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Preparation and Characterization of Chitosan and k-Carrageenan-Based Nanocomposite Coatings Utilizing Different Technologies for Food Packaging Applications

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Abstract: *Perishable food products, including fruits, vegetables, and seafood, require preservation techniques to extend their shelf life. In recent years, nanotechnology has emerged as a promising approach to enhance the properties of edible coatings. Nanocomposite coatings incorporating various materials and technologies have been developed to optimize coating performance. PSA, SEM, XRD, and FT-IR analyses were conducted to characterize the physical and morphological properties of these nanocomposite coatings. The findings indicated that the use of Ultra-Turrax (UT) technology in the preparation of the coating solution resulted in smaller particle sizes (458.9-1037.2 nm), improved visual appearance, and smoother films with uniformly distributed nanoparticles on the surface. XRD and FT-IR analyses confirmed the crystallinity and functional groups of ZnO and TiO_2 within the nanocomposite coatings. These newly developed coatings have significant potential as environmentally friendly packaging materials and preservation technologies to extend the shelf life of perishable food products.*

Keywords*: Nanocomposite coatings, chitosan, carrageenan, nano ZnO, nano* TiO_2

1. Introduction

Recent research has increasingly focused on natural biopolymers as sustainable alternatives to non-biodegradable plastics for packaging applications [1]. Polysaccharides, proteins, and lipid-based materials derived from plant and animal sources are commonly employed for this purpose [2]. Among these, polysaccharides exhibit favorable film-forming capabilities, moderate mechanical strength, and excellent barrier properties against gases such as oxygen and carbon dioxide. Various polysaccharides, including chitosan, carrageenan, and cellulose, along with their derivatives such as alginate, pectin, starch, and pullulan, have been utilized in the development of edible packaging materials [3-9].

Chitosan is a natural polysaccharide known for its remarkable film-forming properties, high mechanical strength, and strong antimicrobial activity [10]. Pavinatto et al. [11] reported that chitosan can be effectively employed as a coating to extend the shelf life of strawberries. Additionally, research by Hong et al. [12] showed that a 2.0% (w/v) chitosan coating, when combined with low-temperature storage, significantly inhibits fruit ripening and preserves fruit quality. In addition, κ-carrageenan is a polysaccharide extracted from certain species of red seaweed, consisting of linear chains of sulfated galactans [13]. It holds significant potential for development due to its excellent transparency, tensile strength, gelling ability, and film-forming properties [14]. κ-carrageenan has been widely utilized in various food industries for applications such as food films and coatings.

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These include preventing superficial dehydration in fresh and frozen meat, poultry, and fish [15], as well as in ham or sausage casings, dry solid foods, and oily products. Additionally, it is employed in the cosmetics and pharmaceutical industries [16]. Although chitosan and carrageenan are used in many applications, it forms films that do not have good mechanical and water vapour barrier properties. Therefore, further improvements are required to enhance their physical and mechanical performance. Numerous studies have concentrated on the incorporation of nano-sized reinforcing materials into polymer matrices to develop nanocomposite materials.

Nanomaterials such as nano-TiO_2 and nano-ZnO have been utilized as nano-fillers in polymer coatings to enhance their properties. TiO_2, a chemically inert material, is extensively applied in food, medical, and biological products due to its antimicrobial properties [17-19]. In contrast, ZnO is an inorganic compound known for its ability to inhibit microbial growth, protect food from damage caused by ultraviolet (UV) radiation, and is considered safe for use in controlled quantities in food products [20-22]. Several studies have investigated the application of chitosan and carrageenan-based nano-composite coatings. Xing et al. [17] reported that a chitosan/nano-TiO_2 nanocomposite coating effectively preserves the nutritional composition and quality of mangoes stored at 13°C. Karthikeyan et al. [23] reported that chitosan/nano-TiO_2 composites exhibit excellent antimicrobial properties. Additionally, Li et al. [8] showed that chitosan/nano-ZnO nanocomposite coatings applied to cherry tomatoes inhibit gas exchange, reduce respiratory intensity, maintain soluble solids content (SSC) and color, and effectively suppress microbial growth. Meindrawan et al. [24] found that carrageenan/nano-ZnO nanocomposite coatings on mangoes reduced total acidity, preserved texture, delayed discoloration and decay, and extended shelf life, attributed to the antimicrobial activity of ZnO. Furthermore, the properties of the resulting nanocomposite coatings are significantly influenced by the manufacturing technology employed in their production.

The technology employed in the fabrication of nanocomposite coating solutions significantly influences the physical, mechanical, and chemical properties of the resultant coatings [25]. Precise control of the synthesis process, nanoparticle size and distribution, and application method can produce coatings with desired properties for various applications, including material protection, food storage, and other industrial applications. Ultra-Turrax, ultrasound, and magnetic stirrer technologies are utilized to mix, mediate, and homogenize nanoparticles within polymer matrices or solutions. Each method offers unique strengths and applications, and they are often employed either sequentially or simultaneously to achieve optimal dispersion and stability of the nanoparticles [5, 26-28]. UT technology has been widely utilized in various studies for applications requiring homogenization, emulsification, and particle size reduction [29-31]. Additionally, UB and MS technologies are commonly employed by researchers in the development of edible nanoemulsions, edible films, and nanocoatings [32–34].

This study investigates the preparation and characterization of nanocomposite coatings, including CS/nano TiO_2, CG/nano ZnO, and CS/nano ZnO, utilizing various technologies for food packaging applications. The particle size of the nanocomposite coatings was analyzed using particle size analysis (PSA), and their morphological properties and visual appearance were examined using scanning electron microscopy (SEM). The presence of nanoparticle crystals was confirmed by characteristic diffraction peaks observed in the theta region through X-ray Diffraction (XRD). Additionally, the functional groups of the nanocomposite coatings were identified using Fourier-transform infrared (FT-IR) spectroscopy.

2. Materials and methods

2.1. Materials

Commercial food-grade chitosan with a deacetylation degree of 97.21% was obtained from CV. Phy Edumedia, Indonesia. K-carrageenan, with a food-grade purity of 99.6%, was sourced from Indo Food Chem. Anatase titanium dioxide nanopowders (≥99.9% trace metal basis, 10 nm particle size) and ZnO nanopowders (≥99.8% trace metal basis, 20-30 nm particle size) were procured from Hongwu Materials, China.

2.2. Nanocomposite coatings preparation

The chitosan/TiO_2 nanocomposite was prepared following the method described by Xing et al. [17], with slight modifications. Specifically, 0.03 g of nano TiO_2 powder was dissolved in 2 mL of glycerol, followed by the addition of 100 mL of a 1% (v/v) glacial acetic acid solution. Subsequently, 1 g of chitosan powder was added, and the mixture was heated on a hot plate at 90°C for 20 min (Figure 1a). The CS/nano TiO_2-MS treatment involved heating and stirring the mixture with a magnetic stirrer at 1500 rpm and 40°C for 2 h. The CS/nano TiO_2-UB1 and CS/nano TiO_2-UB2 treatments were subjected to ultrasonic bath heating, with the ultrasonic bath applied at the beginning of the process for CS/nano TiO_2-UB1 and at the end for CS/nano TiO_2-UB2, at 50°C for 40 min. The CS/nano TiO_2-UT treatment was stirred using an Ultra-Turrax at 15000 rpm, followed by ultrasonic bath heating for 15 min at 50°C. The membrane solution was then filtered using cheesecloth.

