Egyptian Journal of Food Science
http://ejfs.journals.ekb.eg/

Enhancement of Chitosan Film Characteristics with Nanoparticles

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FOOD packaging is mainly made from plastics. New techniques, such as biodegradable films or coatings were used to meet the environmental concerns and consumer demands for natural products. This research aimed to investigate the effect of adding zinc oxide and selenium nanoparticles (ZnO-NPs and Se-NPs) to chitosan films on its characteristics. The chitosan films incorporated with ZnO-NPs and Se-NPs were prepared to contain ZnO-NPs and Se-NPs as follows: Ch/3%ZnO-NPs and Ch/1%Se-NPs. The results revealed that the incorporation of ZnO and Se-NPs in chitosan films had significantly decreased thickness (from 0.149 µm to 0. 124µm), Transparency (from 0.77% to 0.53%) solubility (from 24.38% to 18.64%) and water vapor permeability (from 40.37 g/m^{2}h to 37.02 g/m^{2}h m) whereas tensile strength and elongation were increased from 33.50 N to 63.71N and from 20.95% to 28.18%, respectively. In general, the chitosan films incorporated with ZnO-NP and Se-NPs will have an important role in food-active packaging.

Keywords: Zinc, Selenium, Chitosan film, Coating

Introduction

Nanomaterials consist of one atom or one molecule and have at least one dimension with nano-scale (one-billionth of a meter) and have a huge potential to bring benefits in different areas such as drug development, water decontamination, and food production (Faisal et al., 2023). Nanoparticles with dimensions in the range of 1–100 nm have a growing interest because of their unique properties, arrangement, and applications which are superior to their bulk counterparts (Jeevanandam et al., 2018). The importance of nanomaterials comes from that size can influence the physio-chemical properties of a substance as the optical properties which can be utilized in bio-imaging applications (Dreaden et al.,2012).

Metal NPs are possessing unique optoelectrical properties so it used in many research applications (Lou-Franco et al., 2021). Plastic packaging materials are widely used as food packages but because of their non-biodegradability, researchers resorted to biodegradable packaging materials to reduce plastic waste and use renewable resources such as proteins, lipids, and polysaccharides (Rhim et al., 2013; Jeevahan et al., 2020; Mellinas et al. 2020). Chitosan is a biodegradable, non-toxic, film-forming polysaccharide that has antimicrobial and antifungal efficacy, able to carry active materials used as film or coating material for food products (Souza et al., 2021 and Severo et al., 2021), but chitosan has poor mechanical and barrier properties, therefore reinforcement materials can be used to impart it these properties

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Received :21/2/2024; Accepted :25/5/2024
DOI : 10.21608/EJFS.2024.271728.1176

(Pires et al., 2021). Biopolymer-based films are incorporated with functional such as antibacterial, antioxidant, and UV-blocking properties materials to improve their physicochemical properties (Roy and Rhim, 2021).

The incorporation of nanoparticles (NPs) into edible films can modify their thermal, mechanical, and gas barrier properties and functionality (Etxabide et al., 2017). So, various nanomaterials such as zinc oxide nanoparticles (ZnONPs) and selenium nanoparticles (SeNPs) have been used to enhance the functionality of the edible films (Hoseinnejad et al., 2018). ZnO NPs can be used to improve the mechanical, chemical, antibacterial, and antioxidative characteristics of the edible films which elongate the shelf life of foods coated with these films. ZnO NPs improve the barrier properties of the edible films which reduce the passage of water or oxygen since the NPs fill the porous spaces within the film matrix (Anbukkarasi et al., 2015). ZnO-NPs are nontoxic to human cells but harmful to microorganisms since the U.S. Food and Drug Administration (FDA) has listed ZnO-NPs as a safe material (Kim et al. 2022). Also, SeNPs have unique antimicrobial, antioxidative, and UV-barrier properties, therefore SeNPs are incorporated into food packaging material (Menon et al., 2019). SeNPs have minimal toxicity and higher biocompatibility when compared to organic/inorganic Se compounds. The Se toxicity could appear with consumption of ≥ 3200 µg/day. SeNPs had antimicrobial, antioxidant, antifungal, anticancer and immune-stimulation properties (Youssef et al., 2022). The research aimed to incorporate ZnO and Se nanoparticles into chitosan films to investigate their nanostructure and functional properties.

Materials and Methods

Materials

Chemicals and reagents used

Zinc-acetate, Methanol, Sodium hydroxide, Sodium selenite, Ascorbic acid, Chitosan, Glycerin, and Glacial acetic acid were obtained from EL-Gommhouria Chemical Company, Cairo, Egypt.

Methods

Preparation of nanoparticles

Zinc oxide nanoparticles (ZnO-NPs) were prepared by the method of Youssef et al. (2016), using stock solutions of Zn $(CH_3COO)_2 \cdot 2H_2O$ (0.2 M), methanol, and NaOH (0.3 M). Selenium nanoparticles (Se-Nps) were prepared according to the method of Li et al. (2010), using stock solutions of Na_2Seo_3 and ascorbic acid.

Preparation of chitosan (Ch) nanocomposites films:

Chitosan nanocomposite films were prepared as described by Souza et al. (2020) using the formulas in Table 1.

Characterization of nanoparticles and nanocomposites films

Particle size, polydispersity index (PDI), and zeta potential.

