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A Study on Sustainable Eggshell-Derived Hydroxyapatite/CMC Membranes: Enhancing Flexibility and Thermal Stability for Sustainable Development Goals (SDGs)

Ardanari Wahyu Waardhani[1], Atiek Rostika Noviyanti[1], Eny Kusrini[2], Khoirina Dwi Nugrahaningtyas[3], Agus Budi Prasetyo[4], Anwar Usman[5], Ferli Septi Irwansyah[6], Juliandri Juliandri[1]*

[1]Universitas Padjadjaran, Sumedang Indonesia
[2]Universitas Indonesia, Depok, Indonesia
[3]Sebelas Maret University, Surakarta, Indonesia
[4]National Research and Innovation Agency (BRIN), Tangerang Selatan, Indonesia
[5]Universiti Brunei Darussalam, Gadong, Brunei Darussalam
[6]UIN Sunan Gunung Djati Bandung, Bandung, Indonesia
*Correspondence: E-mail: atiek.noviyanti@unpad.ac.id

ABSTRACT

Carboxymethyl cellulose (CMC) is a biopolymer with promising biomedical applications, and its properties can be enhanced through hydroxyapatite (HA) incorporation. This study synthesized HA from chicken eggshells via the hydrothermal method, aligning with Sustainable Development Goals (SDGs) by valorizing biowaste. The synthesized HA exhibited 35.24 nm crystal size and 86.98% crystallinity. HA was integrated into CMC membranes (i.e. 1 and 5%), with and without polyethylene glycol (PEG-400; as a plasticizer). Increased HA content reduced membrane flexibility, but PEG-400 improved structural cohesion. Microscopic analysis revealed better HA dispersion at 5% loading, enhancing membrane performance. Thermal gravimetric analysis confirmed improved thermal resistance, evidenced by a higher decomposition onset temperature. These findings suggest that CMC/HA composite membranes, especially with PEG-400, offer sustainable solutions for biomedical applications, demonstrating superior mechanical and thermal properties while promoting eco-friendly material utilization from biowaste.

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1. INTRODUCTION

Polymer-based membranes play a crucial role in various applications such as separation, filtration, and medical technologies. One commonly used polymer is Carboxymethyl Cellulose (CMC), known for its biodegradable and biocompatible properties [1]. However, for more advanced applications, modifications and enhancements of the polymer's properties are often required.

One of the most widely studied fillers is Hydroxyapatite (HA), a naturally occurring calcium phosphate that constitutes the main component of human bone and teeth. HA is well known for its biocompatibility, bioactivity, and osteoconductive properties, making it highly valuable in biomaterial applications [2]. HA can improve mechanical strength, thermal stability, and chemical resistance when incorporated into polymer matrices like CMC. However, a major drawback of HA is its inherent brittleness, which often reduces membrane flexibility and introduces rigidity into the polymer structure [3]. This challenge necessitates further optimization, particularly in applications requiring a balance between mechanical strength and flexibility.

To address this issue, plasticizers such as polyethylene glycol (PEG) are often introduced into polymer-based membranes. These additives function by reducing intermolecular forces within the polymer chains, thereby improving elasticity and flexibility [4]. The use of plasticizers is particularly important in HA-reinforced membranes, as they help mitigate the brittle nature of HA and enhance the overall mechanical performance of the composite. While HA improves thermal stability, plasticizers generally lower thermal resistance by increasing polymer chain mobility.

The combination of natural polymers like CMC with inorganic fillers such as HA not only improves the mechanical properties of the composite membranes but also enhances their thermal and chemical stability. Recent studies have highlighted the potential of such composites in biomedical applications, including tissue engineering scaffolds and wound dressings, due to their bioactivity and capability to mimic natural extracellular matrices [5-8]. Moreover, the use of these composite membranes in filtration technologies has gained prominence, especially in water treatment processes, where the membranes demonstrate improved durability and contaminant rejection rates [9].

Thermal stability is a crucial factor in membrane applications, especially in environments exposed to high temperatures, such as biomedical sterilization, filtration systems, and electronic components. HA has been reported to increase the degradation temperature of polymer matrices, making them more resistant to thermal decomposition [10,11]. However, most studies have only investigated HA as a standalone additive, without considering the combined influence of HA and plasticizers on both mechanical and thermal properties. Understanding these synergistic effects is essential for designing membranes that can withstand temperature fluctuations while retaining their structural integrity.

