Physicochemical Properties of Films from Semirefined Carrageenan/TiO_2 Integrated with Cinnamaldehyde Pickering Emulsion for Active Food Packaging

Khadijah Husna Abd Hamid[1], Azilah Ajit[1], Azren Aida Asmawi[1], Mohd Hafiz Arzmi[2] and Nurul Aini Mohd Azman[1,*]

[1]*Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuh Persiaran Tun Khalil Yaakob, 26300, Kuantan, Pahang, Malaysia*

[2]*Department of Fundamental Dental and Medical Sciences, Kulliyyah of Dentistry, International Islamic University Malaysia, Pahang, Malaysia*

Abstract: Plastic waste has become a significant global environmental issue, particularly in the context of food packaging. In the present study, active packaging films were fabricated by integrating chitosan-stabilized cinnamaldehyde Pickering emulsion (PE) and titanium dioxide particles (TNPs) into the semirefined carrageenan (SRC) matrix. The impact of cinnamaldehyde PE and TNPs on the physical and mechanical attributes of the SRC films was explored. The integration of TNPs (3%, w/v) and 0.5% cinnamaldehyde PE revealed promising mechanical properties, with 21.86 MPa tensile strength and 34.21% of elongation at break value. The inclusion of TNPs and cinnamaldehyde PE led to enhancements in the moisture content and water solubility of the SRC films. The thermal stability of the film was marginally increased with 0.5% cinnamaldehyde PE. Scanning electron microscopy (SEM) revealed a uniform distribution of active compounds in the SRC matrix. The study findings highlight the potential of cinnamaldehyde PE and TNPs in active food packaging films as eco-friendly alternatives to conventional petrochemical-derived plastics in food packaging.

Keywords: Active food packaging, plastics waste, nanoparticle, pickering emulsion, cinnamaldehyde, titanium dioxide.

1. INTRODUCTION

Renewable polymers like polysaccharides, proteins, and lipids are being explored as eco-friendly packaging materials for food products, as a replacement for non-degradable petrochemical-based alternatives [1,2]. Carrageenan-derived polysaccharides from red algae are abundant biopolymers with strong gel properties, used in packaging as film-forming material due to their superior mechanical properties and effective barrier against gases, lipids, and oils (Aga *et al*., 2021). Moreover, semirefined carrageenan (SRC) has a lower purity than other carrageenan products, with cellulose remaining from seaweed for enhanced binding and gelling properties at a lower cost [3]. Nonetheless, because of their hydrophilicity, most of the biopolymers are restricted in their application in food packaging due to the fact that the materials possess an affinity for water [4]. Utilizing carrageenan in conjunction with other biopolymers like cellulose nanofibril (CNF) improves the mechanical, barrier, and thermal properties of biopolymer packaging films [5]. Cellulose, comprised of the major substance in plant cell walls, is abundant, cost-effective, and coupled with its outstanding capability to form packaging films [6,7].

Nowadays, researchers have recently shown significant interest in incorporating nanofiller compounds to improve the functional properties of biopolymer-based packaging films, such as nanocellulose/gellan gum [8], gelatin/cellulose nanofiber/zinc oxide nanoparticles [9], chitosan/NiO nanoparticles [10], and cellulose nanofibrils/ZnO nanoparticles/Pickering emulsion-oregano essential oil [11]. In this scenario, titanium dioxide nanoparticles (TNPs) have received a lot of attention as a safe, cost-effective, and stable metal oxide nanoparticle used as a functional filler for packaging films [12,13]. Furthermore, TNPs presents numerous advantages, including antibacterial properties, biocompatibility, photocatalytic activity, high refractive index, and ultraviolet absorption [12,14]. Packaging films incorporating various TNPs such as those made from sago starch [15], gelatin [16], chitosan [17], and hydroxypropyl methylcellulose [18], demonstrated enhanced antibacterial activities, tensile properties, and water vapor permeability.

