

Article

Rice Bran Valorization through the Fabrication of Nanofibrous Membranes by Electrospinning

María Alonso-González ^{1,2,*} , Manuel Felix ^{2,*}  and Alberto Romero ¹ 

¹ Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, 41012 Sevilla, Spain; alromero@us.es

² Departamento de Ingeniería Química, Escuela Politécnica Superior, Universidad de Sevilla, 41011 Sevilla, Spain

* Correspondence: maralonso@us.es (M.A.-G.); mfelix@us.es (M.F.); Tel.: +34-954557179 (M.F.)

Abstract: The high production rate of fossil-based plastics, coupled with their accumulation and low degradability, is causing severe environmental problems. As a result, there is a growing interest in the use of renewable and natural sources in the polymer industry. Specifically, rice bran is a highly abundant by-product of the agro-food industry, with variable amounts of protein and starch within its composition, which are usually employed for bioplastic development. This study aims to valorize rice bran through the production of nanofiber membranes processed via electrospinning. Due to its low solubility, the co-electrospinning processing of rice bran with potato starch, known for its ability to form nanofibers through this technique, was chosen. Several fiber membranes were fabricated with modifications in solution conditions and electrospinning parameters to analyze their effects on the synthesized fiber morphology. This analysis involved obtaining micrographs of the fibers through scanning electron microscopy (SEM) and fiber diameter analysis. Potato starch membranes were initially investigated, and once optimal electrospinning conditions were identified, the co-electrospinning of rice bran and potato starch was conducted. Attempts were made to correlate the physical properties of the solutions, such as conductivity and density, with the characteristics of the resulting electrospun fibers. The results presented in this study demonstrate the potential valorization of a rice by-product for the development of bio-based nanofibrous membranes. This not only offers a solution to combat current plastic waste accumulation but also opens up a wide range of applications from filtration to biomedical devices (i.e., in tissue engineering).

Keywords: rice bran; electrospinning; co-electrospinning; potato starch; membranes



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1. Introduction

Electrospinning is a processing technique that allows the fabrication of polymer nanofibers using electrical forces, which has gained significant importance in recent years due to its versatility and potential applications in various fields. It stands out for being a highly efficient, simple, and non-expensive technique that has become increasingly relevant for multiple researchers, given the scientific importance of obtaining fiber diameters in the order of tens and a few hundreds of nanometers [1–3]. These fibers exhibit excellent characteristics, such as a very large surface-to-volume ratio (up to 1000 times larger than microfibers with diameters in the micrometer range) and superior mechanical properties like tensile strength and rigidity [4].

The electrospinning process is influenced by various parameters broadly categorized into the following three groups: (a) compositional parameters, including polymer concentration in the solution, density, conductivity, viscosity, pH, molecular weight and surface tension; (b) process parameters, including hydrostatic pressure in the capillary tube, applied electrical potential between the capillary tube tip and the metal collector, needle-to-collector distance, flow rate and collector type; and (c) environmental parameters, such as temperature, humidity and airspeed in the electrospinning chamber [5]. Each of these parameters

affects the morphology of the electrospun nanofibers, and appropriate adjustment can lead to the desired fiber morphology and diameter [6,7].

Different polymers, both synthetic and natural, have been electrospun using this technique [8,9]. Synthetic polymers exhibit better mechanical properties and adjustable degradation rates [10]. Some examples of synthetic polymers that have been electrospun to form biodegradable nanofiber membranes include polyglycolic acid (PGA), polylactic acid (PLA), and polycaprolactone (PCL). Examples of electrospun nanofibers from natural polymers include collagen, starch, chitosan, gelatin, cellulose acetate, silk proteins, fibrinogen, chitin, and hyaluronic acid, among others [11–13].

Starch is an abundant, versatile, biodegradable, and cost-effective resource. It consists of two distinct glucose polymers: amylose and amylopectin. Potato starch, with an intermediate amylose content (25–30%) compared to other types of starch, has been electrospun successfully using a 40% concentration in formic acid, resulting in a morphology with beads and an average diameter in the range of 128–143 nm [3]. Additionally, the use of by-products rich in biopolymers like proteins and starch in electrospinning opens avenues for creating high-added value membranes. These membranes hold promise for diverse applications, including biomedical uses, water capture, and the filtration of water or air, offering innovative solutions to pressing environmental and healthcare challenges [14–16].

In this way, rice bran contains significant amounts of both starch and proteins (around 20% and 15%, respectively). It constitutes the outer layer of the rice grain, which is removed during refining for consumption. Although rice bran makes up approximately one-tenth of the weight of rice, the most cultivated cereal globally, it remains underutilized. Utilizing these by-products as raw materials for membrane production not only reduces waste from the agro-food industry, which currently lacks a significant valorization pathway but also decreases the production of plastics from fossil resources [17]. Nevertheless, electrospinning by-products can pose a challenge due to their complex composition. One effective approach to address this issue is through co-electrospinning using a biopolymer capable of forming membranes via this technique. The co-electrospinning of different polymers presents a versatile approach, offering advantages such as enhanced mechanical properties, variable porosity, and improved functionality. This technique addresses challenges encountered when electrospinning certain polymers individually while also enabling the creation of novel composite materials with tailored properties for various applications.

The first step in the electrospinning process is polymer dissolution in a suitable solvent with specific properties. The choice of an appropriate polymer–solvent system is crucial for successful fiber electrospinning. Common electrospinning solvents include acetone, acetic acid, formic acid (FA), ethanol, chloroform, dimethylformamide (DMF) and water. Formic acid is the strongest unsubstituted fatty acid, approximately ten times stronger than acetic acid [18]. Under atmospheric conditions, it is a highly volatile, colorless liquid with strong corrosive properties, releasing gases that can be toxic if inhaled [19]. These properties make it ideal for dissolving polymers and evaporating during the electrospinning process, thereby producing polymeric fibers.

The excellent characteristics of nanofibers obtained through electrospinning make them ideal for various applications, such as filtration, biosensors, protective coatings, and biomedicine. Electrospun nanofibers are found to be extensively used in biomedical applications, especially as scaffolds for tissue engineering. Additionally, they are employed in wound healing, localized drug delivery, filters, enzyme immobilization, small-diameter vascular graft implants, healthcare, biotechnology, environmental engineering, energy storage, and generation, among other ongoing research areas [20–22].