The particle size and size distributions of ZnO-NPs, Se-NPs, and bio nanocomposites film solutions were determined in terms of average volume diameters, Size range (0.6:6000nm), Zeta potential range (-200:200mV) and polydispersity index (PDI) by photon correlation spectroscopy using particle size analyzer Dynamic light scattering (DLS) (Zeta seizer Nano, Malvern analytical Ltd, United Kingdom) at fixed angel of 173 at 25 as described by Anean et al. (2023).

TABLE 1. chitosan nanocomposites films formulas.

*Films	Film ingredients				
	Chitosan	Glacial acetic acid	Glycerol	ZnO-Nps	Se-Nps
Ch-Control	2%	2 mL	30%	-	-
ChZn	2%	2 mL	30%	3%	-
ChSe	2%	2 mL	30%	-	1%

*Ch-Control, Chitosan; ChZn, Chitosan / 3% ZnO-NPs; ChSe, chitosan/1% SeNPs; ChZn/Se, chitosan / 3% ZnO-NPs / 1% Se-NPs.

Scanning electron microscopy (SEM)

The morphological properties of chitosan films were assessed by scanning electron microscopy (SEM), (JSM 6360LV, JEOL/ Noran) according to the method of Youssef et al. (2016.)

Mechanical and physical properties of nanocomposite films

Films thickness

The film thickness was measured with a digital micrometer (Mitutoyo type Digital Indicators, the company's models: pk-1012 E, Japan) as described by Tien et al. (2004).

Tensile strength and elongation

Tensile strength and elongation were measeared using a texture analyzer (type CT3) by the method of Hernandez-Muñoz et al. (2004).

Films transparency

UV-Visible spectrophotometer (Model UV5704SS) was used to dertermine the transperancy of films as described by sun et al.(2020), the transperancy calculated using the following equation:

$$\text{Transparency} = \frac{A600}{T}$$

Where :

A600 was absorbance at 600 nm

T was film thickness in mm

The percentage of water solubility (weight loss) of films was determined according to the method of Munoz et al. (2004), and calculated by the following equation:

$$\%\ \text{water solubility} = \frac{\text{wt.of intial dry matter} - \text{wt.of dry matter not solubilized}}{\text{wt.of intial dry matter}} \times 100$$

Measuring water vapor transmission rate (WVTR)

The water vapor transmission rate (g/hr.m^2) was determined by the method of the ASTM E96-95 (ASTM, 1995), and the water vapor transmission rate (WVTR) was calculated using the following equation:

$$WVTR = \Delta m / \Delta t.\ A$$

Δm/Δt = is the moisture gain weight per time (g/hr)

A = is the surface area of the film(m^2)

Results and Discussion

Characterization of ZnO-NPs and Se-NPs:

Particle size, polydispersity index (PDI), and zeta

The particle size (diameter) of nanoparticles is an important characteristic for the application of nanoparticles in food technology. Table 2 demonstrates the particle size distribution of ZnO-NPs and Se-NPs. The results indicated that the size of ZnO-NPs was 256.7 nm while Se-NPs recorded a smaller particle size (72.96 nm) as compared to ZnoNPS. On the other hand, the Polydispersity index is a dimensionless measure of the heterogeneity of particle size and is used to show the distribution pattern of particles as the (PDI) indicates the level of dispersion homogeneity, which ranges from 0 to 1. If PDI is close to 0 it suggests that the size distribution of nanoparticles is more homogeneous (Yadav and Sawant, 2010). In this context, Se-NPs exhibited the lowest PDI value (0.186) (more homogeneous) as compared to Zno-NPs (0.478). Regarding, the zeta potential of nanoparticles is useful in the determination of nanoparticles' stability during storage time (Abbas et al., 2008). The nanoparticles are more stable when the zeta potential is higher, whether it is positive or negative (wiacek and chibowski, 2000). The results showed that the zeta potential values of ZnO-NPs and Se-NPs were -18 and -23 mv, respectively. The higher zeta potential was recorded for SeNPs (-23mv), in which a small particle size (72.96nm) was also achieved because had a higher negative value charge that indicates higher stability of the Se-NPs as compared to ZnO NPs. These results agreed with that obtained by Farag et al. (2023) who demonstrated that the particle size of ZnO-NPs and Se-NPs, were 219 and 190 nm, respectively. Also, Hassanein et al. (2021) reported that the average size of prepared ZnO-NPs with the chemical method without using a stabilizer was (282.6 nm) and the zeta potential for it was -21.6 mv. Similarly, Mohanraj and Chen (2006) showed that the size of the nanoparticles ranged between 10 and 1000 nm which is accompanied by the obtained result.

Characterization of nanocomposite films

Surface morphology of nanocomposite films

The recognizing microstructure and morphology of the edible films helps in choosing the proper film formula for food application. Fig.1 presents the SEM micrographs of the surface of different films. The results showed that the control film (Ch without nanoparticles) had a smooth surface enough to be homogenous and to form a continuous matrix with some pores

TABLE 2. Particle size, Poly Dispersity index (PDI) and Zeta potential of ZnO-NPs and Se-NPs.

