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Unveiling the Structural Evolution of Starch-Sodium Salt Complex Membrane: A Morphological Perspective

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ABSTRACT

The development of sustainable and biodegradable materials for energy storage and functional applications has gained significant attention. This study aims to investigate the structural evolution and morphological modifications of starch-sodium salt complex membranes, focusing on the impact of sodium methanoate incorporation on the polymer matrix. Solid-state membranes were prepared using a solution casting technique with starch, sodium methanoate, distilled water, and glycerin. The pure membrane exhibited a smooth and transparent surface, indicating a uniform polymer network. However, increasing sodium methanoate concentrations led to notable changes in surface morphology, including enhanced opacity and structural heterogeneity. Characterization using a high-resolution camera, SEM, and EDS confirmed the formation of distinct macro- and microstructures, alongside a uniform distribution of sodium ions within the polymer matrix. Among the tested compositions, the 30 wt.% sodium methanoate membrane exhibited the most optimized structure, with a uniformly distributed opaque appearance, a highly veiny morphology observed in SEM, and an evenly dispersed sodium ion distribution in EDS analysis. These findings contribute to the understanding of salt-mediated structural modifications in starch-based materials, offering insights into their potential applications in biopolymer electrolytes and other advanced materials.

1. Introduction

The growing demand for sustainable and eco-friendly materials has spurred extensive research into biopolymer-based systems. Among these, starch has emerged as a promising candidate due to its renewable nature, biodegradability, and low cost. Its inherent polysaccharide structure, composed of amylose and amylopectin, makes it a versatile polymer matrix for various applications. Starch-based materials have been widely explored in areas such as bioplastics, packaging, and biomedical devices. However, their utilization in advanced technologies, such as solid polymer electrolytes, remains underexplored. These insights are particularly relevant not only to energy storage systems

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but also to other electrochemical and functional materials that demand innovative, sustainable, and adaptable solutions.

Incorporating sodium salts into starch matrices offers a novel route to enhance the functionality of starch-based membranes. Sodium salts, such as sodium methanoate, act as dopants that interact with the polymer chains, disrupting the crystalline regions and promoting amorphization. These interactions lead to significant changes in the physical properties of the membranes, including ionic conductivity, mechanical strength, and surface morphology. As in starch-sodium systems, the presence of granular cavities and reduced molecular entanglement enhances the influence of salts on the thermal and structural properties of starch, with higher salt concentrations inhibiting retrogradation in amylose-rich matrices. These co-solute interactions significantly modulate the physical properties of the complexes, such as gelatinization and gel strength [1]. These effects, tied to salt accessibility and polymer interactions rather than hydration changes and offer insights for optimizing starch-based solid polymer electrolytes. In the system studied by Chiotelli, involving wheat and potato starches with sodium chloride, further evidence demonstrated that the physical properties of starch-salt complexes change significantly with salt concentration. Sodium chloride was shown to influence gelatinization parameters, such as onset, peak, and end temperatures, as well as gelatinization enthalpy, storage modulus, and rotational mobility. These changes were attributed to the dual effects of salt on water properties and direct polymer-salt interactions, which varied based on salt concentration and highlighted the complex interplay between solute and starch structures. [2]. As in starch-salt systems, the exclusion of salts at low concentrations and increased salt binding at higher concentrations significantly influence the starch matrix [3]. In multiple systems, where starch was combined with various salts (sodium chloride, sodium sulfate, potassium chloride, calcium chloride, and sodium phosphate), it was shown that these salts significantly influence the physical properties of the complexes. Studies revealed changes in viscosity and gelatinization temperature when starch was pasted with xanthan in the presence of salts, as measured using Brabender amylograph. Rheological analysis further confirmed that the salts affected the starch-gum interactions under varying shear rates, highlighting their role in modifying the texture and structural behavior of the complexes [4]. Vilwock and BeMiller provided compelling evidence of the interaction between starch and sodium salts in their study, which supports the structural alterations in this combination. Their research demonstrated that salts, depending on their position in the lyotropic series, significantly impact starch gelatinization. Sodium sulfate, for example, restricted swelling due to a moderately lyotropic effect and the generation of Donnan potential, while sodium chloride was ineffective as a swelling inhibitor, leading to granule pasting. These findings highlight how salts influence granule swelling, gelatinization inhibition, and reaction efficiency, offering insights into the mechanism underlying starch-salt interactions [5]. By tailoring the concentration of the added salt, it becomes possible to modulate the structural properties of the complexes, making them suitable for diverse applications, particularly in energy storage devices.