The objective of this work is to valorize rice bran by producing nanofibers using the electrospinning technique. This involves selecting an appropriate biopolymer, such as potato starch, for co-electrospinning with rice bran, choosing a suitable solvent, determining dissolution conditions, and selecting electrospinning conditions. Scanning electron microscopy (SEM) has been employed to study systems with variations in both solution

preparation and processing parameters. The goal is to identify a combination of parameters that yield more uniform, smaller-diameter fibers without defects.

2. Materials and Methods

2.1. Materials

The rice bran was supplied by Herba Ingredients (San José de la Rinconada, Seville, Spain). It is a by-product of the production process of a rice variety called ‘indica’, subjected to a steam treatment. The rice bran was defatted following the procedure established by Alonso-González et al. [23], resulting in a raw material with 15.9% water content, 13.4% ashes, 1.8% lipids, 16.8% proteins, 27.9% fiber, and 24.2% starch. The chemical composition was evaluated following the A.O.A.C. methods [24]. Soluble commercial potato starch with a molar mass of 162.15 g/mol was provided by PanReac AppliChem, ITW Reagents (Barcelona, Spain), and the solvents used were distilled water (W), formic acid (FA), dimethyl sulfoxide (DMSO), and hexafluoroisopropanol (HFIP).

2.2. Preparation of Solutions

2.2.1. Rice Bran Solutions

Firstly, rice bran solutions were prepared using different solvents and concentrations. The procedure is always the same: the desired amount of solute (in this case, rice bran) is mixed with the solvent by magnetic agitation at 450 rpm at the selected temperature. Once the dissolution is complete, it is allowed to cool at room temperature, and the solution is then ready for electrospinning. Due to the limited solubility of rice bran, it is not completely dissolved. Therefore, certain systems underwent centrifugation at 5000 rpm and 25 °C using a 3-18KS refrigerated centrifuge (Sigma, Steinheim, Germany). Undissolved rice bran was discarded, and the supernatant, composed of the dissolved fraction of rice bran, was collected to evaluate its concentration by subtracting the initial mass of rice bran and the undissolved mass. For this purpose, the undissolved bran was collected and dehydrated in a conventional oven (Memmert B216.1126, Schwabach, Germany) for 24 h at 105 °C. Once the sample was dry, it was weighed, and the mass of undissolved rice bran was calculated. The volume of the supernatant solution was measured after centrifugation, as some of the volume was absorbed by the undissolved rice bran and removed in the oven. The mixing time (t_d) was fixed to 30 min, and the mixing temperature (T) was always between 25 and 80 °C depending on the solution.

In an attempt to improve the solubility of rice bran, some systems were processed at 80 °C for 1 h and 200 rpm in the Haake PolyLab QC mixing rheometer (Thermo Fisher Scientific, Waltham, MA, USA) prior to its solution, as it is known that starch granules break under these conditions [25]. Subsequently, the mass of rice bran obtained after processing in the rheometer is dissolved, and centrifugation is carried out, as explained earlier. The mixing time was maintained at 30 min.

2.2.2. Potato Starch Solutions

Potato starch solutions were prepared in different solvents following the procedure explained earlier. The various solutions produced did not present solubility issues. Therefore, there is no need for centrifugation.

2.2.3. Rice Bran/Potato Starch Solutions

The final systems involve dissolving both potato starch and rice bran in formic acid. To achieve this, rice bran was first dissolved, without prior processing, in the mixing rheometer in FA at 70 °C for 1 h. Due to the low solubility of rice bran, only a portion of the initially added amount was dissolved, so the solutions were centrifuged, and the concentration of the obtained supernatant was calculated. Subsequently, FA and potato starch were added to reach the desired concentrations, and they were mixed for 30 min at 70 °C. The ratios of rice bran/potato starch in formic acid were 5/45% w/v and 10/40% w/v .

2.3. Solution Characterization

The prepared solutions were characterized by density measurements at room temperature using the Densito 30P densimeter (Mettler Toledo, Columbus, OH, USA) and electrical conductivity measurements using the EC-Meter BASIC 30+ equipment (Crisson Instruments, Barcelona, Spain) to correlate solution characteristics with membrane microstructure.

2.4. Electrospinning

The electrospinning equipment Fluidnatek LE-50 (Bioinicia, Valencia, Spain) was employed with a horizontal setup for membrane production. For each prepared solution, electrospun nanofibers were manufactured on the collector for 30 min/1 h. Numerous tests were conducted, varying the processing parameters, always favoring the formation of the Taylor cone. In this way, the evaluated parameters were the needle-to-collector distance ($d = 6, 9$, and 12 cm), the potential difference ($V = 14, 18$, and 22 kV), and the flow rate ($Q = 0.05, 0.1, 0.2, 0.3$, and 0.4 mL/h).

The environmental conditions in the electrospinning equipment were fixed at $25\text{ }^{\circ}\text{C}$ and $25 \pm 5\%$ humidity. These environmental parameters have been used in previous tests with formic acid and potato starch [3].

2.5. Membrane Characterization

The microstructure of the membranes is studied by scanning electron microscopy using the Zeiss EVO device (Carl Zeiss Microscopy, White Plains, NY, USA) to establish a relationship between processing parameters and the membrane structure. Firstly, the samples were coated with Pd/Au (13 nm) by sputtering using the Leica AC600 metallizer, and then they were observed at an acceleration voltage of 10 kV and magnifications of $\times 500$, $\times 1000$, and $\times 2000$. Images obtained with SEM were analyzed using the Image J software v1.54i, a Java-based digital image processing program developed at the National Institutes of Health. The average diameter, as well as its standard deviation, was measured using at least 100 measurements for each sample.

2.6. Statistical Analyses

At least 100 replicate measurements were taken. Statistical analyses were carried out with t -tests and one-way analyses of variance (ANOVA) ($p < 0.05$) using STATGRAPHICS 18 software (Statgraphics Technologies, Inc., The Plains, VA, USA). Some selected parameters are shown along with their standard deviations and coefficient of variation (CV), and different letters were added to indicate significant differences in certain parameters.

3. Results and Discussion

3.1. Rice Bran Membranes

The rice bran solutions prepared in different solvents and conditions highlighted the insolubility of the rice bran. A turbid solution was formed, which was centrifuged (CS) in some cases to work with the supernatant, although some tests were also conducted without centrifugation. For this reason, the maximum concentration achieved was 20% w/v , as higher concentrations resulted in very thick masses that hindered centrifugation, yielding limited supernatant. Furthermore, electrospinning parameters such as the flow rate, the voltage, and the needle-to-collector distance were varied, always favoring the formation of the Taylor cone. The solution and electrospinning conditions for the different electrospun tests are shown in Table S1.