On the other hand, essential oils (EOs) have garnered significant attention as a potential substitute for food preservation because of their bacteriostatic

*Address corresponding to this author at the Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuh Persiaran Tun Khalil Yaakob, 26300, Kuantan, Pahang, Malaysia; E-mail: ainiazman@umpsa.edu.my

E-ISSN: 1929-5995/24

[19]. Cinnamaldehyde, found in natural EOs like cinnamon cassia, rose, and cinnamon bark has various pharmacological functions including antioxidant, antiviral, antibacterial, antifungal, anti-inflammatory, and anticancer [20]. Employing EOs that are potent with antibacterial and antioxidant compounds in food packaging materials can mitigate food safety risks related to oxidation [21,22]. Nevertheless, the utilization of EOs constrained by the active compound's high volatility, and the compatibility between EOs and matrix polymers is poor and susceptible to phase separation, leading to the deterioration of film's properties [23,24]. Therefore, it is essential to choose suitable carriers for encapsulating EOs as an approach to safeguarding against the evaporation and oxidation of EOs. To address these limitations, a Pickering emulsion (PE) are utilized to enhance the dispersion of hydrophobic substances stabilized by solid particles such as chitosan, starch and zein [23]. The preparation of PE involves techniques such as, high shear homogenization and ultrasonication to create stable oil droplets [25]. The integration of PE, which contains EO stabilized by hydrophilic polymers, improves the biological performance of biodegradable packaging films [26].

However, limited research exists on the impact of SRC incorporated with TNPs and cinnamaldehyde EO stabilized by PE on the physicochemical properties of active packaging films. Our previous study showed excellent mechanical properties on the film formulation with SRC/TNPs [27] and SRC/cellulose nanofibril (CNF) [28]. In this study, cinnamaldehyde PE was prepared by chitosan as a stabilizer. Then, SRC/CNF packaging films loaded with TNPs and varying concentration of cinnamaldehyde PE were developed. The resulting films will be analyzed for their structure morphology, mechanical, thermal, and physical properties.

2. MATERIAL AND METHODS

2.1. Materials

Semirefined carrageenan was obtained by CV Simpul Agro Globalindo, Indonesia. Titanium dioxide (size: 20–25 nm, 99.7% purity), glacial acetic acid (99 %), chitosan (medium molecular weight), cinnamaldehyde (natural, ≥95%) and glycerol were provided from Sigma-Aldrich, USA. Cellulose nanofibril was supplied from UPM Biomass Centre. Ultra-pure water was used to fabricate films and Pickering emulsion.

2.2. Preparation of Cinnamaldehyde PE

Cinnamaldehyde PE was prepared following a previously described method with minor modifications [29]. First, chitosan (2%, w/v) was dissolved in 10 mg/mL glacial acetic acid solution using magnetic stirrer at 1500 rpm for 16 h. The chitosan nano-suspension was prepared by ultrasonication (Q700 Sonicator, Newtown) at an amplitude of 20 for 10 min while maintaining a constant temperature by immersing the suspension in cold water. Subsequently, cinnamaldehyde (1%, v/v) was blended into the chitosan nano-suspension and agitated using homogenizer (T25 UltraTurrax, IKA Werke GmbH & Co, Germany) at 10,000 rpm for a duration of 10 min. The sample was transferred to a transparent vial and stored at 4 °C prior to the analysis. The droplet size and the polydispersity index (PDI) of cinnamaldehyde Pickering emulsion was measured by Zetasizer Nano ZS (Malvern Instruments, UK) at room temperature.

2.3. Preparation of SRC/Cinnamaldehyde PE Films

The SRC/cinnamaldehyde PE films were fabricated by solution casting method with minor modifications [30]. Initially, SRC (2%, w/v) was added into ultra-pure water and subjected to continuous stirring at 80 °C for 30 min. Glycerol (45%, v/v, based on SRC) was introduced as a plasticizer, and CNF (10%, v/v) was added as a reinforcing material [31] into the film-forming solution. The TNPs (3%, w/v) were initially suspended in ultra-pure water and subjected to sonication (Q700 Sonicator, Newtown) for 30 min. Afterwards, TNPs and cinnamaldehyde PE at various concentrations (0.1, 0.5, 1, and 3%, v/v) were added to the film solution at a constant temperature. Film without cinnamaldehyde PE was prepared as a control film. The film solution was subsequently cast onto a non-stick casting plate. The films were dried in an oven at 40 °C overnight and then stored at room temperature for further analysis. The film samples were developed as the following Table **1**.

2.4. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of the film sample within the wavelength range of 600 to 4000 cm^{-1} was evaluated using the attenuated total reflection (ATR) component (Nicolet iS5 spectrometer, Thermo Fisher Scientific, United States).

