

# Review Article

## Effect of nanoparticle and essential oil addition on Kappa carrageenan-based bionanocomposite films: A Review

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### ABSTRACT

The issue of plastic waste has become a global concern due to its negative impact on environmental sustainability. Bionanocomposites are a combination of composite materials made from natural materials with nano-sized organic or inorganic fillers that are biodegradable. Carrageenan is one of the natural polymers that can be used as a biofilm constituent material which is recognized to form a good film due to its ability to form a strong and stiff gel, but still has limitations in water vapor permeability and lower mechanical properties. The use of nanoparticles and essential oil into carrageenan-based films can improve the characteristics including mechanical properties, optical properties, barrier properties, and act as antibacterial and antioxidant in the films

*Keywords: nanoparticles, bionanocomposite film, essential oil, kappa carrageenan*

### 1. INTRODUCTION

The issue of plastics is a global concern with a drastic increase in production over the last few decades [1]. The high use of plastics has a negative impact on environmental sustainability [2]. Petroleum-based synthetic polymers have been widely used in various types of plastic packaging, but are a major source of waste problems [3]. Petroleum polymer-based plastics are difficult to degrade, require tens to hundreds of years to disintegrate and if burned, plastics will produce carbon emissions that pollute the environment [4], [5]. Because of these weaknesses, a plastic packaging technology solution that is easily degradable and environmentally friendly is needed.

Several studies have led to technologies to make plastics from rapidly degradable natural materials, known as biodegradable plastics or bioplastics. Bionanocomposites are attracting great attention as potential replacements for petroleum-based plastics as they can extend the shelf life of food products serving as barriers against the transfer of water vapor, gases, lipids, and flavor components [6].

These bionanocomposites are made from biopolymers (natural polymers) such as starch, cellulose, and fats [7]. Biopolymers are polymeric materials obtained from natural resources (animals, plants, and algae). Commonly used biopolymers in the formulation of bionanocomposite films are polysaccharides, proteins, and lipids [8]. Among those biopolymers, mainly seaweed-based polysaccharides (alginate and carrageenan) have received great attention in recent years due to their good barrier properties as well as mechanical properties [9].

Processing carrageenan into biofilm is expected to boost the growth of the carrageenan industry. Kappa carrageenan is one type of carrageenan that is recognized as a good film-former because it has the ability to form strong and rigid gels with hydrophobic properties towards water [10], [11]. However, kappa carrageenan-based films still have limitations in water vapor permeability and lower mechanical properties [12]. One way to improve the mechanical properties and permeability of films from kappa carrageenan is to incorporate nanoparticles as fillers [13]. In addition to nanoparticles, the addition of essential oils can be used as additives in bionanocomposites. Essential oils extracted from plants and spices are proven to provide antioxidant, antimicrobial effects, and reduce water vapor permeability of hydrophilic films [14]. Based on this information, it can be seen that the addition of nanoparticles and essential oils to kappa carrageenan-based bionanocomposite films can improve the characteristics of bionanocomposite films for the better. Further study needed to

see the effect of the addition of nanoparticles and essential oils on mechanical properties, optical properties, barrier properties, especially antioxidant active properties and antimicrobial properties.

## 2. EFFECTS OF EO AND NANOPARTICLES ON MECHANICAL PROPERTIES OF BIONANOCOMPOSITE FILMS

The mechanical properties of bionanocomposite films include characteristics such as thickness, tensile strength, and elongation. Most studies have reported that the addition of nanoparticles and essential oils has a significant effect on the mechanical properties of bionanocomposite films (**Table 1**). Tensile strength, elongation, and thickness are key factors that help to explain the relationship between the mechanical properties of film materials and their chemical structure [15].

The addition of nanoparticles such as SiO<sub>2</sub> and ZnO to the carrageenan biofilm was shown to improve the mechanical properties of the film. This can occur because the bead milling process of these nanoparticles results in better dispersion, reduced particle size, and improved distribution within the biofilm matrix [16]. Based on research [13] stated that the addition of ZnO nanoparticles with an optimal concentration of 0.5% in kappa carrageenan/ZnO-based films increased tensile strength and decreased elongation, but beyond this concentration, tensile strength actually decreased.

Essential oils such as clove oil, tea tree oil, and oregano oil can also improve the flexibility and elongation of bionanocomposite films. Essential oils can interact with polymer chains, thereby increasing the plasticity of the film and its ability to stretch without breaking [17]. The use of essential oils decreases the stiffness and increases the flexibility of the material in the film which contributes to the increased toughness of the biofilm. The combination of using nanoparticles and essential oils together can optimize the mechanical performance of biofilms. Nanoparticles provide the necessary stiffness and strength, while essential oils contribute to flexibility and toughness, resulting in biofilms with balanced and enhanced mechanical properties [18]. This combination results in a bionanocomposite film 80 that is not only strong but also flexible enough for applications that require high stretchability.

In several studies of bionanocomposite films, it was reported that film thickness can be increased by the presence of nanoparticles. The addition of TiO<sub>2</sub> nanoparticles to semi-refined carrageenan-based films creates a more complex matrix, which directly increases the thickness of the film [19]. This was added by [20] which states the addition of ZnO nanoparticles as a film admixture acts as a good filler.

This is because nanoparticles have a large surface area and surface energy so that they can build strong interactions and can be well dispersed in the matrix. The addition of nanoparticles can increase the total solid content in the film-forming solution so that the thickness of the film increases [21]. In addition to nanoparticles, the addition of essential oil to the bionanocomposite film significantly increases the film thickness.

The addition of ginger essential oil to chitosan-based films significantly increases the film thickness as the concentration of GEO (Ginger Essential Oil) increases due to the interaction between chitosan and GEO, which reduces the polymer chain arrangement [22]. The incorporation of nanoparticles and essential oil also significantly increases the thickness of bionanocomposite films. This is evidenced in the study [23] that the incorporation of TiO<sub>2</sub> nanoparticles with ZEO (Zataria multiflora Essential Oil) increased the thickness significantly to 0.071 and 0.073 mm.

Overall, the addition of nanoparticles and essential oils in bionanocomposite films offers significant improvements to the mechanical and functional properties of the films. The synergy between these two components creates a superior material that can be optimized for various applications including food packaging.

**Table 1. Mechanical Properties in Bionanocomposite Films**

Polymer Matrix		Nanocomposites and Essential Oils	Thickness (mm)	Tensile Strength (MPa)	Elongation (%)	References
SR Carrageenan	Kappa	SRkC/ZnO (0,5%)	-	32.03 ± 1.1	5.17 ± 1.0	[13]
		SRkC/ZnO (1,0%)		26.40 ± 3.7	4.70 ± 0.8	
		SRkC/ZnO (1,5%)		22.77 ± 0.8		
Carrageenan		Car/agar	51.9 ± 5.5	45.4 ± 6.4	2.5 ± 0.8	[17]
		Car/agar/ZnS (2 wt%)	57.8 ± 5.5	60.4 ± 7.2	4.0 ± 1.0	
		Car/agar/PET	53.1 ± 6.5	41.3 ± 9.6	3.7 ± 1.1	
		Car/agar/ZnS (2 wt%)/PET	56.3 ± 3.7	45.8 ± 9.3	5.3 ± 0.9	

