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The Effects of SiO_2 Nanoparticles on Mechanical and Physicochemical Properties of Potato Starch Films

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Abstract: In this paper effect of SiO_2 nanoparticles was investigated on potato starch films. Potato starch films were prepared by casting method with addition of nano-silicon dioxide and a mixture of sorbitol/glycerol (weight ratio of 3 to 1) as plasticizers. SiO_2 nanoparticles incorporated to the potato starch films at different concentrations 0, 1, 2, 3, and 5% of total solid, and the films were dried under controlled conditions. Physicochemical properties such as water absorption capacity (WAC), water vapor permeability (WVP) and mechanical properties of the films were measured. Results show that by increasing the concentration of silicon dioxide nanoparticles, mechanical properties of films can be improved. Also incorporation of silicon dioxide nanoparticles in the structure of biopolymer decrease permeability of the gaseous molecules such as water vapor. In summary, addition of silicon dioxide nanoparticles improves functional properties of potato starch films and these bio Nano composites can be used in food packaging.

Keywords: SiO_2 nanoparticle, Starch film, Mechanical Properties, Bionanocomposite

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INTRODUCTION

Starch is found in abundance in nature and due to the low price, biodegradability, good mechanical and barrier properties, is one of the raw materials used for food packaging. The use of nanotechnology in the field of polymer science has led to the production of nanocomposites polymers. The nanocomposites are biodegradable and have good functional properties. The growth of biological products and the development of innovative technologies, reduce dependence on fossil fuels. In recent decade the demand for such environmentally friendly polymers is growing and has been focus of many researcher efforts.

Sustainable and biodegradable packages are being developed worldwide and make great efforts to produce the packaging material of natural origin (proteins, fats and carbohydrates) to take films or coatings. In comparison these biopolymers have less adverse effect on environment than synthetic plastic. Biopolymers have advantages over the synthetic polymers; biopolymers are biodegradable and renewable materials. Permeability inhibition of gases by biopolymers increases shelf life of fresh products such as fruits and vegetables. Inhibitory to volatile compounds and oils maintain the quality of the food in production and

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distribution cycle however, poor mechanical properties and high permeability to water vapor are two main disadvantages of biopolymers that recently nanotechnology helps to solve these problems. Bionanocomposites as a new generation of nanocomposites represent the combination of a biopolymer and an inorganic material that shows at least one nanometer scale dimension. These generations of biocomposites have more desirable functional properties like good mechanical strength and low water vapour permeability. Increasing the barrier properties against gases, increasing efficiency in the use of film as an active packaging, increasing heat resistance and transparency and improving appearance of bionanocomposites are other advantages [1].

Starch films stronger than other biopolymer films and mechanical properties of the starch films are better than polysaccharides and proteins film. Mechanical properties of starch films are influenced by many factors such as amylose to amylopectin ratio in starch that plays an important role in the mechanical properties of the films. Another important factor effect on mechanical properties of the films is the components used in film formulation. One of the factors affecting on mechanical properties of starch films is other chemicals used in the formulation of film-forming solution. The most important factor is the amount of plasticizer that overuse can lead to weakening of the mechanical properties of the final film and limits its application [2,3].

Starch films are transparent, semi-transparent, tasteless, colourless and flavourless. Starch because of its nature, cost and reliability of thermo plastics has a great interest as packaging materials. However, starch alone has some disadvantages such as hydrophilic nature and poor mechanical properties [4].

Potato starch has some number of desirable features to improve and to enhance the stability and rigidity of the gel in some foods, and as a major component prefers to corn, wheat and other starches. Moreover, compared to other starches, has swelling power and high binding and lower gelatinization temperature [5].

Rogr and his colleagues (1998) stated that one of the factors influences on retro gradation is amylose content of starch so potato starch compared to wheat starch, has less tendency toward self-retro gradation. The amount of phosphorus present in the amylopectin of potato starch has negative charge and repulsive little faster because there may be swelling of potato starch granules in hot water and high viscosity, high transparency and it is involved in low retro gradation speed of potato starch pastes [6].

The silicon dioxide (SiO_2) chemical compound, which is known as silica, is an oxide of silicon. Silicon dioxide has been known since ancient times because of its hardness. Usually in nature it is found as silica sand, quartz, crystal, vapor-silica, colloidal silica, silica gels and aerogels [7].

Starch films are made in two ways, thermoplastic (extrusion blow or roller) and casting method. The method used in this research is casting method comprising the steps of gelatinization, pasting, bursting of granules, and starch retro gradation. Starch films in the absence of plasticizers are very hard and brittle. Therefore it is necessary to use a plasticizer in the production of starch films. The most common plasticizer is glycerol used in starch films fabrication [8].

