

Article

Influence of Plasticizers Concentration on Thermal, Mechanical, and Physicochemical Properties on Starch Films

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Abstract: The increasing demand for sustainable packaging materials has driven the exploration of biodegradable alternatives to synthetic plastics. This study investigates the thermal and mechanical properties of starch-based films plasticized with varying concentrations of glycerol and sorbitol. Cornstarch films were prepared with glycerol and sorbitol plasticizers in different ratios, and their physical characteristics, including swelling index, water solubility, and thermal stability, were assessed using Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), and tensile testing. The results indicate that the incorporation of plasticizers significantly influenced the films' properties. Films with higher glycerol content exhibited greater flexibility and solubility, while sorbitol-plasticized films showed enhanced thermal stability. The combination of both plasticizers yielded films with balanced properties suitable for food packaging applications. This study demonstrates the potential of glycerol and sorbitol as effective plasticizers in developing biodegradable starch-based films, offering a promising alternative to conventional plastic packaging.



Citation: Sirbu, E.-E.; Dinita, A.; Tănase, M.; Portoacă, A.-I.; Bondarev, A.; Enascuta, C.-E.; Calin, C. Influence of Plasticizers Concentration on Thermal, Mechanical, and Physicochemical Properties on Starch Films. *Processes* **2024**, *12*, 2021. <https://doi.org/10.3390/pr12092021>

Academic Editors: Giancarlo Cravotto, Jose V. Garcia-Perez and Zhen Fang

Received: 12 August 2024

Revised: 12 September 2024

Accepted: 18 September 2024

Published: 19 September 2024



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Keywords: biodegradable films; starch-based films; glycerol; sorbitol; plasticizers; thermal stability; mechanical properties; food packaging; sustainable materials

1. Introduction

Globally, plastic pollution is a major issue. Global plastic bag production by the end of the 20th century was estimated to be 260 billion bags, with an industrial output valued at USD 1 trillion [1]. The price of plastics will rise since the non-renewable resource oil is used as a raw material in the production of plastics. In 2018, 39.9% of all plastics produced in Europe (61.8 million tons) were utilized for packaging purposes. Annually, 350 million tons of plastics are manufactured worldwide, which represents 6% of total oil production. Only 1% of globally produced plastics is bio-based; the rest is sourced from fossil fuels, carrying a significant carbon footprint comparable to that of the aircraft industry. Thus, the development of a suitable procedure for making biodegradable packaging is imperative [2].

The food industry is an important branch of the mass production of widespread consumables and has a great need for biodegradable packaging to reduce environmental stress. So the potential for natural polymers to replace synthetic materials such as polyethylene (PE) and polypropylene (PP) is currently under investigation [3]. Using plastic-free materials in the food industry offers numerous advantages. Environmentally, they contribute to the reduction of plastic pollution, lower carbon footprints, and support biodegradability, thus helping in preserving wildlife and ecosystems [4]. Many plastic-free materials are derived from renewable resources, reducing reliance on fossil fuels [5]. Health-wise, they

minimize exposure to harmful chemicals like BPA and phthalates, which can leach from plastics into food [6].

Economically, plastic-free packaging can differentiate brands in a competitive market, appeal to environmentally conscious consumers, and ensure compliance with tightening regulations on plastic use [7]. Consumer demand for sustainable products is growing, driving sales and loyalty for businesses offering eco-friendly options. Aesthetically, materials like glass, paper, and wood enhance product appeal and promote a premium feel [8].

The durability and reusability of some alternatives like glass and metal support waste reduction efforts. Moreover, the transition to plastic-free solutions fosters innovation in packaging technologies, aligning businesses with future market trends and consumer behaviors [9].

Starches are a promising biopolymer due to their biodegradability, renewable nature, wide availability, and cheap cost. Amylose and amylopectin are the two distinct macromolecules that compose starches. The proportion of highly branching amylopectin to linear homopolymer amylose is responsible for the brittle nature of starches when they are dried in ambient conditions, due to the strong intermolecular hydrogen bonding between the amylose and amylopectin [10,11]. To overcome these drawbacks, plasticizers are frequently added to increase film flexibility and reduce brittleness by decreasing intramolecular hydrogen bonding along polymer chains, hence increasing intermolecular space. Water, polyols like sorbitol and glycerol, and amide-functionalized chemicals, such as urea, formamide, and ethylene-bisformamide, are examples of common plasticizers. One of the most widely utilized plasticizers for starch films is glycerol because its molecular structure is similar to the glucose units of starch, enhancing the possibility of chemical interaction with starch [12]. Furthermore, glycerol has been classified as a non-toxic substance, making it suitable for application in the food industry [13]. Numerous studies have shown the effectiveness of glycerol as a plasticizer at concentrations ranging from 20% to 40% of the starch weight. J. Tarique et al. [14] studied the influence of different concentrations of glycerol (15, 30, and 45%) on the physical, structural, mechanical, thermal, environmental, as well as barrier properties of arrowroot (*Maranta arundinacea*) starch (AS) biopolymers. The results showed that the control AS films were brittle, fragile, and not peelable from the Petri dishes. Hence, the incorporation of glycerol as a plasticizer to AS film-forming solutions led to a decrease in the brittleness and fragility and increased the flexibility and peel ability of AS films. These results also demonstrated that the addition of glycerol to AS films resulted in the increment of the film thickness, moisture content, solubility in water, and density [14]. Another polyol that is utilized as a starch plasticizer is sorbitol, which possesses a small, water-resistant molecule that reduces its affinity for water and increases its molecular interaction with polymer chains [15]. The use of various plasticizer mixtures, such as formamide/urea, sorbitol/glycerol, ethylene-bisformamide/sorbitol, and glycerol/maltose, has been studied recently to overcome issues regarding starch retrogradation, long-term plasticizer migration, and starch embrittlement. Using plasticizer mixes may also make it possible to adjust the material's tensile and water resistance characteristics [16]. For example, the proportion of glycerol and sorbitol affects the starch biofilm properties. Sorbitol gives shine, less water vapor transmission, and more mechanical support, while glycerol has long water vapor transmission, high solubility, greater elongation, and low tensile strength [15]. The study [17] showed that biodegradable potato starch/PVA samples with varying rosin concentrations were prepared by melt-mixing to enhance native starch film properties. Glycerol and PVA were used as plasticizers. The samples, in cause, were analyzed for water content, solubility, mechanical properties, microstructure, and dynamic mechanical behavior. Adding 8% rosin resulted in a tensile strength over 10 MPa and an elongation at break near 2000%, comparable to conventional food packaging polymers like LDPE. Additionally, starch compounds are cost-effective and highly biodegradable.

