Biodegradation Behaviour of Acetylated Manihot Esculenta Crantz CV. TMS 92/0326 Starch-Based Bioplastics Films Reinforced with Rice Husk Ash Filler and Plasticize with Sorbitol

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Abstract
This study investigates the biodegradability of acetylated Manihot esculenta Crantz cv. TMS 92/0326 cassava starch-based bioplastics reinforced with Rice husk ash and plasticized with Sorbitol. Starch was extracted from Manihot esculenta Crantz cv. TMS 92/0326 cassava variety and modified through acetylation, confirmed using Fourier Transform Infrared (FTIR) by the appearance of a carbonyl (C=O) peak at 1740 cm^{-1} in the FTIR spectrum. The results from the percentage yield of the extracted starch was high (85.2%), which is typical for starch extracted from such variety (TMS 92/0326). Modification by acetylation reduces the percentage yield to 79% ,this arises as a result of the substitution of hydroxyl groups with acetyl groups in the starch molecules. The films were prepared by varying the concentrations of Sorbitol (plasticizer) (2–5 g) and Rice husk ash filler (0–1 g). Biodegradability was evaluated using soil burial tests, and the films were found to degrade significantly within four weeks, with the formulation of 5 g Sorbitol and 0.g Rice husk ash filler showing the highest biodegradability at the third week, however all formulations reaches complete degradation at the end of the fourth week. These results indicate that the acetylated cassava starch-Rice husk ash composites offer a promising approach to sustainable, biodegradable packaging materials.

Keywords: Manihot esculenta Crantz cv. TMS 92/0326 Acetylated Starch, Rice husk ash, Biodegradable Bioplastics.

1. Introduction

The growing global population is a major factor in many environmental challenges, such as global warming, soil erosion, and the

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accumulation of plastic waste. Additionally, the increasing use of plastic products is linked to population growth. For example, the global production of plastic reached 390.7 million tonnes in 2021 (Plastics Europe, 2021).

The United States Environmental Protection Agency (EPA) reported that 12% of the 292.4 million tonnes of Municipal Solid Waste (MSW) generated in 2018 was plastic. Of the total municipal waste (MSW) produced that year, 146.1 million tonnes of it went to landfills, with plastics making up 18.46% of that. In addition, 69.1 million tonnes of municipal waste (MSW) were recycled, but only 4.47% of that was plastic (EPA, 2022).

The persistence of plastic waste in the environment stems from the non-degradability of petroleum-based plastics, which can endure for extended periods. Consequently, the environmental consequences of plastic waste accumulation have become a subject of heightened concern. Considering these statistics, plastic waste contamination presents an escalating environmental challenge. Should plastic production and waste accumulation proceed at their current pace, landfills and natural ecosystems, including soils and oceans, could collectively amass approximately 12,000 MT of plastic waste by the year 2050 (Geyer *et al.,* 2017).

Unmodified starch's inherent hydrophilicity leads to films that are both brittle and sensitive to moisture, as well as thermally unstable, thereby restricting their practical utility (Shogren, 2002). Chemical modifications, such as acetylation, offer a potential solution to these drawbacks. Acetylation, which involves substituting hydroxyl groups in starch with acetyl groups, increases the material's hydrophobicity, flexibility, and thermal stability, as evidenced by research (Awokoya *et al.,* 2020). Consequently, this modification improves the performance of starch-based bioplastics in applications where moisture resistance and thermal stability are critical. Furthermore, acetylated starch films demonstrate enhanced flexibility, thus broadening their applicability, including in food packaging, as shown in recent studies (Pooja *et al.,* 2024).

Studies have shown that fillers improves the stability and mechanical strength of starch-based bioplastics by acting as a reinforcement within the polymer matrix. The incorporation of fillers into starch-based films also improves their biodegradability; this is achieved by forming a structure that promotes microbial breakdown during the biodegradation process (Adebowale *et al.,* 2019).

Incorporating rice husk ash as a filler in bioplastics presents a promising strategy for producing sustainable, economical, and high-performance materials. This approach addresses several environmental issues, including waste management and the reduction of dependence on petroleum-based plastics. Consequently, as bioplastics gain momentum, the integration of agricultural waste, such as rice husk ash, into their formulation constitutes a crucial advancement toward a more sustainable and circular economy.

Furthermore, sorbitol, a polyol, demonstrate effective interaction for biopolymers, including starch, cellulose, and protein matrices.