Sodium methanoate (HCOONa) was specifically selected as the doping salt for this study due to its unique ionic profile and its emerging potential in cost-effective sodium-ion energy applications. Structurally, the methanoate anion ($HCOO^-$) possesses a relatively small ionic radius coupled with high electronegativity compared to larger organic anions. We hypothesized that this compact size would facilitate deeper and more uniform penetration into the dense biopolymer matrix, making it an ideal candidate to study salt-induced structural transformations.

At the molecular level, the native starch matrix consists of tightly packed amylose and amylopectin chains held together by an extensive network of strong intra- and intermolecular hydrogen bonds, which typically yields a rigid, semi-crystalline morphology. Upon the incorporation of sodium methanoate, the sodium cations (Na^+) and methanoate anions ($HCOO^-$) actively compete

for the abundant hydroxyl (–OH) groups along the starch backbone. The resulting ion-dipole electrostatic interactions effectively disrupt and replace the native hydrogen bonds between the polymer chains. This molecular decoupling plasticizes the matrix, reduces overall crystallinity, and provides the mechanistic driver for the distinct morphological shifts—such as the transition from a uniform surface to the highly amorphous, phase-separated veiny structures—observed in the microscopic analysis.

Morphological characterization plays a critical role in understanding the structural evolution of these starch-sodium salt membranes. Techniques such as scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) provide detailed insights into the surface features and elemental distribution of the membranes. These methods, coupled with visual analysis using standard optical imaging, help to reveal the impact of salt concentration on the membrane's appearance, texture, and homogeneity. Morphological changes, such as increased opacity or the formation of distinct microstructures, can be directly linked to the interaction between the polymer and salt ions. Although previous studies have touched upon these physical effects, there is a notable gap in the literature concerning the use of imaging technologies to explore the morphology of complex compounds, especially those involving starch and sodium salts. This area remains underexplored, highlighting an opportunity for further research into how these imaging methods can reveal intricate details about these materials' structures.

Despite the growing interest in biopolymer electrolytes, a distinct research gap remains regarding the specific microstructural evolution of starch-based membranes when doped with sodium methanoate. While general salt-polymer interactions are documented, the precise morphological mechanisms—specifically how varying concentrations of sodium methanoate interact with starch chains to disrupt hydrogen bonding and induce phase separation—are not fully understood. Therefore, the research objective of this study is to systematically investigate the structural transformations of starch-sodium methanoate complex membranes from a purely morphological perspective. The significance of this study lies in establishing a foundational structural understanding of these specific salt-polymer dynamics. By mapping the morphological shifts that occur at different weight percentages, this work provides the prerequisite framework necessary to connect physical structure to performance, serving as a critical steppingstone for the future optimization of these membranes in energy storage applications.

2. Methodology

2.1 Preparation of Solid Biopolymer Electrolyte (SBE) membrane

The starting materials, starch ($C_6H_{10}O_5$) and sodium methanoate (HCOONa), were procured from Sigma-Aldrich. To fabricate the solid biopolymer electrolytes (SBEs), a range of sodium methanoate concentrations, specifically from 5 wt.% to 45 wt.% (detailed in Table 1), was incorporated. The preparation process involved dissolving the designated quantities of HCOONa in a carefully selected solvent system comprising distilled water and glycerin. The mixture was stirred continuously until a clear, homogenous solution was obtained, ensuring the complete dissolution of all components without any residual particles. The weight percentages (wt.%) of the components were determined using Eq. (1), which provides a systematic approach to calculating the composition of the SBEs.

$$wt.\% = \frac{x}{x+y} \times 100 \quad (1)$$

where, *x* is the amount of HCOONa (g) and *y* is the amount of polymer host (g).

Table 1
Compositions of polymer and ionic dopant

SBE sample	Sodium methanoate		Distilled water (*ml*)	Glycerin (*ml*)
	wt.%	g		
A	0	0.000	20	0.6
B	5	0.053	20	0.6
C	10	0.111	20	0.6
D	15	0.176	20	0.6
E	20	0.250	20	0.6
F	25	0.333	20	0.6
G	30	0.429	20	0.6
H	35	0.538	20	0.6
I	40	0.667	20	0.6
J	45	0.818	20	0.6

To continue the preparation process, 1 g of starch was carefully added to the pre-mixed solution of distilled water, glycerin, and sodium methanoate. The mixture was stirred consistently at a temperature range of 60–70°C until a homogeneous and uniform solution was achieved. The resulting solution was then poured into a clean glass petri dish, where it was left to dry naturally at room temperature. This process allowed the formation of solid biopolymer electrolyte (SBE) membranes. To ensure complete removal of residual moisture and to preserve the membranes' solid-state properties, they were transferred to a desiccator containing silica gel. This drying step was critical for stabilizing the membranes and preventing moisture-induced degradation. The entire preparation methodology, referred to as the solution casting technique, is illustrated schematically in Figure 1.

