The Influence of Filler Concentration on Mechanical and Thermal Properties of Whey Protein Isolate/Silica Biocomposite Film

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Abstract. The incorporation of silica (SiO_2) into whey protein isolate (WPI)-based biocomposites film has been explored. This study aimed to determine the effect of SiO_2 addition on the characteristics of WPI by casting. WPI was prepared with variations in SiO_2 concentration ranging from 0% to 7% (w/w). The resulting biocomposite film was then studied for its mechanical, thermal, and morphological properties. According to the results, adding 7% SiO_2 decreased the tensile strength by 13.82 MPa. In contrast, the elongation tendency increased by 50.57%. The increase in temperature indicates that the addition of SiO_2 improves the thermal stability of WPI biocomposites. The WPI biocomposites have three temperature ranges: 38 to 50°C, 106 to 130°C, and 172 to 192°C. In addition, the incorporation of SiO_2 causes the shape of the biocomposite to be granular, more heterogeneous and made of small particle aggregates. Overall, SiO_2 has the potential to be used as a filler in biocomposites and in various food packaging applications due to its enhanced thermal characteristics.

Keywords: Filler Concentration, Mechanical and Thermal Properties, Whey Protein Isolate, Silica Biocomposite Film.

1 Introduction

Plastic is a marvelous substance and invention that has altered the globe. Everywhere and every day, plastics are utilized globally. Despite its numerous applications, however, its disposal has endangered the biosphere. Using biodegradable materials, the approach is to create biodegradable plastics. As packaging biocomposite materials, starch, cellulose, and protein offer potential [1]. Biodegradable and generated from renewable resources, biocomposite materials are biodegradable [2].

The usage of protein-based biocomposites has garnered considerable interest. Whey protein isolate (WPI) has superior mechanical and oxygen resistance in comparison to

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other proteins. These are the conditions resulting from the high intramolecular binding structure that the molecule possesses. WPI is a byproduct of cheese, milk, and tofu [3,4]. In wealthy nations, milk output will increase by 9% by 2027, with cheese production accounting for 37% of the increase [5]. WPI is high in nutrients, has a good oxygen barrier quality, has no flavor and is colorless; nonetheless, it is brittle, has low tensile strength, and has poor water moisture control [6,7]. This is due to the intermolecular disulfides produced during heating with amino acids and the solubility in the water of protein molecules. Combining WPI with other biocomposites is a strategy for obtaining the targeted characteristics. It has been attempted to combine WPI with chitosan. However, the outcome was unsatisfactory mechanical, physical, and permeability qualities [8]. It is possible to improve the physical and mechanical by including silica (SiO_2) as a filler.

SiO_2 has found many uses in the biological industry, such as an energy storage medium, a bioremediation agent, and a component in building materials. In general, SiO_2 particles have been mixed with polymers to improve their heat, radiation, and mechanical resistance [6]. The number of applications for SiO_2 as a reinforcing agent has steadily increased over the past few decades. According to previous research findings, incorporating SiO_2 into pullulan coatings improves their resistance properties, strength properties, and barrier qualities [9]. Adding SiO_2 to the PVOH/xylan coating has also improved the mechanical, thermal stability, morphological, and barrier properties [10]. The thermal conductivity of the polymer matrix can be enhanced by incorporating fillers for packaging purposes, such as SiO_2, Al_2O_3, and SiC. When Cu was combined with SiO_2, the value of the conductivity rose [11]. It is feasible to improve the flexibility and brittleness of the WPI coating by adding 30% PVOH to the WPI matrix. However, it will result in a decrease in tensile strength and spontaneous water absorption [12]. More studies are needed on using WPI and SiO_2 as biocomposite materials.

This research aims to explore the capabilities of WPI biocomposites with SiO_2 additions of 0%, 1%, 3%, 5%, and 7% via casting based on the favorable characteristics and economic potential of WPI and SiO_2. The Mechanical properties (tensile strength and elongation), thermal properties, particularly thermogravimetric (TGA), and the effect of SiO_2 on the surface as assessed by scanning electron microscopy (SEM), were investigated.

2 Method

2.1 Biocomposite Film Preparation

Ten grams of WPI dissolved in 190 ml of aquades were stirred on the hot plate at 60°C for 30 minutes. Next, 70% glycerol was added. SiO2 was incorporated 0%, 1%, 3%, 5%, and 7% w/w dispersed in distilled water and sonicated for 60 minutes. Then, the WPI and glycerol solutions were mixed with SiO2 and heated to 80°C for 1 hour. Finally, the film solution was molded in silicone and baked for 24 hours at 55°C. The obtained biocomposite films were peeled off and stored in a desiccator before being characterized.

