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THE POTENTIAL OF NATIVE STARCH BIOMASS TO PRODUCE MATERIALS FOR ENERGY APPLICATIONS

Omar P. Troncoso, Fernando G. Torres * and Virgilio B. Delgado

Department of Mechanical Engineering, Pontificia Universidad Católica del Perú, Av. Universitaria 1801, 15088, Lima, Peru

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ABSTRACT

Starch is widely used in the food, packaging, paper, and biomedical industries, primarily sourced from commercial crops such as potato, maize, corn, cassava, and wheat. However, native Andean potatoes, despite their high starch content and genetic diversity, remain underutilized in industrial applications. These varieties are often overlooked in favor of commercial starch sources. They are usually considered non-commercially viable due to cosmetic defects, irregular sizes, or overproduction surpluses. In this study, starch extracted from a native Andean potato variety was reinforced with Barium Titanate Oxide (BTO) to fabricate a biopolymeric film with a high dielectric constant. This composite film was employed as the triboelectric layer in a freestanding sliding Triboelectric Nanogenerator (TENG), which achieved a maximum output voltage of 25 V and a short-circuit current of 2.5 μA. This TENG was used to charge a 3.4 μF capacitor, demonstrating the potential of Andean potato starch-based films for energy harvesting applications, particularly in self-powered sensors and low-power electronic devices.

1. INTRODUCTION

Starch is a crucial food source and a renewable biomass resource widely used in industrial applications as a thickening and adhesive agent (Troncoso and Torres, 2020). Structurally, it is composed of two biopolymers, amylose and amylopectin, which have been utilized in the development of biodegradable polymers for packaging applications. The advantages of starch-based biopolymers include their biodegradability, low cost, and abundant availability (Yu et al., 2021). Moreover, it is present in a variety of plant sources, including roots, tubers, stalks, and seeds, but commercially significant starch production is primarily derived from crops such as corn, wheat, and potato (Buléon et al., 1998). The starch extracted from these crops plays a significant role in industries such as food, textiles, and paper manufacturing (Eliasson, 2004). However, the physicochemical properties of starch and its derived materials depend on their botanical origin. Previous studies have analyzed the properties of starches extracted from more than 30 varieties of Andean tubers, including various native potato species (Torres et al., 2011). It has been observed that factors such as granule size, amylose-to-amylopectin ratio, gelatinization temperature, and enthalpy vary significantly based on the starch source. Similarly, starch-derived nanoparticles exhibit distinct properties, such as variations in size and crystallinity, even when derived from potato varieties with similar amylose content and gelatinization temperatures (Torres et al., 2015).

The study of native starches is justified by several factors, including their potential for sustainable and eco-friendly production and their local availability, which can provide economic and cultural benefits (Zhu, 2020). For instance, in Peru, smallholder farmers cultivate more than 4,000 native potato varieties (Meinzen-Dick et al., 2009), each one of them with different morphological and thermal properties (Torres et al., 2011). However, these varieties are primarily used for direct human consumption rather than for starch extraction, leading to potential underutilization of a valuable resource. The International Potato Center has shown that potato processing in Andean countries, such as Peru and Bolivia, is primarily oriented toward fresh table potato consumption. The percentage of processed potatoes relative to the total production in these countries is in the range of 1.5%-3.3% (Devaux et al., 2024). This underscores the limited utilization of starch in the industry of Andean countries. Despite the limited industrial utilization of native potato starch, studies have highlighted its promising functional properties for different applications. Vilpoux (2023) studied the economic opportunities for underutilized raw materials of South American origin in the starch markets. He found that as the main cost of native starch is the cost of raw material, agricultural yields are of great importance to identify the most promising starch sources. Consider-

* Corresponding author:
Fernando G. Torres
email: fgtorres@pucp.pe

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ing dry matter productivity per hectare, potato remains the most productive crop in the Andean countries with great economic potential.

Choque-Quispe et al. (2024) evaluated the rheological, thermal, and techno-functional properties of starch extracted from two native Andean potato varieties. They concluded that these starches have potential applications in the food industry. While starch-based products generally have lower CO_2 emissions compared to fossil-based products when a Life Cycle Assessment (LCA) is conducted, studies indicate that their impact on eutrophication and acidification may be greater due to agricultural practices (Forfora et al., 2024). Several studies have evaluated the environmental impact of the production of starch-based biocomposites using the LCA methodology. Rojas et al. (2021) evaluated the environmental impact of bioplastics made from different type of starches. Thermoplastics made from Andean potato starches featured lower environmental impact compared to other biopolymers, such as polylactic acid (PLA). Global warning (GW), freshwater ecotoxicity (FEC), freshwater eutrophication (FEU), fossil resources (FR) and mineral resources (MR) present a lower impact for Andean potato starch compared to PLA. Their results also found that agricultural practices and starch extraction efficiency are key factors to obtain sustainable products.