Figure 1 is representative of the images obtained by SEM, revealing that the material was deposited in granules with no fibers in any of the systems due to the complex composition and limited solubility of the different phases. Furthermore, it seems that the solvent did not fully evaporate, resulting in the formation of a continuous film.

As indicated before, the solubility of the rice bran was also evaluated after processing the material in the mixer rheometer to destroy the granular structure of the starch granules [26]. Once again, different systems were obtained by varying the solution and elec-

trospinning conditions, as reflected in Table S2. Despite processing in the mixing rheometer, all of these solutions also encountered solubility issues, so once again, low concentrations were selected, and the systems were subjected to centrifugation.

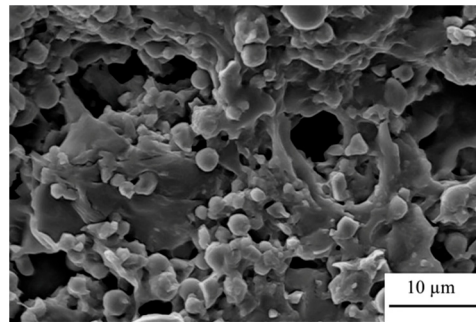


Figure 1. SEM micrograph ($\times 2000$) of the system obtained from the 20% *w/v* solution in DMSO mixed at 80 °C for 30 min without centrifugation. The electrospinning parameters were 18 kV, 12 cm, and 0.4 mL/h.

During the electrospinning process, the solutions were processed discontinuously, and the images obtained by SEM once again reflected the absence of fibers, as can be observed in Figure 2.

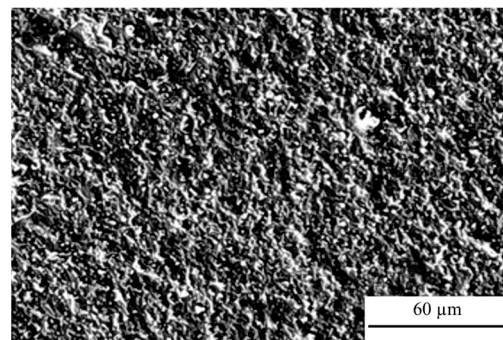


Figure 2. SEM micrograph ($\times 500$) of the system obtained from the 20% *w/v* solution of rice bran processed in the rheometer mixer in DMSO/W (1:1) mixed at 70 °C for 30 min and centrifuged. The electrospinning parameters were 22 kV, 12 cm, and 0.2 mL/h.

These issues in the processed membranes may be attributed to the fact that rice bran is a highly complex material consisting of proteins, starch, fibers, ashes, etc., whose interactions are not entirely known and could be hindering fiber formation during electrospinning. Due to the processing challenges and the absence of fibers, the following alternative approach was chosen: the co-electrospinning of rice bran and potato starch, which is able to produce fibers on its own as it has previously been used for the production of ultrafine fibers with diameters in the range of 128 to 143 nm [3]. Once this method is established, potato starch electrospun membranes are first developed under different conditions, and then, the co-electrospinning of rice bran/potato starch solutions is carried out. In this way, the aim is to select conditions that yield homogeneous membranes with fine and uniform fibers.

3.2. Optimization of Potato Starch Membranes

3.2.1. Effects of the Solvent

The potato starch solution began by using different solvents as follows: water, a mixture of FA and water (3:1), and FA. These solvents were selected based on their previous use in other studies [3]. The concentration of potato starch within each solvent was selected based on the solubility limit. The solution of 50% *w/v* potato starch in FA was complete, with no need for centrifugation. The flow rate was maintained at 0.2 mL/h. Table 1

shows the different solution conditions and electrospinning parameters for the initial tests conducted with potato starch. The mixing time ranged from 30 to 50 min until complete dissolution was achieved, and the temperature varied between 70 and 80 °C, which is a range known to favor gelatinization [27]. The electrospinning parameters were selected to promote the formation of the Taylor cone. Figure 3 shows the micrographs obtained by scanning electron microscopy for the different systems.