Carrageenan/Gelatin	Ge/Car	0.304	± 14.42	± 19.59 ± 0.8	[18]
	Ge/Car/TEO (10%)	0.01	0.5	45.21 ± 1.0	
	Ge/Car/ZNP(10%)	0.425	± 12.28	± 65.74 ± 1.4	
	/TEO (10%)	0.01	0.7		
		0.504	± 16.93	±	
SR Carrageenan	SRC	0.095	± 19.72	32.06	[19]
	SRC/TiO2 (1%)	0.001	26.58	17.20	
	SRC/TiO2 (3%)	0.100	± 20.35	15.00	
	SRC/TiO2 (5%)	0.007	20.45	19.21	
	SRC/TiO2 (7%)	0.105	± 20.86	15.30	
		0.005			
		0.104	±		
		0.003			
		0.100	±		
		0.004			
Corn starch	CS/CMC/ZnO (0%)	0.26	-	-	[20]
	CS/CMC/ZnO (3%)	0.28			
	CS/CMC/ZnO (5%)	0.28			
Carrageenan/gelatin	Car/Ge	0.078	± 16.64	± 84.63 ± 2.2	[22]
	Car/Ge/ oregano essential oil (OEO) (2%)	0.002	0.9	87.71 ± 0.7	
	Car/Ge/OEO (2%) /ZnO (2%)	0.103	± 10.09	± 43.61 ± 0.9	
	SA/ Car/Ge/OEO (2%) /ZnO (2%)	0.002	0.3	31.85 ± 1.3	
		0.093	± 21.01	± 27.43 ± 1.0	
		0.003	0.5		
		0.133	± 30.23	±	
		0.002	1.6		
Chitosan/Wheat	Kontrol	66.93 ± 1.2	6.03 ± 0.2	22.37 ± 1.1	[23]
	TiO2 1%	64.37 ± 1.1	8.80 ± 0.8	17.39 ± 0.9	
	TiO2 1%/Zattaria flower essential oil ZEO	71.31 ± 1.1	8.14 ± 0.4	13.62 ± 1.1	
	TiO2 2%	66.81 ± 1.2	9.44 ± 0.4	12.88 ± 1.3	
	TiO2 2%/ZEO	73.50 ± 1.2	8.71 ± 0.5	11.28 ± 1.7	
		0.002	0.8		

### 3. EFFECT OF EO AND NANOPARTICLES ON BARRIER PROPERTIES OF BIONANOCOMPOSITE FILMS

Barrier properties are important parameters that determine efficiency in food packaging. Packaging materials must be able to protect food from spoilage and deterioration [21]. The ability of the film to slow down the loss of moisture from the product is an important characteristic that affects product quality [24], [25]. The water vapor permeability (WVP) of packaging films is one of the important properties for assessing their suitability as packaging materials as well as an important component for predicting product shelf life [26]. This parameter can be used to estimate the barrier properties of the film by measuring the rate of diffusion of water molecules through the cross-section [27]. Most studies have reported that the addition of nanoparticles and essential oils has a significant effect on the barrier properties of bionanocomposite films (Tabel 2).

The addition of nanoparticles into the biocomposite film matrix significantly reduces water vapor permeability. The nanoparticles act as a physical barrier that extends the diffusion path of water vapor molecules through the film. In an article [28], the addition of ZnO and TiO<sub>2</sub> nanoparticles in kappa carrageenan-based films has been shown to improve the barrier properties against water vapor. These nanoparticles fill the gaps in the polymer matrix and strengthen the bonds between polymer chains, thereby reducing water vapor permeability. In research [29], the addition of SiO<sub>2</sub> nanoparticles in kappa carrageenan-based films also showed a significant reduction in water vapor permeability. This was attributed to the barrier properties of the SiO<sub>2</sub> nanoparticles. SiO<sub>2</sub> nanoparticles, having a high surface area, will block or trap water vapor molecules [30].

Essential oils are known to have antimicrobial properties and can affect the barrier properties of biocomposite films. In research [31], the addition of Zattaria multiflora Boiss (ZEO) and Mentha pulegium (MEO) essential oils into kappa carrageenan films reduced water vapor permeability. Essential oils reduce the density of the film structure, thereby reducing the WVP of the film. Other studies in the research [32] showed that the addition of essential oils into chitosan films also

reduced water vapor permeability. Essential oils increase the resistance to water vapor by modifying the microstructure of the film and filling the existing gaps, thereby reducing the diffusion path of water vapor.

The combined use of nanoparticles and essential oils in the formulation of biocomposite films provides a stronger synergistic effect toward reducing water vapor permeability. For example, in a study by [33], the combination of ZnO nanoparticles and cinnamon essential oil in PLA films resulted in a significant reduction in water vapor permeability compared to the use of nanoparticles or essential oil separately. This combination creates a denser and more homogeneous structure, making it more effective in inhibiting water vapor diffusion.

Solubility is another important property that affects the barrier ability of the film. Literature study [13] on kappa carrageenan-based bionanocomposite films showed the addition of ZnO nanoparticles significantly increased the solubility, but the higher concentration of ZnO decreased the solubility. This is because the addition of ZnO nanoparticles to the film increases the formation of hydrogen bonds between ZnO and matrix components, so free water molecules interact less with the film. Similar results were obtained by carrageenan-based bionanocomposite films with the addition of SiO<sub>2</sub> nanoparticles, ZnO nanoparticles, and CuO nanoparticles. Showing that the added nanomaterials can reduce the solubility of the film [28].

The addition of essential oils (ZEO and MEO) to carrageenan-based films showed effects on their solubility. Films with *Zataria multiflora* Boiss (ZEO) and *Mentha pulegium* (MEO) added significantly decreased the solubility of the films. This is due to the increased interaction between the hydroxyl groups of carrageenan and essential oil components which reduces the availability of hydroxyl groups and water-polymer interactions [31]. This decrease in solubility is beneficial for product integrity and water resistance. Similar results were also found in the research [34] with the addition of Clove essential oil (CEO) to Alginate/kappa-carrageenan film slightly decreased its water solubility. This is due to the hydrophobic nature of CEO which reduces the interaction between film particles and reduces the interaction of polysaccharides with hydroxyl groups, thereby increasing the hydrophobicity of the film and reducing water solubility.

Another parameter that can describe the barrier properties in films is the water contact angle. The water contact angle is usually used to determine the hydrophilicity or hydrophobicity of the film. A study [28] showed that the addition of CuO nanoparticles to carrageenan films increased the water contact angle (WCA) significantly. This was due to increased bonding, nanoparticle equalization, and air trapping in the biopolymer matrix. Similar results were found in the addition of essential oils to the water contact angle of bionanocomposite films. Research [35] showed that increasing the concentration of palm oil can increase the WCA of the film. This indicates that essential oil makes the surface of the bioplastic film more hydrophobic. Similar results were found in the research [36] which showed the incorporation of thyme and clove essential oils into PLA/PBAT bioplastic films at higher concentrations significantly increased the water contact angle. This could potentially improve the suitability of the film for applications that require moisture resistance.

**Table 2. Barrier Properties in Bionanocomposite Films**

Polymer Matrix	Nanocomposites and Essential Oils	WVP (g/m <sup>2</sup> s Pa)	Solubility (%)	Water Contact Angle (°)	References
Gelatin/Kappa Carrageenan	Kontrol	8.90 ± 0.31	-	-	[29]
	Gel/KC/SiO <sub>2</sub> 1%	7.10 ± 0.33			
	Gel/KC/SiO <sub>2</sub> 3%	2.62 ± 0.33			
	Gel/KC/SiO <sub>2</sub> 5%	1.61 ± 0.13			
SRkC/Gelatin	SRkC	2,590	± 88.50	± 82,03 ± 3,2	[30]
	SRkC/SiO <sub>2</sub> -ZnO	0,05	± 2.8	± 82,58 ± 7,1	
	Gel	2,424	± 78.46	± 63,82 ±	
	Gel/SiO <sub>2</sub> -ZnO	0,05	± 2.4	± 10,4	
	SRkC/Gel 1;3/SiO <sub>2</sub> -ZnO	1,625	± 65.75	± 74,75 ± 7,3	
	SRkC/Gel 1;1/SiO <sub>2</sub> -ZnO	0,08	± 6.0	± 95,80 ± 6,3	
	SRkC/Gel 3;1/SiO <sub>2</sub> -ZnO	1,343	± 61.30	± 97,72 ± 4,8	
		0,26	± 4.8	± 83,72 ± 7,3	
		2,348	± 37.86	±	
		0,01	± 4.5		
	2,395	± 43.79	±		
	0,13	± 7.2			
	2,665	± 54.58	±		
	0,18	± 3.7			