In some cases, surplus or non-commercially viable potatoes could be repurposed to generate starch-based materials for other applications, contributing to waste reduction and promoting circular economy practices. One of the most interesting possible applications is its use in Triboelectric Nanogenerators (TENGs). TENGs operate based on the contact electrification phenomenon, in which charge transfer occurs between two dielectric materials during periodic contact-separation cycles (Torres et al., 2023; Torres and De la Torre, 2021). These devices can convert mechanical energy into electrical energy, potentially serving as power sources for small portable electronics such as wearable devices, sensors, LEDs, and implantable devices for wireless cardiac monitoring, among others (Kim et al., 2021).

There are many reports of the use of waste and biopolymers in TENGs. For instance, Saqib et al. (2020) developed an economical and environmentally friendly TENG using peanut shell powder (PSP) as the active material. The PSP-TENG demonstrated high performance being capable of powering LEDs and a calculator. The use of biodegradable materials, such as chitosan and cellulose nanofibrils, has also been remarked for their potential in creating self-powered devices that can degrade in physiological environments, thus minimizing environmental impact (Chaturvedi and Roy, 2024). This is particularly relevant for implantable medical devices, where the need for secondary surgeries to remove non-biodegradable components can be eliminated (Mi et al., 2022). Recent advancements have also focused on the use of recycled plastics, such as take-out boxes and plastic bags, in TENGs. For instance, a TENG constructed from waste take-out boxes achieved an output voltage of 186 V and a power density of 34 μW (Gu et al., 2023). Furthermore, the use of polyethylene waste has been explored, with findings indicating that it can effectively serve as a triboelectric material, thereby contributing to a circular economy by mitigating plastic waste (Das et al., 2024).

A notable application of Andean potato starch involves its use in the development of biopolymeric films for energy harvesting technologies. While previous studies have investigated starch-based triboelectric materials, their performance has remained limited, particularly in terms of electrical output (Ccorahua et al., 2019a; Ccorahua et al., 2019b). Herein, starch extracted from the "Yungay" variety has been used to fabricate a triboelectric layer for a TENG device, aiming to develop a more ecofriendly device with competitive electrical output for energy harvesting applications. Typically, triboelectric materials are synthetic polymers such as PTFE, and Kevlar®, which may have significant environmental impacts (Hao et al., 2024). Unlike PTFE and Kevlar®, starch-based materials degrade naturally and are extracted from bioresources. In order to improve the dielectric properties of starch, and make it a viable alternative, a starch-based composite incorporating Barium Titanate Oxide (BTO) has been developed. This composite material has demonstrated its suitability for TENG applications, offering an alternative to conventional synthetic polymers.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

Potatoes (solanum tuberosum var Yungay) were bought in Lima, Peru. Barium titanate oxide (BTO, $BaTiO_3$), glycerol, hydrochloric acid (HCl), and sodium hydroxide (NaOH) were analytical grade and obtained from Sigma-Aldrich and Himedia Laboratories LLC. Kapton® films were sourced from Fuel Cell Store, while Teflon® films were acquired from Sigma-Aldrich.

2.2 Fabrication of starch-based TENGs

TENGs operate based on the principles of contact electrification and electrostatic induction. For effective charge transfer, two dielectric layers composed of materials with distinct electron affinities must be employed. Before contact, there is no charge transfer, and thus no potential difference. However, upon contact, electrons transfer from the material with lower electron affinity to the one with higher electron affinity, leading to one surface acquiring a negative charge while the other becomes positively charged. Upon separation, this charge imbalance induces an electron flow in the external circuit until electrostatic equilibrium is reached. To develop a functional starch-based TENG, it was first necessary to extract and process the starch used as the triboelectric material. For the starch extraction, fresh Yungay potatoes were washed with tap water, chopped, and homogenized using a blender. The resulting slurry was sieved and allowed to settle for 4 hours. The supernatant was discarded, and the precipitate was degreased by resuspension in a 1:1 methanol-water mixture, followed by decantation. The final starch precipitate was dried at 60°C for 24 hours.

