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Keywords

Biopolymer films, Nanoparticles, Protein isolates, Thermal properties, Mechanical properties

Disciplines

Bioresource and Agricultural Engineering | Food Chemistry | Nanoscience and Nanotechnology | Polymer and Organic Materials

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Preparation and characterization of whey protein isolate films reinforced with porous silica coated titania nanoparticles

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Abstract

Whey protein isolate (WPI) films embedded with $\text{TiO}_2@ \text{SiO}_2$ (porous silica (SiO_2) coated titania (TiO_2)) nanoparticles for improved mechanical properties were prepared by solution casting. A WPI solution of 1.5 wt% $\text{TiO}_2@ \text{SiO}_2$ nanoparticles was subjected to sonication at amplitudes of 0, 16, 80 and 160 μm prior to casting in order to improve the film forming properties of protein and to obtain a uniform distribution of nanoparticles in the WPI films. The physical and mechanical properties of the films were determined by dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and tensile testing. Water vapor permeability (WVP) measurements revealed that the water vapor transmission rates are slightly influenced by sonication conditions and nanoparticle loading. The DMA results showed that, at high sonication levels, addition of nanoparticles prevented protein agglomeration. The thermal stability of the materials revealed the presence of 3–4 degradation stages in oxidizing the protein films. The addition of nanoparticles strengthens the WPI film, as evidenced by tensile stress analysis. Sonication improved nanoparticle distribution in film matrix; such films can potentially become effective packaging materials to enhance food quality and safety.

Keywords

- Biopolymer films;
- Nanoparticles;
- Protein isolates;
- Thermal properties;
- Mechanical properties

1. Introduction

Whey protein isolate (WPI), an abundant by-product in the cheese-making industry, has been successfully employed as a raw material for preparation of biodegradable polymers (Mulvihill and Ennis, 2003). WPI has desirable film forming and barrier properties, which compare well to petrobased products (McHugh et al., 1994a, McHugh et al., 1994b, McHugh and Krochta, 1994, Fairley et al., 1996, Sothornvit and Krochta, 2000, Fang et al., 2002, Hong and Krochta, 2003, Khwaldia et al., 2004, Perez-Gago et al., 2005, Gounga et al., 2007, Pallas-Brindle and Krochta, 2008 and Min et al., 2009). However, the low tensile strength and high water vapor permeability (WVP) of WPI films limit its applications in food-related packaging. Nanoscale fillers (e.g., nanoclays) have been used as reinforcements to strengthen whey protein polymer matrices (Zhao et al., 2008).

Nanoscale fillers need to be well dispersed in the polymer matrix for better film forming properties. High-power ultrasonication has been shown to create better dispersions of nanoparticles (Li et al., 2005) during mixing. Sonication is a highly system-specific dispersion procedure involving a variety of concomitant complex physicochemical interactions. These interactions can result in cluster breakdown or further agglomeration, as well as other effects including chemical reactions (Taurozzi et al., 2010). Ultrasonic waves are generated in a liquid suspension either by immersing an ultrasound probe or “horn” into the suspension (direct sonication), or by introducing a sample container with the suspension into a liquid bath through which ultrasonic waves propagate (indirect sonication).

Efforts are being made to find new uses for whey proteins, including edible films (Anker et al., 1998 and Kokoszka et al., 2010) and films with antimicrobial functionality for more effective protection of food products, which would reduce the risk of outbreaks of foodborne diseases (Appendini and Hotchkiss, 2002). Unlike chitosan films, whey protein films do not inherently possess antimicrobial activities but incorporation of antimicrobial agents, such as sorbic acid, p-aminobenzoic acid (Cagri et al., 2001), and lysozyme have been reported (Kristo et al., 2008). Another potential method of imparting antimicrobial functionality to packaging films is through the utilization of antimicrobial nanoparticles such as titania (TiO₂) nanocomposites. Titania is a nontoxic and inexpensive material exhibiting bactericidal activity against a wide variety of microbes due to its photocatalytic activity. When incorporated into a polymer matrix, TiO₂ can provide protection against foodborne microorganisms as well as odor, staining, deterioration, and allergens in the presence of relatively low-wavelength radiation near the ultraviolet region (Rajh et al., 1999 and Zhou et al., 2009). However, TiO₂ particles easily aggregate and thus deteriorate the properties of the film (Zhou et al., 2009). In addition, the direct contact between TiO₂ and the polymer matrix may lead to rapid degradation of the polymer films themselves. Recently, we developed novel core (TiO₂) and shell (SiO₂) nanoparticles (TiO₂@SiO₂) with a void layer between the titania core and the porous silica outer layer as a reaction/enrichment zone for free radicals. This void layer acts as a phase-selective photo-catalyst for the photodecomposition of gas phase organic pollutants without any damage to their solid phase organic supports (Wang et al., 2008). With the improvement in film properties, the nanoparticle-embedded films can potentially become more effective packaging materials to enhance food quality and safety. The main objectives of the present work are to develop WPI films embedded with TiO₂@SiO₂ nanoparticles by utilizing sonication to achieve uniform distribution of nanoparticles inside the