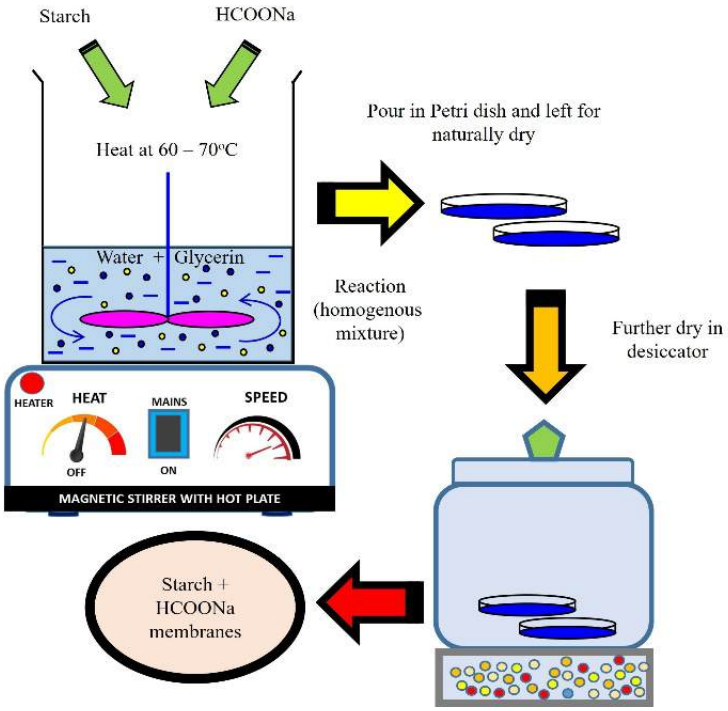

Fig. 1. A schematic diagram for preparation of solid biopolymer electrolyte membranes

2.2 Characterization

The prepared samples were photographed using a 20 MP high-definition camera to observe macroscopic effects of sodium salt incorporation, such as changes in opacity, surface texture, and color. This technique provides a qualitative perspective on the physical changes induced by varying salt concentrations and serves as a preliminary indicator of structural evolution in the membranes.

For a detailed surface morphology analysis, scanning electron microscopy (SEM) was employed. The analysis was performed using the JEOL JSM-6350LA model SEM with an acceleration voltage of 20 kV to achieve high-resolution images of the membrane's microstructure. SEM enables the observation of surface features such as roughness, pore formation, and morphological changes because of sodium salt addition. Variations in surface morphology, such as the transition from a smooth to a more irregular and textured structure, were captured at magnifications of up to 1,000×. These microstructural changes offer insights into the interaction between the polymer matrix and the sodium salt.

The elemental composition and distribution within the membranes were further analysed using energy dispersive spectroscopy (EDS), an analytical tool integrated with the SEM system. EDS mapping provided detailed information about the spatial distribution of key elements such as sodium (Na), oxygen (O), and carbon (C) within the membranes. The technique was critical for confirming the uniform dispersion of sodium methanoate within the polymer matrix and identifying regions of phase separation, if present. The data from EDS not only validated the successful incorporation of the salt into the matrix but also shed light on the role of ionic interactions in altering the microstructure.

To ensure accurate SEM and EDS measurements, the sample surfaces were coated with a thin layer of gold using a sputter coater. This step was necessary to prevent electrostatic charging during the analysis, which can distort the images and reduce the quality of data collected. The coated samples were carefully mounted onto specimen holders with double cellophane layers for stability during observation.

Additionally, the SEM images were analysed to discern crystalline versus amorphous characteristics of the samples. These structural features are directly linked to the ionic conductivity of the membranes, as the transition from a crystalline to a more amorphous structure often enhances the mobility of charge carriers. This characterization provided a direct correlation between surface morphology and the electrochemical properties of the membranes.

3. Results and Discussion

The solid biopolymer electrolytes (SBEs) based on starch were synthesized through the solution casting technique using starch, glycerine, and sodium methanoate as primary components. The pure starch membrane, as depicted in Figure 2(a), demonstrated a smooth and transparent surface, which reflects the homogeneity and uniformity of the polymer matrix Upon incorporating sodium methanoate at varying concentrations ranging from 5 wt.% to 45 wt.% (Figure 2(b)–2(j)), notable transformations in the surface morphology of the membranes were observed, highlighting the impact of salt addition on the structural characteristics of the starch-based biopolymer electrolytes (SBEs). Initially, at lower concentrations of sodium methanoate (5 wt.% and 10 wt.%), the membranes began to show subtle changes in their appearance. The transparency of the pure starch membrane, which had previously exhibited a smooth and homogeneous surface, gave way to a slightly opaquer appearance. This change suggests the onset of interactions between the sodium methanoate and the polymer matrix, likely disrupting the regular arrangement of starch molecules [6,7].