0.16 g of ZnO NPs was dispersed into 100 mL of aquadest (Figure 1b). 2 g of carrageenan was slowly added and stirred at 60°C until completely dissolved. A glycerol plasticizer (0.5 mL) was added to the solution heated to 80°C, and maintained for 5 min. The next steps were the same as those carried out in the preparation of pure carrageenan-ZnO nanocomposite [9, 24]. The CG/nano ZnO-MS treatment was followed by heating and stirring with a magnetic stirrer at 1500 rpm at a temperature of 40°C for 2h. CG/nano ZnO-UB1 and CG/nano ZnO-UB2 were heated with an ultrasound bath at the beginning and end at 50°C for 40 min. The CG/nano ZnO-UT treatment was stirred using ultra-turrax at 15000 rpm and continued with ultrasound bath heating for 15 min at 50°C. The membrane solution was filtered using a cheesecloth.

Chitosan-ZnO nanocomposites were prepared by the method of Li et al. [8], with slight modifications (Figure 1c). A total of 2 g of chitosan was added to a 0.5% (v/v) glacial acetic acid solution and stirred at 30°C until a homogeneous solution was obtained. Glycerol (1 mL) and ZnO nanoparticles (0.6 g) were then introduced into the mixture. The solution was heated on a hot plate at 80°C for approximately 5 min. Subsequent steps followed the same procedure used in the preparation of the pure chitosan-ZnO nanocomposite. For the CS/nano ZnO-MS treatment, the solution was heated and stirred with a magnetic stirrer at 1500 rpm at 40°C for 2 h. In the CS/nano ZnO-UB1 and CS/nano ZnO-UB2 treatments, the solution was subjected to ultrasonic bath heating at 50°C for 40 min at both the beginning and end of the process. The CS/nano ZnO-UT treatment involved stirring the solution using an Ultra-Turrax at 15,000 rpm, followed by ultrasonic bath heating for 15 min at 50°C. Finally, the membrane solution was filtered using cheesecloth.

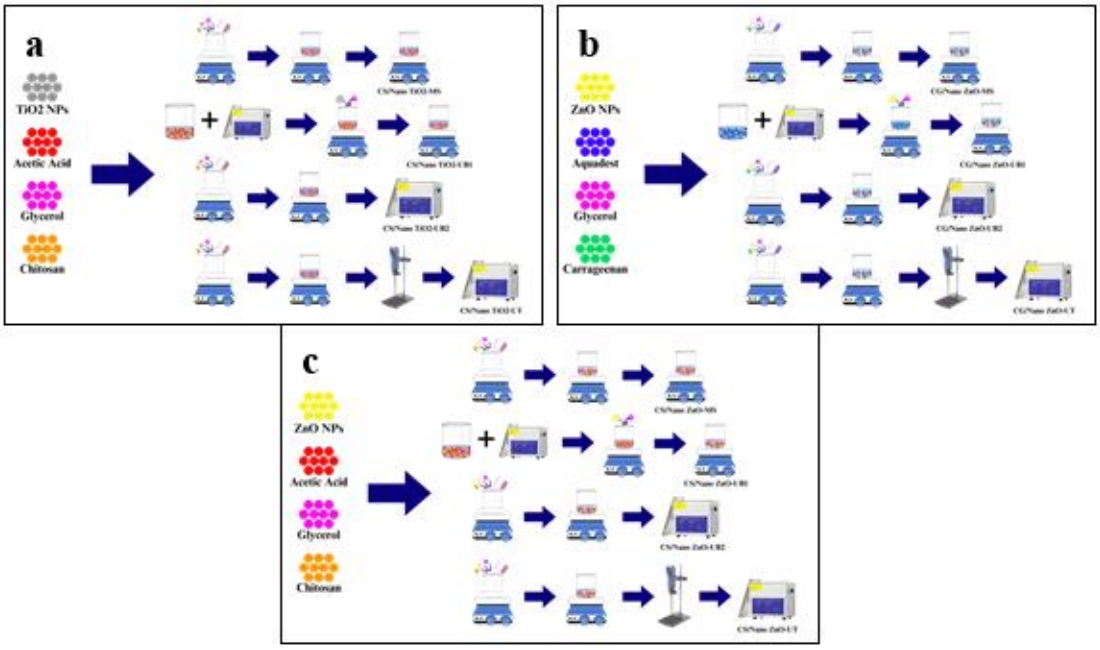


Figure 1. Nanocomposite coatings preparation on chitosan/nano TiO_2 (a), carrageenan/nano ZnO (b) and chitosan/nano ZnO (c)

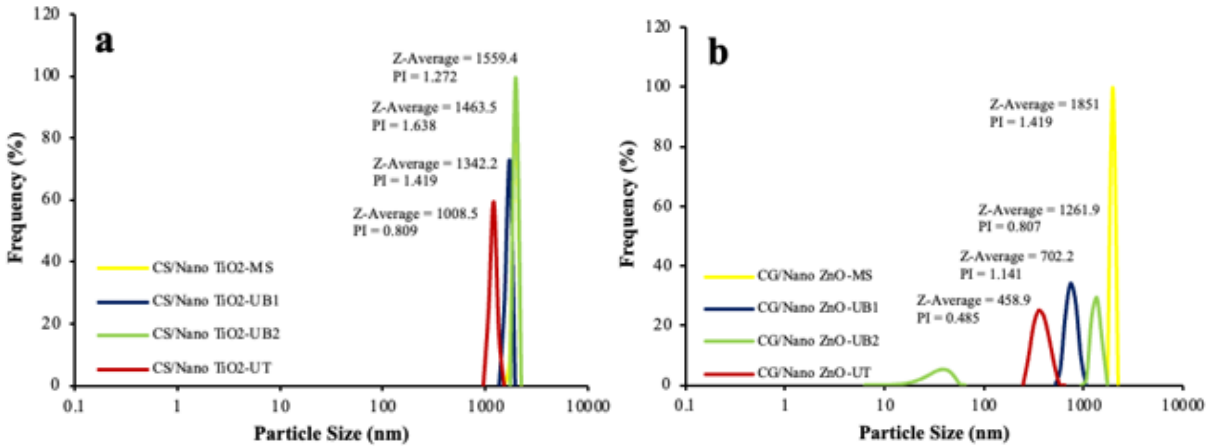
2.3. Characterization

The particle size of the nanocomposite coatings was characterized using particle size analysis with a Horiba Sz-100 instrument. The morphological characteristics of the samples were examined using a Scanning Electron Microscope (SEM) at magnifications of 200x and 500x, specifically the Hitachi SU3500 model and Quanta-650. The crystal structure of the nanocomposite coatings was analyzed using an X-ray diffractometer (XRD), specifically the X'Pert PRO, PANalytical MPD PW3040/60, with a scanning angle range of 10° to 100°. The functional groups and properties of the nanocomposite coatings were characterized using Fourier Transform Infrared (FTIR) spectroscopy with a Vertex 80 instrument in the wavenumber range of 4000 cm^{-1} to 400 cm^{-1}.