This interaction occurs through a reduction in intermolecular forces and an increase in flexibility, thus mitigating the inherent brittleness of numerous bio-based films and enhancing their elongation and tensile characteristics, which is crucial for their application in packaging (Ballesteros Mártinez *et al.,* 2020). When contrasted with traditional plasticisers like glycerol, films plasticised with sorbitol frequently display improved thermal stability, mechanical support, and reduced hydrophilicity. These attributes contribute to better moisture resistance and barrier properties, both of which are essential for preserving food quality and extending shelf life (Santana *et al.,* 2024). Furthermore, sorbitol's higher molecular weight and strong hydrogen bonding with polymer chains facilitate slower migration within the polymer matrix, thereby enhancing film stability over time and rendering it appropriate for prolonged food storage conditions (Ballesteros Mártinez *et al.,* 2020).

The use of cassava starch, particularly the TMS 92/0326 variety, as a raw material for starch-based bioplastics offers a more sustainable solution compared to traditional petroleum-based plastics. Unlike their petroleum-based counterparts, which can persist in the environment for centuries, starch-based bioplastics are biodegradable and break down naturally, helping to reduce plastic waste and contribute to a cleaner, more sustainable world (Zhang *et al.,* 2022).Given its high starch content, TMS 92/0326 presents

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a promising option for the development of biodegradable plastics. This characteristic is particularly relevant in light of the increasing global interest in environmentally sustainable materials, thereby contributing to a reduction in the dependence on non-renewable plastics and promoting a more environmentally conscious future (Müller *et al.*, 2023).

Cassava, a major crop in several tropical areas such as Africa, Asia, and Latin America, serves as a fundamental food source. The incorporation of cassava starch-based bioplastics into the market landscape offers novel avenues for this crop, potentially generating additional employment opportunities and stimulating local economies. Furthermore, this transition encourages the adoption of sustainable agricultural approaches, thereby reconciling food production with the cultivation of industrial crops (Adeoti *et al.*, 2021).

The TMS 92/0326 cultivar, engineered for elevated yield and disease resistance, presents an optimal solution for large-scale starch production, thereby mitigating any detrimental impact on the availability of food crops. Consequently, it represents a strategic option for maximising cassava's economic value while simultaneously safeguarding food security(IITA,2020).

Furthermore, TMS 92/0326 suitability for industrial applications is enhanced by its classification as a bitter cassava variety, characterised by high concentrations of cyanogenic compounds. This characteristic renders it unsuitable for direct human consumption without appropriate processing. Given that this variety is not primarily cultivated for food, its utilisation in industrial applications, such as bioplastics, minimises competition with food crops. This, in turn, facilitates the effective allocation of land and resources to address both food and industrial requirements (IITA, 2020).

This study will investigates the Soil Biodegradability of bioplastics made from acetylated Manihot esculenta Crantz cv. TMS 92/0326 variety cassava starch. These bioplastics were reinforced with rice husk ash and plasticised with sorbitol. The biodegradability was assessed using soil burial tests over four weeks, with the goal of identifying formulations that would degrade down within that period of time.

2.0 **Methodology**

2.1 SampleCollection/Sample Area:

Cassava tuber were purchased from a farm in Ekosodin community Benin City, Edo State. It is located along the longitude 5.6028° E and latitude 6.3589° N of the central province of Edo state, Nigeria. Additional materials such as HCl (Reagent 36%- WW), Sodium hydroxide pellets (MOLYCHEM-98% Purity), Acetic Anhydride (APC- 98% Purity), Sorbitol (SRL-98% Purity), were sourced from Pyrex-IG Scientific company Benin City, Edo State Nigeria and were all of analytical standard. Rice husk were purchased from a local rice processing factory at Illeh community, Ekpoma, Edo State. It is located along the longitude 6.0814° E and latitude 6.7583° N of the southern province of Edo state, Nigeria.

Figure 1.0: Map of Edo state, Nigeria, describing the location of sample area

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Figure 1.1: **Manihot esculenta Crantz cv. TMS 92/032 tubers**

Figure 1.2: Rice husk

2.2.0. Extraction of Starch:

Extraction of cassava starch was carried out using methodology described by (Ezeoha and Ezenwanne 2013). The cassava tubers were mechanically grated after being manually peeled and cleaned with distilled water, three times as much water as the shredded cassava was added to the mixture. A coarse sieve and a filter cloth were used to sieve and filter the mixture, respectively. The filtrate was allowed to settle for six hours, then mixed with an equal amount of water and left to settle for a day. At the end of 24 hours, the wet starch was decanted, manually dewatered and then oven-dried at 105 °C for 4 hours to reduce its moisture content.

