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The Impact of Silica Nanoparticles on the Properties of WPI/CMC Biocomposite Films for Packaging Applications

Mukhlishien, Syahiddin DS*, Medyan Riza, Azwar

Chemical Engineering Department, Engineering Faculty, University Syiah Kuala, Banda Aceh, Indonesia
***Corresponding author**: syahiddindahlan@usk.ac.id

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Abstract
WPI/CMC biocomposite films reinforced with silica offer a biodegradable alternative to traditional plastics. The primary aim was to assess the impact of silica reinforcement on the films' physical, mechanical, water barrier, and thermal properties, which are crucial for packaging applications. Silica nanoparticle reinforcement significantly enhanced the tensile strength of WPI/CMC biocomposite films, reaching a maximum of 27.07 MPa at a 7% silica concentration. This enhancement in tensile strength came at the cost of reduced elongation, which decreased from 26.48% to 8.32%. The thickness of WPI/CMC biocomposite films with silica addition ranged from 0.126 to 0.371 mm. Silica incorporation significantly reduced water absorption, with a decrease from 83.23% to 63.33%. Tensile strength varied significantly, ranging from 2.02 to 27.07 MPa. Similarly, the elongation values ranged widely, from 7.42% to 26.48%. Thermal properties increased with the increase of silica. The morphology of the biocomposite films with 1%, 3%, 5%, 7%, and 9% silica additions exhibited uneven surfaces. The morphology of the biocomposite films was also affected by silica incorporation. The addition of silica nanoparticles resulted in uneven surfaces, which may influence the film's barrier properties and overall performance. Silica nanoparticle reinforcement offers a promising approach to enhance the mechanical properties of WPI/CMC biocomposite films. However, careful optimization of silica concentration is crucial to balance strength and flexibility.
Keywords: *Silica nanoparticle, WPI, CMC, biocomposite films, Thermal properties*

Abstrak
Film biokomposit berbasis whey protein isolate (WPI) dengan penambahan karboksimetil selulosa (CMC) yang diperkuat dengan silika menawarkan alternatif biodegradable untuk plastik tradisional. Tujuan utama penelitian ini adalah untuk menilai dampak penguatan silika terhadap sifat fisik, mekanik, penghalang air, dan termal film, yang sangat penting untuk aplikasi kemasan. Penguatan dengan nanopartikel silika secara signifikan meningkatkan kekuatan tarik film biokomposit WPI/CMC, mencapai nilai maksimum 27,07 MPa pada konsentrasi silika 7%. Peningkatan kekuatan tarik ini diimbangi dengan penurunan perpanjangan, yang menurun dari 26,48% menjadi 8,32%. Ketebalan film biokomposit WPI/CMC dengan penambahan silika berkisar antara 0,126 hingga 0,371 mm. Inkorporasi silika secara signifikan mengurangi penyerapan air, dengan penurunan dari 83,23% menjadi 63,33%. Kekuatan tarik bervariasi secara signifikan, berkisar antara 2,02 hingga 27,07 MPa. Demikian pula, nilai perpanjangan bervariasi secara luas, dari 7,42% hingga 26,48%. Sifat termal meningkat dengan peningkatan konsentrasi silika. Morfologi film biokomposit dengan penambahan silika 1%, 3%, 5%, 7%, dan 9% menunjukkan permukaan yang tidak rata. Morfologi film biokomposit juga dipengaruhi oleh inkorporasi silika. Penambahan nanopartikel silika menghasilkan permukaan yang tidak rata, yang dapat mempengaruhi sifat penghalang dan kinerja keseluruhan film. Penguatan dengan nanopartikel silika menawarkan pendekatan yang menjanjikan untuk meningkatkan sifat mekanik film biokomposit WPI/CMC. Namun, optimasi konsentrasi silika yang cermat sangat penting untuk menyeimbangkan kekuatan dan fleksibilitas.
Kata Kunci: *Nanopartikel Silika, Film Biokomposit, WPI, CMC, Sifat Termal*

1. Introduction

The fast increase in using biodegradable materials for food packaging is to keep food fresh longer and protect the environment [1]. Natural-based materials are a preferable alternative to oil-based plastics for food packaging. This helps us use less harmful materials and makes use of the many natural resources we have [2]. Natural materials like PLA, starch, and chitosan are being utilized to develop innovative, eco-friendly food packaging films [3-4].