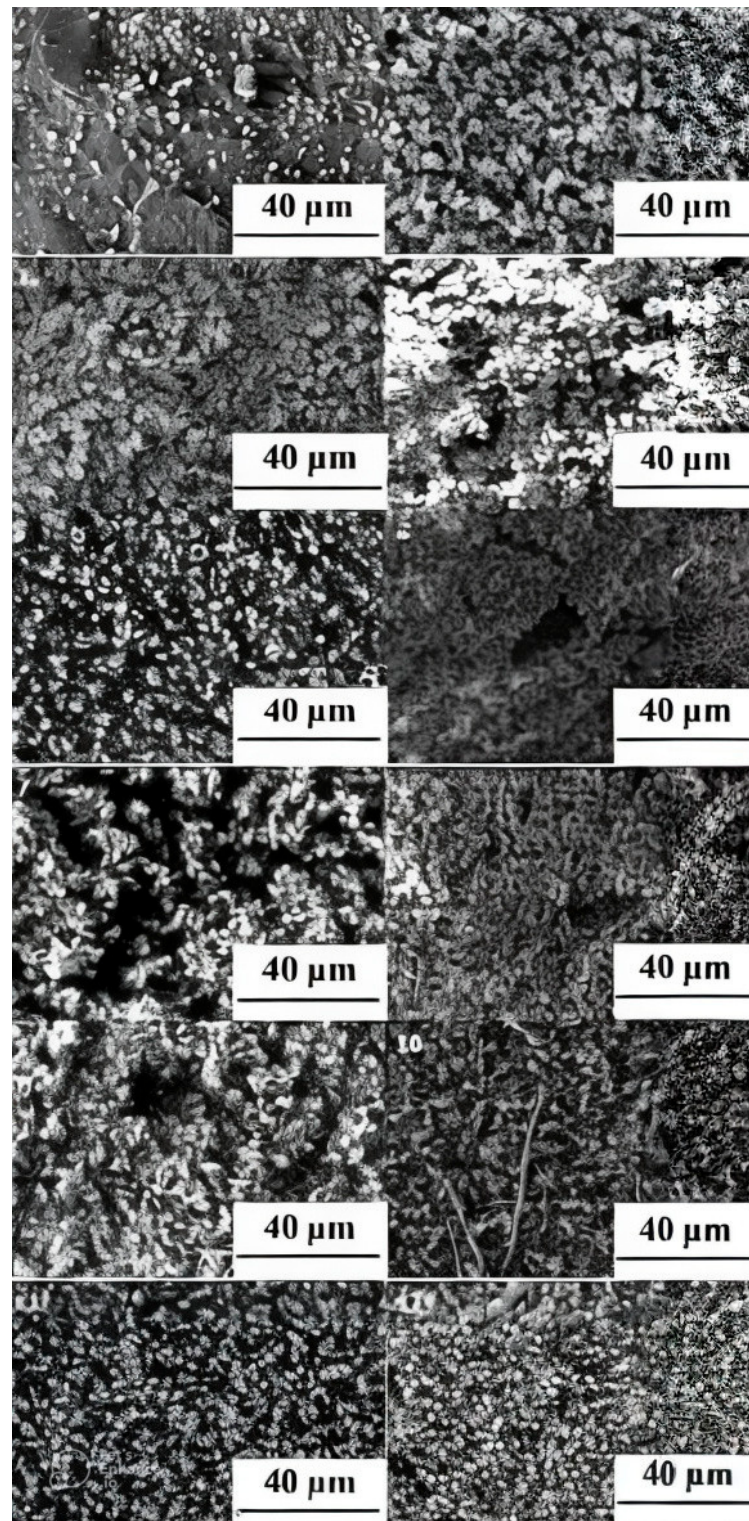


Figure 3. SEM micrographs ($\times 1000$) of the different potato starch systems defined in Table 1.

Table 1. Solution conditions and electrospinning parameters selected for potato starch systems. During electrospinning, the temperature was 25 °C and the humidity was 25 ± 5%.

System	Solution Conditions				Electrospinning Parameters	
	Solvent	t_d (min)	T (°C)	Concentration (% w/v)	V (kV)	d (cm)
1	W	30	70	30	18	6
2	FA/W (3:1)	50	80	40	18	6
3					18	9
4					18	12
5					18	9
6	FA	50	80	30	18	9
7				40	14	9
8					18	9
9					22	9
10				50	18	6
11					18	9
12					18	12

Despite connecting some nodules, the presence of fibers was observed for the first time in the 40% w/v starch solution in FA/W (3:1) mixed at 70 °C (system 5) and in the 50% w/v starch solution in FA mixed at 80 °C, specifically in systems 10 and 11. Consequently, FA was selected as the solvent for the subsequent systems to simplify the solution process using a single solvent instead of a mixture. Furthermore, it seemed that both 70 and 80 °C were suitable mixing temperatures for the gelatinization of potato starch in FA, as confirmed in previous studies [27]. In this way, 70 °C was set as the solution temperature to minimize energy consumption after corroborating its suitability. As mentioned earlier, the concentration will not exceed 50% w/v to avoid solubility issues. It was observed that within 30 min, complete dissolution was achieved, so the mixing time was fixed at 30 min for the following tests.

3.2.2. Effects of Potato Starch Concentration

The next step was the evaluation of the effects of polymer concentration, in this case, potato starch, on the electrospun membranes. To conduct this, the systems gathered in Table 2 were analyzed. The results from conductivity and density measurements for the different solutions used, as well as measurements of the average diameter of the fibers ($\bar{d}_f$), their standard deviation (σ), and their coefficient of variation (CV), are also included in Table 2.

An increase in solution density was observed with a higher starch concentration. In the same way, conductivity values increased with the concentration because, as the solution concentration increased, the number of electric charges also did [28,29]. In Figure 4, SEM images corresponding to systems 13–18 are displayed.

To begin with, the 30% w/v solution did not lead to the formation of fibers for any of the distances evaluated (6 or 9 cm); instead, the material deposits were in the form of granules. On the contrary, both the 40 and 50% w/v solutions produced fibers with varying mean diameters depending on the distance employed, although they formed a more homogeneous membrane with fewer nodules for the 50% w/v solution. Thus, the concentration of 50% w/v potato starch in FA seemed to be more suitable for the formation of electrospun fibers. In the study by Jun et al. [30], it was also found that the fiber diameter increased with the polymer concentration using a PLA solution.

Table 2. Solution conditions, electrospinning parameters, solution characteristics, and fiber diameter for potato starch systems. The solvent was FA, and dissolution was carried out at 70 °C for 30 min. During electrospinning, the temperature was 25 °C, and the humidity was $25 \pm 5\%$. The flow rate was fixed at 0.2 mL/h.

System	C (% w/v)	Electrospinning Parameters		Solution Characteristics		Fiber Diameter		
		V (kV)	d (cm)	σ_e (mS/cm)	ρ (g/cm ³)	$\bar{d}_f$ (nm)	σ (nm)	CV
13	30	18	6	2.16	1.261	-	-	
14	40			2.27	1.270	238 ^A	96	0.40
15	50			2.33	1.283	291 ^B	146	0.50
16	30	18	9	2.16	1.261	-	-	
17	40			2.27	1.270	285 ^B	141	0.49
18	50			2.33	1.283	549 ^C	244	0.44

C = concentration, σ_e = electric conductivity, and ρ = density. Different letters indicate significant differences.

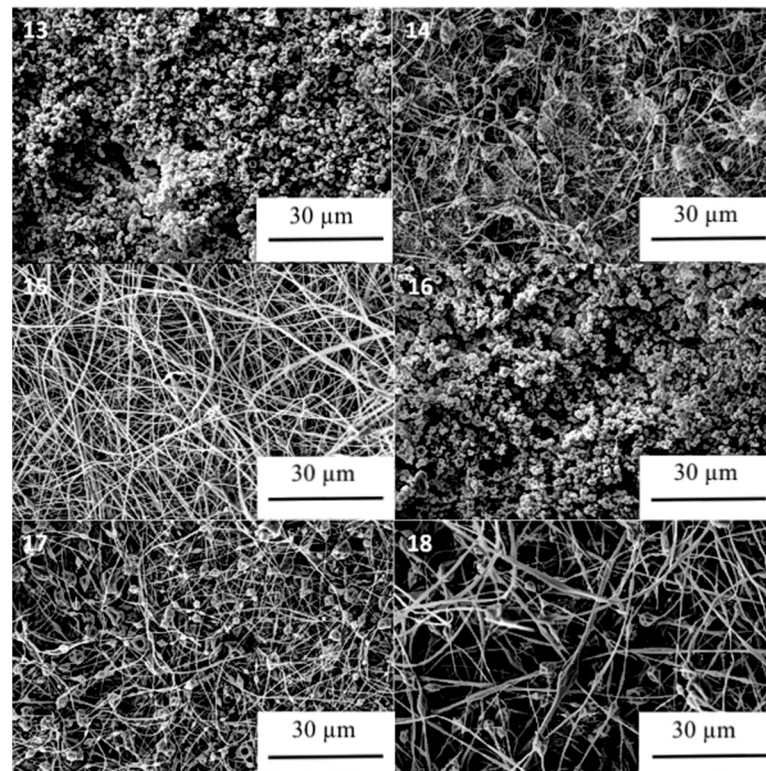


Figure 4. SEM micrographs ($\times 1000$) of the different potato starch systems defined in Table 2.