2.5. Mechanical Properties

The film thickness was determined as the average of measurements taken at five randomly selected

Table 1: Film Formulation

Sample	TNPs (%, w/v)	Cinnamaldehyde PE (%, v/v)
SRC	–	–
SRC/TNPs	3	–
SRC/TNPs/0.1PE	3	0.1
SRC/TNPs/0.5PE	3	0.5
SRC/TNPs/1PE	3	1.0
SRC/TNPs/3PE	3	3.0

positions (Vernier caliper). The tensile strength (TS) and elongation at break (E) of the film samples (10 × 1 cm^2) were determined in accordance with the ASTM D 882 standard method (ASTM International) using tensile testing machine (AG-X plus, Japan) at a constant speed of 10 mm/min. The stress-strain curves offered the film values for TS (MPa) and E (%).

2.6. Water Solubility

The film samples (2 × 2 cm²) were subjected to drying in an oven at 100 °C until a constant weight, W_0, was achieved [31]. Following this, the film samples were immersed in 30 mL of distilled water for 24 hours at room temperature. Subsequently, the undissolved film samples were dried at 100 °C to a constant weight, W_f. The water solubility was calculated using the following equation:

$$Water\ solubility\ (\%) = \frac{W_0 - W_f}{W_0} \times 100 \quad (1)$$

2.7. Moisture Content

The moisture content of the film samples was determined by measuring the weight loss of the films (2 × 2 cm²) before drying (W_1) and after undergoing a 24-hour drying process in an oven at 100 °C (W_2) [31]. Moisture content was then calculated using the specified equation.

$$Moisture\ content\ (\%) = \frac{W_1 - W_2}{W_1} \times 100 \quad (2)$$

2.8. Opacity

The opacity of the films was assessed using a UV-visible spectrophotometer (U-1800, Japan) at a wavelength of 600 nm, employing an empty plastic cuvette as the reference [31]. The opacity of the films was then determined through the following equation:

$$Opacity = \frac{Abs_{600}}{d} \times 100 \quad (3)$$

where *Abs* is the absorbance, and *d* is the thickness of the film (mm).

2.9. Scanning Electron Microscope (SEM)

SEM a technique used to study the surface morphology and topography of materials at high magnification. When applied to semi-refined carrageenan films, SEM can provide detailed information about its micro-surface of films.

2.10. Thermogravimetric Analysis (TGA)

The thermal stability of the films was assessed employing a TGA (SDT Q600 V20.9 Shimadzu, Tokyo) analyzer. Samples weighing 1–2 mg were positioned in the heating chamber, enveloped by an inert nitrogen atmosphere (with a flow rate of 50 mL/min), and subjected to a heating rate of 10 °C/min. The examination of thermal stability was conducted within the temperature range of 25 °C to 400 °C.

3. RESULT AND DISCUSSION

3.1. Characterization of Cinnamaldehyde PE

The particle size and PDI of cinnamaldehyde PE were 314.7 nm and 0.520, respectively. Previous study demonstrated a similar trend with droplet diameter of chitosan-loaded nanoemulsion with 0.5% EO (342.33 nm) than that of chitosan-loaded NE with 1% EO (455.13 nm) [32]. The mean droplet size of nanoemulsions that is smaller than 500 nm and PDI<0.7 has been recognized as colloidal dispersion droplets, which bring homogeneity and stability and prevent droplet aggregation [19,33].

3.2. FTIR Analysis

The FTIR were employed for the analysis of chemical bonding and alterations in the functional

