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Synthesis and Characterization of a Cassava Starch and Corn husk Mixture for Biofilm Production

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The need to use solid waste generated in cities after crops are transformed into final consumer products motivates efforts aimed at creating alternatives and strategies for this purpose. Usually, the largest component of municipal waste is the organic fraction which is often not properly reused. This fact results in significant negative environmental and social impacts, such as high CO_2 emissions, particles released from uncontrolled burning, water pollution from leachates, generation of foul odors, and the proliferation of rats and insects. These impacts could be prevented by applying different techniques, ranging from proper separation to obtaining energy from the waste and obtaining new products with characteristics and properties that confer a high potential for reuse. One possible alternative focus in creating new materials that use waste as raw materials, which can include agriculture and municipal waste.
This study aims to present the creation of biofilm as a possible substitute for using virgin plastic materials as an alternative to manage one type of solid waste generated in the domestic sector but in greater quantities such as with corn husks found in marketplaces. This waste was used to develop a composite material with a polymeric matrix made of cassava starch that uses glycerol and polyvinyl alcohol (PVOH) as a plasticizer. The film created was evaluated to determine its mechanical tension and impact strength properties. Furthermore, a thermal characterization was performed via differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic-mechanical analysis (DMTA). The films were prepared to contain 95% gelatinized cassava starch, 0.3% corn husk dry residue, 3% glycerin, and 1.7% % PVOH. This biofilm represents an alternative to support circular economy policies and is a technological strategy aimed at material innovation.

1. Introduction

The global population increase has led to a rise in the production of agro-industrial products, which in turn has resulted in an increase in waste generation from this sector. Worldwide, approximately 2.0 billion tons/year of agricultural waste is being produced, with an average annual growth rate between 5 and 10% (Huzairi et al., 2022). Therefore, the management and innovation of technologies for the utilization of these waste materials are essential to reduce the exploitation of natural resources, mitigate emissions, and promote sustainable development in society.Recent research aimed at studying new materials has explored opportunities in the field of eco-friendly composites made from natural fibers given their excellent properties, such as being lightweight, widely available, sustainable, and their propensity to respect the environment. The cost-effectiveness, diversity, and renewability of these fibers, as well as their added advantages, have attracted both the academic and industrial sectors (Devnani, 2021). As such, concerns for ecological safety and natural resources have presented opportunities for research on developing ecologically safe and nature-friendly materials, i.e., bioplastics, which focus on using plants and agricultural wastes such as fruit and vegetable wastes to produce these materials due to their variable characteristics (Kharb & Saharan, 2022).

Pollution from plastic waste is a current environmental concern because due to its composition, these plastics can release toxins. Consequently, biofiber-based polymer composite materials are emerging as a suitable

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substitute for these materials as they are low-cost, lightweight, and eco-friendly. These materials represent an opportunity for a sustainable environment, as well as future market trends given the potential applications of these polymer composites made from natural fibers (Das & Chaudhary, 2021). As these materials prove to be ecological, sustainable, and nature-friendly compared to conventional petroleum-based synthetic plastics, a research trend has emerged of exploring bioplastic films made from mixtures of starch and other organic wastes (Kharb & Saharan, 2022). Biobased plastics have demonstrated that they have a market and a wide range of applications, resulting in their increasing popularity in research and economics. The limitation of fossil resources, as well as environmental issues, have led to the development of an innovative bio-economy while also fueling the shift from fossil-based plastics to bio-based plastics (Spierling et al., 2018).

Moreover, by-products or waste are generated during agro-industrial processes, which if not recycled or processed correctly, create various environmental problems given that they are generally burned or dumped in sanitary landfills. These actions result in the release of carbon dioxide, contamination of water courses, odor nuisance, as well as the proliferation of vectors such as rats, flies, and other insects (Barragan et al., 2008).