As the concentration of sodium methanoate increased to 20 wt.% and beyond, the morphological changes became more pronounced. The membranes began to exhibit a more distinct heterogeneous

surface, characterized by visible irregularities and textural changes. These changes can be attributed to the progressive incorporation of sodium ions into the polymer matrix, which likely caused localized disruptions in the crystalline regions of the starch. The sodium ions interacted with the hydroxyl groups of the starch, leading to a reduction in intermolecular hydrogen bonding within the matrix and promoting a more amorphous structure. This phenomenon not only affected the optical properties of the membranes, making them opaquer, but also altered their surface features, as observed in the form of increased roughness and irregularities [8].

At concentrations between 30 wt.% and 45 wt.%, the membranes displayed significant heterogeneity. Small structural features resembling belts or ridges were observed, indicating a higher degree of phase separation within the polymer matrix. This can be explained by the uneven distribution of sodium methanoate throughout the membrane, resulting in regions enriched with salt while others remained primarily polymer-rich. Such phase separation is a well-documented occurrence in polymer-salt systems and is typically driven by the limited solubility of the salt in the polymer at higher concentrations. The interaction between the salt ions and the starch molecules not only disrupted the uniformity of the matrix but also influenced its mechanical and optical properties. The increased salt content led to enhanced light scattering, further contributing to the opaquer appearance of the membranes [9,10].

Interestingly, while the addition of sodium methanoate brought about significant changes in morphology, it was observed that when the salt concentration exceeded 45 wt.%, the membranes became increasingly fragile and brittle. This brittleness can be attributed to the overloading of the polymer matrix with salt, which likely resulted in excessive phase separation and precipitation of sodium methanoate. These factors compromised the structural integrity of the membranes, rendering them unsuitable for further evaluation. The observed morphological evolution with increasing salt concentration underscores the complex interplay between polymer-salt interactions, phase behaviour, and the resulting physical properties of the membranes [11].

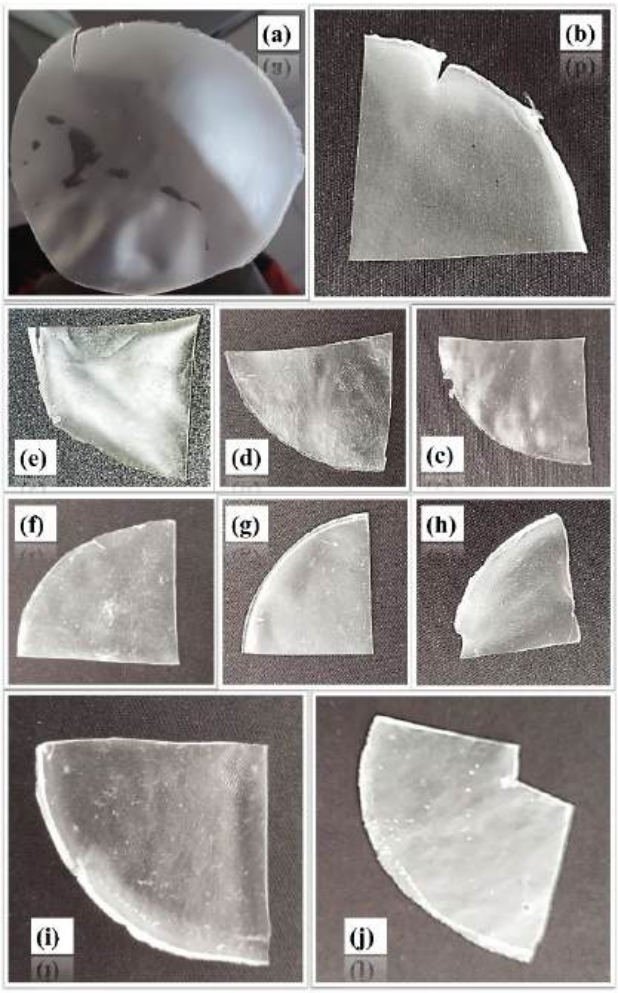

Fig. 2. SBE membranes at different weight % of HCOONa. Corresponding image for (a) pure starch, (b) 5 wt.%, (c) 10 wt. %, (d) 15 wt. %, (e) 20 wt. %, (f) 25 wt. %, (g) 30 wt. %, (h) 35 wt.%, (i) 40 wt.%, (j) 45 wt.% of HCOONa

The morphology and microstructure of the starch-based solid biopolymer electrolyte (SBE) membranes were comprehensively investigated using scanning electron microscopy (SEM) at a magnification of 1000×. This characterization provided insights into the structural changes induced by varying concentrations of sodium methanoate (HCOONa) within the polymer matrix. Figures 3(a)–3(j) illustrate the SEM images of SBE membranes with sodium salt content ranging from 0 wt.% to 45 wt.%, highlighting the progression of morphological changes as a function of salt concentration.