Whey protein isolate (WPI) is a protein-rich biological substance. The compound is extracted from milk by-products during the production of cheese and tofu. Previous studies have demonstrated that WPI has superior film-forming and gas barrier capabilities in comparison to other polymers derived from petroleum [5-7]. Nevertheless, the films produced from WPI exhibit limitations in their packing capabilities due to their inadequate performance as a moisture barrier and their weak mechanical properties, which can be attributed to a significant presence of hydrophilic amino acids [8-9]. This work investigates the incorporation of nanoscale elements into the structure of WPI films as a means of reinforcing or chemically modifying them to address their inherent weaknesses. Hence, the issue above was successfully resolved with the incorporation of carboxymethyl cellulose. CMC, a readily available and affordable biopolymer, can effectively improve the flexibility and processability of the films. By combining WPI with CMC, we can create innovative biocomposite films with enhanced properties, offering a more sustainable and functional packaging solution. Figure 1 illustrates the process of creating and the potential applications of protein-polysaccharide-based biocomposites in food packaging [10].

CMC, a versatile cellulose derivative, is produced through the etherification of cellulose. This biomaterial finds widespread application as a stabilizer, food thickener, and even in the production of bioplastics, often used in conjunction with crosslinking techniques [11]. Research by Hasanah et al. has shown that the addition of CMC to bioplastics can significantly accelerate their biodegradation rate [12]. The research suggests a positive correlation between CMC concentration and microbial degradation rate. However, the presence of starch can impede water solubility. To address this challenge, Bayu et al. proposed adding CMC to the plastic mixture to improve its surface texture and water solubility. To address this challenge Ihsan et al. [12] proposed adding CMC to the plastic mixture to improve its surface texture and water solubility. This, combined with the use of CMC, leads to a more eco-friendly and long-lasting plastic material.

Fig. 1: Protein-polysaccharide biocomposites for food packaging [10]

Silica can be utilized as a filler in biopolymer films due to its notable porous structure, significant surface activity, and compatibility with biological systems [13]. The mechanical properties of maize starch and LDPE biocomposites were enhanced through the integration of silica into their matrix [14]. There is a need to augment the concentration of filler integrated into biocomposite films. Hence, the augmentation of silica content can impact the physical, mechanical, and thermal characteristics of WPI/CMC biocomposite films, owing to the advantageous features and functional attributes associated with silica. The effects of silica addition on the performance of WPI/CMC films, including their flexibility, strength, and heat resistance, will be investigated through specific tests in this research.

2. Material and Methods

The study utilized standard laboratory equipment (beakers, Petri dishes, spatulas) and specialized instruments (magnetic stirrer, thermometer, digital balance, hot plate, oven). The primary materials employed in this study were CMC, whey, and silica. The main materials used were CMC, whey, and silica. Distilled water, aluminum foil, and tissue paper were also utilized as auxiliary materials in the biocomposite fabrication and testing processes. The variables held constant in this study were whey concentration, stirring speed, heating and drying temperatures, and cooling time. Meanwhile, the variables that were manipulated were CMC and silica concentrations to observe their effects on the properties of the resulting biocomposites.

Silica dissolution stage with distilled water. Silica was dispersed into 50 mL of distilled water using an ultrasonic bath for 1 hour at room temperature. The concentrations of silica dispersion used were 1%, 3%, 5%, 7%, and 9% (b/v) by weight of WPI. Silica that has been dispersed into distilled water was then heated at 70°C for 30 minutes.