Therefore, the valorization of agro-industrial waste and implementing management strategies have become indispensable and a priority integrated into countries' environmental policies and development plans in response to the environmental problems caused by these wastes. If they are not properly disposed of or used, they can alter different natural resources, including soil, water, and air, in addition to being a possible source of contamination and risk to human health (Gómez et al., 2022). Creating plastic films made from residual fibers and biodegradable polymers that result from different processes generated in this sector has demonstrated the ability to create potential substitutes for conventional non-biodegradable plastic films. For example, one alternative is using the new material as a covering material for agricultural production (Tan et al., 2016). Utilizing starch-based films is projected as a potential alternative to petroleum-based plastics. Therefore, priority has been given to this subject of great importance for environmental waste management (Sanyang et al., 2015).

As such, this research study aims to propose an alternative to replace plastic materials by synthesizing and characterizing a biofilm made from a polymeric matrix composed of cassava starch and corn husk to create a thermoplastic material. The mechanical properties are basic functional properties, determined by measuring the starch-based films to project their possible use for packaging purposes (Żołek-Tryznowska & Kałuża, 2021). And their potential use is established in accordance with the values obtained of their properties during the experimentation process.

2. Materials and Methods

This study was conducted following prior research (Gómez et al., 2022) in order to perform a coherent and comparative analysis of the generation of new materials from starch and natural fibers. The aim was to obtain a composite material formulation derived from renewable sources that can be used as an alternative to conventional polymeric materials in the manufacturing of films. The films were created via the casting method using cassava starch, corn husk, PVOH, industrial-grade glycerol, and water. Once the gelatinized starch mixtures with all the aforementioned components were formed, they were poured into molds with a drying process performed in an oven for 24 hours at 60°C. After the drying process was completed, the films were demolded for the characterization process.

The preliminary experimental trials made it clear that the best formulation for the films contains 95% p/p of gelatinized cassava starch, 0.3% p/p of dried corn leaf residue, 3% glycerin, and 1.7 % PVOH. Adding more residue content caused agglomeration, preventing a homogeneous film to form. The gelatinized starch was obtained at a temperature of 67°C with a composition of 6% p/p of cassava starch and water. Once the gelatinization point was reached, glycerin, corn husk particles approximately 0.297 mm in size, and PVOH were added. After the films were created, their mechanical and impact properties were determined, along with a thermal characterization via differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA). The biofilm characterization tests were performed in accordance with American Society for Testing and Materials (ASTM) standards.

3. Results and Discussion

3.1 Mechanical Characterization

Tensile Test

The maximum stress at break and the deformation percentage of the films were measured according to ASTM 882 Standard Test Method for Tensile Properties of Thin Plastic Sheeting. The test was performed on an EZ-XL-Shimadzu universal testing machine at a speed of 5 mm/min and a separation distance between the grips of 50 mm. The values obtained for maximum stress at break and deformation percentage for the composite material and the thermoplastic starch (TPS) reference material are shown in Table 1. The addition of corn husk worsened the material's mechanical properties, decreasing its maximum stress at break and percentage elongation values. This behavior was most likely due to the low adhesion and cohesion between the matrix and the corn husk particles.

Table 1. Tensile Test Results

Material	*Strength at break (MPa)*	*Deformation (%)*
TPS	2.99 ± 0.46	62.49 ± 0.44
TPS + Corn	1.88 ± 0.21	33.37 ± 4.12

Shore hardness

Table 2 shows the average hardness values found for the two films, which were determined using the method established by ASTM D2240 - Standard Test Method for Rubber Property-Durometer Hardness. A manual durometer was used for the test and ten points were taken on each film. Based on this standard, the films obtained are classified in the range of soft plastics.

Table 2. Hardness Test Results

Material	*Shore hardness A*
TPS	81.9
TPS + Corn	86.3

3.2 Thermal Characterization

Differential Scanning Calorimetry (DSC)

A differential calorimeter TGA/DSC 1 - Mettler Toledo was used for this test. The analysis of the materials was carried out at a heating rate of 5 °C/min under inert atmosphere (N_2) with a flow rate of 180 L/min in a temperature range from -20 °C to 400 °C. The results obtained from the DSC analysis are shown in Table 3.