*Nano material	particle size distribution (nm)		Zeta potential (mv)
	Particle size	PDI	Z-Potential
ZnONPs	256.7	0.478	-18.4
SeNPs	72.96	0.186	-23.8

*ZnO-NPs: Zinc oxide nanoparticles and Se-NPs: Selenium nanoparticles

on the surface. On the other hand, the films prepared with the incorporation of nanoparticles became rougher (the size of the nanoparticle is increased) because of the recrystallization of chitosan molecules during the film drying (Ndwandwe et al., 2022). The SEM images of the film which was prepared with the addition of 3% ZnO-NPS showed that the film is uniform with a homogeneous surface because of the absence of noticeable ZnO-NPs aggregates.Also, the SEM micrographs of the film that contained 1% SeNPs exhibited an equal distribution of particles through the surface, because SeNPs filled interspaces that existed in the control film. These results agreed with Mirjalili & Ardekani (2017) who reported that nanoparticles improved the mechanical and physical properties of starch edible film supplemented with nanoparticles of zinc. Also, Ndwandwe et al. (2022) reported that the scanning electron microscopy of potato starch film with Se-NPs showed a slight increase in surface roughness and high affinity between the Se-NPs and the starch film matrix which enhanced the mechanical and physical properties.

Mechanical and physical properties of nanocomposite films

The effect of ZnO and Se nanoparticles addition on the thickness of films

The thickness of the film mainly depends on the preparation methods and drying conditions and is influenced by the component's interaction (Kanamani et al., 2013). Figure 2 shows the effect of nanoparticles (Zn and Se) on the thickness values of films. It could be seen that the thickness values of chitosan films; Ch, Ch/Zn, and Ch/Se were 0.149, 0.124, and 0.147µm, respectively. The results cleared that the highest thickness was observed for the control film (Ch) followed by Ch/Se while the lowest thickness was observed for Ch/Zn film. These results indicated that the thickness of chitosan film was affected by the addition of Zno and Se- NPs because of the tight network structure between NPs and chitosan. These results agreed with that of Goudarzi et al. (2017) who stated that the addition of Nano TiO_2 to starch film decreased the thickness. Also, these results on line with Abo-Gabal et al. (2022) who reported that the addition of nano TiO_2 and Ag decreased the thickness of hydroxy propyl methyl cellulose film.

The effect of Zno and Se nanoparticles addition on tensile strength (N) and elongation at break (%) of films

Figure 3 exhibits the influences of nanoparticles on the strength property of chitosan film. The tensile strength of prepared films was determined as resistance obtained to rupture when subjected to a pulling force or maximum load. The data indicated that the tensile strength of prepared films was greatly affected by the nanoparticles. The maximum tensile strength at chitosan films was recorded for Ch/zn (63.71N) followed by Ch/se (55.07N) compared to the control film, Ch (33.50N). On the other hand, the elongation property of flexible films measures the extent to which a martial will stretch before breaking. The results indicated that the highest value of elongation in chitosan composite films (28.18%) was observed for Ch/Zn and the lowest elongation value (20.95%) was noticed for control film (Ch). The obtained data showed that tensile strength and elongation reached maximum value when nanoparticles were added. The enhancement of tensile strength and elongation of films is due to NPs existing in between polymer chains and an intermolecular cross-linking is generated. This observation is compatible with SEM analysis. These results were in agreement with that of Ndwandwe et al. (2022) who reported that the tensile strength and elongation of potato starch film were improved with the addition Se-NPS. Also, these results were supported by the findings of Anwar et al. (2022) who reported that adding ZnO-NPs to carboxyl methyl cellulose film increased the tensile strength and elongation compared to control film formulated without nanoparticles.