3.2.3. Effects of the Needle-to-Collector Distance

The membranes are processed under different electrospinning conditions, as reflected in Table 3, with a particular focus on the needle-to-collector distance. The corresponding values for fiber diameter, their deviation, and their CV obtained from SEM microscopy images are also presented in the table based on the micrographs shown in Figure 5. The processed tests are grouped in sets of three, where only the needle-to-collector distance parameter varied within each group. The effect of the distance on the obtained membranes was studied by observing the differences in SEM images and comparing the fiber diameter and its deviation.

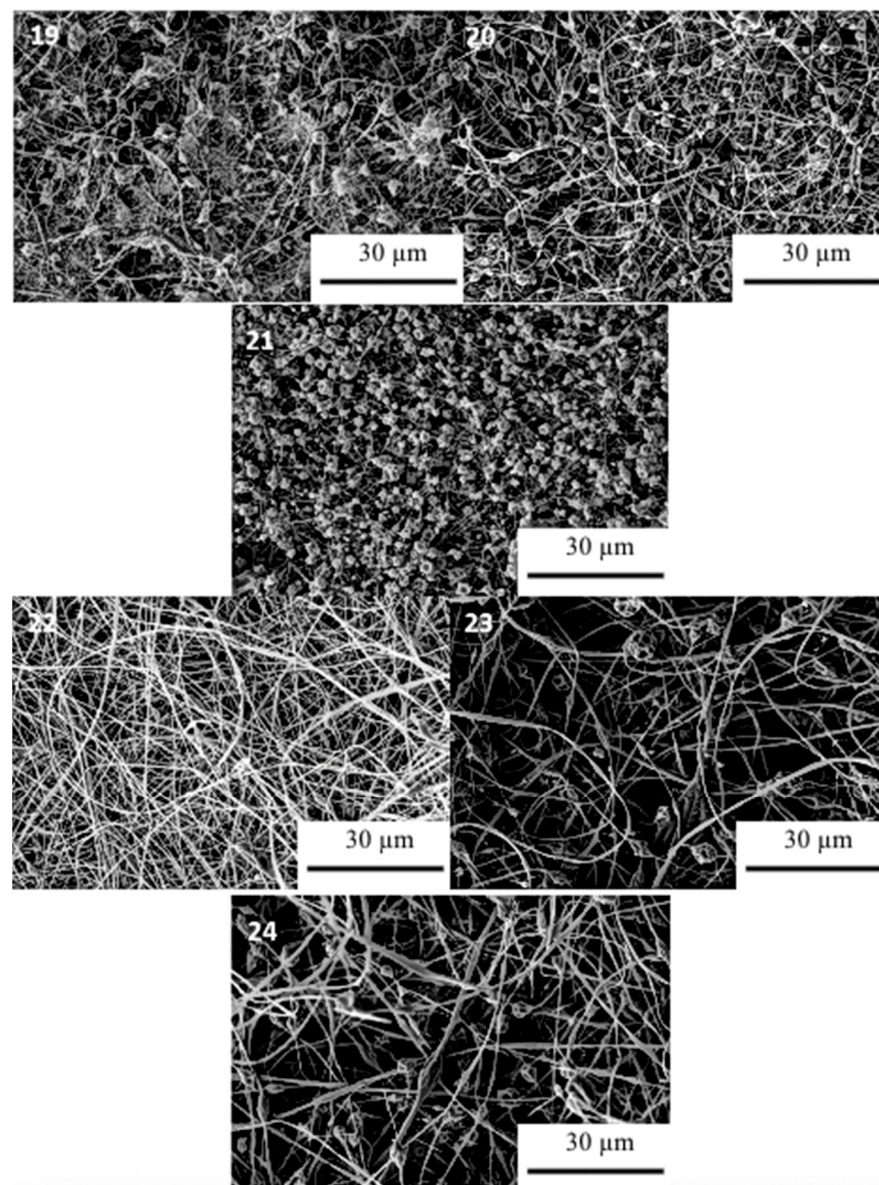


Figure 5. SEM micrographs ($\times 1000$) of the different potato starch systems defined in Table 3.

When comparing the SEM images of systems 19, 20, and 21, it can be observed that at a 6 cm distance, highly heterogeneous membranes were produced, featuring fibers of different diameters with small fiber agglomerations adhering to larger ones. It seems that for shorter needle-to-collector distances in the 40% *w/v* solution, fibers tended to agglomerate due to incomplete solvent evaporation. The size of these fibers makes diameter measurements challenging; therefore, the average diameter and its deviation are non-representative, with the latter being much higher. A 6 cm distance is excessively short for this concentration, inducing erratic polymer depositions. This behavior was also observed by other authors in the electrospinning of an aqueous chitosan solution [31]. When the distance was set at 9 cm, more homogeneous fibers formed with some nodules of similar size, but the majority of the polymer was deposited in the form of fibers. Thus, fibers processed at 9 cm exhibited larger fiber diameters and more homogeneous fiber membranes with fewer nodules.

Finally, when the distance was set at 12 cm, the membrane exhibited a higher number of nodules, along with thinner fibers, than at 9 cm since more of the polymer was deposited in the nodules. It seems that, as the distance increases, greater fiber stretching occurs, lead-

ing to smaller fiber diameters. Additionally, these fibers can occasionally break, resulting in a heterogeneous membrane with shorter fibers.

Table 3. Solution concentration, electrospinning parameters, and fiber diameter for potato starch systems at different needle-to-collector distances. The solvent was FA, and dissolution was carried out at 70 °C for 30 min. During electrospinning, the temperature was 25 °C and the humidity $25 \pm 5\%$. The flow rate was fixed at 0.2 mL/h.