Table 3. Melting temperature for TPS and TPS + Corn

Material	*Melting Temperature (°C)*	*Initial Temperature (°C)*	*Final Temperature (°C)*
TPS	279.85	269.30	301.67

The material containing corn husk had a lower melting temperature, most likely due to poor adhesion between the thermoplastic starch and the corn husk particles.

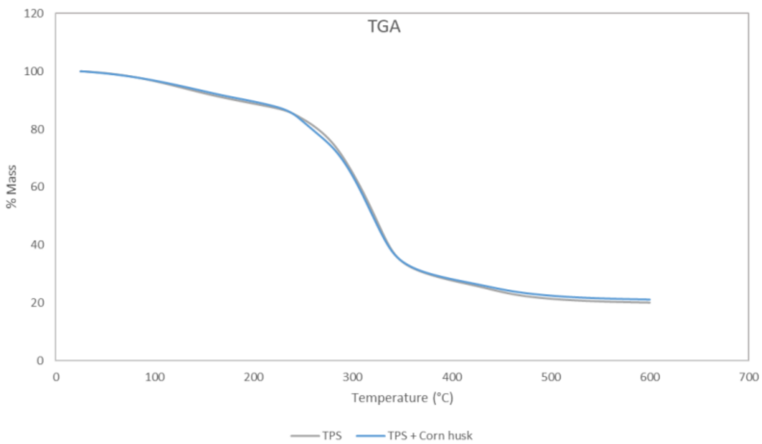

Figure 1. TGA curves

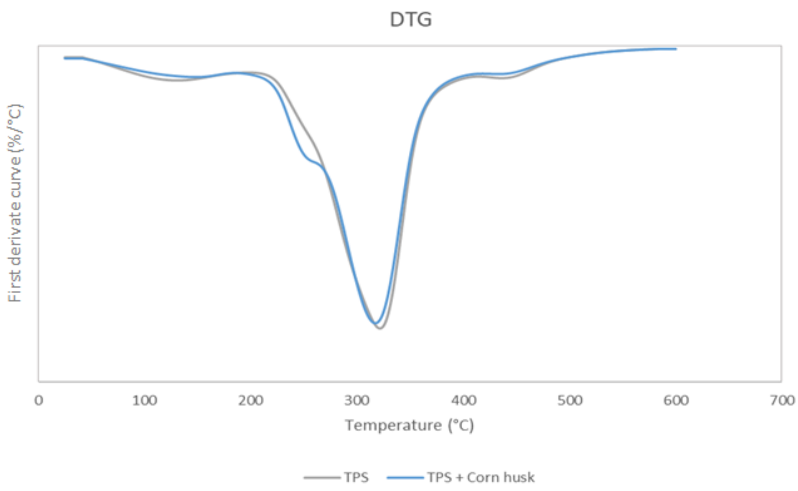

Figure 2. First derivative (DTG) of the TGA curve

Thermogravimetric Analysis (TGA)

The thermogravimetric analysis was carried out in a temperature range between 25 °C and 600 °C at a heating rate of 5 °C/min. A Mettler Toledo TGA/DSC 1 - Mettler Toledo TGA/DSC 1 was used for the test. The thermograms obtained are shown below in Figures 1 and 2.

The TGA thermograms of the two samples show a loss of mass between 50 °C and 170 °C, which can be attributed to water evaporation. The degradation of the two materials TPS and TPS-corn husk was seen in the temperature range between 200 °C and 390 °C where there is a sharp drop in mass which is attributed to the decomposition of starch and corn husk particles. The DTGA thermogram shows that TPS and TPS-corn husk have a maximum decomposition temperature of 320 °C and 317 °C, respectively. Mass losses at temperatures higher than 390 °C are considered to be due to polymer degradation.

Dynamic Mechanical Analysis (DMA)

For this analysis, a DMA 850 machine was used at a frequency of 1Hz and a heating rate of 5 °C/min in a temperature range between -70 °C and 100 °C, with a deformation of 1 mm. The results obtained for the storage modulus (E') and the loss tangent, tan δ, as a function of temperature for the films obtained are shown in Figures 3 and 4.