WPI film, and to characterize the effects of different levels of sonication used. Furthermore, the effect of film thickness on the physical and mechanical properties of the films is also of interest.

2. Material and methods

2.1. Materials

TiO₂@SiO₂ nanoparticles (particle size between 100 and 180 nm) were made following a previously reported procedure (Wang et al., 2008). Briefly, TiO₂ nanoparticles were coated by glucose (i.e., carbon) to form particle complex denoted as C@TiO₂. The C@TiO₂ particles were then coated with a layer of silica via a sol-gel method to form SiO₂@C@TiO₂. Finally, the SiO₂@C@TiO₂ nanoparticles were calcined at an elevated temperature (~773 K for 3 h) to remove the interior carbon layer and create pores on the outer layer to yield nanovoid core/shell nanoparticles denoted as SiO₂@@TiO₂. A schematic illustration and TEM image of the TiO₂@@SiO₂ nanoparticles used in the WPI films are shown in Fig. 1.

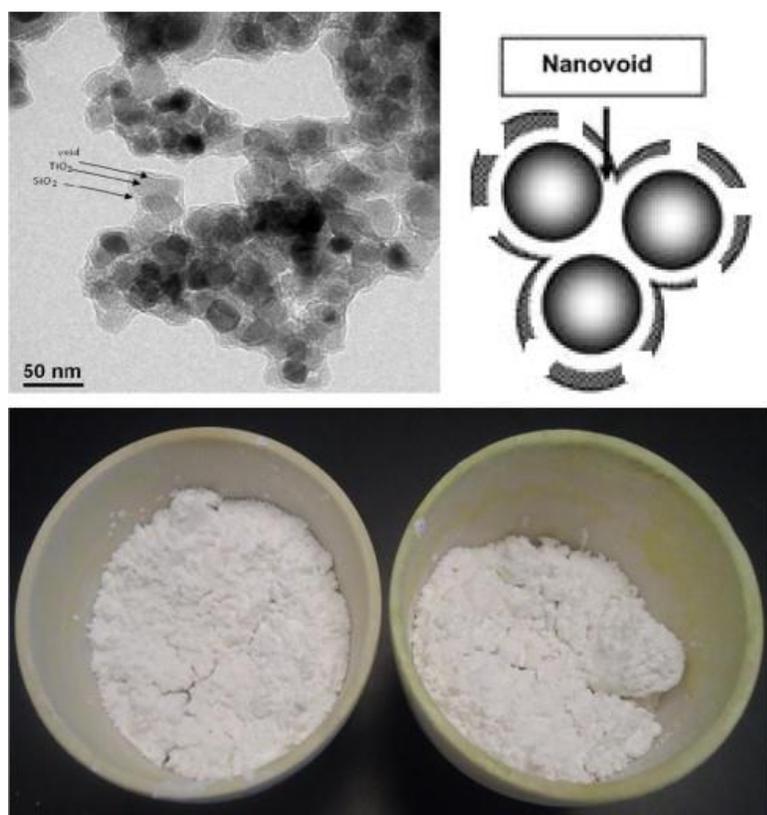


Fig. 1: Transmission electron micrograph (top), and picture (bottom) of TiO₂@@SiO₂ nanoparticles used in WPI films to improve mechanical and antimicrobial properties.

Whey protein isolate (WPI) was purchased from Pure Bulk (Roseburg, Oregon, USA) which was processed using cold micro-filtration. WPI protein analysis was done using the Dumas Nitrogen Combustion method which revealed an 86.01% protein content (as-is basis) with a moisture

content of 6.96 wt%. All other reagents were of analytical grade. Deionized and distilled (DD) water was used for preparation of all samples.