%Starch yield was calculated using:

$$\text{Starch yield } (\%) = \frac{weight\ of\ extracted\ starch\ (g)}{weight\ of\ cassava\ tubers} \times 100 \quad (1)$$

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Figure 2.0: Extracted starch(native) without modification.

2.2.1 Preparation of Rice husk ash *:* Rice husk ash was obtain by collecting clean, dry rice husks, ensuring they are free from dirt and contaminants. The combustion process were carryout with a furnace at a temperature of 650°C . This temperature promotes the complete combustion of the organic material. The rice husks was allow to burn for several hours until they transform into a fine, light gray ash. Once the burning process is complete, the ash is allow to cool naturally within the furnace, ensuring it is not disturbed while still hot. The cooled rice husk ash were grounded into fine powder using Ball Mill. The ash is stored in a dry, airtight container to prevent moisture absorption, which could compromise its properties.

Figure 2.1: Rice husk ash

2.3 preparation of Acetylated Starch.

The extracted starch was modified via acetylation using the method reported by (Henry 2007) with some modification. Starch (20g) was dispersed in 100cm^3 of distilled water and then constantly stirred for 30 minutes.The slurry was adjusted to pH 8.0 with 3%NaOH, 1.2g of acetic anhydride was added to the slurry. After the addition of the acetic anhydride, the reaction was allowed to proceed for another five minutes. The pH of the slurry was adjusted to 4.5 with 0.5M HCl and filtered through whatman No 1 filter paper. The residue obtained was washed for four times with distilled water to remove completely some acids that may be present in the product and finally air- dried at room temperature. The yield was calculated

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$$\text{yield (\%)} = \frac{weight\ of\ modified\ starch\ (g)}{weight\ of\ native\ starch\ (g)} \times 100 \quad \text{------------------(2)}$$

Figure 2.2: Chemical modified starch (Starch acetate).

2.4 Fourier Transform Infrared (FT-IR) spectroscopy determination of extracted native starch and modified starch.

The FT-IR spectrum of extracted native starch and modified starch were acquired on a Perkin Elmer FT-IR spectrophotometer (Perkin Elmer, Inc., MA, USA) using a potassium bromide (KBr) disc prepared from powered samples mixed with dry KBr. The spectra were recorded (16 scans) in the transparent mode from 4000 to 400 cm-1 (Bernardino-Nicanor *et al*., 2017).

2.5 Preparation of Biodegradable Plastic Film and Casting of films

The preparation was done following a refined modification of the method proposed by (Nwaka *et al.*, 2025). 10 g of the acetylated starch powder was weighed in a beaker to which 100 mL of distilled water was added. It was stirred at 350 rpm for 10 min on a magnetic stirrer.Rice husk ash powder was then added at different weights, 0g : 0% (w/w), 0.5g :5% (w/w), 1g: 10% (w/w) and stirred. Sorbitol was also added at different weights (2g, 3g, 4g, 5g) and stirred at 350 rpm for 15 min. The solution was heated at about 80 ⁰C to form gel with continuous stirring. The slurry was then poured onto a Mold, dried in a hot air oven at 50 ⁰C and stored at room temperature.

Table 1: Experimental Design for Biodegradable plastic Film Formulation

	Sorbitol (plasticizer)	**RICE HUSK ASH (FILLER)**
starch acetate	2g	0g
		0.5g
		1.0g
	3g	0g
		0.5g
		1.0g
	4g	0g
		0.5g
		1.0g
	5g	0g
		0.5g
		1.0g

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2.6 Bioplastic Film Soil Degradability Test

The biodegradable behaviour of the bioplastic film samples was determined using soil burial decomposition test. Biodegradability test on the film samples were carried out using method proposed by Nwaka *et al.*, (2025) with slight modifications. Bioplastic films (3 inches by 3 inches) were weighed (W_1), buried in moist soil at a 3-inch depth for one week, and reweighed (W_2). The percent weight loss was calculated using:

$$(\%)Weight\ Loss = \frac{W1-W2}{W1} x100 \quad \text{---------------(3)}$$

3.0 Results and Discussion

Table 2: Percentage Yield of the Extracted Cassava and modified starch acetate

%yield of extracted starch	% yield of Starch acetate
85.2	79

The percentage yield of 85.2% for the extracted starch reflects a high extraction efficiency, which is typical for cassava starch extraction processes of this variety (IITA, 2020). The modification of cassava starch through acetylation resulted in a percentage yield of 79%, slightly lower than the extracted-native starch yield, suggesting some loss during the acetylation process. This result agrees with previous findings indicating a reduction in yield that results from the acetylation process, which involves the substitution of hydroxyl groups with acetyl groups, possibly causing some degradation (Gani *et al.*, 2019).