Mechanical properties of starch-based films, assessed through tensile tests, are essential in determining their potential as viable alternatives to conventional plastics. These tests

provide essential data on the strength, flexibility, and durability of the films, which are key factors in their practical application [3,17–24].

Natural materials were investigated for obtaining starch films in reference [18], in which various Andean crops were utilized as raw materials for producing biodegradable polymers. From these starches, biodegradable films were created through casting, with water and glycerol serving as plasticizers. The mechanical properties of the starch-based films were evaluated using tensile tests, while compost and FTIR tests assessed their biodegradability. The results revealed that the mechanical properties (UTS, Young's modulus, and elongation at break) were highly dependent on the starch source. All starch films biodegraded in three stages, with a higher weight loss rate compared to the cellulose control film.

Reference [20] aimed to evaluate the film-forming capacity of various starch sources (cassava, corn, potato, and wheat) by casting with starch contents ranging from 2% to 6%. Cassava starch films demonstrated lower wettability and good mechanical properties, suggesting their suitability for packaging products with higher water activities, such as fruits and vegetables.

To address the mechanical and thermal limitations of starch films, N. Nordin and collaborators employed the bio-composite concept [21]. They incorporated microcellulose fibers (MCF) into thermoplastic starch (TPS) films at varying concentrations (1, 5, and 10 wt%). The MCF was prepared through NaOH/urea dissolution and ultrasonication. Due to similar polysaccharide structures and good interfacial interactions, the tensile strength (TS) and elongation at break (EAB) of the films improved with the addition of MCF, but this enhancement was observed only at the 1 wt% loading content.

The impact of each starch's grain structure on the microstructure, transparency, hydration properties, crystallinity, and mechanical properties of the films was assessed in [25]. The study found that potato starch films were the most transparent, while corn-starch films were the opaqueness. All films exhibited homogeneous, highly amorphous internal structures without pores, indicating effective starch gelatinization. The tensile strength (4.48 MPa–8.14 MPa), elongation at break (35.41–100.34%), and Young's modulus (116.42–294.98 MPa) of the films were significantly influenced by the amylose content, molecular weight, and crystallinity of the film.

Storage conditions can affect the properties of starch-based films. The starch gel's surface microstructure and functionalities are significantly impacted by storage temperature and time. The drying of starch gel leads to the retrogradation phase characterized by re-association of amylose-amylopectin chains. The drying temperature determines the degree of reorganization or crystallinity of the developed films, which can induce changes in the optical, mechanical, and barrier properties [22]. Moreover, the quality of most packaging materials based on starch films degrades when subjected to specific external conditions over extended periods, due to protein aggregation, plasticizer migration, or small-molecule component diffusion, thereby decreasing their protective efficacy against environmental factors on stored foods [26,27]. Plasticizer migration occurs naturally during storage, but the process is difficult to observe and control [26]. Chen C. et al. [28] investigated the influence of different storage temperatures, relative humidity (RH), and time on the apparent form, barrier properties, mechanical properties, and microstructure of corn-wheat starch/zein bilayer films. The results indicated that as storage duration extended, the oxygen barrier characteristics of the bilayer films decreased; meanwhile, the moisture content initially increased and subsequently decreased. After 150 days, the bilayer film maintained at 25 °C with 54% relative humidity exhibited superior water resistance properties. The tensile strength of bilayer films held at 25 °C with relative diminished humidity levels of 43%, 54%, and 65%, although it remained superior to those maintained at lower temperatures (−17 °C, 4 °C), which exhibited increased toughness due to their elevated elongation at break [28]. In the article [29], pea starch (S) and poly(vinyl alcohol) (PVA) blends were produced in various ratios (2:1, 1:1, 1:2) to address the common drawbacks of starch films. These blends, obtained by casting, were analyzed for microstructure, thermal behavior,

and barrier, mechanical, and optical properties after 1 and 5 weeks of storage at 25 °C and 53% relative humidity. Incorporating PVA into pea starch films significantly improved their mechanical properties, making them more extensible and stable during storage. Additionally, the blends demonstrated enhanced water barrier properties and reduced water sorption, especially at S ratios of 1:1 and 1:2. Mali et al. [30] compared the thermal, mechanical, and barrier properties of corn, cassava, and yam starch plasticized with glycerol (0–40%) under a controlled storage (64% RH and 20 °C) time of 90 days. With 90 days of storage, the crystallinity was affected by plasticizer concentration and storage time; in unplasticized samples, the increase in crystallinity was higher than in plasticized ones during storage; thus, unplasticized stored samples became more brittle and less permeable during storage. Regardless of starch types, the tensile strength decreased, whereas the elongation at break improved with increasing the concentration of glycerol.

Therefore, in this current study, thermal and physicochemical properties correlated with mechanical properties were assessed to characterize the behavior of starch films containing different proportions of glycerin and/or sorbitol from 1.67 to 30% and stored at room temperature for 4 weeks. The novelty of the present paper consisted of providing critical insights into how varying concentrations of plasticizers can optimize the performance of starch films also how the storage time influence the properties of cornstarch films. Such research is very important for advancing the development of more effective and sustainable biodegradable packaging materials, aligning with current trends toward improving the functionality and environmental impact of food packaging.

2. Materials and Methods

2.1. Film Preparation

Food-grade cornstarch (20% amylose and 11% moisture) was bought from a local market (Romania). Acetic acid, sorbitol, and glycerol (analytical reagent) were purchased from Merck Millipore, Darmstadt, Germany.

Film preparation was adapted from N. Usman, et al. (2022) [31], with some modifications. Starch films were prepared by adding 10 g of cornstarch powder, 60 mL of distilled water, and 10 cm³ of 9% acetic acid into 100 cm³ beakers. After that, the two plasticizers, glycerol and sorbitol, were added to the solutions in percentages between 0 and 30% (*w/w*, compared to starch), and the reaction mixture was heated to boiling under continuous stirring for 10–15 min until it became homogeneous. Finally, the solutions mixtures were poured into Petri dishes and labeled from R1 to R10 based on the plasticizer category and concentration, as can be seen in Table 1. The films were kept at room temperature for 4 weeks before characterization and testing. Acetic acid was used for the hydrolysis of starch, facilitating the breakdown of branched amylopectin molecules into linear amylose molecules [32,33], thereby enhancing the solubility of starch [34]. In addition to its function as a hydrolyzing agent, acetic acid is recognized for its antibacterial effects [33].

