The Mechanical Strength of Composite Solid Electrolyte Membranes Based on Carboxymethyl Chitosan as a Function of Amount ZSM-5 Zeolite Paracrystalline Filler

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**Abstract.** This study investigated how different weights of ZSM-5 zeolite paracrystalline impact its role in the mechanical strength of Composite Solid Electrolyte (CSE) with a carboxymethyl chitosan (CMCh) matrix. Specifically, ZSM-5 zeolite paracrystalline was incorporated at concentrations of 0.5% (CZ0.5), 1.5% (CZ1.5), and 3% (CZ3) relative to the total mixture weight. The influence of ZSM-5 zeolite weight on membrane strength was primarily assessed through tensile strength measurements. The tensile strengths of membranes composed of pristine CMCh, CZ0.5, CZ1.5, and CZ3 were 53.12 MPa, 42.74 MPa, 48.21 MPa, and 82.59 MPa, respectively. These findings demonstrate that at low, moderate, and high levels of ZSM-5 zeolite paracrytalline content, the material respectively decreases, maintains, and increases the tensile strength of the CSE compared to pristine CMCh membranes. This effect is attributed to the occupancy of membrane spaces by ZSM-5 zeolite paracrystalline and its ability to transmit stress to the CMCh matrix effectively. These results suggest that ZSM-5 zeolite paracrystalline shows promise as a filler to sustain and enhance the mechanical durability of solid electrolyte membranes in potential applications.

**Keywords**: Carboxymethyl chitosan, composite solid electrolyte, ZSM-5 zeolite paracrystalline, mechanical strength of CSE

# Introductions

The demand for safe and eco-friendly energy has spurred diverse research efforts, including research about lithium-ion battery composite solid electrolytes. Composite solid electrolytes are solid polymer electrolyte membranes comprising polymer materials, electrolytes, and additional fillers. They serve as an electrolyte and a separator in lithium-ion batteries [1,2] The primary objective of developing solid electrolytes from various polymers is to enhance ionic conductivity properties at room temperature while preserving mechanical strength and thermal stability. Increasing the electrolyte concentration in polymers boosted conductivity [3,4], but excessive concentrations diminished mechanical strength and thermal stability [4,6]

To mitigate the decrease in mechanical strength of polymer-based solid electrolytes, researchers have explored the addition of fillers other than electrolyteS [7]. These fillers, typically inorganic solids known for their high mechanical strength, include substances like clay [8,10] metal oxides [11,12], and zeolites [15-15]. Those studies showed that incorporating clay and metal oxides as fillers in solid electrolyte membranes has not significantly enhanced mechanical strength. The X zeolite employed in solid electrolytes demonstrated improved mechanical strength, with tensile strength and Young's Modulus reaching approximately 15 MPa and 55 MPa, respectively [13]. In contrast, zeolites, specifically clinoptilolite zeolite, when added as a filler to PVDF-based copolymer membranes, exhibited a tensile strength of approximately ~6.5 MPa and a Young's Modulus of 92 MPa [15].

Silicalite-1, MFI zeolite, was studied as an additive in battery separator applications within a Poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) polymer matrix with BMIMSCN ionic liquid serving as a solid polymer electrolyte for lithium batteries [14]. When incorporated into the polymer, silicalite-1 enhances tensile strength and Young's Modulus to approximately 14 MPa and 350 MPa, respectively. However, it does not significantly improve ion conductivity compared to PVDF-HFP, which remains around ~10-11 S.cm-1.Structurally, silicalite-1 is identical to ZSM-5 zeolite but differs in having an infinite Si/Al ratio [16]. Consequently, PVDF-HFP alone does not achieve tensile strengths exceeding 15 MPa. Silicalite-1, which lacks Al, is hydrophobic and forms weak interactions with PVDF-HFP. The similar hydrophobic properties between silicalite-1 and PVDF-HFP did not ensure the strength of the resulting membrane. As a result, this study will use zeolite ZSM-5, which has lower hydrophobicity or higher hydrophilicity compared to silicalite-1, as a filler in the CMCh polymer matrix, which is also hydrophilic [17,18].