3. Results and discussions

3.1. Particle size and polydispersion index

Particle size is the most important parameter in nanocomposite coatings (Figure 2). A composite can be considered nanosized if it falls within the range of 10-1000 nm [35-38]. This study measured the particle size and polydispersion index (PI) twice for each sample and the average value was calculated for analysis. The results showed that the average diameter of the nanocomposite ranged from 458.9 to 1851 nm. UT technology treatment and CG/nano ZnO nanocomposite produced smaller particle sizes ranging from 458.9 to 1037.2 nm compared to other treatments in Figure 2. The high shear force generated by ultra-turrax causes the particles in the sample to be well dispersed. This is consistent with the findings of Zambrano-Zaragoza et al. [39, 40] reported particle sizes of around 187-326 nm. Followed by the lowest polydispersity index (PI) value of 0.485. This PI value indicates a homogeneous particle distribution because a PI value of <0.7 is considered optimal. In the particle size analyzer (PSA) measurement process, agglomeration is a critical factor. During PSA measurements, particles are analyzed in a liquid medium dispersed in dispersants, which significantly affects the measurement process [41]. The high-speed rotation of the UT rotor-stator generates intense shear forces and turbulence, effectively breaking larger particles into smaller ones and homogenizing the solution [42]. In contrast, magnetic stirrer and ultrasound bath technologies are less effective, as the shear forces they generate are comparatively weaker than those produced by the UT.



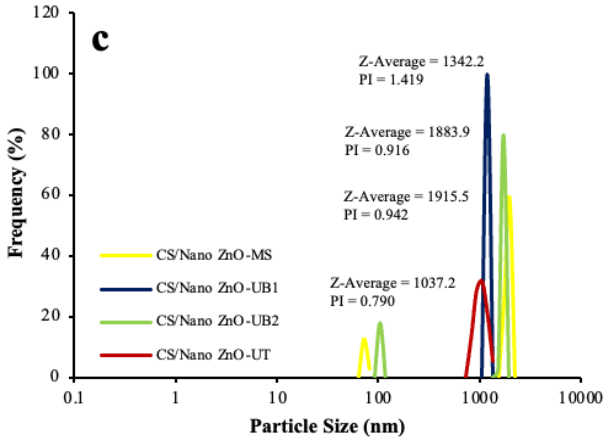


Figure 2. Particle size and polydispersion index of chitosan/TiO_2 (a), carrageenan/ZnO (b) and chitosan/ZnO (c) Nanocomposite Coatings

3.2. Visual appearance and SEM images

Nanocomposite-based films were formed using various manufacturing methods and material concentrations. The resulting films exhibited homogeneous (smooth) and bubble-free surfaces (Figure 3). The right technology is required to disperse the particles evenly in the solution to achieve such films, preventing clumping [43]. The surface of the nanocomposite film is generally similar to those produced by other treatments, except for the CS/nano TiO_2 nanocomposite film, which has a less transparent appearance compared to the CG/nano ZnO and CS/nano ZnO treatments (Figure 3). This difference is influenced by the filler material, specifically nano TiO_2, used in the process of making the nanocomposite films. The nano TiO_2 solution is white and opaque due to the inherent optical properties of the nanoparticles [3].

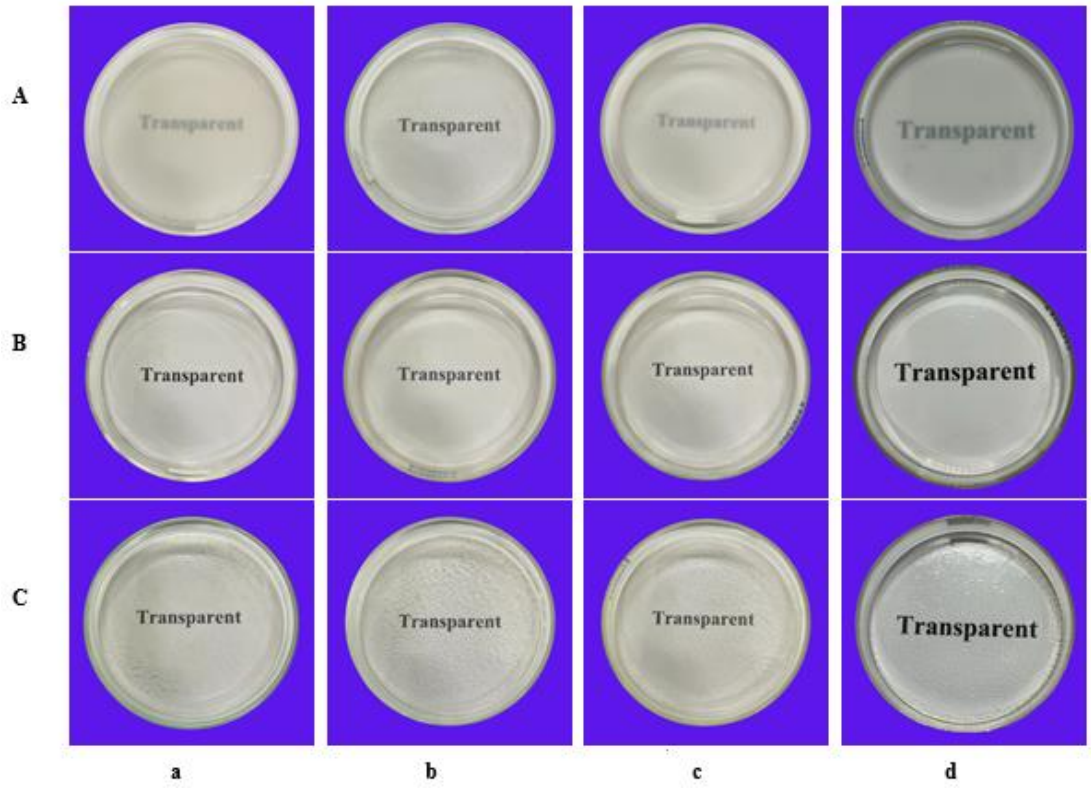
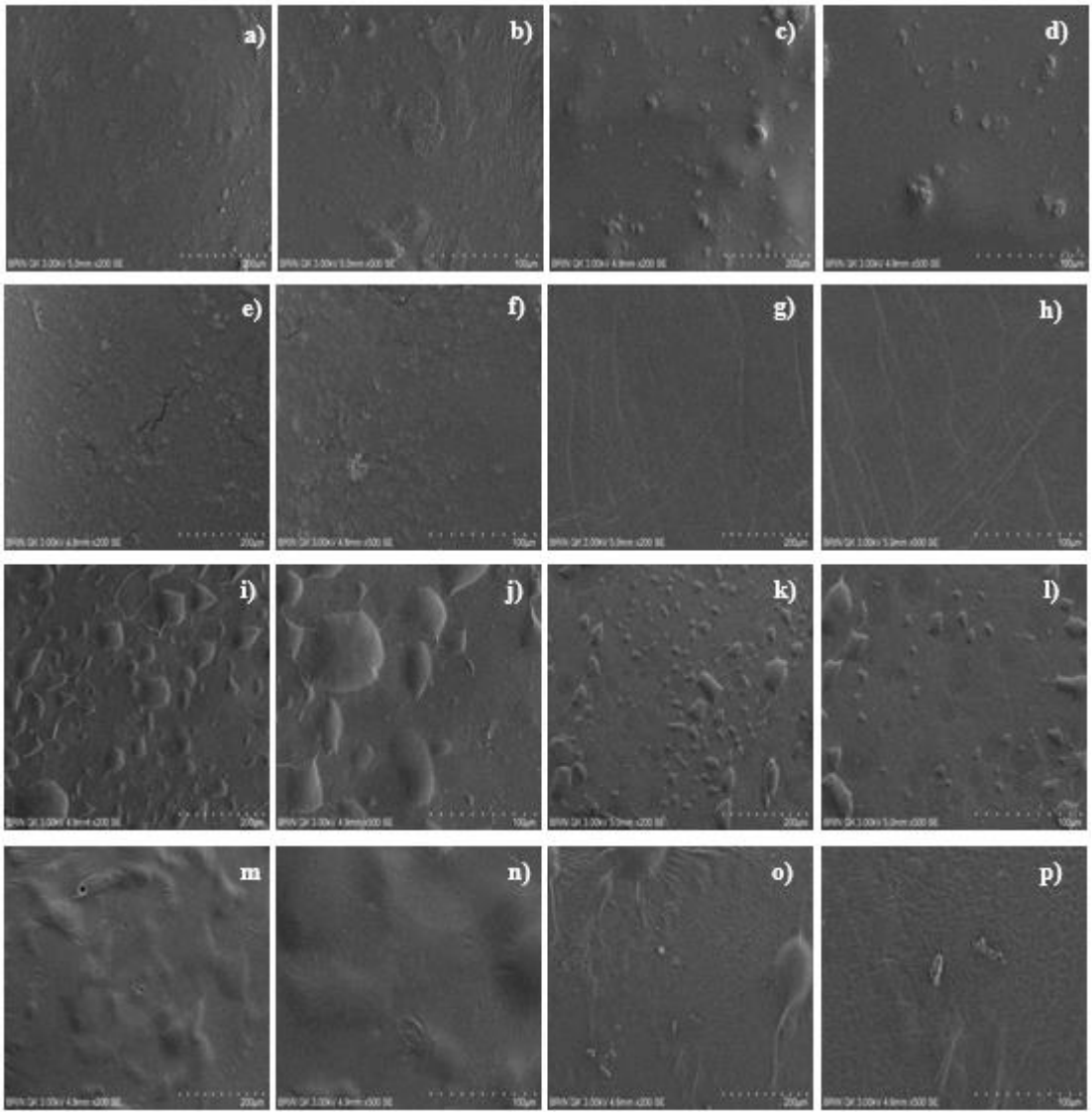