Table 1. The content of the analyzed samples.

Abbreviation	Glycerol (%)	Sorbitol (%)
R1	5	0
R2	30	0
R3	0	5
R4	0	30
R5	2.5	2.5
R6	1.67	3.33
R7	3.33	1.67
R8	10	20
R9	20	10
R10	15	15

2.2. Physical Characteristics

2.2.1. FTIR Analysis

Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR), model Shimadzu IRTRACER-100, Kyoto, Japan, equipped with a QATR-10 single bounce—diamond extended range, controlled by LabSolution IR software version 2.27, was used to characterize the samples after four weeks of storage, in the region of 4000–400 cm^{-1} with a resolution setting of 4 cm^{-1} .

2.2.2. Film Swelling Degree

During the swelling process, the molecular chain structure of starch changes from tightly ordered to relatively loose and disordered, leading to the dissolution of starch molecules; therefore, the swelling test was performed [35]. The samples were weighed on the analytical balance, noting the initial mass (M_{Dry}). The samples were placed in the water bowl one at a time and left for 24 h. After this time, the samples were removed, blotted on filter paper, and then weighed. The mass after weighing was noted (M_{Swollen}).

The degree of swelling of polymers is calculated using the expression:

$$\text{Swelling degree (\%)} = (M_{\text{Swollen}} - M_{\text{Dry}}) / M_{\text{Dry}} \times 100 \quad (1)$$

where M_{Dry} = the initial mass of the polymer sample, and M_{Swollen} = mass of the sample after swelling.

2.2.3. Film Solubility in Water

This test was conducted according to the method of J. Tarique [14], with some modifications. This test was carried out in static mode. The samples were prepared and weighed on the analytical balance, noting the initial mass (W_i , gram). The samples were placed in the water dish, each in its own dish, and were left for 24 h. After this time, the samples were removed, placed on watch bottles and allowed to dry in an oven for 48 h at 105 °C, and then weighed. The mass after drying was noted (W_f , gram). The degree of solubility of polymers was calculated using the expression:

$$\text{Solubility (\%)} = [W_i - W_f] \times 100 / W_i \quad (2)$$

2.2.4. The Contact Angle

Angle measurements were carried out using dropping water method. Water droplet pictures were measured by the Image-J application version 1.54. The contact angle was photographed when the droplet contacted the starch film for 10 s.

2.2.5. Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of samples were studied using a thermogravimetric/derivative equipment TGA/DTG (TGA 2 Star System Mettler Toledo, Zurich, Switzerland). The method used for our study was to vary the temperature from 25 to 600 °C with 5 °C/min in a controlled nitrogen atmosphere. In order to study the temperature stability of the samples, 5 mg of each sample were taken and heated in the aluminum tray. TGA analysis illustrates this mass loss with temperature.

2.2.6. Thickness and Density

An electronic caliper (TESA-CAL IP6, Wetzlar, Germany) with an accuracy of ± 0.03 mm was used to measure the film thickness. The density of the films was determined directly from their volume (v) and weight (m), where the volume of each film was calculated from the result of the suggested film dimensions (10 mm $\times$ 10 mm) times the previously obtained thickness. Thus, the film density (ρ) was calculated using the following equation:

$$\rho = m / v \text{ (g/cm}^3\text{)}$$

2.2.7. Moisture Content (MC)

The total moisture content was determined according to the method used by M.I.J. Ibrahim [36]; namely, a known amount of film was kept in the oven at 105 °C for 24 h. The weight differences before heating (w_1) and after heating (w_2) were calculated for each sample; thus, the moisture content percentage was according to the relationship below:

$$MC\% = (w_1 - w_2)/w_1 \times 100$$

To study the influence of the storage conditions on the humidity of the film samples, samples with dimensions of 1 cm × 1 cm were left at room temperature and weighed after 3 and 7 days. The moisture content was calculated using the formula above.

2.2.8. Mechanical Properties

Due to the way of obtaining these types of materials, it is difficult to apply certain applicable standards and regulations: D882-18 [37]; ASTM D638-14 [38]; ISO 527-1:2019 [39].

The free plastic samples were tested using the Lloyd Instruments equipment with a maximum load of 2.5 tons, as shown in Figure 1. The analyzed materials (R1 ... R10) were tensile tested using a gripping grip displacement speed of 20 mm/min.

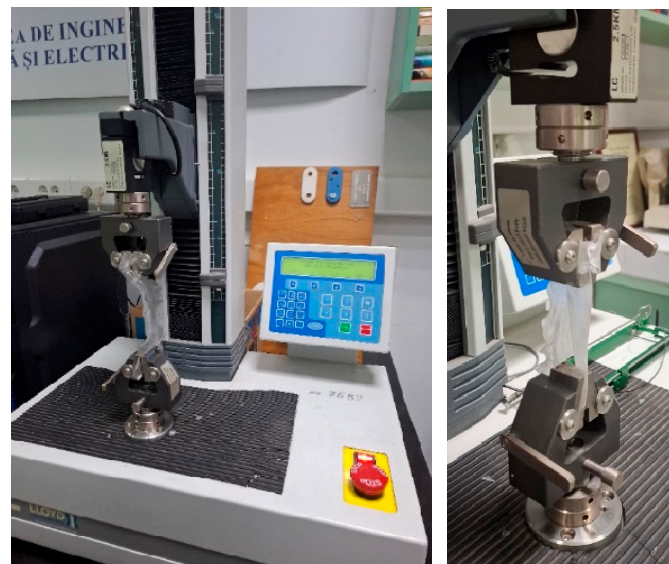


Figure 1. Tensile testing machine used for mechanical characteristic properties.

In this study, the evaluation of tensile strength was conducted to assess the mechanical properties of the samples. Tensile strength was selected as the primary parameter because it indicates the material's capacity to resist forces that attempt to pull it apart, which is essential for various practical applications where durability and flexibility are important. The samples were tested at two intervals—1 day and 4 weeks—to capture both the initial mechanical properties and any potential changes in strength over time due to environmental factors such as moisture uptake or loss. The goal was to understand how different concentrations of glycerol and sorbitol affect the long-term mechanical behavior of the samples, especially in terms of flexibility, brittleness, and overall durability. This methodology enabled the evaluation of the influence of plasticizers, such as glycerol and sorbitol, on the material's tensile strength over time. Additionally, it facilitated the identification of changes in mechanical properties, including both deterioration and improvement, particularly in samples that became too brittle to be tested.