Kappa Carrageenan	Kontrol	2.383	± 26.32	± -	[31]	
	ZEO 1	0.04	1.03			
	ZEO 2	0.692	± 25.88	±		
	ZEO 3	0.10	0.75			
	MEO 1	0.577	± 22.06	±		
	MEO 2	0.09	0.49			
	MEO 3	0.425	± 17.98	±		
		0.07	1.66			
		0.945	± 23.46	±		
		0.08	1.23			
		0.665	± 20.87	±		
		0.05	0.94			
		0.496	± 16.04	±		
		0.03	1.35			
Polylactic acid	PLA	103.86	± -	69.72 ±	[33]	
	PLA/fenugreek essential oil (FEO)-5%	0.22		1.34		
	PLA/Cur-1%	104.67	±	76.13 ±		
	PLA/FEO (5%)/Cur (1%)	0.58		1.30		
		103.42	±	73.12 ±		
		0.12		0.45		
Kappa Carrageenan	Kontrol	10.6	95.00 ±	-	[28]	
	KC/ZnO (0,5%)	3.14	3.79			
	KC/CuO (0,5%)	8.83	82.15 ±			
	KC/SiO2 (0,5%)	7.51	4.63			
			71.44 ±			
			11.18			
			72.74 ±			
			11.64			
	SR Carrageenan	Kappa SRkC/ZnO (0,5%)	-	61.38 ±	-	[13]
		SRkC/ZnO (1,0%)		2.47		
SRkC/ZnO (1,5%)			91.85 ±	±		
			2.36			
			83.80 ±	±		
			0.65			
Alginate/Kappa Carrageenan	SA/KC/Clove essential oil (CEO)- (1,5%)	-	59.04 ±	-	[34]	
	SA/KC/ CEO (2,0%)		3.06			
	SA/KC/ CEO (2,5%)		57.00 ±	±		
	SA/KC/ CEO (3,0%)		1.02			
			54.98 ±	±		
			0.99			
Cassava starch	CS	-	-	45.95 ± 0.0	[35]	
	CS/Palm Oil (2,5%)			46.83 ± 0.5		
	CS/Palm Oil (5,0%)			61.98 ± 0.2		
	CS/Palm Oil (7,5%)			49.46 ± 0.6		
				1.47		
PBAT (poly (butylene adipate-co-terephthalate)/ Poly (lactide)	PLA/PBAT	-	-	61.61 ±	[36]	
	PLA/PBAT-Clove (1%)			2.82		
	PLA/PBAT-Clove (5%)			62.24 ±		
	PLA/PBAT-Clove (10%)			5.75		
				64.69 ±		
			2.15			
			74.74 ±			
			4.11			

#### 4. EFFECTS OF EO AND NANOPARTICLES ON OPTICAL PROPERTIES OF BIONANOCOMPOSITE FILMS

Optical characteristics are one of the important properties of packaging films as they relate to UV blocking ability which prevents food oxidation and transparency which influences consumer preferences in assessing food freshness [12]. Two optical properties that are often analyzed are UV-screening and transparency properties. UV-screening refers to the film's ability to block ultraviolet radiation, while transparency refers to how much visible light can pass through the film unimpeded [20]. Most studies have reported that the addition of nanoparticles and essential oils has a significant effect on the optical properties of bionanocomposite films (**Tabel 3**).

The addition of nanoparticles to bionanocomposite films can improve UV-screening properties. In research [37], It was found that films with the addition of SiO<sub>2</sub> nanoparticles in kappa-carrageenan films showed a decrease in light transmission and improved UV-screening properties. This is due to the ability of SiO<sub>2</sub> nanoparticles to absorb and scatter UV light, thus preventing damage due to UV radiation. The addition of nanoparticles decreases transparency, due to the nature of the polymer and the agglomeration of nanoparticles which affects the light transmission of the film. In addition, research [38] proved that the incorporation of amorphous cellulose nanocrystals (CNCs) into carrageenan films improved the UV barrier properties of the films, with films having the highest CNC content showing the lowest transmittance due to the UV-blocking properties of the CNCs.

The addition of essential oils (EOs) to bionanocomposites can significantly alter their optical properties. This modification is particularly important for applications in food packaging. As in the study of [39] which states the addition of orange essential oil (OEO) and trehalose significantly affects the transparency of carrageenan-based films. This suggests a synergistic essential oil effect in reducing transparency. In addition, combining OEO and trehalose showed effective barrier properties against UV radiation. This was also the case in the study of [40] which incorporated grapefruit essential oil (GFO) into kappa carrageenan films resulting in a slight decrease in transparency. This was due to the interactions within the polymer matrix and the higher concentration of essential oil, which caused a slight change in the color and transparency of the film.

Transparency values decrease with the addition of essential oils due to the formation of lipid droplets, which scatter light and reduce clarity. This is evident in various studies where essential oils such as oregano and cinnamon have been used in different bioplastic matrices[31], [41]. Essential oils contain compounds such as terpenes, which inherently have UV light-blocking properties. Integration of essential oils into the bioplastic film enhances the UV barrier ability, making it suitable for food packaging applications that require UV protection[31], [42].

In yam starch-based bioplastics incorporated with clove oil, it was shown that transparency decreased as the concentration of clove oil increased. Higher concentrations of clove oil led to increased interactions between the polymer chains, modifying the refractive index and limiting the passage of light through the bioplastic [43]. Thus, essential oils and nanoparticles also play an important role in enhancing the protective function against UV radiation.

**Table 3. Optical properties in Bionanocomposite Films.**

Polymer Matrix		Nanocomposites and Essential Oils	UV-Light absorbance (%)	Transparency (%)	Reference
SR Carrageenan/Cassava starch	Kappa	SRkC	25.14	62.69	[12]
		SRkC-NPs	6.34	53.33	
		CS:SRkC 1:3	8.05	58.26	
		CS:SRkC 1:1	9.17	61.86	
		CS:SRkC 3:1	9.72	63.57	
Chitosan		Chit/ /chito-oligosaccharide (COS) (1,5%)	-	0.42±0.27	[44]
		Chit/ /chito-oligosaccharide (COS) (2,0%)	-	0.47±0.27	
PVA/gelatin		PVA/gelatin	14.3	0.48	[37]
		PVA/gelatin/SiO <sub>2</sub> (0,5%)	12	0.41	
		PVA/gelatin/SiO <sub>2</sub> (1,0%)	15.2	0.35	
		PVA/gelatin/SiO <sub>2</sub> (1,5%)	13.1	0.39	
Kappa Carrageenan		Kontrol	-	76.28	[38]
		KC/ Cellulose nanocrystals (CNC) (1%)	-	63.52	
		KC/ CNC (3%)	-	48.14	
		KC/ CNC (5%)	-	46.06	
		KC/ CNC (7%)	-	21.42	