The hydrophilicity of ZSM-5 zeolite which is higher than silicalite-1 in synthesizing of chitosan-based solid electrolytes is a reason for its selection as a filler. Apart from being related to the Si/Al ratio, its functional groups also contribute the hydrophilic properties of ZSM-5 zeolite. The functional groups of ZSM-5 zeolite consisting of OH, Si-O-Si, and Si-O-Al have been reported by many researchers [16, 19-22]. The Si-O-Al group of ZSM-5 zeolite differentiates its hydrophilicity from silicalite-1.

Carboxymethyl chitosan (CMCh) is a derivative of chitosan, a natural polymer extracted through carboxymethylation.23 Since CMCh is derived from the natural chitosan, it is eco-friendly. Chitosan is sourced from various marine organisms such as crab chitin [24-27], shrimp [3,28,29], and shellfish [30]. The utility of chitosan as a polymer matrix is hindered by its low solubility in water. However, once chitosan is transformed into a semi-synthetic material like CMCh, it becomes amphiphilic and dissolves in water due to its hydrophilic components. The hydrophilicity of CMCh is attributed to functional groups like hydroxyl, carboxyl, and amine. These groups can serve as cross-linking agents with electrolytes, which is why CMCh has been utilized as a polymer matrix in the creation of solid polymer electrolytes (SPE) [3,31]. In the SPE synthesized by Triandani et al., the ion conductivity increases with higher electrolyte concentration, although the mechanical strength of the membrane decreases [3].

In addition to the similar hydrophilic properties of CMCh and ZSM-5, the decision to use ZSM-5 zeolite as a filler in CSE synthesis is based on the structural similarity between the SBU of ZSM-5 zeolite paracrystalline and CMCh [32]. This structural similarity ensures compatibility between the two, so the mechanical strength of the CSE membrane, after the addition of LiClO4 electrolyte, is comparable to that of pure CMCh.

In the our group's research, the mechanical strength properties of ZSM-5 zeolite paracrytalline in relation to the its varying amounts added to the CMCh polymer matrix have not been thoroughly explored [32]. Therefore, this study focuses on optimizing the variations in the weight of ZSM-5 zeolite paracrystalline and its impact on the mechanical strength of the membrane. Additionally, the study investigates in detail the presence of functional groups and chemical interactions, thermal stability, morphology, crystallinity, and ionic conductivity of the CSE membrane, all of which contribute to its mechanical properties.

# Experiments

## Materials

CMCh was purchased from Chi Multiguna, characterized by its molecular weight of 1.13x106 Daltons, an intrinsic viscosity of 73.08 dL/g, a degree of polymerization of 2081.10, and a degree of substitution of 1.02. ZSM-5 zeolite paracrystalline was synthesized without organic structure direction agents.19 Anhydrous technical sodium aluminate (Sigma-Aldrich), sodium hydroxide 50 % pro analysis (Merck), Ludox® HS-40 colloidal silica (Sigma-Aldrich) were used as precursors of ZSM-5 zeolite paracrystalline.

## Synthesis of zeolite ZSM-5 paracrystalline

Synthesis of ZSM-5 zeolite paracrystalline follows the procedure outlined by Tawa et al.32 The synthesis was conducted without an organic structure-directing agent, using a molar ratio of 12 Na2O: 100 SiO2: 2 Al2O3: 2500 H2O.19 Anhydrous technical sodium aluminate was dissolved in distilled water to form mixture A, then 50% pro analysis sodium hydroxide solution was added as a source of Na2O, creating mixture B. Ludox® HS-40 colloidal silica, as a source of SiO2, was added dropwise to mixture B. The mixture was stirred at 300 rpm for 5 hours at 80°C, left at room temperature for 24 hours, and then subjected to a hydrothermal process at 180°C for 24 hours. Afterward, the mixture was washed to a pH of 7 and dried at 80°C for 24 hours [19,32]. The hydrothermal product obtained is referred to as ZSM-5 zeolite paracrystalline (Z5AH), which has been characterized and reported in the previous work [32].