Despite significant research on HA-polymer composites, existing studies tend to focus either on HA reinforcement or plasticizer effects independently, without addressing their combined role in improving membrane properties.

This study aims to investigate the effect of HA addition on the mechanical and thermal properties of CMC membranes, with a primary focus on how HA incorporation influences membrane flexibility, strength, and thermal resistance. Additionally, the study explores how plasticizer additives contribute to improving membrane properties by enhancing elasticity while maintaining sufficient thermal stability. However, their interaction with HA filler particles introduces additional complexity, as it affects homogeneity, morphology, and overall

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membrane performance. By gaining a deeper understanding of these interactions, this research aims to contribute valuable insights for the development of efficient and high-performance polymer membranes.

Additionally, the majority of HA used in previous research is derived from synthetic or geological sources [12,13], which are often costly and environmentally taxing. In this study, HA is synthesized from a sustainable calcium source (such as chicken eggshells) using a hydrothermal method, providing an eco-friendly alternative while ensuring high purity and crystallinity. Many reports regarding eggshells have been well-documented [14-23], however not many papers use this material as a source for HA.

The novelty of this research lies in investigating the synergistic effects of HA incorporation and plasticizer addition on the mechanical and thermal properties of CMC membranes. By systematically varying HA content, this study seeks to optimize membrane flexibility, strength, and thermal stability, paving the way for more efficient biopolymer membranes suited for biomedical, environmental, and filtration applications.

This study is expected to provide important contributions to the advancement of biopolymer-based membranes for various real-world applications, including biomedical materials, environmental remediation, and sustainable membrane technologies. In biomedical applications, HA-CMC membranes have the potential to be utilized in wound dressings, drug delivery systems, and tissue engineering scaffolds, where biocompatibility, flexibility, and thermal stability are essential [24-28]. In the environmental sector, these membranes could be applied in water purification and filtration systems, where improved mechanical strength and durability can enhance performance and longevity. Furthermore, by utilizing HA derived from eggshell waste, this study aligns with green chemistry principles, contributing to environmentally sustainable material development [29].

As global efforts continue to focus on sustainability and reducing plastic waste, the development of biopolymer-based membranes enhanced with natural fillers like HA presents a promising alternative to conventional synthetic polymers [30]. Indeed, this supports current issue in the sustainable development goals (SDGs) [31-37]. By refining these properties through the strategic integration of HA and plasticizers, these membranes could be further optimized for applications in medical, environmental, and industrial fields. Ultimately, this research contributes to advancing biopolymer-based membrane technology, paving the way for durable, thermally stable, and flexible materials that can be implemented in emerging technologies and sustainable innovations.

2. METHODS

2.1. Materials

The materials used in this study include distilled water, diammonium hydrogen phosphate ($(NH_4)_2HPO_4$, 99%, Merck), 25% ammonia solution (Merck), CMC, PEG-400 (Sigma Aldrich), and chicken eggshells.

2.2. Synthesis of Hydroxyapatite Nanoparticles via Hydrothermal Method

HA synthesis was carried out using the hydrothermal method with CaO as the precursor, derived from chicken eggshells. CaO and DHP with a molar ratio of Ca/P = 1.67 were dissolved in 50 mL of distilled water. The solution's pH was adjusted to 10 by adding ammonia. The mixture was then transferred into a 100 mL autoclave and heated to 230°C for 48 hours. The resulting HA was washed with distilled water until the pH reached 7 to remove any residual NH_4OH and then dried at 110°C for 2 hours [38].

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2.3. Fabrication of HA-CMC Membrane

The CMC/HA membranes were fabricated using the solution casting method on a glass plate. In this process, a 10% CMC solution was mixed with HA at concentrations of 1 and 5%, with or without the addition of PEG-400. The resulting solution was then cast on the glass plate and dried at 60°C [39].