Kappa Carrageenan	(0,5g) KC/orange essential oil-OEO (0,45 ml)/T80	7.07 ± 1.22	42.06 ± 1.15	[39]
		10.81 ± 0.04	84.31 ± 0.03	
	(0,5g) KC/orange essential oil-OEO (0,45 ml)/T20	28.23 ± 0.13	87.81 ± 0.35	
		11.77 ± 0.01	82.14 ± 0.04	
	(0,3g) KC/orange essential oil-OEO (0,45 ml)/T80			
Carrageenan	(0,3g) KC/orange essential oil-OEO (0,45 ml)/T20			[40]
	Car/grape fruit essential Oil-CEO (0,1%)	-	76.13 ± 3.14	
	Car/grape fruit essential Oil-CEO (0,2%)		70.59 ± 2.74	
	Car/grape fruit essential Oil-CEO (0,3%)		67.10 ± 1.56	
Chitosan	Clove oil-CO (0,3%)	-	12.28 ± 1.20	[43]
	Clove oil-CO (0,6%)		10.42 ± 1.10	
	Clove oil-CO (0,9%)		8.67 ± 1.30	
	Clove oil-CO (1,2%)		8.58 ± 1.40	
	Clove oil-CO (1,5%)		5.95 ± 2.90	

## 5. EFFECTS OF EO AND NANOPARTICLES ON ANTIMICROBIAL PROPERTIES OF BIONANOCOMPOSITE FILMS

Antimicrobial packaging can reduce and increase the shelf life of food products [45]. Packaging with antimicrobial properties is a highly effective technique to inhibit the growth of pathogenic microorganisms in food products, for example, by adding nanoparticles [46]. In some of the literature studies found it was observed that the trend of using silver or zinc nanoparticles is increasing compared to other types of metal nanoparticles on the antibacterial properties of bionanocomposite films. **Table 4** shows some of the recent studies related to the effects of adding nanoparticles and essential oils on the antimicrobial properties of bionanocomposite films

Proven in the study [47] in the use of  $\kappa$ -carrageenan/cassava starch-based films to coat fresh strawberries, the addition of ZnO nanoparticles significantly inhibited microbial spoilage and extended the shelf life to 11 days. This is due to the increased surface area of the nanoparticles by contact with oxygen-reactive species that damage the bacterial cell membrane resulting in membrane rupture and preventing bacterial [48]. Similar results were obtained in the addition of Zein nanoparticles to kappa carrageenan/gelatin-based bionanocomposite films showing significant antibacterial effects on *E. coli* (gram-negative) and *S. aureus* (gram-positive) bacteria [49]. The antimicrobial activity of the film with nanoparticle incorporation was higher against gram-positive bacteria compared to gram-negative bacteria (*E. coli*). This is because the cell wall of gram-negative bacteria is more complex and difficult to penetrate, while the cell membrane of gram-positive bacteria is porous and easily penetrated [46].

The integration of essential oils into bioplastic films has been studied for its potential to enhance antibacterial and antioxidant properties. Oregano Essential Oil (OEO)-loaded films showed significant antibacterial activity against pathogenic bacteria commonly present in food including *Bacillus subtilis*, *Escherichia coli*, and *Staphylococcus aureus*. This is influenced by the hydrophobicity of essential oils which can disrupt bacterial cell membranes by interacting with lipids, increasing permeability and causing leakage of vital components, ultimately leading to cell death [50]. In addition, research [45] showed that combining nanoparticles with essential oils effectively increased the antibacterial effectiveness of the film against *Escherichia coli* and *Staphylococcus aureus* with the addition of titanium dioxide (TiO<sub>2</sub>) nanoparticles and neem essential oil (NEO). In addition, research [51] CA nanoclay film / CEO clove essential oil showed significant antibacterial activity against *Escherichia coli*, *Listeria monocytogenes*, and *Lactobacillus sakei* as the concentration of nanoclay and CEO increased. This is because Nanoclay can increase the surface area while the essential oil dispersion in the polymer matrix contains the main component, Eugenol, which can disrupt the bacterial cell membrane, increase permeability, and cause cell death.

**Table 4. Antimicrobial properties in Bionanocomposite Films**

Composition	Nanocomposites and Essential Oils	Type of Bacteria	Method	Antimicrobial activity of film	References
SR Iota Carrageenan-Fish Gelatin (1:3)/NP SiO <sub>2</sub> -ZnO	SiO <sub>2</sub> -ZnO	Escherichia coli dan Staphylococcus aureus	Disc diffusion method	Antibacterial activity of bionanocomposite films increased with the addition of nanoparticles. The antimicrobial activity of the film was higher against gram positive bacteria ( <i>S. aureus</i> ) than gram negative bacteria ( <i>E. coli</i> ) this was attributed to the cell wall complexity of gram-negative bacteria compared to gram-positive bacteria.	[46]
Kappa Carrageenan/PVA/Starch/NP ZnO	ZnO (1, 1.5, and 2 % wt/wt)	Escherichia coli Salmonella Typhimurium, dan Staphylococcus aureus	Broth dilution method	Showed growth inhibitory against Salmonella potential <i>E. coli</i> , Typhimurium, and <i>S. aureus</i> microorganisms. This antimicrobial activity may be due to the increased surface area of ZnO NPs and contact with oxygen-reactive species on the nanoparticle surface, leading to the rupture of bacterial cell membranes and inhibiting their replication.	[47]
Gelatin/Kappa Carrageenan/ZNPs	Zein nanoparticles (15 mg/ml)	<i>S. aureus</i> dan <i>E. coli</i>	Disc diffusion method	The addition of Zein nanoparticles showed a significant inhibitory effect against <i>S. aureus</i> and <i>E. coli</i> . For <i>S. aureus</i> , the diameter of the inhibition zone was $8.6 \pm 1.3$ mm and $10.3 \pm 1$ mm in <i>E. coli</i> , the diameter of the inhibition zone was $4.2 \pm 1.2$ mm and $6.2 \pm 1.3$ mm.	[49]

Starch/CMC/ Oregano essential oil	Oregano essential oil Rosemary essential oil Thyme Essential oil	B. subtil E. coli S. aureus P. aeruginosa	Disc diffusion method	Oregano essential oil (OEO) had strongest the antibacterial activity compared to other oils. The Diameter of Inhibition Zone (DIZ) values of OEO against B. subtilis, E. coli, S. aureus, and P. aeruginosa were 39.70 ± 1.80 mm, 29.67 ± 0.75 mm, 55.41 ± 7.47 mm, and 8.62 ± 0.42 mm, respectively. Essential oils are more effective Maroufi et al 2021 Shen et al 2023 gram against positive bacteria because they can directly damage their cell membranes, while the outer cell membranes of gram negative bacteria are more hydrophilic blocking interaction.	[50]
Agar / TiO2 / Radish anthocyanins / Neem Essential Oils	Neem essential oil (NEO)	S. aureus dan E. coli	Disc diffusion method	The addition of Neem essential oil significantly improved the antimicrobial ability against S. aureus and E. coli. This was attributed to abundance antimicrobial the of compounds in NEO (sterols, triterpenoids, active derivatives), and ester which can effectively inhibit microbial growth.	[45]
Cellulose acetate / Nanoclay/Clove Essential Oil	Clove Essential Oil (CEO)	Escherichia coli Listeria monocytogenes dan Lactobacillus sake	Contact method	Addition of nanoclay impregnated with clove essential oil inhibited or reduced proliferation for all the bacterial strains studied. This is related to eugenol which is encapsulated in clove essential oil, a phenolic monoterpenoid compound with a reactive hydroxyl (OH) group. Eugenol can form hydrogen Yang	[51]

et al 2022 cândido et al-2024 bonds with the active sites of bacterial enzymes. This causes disruption or rupture of the bacterial cell membrane.