2.2. Preparation of WPI-based films

The WPI films were formed following the method described by [Kim and Ustunol \(2001\)](#) with some modifications. WPI and glycerol at 5 wt% each were dissolved in DD water (90 wt%) with continuous stirring to obtain a film-forming solution. The pH of the film forming solution was adjusted to 8.0 with 2 M NaOH. Then, the solution was heated to 90 ± 2 °C for 30 min in a water bath while being stirred continuously, and rapidly cooled in an ice bath for 10–15 min to avoid further denaturation. The solution was then filtered through two layers of muslin cloth to remove any coagulation. The filtered WPI solution was subjected to ultrasonication levels of 0%, 10%, 50% and 100% sonication (i.e. 0, 16, 80 and 160 μm amplitudes), denoted as A, B, C and D respectively. The film forming solutions of 10, 15 and 20 g were cast on sterile polystyrene petri dishes (Fisher brand, USA). These were dried at 35 ± 1 °C for 24 h in a hot air dryer having 24% relative humidity (RH), then kept in a $50\% \pm 2\%$ RH chamber for at least 24 h before the films were peeled and tested at room temperature (24 ± 1 °C).

2.3. Film thickness

The film thicknesses were measured by a digital micrometer (Model: IP-65, Mitutoya Corp., Tokyo, Japan) to the nearest 0.001 mm. Measurements were taken at five positions along the rectangular strips cut for the mechanical properties determination. Thickness measurement for water vapor permeability (WVP) was done at five random positions around the perimeter of each film prepared in petri dish. The mechanical properties and WVP were calculated using the average thickness of each film.

2.4. Film surface wettability/contact angle

The contact angle measurements were carried out with a Ramé-hart 100-00 115 NRL contact angle goniometer (Ramé-hart instrument co, NJ). A droplet of distilled water (4 μL) was deposited on the leveled film surface to determine the contact angle of water on the biopolymer films. All films were pre-conditioned in a humidity chamber at $50\% \pm 2\%$ relative humidity to avoid interference due to competing moisture exchange at the surface around the droplet ([Marcuzzo et al., 2010](#)).

2.5. Water vapor permeability

Water vapor transmission rate (WVTR), a film barrier property, was evaluated using a gravimetric method per ASTM E 96-95 with modifications described by [Anderson et al. \(2012\)](#). An open area of film with a diameter of 62 mm was placed on top of a flat-lipped glass beaker containing 3 ± 0.01 g of anhydrous calcium sulfate (Drierite) to maintain nearly 0% RH inside the cell. The lip of the beaker was vacuum-greased and the film was sealed with a custom-made flange and an O-ring to secure the film between the beaker and flange. A saturated solution of calcium nitrate was used to maintain $95\% \pm 2\%$ RH outside the beakers in a closed chamber. The films were left in the closed chamber for 48 h. Two different thicknesses of films, formed using

10 and 20 g of film forming solution, were tested at 24 ± 1 °C. The WVP was calculated by plotting the weight gain by the film over time using the following equation (Anderson et al., 2012):

$$\mu = WL/tAP$$

where μ is the water vapor permeability (i.e. 10^{-11} g m/m² s Pa), W is the amount of the water gained by the cup (g), L is the film thickness (m), t is the elapsed time (s), A is the film cross sectional area (m²), and P is the difference in pressure between the inside and outside of the vial (Pa).

2.6. Dynamic mechanical analysis

The DMA measurements were performed on rectangular film samples with dimensions ($l \times w \times t$) of 13 ± 1 mm \times 7 ± 1 mm \times actual thickness, respectively, using a Q800 DMA (TA Instruments New Castle, DE, USA). Samples were evaluated in tension mode using a dynamic temperature sweep to measure the storage and loss moduli as a function of temperature at a fixed frequency (1 Hz). The specimen's temperature was equilibrated at -120 °C using liquid N₂ cooling followed by a constant heating rate of 5 °C/min to 150 °C.

2.7. Determination of mechanical properties

The tensile testing of the mechanical properties of the biopolymer samples were as performed with an Instron Universal Testing machine (Model 5569, Instron Engineering Corp., Canton, MA) at an extension rate of 50 mm/min using a 2 kN load cell. The samples for the tensile tests were prepared by stamping dog-bone shaped specimens from the biopolymer films according to ISO 527 type 5A. The strain in the sample was measured by keeping a gauge length of 30 mm between the clamps. The Young's modulus was measured at 0.1–0.5% strain using the Bluehill software supplied with the machine. For each film type, five specimens were cut from a single petri plate film sample and the highest four results were averaged. The test cross section was measured for length, width and thickness using a digital caliper.

2.8. Thermogravimetric analysis

The thermal stability of the WPI films with and without TiO₂@SiO₂ was investigated using a thermogravimetric analyzer, TGA model Q50 (TA Instruments, DE, USA) in a nitrogen atmosphere. The mass of the samples used was 15 ± 1 mg. The samples were heated from room temperature to 800 °C at a heating rate of 10 °C/min to measure weight changes as a function of temperature and/or time under a controlled atmosphere and to determine the material's thermal stability and composition.