Figure 3. Visual images of CS/nano TiO_2-MS (Aa), CS/nano TiO_2-UB1 (Ab), CS/nano TiO_2-UB2 (Ac), CS/nano TiO_2-UT (Ad), CG/nano ZnO-MS (Ba), CG/nano ZnO-UB1 (Bb), CG/nano ZnO-UB2 (Bc), CG/nano ZnO-UT (Bd), CS/nano ZnO-MS (Ca), CS/nano ZnO-UB1 (Cb), CS/nano ZnO-UB2 (Cc) and CS/nano ZnO-UT (Cd) Nanocomposite materials

Scanning Electron Microscopy (SEM) analysis was performed to examine the morphology of chitosan/nano TiO_2, carrageenan/nano ZnO, and chitosan/nano ZnO coating films. Figure 4 illustrates the surface morphology of these films, revealing a rough texture with small bulging areas corresponding to particle aggregates. The results suggest that the film structure is altered by the incorporation of nanoparticles. Previous studies have shown that composite membranes, such as those containing nanoparticles, are prone to agglomeration [44]. The addition of nanoparticles to the composite films induces this agglomeration, which in turn affects their physical and mechanical properties [45]. Agglomeration occurs primarily due to the challenges in dispersing nanoparticles in viscous solutions, as nanoparticles tend to cluster due to strong electrostatic attraction forces [46]. Treatment with an Ultra-turrax (UT) system can mitigate particle agglomeration by applying intense frictional forces through rapid impeller rotation [27]. Moreover, Ultra-Turrax treatment enhances nanoparticle dispersion within the matrix, particularly in liquid or semi-liquid systems. In the production of nanocomposite coatings, the choice of processing technology is crucial to preventing particle agglomeration and ensuring uniform nanoparticle distribution within the matrix.



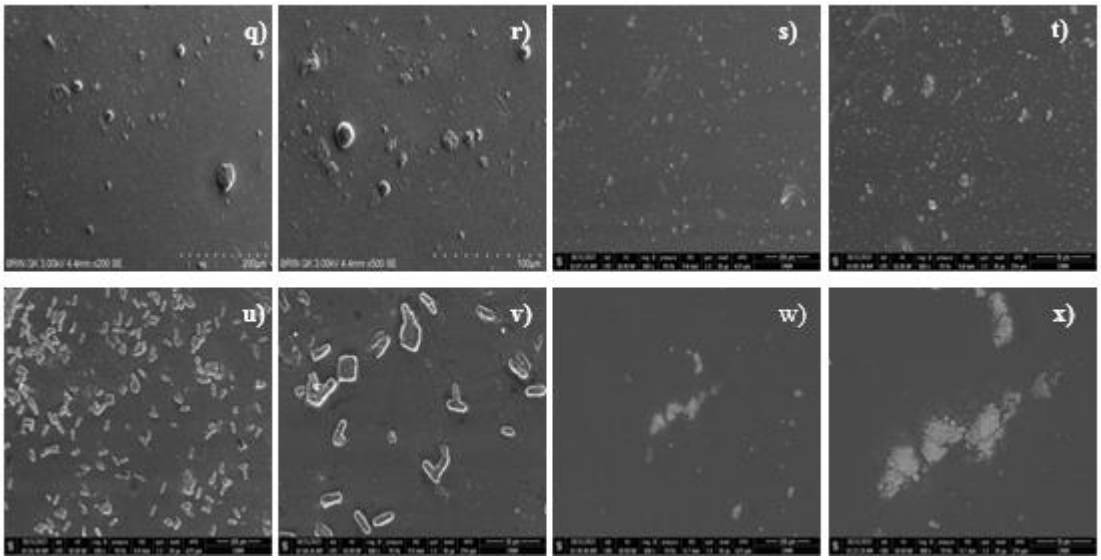
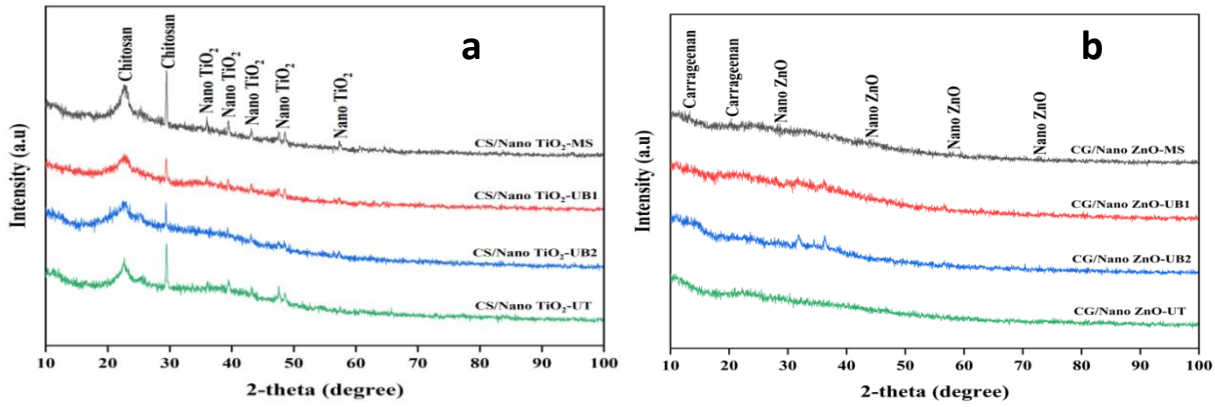


Figure 4. SEM Images of CS/Nano TiO_2-MS (a-b), CS/Nano TiO_2-UB1 (c-d), CS/Nano TiO_2-UB2 (e-f), CS/Nano TiO_2-UT (g-h), CG/Nano ZnO-MS (i-j), CG/Nano ZnO-UB1 (k-l), CG/Nano ZnO-UB2 (m-n), CG/Nano ZnO-UT (o-p), CS/Nano ZnO-MS (q-r), CS/Nano ZnO-UB1 (s-t), CS/Nano ZnO-UB2 (u-v) and CS/Nano ZnO-UT (w-x) with 200x dan 500x magnification