System	Concentration (% <i>w/v</i>)	Electrospinning Parameters		Fiber Diameter		
		V (kV)	<i>d</i> (cm)	$\overline{d_f}$ (nm)	σ (nm)	CV
19	40	18	6	238 ^{AB}	96	0.40
20			9	285 ^{BC}	141	0.49
21			12	227 ^A	69	0.30
22	50	18	6	291 ^C	147	0.51
23			9	549 ^D	244	0.44
24			12	507 ^D	274	0.54

Different letters indicate significant differences.

However, upon comparing systems 22, 23, and 24, it was observed that 6 cm led to a very homogeneous membrane exhibiting few nodules and thin fibers. Since these systems have been processed with a more concentrated solution (50% *w/v*), it seems that the influence of the needle-to-collector distance on fiber morphology depends on the polymer concentration. Additionally, it can be observed that at 9 and 12 cm distances, membranes present more nodules.

Fibers with small diameters, that is, with a high specific surface area, are interesting for numerous applications. Another crucial aspect is the absence of irregularities in the membranes, such as numerous nodules or wet fibers, due to incomplete solvent evaporation in the polymer jet during the process. In this way, needle-to-collector distances of 6 and 9 cm, due to their positive effects on 50 and 40% *w/v* solutions, respectively, are selected as potential optimal values.

3.2.4. Effects of the Potential Difference

In this section, the effect of the potential difference on electrospun membranes is studied. To achieve this, membranes were processed with different voltages, and measurements of the average fiber diameter and their deviation and CV were taken to quantify these results. Table 4 displays all relevant data for each electrospinning test conducted on 40% *w/v* samples with a needle-to-collector distance of 9 cm based on the results obtained in Section 3.2.3. Figure 6 shows the SEM images for these systems.

Table 4. Solution concentration, electrospinning parameters, and fiber diameter for potato starch systems at various potential differences. The solvent was FA, and dissolution was carried out at 70 °C for 30 min. During electrospinning, the temperature was 25 °C and the humidity $25 \pm 5\%$. The flow rate was fixed at 0.2 mL/h.

System	Electrospinning Parameters		Fiber Diameter		
	V (kV)	<i>d</i> (cm)	$\overline{d_f}$ (nm)	σ (nm)	CV
25	14	9	291 ^A	189	0.65
26	18		367 ^B	148	0.40
27	22		500 ^C	210	0.42

Different letters indicate significant differences.

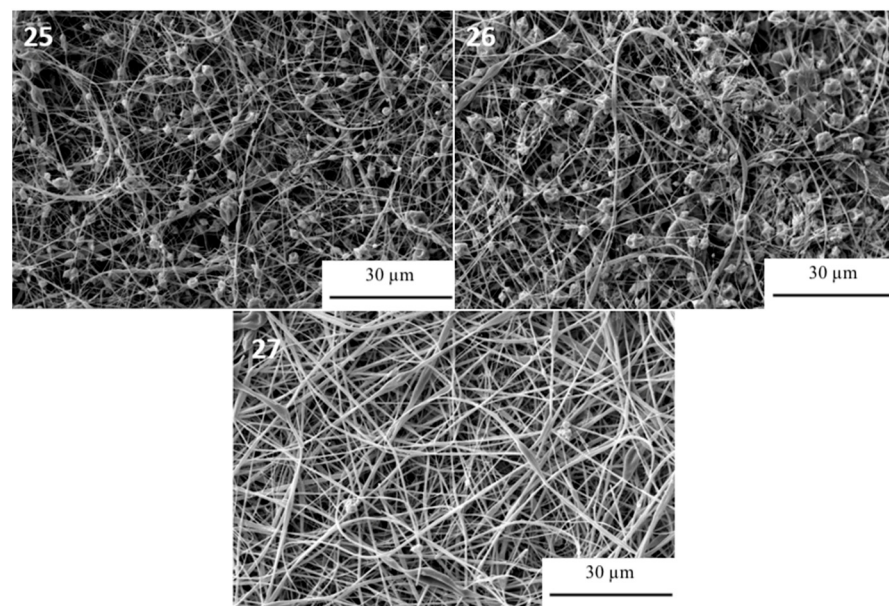


Figure 6. SEM micrographs ($\times 1000$) of the different potato starch systems defined in Table 4.

With these results, the effect of the potential difference can be analyzed. The membranes obtained at 14 and 18 kV exhibited a smaller fiber diameter but also a high number of nodules. As the potential difference increased, the fiber diameter also increased because a greater amount of polymer was deposited into the fibers instead of in the form of granules. Bakar et al. [32] observed a similar increase in fiber diameter with increased applied voltage for acrylonitrile electrospun fibers. At 14 kV, the average fiber diameter was 291 nm, whereas at 18 kV, the value obtained was 367 nm, but these voltages induced the formation of high numbers of nodules. On the contrary, although at 22 kV, the fiber diameter increased from 367 nm (at 18 kV) to 500 nm, a homogeneous fiber membrane with hardly any nodules was obtained. In this way, 22 kV was selected as an optimal potential difference, but since the effects of other electrospinning parameters depended on solution concentration, other values were also considered for 50% *w/v* solutions.

3.2.5. Effects of the Flow Rate

In this section, the effect of flow rate on fiber electrospinning is evaluated. For this purpose, the flow rate was decreased in order to achieve a more homogeneous electrospinning process. Specifically, tests were conducted at 0.05 mL/h and 0.1 mL/h, and comparisons were also made with some tests at 0.2 mL/h. The conditions of the evaluated systems are listed in Table 5, along with the measured values of the mean diameter, their standard deviation, and their CV.

The images obtained by SEM for these systems are shown in Figure 7. When comparing system 28 with systems 29 and 30, it seems that decreasing the flow rate from 0.2 mL/h to 0.1 and 0.05 mL/h led to thinner and more continuous electrospun fibers. Thus, for 0.05 mL/h and 0.1 mL/h flow rates, more homogeneous membranes with fewer nodules were observed. However, when decreasing the flow rate from 0.1 to 0.05 mL/h in systems 31 and 32, an increased mean diameter was observed, but both membranes were homogeneous and did not show any nodules, so it was determined that the effect of the flow rate was also dependent on other parameters being both 0.1 and 0.05 mL/h optimal values for the flow rate. With these results, a flow rate of 0.1 mL/h was fixed because it allowed faster material deposition while providing homogeneous membranes.