The mechanical properties of starch films largely improved by addition of glycerol, but, barrier properties of starch films like protein films change with the addition of plasticizer and weaken somewhat [8].

MATERIALS AND METHODS

Materials

Starch from potato was purchased from Glucosan Company (Ghazvin, Iran). Glycerol was purchased from Merck. Nanosilicon dioxide was obtained from Sigma Chemical Co (St. Louis, MO, USA).

Film preparation

Nano-silicon dioxide was dispersed in water at different concentrations (1, 2, 3, and 5% of total starch solid) and heated to 60 °C with continuous stirring for 1 h, then sonicated in an ultrasonic bath (Marconi modelUnique USC 45 kHz) for 15 min to ensure homogenization was completed. The solution was cooled to room temperature and was used to prepare the aqueous starch dispersion 4% (w/w). The starch dispersion was heated to 90°C and held at this temperature for 45 min to complete the gelatinization. A 3:1 mixture of sorbitol-glycerol at 40% (w/w of starch) was added as plasticizers; the choice of the plasticizers was based on the previous research by Abdorreza and his colleagues [9]. Starch nanocomposites were heated to 85±5 °C and held for 45 min to allow gelatinization. Upon completion of starch gelatinization, the solution was cooled to room temperature. A portion (92 g) of the dispersion was cast on Perspex plates fitted with rims around the edge to yield a 16×16 cm^2 film-forming area. Films were dried under controlled conditions in a humidity chamber (25 °C and 50% RH). Control films were prepared similarly but without addition of nanoparticles. Dried films were peeled and stored at 23 ± 2 ºC and 50 ± 5% relative humidity (RH) until experimentation. All films (including control) were prepared in duplicate.

Mechanical Properties

ASTM D882-10 [10] was used with some modifications to determine the mechanical properties under standard conditions. Film strips were cut to 100 mm long and 20 mm wide and conditioned for 48 h in 23 ºC and 53% relative humidity. Texture analyzer (TA.XT2, Stable Micro System, Surrey, UK) equipped with Texture Exponent 32 software was used for measuring mechanical properties of the films. The initial grip separation and crosshead speed were 50 mm and 30 mm/min, respectively. Elongation and tensile strength at break were calculated from the deformation and force data recorded by the software. Eight replicates for every sample were evaluated.

Solubility in water

Solubility of the films in water was determined according to Maizura and others [11] and Laohakunjit and Noomhorm [12] with some modifications. Pieces of film (2 × 3 cm ≈500 mg) were cut from each film and were stored in a desiccators with P_2O_5 (0% RH) for 2 days. Samples were weighed to the nearest 0.0001 g and placed into beakers with 80 mL deionized water (18 MΩ). The samples were stirred with constant agitation for 1 h at room temperature. The remaining pieces of film after soaking were filtered through filter paper (Whatman no.1), followed by oven drying at 60 °C to constant weight. Samples were measured in triplicates and the percentage of total soluble matter (% solubility) was calculated as follow:

$$Solubility\ (\%) = \frac{(Initial\ dried\ weight\ of\ film - Final\ dried\ weight\ of\ film)}{Initial\ dried\ weight\ of\ film} \times 100$$

Water Vapor Permeability

The modified gravimetric cup method [13] based on ASTM E96-05 [13] was used to determine the water vapour permeability (WVP) of films. The test cups were filled with water 1.5 cm below the film. A plot of weight gained versus time was used to determine the WVTR. The slope of the linear portion of this plot represented the steady state amount of water vapour transmission through the film per unit time (g/h). Six samples per treatment were tested. The slopes yielded regression coefficients of 0.99 or greater. The WVP of film was calculated by multiplying the steady WVTR by the film thickness and dividing that by the water vapour pressure difference across the film.

Water Absorption Capacity

The water absorption capacity measured as adapted method by Kiatkamjornwong and his colleagues [15]. Nanobiocomposite films first were dried in a P_2O_5 for one week and then a piece of $2\times 2\ cm^2$ ($\approx$50 mg) of dried films was added to 100 ml of distilled water and allowed to stand for 30 min for swelling. The swollen films were drained and weighted. The amount of water retained by films per dried weight of the films calculated as water absorption capacity.

STATISTICAL ANALYSIS

ANOVA and Tukey's Post Hoc tests were used to compare means of physical, mechanical, thermal, and antimicrobial properties of starch based or gelatin based films at the 5% significance level. Statistical analysis was conducted using PASW 18.0 for windows (SPSS Inc. Chicago, IL) and GraphPad Prism 5 (GraphPad Software Inc., 2236 Avenida de la Playa, La Jolla, CA 92037, USA).