## Preparation of solid composite electrolytes

The CMCh/ZSM-5 membrane was prepared by blending carboxymethyl chitosan with 0.5, 1.5, and 3 wt % ZSM-5 zeolite based on a total sample weight of 1 gram dissolved in 40 mL of distilled water [33]. The weight ratios of zeolite to CMCh were 0.5:99.5, 1.5:98.5, and 3:97, denoted as CZ0.5, CZ1.5, and CZ3 respectively. The mixture was stirred for 20 hours at room temperature, then poured into a petri dish using the solution casting method, and dried at 80°C for 6 hours in an oven. The CSE membranes were subsequently released from the petri dish with the addition of a small quantity of methanol.

1. Top of Form
2. Bottom of Form

## Characterizations

The mechanical strength of the CSE was assessed using the Universal Testing Machine, Tensilon, at the Bandung Ceramics Center. Thermal stability analysis of the CSE membrane was conducted using TG/DTA on a Hitachi STA7300 PPNN ITB. Functional groups and interactions of the CSE were characterized via attenuated total reflection-FTIR (ATR-FTIR). FTIR analysis of CMCh and ZSM-5 zeolite functional groups was performed in the range wave numbers of 4000-500 cm-1 with a resolution of 4 cm-1 using a Bruker Alpha FTIR Spectrometer, the morphology of the CSE membrane was investigated using SEM SU 3500 at PPNN ITB, and its crystallinity degree was assessed by XRD. The conductivity of the CSE was analyzed using electrochemical impedance spectroscopy (EIS), measuring electrical resistance across frequencies ranging from 1 MHz to 1 Hz with the Gamry Ref 3000 instrument at FMIPA ITB Electrochemistry Laboratory.

The equation used to calculate ionic conductivity (σ) is as follows.34

Top of Form

Bottom of Form

(1)

where *l* represents the thickness of the electrolyte membrane, *Rb* denotes the resistance measured through EIS measurements, and S indicates the area of the stainless steel block electrode.

# RESULTS and discussions

## Functional groups and interactions in CSE membranes

Figure 1 displays the FTIR spectra of CMCh, Z5AH, CZ0.5, CZ1.5, and CZ3 membranes. The functional groups in these materials are identified based on the peaks appearing from higher to lower wavenumbers. In the CMCh FTIR spectrum, the wavenumbers of 3431, 2923, 1632, 1060, and 698 cm⁻¹ correspond to the axial stretching vibrations of O-H and N-H, -CH-, asymmetric stretching vibrations of -COO- groups overlapping with -NH2 bending vibrations, stretching vibrations of C-O-C from the glucosamine ring, and vibrations of saccharide ring, respectively [3,4,23,32]. In the FTIR spectrum of Z5AH, the wavenumbers of 3446, 1635, 1094, 960, 796, and 545 cm⁻¹ confirm the presence of -OH group stretching vibrations, H2O bending vibrations, T-O-T internal asymmetry stretching vibrations (where T = Si or Al), ring vibrations of the SBU of ZSM-5 zeolite paracrystalline, T-O-T external symmetry stretching vibrations, and the double-five ring (D5R) vibrations, respectively [19-21,32,35].