Starch-based films were prepared using the casting method. A total of 10 g of dried starch was dissolved in 200 mL of distilled water at 95°C. Then, 0.075 g of BTO was added to the starch solution. The solution underwent partial hydrolysis in 0.1 N HCl, adjusting the pH to 2.0. Glycerol was incorporated at a 2:5 ratio (glycerol:starch, dry basis). The mixture was homogenized by stirring for 15 minutes at 95°C, after which it was neutralized with 0.1 N NaOH, adjusting the pH to 10 to halt hydrolysis. The final solution was spread onto Petri dishes and dried in an oven at 40°C for 16 hours. The resulting films were approximately 200 μm thick. Pure starch films were also prepared for comparison. The starch-based films served as one triboelectric surface, while Teflon® was used as the counterpart. The starch-based films functioned as a freestanding layer (Figure 1a), while the Teflon® layer remained stationary as the stator. A linear motor facilitated a sliding motion (Figure 1b), generating contact-separation states in the TENGs. Copper films were used as electrodes (current collectors).

2.3 Characterization techniques

Scanning Electron Microscope (SEM) was used to study the morphology of the starch-based films. The analysis was performed using an Axia ChemiSEM (Thermo Fisher) equipped with an energy-dispersive X-ray spectroscopy detector. Tests were carried out in low vacuum with a voltage of 20 kV and a working distance of ~10 mm. Fourier Transform Infrared (FTIR) spectroscopy was employed to identify functional groups in the starch-based films. Spectra were recorded using a Spectrum Two PerkinElmer spectrometer equipped with a universal ATR accessory. The spectral range was 500-4000 cm^{-1}, with a resolution of 4 cm^{-1} and 64 scans. The dielectric properties of the films were analyzed using a NOVOCONTROL Broadband Dielectric Spectrometer (BDS) with an Alpha A-High Performance Frequency Analyzer. Measurements were conducted over a frequency range of 10^{-2} to 10^{-7} Hz under an inert nitrogen (N_2) atmosphere. Temperature control was achieved using a QUATRO Cryosystem nitrogen jet. The starch-based films were cut into 30 mm diameter circular discs and placed between gold-plated electrodes. Film thickness was measured using a Mitutoyo 293-240 micrometer. The electrical output of the TENGs was assessed using a Tektronix DPO2022 oscilloscope. The generated voltage signal was recorded directly, including rectified voltage measurements. Data were collected over a 10-second interval. The short-circuit current was measured using an SR570 Stanford current preamplifier in a circuit with an equivalent resistance of 9.3 MΩ. Electrical measurement were conducted at least three times. Mechanical tests were conducted to analyze the stress-strain curves and determine the stiffness of the films. These tests were performed using a Shimadzu EZ-SX Universal Testing Machine equipped with a 500 N (±0.5%) load cell. The crosshead speed was set at 10 mm/min. The samples were cut into 5 mm x 60 mm strips. The tests were performed at room temperature (20°C). Three repetitions were conducted.

3. RESULTS AND DISCUSSION

TENGs work as a voltage source coupled with a capacitor (Niu and Wang, 2015). Like any capacitor, its energy storage capacity depends on the relative permittivity (ε_r) of the charge-storing surface. Relative permittivity quanti-