2.4. Characterization

The crystal structure of the synthesized material was analyzed using X-ray diffraction (XRD) with Ni-filtered monochromated Cu-Kα radiation (λ = 1.54 Å) [40]. The diffraction patterns were recorded over a 2θ range of 10° to 80° at a scanning speed of 10°/min. To perform the Rietveld refinement of hydroxyapatite (HA), HighScore Plus software (PANalytical 3.0.5) was utilized in conjunction with the Inorganic Crystal Structure Database (ICSD) 98-020-3027 [41]. The crystallite size of HA was determined using the Scherrer equation (1):

$$D = K.\lambda / B \cos\theta \quad (1)$$

where D is the crystallite size (nm), K is the Scherrer constant (0.9), λ is the X-ray radiation wavelength (0.15406 nm), B is the value of the peak full width at half maximum (FWHM, radians), and θ is the diffraction angle [42,43].

The morphology of HA was analyzed using a scanning electron microscope (SEM-EDS, TM3030 Plus, Hitachi, Tokyo, Japan) to observe the composite structure and assess the dispersion of HA within the CMC matrix. This characterization offered valuable information regarding the material's morphological features and overall properties [44]. The SEM analysis was conducted at an accelerating voltage of 15.0 kV with a magnification of 1000×. The thermal stability of HA was examined using thermogravimetric analysis (TG-DTA8120, Rigaku, Tokyo, Japan) at a heating rate of 10 °C/min, with temperatures reaching up to 900 °C. TGA is a commonly employed technique for evaluating the thermal properties of materials by tracking weight variations in response to temperature changes. This analysis offers valuable information on material degradation, stability, and phase transformations [45].

3. RESULTS AND DISCUSSION

3.1. Conversion of CaCO3 into CaO

Calcium carbonate ($CaCO_3$) begins to thermally decompose at temperatures between 700°C and 750°C [46]. This decomposition is an important precursor step in the production of calcium oxide (CaO), which has extensive applications in various industrial processes. At temperatures reaching 1000°C, $CaCO_3$ undergoes complete thermal decomposition, resulting in the formation of CaO and the release of carbon dioxide (CO_2) gas, as described by reaction (2) **[38]**.

$$CaCO_{3\,(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_{2\,(g)} \quad (2)$$

In this reaction, the solid calcium carbonate transitions into calcium oxide, a crucial intermediate for numerous chemical reactions, including the synthesis of HA The phase composition of the eggshells after calcination at 1000°C for 5 hours, as summarized in **Table 1**, shows a predominant conversion to CaO, which is consistent with the expected behavior of $CaCO_3$ under high temperatures.

The yield of CaO from this thermal decomposition process was calculated to be 54.88%, which approaches the theoretical yield of 56%. This yield efficiency demonstrates that the calcination process was effective, though some material loss or incomplete decomposition

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may account for the small deviation from the theoretical value. To further characterize the composition of the calcined eggshells, XRF (X-ray fluorescence) analysis was conducted. This analysis revealed that the CaO content in the sample was 91.14%. The remaining 8.86% could be attributed to minor impurities or residual unreacted materials, which is typical in natural sources such as eggshells [47].

This CaO was subsequently utilized for the formation of HA by reacting it with diammonium hydrogen phosphate (DHP), serving as the phosphate source. The molar ratio of calcium to phosphate ions is critical in forming stoichiometrically pure hydroxyapatite [48]. Based on the XRF data, the precise amount of calcium oxide was calculated, ensuring that the Ca molar ratio was maintained at approximately 1.67, which is the ideal ratio for hydroxyapatite formation [38]. This ratio not only influences the phase purity of the hydroxyapatite but also plays a crucial role in its crystallinity and bioactivity when used in biomedical applications, such as bone regeneration. By optimizing the calcination conditions and controlling the molar ratio in the subsequent reaction, this study successfully produced high-purity hydroxyapatite from a natural and sustainable source. This highlights the potential of eggshells as an eco-friendly and cost-effective raw material for producing calcium-based compounds, contributing to both waste valorization and material innovation in various fields.

Table 1. The phase composition of the eggshell after calcination.