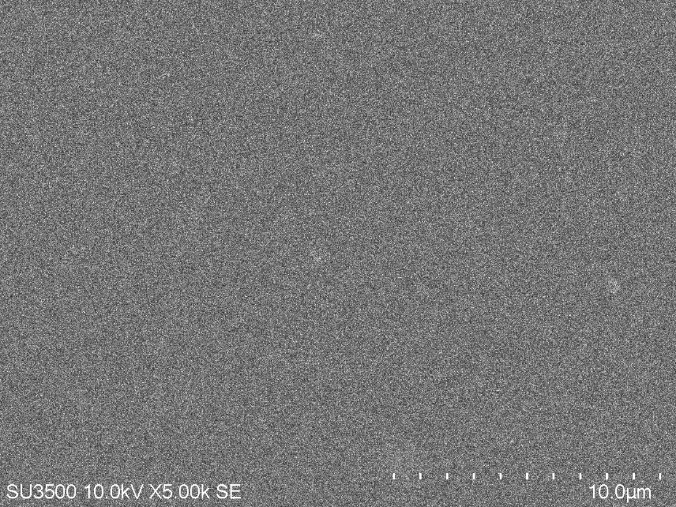
The shift in the wave number of the functional groups of CMCh and Z5AH to lower values in the CMCh/Z5AH (CZ) membranes indicates that an interaction has occurred between the materials forming the solid electrolyte membrane. This interaction is evidenced by the shifts in peaks at the wave numbers 3431, 1632, 1061 cm⁻¹ for CMCh and 3446, 1635, 1094 cm⁻¹ for Z5AH, which move to lower wave numbers: 3252, 1581, 1018 cm⁻¹ for the CZ0.5 membrane, 3242, 1582, and 1017 cm⁻¹ for CZ1.5, and 3246, 1581, and 1018 cm⁻¹ for CZ3.



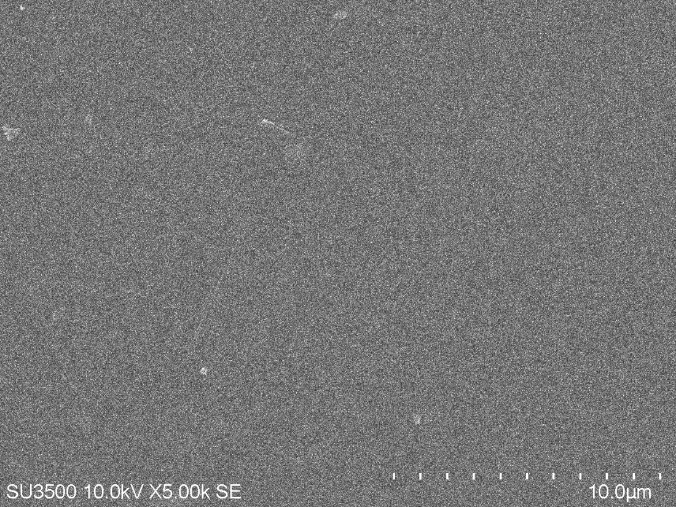
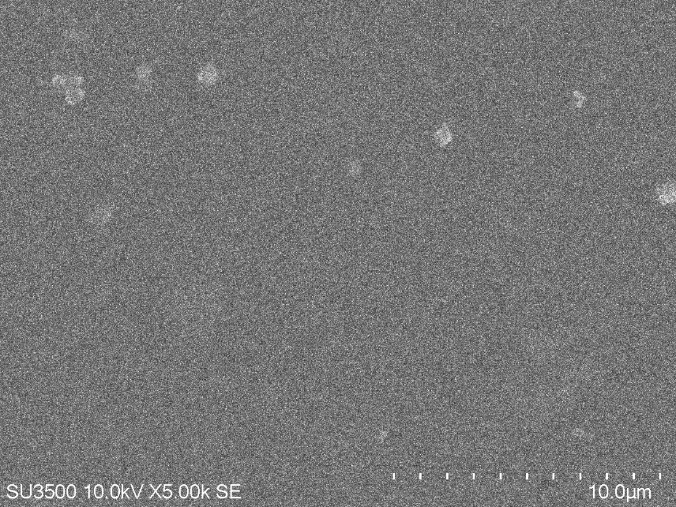
**FIGURE 1.** FTIR spectra of CMCh, Z5AH, and CSE membranes.