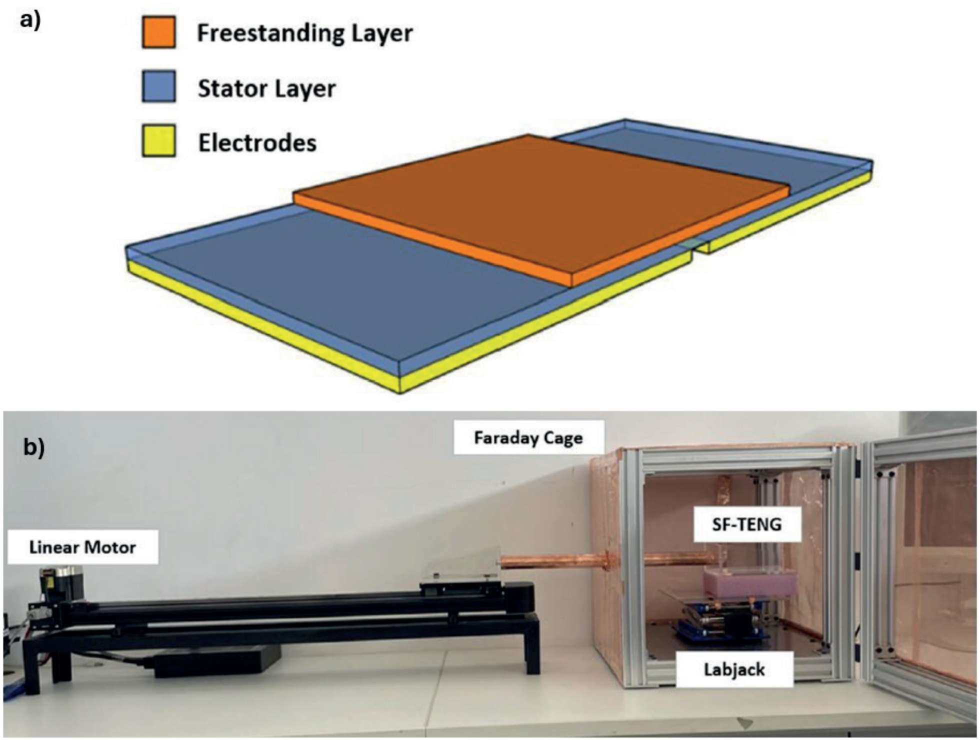

FIGURE 1: Schematic representation of the TENGs prepared for this study. Starch and starch/BTO films were used as freestanding layers. Teflon® films were used as stator layers (a). The sliding mode TENG fabricated was prepared using a linear motor that provides an oscillating movement between a starch/BTO film and a Teflon® film. The TENG was kept in a Faraday cage to avoid electric interference (b).

fies a material's ability to polarize in response to an electric field. To maximize TENG power generation, the dielectric materials used as active surfaces should have the highest possible permittivity. Several synthetic polymers, such as polytetrafluoroethylene (PTFE), Kapton®, and Kevlar®, exhibit relatively high ε_r values. However, their permittivity remains lower than that of high-permittivity ceramics (Prateek et al., 2016). To address this limitation, a high-permittivity composite was developed by incorporating BTO into a starch matrix. This starch/BTO composite was then used as one of the active surfaces in the TENGs prepared for this study.

A higher permittivity leads to a greater charge density (σ), as described for the following equation for a sliding TENG (Niu et al., 2013):

$$\sigma = \frac{\varepsilon_0 (l-x) V_{oc}}{x}\left(\frac{\varepsilon_{r1}}{d_1}+\frac{\varepsilon_{r2}}{d_2}\right) \qquad (1)$$

where ε_0 is the vacuum permittivity, V_{oc} is the open-circuit voltage, d_1 and d_2 are the thickness of the triboelectric layers (in this case, the starch-based and the Teflon® films), εr_1 and εr_2 are the relativities permittivities of these films, x is the separation between the triboelectric layers and l is the longitudinal size of these layers.

The output voltage of a typical TENG operating in sliding mode also depends on the charge density and can be expressed as follows (Niu et al., 2013):

$$V = -\frac{1}{w\varepsilon_0(l-x)}\left(\frac{d_1}{\varepsilon_{r1}}+\frac{d_2}{\varepsilon_{r2}}\right)Q + \frac{\sigma\, x}{\varepsilon_0(l-x)}\left(\frac{d_1}{\varepsilon_{r1}}+\frac{d_2}{\varepsilon_{r2}}\right) \qquad (2)$$

where Q is the amount of transferred charge and w is the width of the whole structure. These equations highlight the importance of using films with high permittivity to get devices with improved performance, justifying the incorporation of BTO.

The incorporation of BTO was assessed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX). Figure 2a depicts the SEM image of the pristine starch film. The surface morphology reveals a relatively homogeneous structure with a smooth texture, accompanied by small pores and irregularities distributed throughout the film. The presence of these pores suggests a non-compact arrangement of the starch polymeric matrix. The Energy Dispersive X-ray (EDX) identified carbon (55.2% wt), oxygen (36.9% wt) and Na (4.4% wt) as the principal components (Figure 2c), with sodium likely originating from the extraction process. Figure 2b displays the morphology of the starch/BTO film. In contrast to the pristine film, the surface morphology exhibits a more heterogeneous structure, characterized by the presence of dispersed bright regions corresponding to BTO particles. These particles appear aggregated in certain areas, forming irregular clusters distributed throughout the polymeric matrix. EDX analysis indicate a composition of carbon (46.5%wt), oxygen (36.4% wt), titanium (9.9% wt) and sodium (4.2% wt) (Figure 2d).

FTIR also confirmed the incorporation of BTO into the starch-based films. Figure 3 presents representative spectra of pure BTO and starch/BTO films. The spectrum of pure BTO exhibits a characteristic peak at 1421 cm^{-1}, attributed to bending vibrations in the COO group, a result of acetic acid usage during BTO synthesis (Singh et al., 2017). The same peak appears in the starch/BTO spectrum, confirming the presence of BTO in the composite. Additional peaks correspond to typical starch features. The band at 930 cm^{-1} is associated with glycosidic linkages, while the 1642 cm^{-1} band corresponds to water absorption in the amorphous regions of starch. The CH deformation band at 2933 cm^{-1} is also observed (Torres et al., 2015).

