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Análisis de películas biopoliméricas de almidón para potencial aplicación en optoelectrónica.

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Hariana Farfán Benavides

Industrial Engineer
hariana.farfan@uptc.edu.co;
Universidad pedagógica y tecnológica de Colombia,
Sogamoso, Colombia.

Karol Roa Bohórquez

Master's Degree in Advanced Technology,
karol.roa@uptc.edu.co;
Instituto Politécnico Nacional,
Mexico City, Mexico
Universidad pedagógica y tecnológica de Colombia.

Raúl Sánchez Alarcón

PhD in Advanced Technology,
raul.ivan.sanchez@uv.es
Universidad de Valencia,
Valencia, España.

Ricardo Paredes Roa

Industrial Engineer,
ricardo.paredes@uptc.edu.co,
Universidad pedagógica y tecnológica de Colombia,
Sogamoso, Colombia.

***Autor para correspondencia:**
hariana.farfan@uptc.edu.co

Analysis of biopolymeric starch films for potential application in optoelectronics

Abstract

The research on energy-efficient materials, such as perovskites, has experienced a surge due to their characteristics, low cost, and various synthesis methods, which enable the development of optoelectronic devices. However, their susceptibility to instability when exposed to air, moisture, or temperature variations has motivated the search for alternative structures that utilize sustainable materials, aiming to improve durability, optimize manufacturing, and reduce costs. In this context, the synthesis of starch-based polymeric matrix is proposed, applying a biopolymer, with the objective of mitigating the use of hydrocarbon-based polymers. The selected polysaccharides are derived from potatoes and aquatic plants from Lake Tota (Elodea). They were dissolved in dimethyl sulfoxide and dimethylformamide under ambient conditions, evaluating the feasibility of their application in perovskite-based technologies. The process resulted in the formation of homogeneous films, demonstrating the partial and complete dissolution of starches and establishing the foundation for their potential application in these perovskite-based devices.

Key words: biopolymer, starch, aquatic plants, dimethyl sulfoxide, optoelectronic.

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Resumen

La investigación de materiales energéticamente eficientes, como las perovskitas, ha experimentado un aumento debido a que por sus características, bajo costo y variedad de métodos de obtención, se pueden desarrollar dispositivos optoelectrónicos. Sin embargo, su susceptibilidad a la inestabilidad cuando se exponen al aire, la humedad o variaciones de temperatura ha motivado la búsqueda de estructuras alternativas que utilicen materiales sostenibles, buscando así mejorar su durabilidad, optimizar la fabricación y reducir costos. En este contexto, se propone la síntesis de una matriz polimérica de almidón mediante la utilización de un biopolímero, con el objetivo de mitigar el uso de polímeros basados en hidrocarburos. Los polisacáridos seleccionados provienen de papa y plantas acuáticas del lago de Tota (Elodea). Estos fueron disueltos en dimetilsulfóxido y dimetilformamida en condiciones ambientales, evaluando la viabilidad de su aplicación en tecnologías que emplean perovskitas. El proceso resultó en la obtención de películas homogéneas, demostrando la disolución parcial y completa de los almidones y estableciendo así las bases para su potencial aplicación en estos dispositivos basados en perovskitas.

Palabras clave: biopolímero, almidón, plantas acuáticas, dimetilsulfóxido, optoelectrónica.

Introduction

Devices crafted from energy-efficient materials, such as perovskites, showcase excellent properties that enable their use in photonic and optoelectronic applications [1]. Perovskite metal halide films are particularly advantageous due to their wavelength tunability from green to infrared, long carrier diffusion length, and cost-effective processing [2]. However, it have encountered challenges in terms of structural stability and properties when exposed to environmental conditions such as air, humidity, and thermal stress, limiting their applicability and processability [3]. Issues during synthesis, including phase segregation and photoluminescence deterioration, have prompted the exploration of substances capable of forming luminescent components directly within matrices, such as polymeric ones [4]–[6].

Among biopolymers, starch stands out as one of the most abundant organic substances globally. It is present in grains with layers of polymeric macromolecules, amylose (gelatinization), and amylopectin (viscosity). These macromolecules exhibit intramolecular organization with hydrogen bonds between OH groups, either directly or through water molecules, in a semicrystalline structure (dense layers and branches) and amorphous regions (less organized layers). Starch serves as an energy reserve in tubers such as potatoes and in plants like aquatic weeds [7]–[9]. The latter, besides being considered invasive and common, contributes to pollution in water bodies such as lakes and rivers due to its excessive growth, causing ecological imbalances, affecting water quality, and excluding native species. This phenomenon is attributed to the concentration of macronutrients (potassium and phosphorus) from fertilizers and wastewater discharges, among other factors [10], [11].