3. Results and Discussion

3.1. FTIR Analysis

The FTIR spectra of the cornstarch films are presented in Figure 2. As can be seen, all the samples exhibited almost identical bands, mainly due to the vibrational modes of amylose and amylopectin from starch. The most significant differences were observed in the stretching regions of alcohols, possibly due to differences in content. The 3300–3200 cm^{-1} region was characteristic of the stretching vibrations of the hydroxyl groups (O-H). This was observed in all samples, but the shape changed depending on the amount of plasticizer added because both glycerin and sorbitol contained more hydroxyl groups. It can be observed in the case of the film with the highest amount of glycerin (30%), R2, and the highest amount of sorbitol (30%), R4. The results demonstrated that all films showed absorption peaks in the same regions, regardless of glycerin or sorbitol content; this indicates that the plasticizers have similar functional groups and are all classified as polyols [10]. The peaks at 2922 and 2852 cm^{-1} were characteristic of stretching vibrations of C-H bonds in methyl and methylene groups. These bands were more pronounced in the samples R2, R10, and R6 due to the high content of C-H bands from glycerol and/or sorbitol. The bands in the 1145–1074 cm^{-1} region corresponded to the stretching vibrations of the C-O bonds in starch and plasticizer structures. The peak at 1078 cm^{-1} indicated C-O-C stretching vibrations, specific to ether bonds in starch; meanwhile, the peak at 1145 cm^{-1} indicated the presence of C-OH stretching bands [24]. The bending vibrations of the C-H bonds in the cyclic rings of starch were present through the peaks at 756 cm^{-1} , and the bands at 1640 cm^{-1} were also distinct for the starch structure. Bending vibrations at 1640 cm^{-1} were associated with O-H groups [40]. The effect of water interactions with glycerol and/or sorbitol can be analyzed by comparing the spectra of starch powder to the spectra of starch films with 10–30% of glycerol and/or sorbitol. The peaks at 3600–3020 cm^{-1} shifted to a lower wavenumber after the addition of polyols, indicating that the interaction between polyols and starch was stronger than the interaction between starch itself, as shown by Chenyu Ma et al. [41].

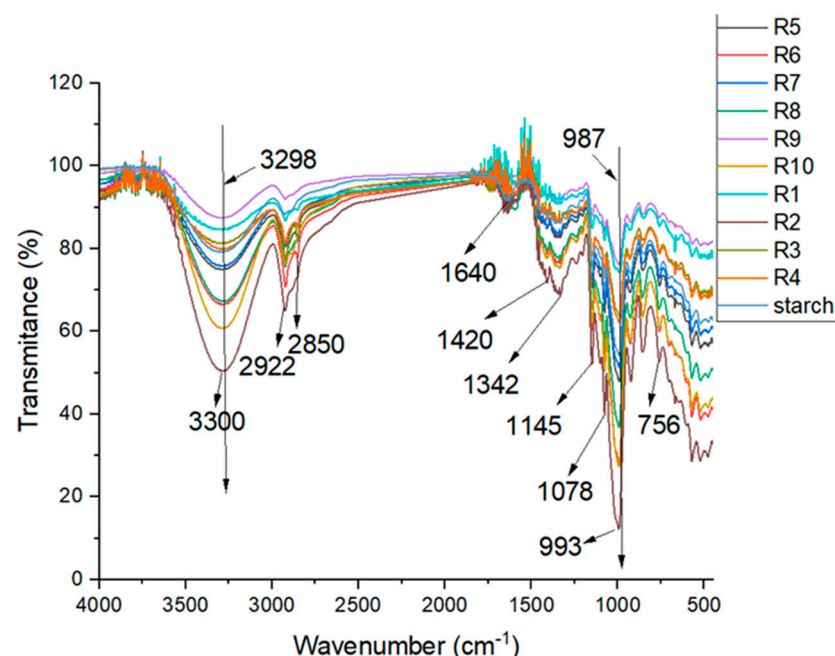


Figure 2. FTIR curves of starch films with various sorbitol/glycerol concentrations.

By adding glycerol to the starches, the band of O-H stretching reduced, so the films containing glycerol formed stronger hydrogen bonds with water [12]. The characteristic peak at 3298 cm^{-1} (affiliated to O-H bond) was shifted to 3300 cm^{-1} for the films comprised of 10–30% glycerol. These shifts indicated that the addition of glycerol promoted the hydrogen bonding interactions among starch and glycerol. Also, with the addition of

sorbitol, the increase in the number of methylene groups generated the shift of the peak from 2922 cm^{-1} to 2850 cm^{-1} in the samples with high sorbitol content. Thus, peaks at 987 cm^{-1} could be assigned to C-O stretching vibrations, and they were also shifted to 993 cm^{-1} (starch films with 30% of glycerol) peaks at 1045 cm^{-1} , which could be assigned to C-OH stretching bands were shifted to 1150 cm^{-1} (starch films with 30% of glycerol) [13].

3.2. Film Swelling Degree

Increased concentrations of plasticizer caused a change in the molecular network of the polymer, influencing the swelling capacity, as can be observed in Figure 3. For all films plasticized with sorbitol or glycerol in high concentrations, the degree of swelling decreased from 157.57% (R1) to 124.72% (R2) for glycerol and from 217.95% (R3) to 127.57% (R4) for sorbitol, maybe due to the formation of strong hydrogen bonds formed between the plasticizer molecules, which have hydroxyl groups and polyol structure of starch [14]. The same behavior was observed also for films that contained equal percentages of glycerol and sorbitol, with the swelling index decreasing from 208.91% (R5) to 117.00% (R10). The glycerol plasticized films (R1 and R2) had a lower swelling index compared with sorbitol ones (R3 and R4) because even though glycerol molecules are small, they show a high capacity to interact with starch chains, thus increasing molecular mobility and hydrophobicity [42].