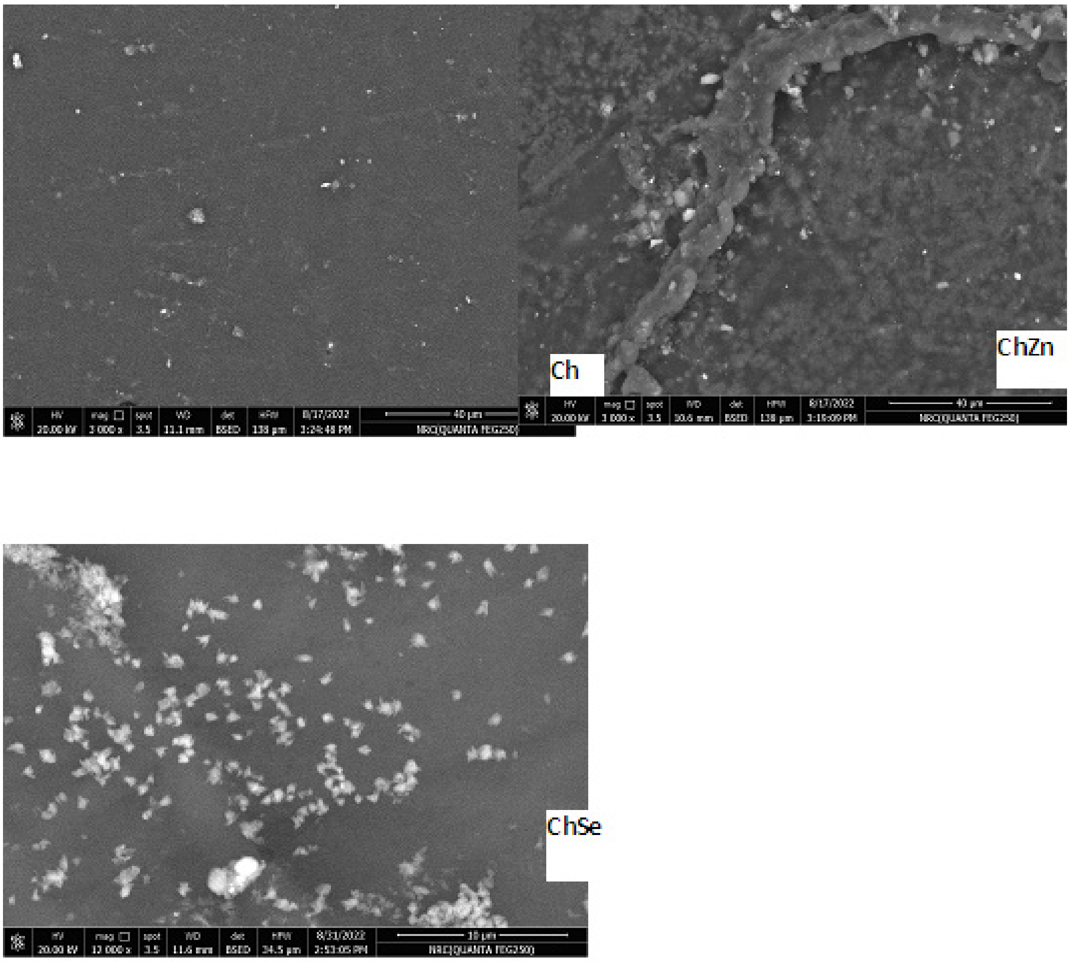

Fig. 1. Scanning electron microscopy images of films.

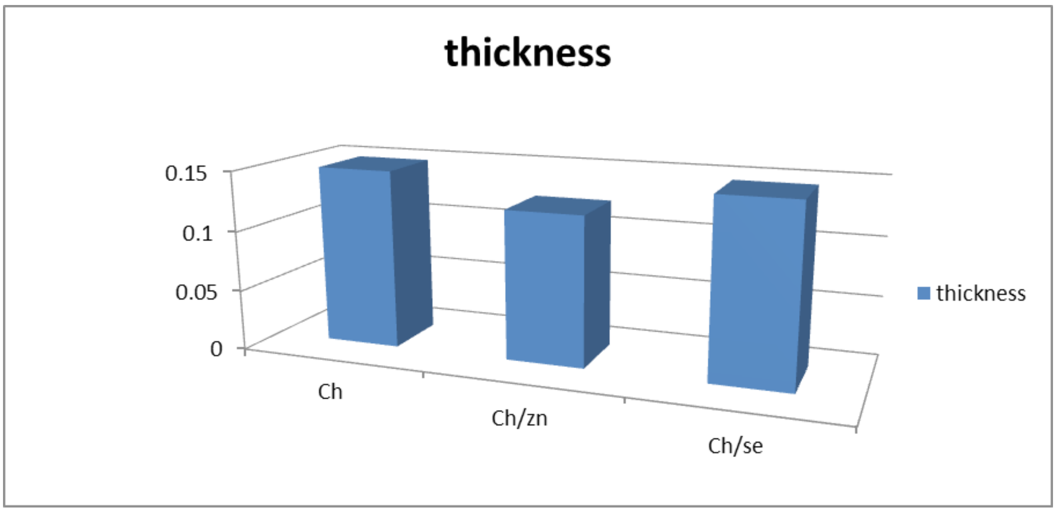

Fig. 2. Effect of ZnoNps and SeNps addition on Thickness of films.

The effect of Zno and Se nanoparticles addition on the Transparency of films

The transparency of film influences consumer acceptance when applied to packaging and food coating. The recorded transparency values of chitosan films with/ without NPs are presented in Fig. 4. The obtained data showed that the transparency decreased by adding nanoparticles, since it decreased from 0.77% for control (Ch) to 0.53 and 0.62 for Ch/Zn and Ch/Se, respectively. These results agreed with Dehankar et al. (2023) who reported that the transparency decreased by adding ZnO-NPs to chitosan/guar gum film. Similarly, Anwar et al. (2022) reported that the transparency of carboxyl methyl cellulose film was decreased by adding ZnO-NPs.

\The effect of Zno and Se nanoparticles addition on % Water solubility (weight loss)

Solubility in water is an important property of edible films which is required to enhance product integrity and water resistance. However, in some cases, water solubility before consumption of the product might be useful. Figure 5 shows the water solubility of chitosan films prepared with/without NPs. The results showed that chitosan films loaded with NPs had lower values of solubility than control film. The solubility value decreased with the addition of NPs since it was lowered