Materials y Methods

Materials

he potato starch was supplied by Brymar S.A.S, and the plant starch was extracted from Elodea Canadensis following the procedure described in Figure 1. Anhydrous dimethyl sulfoxide 99.9% (DMSO) was purchased from Scientific Products, and N,N-dimethylformamide 99.9% (DMF) was acquired from Scientific Products. All materials were used as received without any additional purification.

Methods

Starch extraction

The wet method was employed for the extraction of starch from aquatic plants, based on the findings of a prior research [12]. Initially, the plants were washed with water and

hypochlorite 1% solution, and this process was repeated twice. Subsequently, the plants were triturated to reduce the particle size and separate the crude fiber from the liquid part of the plant. These components were then hydrated and flocculated for 2 hours, facilitating the release of starch particles as starch is not soluble in water at room temperature. The mixture was filtered through cheesecloth to separate the fiber from the polysaccharide, obtaining starch through sedimenting. Finally, the moisture content of the resulting starch was removed by drying at 40°C for 24 hours in preparation for subsequent milling.

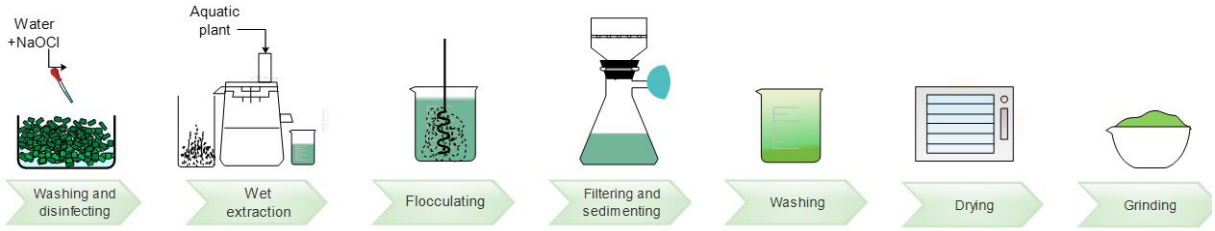

Figure 1. Extraction of starch from aquatic plants

Biopolymer Film Synthesis

The preparation of the biopolymer in DMSO:DMF under ambient conditions was carried out as follows, based on [13] and [14], as illustrated in Figure 2. The starches from aquatic plants and potatoes were mixed in a 1:9 ratio, respectively, and added to a container. The DMSO:DMF solvent system (3:2) was introduced into the container at 92, 95, or 97 % w/w at room temperature. The container was then sealed and placed on a heating plate with magnetic stirring at 80°C, maintaining agitation at 1200 rpm for 6 hours. Finally, a thin film was formed in a Petri dish and dried in an oven at 60°C for 7 hours.