WPI/CMC incorporation with silica

A 5-gram sample of whey protein was dissolved in 100 milliliters of distilled water and stirred at 400 rpm for 90 minutes. The resulting solution was subsequently heated to 70 degrees Celsius for 60 minutes. Then CMC was added with varying concentrations, namely 0.75 and 1 gram, to the solution before cooling. Silica nanoparticles were incorporated into distilled water at concentrations ranging from 1% to 9% by weight. The mixture was then sonicated for one hour to break up any clumps of nanoparticles and ensure a uniform dispersion. The dispersion was then heated to 70 degrees Celsius for 30 minutes to further enhance nanoparticle distribution and improve the overall properties of the solution. The next stage is the process of combining the two solutions. At this stage the silica solution is added to the WPI solution with CMC, after all the solutions mixed, the solution was printed in a petri dish and dried at 55°C, then cooled to room temperature [15].

Analysis of WPI/CMC-silica biocomposite films

The biocomposite films were characterized by measuring thickness (using a push-pull gauge), swelling, tensile strength, elongation, SEM, FTIR, and TGA. The thickness of the biocomposite films was measured using a push-pull thickness gauge with an accuracy of 0.01 mm. Five measurements were taken from different locations on 2 x 5 cm film samples, and the average value was reported. The swelling capacity of the biocomposite films was determined by immersing 50 mm x 50 mm samples in phosphate buffer saline (PBS) solution at pH 7.4 for 30 minutes. The films were then removed, gently blotted dry, and weighed. The swelling percentage was calculated based on the weight gain. Tensile Strength and Elongation: Tensile strength and elongation were measured using a Computer Universal Testing Machine HT-2402 according to ASTM D-682 [16].

The biocomposite film's morphology was analyzed using SEM on 2x2 cm samples. The SEM test results also reveal the distribution of filler particles within the matrix, indicating whether the filler particles are evenly dispersed or not. Functional group analysis of the biocomposite film was conducted using a Shimadzu IR Prestige 21 FTIR spectrometer This test identifies the functional groups in the biocomposite film. For this analysis, the sample was placed in a sample holder and inserted into the spectrometer cavity. This technique entails heating the sample from 40°C to 600°C and recording any mass loss or gain resulting from decomposition, oxidation, or dehydration processes. This information provides insights into the thermal stability and composition of the material. This technique can characterize materials that undergo weight loss or gain due to decomposition, oxidation, or dehydration [17].

3. Results and Discussion

Thickness of biocomposite film

The thickness of WPI/CMC-based biocomposite films, with silica concentrations ranging from 1% to 9%, is depicted in Figure 2. Figure 2 reveals that the biocomposite films with silica additions exhibit a thickness between 0.126 and 0.350 mm. The film thickness obtained in this study increased for all biocomposite films with an increase in silica concentration. The addition of increasing silica concentration can increase film thickness. This is due to the increasing number of silica particles used as fillers in filmmaking, so it can be ascertained that film thickness can increase along with the addition of particles from the filler [17]. The biocomposites with 1-7% silica met food industry standards for food packaging. The maximum thickness of biocomposites is 0.25 mm, following Japanese Industrial Standards (JIS).

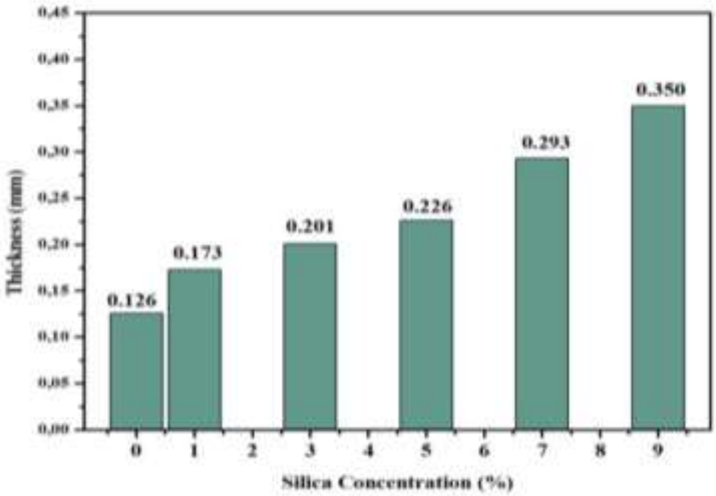

Fig. 2: The effect of silica concentration on WPI/CMC biocomposite film thickness