These results align with the findings from other authors, such as those reported by Zargham S. et al. [33]. In this investigation, it was observed that at lower flow rates, a small amount of the solution was ejected from the needle, leading to the formation of smaller droplets. On the contrary, with higher flow rates, a greater amount of solution

was ejected, which caused a lack of sufficient stretching in the solution jet because the electric field strength was not enough to stretch the solution due to the small amounts of charged ions. Consequently, the authors concluded that there is a threshold value for the flow rate in order to achieve a stable Taylor cone that leads to the formation of narrow fiber diameter distributions.

Table 5. Electrospinning parameters and fiber diameter for potato starch systems at different flow rates. The solvent was FA, and dissolution was carried out at 70 °C for 30 min. During electrospinning, the temperature was 25 °C and the humidity $25 \pm 5\%$. The concentration was always 50% *w/v*.

System	Electrospinning Parameters			Fiber Diameter		
	<i>Q</i> (mL/h)	<i>V</i> (kV)	<i>d</i> (cm)	$\overline{d_f}$ (nm)	σ (nm)	CV
28	0.2	18	9	549 ^C	244	0.44
29	0.1			461 ^B	197	0.43
30	0.05			363 ^A	191	0.53
31	0.1	22	6	307 ^A	179	0.58
32	0.05			484 ^B	285	0.59

Different letters indicate significant differences.

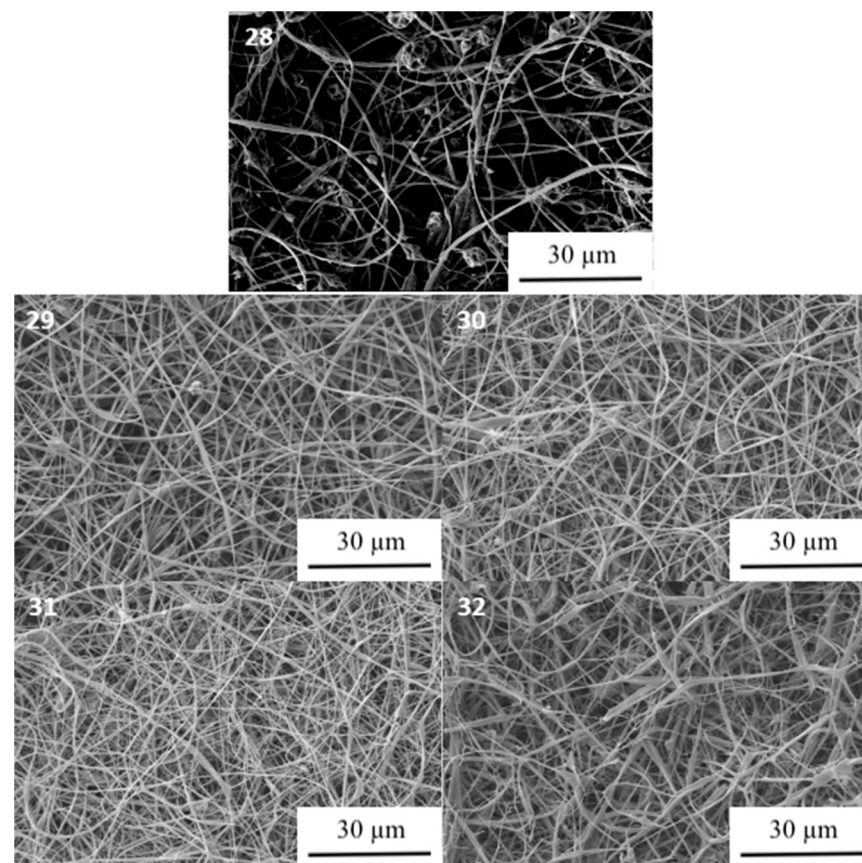


Figure 7. SEM micrographs ($\times 1000$) of the different potato starch systems defined in Table 5.

3.3. Rice Bran/Potato Starch Membranes

The 50% *w/v* concentration was the one selected to carry out the co-electrospinning along with rice bran because it allowed us to deposit higher polymer amounts. Specifically, the concentrations of rice bran/potato starch selected were 5/45% *w/v* (i.e., a solution with 5% *w/v* rice bran and 45% *w/v* potato starch concentrations, respectively) and 10/40% *w/v*. On the other hand, the optimal values for potential differences and the needle-collector

distance for electrospinning potato starch in FA for this concentration were 18 and 22 kV and 6 and 9 cm, respectively. In this way, the co-electrospinning processes of 5/45 and 10/40% *w/v* rice bran/potato starch solutions were performed using these conditions and a flow rate of 0.1 mL/h. For each test, the measurements of mean fiber diameter, standard deviation, and CV were carried out, as shown in Table 6. The SEM images of these systems are shown in Figure 8.