2.2 Mechanical Properties

Mechanical properties, including tensile strength and elongation, were performed with a Universal Testing Machine following ASTM D638 standards. Test samples were prepared with a gauge length of 64.50 mm, a cross-sectional film area of 9.53 mm, and a film size of 7.62 mm. The samples were tested using a load applied at a rate of 10 mm/min, and the tensile strength and elongation of breaks of each sample were recorded [13].

2.3 Thermal Properties

TGA was used to test the thermal stability of the biocomposite film using a Shimadzu DTG-60 from Japan. Under normal air pressure, the biocomposite film was heated from 30°C to 250°C at 10°C per minute-1. The amount of weight loss was based on the temperature.

2.4 Morphology of Biocomposite Film

The surface morphology of the WPI/SiO2 biocomposite films was recorded by SEM (EVO, Carl ZEISS) with 5 kV acceleration. Before testing, the sample was manually cut into 1 cm x 1 cm pieces using liquid nitrogen. The film was taped to the stub, and a thin layer of gold was sputter-coated. The sample was then put into the SEM chamber and observed.

3 Results and Discussion

3.1 Mechanical Properties

Mechanical properties are one of the most critical factors in biocomposites. The mechanical properties of biocomposite films are determined by two critical parameters: tensile strength and elongation at break. Tensile strength indicates the strength of the biocomposite film, while elongation measures the capacity of the film to stretch before breaking. The mechanical properties with various concentrations of SiO2 are shown in Table 1. WPI/SiO2 (0% and 1%) reached 14.12 and 18.63 MPa, but as SiO2 increased (3%, 5%, and 7%), the tensile strength decreased while the addition of SiO2 to the biocomposite increased the elongation. SiO2 has good water binding power, so a gel matrix is obtained, affecting elongation. This is also due to the aggregation of SiO2 particles with WPI during the formation process. Adding hydrophobic particles into the biocomposite film decreases the tensile strength value but increases the elongation value [14]. These results are also the same as research done by Oluwasina et al. [15] tensile strength with dialdehyde starch solution is higher than with the addition of SiO2. The presence of SiO2 in the solution increases elongation resistance but decreases tensile strength. The decrease in tensile strength is due to the lack of cross-linking interactions between components. Basha et al. [16] also reported a decrease in bioplastic film tensile strength with increasing fillers caused by phase separation, poor particle distribution, and particle agglomeration.

Table 1. The effect of SiO_2 concentration on mechanical properties of biocomposites film

Concentration of SiO_2 (%)	Tensile strength (MPa)	Elongation at break (%)
0	14.12	30.70
1	18.63	26.14
3	5.19	22.58
5	11.17	20.97
7	13.82	50.57

3.2 Thermal Properties

TGA is a technique to measure the weight change of a material compound as a function of temperature or time. The curve obtained in TGA analysis is the change in mass against temperature. The effect of SiO2 on the thermal stability of WPI biocomposites has been characterized using TGA. Figure 1 displays the TGA curve with the addition of SiO2.

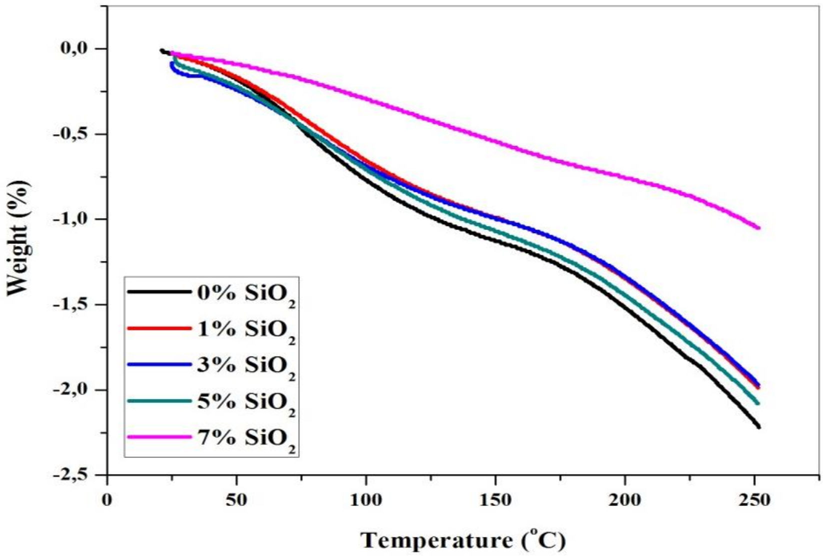

Fig. 1. TGA curves of WPI and WPI/SiO_2 biocomposites film

Based on Fig. 1, all biocomposites show the same decomposition pattern. There are three stages of degradation in these biocomposites, the first stage of degradation occurs at a temperature of 38-50°C. At this stage there is a loss of mass caused by the evaporation of H2O from the biocomposite film. In the second stage, the decomposition of the filler occurs at a temperature of 106-130°C. In the third stage occurs at a temperature of 172-192°C which is the area of transformation of the SiO2 structure of the filler. The initial SiO2 with an amorphous structure is reduced so that it forms crystals which results in increased crystal size. The results obtained in this study are supported by previous research which states that the crystal block adjacent to the amorphous block will affect the structure and crystallinity of other materials. Changes in the amorphous structure into crystals can also affect the surface morphology of the material and temperature stability [17].