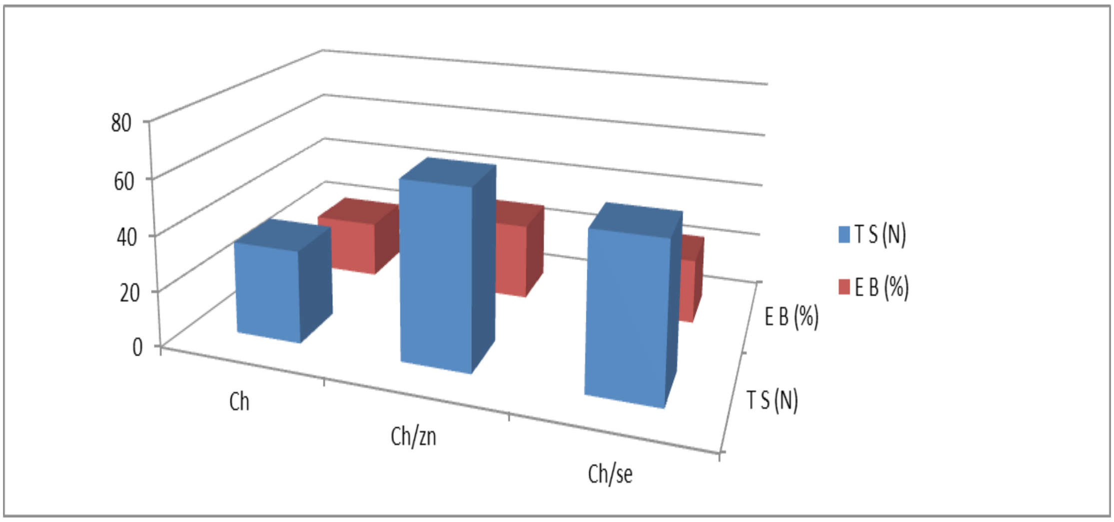

Fig. 3. Effect of ZnO-Nps and Se-Nps addition on Tensile strength(N) and elongation at break (%) of film samples.

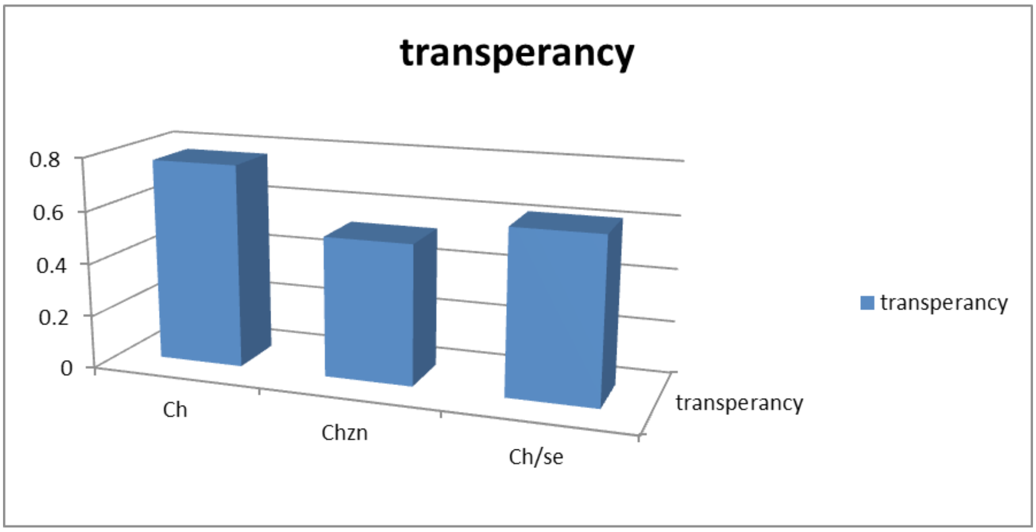

Fig. 4. Effect of ZnoNps and SeNps addition on Transparency of films

from 24% for control (Ch) to 18.64% for ChZn and 21.65% for Ch/Se. The decreased solubility might be attributed to the reduction of free-OH groups of polymers because of NPs/ polymers macromolecule interaction (Mathew et al., 2019) or might be due to strong bonding between polymers and NPs which led to decreased film solubility. These results were in agreement with that of Dehankar et al. (2023) who reported that the solubility in water was decreased by adding ZnO-NPs to chitosan/guar gum film. Also, Anwar et al. (2022) reported that the solubility in water was decreased by adding ZnO-NPs to carboxyl methyl cellulose. Also, Ndwandwe et al. (2022) reported that the solubility in water is decreased by the incorporation of Se-NPs into potato starch film.

The effect of Zno and Se nanoparticles addition on water vapor transmission rate (WVTR) of films.

The water vapor transmission rate: Food applications need effective barriers, such as food packaging, a protective coating, and so on, to reduce WVTR. The values of WVTR are given in Figure 6. The results showed that nanocomposite films exhibited lower WVTR values compared to the control. Where, the lowest values of WVTR were noticed for ChZn (37.02 g/m^{2}h) followed by ChSe (37.18 g/m^{2}h), while the control film (Ch) was recorded as the highest WVTR value (40.37 g/m^{2}h). These results on line with that of Rahman *et al*. (2018) who reported that the WVTR values of chitosan films are decreased by adding ZnO-NPs.

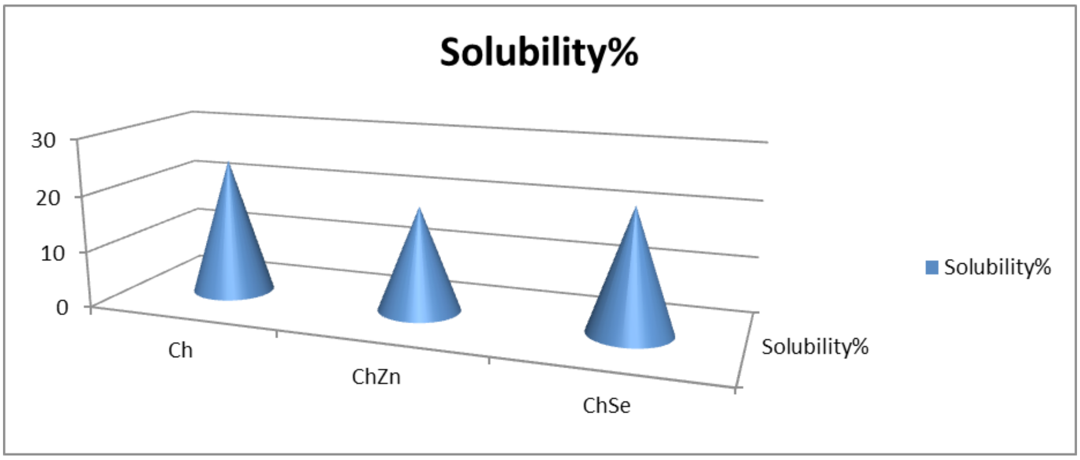

Fig. 5. Effect of ZnO-Nps and Se-Nps addition on % water solubility (weight loss).