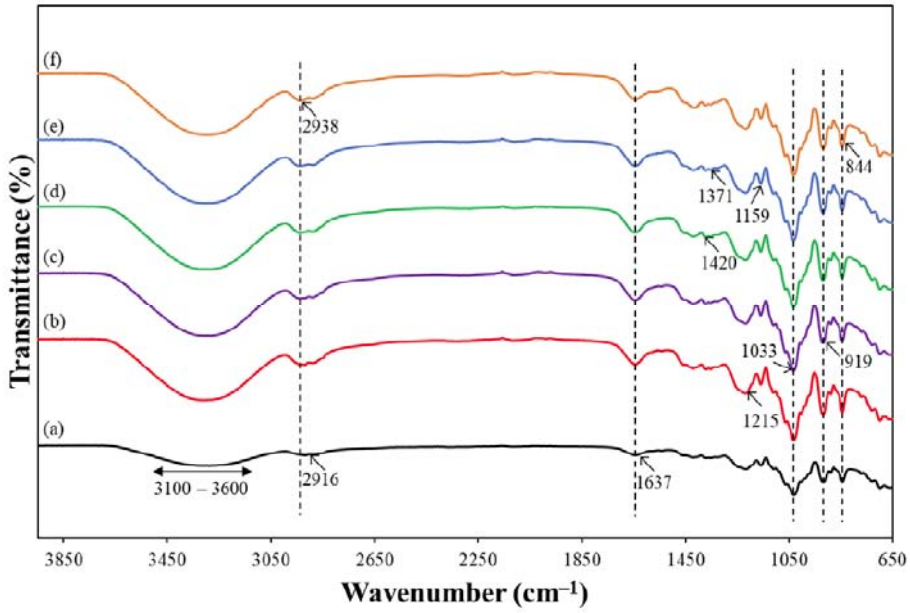

Figure 1: FTIR spectra of (a) SRC, (b) SRC/TNPs, (c) SRC/TNPs/0.1PE, (d) SRC/TNPs/0.5PE, (e) SRC/TNPs/1PE, and (f) SRC/TNPs/3PE.

groups of active packaging films. Figure **1** showed the FTIR spectra in the wavenumbers ranging from 500 – 4000 cm^{-1} of SRC, TNPs and cinnamaldehyde PE. The films displayed a broad band between 3100 and 3600 cm^{-1}, corresponding to the O—H stretching vibration of the hydrogen bond–hydroxyl group in carrageenan and absorbed water [34,35]. The peak detected at ~2916 cm^{-1} corresponds to the vibration of C—H stretching in all the films [36]. In the SRC films, signature bands of kappa carrageenan were noticeable at 1215 cm^{-1}, 844 cm^{-1}, and 919 cm^{-1}. There were attributed with the sulfate ester (O═S═O stretching), galactose-4-sulfate (C—O—S stretching), and 3,6-anhydro-galactose ring, respectively [34,36,37]. The band at 1159 cm^{-1} is associated with the symmetric stretching of C—O—C, while the band at 1033 cm^{-1} corresponds to the stretching of C—O and C—OH groups [38].

The titanium dioxide spectra display a wide band below 600 cm^{-1}, signifying the formation of nanostructures attributed to the metal-oxygen (Ti—O stretching) mode [39]. Previous studies demonstrated a similar trend, with a broad peak below 850 cm^{-1}, indicating the stretching of the TiO for pure titanium dioxide nanostructure [40]. The interaction of various concentrations of cinnamaldehyde PE and TNPs in the SRC matrix led to a subtle change and shifting in the intensity of the bands, evident in all SRC films. Furthermore, the SRC films loaded with cinnamaldehyde PE showed stronger absorption spectra at approximately 1420 cm^{-1} and 1371 cm^{-1} compared to unloaded cinnamaldehyde films. Meanwhile, the characteristic band at 2916 cm^{-1} for the SRC films shifted to 2938 cm^{-1} at a higher concentration of cinnamaldehyde in the films. A comparable pattern was disclosed in the study by Basumatary *et al*. [41], signifying the interaction between the combined active agents in the chitosan films with a shift and alteration in peak intensity.

3.3. Mechanical Properties of the Films

Packaging film with favorable mechanical properties, such as high tensile strength (TS) and elongation at break (E), proves beneficial for the efficient distribution and storage of food items. The TS and E properties of the films are primarily determined by the interaction among compounds and the internal structure within the film matrix [12]. Table **2** shows the thickness, TS and E properties of the films. The TS of TNPs-containing film increased slightly to 15.11 MPa when compared to the TS of SRC/CNF film (14.48 MPa). Furthermore, TNPs-loaded SRC films increased the E value of the SRC films from 15.76% to 20.97%. The higher content of TNPs significantly has a notable impact on the agglomeration of particles within the film matrix, consequently affecting the TS of the films [42]. This study suggests that TNPs at a specific concentration can be evenly distributed, serve as fillers, and reinforce the film network.