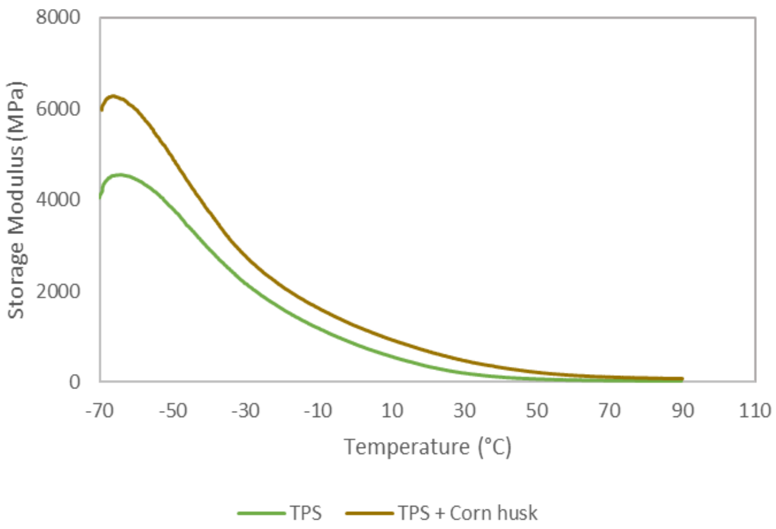

Figure 3. Storage module curve

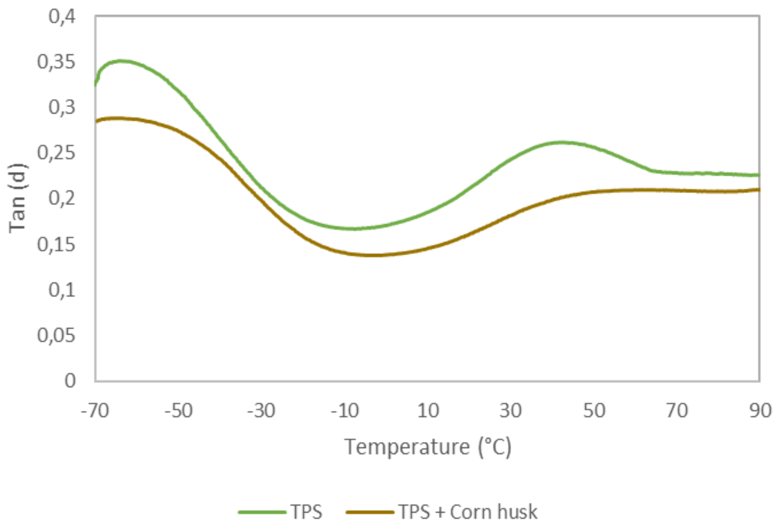

Figure 4. tan δ curve

Two peaks are seen in the tan δ curves for the two materials: TPS and TPS-corn husk. The first peak is seen at approximately -63°C, with the second one having a lower intensity, between 20 °C and 60°C. The storage modulus presents a drop around -63 °C. Therefore, the first peak can be identified as the glass transition temperature of glycerin, which is consistent with what other authors have reported (Famá et al., 2006). This can be attributed to the partial miscibility of starch and glycerin.

Results obtained are important as they allow to understand how a material responds to loads and forces applied at different speeds and temperatures. This information supports the design of more efficient products by identifying weak points and optimizing the product's structure to enhance its strength and lifespan, evaluating the material in terms of its response to dynamic loads. Therefore, results help to understand the material's behavior under real conditions while predicting its performance in different situations. Figure 5 shows the obtained material.

Figure 5. Cassava Starch and Corn husk Biofilm

4. Conclusions

Researching new materials from waste encourages innovation and pushes the boundaries of scientific and technological knowledge. Finding innovative ways to transform waste into valuable materials helps to reduce the amount of waste sent to landfills and incineration facilities. This work contributes to a more sustainable and circular economy and it leads to the appearance of new industries, job creation, and innovative business models centered in waste valorization. For these reasons, this work focus on obtaining a material that incorporates agro-industrial waste into its structure as an alternative to substitute conventional plastic materials.