Kappa Carrageenan/SiO2	SiO2 (1 wt%) SiO2 (3 wt%) SiO2 (5 wt%)	S. aureus dan E. coli	Disc diffusion method	SiO2 nanoparticle based films have good antimicrobial activity. The mechanism involves the release of antimicrobial agents from the surface of SiO2 nanoparticles and the application of antimicrobial effects on bacteria in suspension. Therefore, the KCG/5 wt% SiO2 nanocomposite film showed excellent antimicrobial activity against both microorganisms. [52]
Carrageenan/Orange Essential Oil/Trehalose	Orange essential oil (0.45 mL)	S. aureus dan E. coli	Disc diffusion method	The combination of kappa carrageenan film with OEO showed that it was able to inhibit the growth of E. coli. [39]

## 5. EFFECT OF EO AND NANOPARTICLES ON ANTIOXIDANT PROPERTIES OF BIONANOCOMPOSITE FILMS

Antioxidants are substances that inhibit oxidation reactions caused by free radicals. Antioxidant activity test is needed to determine the content of antioxidant activity in the solubility contained in the packaging film [53]. The addition of natural antioxidants to bioplastics can help prevent oxidation and extend the shelf life of food. Oxidation is the main cause of food degradation, which occurs during processing and storage causing rancidity, deterioration, and the formation of toxic [8]. The table shows some recent studies related to the effects of adding nanoparticles and essential oils on the antioxidant properties of biocomposite films (**Tabel 5**).

Nanoparticles can not only affect the physical, mechanical and characteristics of bionanocomposite films but also the antioxidant properties of bionanocomposite films. Literature study by [54] showed that the antioxidant activity of gelatin/MNP nanocomposite films increased significantly with the addition of melanin nanoparticles (MNP) due to the strong antioxidant content of melanin.

The addition of essential oils can improve the characteristics and add antioxidant compounds to bionanocomposite films [53]. The high use of EOs in the production of Bionanocomposites becomes a natural preservative that contains various components and often works synergistically against free radicals and microorganisms to prevent food spoilage and oxidation [40]. In research [55] it was shown that the addition of ZnO nanoparticles and nutmeg oil in the bionanocomposite significantly improved the antioxidant properties of the film. The increase in antioxidant properties is because the nutmeg

oil used in the bionanocomposite composition contains polyphenols which are the main components responsible for antioxidant properties. Moreover, the presence of polymer matrix and ZnO nanoparticles has significantly enhanced the antioxidant properties due to their compatible biological and chemical properties [56].

Essential oils are known for their phenolic compounds, such as alpha and beta-pinene, which have strong antioxidant properties. The combination of ZnO nanoparticles and *Ferula gummosa* essential oil creates a synergistic effect, which further enhances the antioxidant capacity of the film. ZnO nanoparticles themselves exhibit some degree of antioxidant activity due to their ability to interact with and neutralize free radicals [57]. In addition [58] the incorporation of TiO<sub>2</sub> nanoparticles and dill essential oil DEO into CMC/MG-based bioplastic films markedly improved the antioxidant properties. Bio-nanocomposite films containing TiO<sub>2</sub> nanoparticles and DEO effectively extended the shelf life of refrigerated fish fillet samples. The combination reduced the rate of lipid oxidation and microbial growth. Similarly, the combinations of TiO<sub>2</sub> nanoparticles and grape seed essential oil (GSEO) in bionanocomposite films significantly enhanced antioxidant activity. It is known that TiO<sub>2</sub> nanoparticles themselves have inherent antioxidant properties due to their ability to neutralize reactive oxygen, when combined with GSEO the nanoparticles help create a synergistic effect, which in turn is very effective in delaying the oxidation process [59].

**Table 5. Antioxidant properties in Bionanocomposite Films**

Polymer Matrix	Nanocomposites and Essential Oils	Methods			Reference
		ABTS	DPPH (AA%)	TPC (mg GAEq/g)	
Chitosan/Gelatin	Chit/Gel	65	76	-	[60]
	Chit/Gel/Rosemary	68	78		
	Essential oils (REO) 0.2%	83	80		
	Chit/Gel/REO 0.5%	85	83		
	Chit/Gel/REO 1.0%				
Polyurethane	PU/ZnO/Nutmeg Oils 25 mikro gram mL-1	64.52	± 61.32	± -	[55]
	PU/ZnO/NEO 50	0.10	± 0.22	±	
	PU/ZnO/NEO 100	68.24	± 65.14	±	
		0.56	± 0.52	±	
		69.57	± 66.89	±	
Carrageenan	Kontrol	18.81	± 5.00	± -	[40]
	Car/Gly/Grapefruit	1.23	± 0.73	±	
	Essential oil 0.1%	22.21	± 9.46	±	
	Car/Gly/GEO 0.2%	0.10	± 0.25b	±	
	Car/Gly/GEO .03%	26.56	± 10.12	±	
		0.51	± 0.22	±	
		30.73	± 11.36	±	
Cellulose acetate	Hybrid Nano clay/Clove essential oil 0	-	3 ± 0d	2 ± 0e	[51]
	Hybrid Nano clay/CEO 7.5		63 ± 2c	36 ± 1d	
	Hybrid Nano clay/CEO 15.0		82 ± 1b	80 ± 1c	
	Hybrid Nano clay/CEO 22.5		86 ± 1a	94 ± 1b	
			89 ± 1a	104 ± 0	

Hybrid Nano clay/CEO  
30.0

Carboxymethyl cellulose/						[58]
Refined Carrageenan	Kappa	Kontrol	-	1,05±0,15	-	[53]
		RkC/Lemongrass		2,32±0,14		
		Essential oil 0.1%		6,87±0,09		
		RkC/LEO 0.5%		15,12±0,0		
		RkC/LEO 1%		6		
Starch		Kontrol	-	4	-	[57]
		S+1.5%ZnO+0.5%Ferulla gumamosa boiss EO		24		
		S+1.5%ZnO+1%EO		39		
		S+1.5%ZnO+1.5%EO		48		
Gelatin		Gelatin	7.8 ± 1.9	5.7 ± 1.3	-	[54]
		Gelatin/MNP0.25%	53.4 ± 2.8	19.6 ± 2.3		
		Gelatin/MNP0.5%	69.6 ± 8.7	42.8 ± 3.9		
		Gelatin/MNP1.0%	85.5 ± 2.5	56.5 ± 4.2		

## 6. DISCUSSION

The addition of nanoparticles and essential oils to kappa carrageenan-based biodegradable packaging materials has shown significant improvements in various mechanical, physical, barrier, optical properties, as well as their antioxidant and antibacterial properties. Several studies have shown that the addition of nanoparticles such as ZnO and SiO<sub>2</sub> to kappa carrageenan films can improve their mechanical properties. These nanoparticles can increase tensile strength and resistance to elongation, making the film stronger and more flexible. As in the research by [13] found that the addition of ZnO to kappa carrageenan films increased tensile strength but decreased elongation at optimal concentrations. In addition, essential oils such as clove oil and oregano oil can increase film elasticity by interacting with polymer chains [61].

Another important thing that needs to be considered in biodegradable films is the film's resistance to moisture and oxygen. Nanoparticles function as a physical barrier in the polymer matrix, reducing water vapor and gas permeability by filling gaps in the matrix. This is important for improving the resistance properties of the film. The addition of essential oils also reduces water vapor permeability, providing an additional barrier effect by modifying the film microstructure and reducing water vapor diffusion pathways. Research by [33] showed that the combination of nanoparticles and essential oils in carrageenan films significantly improved the barrier properties against water vapor and gas.

The addition of nanoparticles and essential oils also affected the optical properties of the packaging film. Nanoparticles enhance the UV filtering ability, reducing the transmission of UV light that can damage food products. In contrast, essential oils tend to reduce film transparency due to the formation of lipid droplets that scatter light. As in the study by [39] showed that the addition of orange oil and trehalose in carrageenan films reduced transparency and increased UV barrier properties, which is very useful for protecting food from UV-induced oxidation.