The observed increase in film thickness can be explained by the filler effect of silica nanoparticles, which occupy space within the biocomposite matrix. As more silica particles are added to the biocomposite matrix, they occupy space within the film structure. This increased volume leads to a corresponding increase in film thickness. The biocomposite films produced in this study, with silica concentrations up to 7%, adhere to this standard and are suitable for food packaging purposes. However, further investigation is required to determine the optimal silica concentration for achieving desired film properties while remaining within the thickness limit.

Water absorption (swelling) of biocomposite film

The results of this test for the films with silica are shown in Table 1. The integration of silica nanoparticles within biocomposite films has surfaced as a highly advantageous approach to augment their functional characteristics, particularly with regard to water resistance. The addition of silica nanoparticles significantly reduces the water absorption of the biocomposite films. This reduction leads to diminished water absorption. This augmentation in water resistance can be ascribed to the distinctive attributes of silica nanoparticles and their interactions with the polymeric matrix. Silica nanoparticles, acting as effective fillers, occupy the voids and interstices within the polymer matrix. This filling effect leads to a denser and more compact film structure. The diminished porosity of the film restricts the diffusion of water molecules, consequently impeding water absorption. Furthermore, the hydrophilic properties exhibited by silica nanoparticles may significantly improve water resistance.

Silica nanoparticles possess a hydroxylated surface. These groups interact with polymer chains through hydrogen bonds. This interaction improves the film's structural integrity. Additionally, it decreases the film's water absorption capacity. As the proportion of silica nanoparticles increases, the capacity for water absorption within the biocomposite films notably decreases. This phenomenon is clearly illustrated in the data presented in Table 1, wherein the films containing elevated silica content demonstrate reduced water absorption values. Careful optimization of silica concentration can improve water resistance. This can be done without negatively affecting other film properties. Reduced water absorption enhances the suitability of these films for applications like food packaging. By restricting the transmission of water vapor, these films can significantly prolong the shelf life of food items and preserve their quality. Moreover, the enhanced mechanical characteristics attributed to the incorporation of silica can bolster the resilience and strength of the films, thereby rendering them more appropriate for packaging and various applications.

Table 1: Swelling test results of WPI/CMC biocomposite films with various silica concentrations

Silica concentration (%)	Swelling (%)
0	83.23
1	79.61
3	75.48
5	73.29
7	68.56
9	63.33

The inclusion of silica nanoparticles, as evidenced by Table 1, lowers the hydrophilic nature of the biocomposite film. Silica, acting as a filler, strengthens the biocomposite film. The control biocomposite film, without silica, absorbs 83.23% water. Adding silica (1%, 3%, 5%, 7%, and 9%) reduces water absorption. The associated values of water absorption are 79.61%, 75.48%, 73.29%, 68.56%, and 63.33%. Increased silica concentration leads to decreased swelling. Lower water absorption improves film properties. Higher water absorption compromises film properties. This is because the biocomposite film with the addition of silica has hydrophilic properties, as in silica, which has filler and reinforcement properties. When added to the material, silica fills the gaps between particles or other fibers. This results in increased density and stiffness of the material. Silica limits the available space for water. This reduces the material's water absorption capacity. The combination of the filler effect, namely silica, can cause a decrease in the swelling test value of the biocomposite film [18].