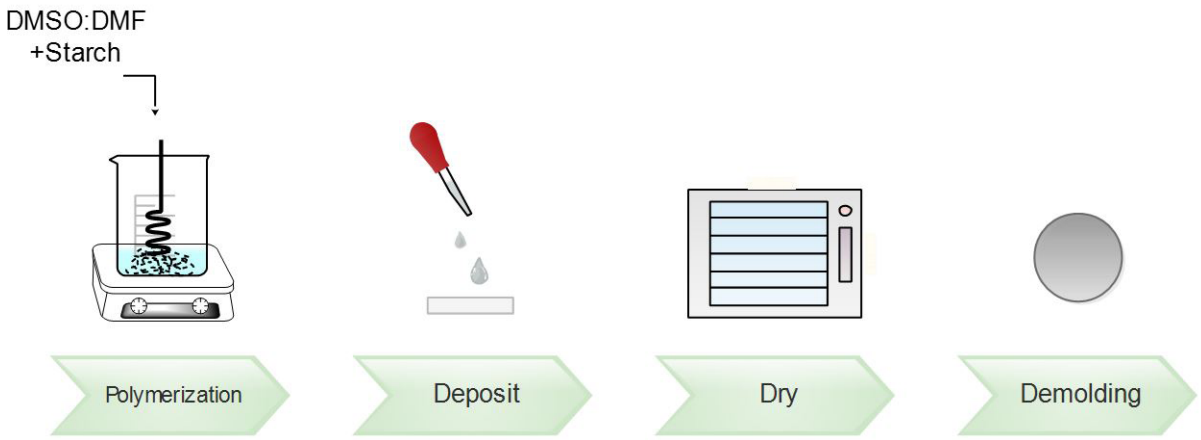

Figure 2. Starch polymerization

Results and Discussion

Efficiency of starch extraction from aquatic plants

The extraction method employed was carried out through a wet approach, demonstrating significant advantages in terms of starch yield from aquatic plants. Compared to the dry method in the previous study [12], a substantial increase in extraction efficiency was achieved, reaching a 50% improvement. This enhancement proved crucial in producing high-quality starch from natural sources. Additionally, the wet method offered the additional advantage of significantly reducing the time required for the comprehensive processing of plants, resulting in the obtainment of fresh starch suitable for subsequent applications.

To calculate the extraction efficiency, Equation (1) was applied, where the efficiency percentages are calculated as the ratio of the obtained starch to the total mass of the plant in grams, expressed as a percentage. The results are summarized in Table 1, showcasing the extraction efficiencies of starch from aquatic plants for the two evaluated methods: dry and wet. The outcomes reveal an extraction efficiency of 4.15% for the dry method, while the wet approach achieved a remarkable 9.04%. These data confirm the superiority of the wet method in terms of efficiency, highlighting its potential to optimize starch production. This improvement in efficiency not only positively impacts resource economics but also contributes to obtaining starches of higher quality and utility in various industrial applications.

$$Extraction\ efficiency\ = \frac{Extracted\ starch\ (g)}{Total\ plant\ mass\ (g)} * 100$$

Table I. Extraction efficiencies of Elodea starches

Method	Extraction Efficiency (%)
Dry	4.15
Moist	9.04

Iodine Test in Elodea starch

Additionally, photometric tests of iodine were conducted to determine the activity of starch-converting enzymes [15]. This assay revealed a color change of starch from blue to black (Figure 3), serving as an indicator of obtaining a polysaccharide with a significant percentage of amylose. This phenomenon is attributed to the interaction of iodine with the helical structures of amylose that compose starch, particularly when starch is in an aqueous medium. The intensity of the color change correlates directly with the intensity and efficiency of starch, where a darker shade indicates a higher concentration and quality of the polysaccharide [16], [17].

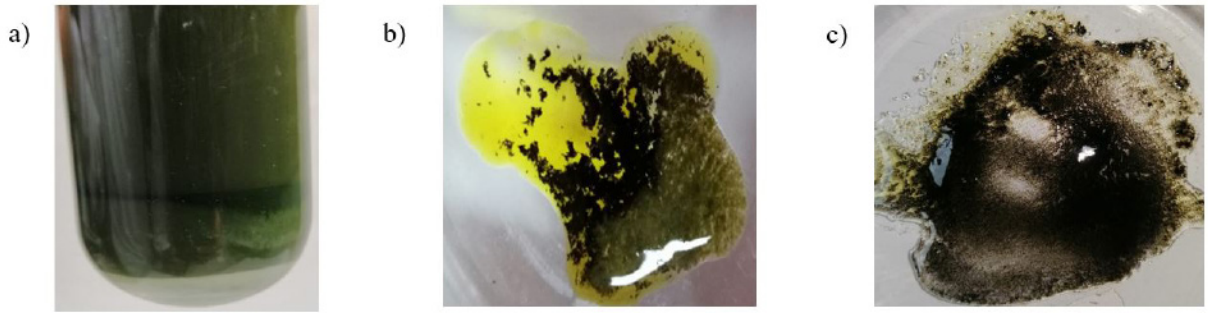

Figure 3. Iodine test on starch of aquatic plant a) 0s; (b) 10s; c) 30s.

Polymerization of the biopolymeric film

The polymerization process resulted in the production of flexible and homogeneous films (Figure 4). This phenomenon is of interest in characterizing the process as it allows for the identification of the involved stages. It was observed that the first gelation phase is triggered after 30 minutes. During this period, signs of swelling and initial ruptures of starch granules are evident, crucial for confirming the formation of the linear amylose structure [18].

The significance of this early gelation phase lies in its contribution to the generation of strong and highly cohesive films [19]. This is because amylose, one of the main components of starch, tends to form linear structures that act as reinforcements in the polymeric matrix. These linear amylose structures facilitate the creation of solid films and, in turn, promote the generation of hydrogen bonds (H-bonds) between the DMSO

solvent and the hydroxyl groups of starch [20].