2.9. Statistical analyses

A single-factor completely randomized experimental design (CRD) was used to determine significant differences among the samples at $p < 0.05$. Analysis of variance (ANOVA) tests (Fisher's LSD) were used to determine the effect of the nano particles in the films.

3. Results and discussion

The whey protein isolate (WPI) films were transparent, smooth, flexible, homogeneous, and without observable pores or cracks. Changes in appearance were observed for films embedded with nanoparticles at various ultrasonication levels of 0%, 10%, 50% and 100% (i.e. tip horn amplitudes of 0, 16, 80 and 160 μm , respectively). The appearance of the film side facing the casting plates was shiny while the other one was slightly dull.

3.1. Film thickness

The average film thicknesses of WPI films with and without nanoparticles are presented in [Table 1](#). It is clear from the [Table 1](#) that the addition of nanoparticles increases the thickness of the cast films. Indeed, the same weight of film-forming solution was casted in 100 mm diameter petri dishes, but the dry matter of the solutions increases with the addition of nanoparticles.

Table 1.

Thicknesses of whey protein isolate films with and without nanoparticles.

Film	Film forming solution (g)	Average thickness (mm)	Std. Dev. (mm)
WPI	10	0.1456	0.0136
	15	0.2276	0.0056
	20	0.3084	0.0145
WPI-NP	10	0.1593	0.0071
	15	0.2329	0.0299
	20	0.3189	0.0189

3.2. Surface wettability

Surface hydrophobicity has been used as an important indicator of a protein film's sensitivity to water or moisture; it could be evaluated indirectly using contact angle (CA) measurement. The hydrophobic interactions on the surface of our film specimen may be influenced by both sonication and nanoparticles. The CA of WPI films without nanoparticles was $40^\circ \pm 3^\circ$, decreasing slightly as the level of sonication amplitude increases. This decrease in the contact angle could be due to the restructuring of the proteins at higher sonication levels that lead to less exposure of hydrophobic regions of the protein to the surface ([Chandrapala et al., 2011](#)). WPI film swelling was observed during the contact angle measurements using a water droplet. Although the observed trend was relatively small in pure WPI films, there was significant

variation of CA in WPI nanocomposite films. It can be observed that the contact angle increased dramatically from 16° to 74° with an increase in sonication amplitude from 0 to 160 μm i.e. 0–100% (Fig. 2). A fine distribution of the nanoparticles is achieved by sonication and results in covering the whole surface of the WPI film. Consequently, the improvement in the contact angle after sonication could be attributed to the domination of surface functionality of the nanoparticles compared to the pure WPI film. Generally, protein films with higher contact angles exhibit a higher surface hydrophobicity (Tang and Jiang, 2007). The contact angles decreased with an increase in measurement time from 60 s to 300 s irrespective of sonication level and nanoparticle loading (Fig. 2). The slight decrease in the contact angle with time could have resulted either from the equilibrium time required to show a stable contact angle or due to the slight absorption of water into the films.

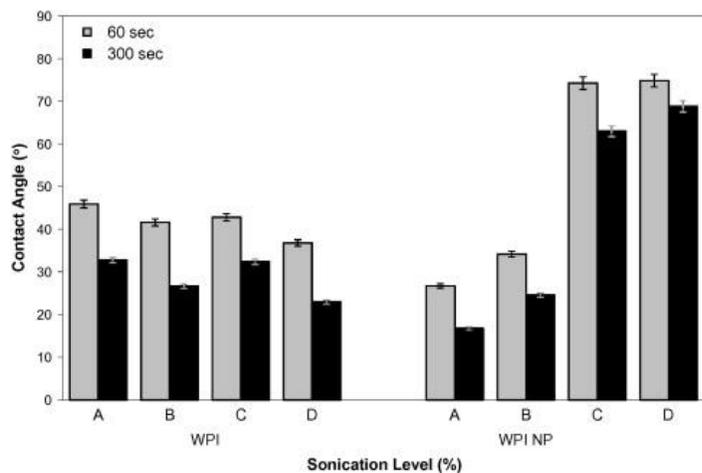


Fig. 2: Effect of sonication levels on water contact angles of 0.23 mm thick pure WPI films and WPI films containing nanoparticles.