Functional groups of the biocomposite film

Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the functional groups present in the biocomposite film samples. The resulting spectrum displayed multiple peaks at specific wavelengths. These peaks indicated the presence of various functional groups within the biocomposite film. Figure 3 illustrates the wavelengths corresponding to these functional groups. As shown in Figure 3, the spectrum displays several absorption peaks. In this case, the six samples have the same absorption peaks, namely at wave numbers 1840-1800 cm^{-1}, there is a C=O functional group, which indicates the presence of anhydride functional groups in the biocomposite film sample. The presence of C≡C functional groups, observed at wave numbers 2100-2260 cm-1, indicates the presence of alkyne groups in the film. The O-H functional groups, evident at wave numbers 2400-3400 cm^{-1}, suggest the presence of carboxylic acid functional groups in the biocomposite film. The absorption peaks at wavenumbers 1103-803 cm^{-1} correspond to the symmetric and asymmetric stretching vibrations of Si-O-Si bonds. This indicates that these functional groups are found in the constituent material of the biocomposite film itself, namely silica.

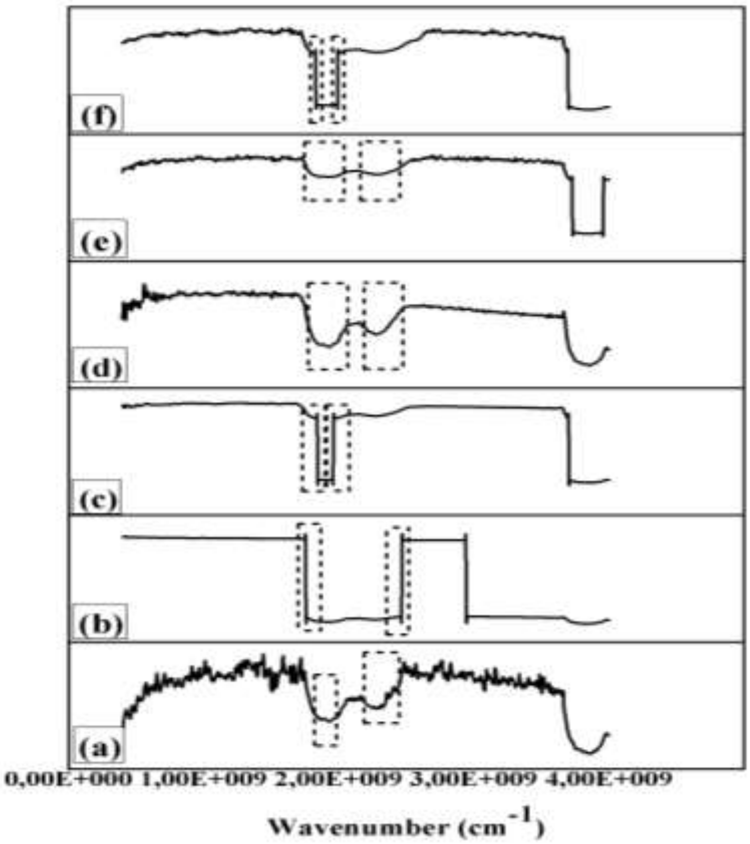

Fig. 3: FTIR spectra of WPI/CMC biocomposite films with 15% CMC with different persen silica (a) without silica, (b) 1% silica, (c) 3% silica, (d) 5% silica, (e) 7% silica, and (f) 9% silica

The absorption region at the wave number showing the C=O functional group is characteristic of CMC, while the absorption band showing the O-H functional group indicates the presence of hydrogen

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bonds in the film. This O-H group comes from CMC, while hydrogen bonding occurs when O atom molecules contained in CMC interact with H atoms from amylose and amylopectin [19]. This shows that the functional groups obtained are in accordance with the film constituent material itself. The presence of C=O functional groups in the synthesized film indicates that the film has biodegradability properties. This is because C=O is a hydrophilic group. The ability of the C=O functional group to bind water molecules from the environment results in more microorganisms that can enter the film matrix along with the higher intensity of the hydrophilic group [20].