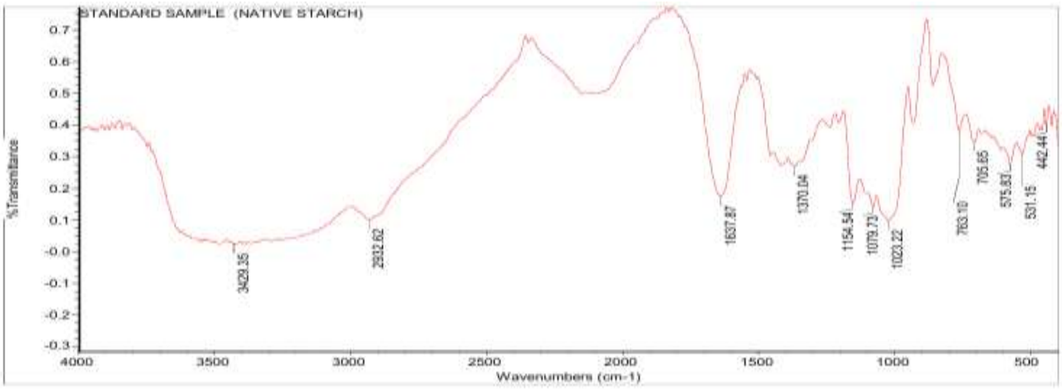

Figure 3.0: FTIR for Native Starch

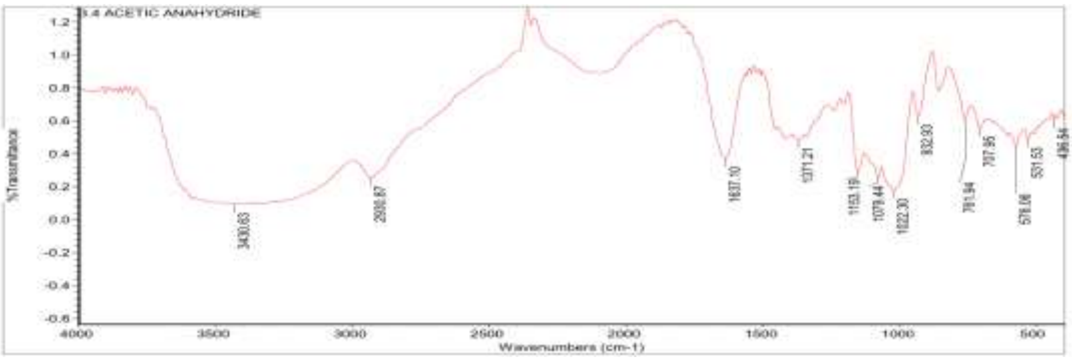

Figure.3.1: FTIR for Acetylated Starch.

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Fourier Transform Infrared (FTIR) spectroscopy was employed to identify and confirm the functional groups present in both the native and chemically modified starch samples. The spectra for native and acetylated starch are shown in Figures 3.0 and 3.1, respectively. The observed differences in absorption bands between the samples substantiate the successful chemical modification of the starch molecules.

The native starch spectrum (Figure 1) displayed characteristic absorption bands associated with polysaccharides. A broad band near 3400 cm^{-1} corresponded to O–H stretching vibrations of hydroxyl groups, which are involved in intra- and intermolecular hydrogen bonding.