## Morphology of CSE membranes

The structure of the CSE membrane was examined using SEM (Figure 2). The surface of CZ0.5 (Figure 2a) appears flat and smooth with minimal zeolite clustering, indicating uniform distribution within the CMCh polymer matrix. Conversely, CZ1.5 (Figure 2b) exhibits slight clustering, while CZ3 (Figure 3c) shows more pronounced agglomeration (marked by red circles). These findings align with previous research, which demonstrated that incorporating small amounts of zeolite into a blend of polyvinyl alcohol and polyvinyl pyrrolidone promotes membrane homogeneity and compatibility [36]. In contrast, higher zeolite content leads to unevenness and reduced uniformity in the membrane structure.



a

b c

**FIGURE 2.** Membrane morphology: (a) CZ0.5 (b) CZ1.5 (c) CZ3.

## Crystallinity of CSE membranes

The diffraction pattern and crystallinity of the CSE membrane were analyzed using graphs and degree of crystallinity calculations with the Origin software (Figure 3 and Table 1). The diffraction pattern reveals that the sequence of 2θ values is CZ1.5 < CZ3 < CZ0.5 (Figure 3), indicating the different degrees of spacing between CMCh polymer chains within the membranes. CZ1.5 exhibits the smallest 2θ value, suggesting the largest inter-chain spacing in CMCh compared to the other membranes.37 In CZ0.5, the inter-chain spacing is presumed to be the narrowest due to insufficient zeolite content to expand the CMCh polymer chains. Meanwhile, CZ3 shows a smaller inter-chain spacing than CZ1.5, likely due to the increased filling of this space by Z5AH and subsequent agglomeration as observed in its morphology (Figure 2c). Furthermore, the phenomenon of different 2 θ in CSE membranes can be elucidated through the concept of zeolite flexibility window. Zeolite Z5AH, synthesized without organic templates and calcination, is thought to possess a density outside the flexibility window, exhibiting flexibility [38,39]. This flexibility is reflected in the 2θ value of Z5AH in the CSE membrane, which shifts to a lower value than pristine Z5AH (2θ of pure Z5AH = 23.18°) [32].

The crystallinity index of the CSE membrane was determined by smoothing the graph in Figure 3 with a resolution of 100 and calculating the areas of crystalline and total (crystalline + amorphous) phases (Table 1). These results indicate that adding zeolite decreases the crystallinity degree of the CSE membranes. This is due to the nano-sized ZSM-5 zeolite paracrystalline [32]. The reduction in crystallinity suggests that ZSM-5 zeolite paracrystalline is evenly dispersed within the CMCh matrix. This observation aligns with mechanical strength data and Young's Modulus, which increases with higher concentrations of ZSM-5 zeolite. In contrast to findings by Barbosa et al., who noted stiffening of PVDF-HFP membranes upon zeolite addition, the hydrophilic nature and lower crystallinity of ZSM-5 zeolite paracrystalline used in this study led to different outcomes [14]. ZSM-5 zeolite paracrystalline exhibits enhanced hydrophilicity and reduced crystallinity compared to silicalite-1, contributing to its distinctive performance characteristics.



**FIGURE 3.** XRD diffraction pattern of the CZ membranes.

**TABLE 1.** Crystallinity degree of CZ membranes.

|  |  |
| --- | --- |
| **Membranes** | **Crystallinity degree (%)** |
| CZ0,5 | 22.10 |
| CZ1,5  CZ3 | 17.51  13.55 |

## Ionic conductivity of CSE membranes

Ion conductivity was indirectly assessed via solid electrolyte resistance following the approach outlined by Halim et al [40]. This method yields ion conductivity values, which are computed using Equation 1. The ion conductivity results for CMCh membranes and CSE membranes are summarized in Table 2.