RESULTS AND DISCUSSIONS

Mechanical Properties

Fig. 1 shows the effect of SiO_2 nanoparticles on tensile strength of potato starch films with 40% plasticizer. Addition of nanoparticles significantly ($p < 0.05$) increased the tensile strength of potato starch films. Wu and others [16] showed that nanoparticles, used as a filling agent, improve the wear performance and tensile strength of starch films. The nanoparticles are likely to bond with hydroxyl groups and other possible hydrogen or Van der Wall's bonds of starch macromolecules strengthening molecular forces between nanoparticles and starch [16].

Figs. 2 and 3 show other mechanical properties of nanoparticle-reinforced starch films: elongation at break and Young's modulus. Elongation at break has a reverse relation with tensile strength in most cases and Young's modulus was directly related to tensile strength. Young's modulus is a measure of the rigidity of the material and improves as nanoparticles were introduced. The elasticity of the films is related to interactions of the macromolecules and can be reduced by addition of plasticizer. As shown in the previous researches nanoparticles significantly reduced moisture content [17]. It is likely that incorporation of nanoparticles occupy the sites on starch that normally would be occupied by water [7,18]. Water that has a plasticizing role [19,20] on the starch and addition of nanoparticles, decrease the water content and consequently reduced the elasticity (elongation at break) of the films.

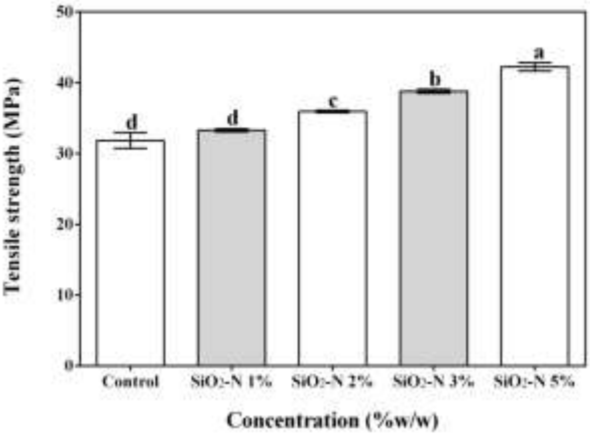

Figure 1. Effects of SiO_2 nanoparticles on tensile strength of potato starch films. The bars show mean (n=8) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

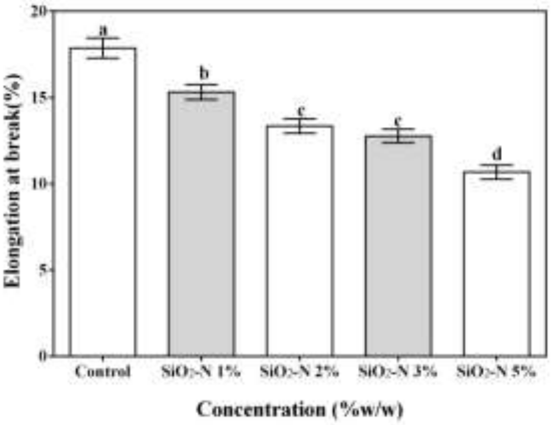

Figure 2. Effects of SiO_2 nanoparticles on elongation at break of potato starch films. The bars show mean (n=8) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

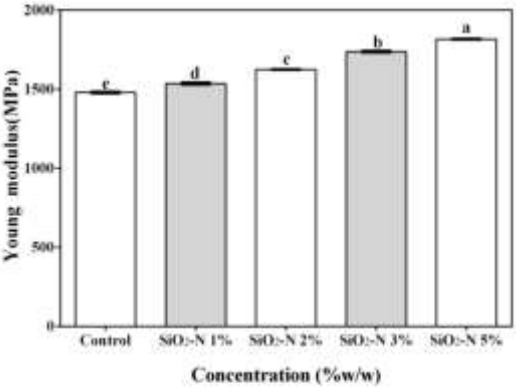

Figure 3. Effects of SiO_2 nanoparticles on Young’s modulus of potato starch films. The bars show mean (n=8) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

Solubility of potato starch films reinforced by SiO_2 nanoparticles in Water

The solubility of the films is one of the important parameter for packaging films. Solubility in water may be an important factor in defining applications for biopolymer composite films. Most of the biopolymers are sensitive to water. By incorporating lipids, crosslinking of the structure or incorporation of nanoparticles sensitivity to water could be decreased [1]. Fig. 4 shows the solubility of potato starch films in deionized water after 1 hr. Incorporation of nanoparticles suppressed the diffusion of water into the structure. The incorporation of nanoparticles had the greatest effect on tapioca and very little effect on sago starch. Effects of nano-silicon dioxide on the water resistance of starch films reported by other researchers and our results are consistent [16,21-23].