Conversely, incorporating cinnamaldehyde PE resulted in an enhancement of both the TS and E, and the film containing 0.5% cinnamaldehyde possessed

the highest TS and E values, measuring at 21.86 MPa and 34.22%, respectively. Nevertheless, as the concentration of the cinnamaldehyde PE increased from 0.5% to 3%, both the TS and E values of the films declined. The integration of the emulsion substances could function as a plasticizer in the matrices, improving the flexibility and strength of the films [25]. On the contrary, with an elevated concentration of cinnamaldehyde PE, there is a possibility of droplet aggregation during the film's casting and drying, resulting in a subsequent decline in the mechanical properties of the films [43]. Larger oil droplets have the potential to disturb the internal structure of the film matrix, resulting in an uneven structure [29]. Hence, the study revealed that incorporating cinnamaldehyde PE and TNPs at a particular concentration markedly improved the TS and E values of the films.

Table 2: Tensile Strength and Elongation Values of SRC Films with TNPs and Varying Concentrations of Cinnamaldehyde PE

Sample	TS (MPa)	E (%)
SRC	14.48 ± 0.67	15.76 ± 0.89
SRC/TNPs	15.11 ± 1.53	20.97 ± 1.87
SRC/TNPs/0.1PE	17.25 ± 1.09	24.98 ± 2.34
SRC/TNPs/0.5PE	21.86 ± 0.42	34.22 ± 1.56
SRC/TNPs/1PE	19.14 ± 3.76	27.63 ± 2.85
SRC/TNPs/3PE	13.79 ± 1.02	26.34 ± 1.54

3.4. Physical Properties of the Films

The water solubility (S) and moisture content (M) of the SRC films are summarized in Table **2**. The M value is an indicator that refers to the total void volume occupied by water molecules in the film matrix [44]. The addition of TNPs and cinnamaldehyde PE to the SRC films slightly decreased the M values from 33.23% to 31.00%. The decrease in M value likely resulted from the robust intermolecular interaction within the compounds in the matrices, impeding the effective absorption of water molecules [45]. In addition, the hydrophobic nature of the oil encapsulated in the O/W emulsion would replace the partial interaction of polymers, active compounds, and water molecules in the matrices, consequently reducing the M value of the film [46]. Shen *et al*. [47] found that combining pullulan-gelatin-based films with PE containing clove essential oil reduced the M value, making the films more moisture-resistant. In particular, the incorporation of TNPs is thought to change the physical properties of the films and reduce the M value of the films. According to the study conducted by Dash *et al*. [44], an increment in the TNPs concentration from 0 to 4% reduced the M values of the starch film, measuring at 23.12% to 15.15%.

The S value is a crucial functional property for biodegradable-based packaging films due to its close linkage with the material's hydrophilicity property [48]. Conversely, high humidity conditions can soften the film's structure, leading to the use of lower-solubility films to minimize wetness for packaging applications [44]. The S value exhibited improvement with the incorporation of TNPs and cinnamaldehyde PE at any concentration, with values ranging from 86.99% to 47.82% (Table **3**). The lowest S value was achieved with the incorporation of 1% cinnamaldehyde, possibly due to the homogeneous structure in biodegradable active films [49]. According to the study by Zhao *et al*. [50], the solubility of chitosan nanoparticle films stabilized with Pickering emulsion is lowest due to stronger hydrogen bond interactions within the polymers and active compounds, which hindered the interaction of hydroxyl groups with water molecules. Hasheminya *et al*. [51] also observed a decrease in the S value of the gum-based films that incorporated EO-based nanoemulsions, and this phenomenon was

Table 3: Moisture Content and Water Solubility of SRC Films with TNPs and Varying Concentrations of Cinnamaldehyde PE

Sample	Moisture Content (%)	Water Solubility (%)
SRC	33.23 ± 0.98	86.99 ± 1.36
SRC/TNPs	33.16 ± 1.25	73.31 ± 0.69
SRC/TNPs/0.1PE	31.45 ± 2.44	74.39 ± 0.73
SRC/TNPs/0.5PE	32.15 ± 0.13	66.34 ± 3.87
SRC/TNPs/1PE	31.00 ± 1.86	47.82 ± 1.93
SRC/TNPs/3PE	32.17 ± 0.23	71.26 ± 0.14

attributed to the hydrophobicity of the oil. Hence, the hydrophilic disadvantage of films can be somewhat mitigated by adding nanoparticles and/or emulsions containing essential oils.