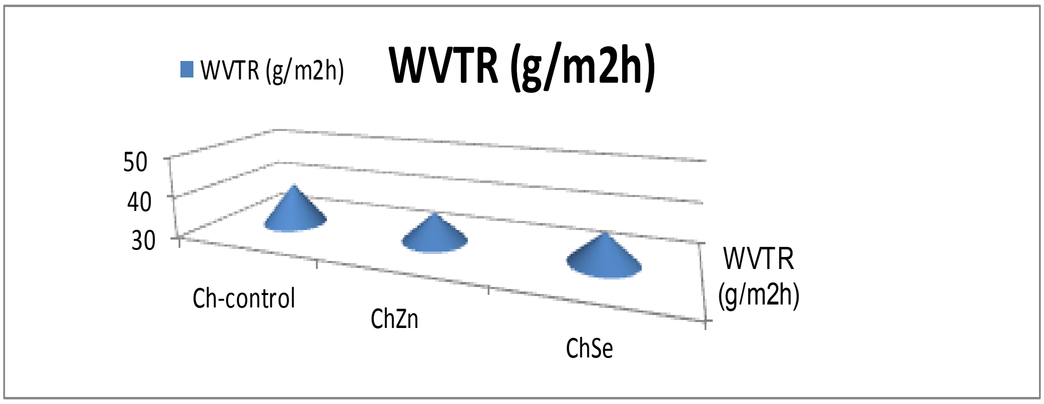

Fig. 6. Effect of ZnO-Nps and Se-Nps addition on water vapor transmission rate(WVTR) of films.

Conclusion

In general, it could be concluded that all properties of chitosan films were affected by the addition of ZnO and Se NPS. For example, ZnO-NPs and Se-NPs improved the mechanical resistance, WVTR, tensile strength, and elongation at the break of chitosan films but lowered their transparency. Finally, the Ch/Zn edible composite film showed better characteristics than other films (Ch/Zn and control).

References

Abbas, Z., Labbez, C., Nordholm, S. and Ahlberg, E. (2008) Size-dependent surface charging of nanoparticles. *The Journal of Physical Chemistry C*, **112**(15), 5715-5723. https://pubs.acs.org/doi/abs/10.1021/jp709667u.

Abo-Gaball, B.H., Bahnasawy, A., and G Khater, E. (2022) Effect of edible films reinforced with nanoparticles on shelf-life and quality of chicken fillet meat during storage. *Misr Journal of Agricultural Engineering*, **39**(2), 205-220. https://mjae.journals.ekb.eg/article_213031.html.

Anbukkarasi, V., Srinivasan, R. and Elangovan, N. (2015) Antimicrobial activity of green synthesized zinc oxide nanoparticles from *Emblica officinalis*. *International Journal of Pharmaceutical Sciences Review and Research*, **33**(2), 110-115. https://globalresearchonline.net/journalcontents/v33-2/23.pdf.

Anean, H. A., Mallasiy, L. O., Bader, D. M. and Shaat, H. A. (2023) nano edible coatings and films combined with zinc oxide and pomegranate peel active phenol compounds has been to extend the shelf life of minimally processed pomegranates. *Materials*, **16(**4), 1569. https://www.mdpi.com/1996-1944/16/4/1569.

Anwar, M. M., Aly, S. S., Nasr, E. H. and El-Sayed, E. S. R. (2022) Improving carboxymethyl cellulose edible coating using ZnO nanoparticles from irradiated Alternaria tenuissima. *AMB Express*, **12**(1), 1-11. https://amb-express.springeropen.com/articles/10.1186/s13568-022-01459-x.

ASTM E 95-96 (1995) Standard Test Methods for Water Vapor Transmission of Materials (E96-E95). *Annual Books of ASTM Standards*, **552**, 785-792. https://codehub.building.govt.nz/resources/astm-e96-95.

Dehankar, H. B., Mali, P. S. and Kumar, P. (2023) Edible composite films based on chitosan/guar gum with ZnONPs and roselle calyx extract for active food packaging. *Applied Food Research*, **3**(1), 100276. https://www.sciencedirect.com/science/article/pii/S277250222300015X.

Dreaden, E. C., Alkilany, A. M., Huang, X., Murphy, C. J. and El-Sayed, M. A. (2012) The golden age: gold nanoparticles for biomedicine. *Chemical Society Reviews*, **41**(7), 2740-2779. https://pubs.rsc.org/en/content/articlelanding/2012/cs/c1cs15237h/unauth.

Etxabide, A., Uranga, J., Guerrero, P. and De la Caba, K. (2017) Development of active gelatin films by means of valorisation of food processing waste: A review. *Food Hydrocolloids*, **68**, 192-198. https://www.sciencedirect.com/science/article/abs/pii/S0268005X1630360.