In the case of the pure starch membrane (Figure 3(a)), the surface appeared remarkably smooth, with no visible structural irregularities, indicating a homogeneously distributed and uniform polymer matrix. This smooth morphology reflects the absence of any significant disruptions in the polymer chains, as no external additives were present to alter the arrangement of the starch molecules. The lack of grain boundaries or irregular features is characteristic of a pristine biopolymer matrix in its native state.

The introduction of 5 wt.% sodium methanoate (Figure 3(b)) initiated observable changes in the surface morphology. The previously smooth surface now displayed the formation of grain boundary-like structures, suggesting the onset of interactions between the polymer chains and the salt ions. These grain boundaries likely arose due to localized disruptions in the polymer matrix, where sodium ions began to interact with the hydroxyl groups of the starch, weakening the intermolecular hydrogen

bonding. This phenomenon marked the first visible indication of sodium methanoate influencing the structural arrangement of the polymer [6,7].

As the salt concentration increased to 10 wt.% (Figure 3(c)), the surface morphology evolved further, exhibiting a combination of grain boundaries and a ripple-like texture. This ripple-like structure suggests enhanced phase separation within the polymer matrix, where regions enriched with sodium methanoate began to emerge alongside polymer-rich areas. This uneven distribution of salt and polymer reflects a more pronounced interaction between the salt and polymer chains, resulting in the disruption of the matrix's crystalline regions.

At 15 wt.% sodium methanoate (Figure 3(d)), the surface underwent a noticeable transformation, with the appearance of vein-like shapes interspersed across the membrane. These vein-like features are indicative of regions where the salt concentration might have exceeded its solubility limit, leading to the precipitation of sodium methanoate within the polymer matrix. Such precipitation contributes to increased surface heterogeneity, further altering the membrane's mechanical and optical properties.

The addition of 20 wt.% and 25 wt.% sodium methanoate (Figures 3(e) and 3(f)) resulted in the membrane surface adopting a soft, wavy, and undulating texture. This change can be attributed to the plasticization effect of sodium methanoate, which reduced the rigidity of the polymer matrix. The interaction between the sodium ions and the starch chains not only disrupted the polymer's crystalline regions but also rendered the matrix more flexible, allowing for the formation of wavy and undulating surface features. This behavior highlights the dual role of sodium methanoate as both a disruptor of crystallinity and a plasticizer.

At 30 wt.% sodium methanoate (Figure 3(g)), the surface morphology underwent a more pronounced transformation, transitioning to a highly veiny structure. This veiny appearance indicates the peak phase separation within the polymer matrix, where salt-enriched regions became distinctly segregated from polymer-rich areas. The veins likely correspond to zones of high salt concentration, where the polymer matrix's structural integrity was significantly altered. This morphological feature is strongly associated with enhanced ionic conductivity, as the formation of distinct salt-rich pathways facilitates the movement of ions within the membrane.

With further increases in sodium methanoate concentration to 40 wt.% and 45 wt.% (Figures 3(h) and 3(i)), the surface morphology exhibited more significant changes, including the development of cracks and pronounced surface irregularities. These features suggest that the polymer matrix had reached its capacity to accommodate additional salt, leading to excessive phase separation and structural instability. The cracks and irregularities are likely the result of salt precipitation, which occurs when the solubility limit of sodium methanoate in the polymer matrix is exceeded [11]. These structural instabilities compromise the membrane's mechanical properties, rendering it fragile and unsuitable for practical applications.

In summary, the SEM analysis revealed a clear progression in the surface morphology of starch-based SBEs with increasing sodium methanoate concentration. The structural evolution, characterized by the emergence of grain boundaries, ripple-like textures, vein-like shapes, and ultimately cracks and irregularities, underscores the complex interplay between sodium methanoate and the starch matrix. These findings provide valuable insights into the design and optimization of biopolymer electrolytes for advanced applications, particularly in energy storage devices where morphological and microstructural properties play a crucial role in determining performance.