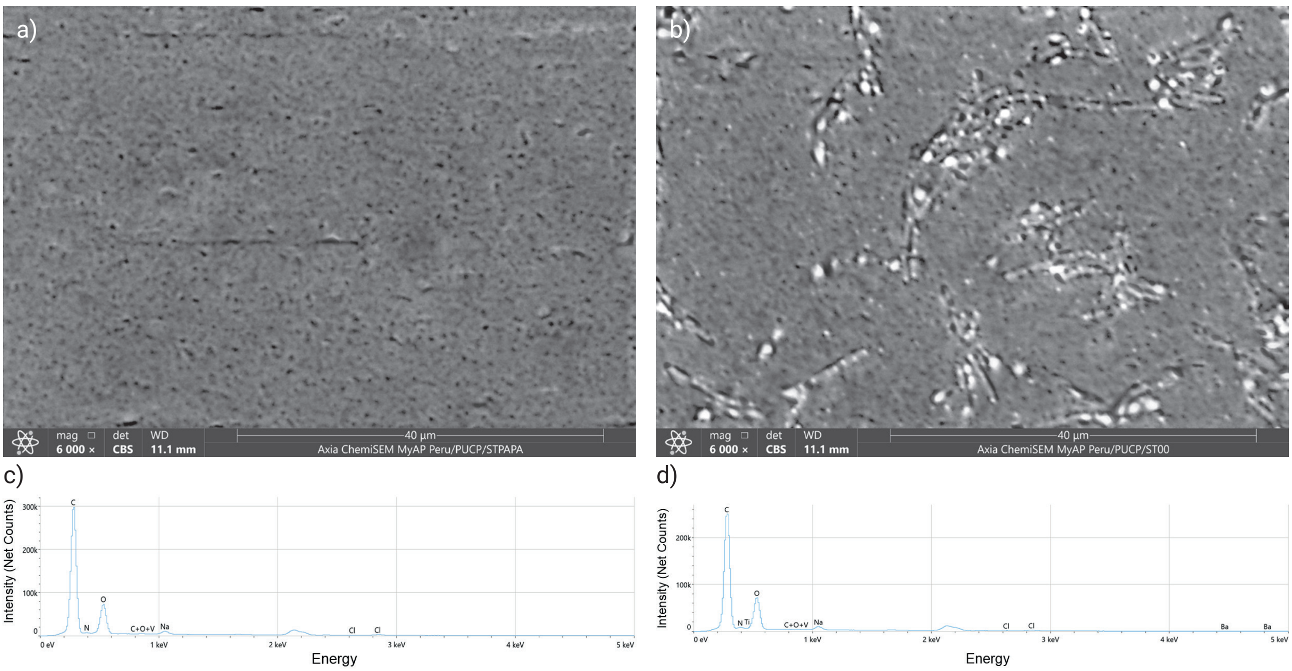

FIGURE 2: SEM images of (a) the pristine starch film and (b) the starch/BTO film, along with their corresponding EDX spectra (c) and (d), respectively.

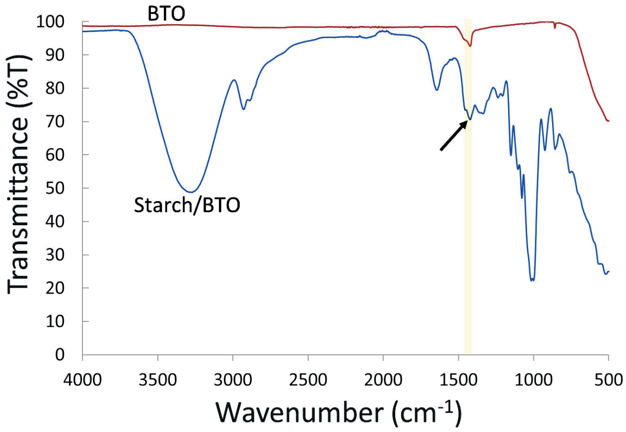

FIGURE 3: Representative FTIR spectra of pure BTO and a starch/BTO film.

BDS was performed to evaluate the dielectric properties of the prepared films. The relative permittivity of native starch films was determined to be $1.02x10^5$. In contrast, the starch/BTO composite films exhibited a significantly enhanced dielectric constant of $3.77x10^6$, an increase by a factor of more than 36.