Essential oils are known to have phenolic compounds with strong antioxidant capacity. The combination of nanoparticles and essential oils showed a synergistic effect in enhancing the antioxidant activity of the film. Research by [57] showed that the combination of ZnO and essential oil from *Ferula gummosa* increased the antioxidant activity significantly compared to the use of one type of additive alone. This is due to the interaction between the nanoparticles and phenolic compounds in the essential oil, which strengthens the antioxidant capacity of the film. Studies combining nanoparticles and essential oils showed a synergistic effect in enhancing the antioxidant properties of the films.

Bionanocomposite films with nanoparticles and essential oil also showed better antibacterial properties. ZnO nanoparticles have significant antibacterial activity against gram-positive and gram-negative bacteria. In addition to nanoparticles, essential oils with compounds such as eugenol and carvacrol are also effective in inhibiting bacterial growth by disrupting bacterial cell membranes. Research by [45] showed that the combination of TiO<sub>2</sub> and neem essential oil increased the antibacterial activity of the film against *Staphylococcus aureus* and *Escherichia coli*.

Overall, the addition of nanoparticles and essential oils to carrageenan-based biodegradable packaging films provided significant improvements in their mechanical, physical, barrier, optical properties, as well as their antioxidant and antibacterial properties. This combination results in a packaging material that is not only environmentally friendly but also provides better protection for food products, making it a potential solution for future food packaging applications.

## 7. CONCLUSION

Bionanocomposites are a combination of composite materials made from natural materials with biodegradable nano-sized organic or inorganic fillers. Carrageenan-based biocomposite films have been widely researched. Nanoparticles and essential oils can be used as film fillers that can improve the characteristics of carrageenan-based biocomposite films. The addition of nanoparticles and essential oils to kappa-carrageenan-based bionanocomposite films significantly improved the film characteristics. ZnO, TiO<sub>2</sub>, and SiO<sub>2</sub> nanoparticles function as a physical barrier that reduces water vapor permeability and increases the mechanical strength 316 of the film. Essential oils, such as *Zataria multiflora* Boiss (ZEO) and *Mentha pulegium* (MEO), also have a positive effect by reducing water vapor permeability and improving the antimicrobial and antioxidant properties of the film. In addition, the addition of nanoparticles and essential oils also affected the optical properties of the bionanocomposite films. The addition of nanoparticles increases the film's ability to block UV radiation, while the addition of essential oil reduces the transparency of the film. The combination of these two materials creates a synergy that results in bionanocomposite films with improved mechanical, barrier, and optical properties, making them potential materials for food packaging applications.

## REFERENCE

- [1] D. K. A. Barnes, F. Galgani, R. C. Thompson, and M. Barlaz, "Accumulation and fragmentation of plastic debris in global environments," *Philos. Trans. R. Soc. B Biol. Sci.*, vol. 364, no. 1526, pp. 1985–1998, Jul. 2009, doi: 10.1098/rstb.2008.0205.
- [2] Y. Tokiwa, B. P. Calabia, C. U. Ugwu, and S. Aiba, "Biodegradability of plastics," *International Journal of Molecular Sciences*, vol. 10, no. 9, pp. 3722–3742, Sep. 2009. doi: 10.3390/ijms10093722.
- [3] E. Rochima, E. Fiyanih, E. Afrianto, I. M. Joni, U. Subhan, and C. Panatarani, "Efek Penambahan Suspensi Nanokitosan pada Edible Coating terhadap Aktivitas Antibakteri," *J. Pengolah. Has. Perikan. Indones.*, vol. 21, no. 1, p. 127, Apr. 2018, doi: 10.17844/jphpi.v21i1.21461. (In Indonesian Language)
- [4] F. Gironi and V. Piemonte, "Bioplastics and petroleum-based plastics: Strengths and weaknesses," *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 33, no. 21, pp. 1949–1959, 2011, doi: 10.1080/15567030903436830.
- [5] M. R. B. Saputra and E. Supriyo, "Pembuatan Plastik Biodegradable Menggunakan Pati Dengan Penambahan Katalis ZnO dan Stabilizer Gliserol," *Pentana*, vol. 1, no. 1, pp. 41–51, 2020. (In Indonesian Language)
- [6] M. Beigomi, M. Mohsenzadeh, and A. Salari, "Characterization of a novel biodegradable edible film obtained from *Dracocephalum moldavica* seed mucilage," *Int. J. Biol. Macromol.*, vol. 108, pp. 874–883, 2018, doi: 10.1016/j.ijbiomac.2017.10.184.
- [7] E. Kamsiati, H. Herawati, and E. Y. Purwani, "The Development Potential of Sago and Cassava Starch-Based Biodegradable Plastic in Indonesia," *J. Penelit. dan Pengemb. Pertan.*, vol. 36, no. 2, p. 67, Dec. 2017, doi: 10.21082/jp3.v36n2.2017.p67-76.
- [8] L. Atarés and A. Chiralt, "Essential oils as additives in biodegradable films and coatings for active food packaging," *Trends in Food Science and Technology*, vol. 48. Elsevier Ltd, pp. 51–62, Feb. 01, 2016. doi: 10.1016/j.tifs.2015.12.001.
- [9] D. Praseptiangga, S. Giovani, G. J. Manuhara, and D. R. A. Muhammad, "Formulation and characterization of novel composite semi-refined iota carrageenan-based edible film incorporating palmitic acid," in *AIP Conference Proceedings*, American Institute of Physics Inc., Sep. 2017. doi: 10.1063/1.5002516.
- [10] A. Rusli, Metusalach, Salengke, and M. M. Tahir, "Karakterisasi Edible Film Karagenan Dengan," *J. Pengolah. Has. Perikan. Indones.*, vol. 20, no. 2, pp. 219–229, 2017. (In Indonesian Language)
- [11] L. R. Rane, N. R. Savadkar, P. G. Kadam, and S. T. Mhaske, "Preparation and Characterization of K-Carrageenan/Nanosilica Biocomposite Film," *J. Mater.*, vol. 2014, pp. 1–8, 2014, doi: 10.1155/2014/736271.
- [12] C. Panatarani et al., "Synthesis, Characterization, and Performance of Semi-Refined Kappa Carrageenan-Based Film Incorporating Cassava Starch," *Membranes (Basel)*, vol. 13, no. 1, 2023, doi: 10.3390/membranes13010100.
- [13] A. . Saputri, D. Praseptiangga, E. Rochima, C. Panatarani, and I. M. Joni, "Mechanical and solubility properties of bio-nanocomposite film of semi refined kappa carrageenan/ZnO nanoparticles," *AIP Conf. Proc.*, 2018.
- [14] M. Viuda-Martos, Y. R. Navajas, E. S. Zapata, J. Fernández-López, and J. A. Pérez-Álvarez, "Antioxidant activity of essential oils of five spice plants widely used in a Mediterranean diet," vol. 25, pp. 13–19, 2010, doi: 10.1002/ffj.
- [15] N. H. Wan, A. Nafchi, and N. Huda, "Tensile Strength, Elongation at Breaking Point and Surface Color of a Biodegradable Film Based on a Duck Feet Gelatin and Polyvinyl Alcohol Blend," *Asia Pacific Jjournal Sustain. Agric. Food Energy*, vol. 6, no. 2, pp. 16–21, 2018, [Online]. Available: <http://journal.bakrie.ac.id/index.php/APJSAFE>
- [16] C. Panatarani, N. Mufida, D. Widyaastuti, D. Praseptiangga, and I. Made Joni, "Dispersion of SiO<sub>2</sub> and ZnO nanoparticles by bead milling in the preparation of carrageenan bio-nanocomposite film," *AIP Conf. Proc.*, vol. 2219, 2020, doi: 10.1063/5.0003068.