3.3. Water vapor permeability

The WVP for WPI films for all levels of sonication, thickness, and nanoparticle loadings ranged between 2×10^{-11} and $\sim 5 \times 10^{-11}$ $\text{g m/m}^2 \text{ s Pa}$ (Fig. 3). The thicker WPI films and desiccant gained more weight compared to the thinner films, irrespective of sonication levels and nanoparticle loadings. A higher WVP is one of the major limitations when using protein-based films as food packaging materials. Therefore, a reduction in WVP is desirable for potential applications in food packaging. The RH gradient is an important parameter when calculating the WVP (McHugh et al., 1993). The actual thickness of the film was mainly responsible for the increase or decrease in its WVP values (Fig. 3) and the same was taken into consideration while calculating WVP.

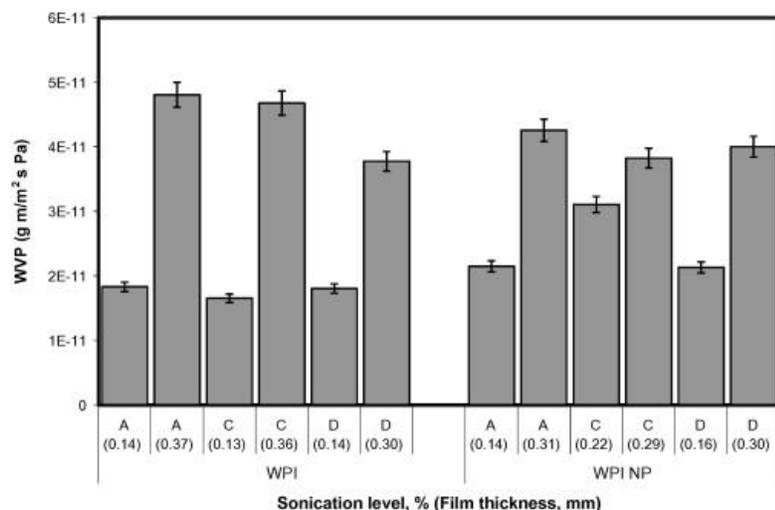


Fig. 3: Water vapor permeability of WPI films as a function of sonication level, nanoparticles and film thickness. Note: A, C, and D represent 0, 80 and 160 μm sonication amplitudes, respectively (film thickness, mm).

The WVP is dependent on the number of polar groups present in the polymer film. The whey protein films are hydrophilic; they are composed of highly polar amino acids. Further, whey powder contains lactose sugar, which is a highly hydrophilic material. The barrier properties of films are influenced by the hydrophobic or hydrophilic nature of the polymer, the presence of voids or cracks, the type, level and compatibility of incorporated plasticizer, and the steric hindrance in the film structure (Santosa and Padua, 1999 and Lawton, 2004). Denaturation of the cowpea protein at higher pH values exposes the hydrophilic residues on the protein surface (Hewage and Vithanarachchi, 2009). This enhances the absorption of migrating water molecules to polar groups, facilitating the transport of water and causing the penetration of more water vapor through the film (Nathalie et al., 1992). The WVP of the cowpea protein film increased with an increasing plasticizer concentration (Hewage and Vithanarachchi, 2009). The plasticizer molecules increase the intermolecular spacing between the protein polymer chains, allowing the water molecules to pass through the films (McHugh et al., 1994a and McHugh et al., 1994b).

3.4. Dynamic mechanical analysis

Thermo-mechanical analysis was used to study the influence of sonication and $\text{TiO}_2@\text{SiO}_2$ nanoparticles on the phase behavior of the WPI films. Fig. 4a and b depict the change in elastic loss modulus (E'') and storage modulus (E') over a temperature range of -120 to 140 $^\circ\text{C}$. The peaks in the loss modulus curves reveal the presence of two distinct transition temperatures. The strong peak at a lower temperature (<0 $^\circ\text{C}$) corresponds to the transition temperature of the sorbitol phase (T_s) in the WPI bulk sample, whereas the shoulder-like peak at 90 $^\circ\text{C}$ corresponds to the α -relaxation (T_α) of WPI (Zinoviadou et al., 2009). The α -relaxation (T_α) is primarily observed due to the glass transition in WPI. A shift in the relaxation temperatures (T_s and T_α) to higher values were observed in pure WPI samples after sonication. Apart from sonication, T_s and T_α also shifted to higher values with the addition of $\text{TiO}_2@\text{SiO}_2$ nanoparticles. The shift of the

relaxation peaks towards higher temperatures in the biopolymer films is primarily attributed to a change in the molecular level interactions that can influence the segmental mobility in the protein. Sonication of the pure WPI resulted in disordering of intramolecular forces in the protein, whereas sonication at high amplitude for an extended period of time could lead to the formation of agglomerations from the disordered phase. Such agglomerations could act as rigid constraints to hinder the relaxation of proteins near T_s and T_α , resulting in a shift of the relaxation peaks to higher temperatures. However, in the case of WPI nanocomposites, the shift in T_s and T_α is mainly attributed to the presence of the $\text{TiO}_2@\text{SiO}_2$ nanofillers. The presence of these rigid fillers in soft protein films could potentially act as a barrier to the protein flexibility.