To fabricate a functional sliding-mode TENG, two different dielectric materials were required. The electrical performance of a starch/BTO-Teflon® TENG was evaluated. Figure 4 illustrates the voltage signals generated by the prepared TENGs. The voltage profile reveals a distinctive alternating pattern resulting from the cyclic mechanical motions. Each oscillation cycle spans approximately one second, with peak values ranging from 23.1 V to -21.9 V. Upon rectification via a full-bridge rectifier, the negative portion of the waveform is mirrored above the time axis, resulting in a fully positive voltage output.

Similarly, Figure 5 presents the short-circuit current signals, which range from 2.46 μA to -2.3 μA. The rectified signal exhibits a peak current of 2.42 μA. These results demonstrate that the starch/BTO composite significantly influences charge transfer efficiency and output current.

To further evaluate the practical applicability of the TENGs, their capability to charge a 3.4 μF capacitor was investigated. Figure 6 presents representative charging curves, illustrating the voltage evolution over time. The charging profile of the pure starch-based TENG reaches a plateau at approximately 1.25 V after 200 seconds. In contrast, the starch/BTO-based TENG exhibits a significantly higher plateau voltage of approximately 2 V, achieved in less than 50 seconds. This improvement is attributed to the higher dielectric constant of the starch/BTO composite, which enhances charge storage capacity and energy conversion efficiency.

These results underscore the potential of biopolymer-based dielectric materials for optimizing TENG performance. By tailoring the dielectric properties of starch-based composites, sustainable and efficient energy harvesting devices can be developed.

TENGs in the freestanding sliding mode generate electrical output through the periodic contact and relative lateral displacement of dielectric films. In this context, evaluating the mechanical properties of these films is essential, as their strength, flexibility, and durability influence their triboelectric performance and long-term stability under repeated sliding motions. Figure 7 presents the stress-strain curves for the pristine starch film and the BTO/starch composite film. These measurements were performed three times, and the elastic module was calculated using the average value. The pristine starch film exhibited an elastic modulus of 17.27 MPa, indicating a more flexible and ductile behavior with a maximum strain of approximately 18%. In contrast, the BTO/starch composite film showed a significantly higher elastic modulus of 41.988 MPa, reflecting an improvement in mechanical strength. The stress at break for the composite film was nearly three times greater than that of the pristine film. However, its elongation at break decreased to approximately 8%, suggesting increased brittleness due to the presence of BTO particles in the matrix.

Compared to other starch-based TENGs, the fabricated device exhibits significant potential for high performance. For instance, Zhu et al. (2018) developed a starch paper-based TENG that achieved an output voltage of 11.2 V, approximated as the open-circuit voltage under a 100 MΩ load resistance. The starch paper was sourced from GILRO Corp. (Israel). In contrast, Ccorahua et al. (2019a) reported

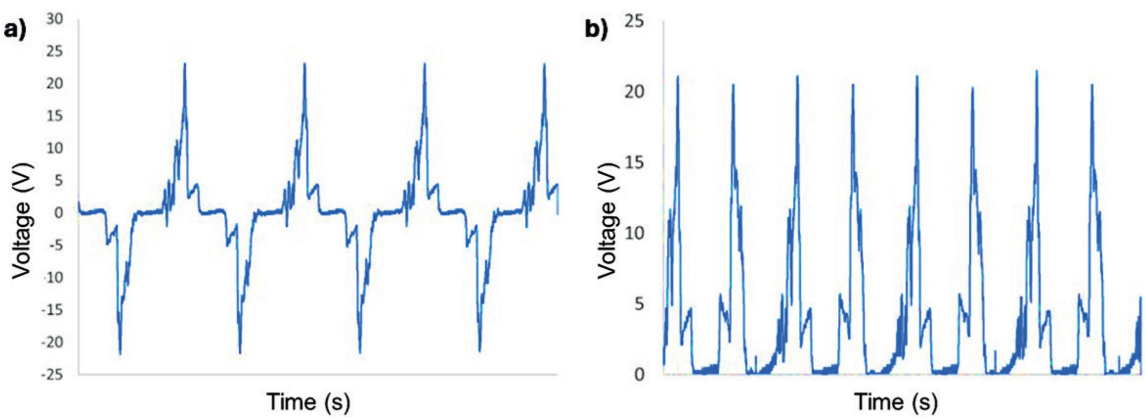

FIGURE 4: Representative open circuit voltage signals from starch/BTO-Teflon® TENGs in an open circuit mode (a) and a rectified circuit (b).