Faisal, S., Hamed, A. A., Shawky, R., and Emara, M. (2023) Chitosan-Silver Nanoparticles: A Versatile Conjugate for Biotechnological Advancements. *Journal of Advanced Pharmacy Research*, **7**(3), 163-169. https://journals.ekb.eg/article_309528.html.

Farag, M. M., El-Sebaie, W., Basalious, E. B. and El-Gazayerly, O. N. (2023) Darifenacin Self-assembled Liquid Crystal Cubic Nanoparticles: a Sustained Release Approach for an Overnight Control of Overactive Bladder. AAPS PharmSciTech, **24**(5), 120. https://link.springer.com/article/10.1208/s12249-023-02575-y.

Goudarzi, V., Shahabi-Ghahfarrokhi, I. and Babaei-Ghazvini, A. (2017) Preparation of ecofriendly UV-protective food packaging material by starch/TiO2 bio-nanocomposite: Characterization. *International Journal of Biological Anmacromolecules,* **95**, 306-313. https://www.sciencedirect.com/science/article/abs/pii/S0141813016318566.

Hassanein, T. F., Mohammed, A. S., Mohamed, W., Sobh, R. A. and Zahran, M. K. (2021) Optimized synthesis of biopolymer-based zinc oxide Nanoparticles and evaluation of their antibacterial activity. *Egyptian Journal of Chemistry*, **64**(7), 3767-3790. https://ejchem.journals.ekb.eg/article_177405.html.

Hernández-Muñoz, P., Villalobos, R. and Chiralt, A. (2004) Effect of cross-linking using aldehydes on properties of glutenin-rich films. *Food Hydrocolloids*, **18**(3):403-411. https://www.sciencedirect.com/science/article/abs/pii/S0268005X03001280.

Hoseinnejad, M., Jafari, S. M. and Katouzian, I. (2018) Inorganic and metal nanoparticles and their antimicrobial activity in food packaging applications. *Critical Reviews in Microbiology*, **44**(2), 161-181. https://www.tandfonline.com/doi/abs/10.1080/1040841X.2017.1332001.

Jeevanandam, J., Barhoum, A., Chan, Y. S., Dufresne, A. and Danquah, M. K. (2018) Review on nanoparticles and nanostructured materials: history, sources, toxicity and regulations. *Beilstein Journal of Nanotechnology*, **9**(1), 1050-1074. https://www.beilstein-journals.org/bjnano/articles/9/98.

Jeevahan, J. J., Chandrasekaran, M., Venkatesan, S. P., Sriram, V., Joseph, G. B., Mageshwaran, G. and Durairaj, R. B. (2020) Scaling up difficulties and commercial aspects of edible films for food packaging: A review. *Trends in Food Science & Technology*, **100**, 210-222. https://www.sciencedirect.com/science/article/abs/pii/S092422442030443X.

Kanamani, P. and Lim, S. T. (2013) Development and characterization of novel probiotic-residing pullulan/starch edible films. *Food chemistry*, **141**(2), 1041-1049. https://www.sciencedirect.com/science/article/abs/pii/S0308814613004482.

Kim, I., Viswanathan, K., Kasi, G., Thanakkasaranee, S., Sadeghi, K. and Seo, J. (2022) ZnO nanostructures in active antibacterial food packaging: Preparation methods, antimicrobial mechanisms, safety issues, future prospects, and challenges. *Food Reviews International*, **38**(4), 537-565. https://www.tandfonline.com/doi/full/10.1080/87559129.2020.1737709.

Li, Q., Chen, T., Yang, F., Liu, J. and Zheng, W. (2010) Facile and controllable one-step fabrication of selenium nanoparticles assisted by L-cysteine. *Materials letters*, **64**(5), 614-617. https://www.sciencedirect.com/science/article/abs/pii/S0167577X09009525.

Lou-Franco, J., Das, B., Elliott, C. and Cao, C. (2021) Gold nanozymes: from concept to biomedical applications. *Nano-Micro Letters*, **13**, 1-36. https://link.springer.com/article/10.1007/s40820-020-00532-z.

Mathew, K., Kolluru, V. S., Mula, S., Steinmann, S. N. and Hennig, R. G. (2019) Implicit self-consistent electrolyte model in plane-wave density-functional theory. *The Journal of Chemical Physics*, **15**1(23). https://pubmed.ncbi.nlm.nih.gov/31864239/.

Mellinas, C., Ramos, M., Jiménez, A. and Garrigós, M. C. (2020) Recent trends in the use of pectin from agro-waste residues as a natural-based biopolymer for food packaging applications. *Materials*, **13**(3), 673. https://rua.ua.es/dspace/handle/10045/102408.

Menon, S., KS, S. D., Agarwal, H. and Shanmugam, V. K. (2019) Efficacy of biogenic selenium nanoparticles from an extract of ginger towards evaluation on anti-microbial and anti-oxidant activities. *Colloid and Interface Science Communications*, **29**, 1-8. https://www.sciencedirect.com/science/article/abs/pii/S2215038218301626.

Mirjalili, F. and Ardekani, Y.A. (2017) Preparation and characterization of starch film accompanied with ZnO nanoparticles. *Journal of Food Process Engineering*, **40**(6), e12561. https://onlinelibrary.wiley.com/doi/full/10.1111/jfpe.12561.