- [17] S. Roy and J. W. Rhim, "Carrageenan/agar-based functional film integrated with zinc sulfide nanoparticles and Pickering emulsion of tea tree essential oil for active packaging applications," *Int. J. Biol. Macromol.*, vol. 193, no. PB, pp. 2038–2046, 2021, doi: 10.1016/j.ijbiomac.2021.11.035.
- [18] M. S. Ali et al., "Development of fish gelatin/carrageenan/zein bio-nanocomposite active-films incorporated with turmeric essential oil and their application in chicken meat preservation," *Colloids Surfaces B Biointerfaces*, vol. 226, no. February, p. 113320, 2023, doi: 10.1016/j.colsurfb.2023.113320.
- [19] K. H. Abd Hamid, T. Jayakumar, S. Gunasegaran, and N. A. Mohd Azman, "Fabrication and Characterization of Semi-refined Carrageenan Films Incorporated with TiO<sub>2</sub> Nanoparticles," *J. Chem. Eng. Ind. Biotechnol.*, vol. 9, no. 1, pp. 1–7, Aug. 2023, doi: 10.15282/jceib.v9i1.9466.
- [20] H. R. Arifin et al., "Corn Starch-Based Bionanocomposite Film Reinforced With ZnO Nanoparticles and Different Types of Plasticizers," *Front. Sustain. Food Syst.*, vol. 6, no. July, pp. 1–13, 2022, doi: 10.3389/fsufs.2022.886219.
- [21] A. V. and L. S. Badwaik, "Recent advancement in improvement of properties of polysaccharides and proteins based packaging film with added nanoparticles: A review," *Int. J. Biol. Macromol.*, vol. 203, no. November 2021, pp. 515–525, 2022, doi: 10.1016/j.ijbiomac.2022.01.181.
- [22] Y. P. Zhang et al., "Preparation and characterization of bio-nanocomposites film of chitosan and montmorillonite incorporated with ginger essential oil and its application in chilled beef preservation," *Antibiotics*, vol. 10, no. 7, 2021, doi: 10.3390/antibiotics10070796.
- [23] M. Gohargani, H. Lashkari, and A. Shirazinejad, "Study on Biodegradable Chitosan-Whey Protein-Based Film Containing Bionanocomposite TiO<sub>2</sub> and Zataria multiflora Essential Oil," *J. Food Qual.*, vol. 2020, 2020, doi: 10.1155/2020/8844167.
- [24] Y. Pranoto, C. M. Lee, and H. J. Park, "Characterizations of fish gelatin films added with gellan and κ-carrageenan," *LWT*, vol. 40, no. 5, pp. 766–774, 2007, doi: 10.1016/j.lwt.2006.04.005.
- [25] D. Turan, "Water Vapor Transport Properties of Polyurethane Films for Packaging of Respiring Foods," *Food Eng. Rev.*, vol. 13, no. 1, pp. 54–65, 2021, doi: 10.1007/s12393-019-09205-z.
- [26] S. R. Kanatt, M. S. Rao, S. P. Chawla, and A. Sharma, "Active chitosan-polyvinyl alcohol films with natural extracts," *Food Hydrocoll.*, vol. 29, no. 2, pp. 290–297, 2012, doi: 10.1016/j.foodhyd.2012.03.005.
- [27] S. Marano, E. Laudadio, C. Minnelli, and P. Stipa, "Tailoring the Barrier Properties of PLA: A State-of-the-Art Review for Food Packaging Applications," *Polymers*, vol. 14, no. 8. MDPI, Apr. 01, 2022. doi: 10.3390/polym14081626.
- [28] M. P. Sudhakar, S. Venkatnarayanan, and G. Dharani, "Fabrication and characterization of bio-nanocomposite films using κ-Carrageenan and Kappaphycus alvarezii seaweed for multiple industrial applications," *Int. J. Biol. Macromol.*, vol. 219, no. August, pp. 138–149, 2022, doi: 10.1016/j.ijbiomac.2022.07.230.
- [29] R. H. Tabatabaei, S. M. Jafari, H. Mirzaei, A. Nafchi, and D. Dehnad, "Preparation and characterization of nano-SiO<sub>2</sub> reinforced gelatin-κ-carrageenan biocomposites," *Int. J. Biol. Macromol.*, vol. 111, no. 2017, pp. 1091–1099, 2018, doi: 10.1016/j.ijbiomac.2018.01.116.
- [30] E. Rochima, D. Octaviani, S. Y. Azhary, D. Praseptiangga, C. Panatarani, and I. M. Joni, "Effect of fish gelatin as a structure forming agent to enhance transparency and speed up degradability of bionanocomposite semi-refined kappa carrageenan film reinforced with ZnO and SiO<sub>2</sub> filler," *Food Hydrocoll.*, vol. 152, no. November 2023, p. 109965, 2024, doi: 10.1016/j.foodhyd.2024.109965.
- [31] S. Shojaee-Aliabadi et al., "Characterization of κ-carrageenan films incorporated plant essential oils with improved antimicrobial activity," *Carbohydr. Polym.*, vol. 101, no. 1, pp. 582–591, 2014, doi: 10.1016/j.carbpol.2013.09.070.
- [32] S. He and Y. Wang, "Antimicrobial and Antioxidant Effects of Kappa-Carrageenan Coatings Enriched with Cinnamon Essential Oil in Pork Meat," *Foods*, vol. 11, no. 18, Sep. 2022, doi: 10.3390/foods11182885.
- [33] M. Subbuvel and P. Kavan, "Preparation and characterization of polylactic acid/fenugreek essential oil/curcumin composite films for food packaging applications," *Int. J. Biol. Macromol.*, vol. 194, no. October 2021, pp. 470–483, 2022, doi: 10.1016/j.ijbiomac.2021.11.090.
- [34] A. Prasetyaningrum, D. P. Utomo, A. F. A. Raemas, T. D. Kusworo, B. Jos, and M. Djaeni, "Alginate/κ-carrageenan-based edible films incorporated with clove essential oil: Physico-chemical characterization and antioxidant-antimicrobial activity," *Polymers (Basel)*, vol. 13, no. 3, pp. 1–16, 2021, doi: 10.3390/polym13030354.
- [35] A. H. D. Abdullah, A. K. Fikriyyah, and R. Dewantoro, "Fabrication and Characterization of Starch Based Bioplastics with Palm Oil Addition," *J. Sains Mater. Indones.*, vol. 20, no. 3, pp. 126–131, 2019.
- [36] S. Sharma, S. Barkauskaite, B. Duffy, A. K. Jaiswal, and S. Jaiswal, "Characterization and Antimicrobial Activity of Biodegradable Active Packaging Enriched with," *Foods*, vol. 9, no. 1117, p. 16, 2020.
- [37] M. Kariminejad et al., "The effect of nano-SiO<sub>2</sub> on the physicochemical and structural properties of gelatin-polyvinyl alcohol composite films," *J. Food Process Eng.*, vol. 41, no. 6, pp. 1–9, 2018, doi: 10.1111/jfpe.12817.
- [38] M. Yadav and F. C. Chiu, "Cellulose nanocrystals reinforced κ-carrageenan based UV resistant transparent bionanocomposite films for sustainable packaging applications," *Carbohydr. Polym.*, vol. 211, no. December 2018, pp. 181–194, 2019, doi: 10.1016/j.carbpol.2019.01.114.
- [39] J. Simona, D. Dani, S. Petr, N. Marcela, T. Jakub, and T. Bohuslava, "Edible films from carrageenan/orange essential oil/trehalose—structure, optical properties, and antimicrobial activity," *Polymers (Basel)*, vol. 13, no. 3, pp. 1–19, 2021, doi: 10.3390/polym13030332.