Element	%mass
Ca	91.14
Al	4.19
Mg	3.70
Si	0.32
Ni	0.16
Sr	0.08
Px	0.37

3.2. HA Crystal Identification

HA phase structure formed was identified using XRD. **Figure 1** displays the XRD diffractogram used to determine the hydroxyapatite phase structure. The XRD analysis results indicate that HA has a hexagonal crystal structure with a space group of $p_{63/m}$. According to ICSD 98-020-3027 [41], hydroxyapatite shows 2θ peaks at angles of 10.8, 16.8, 21.9, 26.1, 28.2, 28.9, 31.8, 32.2, 32.9, 39.8, 42, 43.5, 46.7, 48.2, 49.6, 50.7, 53.2, and 64°, with corresponding hkl planes (110), (101), (020), (111), (002), (102), (210), (211), (112), (300), (202), (130), (131), (113), (222), (132), (213), (321), (004), and (323), respectively.

In this study, the crystallite size of HA was calculated based on X-ray diffraction (XRD) analysis on the (211) crystal plane using the Debye-Scherrer equation [49]. This equation is a tool for estimating the average crystallite size from XRD patterns [50]. The crystallite size was determined by utilizing the width of the diffraction peak at the 2θ angle corresponding to the observed crystal plane. Additionally, crystallinity was also calculated in this study. Crystallinity is the ratio between diffraction peaks that indicate a crystalline structure and the amorphous or disordered regions in the X-ray diffraction pattern [51]. It provides information on the degree to which the material possesses an ordered crystal structure.

The results of this study were compared to previous research conducted by Noviyanti *et al*. [38], as shown in **Table 2**. In this comparison, the average crystallite size of hydroxyapatite obtained in this study was slightly smaller than the crystallite size reported in the previous

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research. Moreover, the crystallinity of the sample in this study was higher compared to the sample from the previous study.

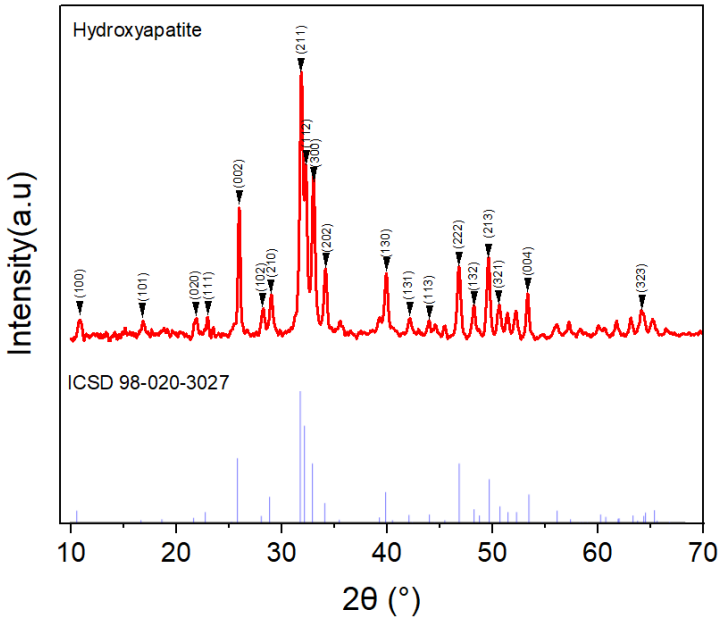

Figure 1. XRD pattern of hydroxyapatite.

Table 2. Lattice parameter, crystallite size, and crystallinity of HA.

Sample	Lattice Parameter		Crystallite Size (nm)	Crystallinity (%)
	A=B (Å)	C (Å)		
HA (this work)	9.4168	6.8765	35.24	86.98
HA [21]	9.4168	6.8794	35.28	72.76

The variation in lattice parameter c observed in this study compared to Noviyanti *et al*. [38] can be attributed to the differences in CaO content used during the synthesis of HA. In Noviyanti *et al*. [38], the CaO content was 97%, while in this study, a lower concentration of 91% was employed. The reduced CaO content likely introduced calcium vacancies or led to a non-stoichiometric phase in the HA crystal structure. This deficiency of calcium ions (Ca^{2+}) in the crystal lattice can induce slight distortions, particularly along the c-axis, which is more susceptible to compositional changes due to its orientation in the hexagonal structure of HA. In contrast, the higher CaO content used by Noviyanti et al. would result in a more complete and stable calcium distribution, yielding a slightly larger lattice parameter c. Thus, the CaO content plays a crucial role in determining the crystal structure and lattice parameters, particularly along the c-axis, influencing the overall properties of the synthesized HA [52,53].