3.3. XRD analysis

X-ray diffraction (XRD) is a technique that provides valuable information regarding the chemical composition, crystallographic structure, phase identification, and unit cell dimensions of crystalline materials [47]. Figure 5 presents the X-ray diffraction pattern of the sample, revealing prominent peaks at specific 2θ angles, namely 23.09° and 29.48°. These peaks correspond to the (202) and (241) crystallo-graphic planes, respectively. The measured 2θ angles for the chitosan sample are consistent with the values listed on card 39-1894 of the JCPDS, which serves as a reference for established crystallo-graphic data [48]. The peaks at 39.43°, 43.20°, 47.61°, and 64.65° correspond to the (004), (112), (200), and (204) crystallographic planes, respectively. The measured 2θ angles for anatase TiO_2 are in good agreement with the values reported on card 21–1272 of the JCPDS [49]. Additionally, the peaks at 45.68°, 51.20°, and 66.23° correspond to the (102), (110), and (200) crystallographic planes for ZnO, with the measured 2θ angles aligning well with the values given on card 043-0002 of the JCPDS [50]. The XRD pattern of the nanocomposite also displays an amorphous peak of κ-carrageenan at approximately 2θ = 10–30° [51].



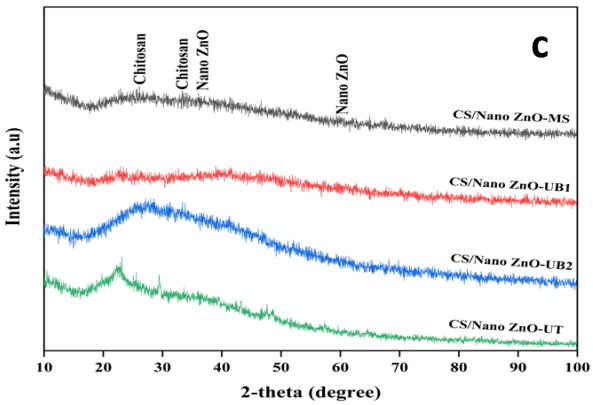
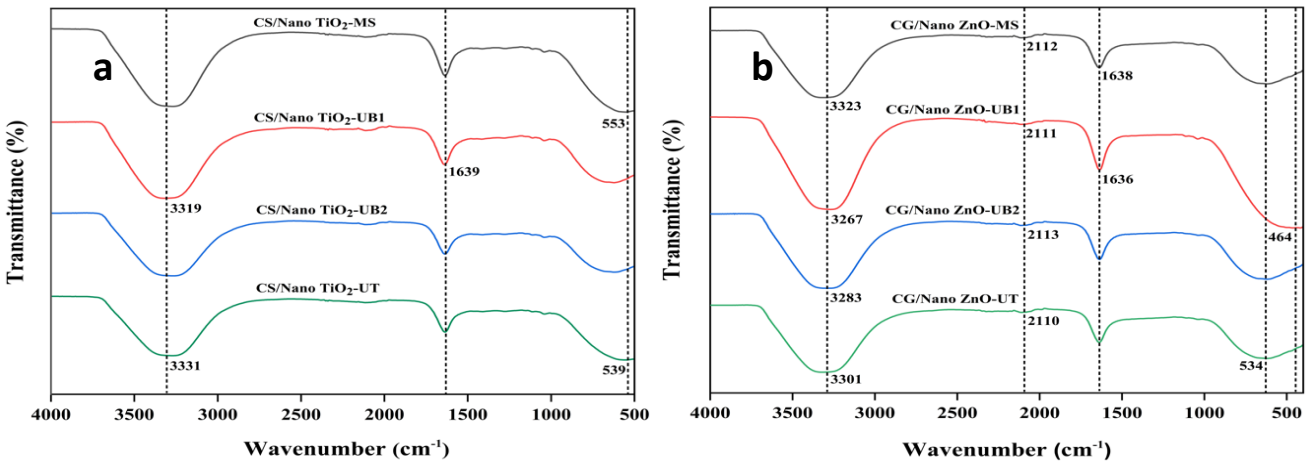


Figure 5. X-ray diffraction of chitosan/TiO_2 (a), carrageenan/ZnO (b), and chitosan/ZnO (c) Nanocomposite materials

3.4. FT-IR

FT-IR (Fourier Transform Infrared) spectroscopy was employed to identify the functional groups in the sample based on their characteristic vibrations [52], with the most significant vibrations occurring within the wavenumber range of 4000-400 cm^{-1}. The FT-IR spectra of chitosan, carrageenan, glycerol, TiO_2, and ZnO nanoparticles are presented in Figure 6. The spectra for chitosan and carrageenan exhibit functional groups characteristic of polysaccharides and amino acids. Intense bands in the range of 3200-3500 cm^{-1} are attributed to O-H and N-H stretching vibrations, corresponding to the hydroxyl and amine groups present in polysaccharide and amino acid molecules (Table 1-3) [53]. Absorption bands observed at 2113 cm^{-1} and 1637 cm^{-1} correspond to C≡C and C=O (amide-I) stretching vibrations, respectively [11, 51, 55]. The band at 1416 cm^{-1} is associated with the stretching of the -NH_2 group in the chitosan spectrum (Table 1 and 3) [56]. Additionally, the absorption band at 1041 cm^{-1} indicates an interaction between the nanocomposite structure and the hydroxyl (-OH) group of glycerol (52). TiO_2 nanoparticles display characteristic vibrations in the 530–720 cm^{-1} region, related to the O-Ti-O bonds in the chitosan-nano TiO_2 nanocomposite [57]. In contrast, the absorption peaks observed in the 673–433 cm^{-1} region correspond to the Zn-O bond stretching frequencies for ZnO nanoparticles [20, 58, 59].



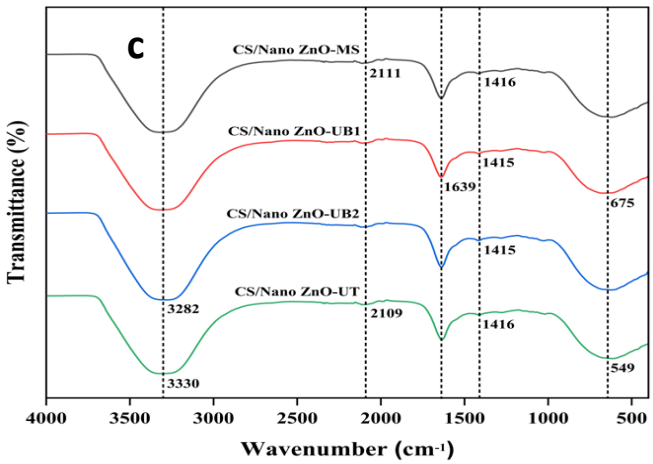


Figure 6. FT-IR of chitosan/TiO_2 (a), carrageenan/ZnO (b), and chitosan/ZnO (c) Nanocomposite Coatings

Table 1. The wavenumber of chitosan/TiO_2 nanocomposite coatings

Functional Groups	Wavenumber (cm^{-1})				Reference
	CS/Nano TiO_2-MS	CS/Nano TiO_2-UB1	CS/Nano TiO_2-UB2	CS/Nano TiO_2-UT	
O-H and N-H	3269	3319	3269	3331	3500-3200 [53]
C≡C	2112	2112	2112	2111	2140-2100 [54]
C=O	1636	1639	1636	1636	1680-1630 [11,55]
$-NH_2$	1416	1416	1416	1416	1600-1300 [56]
-OH	1041	1041	1040	1077	1200-1000 [52,56]
Ti-O	553	622	622	539	720-530 [57]