**TABLE 2.** CMCh and CSE membrane ion conductivity.

|  |  |  |
| --- | --- | --- |
| **Membranes** | **Thickness (mm)** | **Ionic conductivity (S cm-1)** |
| CMCh | 0.05±0.000 | 3.94x10-7 |
| CZ0.5  CZ1.5  CZ3 | 0.05±0.000  0.05±0.002  0.05±0.005 | 2.70x10-6  2.75x10-6  7.22x10-7 |

According to the results in Table 2, the ion conductivity of the CSE membrane has increased compared to that of the CMCh membrane. This improvement is attributed to the presence of ZSM-5 zeolite paracrystalline, which creates additional free space between CMCh polymer chains, enhancing membrane flexibility, particularly evident in the CZ1.5 membrane as indicated by its 2θ value (Figure 3). The CZ0.5 membrane, with 0.5% Z5AH added, shows improved ion conductivity, primarily due to increased space between chains, although it exhibits the least flexibility among the tested membranes. Increasing the zeolite concentration to 3% in CZ3 leads to lower ion conductivity, even though it provides increased free space between polymer chains and greater membrane flexibility than CZ0.5. The lower ion conductivity in CZ3 is attributed to significant zeolite agglomeration observed in its morphology (Figure 2c), which restricts ion mobility [14].

## Mechanical strength characteristics of CSE membranes

The mechanical properties of CSE membranes, including tensile strength, strain, and Young's Modulus, are detailed in Table 3. Tensile strength (σ) represents the maximum stress a material can endure before breaking. In the case of the CSE membrane, tensile strength increases with higher concentrations of ZSM-5 zeolite paracrystalline. However, compared to the pure CMCh membrane, each addition of Z5AH results in distinct mechanical behavior. At CZ0.5, adding Z5AH leads to a decrease in tensile strength. This reduction is attributed to interactions between CMCh and Z5AH creating voids and reducing membrane flexibility to its lowest level. In CZ1.5, the tensile strength remains comparable to that of CMCh. Here, the 1.5% ZSM-5 zeolite paracrystlline content maintains the strength of the CMCh polymer within the CSE membrane, fostering interaction and creating significant voids and flexibility.

The most substantial increase in tensile strength occurs in CZ3, where mechanical strength doubles compared to CZ1.5. This enhancement is due to interactions between CMCh and Z5AH that generate voids within the membrane. However, these voids are filled with flexible agglomeration zeolite (Figures 2b and 2c). These findings align with those of Arshad et al.41 Effective interaction between membrane components and the transfer of zeolite stress to polymer chains can significantly enhance membrane tensile strength.

**TABLE 3.** Summarizes the tensile strength, strain, and Young's Modulus values for CMCh and CZ membranes.

|  |  |  |  |
| --- | --- | --- | --- |
| **Membranes** | **σ (MPa)** | **ε (%)** | **Young’s Modulus (MPa)** |
| CMCh | 53,12 | 2,96 | 4533,4 |
| CZ0,5  CZ1,5  CZ3 | 42,74  48,21  82,59 | 4,78  2,99  7,52 | 2831,2  3440,1  4186,5 |

The impact on tensile strength also elucidates strain behavior of the CSE membrane. At CZ0.5, the strain increases twofold compared to CMCh due to interactions between CMCh and Z5AH, creating voids that amplify membrane strain, albeit with the least stress transfer from Z5AH to the membrane. In CZ1.5, strain is nearly equivalent to CMCh because the interaction between CMCh and Z5AH produces voids while maintaining a balanced stress transfer to the membrane. CZ3 exhibits almost a twofold increase in strain compared to CZ0.5 due to interactions between CMCh and Z5AH, generating voids filled with highly agglomerated, flexible Z5AH. Furthermore, effective material interactions increase the strain.41

Young's Modulus is determined using the linear regression method applied to the stress-strain curve segment. Data for Young's Modulus calculation exhibit linearity with an R² greater than 0.99 and include at least 10 data points. The Young's Modulus of the CZ membrane increases with higher concentrations of ZSM-5 zeolite paracrystalline, indicating greater membrane flexibility.41

## Thermal Stability of CSE Membranes

The thermal stability of membranes composed of pure CMCh, CZ0.5, CZ1.5, and CZ3 was analyzed using TG/DTGA graphs (Figure 4). The graphical representation of TGA and DTGA for CSE membranes (Figures 4a and 4b) shows minimal difference but contrasts slightly with CMCh membranes. The variations are observed in their position on the Y-axis graph (Figure 2a) and during the degradation stages (Figure 2b). The CSE membranes exhibit higher water release below 100°C than the pristine CMCh membrane, indicating that zeolite inclusion creates additional space between CMCh chains, enhancing water molecule absorption. These findings are consistent with those of Xu et al., who reported that zeolite in electrolyte membranes can mitigate side reactions [42].