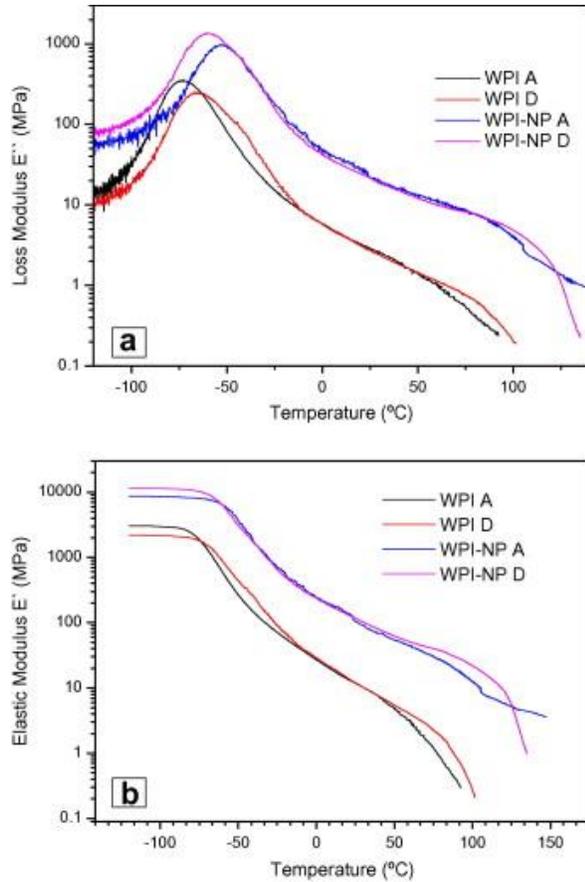


Fig. 4: DMA used for determination of (a) Loss modulus and (b) Elastic modulus of WPI films with or without nanoparticles prepared using different sonication levels. Note: It is one representation of few measurements.

The presence of titania agglomerates in sonicated samples at higher power levels could be reconfirmed from the intensity difference of the T_s relaxation peak. Generally, the intensity of the relaxation peak corresponds to the amount of soft phase in the bulk sample. A decrease in the intensity of the T_s relaxation of WPI-D when compared to WPI-A implies a partial conversion of the overall soft phase to the hard agglomerated phase. However, in contrast to the general trend, the intensity of the T_s relaxation peak in the nanocomposite film WPI-NP-D was higher than in

WPI-NP-A. This difference could be attributed to the ability of $\text{TiO}_2@ \text{SiO}_2$ fillers to protect disordered proteins against forming agglomerations.

The variation in the storage modulus (E') with respect to temperature for all the WPI samples is presented in [Fig. 4b](#). The glassy modulus corresponding to the E' below the T_g (~ -60 °C) decreases after sonication in the case of pure WPI samples, whereas the same increases in nanocomposite films. This change in the glassy modulus could be attributed to a partial agglomeration phenomenon at higher sonication levels. Over the temperature range studied, the elastic moduli of the nanocomposite samples were higher than for pure WPI films. The observed high modulus values could be due the reinforcing effect from the rigid $\text{TiO}_2@ \text{SiO}_2$ fillers in the soft protein matrix. Thus, the $\text{TiO}_2@ \text{SiO}_2$ nanoparticles not only improved the mechanical strength of the samples over a broad temperature range, but also prevented self-aggregation of WPI during sonication at high amplitudes.