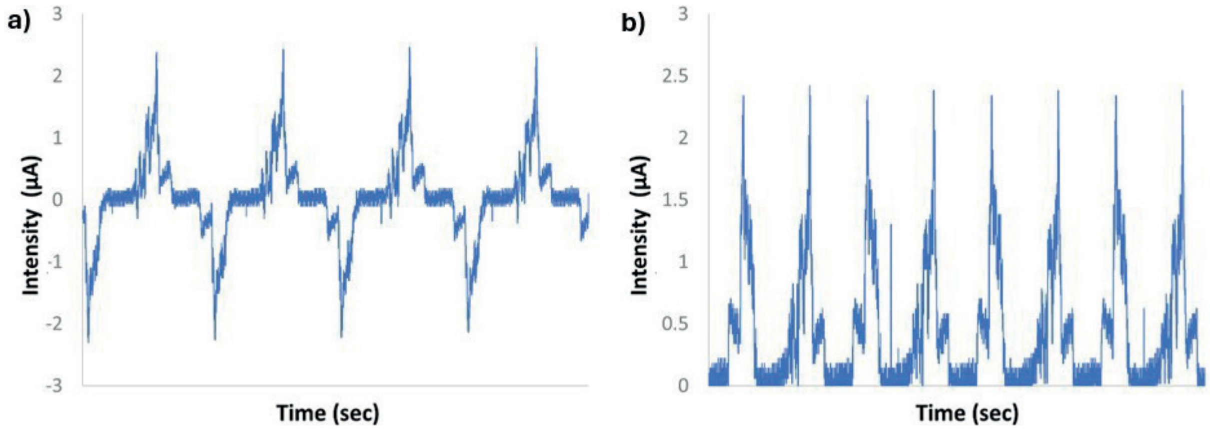

FIGURE 5: Representative short circuit current (µA) signals from starch/BTO-Teflon® TENGs in an open circuit mode (a) and a rectified circuit (b).

lower performance despite also using starch from Andean potatoes (yellow variety). Their starch-cellulose-based TENG generated a maximum output voltage of 300 mV.

It is important to note that while the fabricated TENG demonstrates remarkable performance, other devices have outperformed it. For example, a TENG incorporating a starch gel composite material with a mass ratio of 1:1.02 of corn starch gel and silicone foam produced an output voltage of approximately 280 V (Kamilya et al., 2024), enabling it to power 14 blue LEDs. The TENG using only intrinsic silicone foam achieved an output voltage of 122 V. The superior performance of this device may be attributed to the combination of silicone foam (a highly tribonegative material) and nitrile rubber (a highly tribopositive material), which are positioned far apart in the triboelectric series. Similarly, Khandelwal et al. (2021) extracted starch from the same source and developed a starch/Laver TENG (SL-TENG) that achieved a maximum voltage of 50 V, whereas the pristine starch TENG exhibited a voltage of only 10 V. The difference in performance may also be attributed to the origin of the starch used. While these studies have used wheat starch, our device utilizes starch extracted from Andean potatoes, which could introduce differences in granule size, amylose-to-amylopectin ratio, and dielectric properties. These variations may influence charge transfer mechanisms and triboelectric properties.

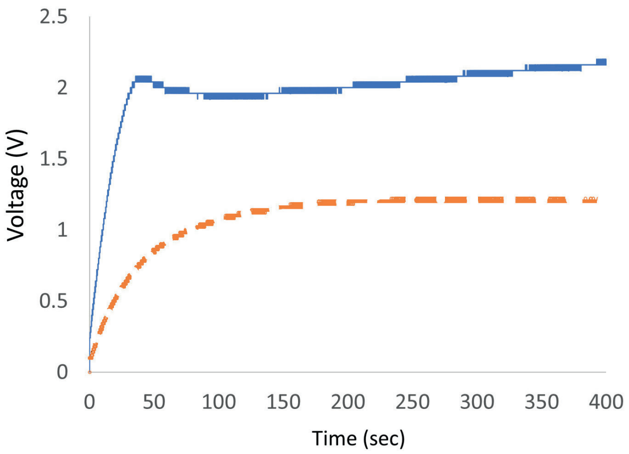

FIGURE 6: Representative time-Voltage curves for a capacitor charged using a starch/BTO-based TENG (solid line) and a pure starch-based TENG (dashed line).