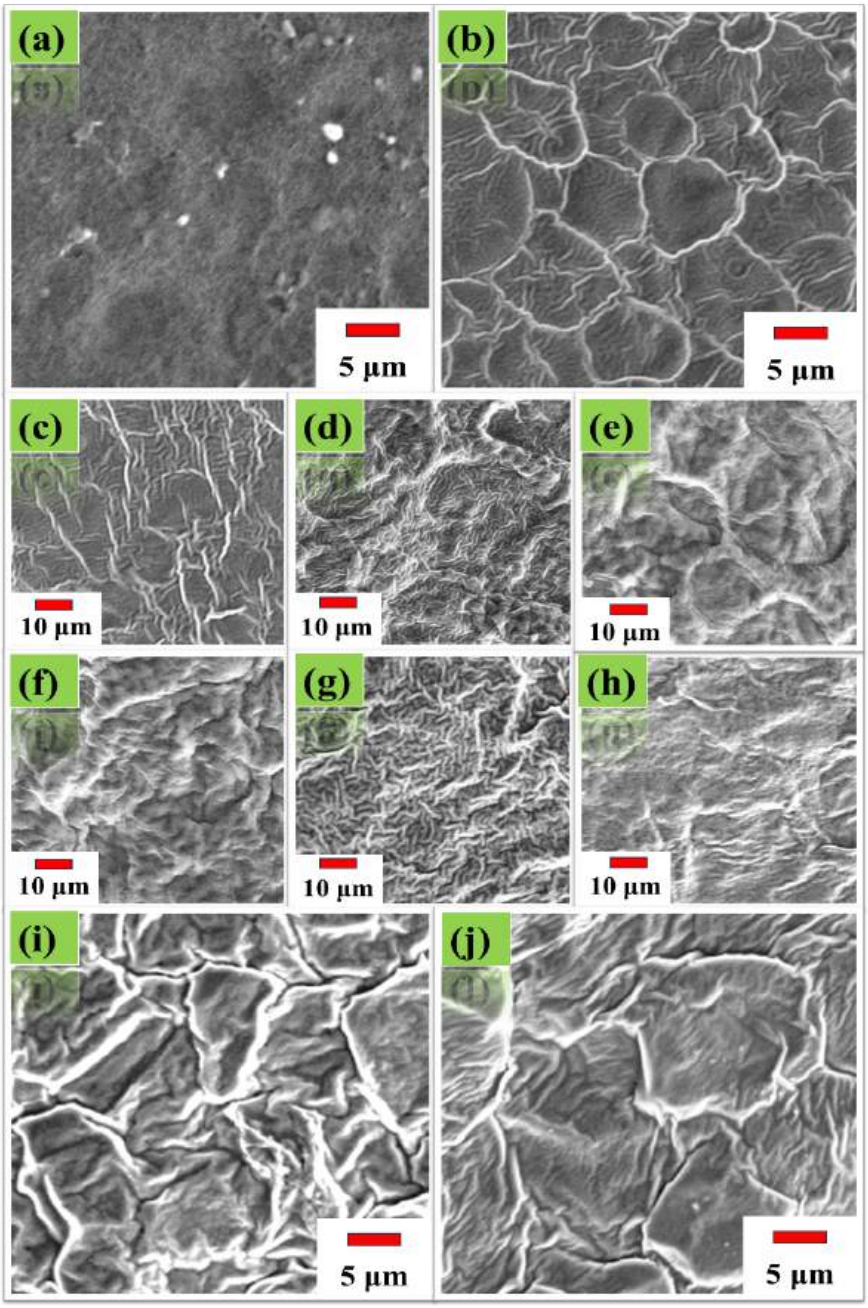

Fig. 3. The surface morphology of SBE membranes. Corresponding image for (a) pure starch, (b) 5 wt. %, (c) 10 wt. %, (d) 15 wt. %, (e) 20 wt. %, (f) 25 wt. %, (g) 30 wt. %, (h) 35 wt.%, (i) 40 wt.%, (j) 45 wt.% of HCOONa

To further substantiate these qualitative observations, the predominant microstructural features observed at key concentrations were estimated using image analysis, as summarized in Table 2.

Table 2
Estimated microstructural feature sizes across varying sodium methanoate concentrations based on SEM analysis.

SBE sample	Sodium Methanoate (wt.%)	Predominant Surface Feature	Estimated Feature Size (μm)*
A	0	Smooth, uniform polymer matrix	N/A
B	5	Onset of grain boundary-like structures	~ 5.0 -10.0 (Grain diameter)
C	10	Ripple-like texture	N/A
D	15	Emergence of vein-like structures	~ 8.0 – 12.0 (Domain width)
E	20	Soft, wavy, undulating texture	~ 6.0 – 10.0 (Domain width)
F	25	Pronounced wavy, undulating texture	~ 5.0 – 8.0 (Domain width)
G	30	Highly veiny, peak phase separation	~ 3.0 – 6.0 (Dense domain width)
H	35	Dense phase separation with minor irregularities	~ 3.0 – 5.0 (Dense domain width)
I	40	Increased structural irregularities and micro-cracks	~ 5.0 – 10.0 (Fractured chunk width)
J	45	Pronounced cracks and severe irregularities	~ 5.0 – 12.0 (Fractured chunk width)

(Note: Feature sizes corresponding to distinct phase-separated domains or vein widths were estimated using ImageJ software calibrated to the SEM scale bars. Values represent the average of 10 measurements. Early-stage morphological changes at lower concentrations did not produce distinct, measurable phase domains.)