Mohanraj, V. J., and Chen, Y. (2006) Nanoparticles-a review. *Tropical Journal of Pharmaceutical Research*, **5**(1), 561-573. https://www.ajol.info/index.php/tjpr/article/view/14634.

Munoz, P. H., Lopez-Rubio, A., Del-Valle, V., Almenar, E. and Gavara, R. (2004) Mechanical and water barrier properties of glutenin films influenced by storage time. *Journal of Agricultural and. Food Chemistry,* **52** (21), 79-83. https://pubs.acs.org/doi/abs/10.1021/jf034763s.

Ndwandwe, B. K., Malinga, S. P., Kayitesi, E. and Dlamini, B. C. (2022) Selenium nanoparticles–enhanced potato starch film for active food packaging application. International *Journal of Food Science and Technology*, **57**(10), 6512-6521. https://ifst.onlinelibrary.wiley.com/doi/full/10.1111/ijfs.15990.

Pires, J., Paula, C. D. D., Souza, V. G. L., Fernando, A. L. and Coelhoso, I. (2021) Understanding the barrier and mechanical behavior of different nanofillers in chitosan films for food packaging. *Polymers*, **13**(5), 721. https://www.mdpi.com/2073-4360/13/5/721.

Rahman, P. M., Mujeeb, V. A., Muraleedharan, K. and Thomas, S. K. (2018) Chitosan/nano ZnO composite films: enhanced mechanical, antimicrobial and dielectric properties. *Arabian Journal of Chemistry*, **11**(1), 120-127. https://www.sciencedirect.com/science/article/pii/S1878535216301526.

Rhim, J. W., Wang, L. F. and Hong, S. I. (2013) Preparation and characterization of agar/silver nanoparticles composite films with antimicrobial activity. *Food Hydrocolloids*, **33**(2), 327-335. https://www.sciencedirect.com/science/article/abs/pii/S0268005X13001057.

Roy, S. and Rhim, J. W. (2021) Gelatin-based film integrated with copper sulfide nanoparticles for active packaging applications. *Applied Sciences*, **11**(14), 6307. https://www.mdpi.com/2076-3417/11/14/6307.

Severo, C., Anjos, I., Souza, V. G., Canejo, J. P., Bronze, M. R., Fernando, A. L. and Ribeiro, I. A. (2021) Development of cranberry extract films for the enhancement of food packaging antimicrobial properties. *Food Packaging and Shelf Life,* **28**, 100646. https://www.sciencedirect.com/science/article/abs/pii/S2214289421000144.

Souza, V. G. L., Alves, M. M., Santos, C. F., Ribeiro, I. A., Rodrigues, C., Coelhoso, I. and Fernando, A. L. (2021) Biodegradable chitosan films with ZnO nanoparticles synthesized using food industry by-products - production and characterization. *Coatings*, **11**(6), 646 (1-16). https://www.mdpi.com/2079-6412/11/6/646.

Souza, V. G., Pires, J. R., Rodrigues, C., Coelhoso, I. M. and Fernando, A. L. (2020) Chitosan composites in packaging industry—current trends and future challenges. *Polymers*, **12**(2), 417. https://www.mdpi.com/2073-4360/12/2/417.

Sun, J., Jiang, H., Wu, H., Tong, C., Pang, J. and Wu, C. (2020) Multifunctional bionanocomposite films based on konjac glucomannan/chitosan with nano-ZnO and mulberry anthocyanin extract for active food packaging. *Food Hydrocolloids*, **107**, 105942. https://www.sciencedirect.com/science/article/abs/pii/S0268005X19328218.

Tien, C., Letendre, M., Ispas-Szabo, P., Mateescu, M. A., Delmas-Patterson, G., Yu, H. L. and Lacroix, M. (2004) Development of biodegradable films from whey proteins by cross-linking and entrapment in cellulose. *Journal of agricultural and food chemistry*, **48**(11): 5566-5575. https://pubs.acs.org/doi/abs/10.1021/jf0002241.

Wiacek, A. and Chibowski, E. (2000) Stability of oil/water (ethanol, lysozyme or lysine) emulsions. Colloids and Surfaces B: *Biointerfaces*, **17**(3), 175-190. https://www.sciencedirect.com/science/article/abs/pii/S0927776599001034.

Yadav, K. S. and Sawant, K. K. (2010) Formulation optimization of etoposide loaded PLGA nanoparticles by double factorial design and their evaluation. *Current Drug Delivery*, **7**(1), 51-64. https://www.ingentaconnect.com/content/ben/cdd/2010/00000007/00000001/art00008.

Youssef, A. M., El-Sayed, S. M., El-Sayed, H. S., Salama, H. H. and Dufresne, A. (2016) Enhancement of Egyptian soft white cheese shelf life using a novel chitosan/carboxymethyl cellulose/zinc oxide bionanocomposite film. *Carbohydrate Polymers,* **151**, 9-19. https://www.sciencedirect.com/science/article/abs/pii/S0144861716305367.

Youssef, D. M., Alshubaily, F. A., Tayel, A. A., Alghuthaymi, M. A. and Al-Saman, M. A. (2022) Application of nanocomposites from bees products and nano-selenium in edible coating for catfish fillets biopreservation. *Polymers*, **14**(12), 2378. https://www.mdpi.com/2073-4360/14/12/2378.