The weak band observed near 2920 cm^{-1} is indicative of C–H stretching vibrations within methylene groups. Conversely, the pronounced absorption within the 1150–1000 cm^{-1} range is representative of C–O–C and C–O stretching vibrations corresponding with glycosidic linkages. A weak band, approximately 1640 cm^{-1}, is ascribed to bound water molecules. The spectrum of acetylated starch (Figure 2) exhibited a distinct absorption peak near 1740 cm^{-1}, which is attributed to the carbonyl (C=O) stretching vibration of ester groups, thereby confirming acetylation. Furthermore, an additional peak within the 1230–1260 cm^{-1} range corresponds to C–O stretching vibrations of the acetyl ester linkage. The observed reduction and narrowing of the O–H stretching band intensity around 3400 cm^{-1} reflects the substitution of hydroxyl groups with acetyl moieties, consequently diminishing intermolecular hydrogen bonding. Slight intensity variations in the 1000–1150 cm^{-1} region also indicate modifications to the starch backbone. Comparative analysis of the spectra clearly demonstrates that the acetylation chemical modifications were successfully achieved.

Table 3: Bioplastic Film Soil Burial Degradability Test

	Sorbitol (g)	Rice husk ash (g)	% degradability Week 1	% degradability Week 2	% degradability Week 3	% degradability Week 4
Acetylated Starch bioplastic	2	0	20.5	41.0	61.0	Degraded
		0.5	15.0	30.0	50.0	Degraded
		1.0	8.0	18.1	38.1	Degraded
	3	0	23.5	47.0	67.0	Degraded
		0.5	16.6	33.2	53.2	Degraded
		1.0	10.0	20.0	50.0	Degraded
	4	0	29.0	56.0	76.0	Degraded
		0.5	20.0	40.0	60.0	Degraded
		1.0	15.0	30.0	50.0	Degraded
	5	0	32.0	59.0	79.0	Degraded
		0.5	24.5	48.0	68.0	Degraded
		1.0	21.5	43.0	63.0	Degraded

The soil burial biodegradation test results, illustrated in Table 3, show a clear increase in biodegradability for all samples, having complete biodegradability in the fourth week. At the start of the test (Week 0), none of the samples had degraded (0% biodegradability), as expected, since no exposure to the soil environment had yet occurred. From Week 1 onward, each sample began to decompose steadily, with the percentage of the sample degraded increases week by week. By the fourth week, complete degradation was observed, with all formulations demonstrating full (100%) biodegradability by the conclusion of the testing phase.

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A significant determinant of the degradation rate was the amount of sorbitol incorporated as a plasticiser within the films. Samples containing a greater sorbitol (plasticiser) concentration (e.g., 5 g) exhibited accelerated degradation compared to those with a lower sorbitol (plasticiser) concentration (e.g., 2 g). This observation implies that an increase in plasticiser content correlates with enhanced biodegradability. A plausible rationale for this is that sorbitol, functioning as a plasticiser, enhances the flexibility of the polymer matrix, thus promoting more efficient penetration and subsequent breakdown by soil microorganisms. Consequently, the films incorporating 5g of sorbitol (plasticiser) displayed exceptionally high biodegradability.

Conversely, the films incorporating 2g of sorbitol (plasticiser), exhibited lowered degradation throughout the same period.

Furthermore, the impact of incorporating Rice husk ash filler on the biodegradation process was also investigated. The presence of Rice husk ash filler affected the degradation rates during the initial stages. During the early weeks of the soil burial test, the films devoid of any filler (0 g) demonstrated a tendency to degrade more rapidly than those containing filler (0.5 g or 1 g). This observation implies that the addition of Rice husk ash filler initially delayed degradation, potentially due to the filler enhancing the bioplastic matrix's rigidity, thereby somewhat obstructing microbial penetration. Nevertheless, this effect proved to be transient.

By the fourth week, all samples, including those incorporating Rice husk ash filler, exhibited complete biodegradability. Consequently, while the Rice husk ash filler may initially impede the degradation process, it does not preclude the complete breakdown of the bioplastic films when subjected to soil burial test.

Conclusion

The biodegradability assessments demonstrated that bioplastic films formulated from acetylated starch displayed a high degree of biodegradability, achieving full degradation within four-week period. Furthermore, the biodegradation rate was influenced by the concentration of sorbitol employed as a plasticiser; specifically, a greater sorbitol content correlated with an accelerated biodegradation rate.

The findings imply that increasing the plasticiser concentration enhances the flexibility of the polymer matrix, thereby accelerating its decomposition by soil microorganisms. Furthermore, while the incorporation of rice husk ash as a filler initially impeded the degradation process, it did not preclude the films from achieving complete biodegradability by the end of the experimental period.