Table 2. The wavenumber of carrageenan/ZnO nanocomposite coatings

Functional Groups	Wavenumber (cm^{-1})				Reference
	CG/Nano ZnO-MS	CG/Nano ZnO-UB1	CG/Nano ZnO-UB2	CG/Nano ZnO-UT	
O-H and N-H	3323	3267	3283	3301	3500-3200 [53]
C≡C	2112	2111	2113	2110	2140-2100 [54]
C=O	1638	1636	1637	1637	1680-1630 [11,55]
-OH	1041	1041	1041	1041	1200-1000 [52,56]
Zn-O	619	464	619	534	673-433 [20,58,59]

Table 3. The wavenumber of chitosan/ZnO nanocomposite coatings

Functional Groups	Wavenumber (cm^{-1})				Reference
	CS/Nano ZnO-MS	CS/Nano ZnO-UB1	CS/Nano ZnO-UB2	CS/Nano ZnO-UT	
O-H and N-H	3319	3319	3282	3330	3500-3200 [53]
C≡C	2111	2113	2113	2109	2140-2100 [54]
C=O	1637	1639	1637	1637	1680-1630 [11,55]
$-NH_2$	1416	1415	1415	1416	1600-1300 [56]
-OH	1041	1041	1041	1041	1200-1000 [52,56]
Zn-O	622	675	622	549	673-433 [20,58,59]

4. Conclusions

In this study, various technologies and nanoparticles were incorporated into biopolymers to develop nanocomposite coatings. Composite solutions were prepared based on previous studies, with slight modifications, and were subsequently subjected to physical characterization. Significant changes were observed in particle size, visual appearance, and the morphological properties of the resulting nanocomposite coatings. FT-IR, XRD, and SEM analyses were employed to further characterize the physical properties of the nanocomposites. A notable variation in particle size was observed between the nanocomposite coatings prepared using different technologies, as analyzed by particle size analysis (PSA).

The use of Ultra-Turrax technology facilitated even distribution of nanoparticles on the nano-composite film surface. XRD analysis confirmed the presence of nanoparticle crystals through the identification of characteristic diffraction peaks in the theta region. Based on these findings, biopolymer-based nano-composite films show promise as environmentally friendly active packaging materials that could extend the shelf life of food products. However, further research is required to evaluate their effectiveness in practical applications aimed at prolonging the shelf life of food products.

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References

1.SHOJAEE-ALIABADI, S., HOSSEINI, H., MOHAMMADIFAR, M.A., MOHAMMADI, A., GHASEMLOU, M., OJAGH, S.M., et al., Characterization of antioxidant-antimicrobial κ-carrageenan films containing Satureja hortensis essential oil, *International Journal of Biological Macromolecules*, 2013, 52, 116-124. http://dx.doi.org/10.1016/j.ijbiomac.2012.08.026

2. SAPUTRA, A., HERPANDI, H., SUPRIADI, A., SAPUTRA, D., *The effects of nano-edible coating on shelf life, physicochemical, microbial and sensory properties in food preservation and horticulture: A mini review*. In: ISEPROLOCAL 2022 E3S Web of Conferences 373, Bengkulu, Indonesia; 2023. pp. 1-6.

3. ALI, H., HAMEED, N., Preparation of Cellulose Acetate Nanocomposite Films Based on TiO_2-ZnO Nanoparticles Modification as Food Packaging Applications. *Journal of Applied Sciences and Nanotechnology*, 2022, 2(3), 115-125. https://doi.org/10.53293/jasn.2022.4542.1122

4. KAZEMEINI, H., AZIZIAN, A., ADIB, H., Inhibition of *Listeria monocytogenes* growth in turkey fillets by alginate edible coating with *Trachyspermum ammi* essential oil nano-emulsion. *International Journal of Food Microbiology*, 2021, 344, 1-5. https://doi.org/10.1016/j.ijfoodmicro.2021.109104

5. NAQASH, F., MASOODI, F.A., AYOB, O., PARVEZ, S., Effect of active pectin edible coatings on the safety and quality of fresh-cut apple. *International Journal of Food Science Technology*, 2021, 57(1), 57-66. https://doi.org/10.1111/ijfs.15059

6. DASH, K.K., ALI, N.A., DAS, D., MOHANTA, D., Thorough evaluation of sweet potato starch and lemon-waste pectin based-edible films with nano-titania inclusions for food packaging applications. *International Journal of Biological Macromolecules*, 2019, 139, 449-458. https://doi.org/10.1016/j.ijbiomac.2019.07.193

7. PRIYADARSHI, R., RIAHI, Z., RHIM, J.W., Antioxidant pectin/pullulan edible coating incorporated with *Vitis vinifera* grape seed extract for extending the shelf life of peanuts. *Postharvest Biology and Technology*, 2022, 183, 1-9. https://doi.org/10.1016/j.postharvbio.2021.111740

8. LI, Y., ZHOU, Y., WANG, Z., CAI, R., YUE, T., CUI, L., Preparation and characterization of chitosan–nano-zno composite films for preservation of cherry tomatoes. *Foods*, 2021, 10(12), 1-15. https://doi.org/10.3390/foods10123135

9.MANUHARA, G.J., PRASEPTIANGGA, D., MUHAMMAD, D.R.A., MAIMUNI, B.H., Preparation and characterization of semi-refined kappa carrageenan-based edible film for nano coating application on minimally processed food. In: 6th Nanoscience and Nanotechnology Symposium (NNS2015) AIP Conference Proceedings 1710, Surakarta, Indonesia; 2016. pp. 1-5.

10.HOSSEINNEJAD, M., JAFARI, SM., Evaluation of different factors affecting antimicrobial properties of chitosan. *International Journal of Biological Macromolecules*, 2016, 85, 467-475. http://dx.doi.org/10.1016/j.ijbiomac.2016.01.022