3.5. Mechanical properties

The stress–strain curves for WPI films with and without nanoparticles are shown in [Fig. 5](#). A slight scattering was observed between the stress–strain curves of different specimens in the same batch. The stress–strain curves shown in [Fig. 5](#) correspond to one of the five specimens tested in each batch. The stress–strain profiles of all the WPI films show a yielding behavior followed by cold drawing prior to failure. The amount of scattering in the stress–strain behavior between different specimens in the same batch of samples can be estimated from the error bars on the Young's modulus and the tensile strength data in [Fig. 6](#). The significant influence of sonication on the stress–strain behavior of the WPI films can also be seen from [Fig. 5](#). With the addition of nanoparticles, the modulus of the pure WPI increased from 19 MPa to 35 MPa ([Fig. 6a](#)) and the tensile strength measured from the stress-at-break also increased from 1.03 MPa to 1.18 MPa ([Fig. 6b](#)). The increase in tensile properties is more prominent after sonication i.e. the modulus seems to be independent of sonication level in pure WPI films when compared to the obvious increase in the nanocomposite films ([Fig. 6a](#)). The tensile strength also showed a similar trend between samples with and without nanoparticles. From the results, it is worth mentioning that both ultra-sonication and $\text{TiO}_2@ \text{SiO}_2$ can collectively contribute to enhance the tensile mechanical properties of the films. Sonication helps in breaking the nanoparticle agglomerations and disperses them finely in the protein matrix. Such well-dispersed nanofillers could improve the reinforcing efficiency of nanoparticles, enhancing the material's mechanical properties. On the other hand, from [Figs. 5](#) and [6c](#) it can be observed that the nanoparticles also affect the strain at break in the samples. In pure WPI films, due to the flexibility of the protein, the material can dissipate more energy resulting in high strain at break; whereas, with the incorporation of reinforcing fillers, the stiffness of the films increases with a simultaneous reduction in film flexibility. Thus, the observed difference in the strain at break between pure WPI and WPI nanocomposite films is due to the change in film flexibility.

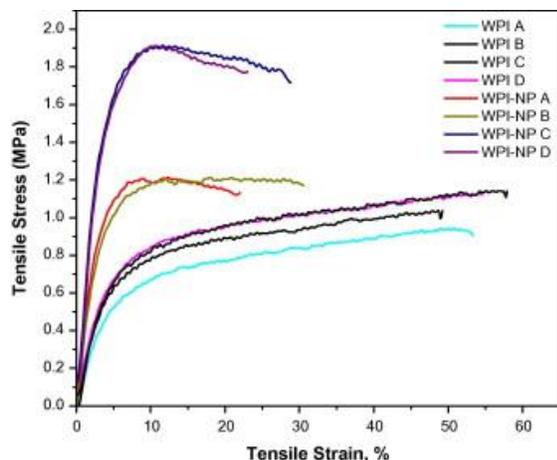


Fig. 5: Typical tensile stress (M Pa)–tensile strain (%) profiles for WPI films at different sonication levels with and without nanoparticles. Note: WPI is whey protein isolate and WPI-NP is whey protein isolate with nanoparticles. A, B, C and D represent the 0%, 10%, 50% and 100% sonication levels, respectively.

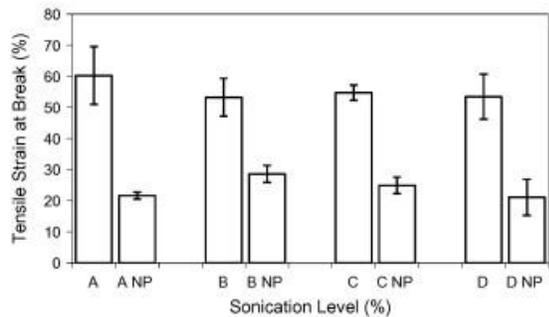
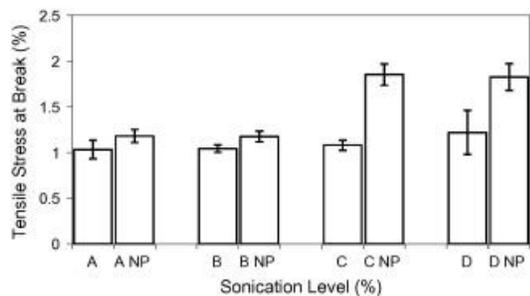
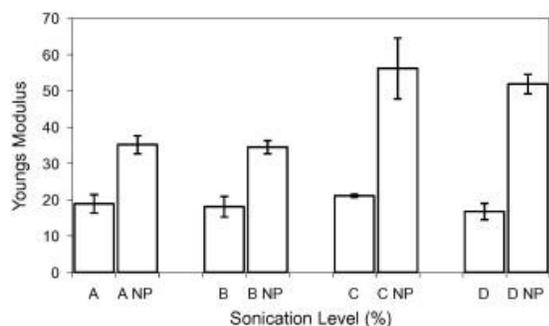


Fig. 6: Effect of sonication level and with or without nanoparticles on Young's modulus, tensile stress and tensile strain of WPI films. The error bars show the standard deviation.