Figure 4 also indicates that the membrane stability of CMCh and CSE is nearly identical. CMCh, CZ0.5, CZ1.5, and CZ3 membranes showed stability at temperatures of 238.6°C, 236.2°C, 238.2°C, and 252.2°C, respectively. These results demonstrate that adding 0.5% Z5AH weight reduces thermal stability, while 1.5% maintains it, and 3% enhances it. This thermal stability data corroborates the mechanical stability findings discussed earlier.



1. (b)

**FIGURE 4**. (a) TGA of CMCh and CZ, (b) DTGA of CMCh and CZ membranes

The DTGA graph (Figure 4b) illustrates three thermal degradation stages for CMCh membranes, whereas CSE membranes show only two prominent degradation stages. The three stages of degradation of membranes are represented by the percentage reduction of pristine CMCh in black and CZ0.5 in red on the TGA graph (Figure 4a). The first stage of degradation of CMCh, CZ0.5, CZ1.5, and CZ3 were 13%, 17%, 17%, and 17%, respectively. These results indicate that the addition of zeolite leads to an increased adsorption of water molecules. The functional groups of Z5AH enhance the hydrophilicity of the membrane, as evidenced by the FTIR data.

The most significant degradation occurs during the second stage, where the saccharide ring of CMCh undergoes depolymerization and decomposition of acetylated and deacetylated units [43,44]. The percentage of molecules released by the CMCh, CZ0.5, CZ1.5, and CZ3 membranes were 24%, 34%, 35%, and 32%, respectively. The degradation of the CZ membranes was higher than that of the pure CMCh membrane, suggesting that the interactions between the polymer chains were reduced, as indicated by the wave number shifts in the FTIR data and the spaces formed between the chains, as shown by the 2θ data from the previous XRD analysis.

The third degradation stage is exclusive to the CMCh membrane, involving the decomposition of carbon and hydrocarbons.45 The percentage of molecules released in the third stage by the CMCh, CZ0.5, CZ1.5, and CZ3 membranes were 32%, 9%, 9%, and 7%, respectively. The much smaller degradation observed in the third stage of the CZ membranes compared to the pure CMCh membrane suggests that Z5AH in CMCh helps to maintain, and even enhance, the thermal stability of the CMCh-based membrane. These findings support the mechanical strength properties observed in the previous section. Incorporating ZSM-5 zeolite paracrystalline into the CMCh matrix suppresses this decomposition, thereby preserving and potentially reinforcing the membrane against further degradation. This finding suggests that the inherent thermal stability of ZSM-5 zeolite paracrystalline obtained after its interaction with CMCh due to their structural similarity [32]. These findings are also consistent with those of Barbosa et al., who utilized silicalite-1, an MFI zeolite type [14].

# conclusions

The addition of ZSM-5 zeolite paracrystalline into the CMCh polymer matrix role to decrease, sustain, and enhance the mechanical strength of the CSE membrane. ZSM-5 zeolite paracrystalline interacts with CMCh to create substantial free space, and its flexibility facilitates balanced stress transfer to the CMCh polymer chains, thereby maintaining the mechanical strength of the CZ1.5 membrane. The flexibility of ZSM-5 has the most significant impact on the mechanical strength of CSE membranes when there is ample free space, as observed in membranes containing higher concentrations like CZ3. The free space in the CZ1.5 composite membrane and the balanced flexibility of ZSM-5 zeolite support ion conductivity and provide adequate room for further addition of electrolyte salts or ionic liquids.

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