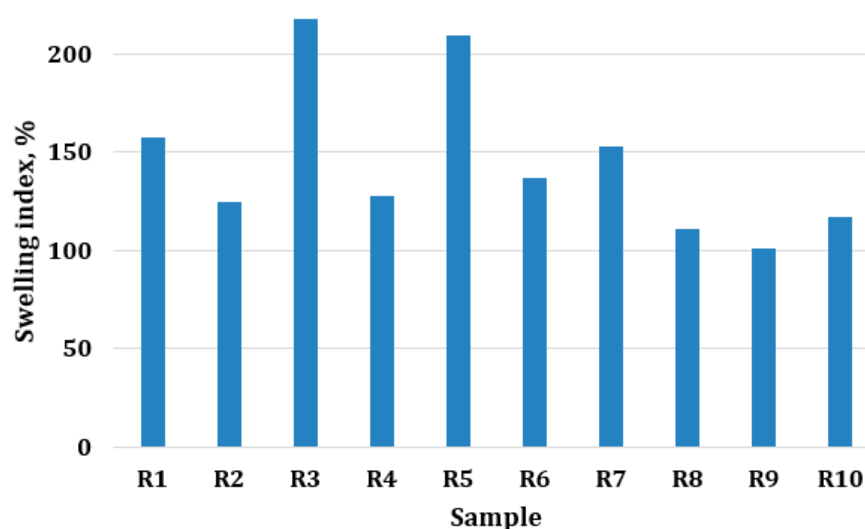


Figure 3. Film swelling index.

3.3. Film Solubility in Water

The main factors that determine the solubility of polymers are the flexibility of the chain, the average molecular weight, the chemical composition, the temperature, the crystalline structure, and the degree of crystallinity of the polymer [43]. From the data obtained and presented in Figure 4, we can understand that the presence of plasticizers in biopolymers significantly influences solubility. Thus, the sample containing only glycerin in proportions of 30% (R2) had a higher solubility than the sample containing only sorbitol in a percentage of 30% (R4). This behavior can be explained by the fact that sorbitol, having a higher molecular mass, is not completely integrated into the polymer matrix, being able to interact directly with water molecules, thus leading to the formation of voids in the matrix of the starch film and thus reducing its solubility in the water [44]. According to L. Ballesteros-Mártinez et al., 2020 [45], a plasticizer can decrease film solubility in water by increasing interactions between biopolymer chains in favor of plasticizer–polymer interactions. The samples containing a mixture of glycerol and sorbitol in percentages of 10–20% also showed high solubilities (R8, R9, R10).

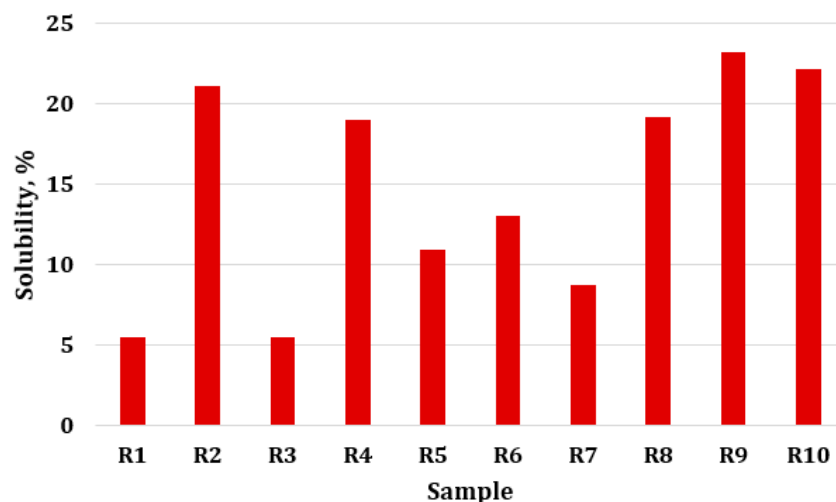


Figure 4. Film solubility in water.

3.4. Thermogravimetric Analysis (TGA)

The TGA analyses of the 10 samples are shown in Figure 5 and Table 2. Every sample exhibited three mass loss regions. The first stage of decomposition, recorded between 25 and 140 °C, can be attributed to the mass loss of bound water and acetic acid and varied between 1.47 and 6.37%. After four weeks of drying at room temperature, the lowest moisture content was observed for sample R4, with maximum sorbitol content, while the highest value of moisture was found for sample R5 with an equal content of glycerol and sorbitol, 2.5%, respectively. It is important to note that all the samples showed thermal stability in the region 140–260 °C. The second stage of thermal decomposition occurs in the temperature range 260–440 °C and was caused by the loss of glycerol, sorbitol, and starch. The highest mass losses were between 81.59 and 84.41% and were observed for films R4, R8, R9, and R10. The maximum degradation temperature varied with the increase of the glycerol and sorbitol content. Thus, for the film with 5% sorbitol (R3), the thermal decomposition occurred at 306.17 °C; meanwhile, for the film with 30% sorbitol (R4), the thermal decomposition occurred at 312.67 °C. The same trend was also observed for the samples containing glycerol. The thermal decomposition of film with 5% glycerol (R1) took place at 300 °C, and for the sample with 30% glycerol (R2), the thermal decomposition occurred at 305.67 °C. This can be attributed to the good interaction that occurred between the glycerol/sorbitol and the starch matrix, as evidenced by the FTIR spectra. This result is also supported by Tarique J. et al. [14] and N. Nordin et al. [46], who found that the onset decomposition temperature of plasticized starch films was higher compared to that of control film due to strong contact between the plasticizer and the starch matrix. It should be noted that the samples containing sorbitol (R3 and R4) had a maximum decomposition temperature up to 7 degrees higher than the samples containing only glycerol (R1 and R2), which may have been caused by the increase in the number of hydroxyl groups and the size molecular structure of the plasticizer which increased the intermolecular interaction with the starch. Samples R6 and R7 showed the same trend; namely, sample R7, which contained more sorbitol, had a maximum degradation temperature higher by 5.67 °C, increasing from 301.67 °C to 306 °C. The same behavior was also reported by A.A. Aydın and V. Ilberg [47].

The last degradation step associated with the mass residue varied between 2.30 and 3.75% over the temperature range 440–600 °C. The samples with low glycerol content (R1 and R5) had the highest amount of mass residue of 3.75% and 3.70%, respectively, while the lowest value of the ash content of 2.30% could be observed for sample R4, which contained a percentage of 30% sorbitol. This finding is probably explained by the plasticizer volatilization from the films, resulting in a lower mass residue [47].