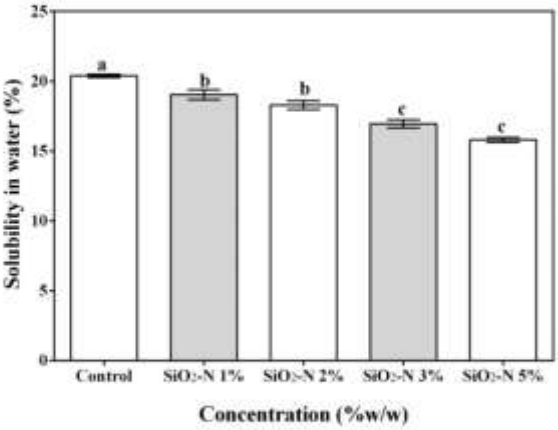

Figure 4. Effects of SiO_2 nanoparticles on water solubility of potato starch films. The bars show mean (n=3) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

Effects of SiO_2 nanoparticles on water vapour permeability

Nanoparticles filling the pores in the macromolecules structures can decrease gas permeability as well as permeability to water vapour [24]. Fig. 5 shows the effect of nanoparticles on the water vapour transmission rate through starch films. As expected, introduction of nanoparticles significantly decreased water vapour permeability (WVP) of potato starch films. Also other researchers have shown positive effects of nanoparticles on WVP. For example, Bajpai and his colleagues [21] have shown that WVP of chitosan films added with zinc oxide nanoparticles decreased significantly.

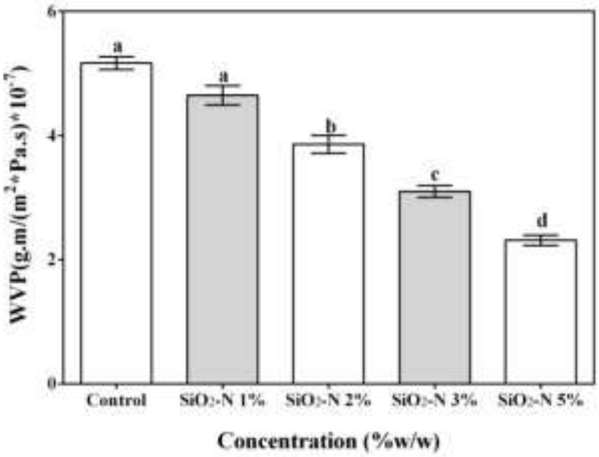

Figure 5. Effects of SiO_2 nanoparticles on water vapor permeability of potato starch films. The bars show mean (n=3) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

Effects of SiO_2 nanoparticles on water absorption capacity

The water absorption capacity of the SiO_2 nanocomposite films are given in Fig. 6. Introducing SiO_2 nanoparticles to the potato starch matrix significantly decrease the water absorption capacity of the nanocomposites. This phenomenon can be described by the interactions between SiO_2 and other compounds in biopolymer film structure. The experimental results were showed that when the nanoparticle (SiO_2) content of films was increased, more hydrogen bonds formed between the SiO_2 and the matrix components [25]. For this reason, free water molecules do not interact as strongly as with nanocomposite films as with composite films alone. These results not only have been supported by the solubility in water but also the other researchers reported the same results on nanobiocomposites [25, 26].

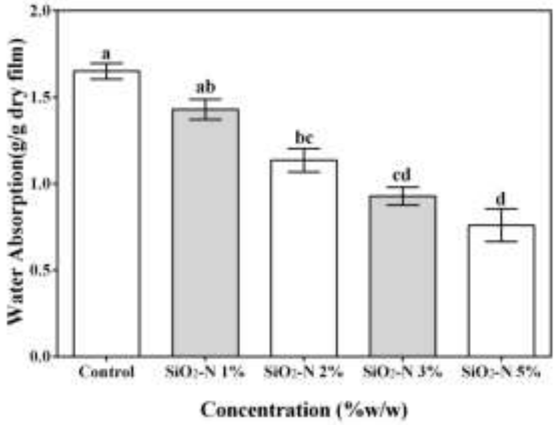

Figure 6. Effects of SiO_2 nanoparticles on water absorption capacity of potato starch films. The bars show mean (n=3) ± SD. Different letters on the bars represent the significant difference at 5% level of probability.

CONCLUSION

In this study, we introduced SiO_2 nanoparticles to the potato starch matrix to fabricate bionanocomposites. Introduction of the nanoparticles improved mechanical properties of the films made from potato starches. Water vapour permeability, water absorption capacity, and water solubility of the films significantly decreased. The results showed that under strict regulation, bionanocomposites based on SiO_2 nanoparticles may have potential applications in the medical, pharmaceutical, and food packaging industries.

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