Thermal Performance of Biocomposite Film Using TGA

The TGA test was conducted within a temperature range of 30-600°C, and every segment of the resulting graph exhibited a reduction in mass. Figure 4 illustrates a significant diminishment in mass, characterized by shrinkage percentages of 71.34%, 71.68%, 68.34%, 68.65%, 68.70%, and 66.40%. The TGA test is used to assess the mass loss of biocomposite film samples and to identify the factors contributing to this loss. Several mechanisms can contribute to mass loss in biocomposite films. These mechanisms comprise moisture evaporation, organic matter degradation, and chemical degradation. During TGA testing, the biocomposite film sample undergoes a gradual heating process under controlled temperature conditions. As the sample is heated, the TGA equipment detects and records changes in mass. A graphical representation is subsequently developed to illustrate the correlation between mass and temperature, thereby facilitating the determination of the temperature at which mass reduction transpires [21].

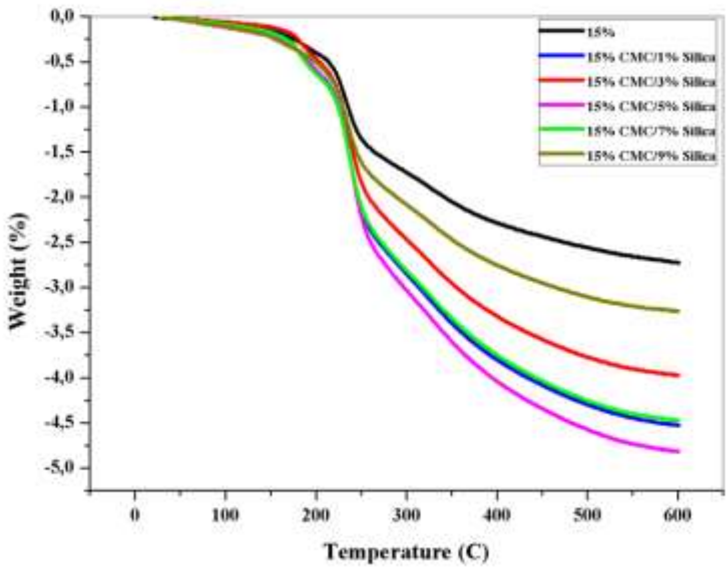

Fig. 4: TGA profiles of WPI/CMC biocomposite film samples at various silica concentrations

Figure 4 illustrates the influence of silica on the thermal characteristics of the biocomposite film. The thermal degradation behavior of the specimen can be influenced by a multitude of factors. Such factors encompass chemical reactions, physical alterations, and the presence of aggregates or non-homogeneously distributed silica particles. Additionally, silica itself has stable thermal properties with a high melting point. As the concentration of silica within the biocomposite film escalates, there is a corresponding tendency for both the initiation and peak temperatures of thermal decomposition to rise. This indicates that the addition of silica enhances the thermal stability of the biocomposite film [22].

4. Conclusion

This study showed that silica nanoparticles can significantly improve the tensile strength of WPI/CMC biocomposite films, but may reduce elongation. Silica also reduced water absorption, making the films more suitable for packaging. Silica nanoparticles significantly increased tensile strength to 27.07 MPa at a 7% concentration, but reduced elongation. They also improved water resistance. The morphological analysis revealed uneven surfaces in the biocomposite films with silica, which may impact their barrier properties. This study looked at how adding tiny silica particles to WPI/CMC films could make them stronger. We found that these tiny particles, called nanoparticles, really helped make the films stronger, especially at a 7% concentration. However, this also made the films less flexible. Silica also improved water resistance, making the films ideal for packaging. This is crucial for maintaining food freshness and preventing moisture damage. Further research is needed to optimize silica concentration and explore other additives. By carefully balancing strength, flexibility, and water resistance, we can develop innovative and sustainable packaging materials.

5. Acknowledgment

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