3.6. Thermogravimetric analysis

The thermal stability of the WPI films with or without nanoparticles was investigated using thermogravimetric analysis (TGA) in an air atmosphere. It can be seen from Fig. 7 that the films experience 3–4 noticeable thermal degradation steps in the temperature range of 30–850 °C. Different stages of degradation can be distinctly observed from the prominent peaks in the derivative weight% curves. The temperature range for the first step of thermal degradation is between 50 and 150 °C, which may correspond to the loss of water from the films. The temperature range for the second step of thermal degradation is between 150 and 300 °C, and this may be due to the decomposition of WPI proteins and the loss of glycerol from the film. The temperatures for the onset of maximum degradation (T_{max}) taken from the peak temperature of derivative weight% curves are listed in Table 2. The T_{max} of pure WPI is at 222 °C, which reduced by only 5 °C after 100% sonication. However, the T_{max} of the nanocomposites samples was significantly reduced to 206 °C and 201 °C for samples before and after sonication, respectively. The decrease in the T_{max} in the samples containing nanoparticles could be attributed to the onset of oxidation of the surface functional groups on the nanoparticle within the temperature limits. An additional third step of thermal degradation in the temperature range of 450–550 °C was observed, which may be due to oxidation of partially decomposed proteins. With the addition of nanoparticles, the nanocomposite films (WPI-NP-A and WPI-NP-D) exhibit a significant delay in the weight loss at temperatures above 300 °C. The difference in the weight loss between WPI and WPI-NP samples at 450 °C is listed in Table 2. Similar results are also reported by Kumar et al. (2010) for soy protein isolate (SPI) and montmorillonite (MMT) bio-nano-composite films. Because the TiO₂@SiO₂ nanoparticles are stable above 650 °C, the residue remaining after the decomposition of nanocomposite samples at 650 °C confirms the presence of a similar weight% of nanoparticles in the investigated samples.

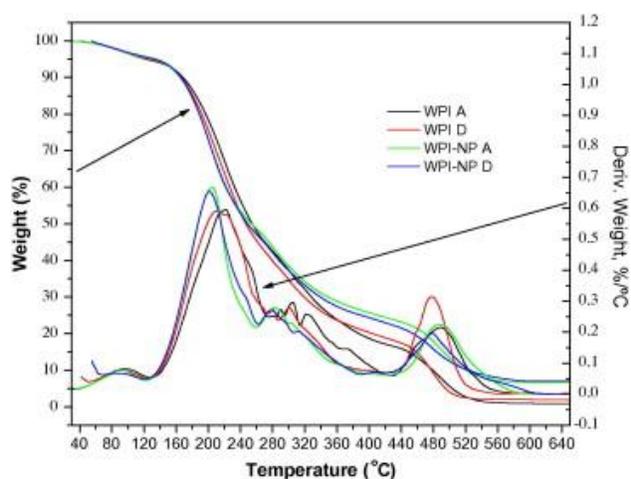


Fig. 7: Effect of sonication level and nanoparticle loadings on TGA of 0.23 mm thick WPI films. Note: It is one representation of few measurements.

Table 2.

TGA investigation of WPI films with and without nanoparticles.

Sample	T_{\max} of derivative curve	Weight loss (%) at 450 °C	Residual weight (%) at 650 °C
WPI-A	222	14.84	0.77
WPI-D	218	16.40	1.76
WPI NP-A	206	22.36	6.64
WPI NP-D	201	20.51	6.96

4. Conclusion

It was observed that whey protein isolate films could sustain their structural integrity under the application of sonication processing, and the incorporation of $\text{TiO}_2@ \text{SiO}_2$ nanoparticles helps to improve their mechanical properties. The optical properties of the WPI films were changed dramatically by the incorporation of nanoparticles, changing from a transparent appearance to opaque. Embedded nanoparticles contributed effectively to increase the thickness of films and to alter the contact angle of the film surface, which may have implications in regard to the hydrophobicity of the films. Film WVP values ($10^{-11} \text{g m/m}^2 \text{ s Pa}$) are shown to be dependent on the film thickness. The presence of nanoparticles in the film was shown to improve certain mechanical properties, but it also caused nearly a 50% reduction in elongation. The storage modulus (E') increased with an increasing level of sonication amplitude, but the presence of nanoparticles led to a reduction in E' , possibly due to phase separation. There were 3–4 steps of thermal degradation of the films in the temperature range of 30–850 °C. The glass transition temperature (T_g) was between -95 °C and -60 °C, and significant differences were observed in the DMA results. The WPI films embedded with nanoparticles have great potential for application in food packaging for extending the shelf life, improving quality, and enhancing the safety of food packaged with them.

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