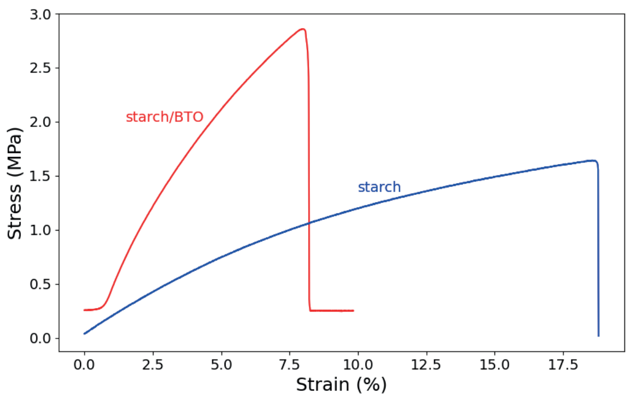

FIGURE 7: Representative stress-strain curves for the pristine starch and starch/BTO films.

Regarding sustainability, Starch Europe, the association of European Starch producers, reported in the Life Cycle Analysis (LCA) of 2022 that the starch industry has managed to reduce its CO_2 emissions by 7% overall and 19% per ton of dry substance since 2009. Its summary report state that potato starch has a carbon footprint of 474.2 kg CO_2 eq per ton of dry substance (DS). In contrast, Corn starch has a carbon footprint of 589 kg CO2 eq per tonne DS and wheat grain cultivation contributes between 480 and 740 kg CO_2 eq per tonne DS of product or coproduct. In summary, potato starch has the smallest carbon footprint which make it more appealing for applications as TENGs that looks for more environmentally friendly solutions to obtain energy. However, it is also necessary to analyze the industrial relevance of starch and its application in TENGs. In food preparation, starch is transformed into starch hydrolysate, which it is used to thicken sauces and soups. Pregelatinized potato starch is used in puddings due to its superior qualities compared to cereal starches. In the confectionery industry, it is used as a thickening agent in synthetic jellies. Potato starch processing generates a significant amount of waste, such as effluent and potato waste.

This potato waste has a high-water content (more than 80%), which makes it difficult to store and can cause serious environmental problems by polluting waterways and generating bad odors (Chauhan et al., 2023). Although it would be costly to dry this waste into dry feed, its disposal or local use as feed can contaminate soil and groundwater. In this context, repurposing potato starch for technological applications such as TENGs provides a more sustainable alternative to disposal, aligning with circular economy principles.

Ahmed et al. (2017) presented two representative TENGs, Module A (high efficiency) and Module B (lower efficiency). These modules were fabricated using synthetic polymers. Their analysis showed that most of the energy consumed in the manufacture of both modules (approximately 90%) was due to raw material requirements. Eco-indicator 99 is a method to evaluate the environmental impact of a process or a product. When comparing these TENGs with photovoltaic (PV) devices, the Eco-indicator 99 results show that both TENG modules achieve the lowest points in ecosystem quality, resources and human health. These were an order of magnitude lower than silicon-based PV modules. On the other hand, energy payback period (EPBP) is the time required for an energy system to generate the same amount of energy that was used in its production, installation, and maintenance. Module A had a 0.5-year EPBP, shorter than traditional PV technologies. Module B's EPBP was competitive but higher than organic and perovskite solar cells. The CO2 emission factor (CEF) of Module A was significantly lower than that of several PV modules. While these findings highlight the environmental advantages of TENGs, further reductions in impact could be achieved by replacing synthetic polymers with biopolymers such as starch. In this context, our TENG emerges as a promising and environmentally friendly alternative to other energy harvesting devices. However, it currently employs a synthetic polymer as one of their films. Therefore, to be considered a fully bio-based product, this component would need to be replaced. Achieving this would require identifying biopolymers that are positioned far apart in the triboelectric series, in order to maximize the output voltage. Future efforts should explore the possibility of replacing the Teflon stationary film with a suitable biological alternative, to further enhance the sustainability of the device.

4. CONCLUSIONS

This study highlights the potential of native Andean potato Yungay variety starch as a sustainable and high-performance material for energy harvesting applications. The incorporation of BTO into starch-based films resulted in a significant enhancement of dielectric properties, leading to TENG output performance. The fabricated starch/BTO-based TENG achieved a maximum output voltage of ~25 V and a short-circuit current of 2.5 μA, demonstrating its feasibility for self-powered electronic devices.

The findings emphasize the importance of utilizing underexploited biomass resources in advanced material applications. Starch from native Andean potatoes represents a valuable yet underutilized agricultural resource, offering a bio-based and biodegradable alternative to synthetic polymers. This approach aligns with circular economy principles by repurposing non-commercially viable potatoes (small or irregular size, cosmetic defects, overproduction surplus, etc.) into functional materials, contributing to waste reduction. Future research should focus on optimizing starch-based composite formulations, exploring additional functional additives, and scaling up production methods to enhance applicability in real world energy harvesting and sensor technologies.

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