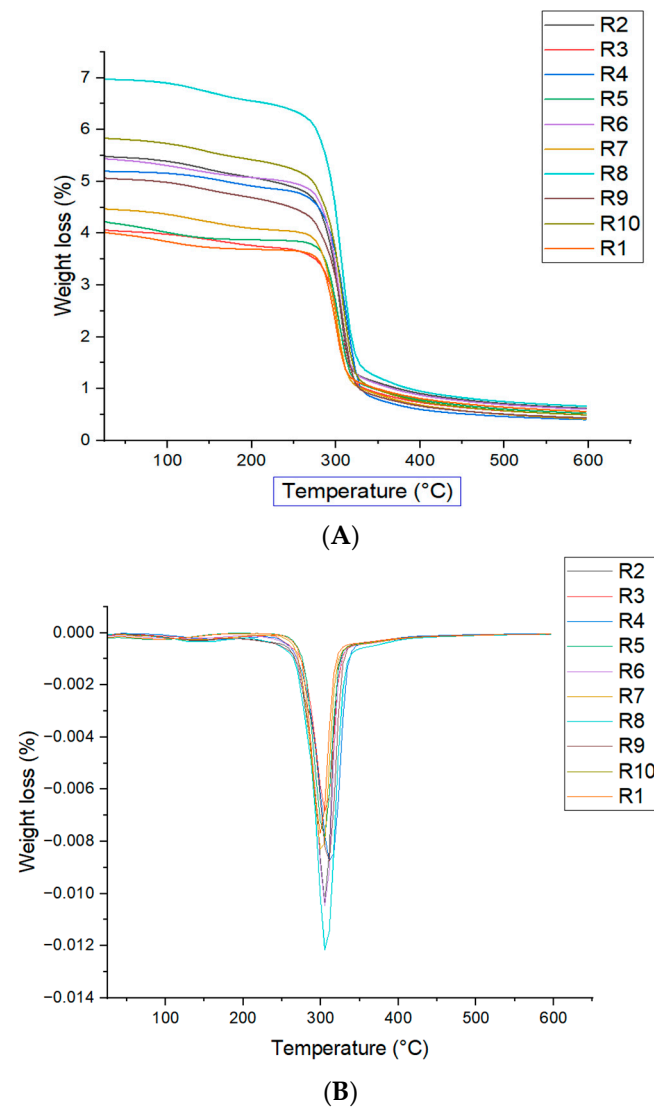


Figure 5. (A) Thermogravimetric analysis; (B) derivate thermogravimetric analysis thermograms.

Table 2. The results of the TGA analysis.

Abbreviation	First Stage of Decomposition (%)	Second Stage of Decomposition (%)	Mass Residue (%)	Td (°C)	T10 (°C)	T50 (°C)	T85 (°C)
R1	6.06	72.41	3.75	300	200	299	526
R2	3.36	77.61	2.94	305.67	229	299	428
R3	3.39	76.48	3.60	306.17	246	305	462
R4	1.47	84.41	2.30	312.67	264	310	351
R5	6.37	74.21	3.70	303.92	235	305	468
R6	3.65	78.86	3.02	306	258	305	421
R7	3.57	77.45	3.61	301.67	205	299	398
R8	2.56	81.59	2.52	306.25	252	305	375
R9	2.82	81.83	2.87	309.5	235	305	369
R10	2.59	82.08	2.71	307.92	246	305	369

The degradation temperatures for weight loss at 10%, 50% and 85% (T10%, T50%, and T85%) are presented in Table 2. An analysis of the degradation temperature at T10% suggests that the thermal stability was improved from 200 °C (R1) to 229 °C (R2) and from 229 °C (R3) to 264 °C (R4) as the percentage of plasticizer increased from 5% to 30%, regardless of the type of plasticizer added. A similar trend was observed for plasticizers' blends.

This can be attributed to the good interaction that occurred between the glycerol/sorbitol and the starch matrix. The highest value of 264 °C was obtained for R4 film which contained 30% sorbitol, maybe due to stronger molecular interactions with glucose units of sorbitol compared with glycerol (229 °C) [48]. On the other hand, the T10% temperature was not strongly influenced by the percentage of added plasticizer, exhibiting values around 300 °C for the films containing only glycerol (R1, R2). The cornstarch film containing only sorbitol or mixtures of sorbitol and glycerol had higher T10 temperatures, with approximately 5 °C (R5, R6, R8, R9, and R10) and 10 °C, respectively (R4), compared with films containing only glycerol (R1 and R2). At T85%, the thermal stability of samples was determined to decrease with the addition of glycerol from 526 °C (R1) to 427 °C (R2) and from 462 °C to 351 °C with the addition of sorbitol, respectively. The films which contained blends of plasticizers had degradation temperatures T85% between 369 °C (R9 and R10) and 468 °C (R5).

3.5. Water Contact Angle

The water contact angle is an important parameter for assessing the hydrophilicity or hydrophobicity of a film material. Thus, if the water contact angle exceeds 90°, the film material is considered hydrophobic, and if the contact angle is lower than 90°, the film is hydrophilic [2]. As shown in Figure 6, the contact angle for all the samples was below 90°, suggesting that the cornstarch-based films were hydrophilic regardless of the type and content of plasticizer. The samples containing glycerol presented lower contact angle values than those with sorbitol. The lowest value of the contact angle of 26.64° was determined for sample R2, which contained the largest amount of glycerin of 30%, followed by sample R9 with a value of 39.22°, which contained 20% glycerin and 10% sorbitol. Samples R3 and R4, which had a content of 5 and 30% sorbitol, respectively, had values of 57.46° and 53.1°, respectively, indicating a higher hydrophobicity. For the samples containing different percentages of glycerol and sorbitol, it was observed that the films with a higher content of glycerol (R7 and R9) had lower values (56.73° and 39.22°) compared with the samples R6 and R8, which contained more sorbitol (67.74° and 42.42°). It can be said that if the contact angle is lower, the degree of solubility is higher, which was also observed from the solubility studies (Table 3). These findings corroborate the studies carried out by Gao W. et al. (2021) [49] and Wang et al. (2022) [2], which also reported that the presence of glycerol in starch films enhanced the hydrophilicity of the films.

Table 3. The results of thickness and density.