3.3. HA-CMC Composite

The pure CMC membrane was successfully obtained through the solution casting method, resulting in a membrane with good flexibility as shown in **Figure 2**. At this stage, it is important to note that HA-CMC composites were also produced by adding various amounts of HA. The effects of HA addition on the membrane properties were then observed. The results indicate that as the amount of HA added to the composite increased, the flexibility of the resulting membrane decreased. This phenomenon can be attributed to the brittle nature of HA [3].

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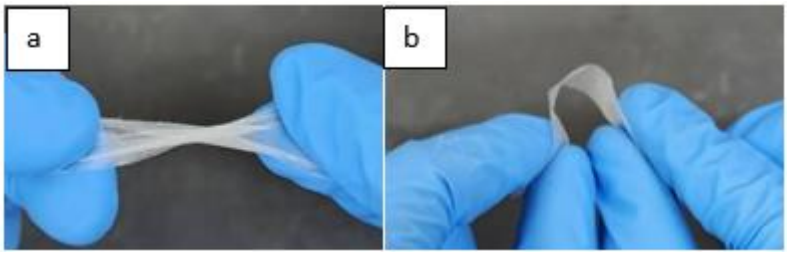

Figure 2. The flexibility of Pure CMC Membrane: (a) Twisted, and (b) Bent.

To address the changes in mechanical properties caused by the brittle nature of HA, PEG-400 was added as a plasticizer. The primary objective of incorporating PEG-400 is to improve the flexibility of the membrane, as maintaining a balance between mechanical strength and flexibility is essential for various applications, such as in biomedicine, packaging, and membrane technologies [54]. PEG-400 acts as a softening agent by reducing the intermolecular interactions between CMC and HA within the membrane matrix, thereby mitigating the brittleness that results from HA inclusion.

The mechanism behind PEG-400's effectiveness lies in its ability to increase the free volume within the polymer network, which enables the polymer chains to move more freely [55,56]. This disrupts the rigid structure formed by the CMC-HA interactions and enhances the membrane's flexibility. Additionally, PEG-400 improves the dispersion of HA particles in the matrix, preventing the formation of agglomerates that could compromise the mechanical properties of the composite [57]. As a result, the membrane can maintain good mechanical integrity, even at higher HA concentrations, which would otherwise cause significant brittleness.

Furthermore, PEG-400 not only enhances flexibility but also improves the overall durability and processability of the membrane. By reducing stiffness, the membrane becomes easier to handle and more adaptable for practical uses. The effect of PEG-400 addition on the HA-CMC membrane is visually represented in Figure 3, where the comparison between membranes with and without PEG-400 demonstrates the improvement in mechanical properties.

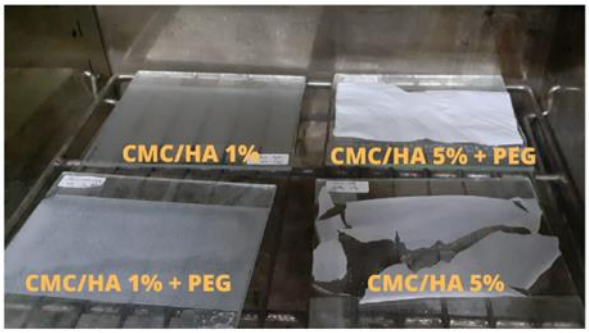

Figure 3. CMC/HA membranes with and without PEG-400.

CMC begins to decompose at approximately 180°C [58]. Testing of membrane shrinkage in an oven at 180°C for 2 hours showed that the pure CMC membrane undergoes significant shrinkage. This shrinkage indicates that CMC is susceptible to thermal degradation at this temperature. When HA is incorporated into the CMC matrix, its presence influences the thermal behavior of the composite. HA is known for its excellent thermal stability and can withstand high temperatures without undergoing significant decomposition or structural changes. As a result, the inclusion of HA in the HA-CMC composites provides several benefits:

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(i) Thermal Protection: HA acts as a thermal barrier [59], helping to protect CMC from reaching its decomposition temperature too quickly. This reduces the rate of thermal degradation of CMC.

(ii) Heat Distribution: HA aids in the even distribution of heat within the composite [10], preventing localized overheating that could accelerate the degradation of CMC.