11. PAVINATTO, A., DE ALMEIDA MATTOS A,V., MALPASS, A.C.G., OKURA, M.H., BALOGH, D.T., Sanfelice, R.C., Coating with chitosan-based edible films for mechanical/biological protection of strawberries. *International Journal of Biol Macromol*, 2020, 151, 1004-1011. https://doi.org/10.1016/j.ijbiomac.2019.11.076
12.HONG, K., XIE, J., ZHANG, L., SUN, D., GONG, D., Effects of chitosan coating on postharvest life and quality of guava (*Psidium guajava* L.) fruit during cold storage. *Sci Hortic*, 2012, 144, 172-178. http://dx.doi.org/10.1016/j.scienta.2012.07.002
13.HILLIOU, L., LAROTONDA, F.D.S., ABREU, P., RAMOS, A.M., SERENO, A.M., GONÇALVES, M.P., Effect of extraction parameters on the chemical structure and gel properties of κ/ι-hybrid carrageenans obtained from Mastocarpus stellatus. *Biomol Eng*, 2006, 23(4), 201-108. https://doi.org/10.1016/j.bioeng.2006.04.003
14.CHENG, C., CHEN, S., SU, J., ZHU, M., ZHOU, M., CHEN, T., et al., Recent advances in carrageenan-based films for food packaging applications. *Front Nutr*, 2022, 9, 1-16. https://doi.org/10.3389/fnut.2022.1004588
15.USTUNOL, Z., *Edible Films and Coatings for Food Applications*. New York: Springer, 2009.
16. SONG, D., HOA, V.B., KIM, H.W., KHANG, S.M., CHO, S., HAM, J., et al., Edible films on meat and meat products. *Coatings*, 2021, 11(11), 1-24. https://doi.org/10.3390/coatings11111344
17.XING, Y., YANG, H., GUO, X., BI, X., LIU, X., XU, Q., et al., Effect of chitosan/Nano-TiO2 composite coatings on the postharvest quality and physicochemical characteristics of mango fruits. *Scientia Horticulturae*, 2020, 263(13), 1-7. https://doi.org/10.1016/j.scienta.2019.109135
18. XING, Y., LI, X., ZHANG, L., XU, Q., CHE, Z., LI, W., et al., Effect of TiO 2 nanoparticles on the antibacterial and physical properties of polyethylene-based film. *Progress Organic Coatings*, 2012, 73(2-3), 219-224. https://doi.org/10.1016/j.porgcoat.2011.11.005
19.KUSTININGSIH, I., RIDWAN, A., ABRIYANI, D., SYAIRAZY, M., KURNIAWAN, T., BARLEANY, D.R., Development of Chitosan-TiO_2 Nanocomposite for Packaging Film and its Ability to Inactive *Staphylococcus aureus*. *Oriental Journal of Chemistry*, 2019, 35(3), 1132-1137. http://dx.doi.org/10.13005/ojc/350329
20.SHEIK, M.S., RAJ, K.R., KOTTAISAMY, M., VASANTHA, V.S., Biosynthesis of ZnO nano-particles through extract from *Prosopis juliflora* plant leaf: Antibacterial activities and a new approach by rust-induced photocatalysis. *Journal of Saudi Chem Soc*, 2020, 24(5), 393-406. https://doi.org/10.1016/j.jscs.2020.03.003
21.NOSHIRVANI, N., GHANBARZADEH, B., MOKARRAM R.R., HASHEMI, M., Novel active packaging based on carboxymethyl cellulose-chitosan-ZnO NPs nanocomposite for increasing the shelf life of bread. *Food Packaging and Shelf Life*, 2017, 11, 106-114. https://doi.org/10.1016/j.fpsl.2017.01.010
22. LI, W., LI, L., CAO, Y., LAN, T., CHEN, H., QIN, Y., Effects of PLA film incorporated with ZnO nanoparticle on the quality attributes of fresh-cut apple. *Nanomaterials*, 2017, 7(8), 1-20. https://doi.org/10.3390/nano7080207
23.KARTHIKEYAN, K.T., NITHYA, A., JOTHIVENKATACHALAM, K., Photocatalytic and antimicrobial activities of chitosan-TiO_2 nanocomposite. *International of Journal Biological Macromol*, 2017, 104, 1762-1773. http://dx.doi.org/10.1016/j.ijbiomac.2017.03.121
24.MEINDRAWAN, B., SUYATMA, N.E., WARDANA, A.A., PAMELA, V.Y., Nanocomposite coating based on carrageenan and ZnO nanoparticles to maintain the storage quality of mango. *Food Packaging and Shelf Life*, 2018, 18(4), 140-146. https://doi.org/10.1016/j.fpsl.2018.10.006
25.ZHANG, S., SUN, D., FU, Y., DU, H., Recent advances of superhard nanocomposite coatings: A review. *Surface and Coatings Technology*, 2003, 167(2), 113-119. https://doi.org/10.1016/S0257-8972(02)00903-9

26.KAEWKLIN, P., SIRIPATRAWAN, U., SUWANAGUL, A., LEE, Y.S., Active packaging from chitosan-titanium dioxide nanocomposite film for prolonging storage life of tomato fruit. *International Journal of Biological Macromolecules*, 2018, 112, 523-529. https://doi.org/10.1016/j.ijbiomac.2018.01.124
27.FERNANDEZ-DIAZ, L., CASTILLO, J., SASIETA-BARRUTIA, E., ARNAIZ, M., CABELLO, M., JUDEZ, X., et al., Mixing methods for solid state electrodes: Techniques, fundamentals, recent advances, and perspectives. *Chemical Engineering Journal*, 2023, 464, 1-18. https://doi.org/10.1016/j.cej.2023.14246
28.PILON, L., SPRICIGO, P.C., MIRANDA, M., DE MOURA, M.R., ASSIS, O.B.G., MATTOSO LHC, et al. Chitosan nanoparticle coatings reduce microbial growth on fresh-cut apples while not affecting quality attributes. *International Journal of Food Sci Technology*, 2015, 50(2), 440-448. https://doi.org/10.1111/ijfs.12616
29.MOHAMADYAN, W., YOUSEFI, S., WEISANY, W., Development of edible nanoemulsions containing vitamin E using a low-energy method: Evaluation of particle size and physicochemical properties for food and beverage applications. *Heliyon*, 2024; 10, 1-13. https://doi.org/10.1016/j.heliyon.2024.e32415
30. FATTAHI, R., GHANBARZADEH, B., DEHGHANNYA, J., HOSSEINI, M., FALCONE, P.M., The effect of Macro and Nano-emulsions of cinnamon essential oil on the properties of edible active films. *Food Sci Nutr*, 2020, 8(12), 6568-6579.
31. CHAUDHARY, S., KUMAR, S., KUMAR, V., SHARMA, R., Chitosan nanoemulsions as advanced edible coatings for fruits and vegetables: Composition, fabrication and developments in last decade. *Int J Biol Macromol*, 2020, 152, 154–170. https://doi.org/10.1016/j.ijbiomac.2020.02.276
32.MENG, X., ZHANG, M., ADHIKARI, B., The Effects of Ultrasound Treatment and Nano-zinc Oxide Coating on the Physiological Activities of Fresh-Cut Kiwifruit. *Food Bioprocess Technol*, 2014, 7(1), 126-132.
33. KARIMIRAD, R., BEHNAMIAN, M., DEZHSETAN, S., Application of chitosan nanoparticles containing *Cuminum cyminum* oil as a delivery system for shelf life extension of *Agaricus bisporus*. *LWT - Food Sci Technol*, 2019, 106, 218-228. https://doi.org/10.1016/j.lwt.2019.02.062
34.MOHAMMADI, A., HASHEMI, M., HOSSEINI, S.M., Chitosan nanoparticles loaded with *Cinnamomum zeylanicum* essential oil enhance the shelf life of cucumber during cold storage. *Postharvest Biol Technol*, 2015, 110, 203-213. http://dx.doi.org/10.1016/j.postharvbio.2015.08.019
35.ARSALAN, A., YOUNUS, H., Enzymes and nanoparticles: Modulation of enzymatic activity via nanoparticles. *International Journal of Biological Macromol*, 2018, 118, 1833–1847. https://doi.org/10.1016/j.ijbiomac.2018.07.030
36. BEAULIEU, M.R., BARAL, J.K., HENDRICKS, N.R., TANG, Y., BRISEÑO, A.L., WATKINS, J.J., Solution processable high dielectric constant nanocomposites based on ZrO_2 nanoparticles for flexible organic transistors. *ACS Applied Materials and Interfaces*, 2013, 5(24), 13096-13103. https://doi.org/10.1021/am404129u
37. HOSEINNEJAD, M., JAFARI, S.M., KATOUZIAN, I., Inorganic and metal nanoparticles and their antimicrobial activity in food packaging applications. *Crit Rev Microbiol*, 2018; 44(2), 161-181. https://doi.org/10.1080/1040841X.2017.1332001
38.MALLAKPOUR, S., BEHRANVAND, V., Polymeric nanoparticles: Recent development in synthesis and application. *Express Polymer Letters*, 2016, 10(11), 895-913. http://dx.doi.org/10.3144/expresspolymlett.2016.84
39.ZAMBRANO-ZARAGOZA, M.L., MERCADO-SILVA, E., RAMIREZ-ZAMORANO, P., CORNEJO-VILLEGAS, M.A., GUTIÉRREZ-CORTEZ, E., QUINTANAR-GUERRERO, D., Use of solid lipid nanoparticles (SLNs) in edible coatings to increase guava (*Psidium guajava* L.) shelf-life. *Food Research International*, 2013, 51(2), 946–953. http://dx.doi.org/10.1016/j.foodres.2013.02.012