Abbreviation	Thickness (cm)	Density (g/cm ³)
R1	0.091	1.195
R2	0.100	1.360
R3	0.103	1.389
R4	0.090	1.530
R5	0.096	1.425
R6	0.084	1.519
R7	0.103	1.533
R8	0.145	1.316
R9	0.206	1.198
R10	0.248	0.925

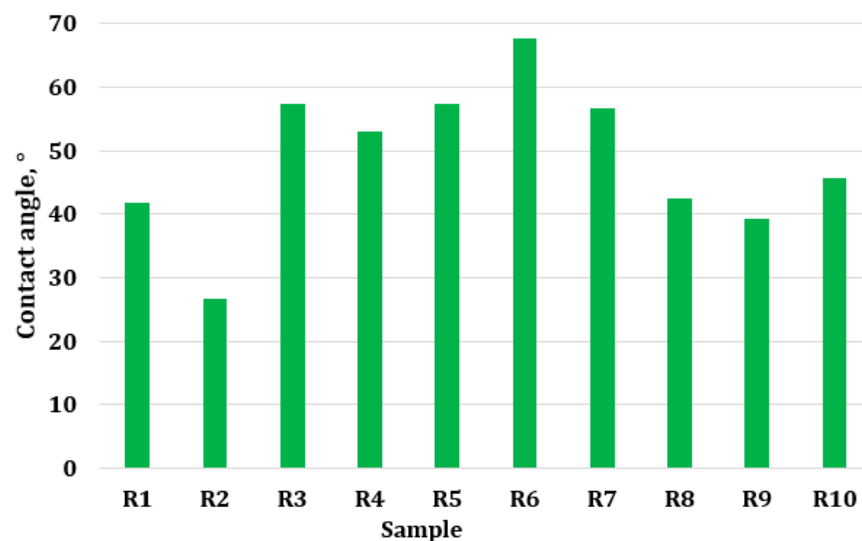


Figure 6. Contact angle results.

3.6. Thickness and Density

It can be seen from the data presented in the table below that the samples with a mixture of plasticizers between 10 and 20% glycerol and between 10 and 20% sorbitol (R8, R9, and R10) were thicker than those that contained only sorbitol and glycerol, respectively (R2 and R4).

This trend indicates that the mixture input of relatively high concentrations of sorbitol and glycerol generates more spaces, resulting in thickening of the film thickness. Regarding the density of the film, it was observed that it increased as the amount of glycerol increased, from 1.195 g/cm³ (R1) to 1.360 g/cm³ (R2), respectively, as the amount of sorbitol increased from 1.389 g/cm³ (R3) to 1.530 g/cm³ (R4). However, the addition of high concentrations of glycerol and sorbitol to the mixture led to a decrease in the density of the film (R8, R9, R10), so as the thickness of the film increased, its density decreased.

3.7. Moisture Content (MC)

Water can be used as an effective plasticizer for starch-based packing materials due to starch's hydrophilic nature [2]. The amount of water absorbed by the film is significantly influenced by the molecular size of plasticizers, particularly when considering the number of hydroxyl groups contained. In general, a decreased polyol molecular weight leads to an increase in the starch-based film's moisture content [44]. As shown in Figure 7, the moisture content increased as glycerol concentration increased from 5 to 30% and from 85.17 to 87.21% for R1 and R2, respectively. According to Sothornvit and Krochta (2001) [50] and A. Farahnaky, B. Saberi and M. Majzoobi (2013) [51], the observed results could be attributed to the hydrophilicity of glycerol, due to its hydroxyl groups that can interact with water through hydrogen bonding. Glycerol molecules are small and possess a significant capacity to interact with starch chains, thereby increasing molecular mobility and enhancing free volume within the film network. Furthermore, glycerol's more hydrophilic nature, in combination with these effects, contributes to the higher water affinity of glycerol films [51]. Similar findings have been reported in several studies [10,51,52]. Cornstarch films (R3 and R4) that have been plasticized with sorbitol exhibited constant moisture content around 84% as the plasticizer concentration rose. DJ Prasetyo et al. (2017) [53] and Awol A.M. et al. (2022) [42] explained the trend by the similarity of the molecular structure of glucose units with sorbitol and by the fact that sorbitol contains more hydroxyl groups than glycerol, thus causing stronger molecular interactions with glucose units compared with glycerol. As a result, sorbitol has fewer hydroxyl groups accessible to interact with water molecules, and therefore less moisture content than films plasticized with glycerol. This outcome correlates with the results [10,48]. The samples containing both plasticizers follow the same

trend, namely the samples with higher glycerin content (R7 and R9), had a slightly higher moisture content than the samples containing more sorbitol (R6 and R8). However, the differences were very small.

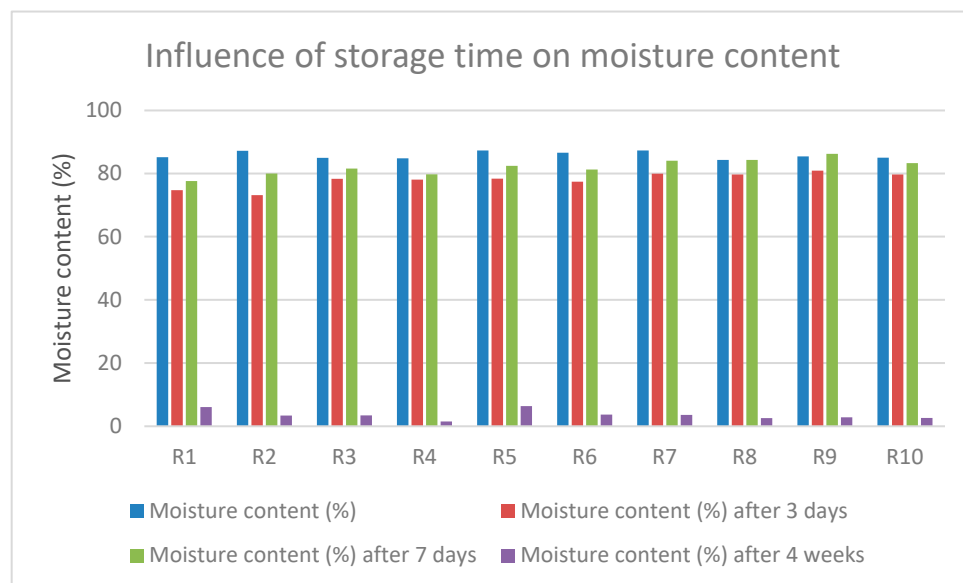


Figure 7. Influence of storage time on moisture content.

The variation in water content in the film during storage can indirectly influence its barrier and mechanical properties. The water content decreased considerably from 0 to 4 weeks, probably due to the migration of plasticizers during storage, resulting in a decrease of the film's water holding ability [54]. After 3 days, under the storage conditions of room temperature and humidity, the moisture content decreased for all samples with percentages between 4.51 for R9 to 14.05 for R2. However, after 7 days, the moisture content of the films that contained 5 and 30% glycerol (R1, R2) increased with 2.91 and 6.85% respectively. The overall increasing trend was observed also for biofilms that contains high glycerol percents compared with sorbitol (R7 and R9), with values of 4.1 and 5.32%, respectively. This phenomenon was related to the hygroscopic characteristic of glycerol [55]. The plasticized films with only sorbitol (R4) or higher content in sorbitol (R8) exhibited low increments of moisture content, with values of 1.66% for R4 up to 4.64% for R8, probably caused by stronger molecular interactions between the sorbitol and the intermolecular polymer chains. Thus, the probability of sorbitol interacting with water molecules was decreased [56]. The moisture content after 4 weeks was very low, with values ranging from 1.47 (R4) to 6.06 (R1). This suggests that the storage environment had a stronger influence on the water content of the film, thus limiting its practical application [54].