- [40] S. Bhatia, Y. Abbas Shah, A. Al-Harrasi, M. Jawad, E. Koca, and L. Y. Aydemir, "Enhancing Tensile Strength, Thermal Stability, and Antioxidant Characteristics of Transparent Kappa Carrageenan Films Using Grapefruit Essential Oil for Food Packaging Applications," *ACS Omega*, vol. 9, no. 8, pp. 9003–9012, 2024, doi: 10.1021/acsomega.3c07366.
- [41] Z. Wu et al., "Preparation and application of starch/polyvinyl alcohol/citric acid ternary blend antimicrobial functional food packaging films," *Polymers (Basel)*, vol. 9, no. 3, Mar. 2017, doi: 10.3390/polym9030102.
- [42] W. Liu et al., "Fabrication of anti-bacterial, hydrophobic and UV resistant galactomannan-zinc oxide nanocomposite films," *Polymer (Guildf)*, vol. 215, no. January, p. 123412, 2021, doi: 10.1016/j.polymer.2021.123412.
- [43] U. Ulyarti et al., "Development of yam-starch-based bioplastics with the addition of chitosan and clove oil," *Makara J. Sci.*, vol. 25, no. 2, pp. 91–97, 2021, doi: 10.7454/mss.v25i2.1155.
- [44] M. H. Arifin, N. E. Suyatma, and D. Indras, "Chito-oligosaccharide Characterization Depolymerized by Different Method and Its Study as Active Film," *J. Pengolah. Has. Perikan. Indones.*, vol. 25, no. 1, pp. 18–33, 2022, doi: 10.17844/jphpi.v25i1.39632.
- [45] Z. Yang et al., "Agar/TiO<sub>2</sub>/radish anthocyanin/neem essential oil bionanocomposite bilayer films with improved bioactive capability and electrochemical writing property for banana preservation," *Food Hydrocoll.*, vol. 123, no. May 2021, p. 107187, 2022, doi: 10.1016/j.foodhyd.2021.107187.
- [46] D. Praseptiangga et al., "Development and characterization of semi-refined iota carrageenan/fish gelatin-based biocomposite film incorporated with SiO<sub>2</sub>/ZnO nanoparticles," *Int. J. Biol. Macromol.*, vol. 271, no. P1, p. 132569, 2024, doi: 10.1016/j.ijbiomac.2024.132569.
- [47] A. R. da Silva Bruni et al., "Characterization and application of active films based on commercial polysaccharides incorporating ZnONPs," *Int. J. Biol. Macromol.*, vol. 224, no. July 2022, pp. 1322–1336, 2023, doi: 10.1016/j.ijbiomac.2022.10.219.
- [48] R. Meraat, A. A. Ziabari, K. Issazadeh, N. Shadan, and K. M. Jalali, "Synthesis and characterization of the antibacterial activity of zinc oxide nanoparticles against salmonella typhi," *Acta Metall. Sin. (English Lett.)*, vol. 29, no. 7, pp. 601–608, Jul. 2016, doi: 10.1007/s40195-016-0439-5.
- [49] L. Y. Maroufi, M. Ghorbani, M. Tabibiazar, M. Mohammadi, and A. Pezeshki, "Advanced properties of gelatin film by incorporating modified kappa-carrageenan and zein nanoparticles for active food packaging," *Int. J. Biol. Macromol.*, vol. 183, pp. 753–759, 2021, doi: 10.1016/j.ijbiomac.2021.04.163.
- [50] Y. Shen et al., "Preparation and characterization of oregano essential oil-loaded *Dioscorea zingiberensis* starch film with antioxidant and antibacterial activity and its application in chicken preservation," *Int. J. Biol. Macromol.*, vol. 212, no. February, pp. 20–30, 2022, doi: 10.1016/j.ijbiomac.2022.05.114.
- [51] G. de S. Cândido, M. S. Silva, N. J. Zeneratto, R. H. Piccoli, E. E. Nunes Carvalho, and J. E. de Oliveira, "Hybrid Nanoclay/Clove Essential Oil in Cellulose Acetate Bionanocomposites for Cooked Ham Active Packaging," *ACS Appl. Nano Mater.*, 2024, doi: 10.1021/acsanm.4c01235.
- [52] R. Venkatesan, N. Rajeswari, and T. T. Thiyagu, "Preparation, characterization and mechanical properties of K-carrageenan/SiO<sub>2</sub> nanocomposite films for antimicrobial food packaging," *Bull. Mater. Sci.*, vol. 40, no. 3, pp. 609–614, 2017, doi: 10.1007/s12034-017-1403-3.
- [53] M. F. Nuansa, T. W. Agustini, and E. Susanto, "Karakteristik dan aktivitas antioksidan edible film dari refined karaginan dengan penambahan minyak atsiri," *J. Pengemb. Dan Biotek*, vol. 6, no. 1, pp. 54–62, 2017. (In Indonesian Language)
- [54] S. Shankar, L. F. Wang, and J. W. Rhim, "Effect of melanin nanoparticles on the mechanical, water vapor barrier, and antioxidant properties of gelatin-based films for food packaging application," *Food Packag. Shelf Life*, vol. 21, no. April, p. 100363, 2019, doi: 10.1016/j.fpsl.2019.100363.
- [55] M. Amina, N. M. Al Musayeib, N. A. Alarfaj, M. F. El-Tohamy, G. A. Al-Hamoud, and H. M. Al-Yousef, "Immunomodulatory and antioxidant potential of biogenic functionalized polymeric nutmeg oil/polyurethane/zno bionanocomposite," *Pharmaceutics*, vol. 13, no. 12, 2021, doi: 10.3390/pharmaceutics13122197.
- [56] C. Wan and J. Li, "Facile synthesis of well-dispersed superparamagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles encapsulated in three-dimensional architectures of cellulose aerogels and their applications for Cr(VI) removal from contaminated water," *ACS Sustain. Chem. Eng.*, 2015.
- [57] H. Sarhadi, F. Shahdadi, A. Salehi Sardoei, M. Hatami, and M. Ghorbanpour, "Investigation of physio-mechanical, antioxidant and antimicrobial properties of starch–zinc oxide nanoparticles active films reinforced with *Ferula gummosa* Boiss essential oil," *Sci. Rep.*, vol. 14, no. 1, pp. 1–14, 2024, doi: 10.1038/s41598-024-56062-w.
- [58] R. Eshaghi, M. Mohsenzadeh, and J. F. Ayala-Zavala, "Bio-nanocomposite active packaging films based on carboxymethyl cellulose, myrrh gum, TiO<sub>2</sub> nanoparticles and dill essential oil for preserving fresh-fish (*Cyprinus carpio*) meat quality," *Int. J. Biol. Macromol.*, vol. 263, no. P2, p. 129991, 2024, doi: 10.1016/j.ijbiomac.2024.129991.
- [59] H. Hemmati, A. R. Yorghanlu, and M. Pirouzifard, "Investigation of some physical properties and antioxidant activity of biodegradable sodium caseinate film containing titanium nanoxide and grape seed essential oil and its effect on the oxidative resistance of virgin olive oil," *J. Food Sci. Technol.*, vol. 19, no. 128, pp. 363–374, 2022, doi: 10.22034/FSCT.19.128.363.
- [60] R. Akhter, F. A. Masoodi, and T. A. Wani, "Chitosan, gelatin and pectin based bionanocomposite films with rosemary

essential oil as an active ingredient for future foods," *Int. J. Biol. Macromol.*, vol. 272, no. P1, p. 132813, 2024, doi: 10.1016/j.ijbiomac.2024.132813.

- [61] X. Zhang et al., "A novel multilayer film based on sodium alginate/k-carrageenan-gelatin incorporated with ZnO nanoparticles and oregano essential oil for active food packing," *Prog. Org. Coatings*, vol. 187, no. September 2023, 2024, doi: 10.1016/j.porgcoat.2023.108170.

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