The most appropriate formulation for obtaining cassava starch and corn husk composite films is the one containing 95 % w/w of gelatinized cassava starch, 0.3% w/w of dried corn husk residues, 3 % of glycerin, and 1.7% of PVOH, which presented a breaking strength of 1.88Mpa and an elongation of 33.37%. The Shore hardness found was 86.3, which classifies it as a soft material. The melting temperature of the material was found to be 262°C, which shows that it is a material resistant to high temperatures. Considering the results obtained in the previous study, it is evident that the films containing dry coffee pulp have a 30% higher resistance to rupture than the films containing corn starch.

With respect to the elongation of the material, the film containing coffee pulp decreases by 135% with respect to the elongation of the films containing corn starch. Considering the results of the hardness test, it is evident that the two materials present similar Shore hardness values and are classified as soft materials according to the ASTM standard used for the test.

Future research will focus on studying the matrix and reinforcement interface of the material to determine the level of adhesion and cohesion between the two materials. Similarly, biodegradability tests and analyses of behavior in the presence of chemical agents will be conducted to determine the most suitable applications for the obtained films. The final goal is to substitute conventional plastic materials, contributing to decrease emissions, while supporting the development of a circular economy model.

References

Barragán-Huerta B., Téllez-Díaz Y., Laguna T., 2008, Use of agro-industrial residues. Rev. Sistemas ambientales, 2(1), 44-50 (in Spanish)

Devnani G. L., 2021, Recent trends in the surface modification of natural fibers for the preparation of green biocomposite. In Green Composites. Springer, Singapore, 273-293, doi.org/10.1007/978-981-15-9643-8_10

Das P.P., Chaudhary V., 2021, Moving towards the era of bio fibre-based polymer composites. Cleaner engineering and technology, 4, 100182, doi.org/10.1016/j.clet.2021.100182

Gómez Rosales Z., Solano J.K., Orjuela D., Rodrigo-Ilarri J., Rodrigo-Clavero M.E., 2022, Synthesis and Characterization of a Cassava Starch (Manihot esculenta) and Dried Coffee Pulp Mixture to Produce Biofilms, Chemical Engineering Transactions, 92, 439-444, doi.org/10.3303/CET2292074

Huzairi, M., Zainudin, M., Zulkarnain, A., Azmi, A., Muniandy, S., Muniandy, S., Sakai, K., Shirai, Y., & Hassam, M., 2022, Enhancement of Agro-Industrial Waste Composting Process via the Microbial Inoculation: A Brief Review. Agronomy 12, 198. https://doi.org/10.3390/agronomy12010198.

Kharb J., Saharan R., 2022, Design and synthesis of eco-friendly cucumber peel-based bioplastic materials. Materials Today: Proceedings, doi.org/10.1016/j.matpr.2022.12.109

Sanyang M.L., Sapuan S.M., Jawaid M., Ishak M.R., Sahari J. 2015, Effect of Plasticizer Type and Concentration on Tensile, Thermal and Barrier Properties of Biodegradable Films Based on Sugar Palm (Arenga pinnata) Starch, Polymers 7, no. 6: 1106-1124, doi.org/10.3390/polym7061106

Spierling S., Knüpffer E., Behnsen H., Mudersbach M., Krieg H., Springer S., Albrecht S., Herrmann C., Endres H.J., 2018, Bio-based plastics-A review of environmental, social and economic impact assessments. Journal of Cleaner Production, 185, 476-491, doi.org/10.1016/j.jclepro.2018.03.014

Tan Z., Yi Y., Wang H., Zhou W., Yang Y., Wang C., 2016, Physical and Degradable Properties of Mulching Films Prepared from Natural Fibers and Biodegradable Polymers, Applied Sciences, 6(5), 147, doi.org/10.3390/app6050147

Żołek-Tryznowska Z., Kałuża A., 2021, The Influence of Starch Origin on the Properties of Starch Films: Packaging Performance, Materials, 14(5), 1146, doi.org/10.3390/ma14051146