3.8. Mechanical Testing

The results of tensile testing are shown in Table 4. After the realization of the biofilms, the samples were stored at room temperature for 2 weeks, in order to study the influence of the temperature and humidity conditions. It can be seen that R2 (30% glycerol and 0% sorbitol) showed the lowest tensile strength (45.8 N), indicating that a higher concentration of glycerol reduced the film's tensile strength. Glycerol acts as a plasticizer, making the film more flexible but less strong, which likely explains this result. In contrast, R8 (10% glycerol and 20% sorbitol) had higher tensile strength (58.9 N) than R2, suggesting that sorbitol might provide better mechanical strength compared to glycerol when used in high concentrations. R10 (15% glycerol, 15% sorbitol) showed the highest tensile strength (76.5 N), indicating that a balanced combination of both plasticizers can lead to optimal mechanical properties. This suggests that both plasticizers work synergistically when

used in equal concentrations, enhancing the film's strength while maintaining flexibility. Similarly, the results of the work [15] showed that the use of glycerol and sorbitol as plasticizers similarly reduced the intramolecular affinity within the starch matrix by forming new hydrogen bonds with the plasticizers. This interaction increased the flexibility of the biofilms and helped prevent breakage. This aligns with findings from Laohakunjit and Noomhorm [57], who observed that glycerol and sorbitol impacted the mechanical properties of rice starch films differently. Specifically, glycerol resulted in lower tensile strength compared to sorbitol but provided greater elongation, highlighting the trade-off between flexibility and strength depending on the plasticizer used.

Table 4. Tensile testing results.

Probe Number	R1	R2	R3	R4	R5	R6	R7	R8	R9	R10
Max. force	1 day	*	43.5 N			49.1 N	28.7 N	68.3 N	58.4 N	88.5 N
		*	/	*	*	/	/	/	/	/
			4.43 kg			5 kg	6.96 kg	6.96	5.89 kg	9.02 kg
	14 days	*	45.8 N				65.8 N	58.9 N	73.1 N	76.5 N
			/	*	*	*	/	/	/	/
			4.67 kg				6.70 kg	6.00 kg	7.45 kg	7.80 kg

* Samples became brittle, and the tensile test could not be performed.

The variations in tensile strength reflect the effect of glycerol and sorbitol concentrations on the mechanical properties of the samples. The R2 sample (30% glycerol, 0% sorbitol) showed a slight increase in maximum force from 43.5 N to 45.8 N after 14 days, indicating minimal degradation or moisture uptake. The R7 sample showed a substantial increase in maximum force from 28.7 N (1 day) to 65.8 N (14 days), indicating a significant improvement in mechanical strength over time, likely due to better interaction between glycerol and sorbitol. R8 and R10 show a notable reduction in strength, while the R9 sample's strength increased from 58.4 N to 73.1 N, showing that this combination of glycerol and sorbitol enhanced the material's strength over time.

R1, R3, R4, and R6 became brittle both after 1 day and 14 days, preventing tensile testing. This brittleness indicates that these samples lacked sufficient plasticizers (glycerol or sorbitol), causing them to lose flexibility and become too rigid for tensile testing.

4. Conclusions

In this study, we investigated the influence of glycerol and sorbitol as plasticizers on the thermal and mechanical properties of cornstarch-based films, demonstrating their effectiveness in enhancing the mechanical properties of starch-based biodegradable films. The findings highlight that the choice of plasticizer, its concentration, and storage time are very important in determining the final properties of the film. Glycerol-plasticized films showed higher flexibility and solubility in water, making them suitable for applications where flexibility is important. On the other hand, films with sorbitol exhibited improved thermal stability, which is advantageous for applications requiring higher temperature resistance.

A notable outcome of the research is the identified trade-off between mechanical properties and thermal stability when selecting plasticizers. While glycerol enhances flexibility, it tends to reduce the thermal stability of the films. On the other hand, sorbitol, though less effective at increasing flexibility, improves thermal resistance. This trade-off is significant and should be carefully considered during the design phase of films for specific applications, particularly in contexts where both properties are critical.

The developed starch-based films, especially those plasticized with glycerol or sorbitol, show promising potential for use in sustainable food packaging. Their biodegradability, coupled with customized mechanical and thermal properties, positions them as suitable candidates for replacing conventional petroleum-based plastics in certain packaging applications. This potential aligns with the growing demand for environmentally friendly

materials that can help reduce the reliance on non-renewable resources and decrease plastic waste.

Looking ahead, further research is needed to optimize the balance between mechanical and thermal properties by exploring different ratios of glycerol and sorbitol. Additionally, studies on the long-term biodegradability and performance of these films in real-world conditions will be essential to confirm their effectiveness and reliability as sustainable packaging materials.

Author Contributions: Conceptualization, E.-E.S. and C.C.; methodology, E.-E.S., A.-I.P., A.D., M.T., C.C., A.B. and C.-E.E.; software, E.-E.S. and C.C.; validation, E.-E.S. and C.C.; formal analysis, A.D.; investigation, E.-E.S., A.-I.P., A.D., M.T., C.C. and A.B.; resources, C.-E.E., E.-E.S., A.-I.P., A.D., M.T., C.C. and A.B.; data curation, E.-E.S., A.-I.P., A.D., M.T., C.C. and A.B.; writing—E.-E.S., A.-I.P., A.D., M.T., C.C. and A.B.; writing—review and editing E.-E.S., A.-I.P., A.D., M.T., C.C. and A.B.; visualization, E.-E.S. and C.C.; supervision, E.-E.S. and C.C.; project administration, E.-E.S. and C.C.; funding acquisition, E.-E.S. and C.-E.E. All authors have read and agreed to the published version of the manuscript.

Funding: This work was carried out through the PN 23.06 Core Program—ChemNewDeal within the National Plan for Research, Development, and Innovation 2022–2027, developed with the support of the Ministry of Research, Innovation, and Digitization, project no. PN 23.06.01.01 (AQUAMAT).

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

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