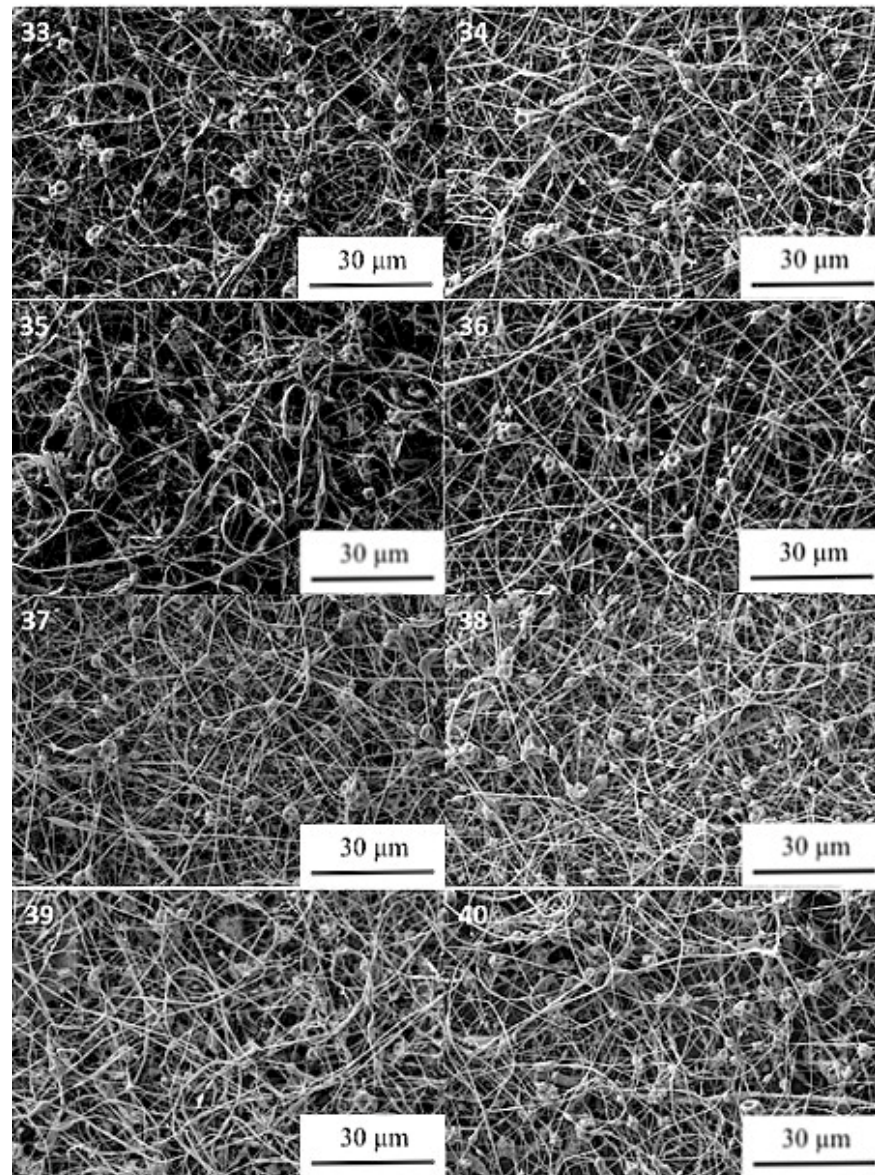


Figure 8. SEM micrographs ($\times 1000$) of the different rice bran/potato starch systems defined in Table 6.

Although it was possible to observe the presence of nodules in the processed systems, nanofiber membranes with approximately 200 and 300 nm diameter containing rice bran were finally achieved through co-electrospinning with soluble potato starch dissolved in FA at concentrations of 5/45 and 10/40% *w/v*, respectively. Since the 10/40% *w/v* solution of rice bran/potato starch led to slightly smaller fiber diameters and had a higher content of rice bran, resulting in the valorization of a larger quantity of by-product, this solution was selected for the co-electrospinning of rice bran and potato starch and the physical characteristics of this solution were measured for density and conductivity. On one hand, the measured density was 1.28 g/cm³, which is similar to that of the 50% *w/v* potato

starch solution. On the other hand, the conductivity was higher since the 10/40% *w/v* rice bran/starch solution had a conductivity of 3.10 mS/cm, while the 50% *w/v* potato starch solution had a value of 2.33 mS/cm. This increase in conductivity led to the greater stretching of the polymer jet during electrospinning, consequently resulting in finer fibers at 18 kV and 9 cm, and the fibers decreased in mean diameter from 549 to 218 nm. Specifically, test 38, at 18 kV and 9 cm, provided a configuration of thinner and more uniform fibers, making these parameters ideal for the co-electrospinning of rice bran with potato starch, allowing a lower proportion of commercial starch to be used by valorizing this low-added value by-product.

Table 6. Rice bran/potato starch concentration, electrospinning parameters, solution characteristics, and fiber diameter for co-electrospun systems. The solvent was FA, and during electrospinning, the temperature was 25 °C, and the humidity was 25 ± 5%. The flow rate was always 0.1 mL/h.

System	RB/PS (% <i>w/v</i>)	Electrospinning Parameters		Fiber Diameter		
		V (kV)	d (cm)	$\bar{d}_f$ (nm)	σ	CV
33	5/45	18	6	308 ^{DE}	145	0.47
34		18	9	318 ^E	154	0.48
35		22	6	326 ^E	154	0.47
36		22	9	295 ^{CDE}	131	0.44
37	10/40	18	6	252 ^{AB}	123	0.49
38		18	9	218 ^A	89	0.41
39		22	6	268 ^{BC}	156	0.58
40		22	9	280 ^{BCD}	150	0.54

PS = potato starch. Different letters indicate significant differences.

4. Conclusions

According to the results obtained, rice bran on its own presents solubility issues that make fiber electrospinning very difficult because low-concentration solutions do not offer suitable properties for this technique. In this way, these multiple attempts to develop nanofiber membranes from rice bran reveal the challenges for the complete valorization of rice bran due to its complex composition. However, membranes can be obtained through co-electrospinning with potato starch after rice bran has undergone degreasing and sieving processes down to 200 µm.

The results reflect that the optimal conditions for the solution using formic acid as a solvent are a rice bran/potato starch concentration of 10/40% *w/v* and a mixing time of 30 min at 70 °C. Under these conditions, the solution has a conductivity of 3.10 mS/cm and a density of 1.28 g/cm³. The electrospinning parameters that optimize fiber formation are an output flow rate of 0.1 mL/h, a potential difference of 18 or 22 kV, and a distance between the needle and the collector of 6 or 9 cm. Under these conditions, membranes with continuous fibers and a 218 nm mean diameter, with a standard deviation of 89 nm, were electrospun. However, these membranes show the presence of nodules, which could hinder their potential application.

Moreover, this technique could be suitable for the valorization of specific phases, particularly proteins or starches, once extracted. Extracting pure protein or starch could mitigate solubility issues at their optimal pH and reduce interactions that might hinder both dissolution and subsequent electrospinning. Furthermore, there are numerous possibilities for further investigation in the valorization pathway of this agro-industrial by-product. Some of them include optimizing the composition and processing parameters to manufacture membranes that meet the necessary requirements for applicability in filter development or

biomedical products. Future research could focus on refining extraction processes to isolate specific components more efficiently, as well as exploring electrospinning parameters in greater depth to enhance the properties of resulting membranes. This ongoing exploration holds the potential for creating value-added products from rice bran while addressing environmental and economic sustainability concerns.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr12061204/s1>, Table S1: Solution conditions and electrospinning parameters for the different rice bran systems. Magnetic agitation was performed for 30 min, and the environmental conditions were fixed (25 °C and 25 ± 5% humidity); Table S2: Solution conditions and electrospinning parameters for the different systems obtained from rice bran previously processed in the mixer rheometer. Magnetic stirring was performed for 30 min, and the environmental conditions were fixed (25 °C and 25 ± 5% humidity).

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