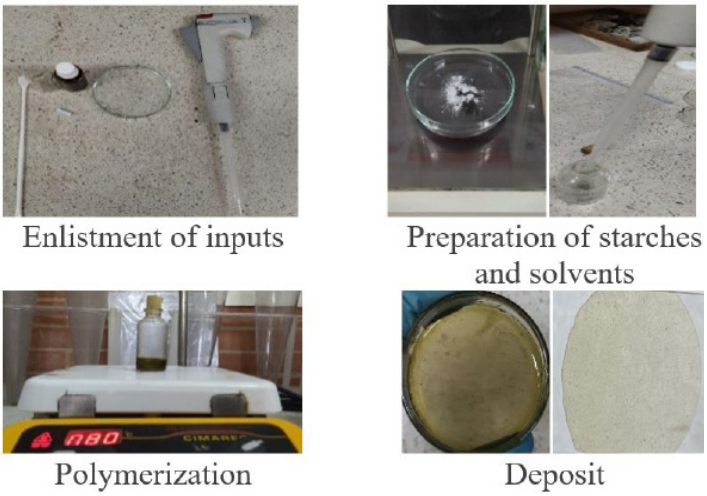

Figure 4. Starch polymerization process in DMSO:DMF

Granulometry of starch dissolved in white light

Additionally, the influence of the particle size of starch derived from aquatic plants on its ability to dissolve completely has been evaluated (Figure 5). To conduct this analysis, the size of ground Elodea starch was varied, decreasing from 425 to 149 μm. The previously detailed methodological procedure was then applied, using the DMSO:DMF solvent mixture in a ratio of 3:2, along with a combination of potato and Elodea starches in a 9:1 ratio. As a result, a substantial decrease in particle size was observed in films P1, P2, and P3.

Particle size analysis was conducted using Image J software. Particularly in P1, the particle size decreased by 59%, averaging from 179.5 to 72.4 μm, indicating an improvement in dissolution. In the case of P2, a more notable decrease of approximately 48% was experienced, dropping from 134.8 to 69.6 μm. This significant reduction in particle size suggests even more efficient dissolution, possibly due to a higher amount of starch present, increasing the probability of interaction with the solvent and hydrogen bond formation. Finally, in P3, a particle size reduction of around 66.5% was observed, decreasing from 477.9 to 160.3 μm. This finding indicates that manipulating the particle size of Elodea starch substantially influences its dissolution capacity.

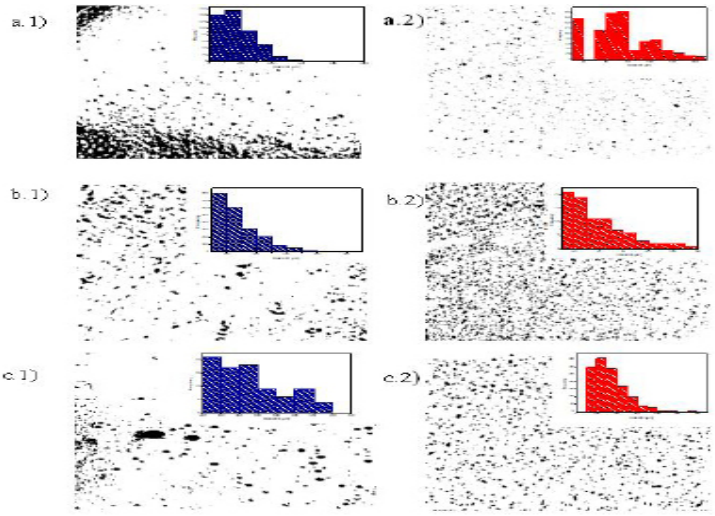

Figure 5. Particle sizes of Elodea starch solution in a) P1 from 179.5 to 72.4 μm; (b) P2 from 134.8 to 69.6 μm; c) P3 from 477.9 to 160.3

Dissolution of starch granules in polarized light

When starch granules have not undergone the gelatinization process and are observed under polarized light, a characteristic "Maltese cross" pattern can be appreciated. This appearance is due to the presence of crystalline regions within the granules, which exhibit a birefringence pattern. As the granules break and give way to the amorphous polymeric material, this property fades away [21], [22].