However, when a lower concentration of HA is used, the membrane exhibits more significant shrinkage compared to higher HA concentrations, as shown in **Figure 4**. This suggests that while HA improves thermal stability, its concentration in the composite impacts the overall thermal behavior. The interaction between CMC and HA, as well as the characteristics of each component, plays a crucial role in determining the thermal stability and performance of the membrane.

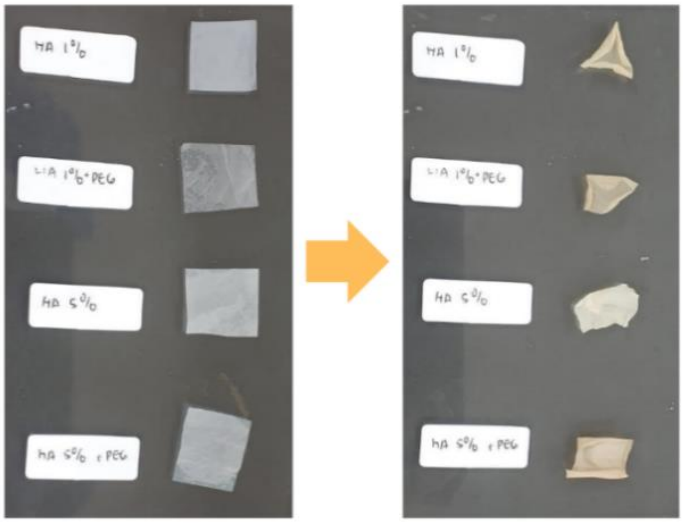

Figure 4. Shrinkage of CMC/HA membranes after heating at 180°C for 2 hours.

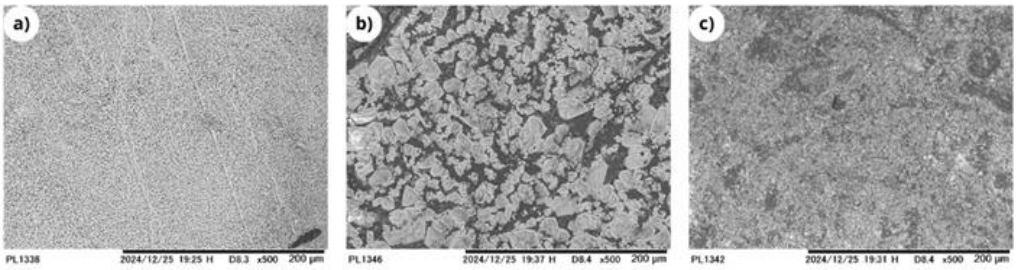

Figure 5. SEM Images. a) pure CMC, b) CMC-HA 1% PEG, c) CMC-HA 5% PEG.

SEM analysis highlights significant differences in the morphology and dispersion of HA particles within the CMC matrix, particularly between samples with varying HA concentrations (Figure 5). The SEM image of pure CMC reveals a smooth and uniform surface, characteristic of a neat polymer matrix without any fillers. While this uniformity indicates structural continuity, it also suggests the absence of reinforcement, which could limit its mechanical strength and thermal stability under demanding conditions.

For the composite containing 1% HA, the SEM image reveals an uneven distribution of HA particles. Clusters or agglomerates are evident, suggesting poor dispersion of HA within the matrix. This non-homogeneous distribution is likely due to the low concentration of HA, which limits the interaction between the filler and the polymer. The agglomerates create localized stress points, potentially reducing the composite's overall mechanical performance and

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flexibility [60]. Furthermore, voids observed in the structure indicate insufficient integration of HA particles, which could further weaken the material. In contrast, the SEM image of the composite with 5% HA shows a much more uniform and homogeneous distribution of HA particles throughout the matrix. The increased HA concentration enhances filler-polymer interactions, minimizing particle agglomeration and promoting even dispersion. This homogeneity contributes to consistent reinforcement across the membrane, resulting in improved mechanical properties such as flexibility and strength.

