.org/10.1039/D2GC02169B
12. I. S. Yun, S. W. Hwang, J. K. Shim, and K. H. Seo, “A study on the thermal and mechanical properties of poly (butylene succinate)/thermoplastic starch binary blends”, *International Journal of Precision Engineering and Manufacturing-Green Technology*, vol. 3, no. 3, pp. 289-296, Jul. 2016, https://doi.org/10.1007/s40684-016-0037-z
13. J. Li, X. Luo, X. Lin, and Y. Zhou, “Comparative study on the blends of PBS/thermoplastic starch prepared from waxy and normal corn starches”, *Starch–Stärke*, vol. 65, no. 9-10, pp. 831-839, Sep. 2013, https://doi.org/10.1002/star.201200260
14. V. C. R. Schmidt et al., “Effect of the degree of acetylation, plasticizer concentration and relative humidity on cassava starch films properties”, *Journal of Food Science and Technology*, vol. 39, no. 2, pp. 491-499, Jun. 2019, https://doi.org/10.1590/fst.34217
15. S. Zhang, Y. He, Y. Yin, and G. Jiang, “Fabrication of innovative thermoplastic starch bio-elastomer to achieve high toughness poly(butylene succinate) composites”, *Carbohydrate Polymers*, vol. 206, pp. 827-836, Feb. 2019.
16. K. Balani, V. Verma, A. Agarwal and R. Narayan, “Physical, thermal, and mechanical properties of polymers”, *Biosurfaces*, pp. 1-23, 2015.
17. W.Y. Jang, B.Y. Shin, T.J. Lee and R. Narayan, “Thermal Properties and Morphology of Biodegradable PLA/Starch Compatibilized Blends”, *Journal of Industrial and Engineering Chemistry*, vol. 13, pp. 457-464, 2007.