3.3 Effect of SiO_2 on The Surface Morphology of Biocomposites Film

The dispersion of filler elements into the matrix polymer is an essential factor in determining the properties of biocomposites. Particle homogeneity plays a vital role in the mechanical performance of biocomposites. The effect of using SiO2 with different concentrations on the morphology of WPI-based biocomposites is shown in Fig. 2.

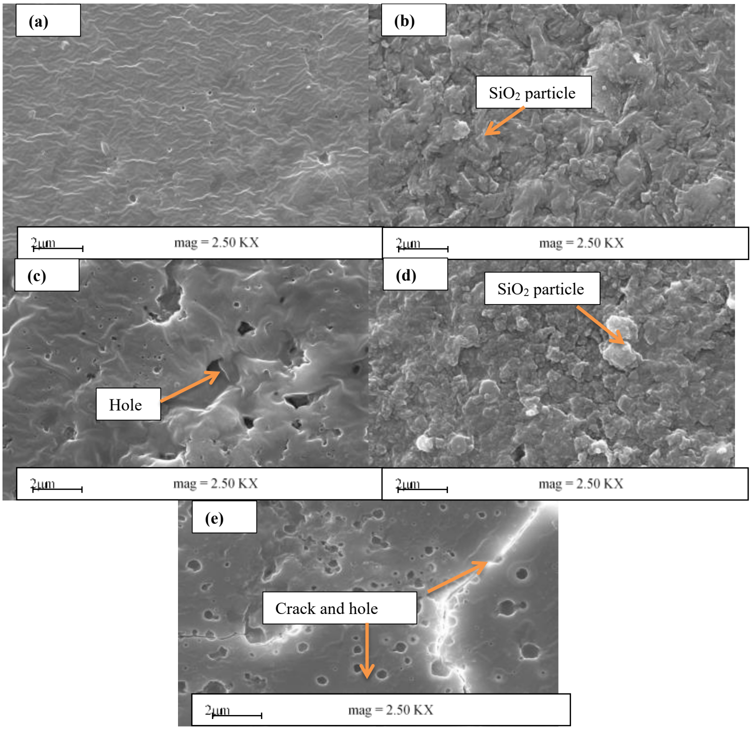

Fig. 2. Morphology of biocomposite films at (a) 0% SiO_2, (b) 1% SiO_2, (c) 3% SiO_2, (d) 5% SiO_2, and (d) 7% SiO_2

Fig. 2 shows biocomposites' morphological structure with the addition of SiO2 on the surface. The surface structure looks flat in (a), showing WPI and 0% SiO2 with the addition of a glycerol plasticizer. The biocomposite (b-e) surface consists of granules (the remaining part of the WPI/SiO2 particles) that are not fully gelatinized during the formation process. Some particles are aggregated at 1% SiO2 content (b), and the number of aggregated particles increases as the SiO2 content increases (b-e). At (e) 7% SiO2 addition, the biocomposite cracked due to weak interaction between WPI/SiO2. This is following research conducted by Hernandez et al. [12]. SEM analysis results showed there are still insoluble granules. Some voids are visible on the surface of the crack, which has an impact on tensile strength. Analysis of the biocomposite surface shows an irregular structure and the presence of SiO2 granules. Similar findings were also presented by Amin et al. [18] regarding the surface of composites exposed to air and TiO2 particles producing rough composites. The morphological structure of cassava starch-clay and glycerin is not homogeneous, and there are some voids on the edges and holes. Cracked composites indicate poor bonding between components [19]. It has been previously published that SiO2 with a mixture of polylactic acid (PLA) and poly ε-caprolactone (PCL) shows an irregular structure with fragment details representing components that are not evenly distributed in the mixture [20].

4 Conclusion

WPI-based biocomposite film with the addition of SiO2 has been successfully developed using the casting method. The addition of SiO2 significantly affected the biocomposites' tensile strength and elongation, thermal properties, and morphology. The tensile strength value at the addition of 7% SiO2 decreased while the elongation value increased to 50.57%. WPI biocomposites with the addition of SiO2 affect the thermal properties from 38°C to 192°C. The morphology of biocomposites in adding 5% and 7% SiO2 is uneven, so there are still small particles and more heterogeneous. These results confirm WPI biocomposites with the addition of SiO2 contribute to improving thermal properties and reducing tensile strength values but increasing elongation values. Thermal properties in biocomposites are significant, so SiO2 has the potential to be used as a filler that can be applied to food packaging.

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