40. ZAMBRANO-ZARAGOZA, M.L., MERCADO-SILVA, E., DEL REAL L. A, GUTIÉRREZ-CORTEZ, E, CORNEJO-VILLEGAS MA, QUINTANAR-GUERRERO D., The effect of nano-coatings with α-tocopherol and xanthan gum on shelf-life and browning index of fresh-cut "red Delicious" apples. Innov Food Sci Emerg Technol 2014; 22: 188–196. http://dx.doi.org/10.1016/j.ifset.2013.09.008
41. TAWALI AB, WAKIAH N, QANITAH K, ASFAR M, SUKENDAR NK, METUSALACH. The Effect of Sonication Time on Physicochemical Profiles of the Nanocalsium from Snake-Head Fish Bone (*Channa striata*). In: The 3rd International Symposium on Agricultural and Biosystem Engineering IOP Conference Series: Earth and Environmental Science 355. South Sulawesi, Indonesia; 2019. pp. 1–6.
42. GALLASSI, M., GONÇALVES, G.F.N., BOTTI, T.C., MOURA, M.J.B., CARNEIRO, J.N.E., CARVALHO, M.S., Numerical and experimental evaluation of droplet breakage of O/W emulsions in rotor-stator mixers. *Chem Eng Sci*, 2019, 204, 270-286. https://doi.org/10.1016/j.ces.2019.04.011
43. SONDI, I., GOIA, D.V., MATIJEVIĆ, E., Preparation of highly concentrated stable dispersions of uniform silver nanoparticles. *Journal of Colloid and Interface Science*, 2003, 260(1), 75–81. http://dx.doi.org/10.1016/s0021-9797(02)00205-9
44. MOTELICA, L., FICAI, D., FICAI, A., TRUŞCĂ, R.D., ILIE, C.I., OPREA, O.C., et al., Innovative antimicrobial chitosan/zno/ag nps/citronella essential oil nanocomposite-potential coating for grapes. *Foods*, 2020, 9(12), 1–26. https://doi.org/10.3390/foods9121801
45.MITTAL, H., RAY, S.S., KAITH, B.S., BHATIA, J.K., SUKRITI., SHARMA, J., et al., Recent progress in the structural modification of chitosan for applications in diversified biomedical fields. *European Polymer Journal*, 2018, 109, 402–434. https://doi.org/10.1016/j.eurpolymj.2018.10.013
46.LIU, Y., CAI, Y., JIANG, X., WU, J., LE, X., Molecular interactions, characterization and antimicrobial activity of curcumin-chitosan blend films. *Food Hydrocolloids*, 2016, 52, 564–572. http://dx.doi.org/10.1016/j.foodhyd.2015.08.005
47. FAN, S., FAN, X., WANG, S., LI, B., ZHOU, N., XU, H., Effect of chitosan modification on the properties of magnetic porous biochar and its adsorption performance towards tetracycline and Cu2+. *Sustainable Chemistry and Pharmacy*, 2023, 33, 1-13. https://doi.org/10.1016/j.scp.2023.101057
48. KOCYIGIT, A., YILMAZ, M., AYDOGAN, S., INCEKARA, U., SAHIN, Y., The performance of chitosan layer in Au/n-Si sandwich structures as a barrier modifier. *Polymer Testing*, 2020, 89, 1-12. https://doi.org/10.1016/j.polymertesting.2020.106546
49.SCARPELLI, F., MASTROPIETRO, T.F., POERIO, T., GODBERT, N., *Titanium Dioxide - Material for a Sustainable Environment*; Intechopen: Canada, 2018, pp. 57-80.
50.SHATNAWI, M., ALSMADI, A.M., BSOUL, I., SALAMEH, B., MATHAI, M., ALNAWASHI, G., et al. Influence of Mn doping on the magnetic and optical properties of ZnO nanocrystalline particles. *Results in Physics*, 2016, 6, 1064-1071. http://dx.doi.org/10.1016/j.rinp.2016.11.041
51. MOHAMMADNEZHADA, G., ARIAEINEZHAD, F., STEINIGER, F., Magnetite/κ-carrageenan Nanocomposites : A Convenient Recyclable Tool for Cu(II) Ions Adsorption from Aqueous Solutio. *Inorganic Chemistry Research*, 2020, 2(2), 129-144. https://doi.org/10.22036/icr.2020.209416.1056
52. ZHOU, Y., WU, X., CHEN, J., HE, J., Effects of cinnamon essential oil on the physical, mechanical, structural and thermal properties of cassava starch-based edible films. *International Journal of Biological Macromolecules*, 2021, 184, 574-583. https://doi.org/10.1016/j.ijbiomac.2021.06.067
53.RUI, L., XIE, M., HU, B., ZHOU, L., SAEEDUDDIN M, ZENG, X., Enhanced solubility and antioxidant activity of chlorogenic acid-chitosan conjugates due to the conjugation of chitosan with chlorogenic acid. *Carbohydrate Polymers*, 2017, 170, 206-216. http://dx.doi.org/10.1016/j.carbpol.2017.04.076
54.NANDIYANTO, A.B.D., OKTIANI, R., RAGADHITA, R., How to read and interpret ftir spectroscope of organic material. *Indonesia Journal of Science Technology*, 2019, 4(1), 97-118. https://doi.org/10.17509/ijost.v4i1.15806

55. PRATAP, S.D., PACKIRISAMY, G., Biopolymer based edible coating for enhancing the shelf life of horticulture products. *Food Chemistry: Molecular Sciences*, 2022, 4, 1-9. https://doi.org/10.1016/j.fochms.2022.100085
56. NANDIYANTO, A.B.D., RAGADHITA, R., FIANDINI, M., Interpretation of Fourier Transform Infrared Spectra (FTIR): A Practical Approach in the Polymer/Plastic Thermal Decomposition. *Indonesian Journal of Science and Technology*, 2023, 8(1), 113-126. https://doi.org/10.17509/ijost.v8i1.53297
57.SIRIPATRAWAN, U., KAEWKLIN, P., Fabrication and characterization of chitosan-titanium dioxide nanocomposite film as ethylene scavenging and antimicrobial active food packaging. *Food Hydrocolloids*, 2018, 84, 125-134. https://doi.org/10.1016/j.foodhyd.2018.04.049
58.DOBRUCKA, R., DŁUGASZEWSKA, J., Biosynthesis and antibacterial activity of ZnO nanoparticles using *Trifolium pratense* flower extract. *Saudi J Biol Sci*, 2016, 23(4), 517-523. https://doi.org/10.1016/j.sjbs.2015.05.016
59.AKBAR, J.F., WAJIDULLAH., ULLAH, R., ULLAH, N., SALMAN., USMAN, M., Exploring the environmental and potential therapeutic applications of *Myrtus communis* L. assisted synthesized zinc oxide (ZnO) and iron doped zinc oxide (Fe-ZnO) nanoparticles. *Journal of Saudi Chemical Society*, 2021, 25(7), 1-16. https://doi.org/10.1016/j.jscs.2021.101278

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