These observations underscore the viability of Acetylated Manihot esculenta Crantz cv. TMS 92/0326 cassava-based bioplastics with the addition of sorbitol and Rice husk ash filler as a sustainable substitute for traditional plastics. The effective modification of this variety of cassava starch with high yield extraction coupled with the favourable biodegradability attributes of the resultant bioplastic films, presents considerable prospects for environmentally sustainable packaging alternatives. Consequently, additional research is necessary to investigate the mechanical properties of these bioplastics and optimise the formulation for industrial-scale utilization.

Acknowledgement

References

- Adebowale, K.O., Olu-Owolabi, B.I. & Lawal, O.S., 2019. ‘Influence of filler loading on starch-based bioplastic composites’, *Journal of Applied Polymer Science*, 136(7), pp. 472–480.
- Adeoti, A., Ogundele, O. & Olaniyi, O., 2021. ‘Economic implications of cassava utilization for industrial applications in West Africa’, *African Economic Review*, 45(3), pp. 350–367.
- Awokoya, K.N., Fadare, D.A. & Oladipo, S.O., 2020. ‘Modification and characterization of starch-based biopolymers for packaging applications’, *Journal of Applied Polymer Science*, 137(23), p. 48761.
- Ballesteros-Mártinez, L., Pérez-Cervera, C. & Andrade-Pizarro, R. (2020) ‘Effect of glycerol and sorbitol concentrations on mechanical, optical, and barrier properties of sweet potato starch film’, *NFS Journal*, 20(20) pp. 1-9
- Bernardino-Nicanor, A., Acosta-García, G., Güemes-Vera, N., Estrada-García, I. & Bello-Pérez, L.A., 2017. ‘Fourier transform infrared and Raman spectroscopic study of

DOI: https://doi.org/10.5281/zenodo.18654304

double-modified starches from ayocote beans', *Journal of Food Science and Technology*, 54(4), pp. 933–943.
- EPA, 2022. *National Overview*: Facts and Figures on Materials, Wastes and Recycling.
- Ezeoha, S.L. & Ezenwanne, J.N., 2013. 'Production of biodegradable plastic packaging film from cassava starch', *IOSR Journal of Engineering*, 3(10), pp. 14–20.
- Geyer, R., Jambeck, J.R. & Law, K.L., 2017. 'Production, use, and fate of all plastics ever made', *Science Advances*, 3(7), e1700782.
- Henry, N.O., 2007. 'Effect of chemical modification on starch of some legume flours', *Pakistan Journal of Nutrition*, 6(2), pp. 167–171.
- IITA, 2020. *Breeding and improving cassava for industrial uses: TMS 92/0326 as a model.* International Institute of Tropical Agriculture (IITA).
- Müller, S., Rajendran, D. & Dufresne, A., 2023. 'Biodegradable plastics from cassava starch: Sustainability and economic impact', *Journal of Bioplastic Research*, 19(2), pp. 125–134.
- Nwaka, E., Akomah, U.C., Maduoma, T.U., Ezeokolie, E.D. & Menankiti, D.T., 2025. 'Optimizing the production of biodegradable chitosan-glycerol bioplastics from potato starch', *European Journal of Sustainable Development Research*, 9(3), p. em0309.
- Pooja, N., Shashank, S., Singh, B.N. & Mazumder, N., 2024. 'Advancing sustainable bioplastics: chemical and physical modification of starch films for enhanced thermal and barrier properties', *RSC Advances*, 14(33), pp. 23943–23951.
- Plastics Europe, 2021. Plastics—The Facts 2021.
- Santana, R.F., Lima, C.M.G., Alves, A.N., Maniglia, B.C., Anjos, L.D., Pires, A.C.S., Santos, L.S., Rodriguez, L.B.,Fontan, R.C.I., Goncalves, J.T.T., Guine, R.P.F., Coutinho, H.D.M & Bonomo, R.C.F. (2024) 'Sorbitol-plasticized jackfruit starch-based films', *Polymer Bulletin* 24(81) pp. 13089-13111.
- Shogren, R.L., Lawton, J.W. & Tiefenbacher, K.F., 2002. Baked starch foams: Starch modifications and additives improve process parameters, structure and properties. *Industrial Crops and Products,* 16(1), pp. 69–79.
- Zhang, Y., Liu, W. & Zhao, L., 2022. 'Environmental benefits of cassava starch-based bioplastics: A review of bioplastics from renewable resources', *Sustainable Materials and Technologies*, 26(1), pp. 110–118.

Declaration

The authors declare that this manuscript is original and unpublished.

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