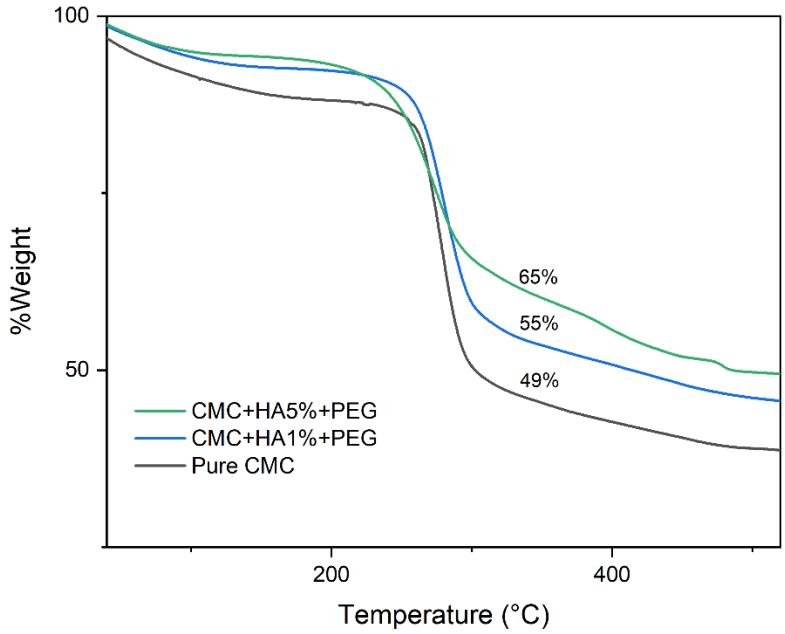

Figure 6. TGA curve of CMC Membranes.

Thermogravimetric analysis (TGA) further supports the enhanced thermal stability imparted by the incorporation of HA (**Figure 6**). The pure CMC membrane exhibits significant weight loss in three major degradation stages. The initial weight loss, observed below 150°C, corresponds to the evaporation of absorbed moisture and residual solvents [61]. The second degradation stage, occurring between 200–350°C [62], is associated with the decomposition of the polymer backbone, leading to a drastic weight reduction. This phase is primarily attributed to the decarboxylation of COO− groups in CMC, leading to the release of volatile decomposition products and CO_2 loss [63]. The presence of PEG in the composite helps to slightly stabilize this degradation process by interacting with the polymer chains, but the overall structural integrity is still largely dependent on the filler content.

Additionally, the decomposition onset temperature (Tonset) shifts positively with increasing HA content, further demonstrating improved thermal resistance. The Tonset for pure CMC is recorded at approximately 250°C, whereas the CMC-HA 5% + PEG composite exhibits a Tonset above 280°C. This upward shift confirms the stabilizing effect of HA, which hinders thermal chain scission and reduces the rate of polymer degradation under high temperatures.

Overall, the findings suggest that increasing HA concentration from 1% to 5% significantly improves the composite's morphology and performance. The more uniform dispersion of HA in the 5% composite ensures balanced mechanical and thermal properties, making it more suitable for advanced applications in filtration, biomedical devices, and energy storage

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systems. These observations underscore the importance of optimizing HA concentrations to achieve a well-integrated and functional composite material.

This research provides an innovative contribution by addressing the dual challenge of mechanical strength and thermal stability in CMC-based membranes through the strategic integration of HA and the addition of PEG-400 as a plasticizer. This approach not only enhances the material properties but also broadens the potential applications of CMC-HA composites across various industrial sectors. The systematic investigation of HA's role in both mechanical and thermal properties offers a comprehensive understanding that is essential for the development of composite materials with improved performance and durability tailored to specific application needs.

4. CONCLUSION

The thermal characteristics of HA, particularly its stability at high temperatures, significantly impact the overall thermal stability of CMC membranes formed through the composite process. The high thermal stability of HA contributes to improving the membrane's resistance to higher temperatures, making it more suitable for applications in environments subject to high temperatures or significant temperature fluctuations.

However, while the addition of HA enhances the thermal stability of the CMC membrane, it also affects the mechanical strength of the composite. High amounts of HA can reduce the mechanical strength of the CMC matrix due to the brittle nature of HA, which leads to decreased flexibility and increased rigidity.

To counteract this reduction in mechanical strength, the addition of plasticizers such as PEG-400 can be beneficial. PEG-400 acts to improve the flexibility and mechanical strength of the membrane by reducing the interactions between CMC and HA, thus mitigating the brittleness introduced by HA.

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6. AUTHORS' NOTE

The authors declare that there is no conflict of interest regarding the publication of this article. The authors confirmed that the paper was free of plagiarism.

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