It is crucial to highlight that the analysis of birefringence in starch granules and its evolution over time provides information about the dissolution dynamics and transformation of the biopolymeric matrix. For this purpose, film P3, which shows a dissolved particle size reduction of approximately 75%, underwent microscopic analysis using polarized light. In Figure 6, the film obtained from Elodea after a 2-hour synthesis process is presented, where birefringence is still observed in the starch particles. This phenomenon indicates that, after a lapse of 6 hours, dissolution will progress significantly, transitioning from a partial to a complete state. This observation is crucial as it suggests that the synthesis process is advancing toward the complete dissolution of starch granules.

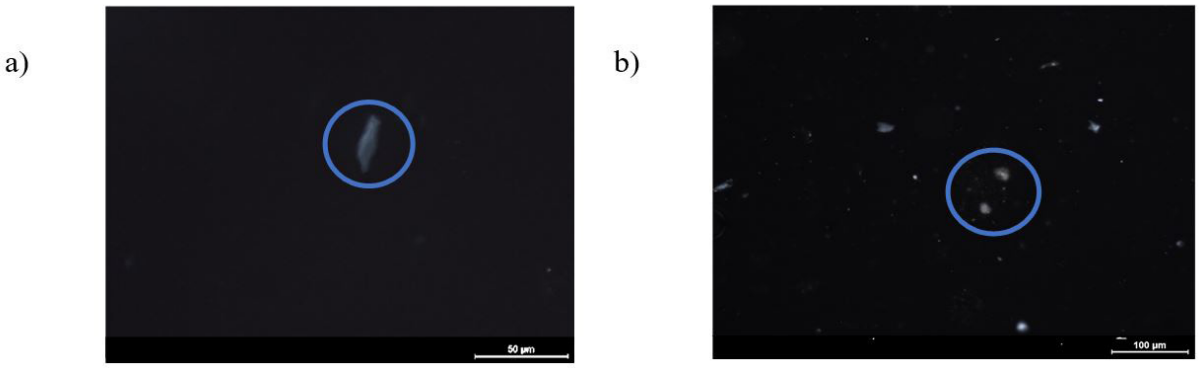

Figure 6. Optical microscopy with polarized light. (a) Elodea 50 µm; b) Elodea 100µm.

Behavior of the biopolymeric film during drying

When carrying out the drying process at a temperature of 60 °C, it was observed that the average drying rate in the film made from Elodea is approximately 2.8 mg/s. The graphical representation of these data (Figure 7) is divided into three significant sections. In the first section, the initial phase of water evaporation in the material is highlighted. The second section shows a phase of constant moisture loss, while in the third phase, it is observed that most of the moisture has been eliminated, and the weight stabilizes. This behavior is consistent with what was identified in previous research [12], [23], where an increase in the elongation of OH groups in Elodea-derived starch was observed. This finding suggests that Elodea starch exhibits hygroscopic properties, promoting greater interaction between the Elodea starch bonds and the DMSO solvent. This may have significant implications when integrating the biopolymeric matrix with perovskite.

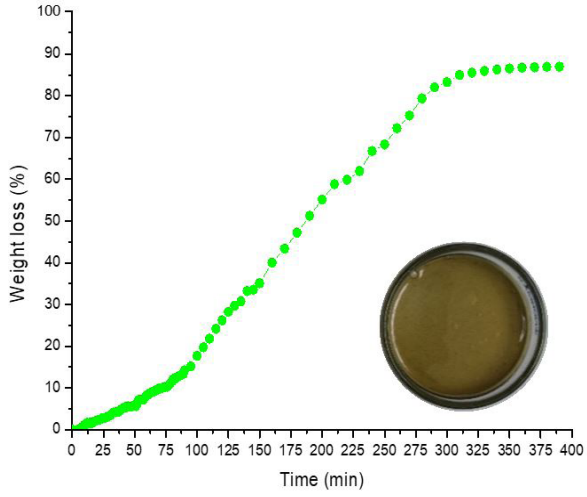

Figure 7. Biopolymer Film Drying Speed

Conclusions

- The research supports the feasibility of using starches from natural sources, such as Elodea and potato, for the creation of homogeneous and flexible films.

- The ability of these starches to form hydrogen bonds with the DMSO:DMF solvent system has been confirmed, opening new perspectives for matrix formulation in perovskite synthesis.

- The potential application of these starches in optoelectronic applications has been corroborated through the synthesis of the Starch-DMSO:DMF film, demonstrating the dissolution of the polysaccharide, specifically Elodea starch. This indicates the formation of hydrogen bonds between dimethyl sulfoxide molecules and the first layer of starch, amylopectin, facilitating the release of amylose, the swelling of granules, and ultimately gelatinization.

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