Energy dispersive spectroscopy (EDS) is an essential analytical technique widely employed for characterizing the elemental composition and distribution within polymer composites. This technique plays a pivotal role in verifying the uniformity of elemental dispersion across the material, providing critical insights into the quality and consistency of the composite structure. The EDS technique is particularly valuable when investigating complex systems such as starch-based solid biopolymer electrolytes (SBEs), where understanding the interactions between polymer matrices and dopant salts is crucial for optimizing performance characteristics. The reliable detection and mapping of elements such as sodium (Na), oxygen (O), and carbon (C) ensure that the fundamental chemical properties of the composite material align with its intended functional applications [12,13].

Figures 4(a)–4(i) illustrate the EDS elemental mappings for Na, O, and C within the starch-sodium salt SBE membranes, corresponding to different concentrations of sodium methanoate (5–45 wt.%). In these mappings, the bright spots of varying colors represent the presence and spatial distribution of each element. Notably, the uniform spread of these bright spots across the membrane surface indicates a homogenous distribution of sodium methanoate throughout the starch matrix. This observation is particularly significant because it underscores the thorough intermixing of the starch and sodium salt particles during the solution casting process. Uniform distribution is crucial for ensuring consistent ionic conductivity and mechanical stability, both of which are essential for the effective performance of SBEs in energy storage applications.

The homogeneous dispersion of sodium methanoate within the starch matrix is consistent with findings from our earlier studies, where we observed a similar distribution pattern in starch-based composites doped with various sodium salts [14-16]. In those studies, the uniform integration of dopant salts within the polymer matrix was identified as a key factor influencing the material's ionic conductivity, mechanical properties, and overall electrochemical performance. By ensuring an even dispersion of sodium ions, the polymer matrix can provide continuous ion-conducting pathways, thereby enhancing the membrane's functionality as an electrolyte in energy storage devices.

Moreover, the results of this study align closely with observations reported by other researchers in the field. Several studies have demonstrated that sodium salts, due to their hygroscopic and soluble nature, are easily distributed within starch-based systems when mixed under appropriate conditions [17-18]. This effortless dispersion is attributed to the strong interaction between the sodium ions and the hydroxyl groups of starch, which facilitates the formation of a well-integrated polymer-salt network. The compatibility between starch and sodium salts is further enhanced by the solution casting technique, which allows for the controlled evaporation of the solvent, leading to the formation of a uniform composite membrane.

In addition to confirming the uniform distribution of elements, the EDS technique also provides valuable insights into the structural evolution of the composite membranes with increasing sodium methanoate content. As the salt concentration increases, the intensity of the Na signal in the EDS mappings becomes more pronounced, reflecting the higher sodium content within the membranes. This incremental increase in sodium concentration is accompanied by subtle changes in the distribution patterns of oxygen and carbon, indicating a shift in the crystalline-amorphous balance of the starch matrix. These changes are consistent with the morphological observations from SEM, where the surface structure of the membranes evolved from smooth and homogeneous to increasingly heterogeneous with the addition of sodium methanoate.

The reliability and reproducibility of the EDS results further enhance the credibility of the observed trends. By consistently demonstrating the homogeneous distribution of sodium methanoate across different membranes, the EDS analysis provides a strong foundation for understanding the interplay between salt concentration and membrane properties. This level of detail is essential for developing a comprehensive understanding of the factors that govern the performance of starch-based SBEs, particularly in the context of energy storage applications.

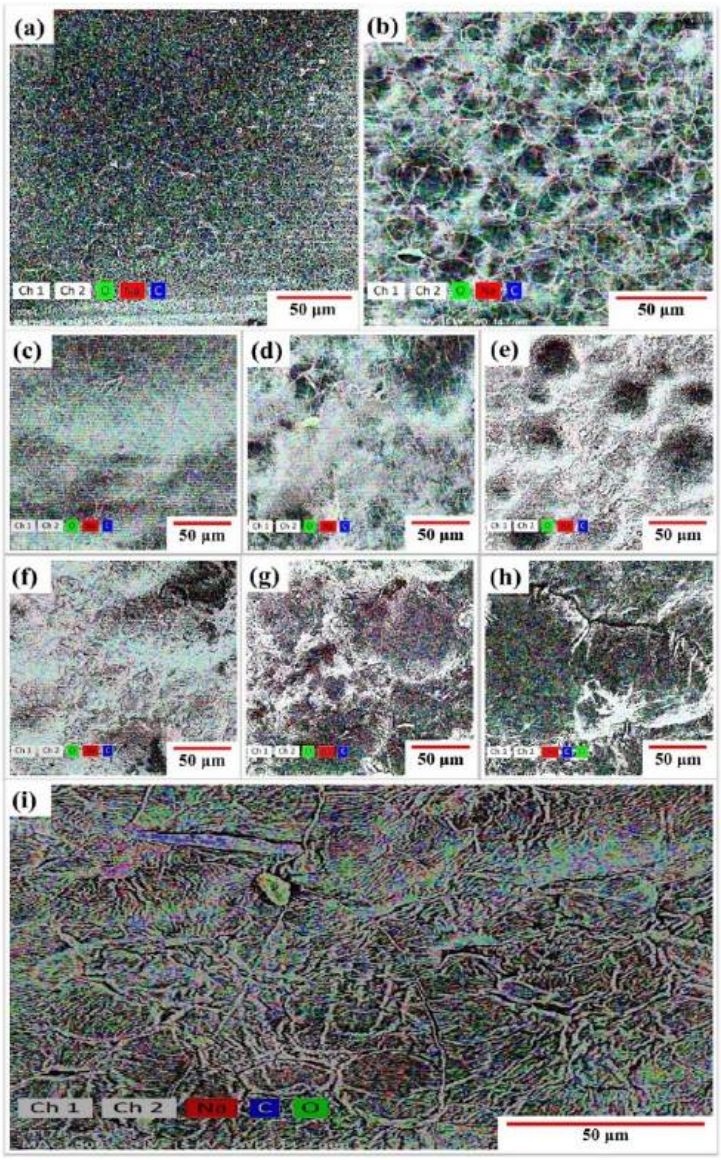

Fig. 3. Scanning electron microscope image of starch-HCOONa complex membranes. Corresponding EDS mappings for sample (a) 5 wt.%, (b) 10wt.%, (c) 15wt.%, (d) 20wt.%, (e) 25wt.%, (f) 30wt.%, (g) 35wt.%, (h) 40wt.% and (i) 45wt.%

While this study provides comprehensive insights into the structural evolution of starch-sodium methanoate complex membranes, certain limitations must be acknowledged. Because the primary objective of this research was to establish a foundational understanding of salt-polymer interactions from a purely morphological perspective, quantitative electrochemical characterizations—such as ionic conductivity, dielectric behavior, and electrochemical impedance spectroscopy (EIS)—were not within the current scope. Furthermore, while visual and microscopic brittleness was noted at higher salt concentrations, formal mechanical property analyses (e.g., tensile testing) and assessments of the long-term environmental stability of the membranes remain to be evaluated.

To fully bridge the gap between these structural findings and practical energy storage applications, future studies must prioritize targeted electrochemical and mechanical testing. Specifically, correlating the optimized veiny microstructures and peak phase separation observed at 30 wt.% sodium methanoate with actual ionic conductivity measurements will be a critical next step in determining the operational viability of these materials as solid biopolymer electrolytes.

4. Conclusions

This study successfully prepared solid biopolymer electrolyte membranes based on starch-HCOONa using the solution casting technique. The structural and morphological effects of HCOONa on the starch matrix were systematically analysed through high-resolution imaging, scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). The incorporation of HCOONa resulted in quantifiable morphological transformations, altering the initially smooth starch matrix into highly textured surfaces. Specifically, the emergence of distinct vein-like structures (~ 8.0 – 12.0 µm in width) began at 15 wt.%, while peak phase separation and an optimized, dense veiny morphology (~ 3.0 – 6.0 µm domain width) were achieved at 30 wt.%. Concentrations exceeding 40 wt.% resulted in structural instability and micro-cracking. These transformations were attributed to interactions between sodium methanoate and the polymer chains disrupting the crystalline-amorphous balance, while EDS confirmed the uniform dispersion of the dopant across all functional concentrations. These findings provide critical baseline insights into tailoring the structural properties of starch-based membranes. To fully realize the potential of these materials as biopolymer electrolytes, future work must focus on correlating these optimized morphologies—particularly the 30 wt.% composition—with targeted electrochemical impedance spectroscopy (EIS), ionic conductivity measurements, and mechanical tensile testing.

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Conflict of Interest Statement
The authors declare that they have no conflicts of interest in this work.

Author Contributions Statement
Muhammad Zulhasnan Mohd Zahari: Methodology, Formal analysis, Investigation, Resources, Data curation. Mohd Faiz Hassan: Conceptualization, Validation, Resources, Visualization, Supervision, Writing – original draft, Writing – review & editing.

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Data Availability Statement
The data of this study are available from the corresponding author upon reasonable request.

Ethics Statement
This study does not contain any studies with human or animal subjects performed by any of the authors.

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