3.5. Thickness and Opacity of the Films

The thickness of the SRC films in this study ranged from 0.0830 to 0.1270 mm (Table **4**). The study found that incorporating active compounds resulted in the creation of more intricate matrices, consequently increasing the thickness of the SRC films [27].

Table 4: Thickness and Opacity of SRC Films with TNPs and Varying Concentrations of Cinnamaldehyde PE

Films	Thickness (mm)	Opacity (mm^{-1})
SRC	0.0830 ± 0.0051	3.10 ± 0.41
SRC/TNPs	0.0900 ± 0.0032	12.47 ± 0.97
SRC/TNPs/0.1PE	0.0870 ± 0.0085	13.78 ± 0.37
SRC/TNPs/0.5PE	0.0930 ± 0.0048	11.47 ± 0.62
SRC/TNPs/1PE	0.0900 ± 0.0091	13.44 ± 0.34
SRC/TNPs/3PE	0.1270 ± 0.0035	10.95 ± 0.73

Film transparency is crucial in food packaging for quality control, especially for perishable foods like meat, but it can also cause oxidation reactions from the light, leading to spoilage [13,40]. The opacity of the film is determined by ultraviolet-visible spectroscopy at the absorbance value of 600 nm with the film thickness [9,16]. Table **4** shows the opacity value of the SRC films incorporated with TNPs and various concentrations of cinnamaldehyde PE. The addition of 3% TNPs increased the opacity of the film from 3.10 to 12.47 mm^{-1}. However, the addition of cinnamaldehyde PE at 0.1% and 1% slightly increased the film's opacity, with values of 13.78 mm^{-1} and 13.44 mm^{-1}, respectively. In contrary, the film with 3% cinnamaldehyde PE exhibited a lower opacity value of 10.95 mm^{-1} as compared to the unloaded cinnamaldehyde film. A previous study revealed that the transparency of pectin/gelatin film decreased with TNPs concentration, and film with 5% TNPs having the highest opacity, possibly due to the light scattering of nano-substances in the film matrix [40]. Nonetheless, the addition of cinnamaldehyde PE increased the opacity of the film, which may be due to the dispersion of droplets in the film matrix. The opacity of a film is significantly influenced by the size and number of scattered oil droplets, which are determined by the difference in refractive index between the two phases [52]. Liu *et al*. [53] showed a similar trend, adding cinnamon oil-Pickering emulsion to cellulose-based film reduced light transmittance due to the oil droplet dispersion.

3.6. SEM Analysis

The SEM analysis (Figure **2**) was employed to examine the surface morphology of the SRC films, revealing their microstructure and the distribution compatibility of compounds within the film matrix. The SEM images exhibited a surface with fold-like features and the absence of any holes or cracks for all of the SRC films. The even distribution of TNPs and cinnamaldehyde PE throughout the polymer matrix showcases the uniform distribution of the compounds in the matrices. The study indicates that incorporating TNPs and cinnamaldehyde PE exhibits compatibility with polymer compounds in the film matrix, resulting in the formation of a continuous structure in the film. Research conducted by Kim *et al*. [6] illustrated a uniform distribution of active compounds in the matrices, and it was observed that the droplet size of the compounds increased with concentration in CNF-based films.

3.7. Thermal Properties of the Films

The thermal degradation and decomposition of the SRC films were evaluated by TGA to observe the thermal stability, which was helpful for determining the films' resistance to incineration [54]. The rapid thermal change (evaporation and decomposition) in the film samples was provided by the DTG peak. The TGA thermogram pattern (Figure **3**) showed that the thermal degradation of the films is classified into multi-stages. First, initial weight loss was observed between 30 – 100 °C indicated to the evaporation of any remaining solvent and water [54,55]. Next, the majority of weight loss took place between 140 – 400 °C, due to the heat degradation of glycerol and polysaccharides, and the highest decomposition of the materials occurring roughly at 222 – 224 °C [56]. The addition of cinnamaldehyde PE at 0.5% slightly increased the thermal stability of the films as compared to the other SRC films. The char residual of the films increased marginally from ~22% to ~26% at 600 °C.

4. CONCLUSION

The addition of TNPs and cinnamaldehyde PE enhanced the mechanical and physical properties of the SRC films. The study found that the incorporation

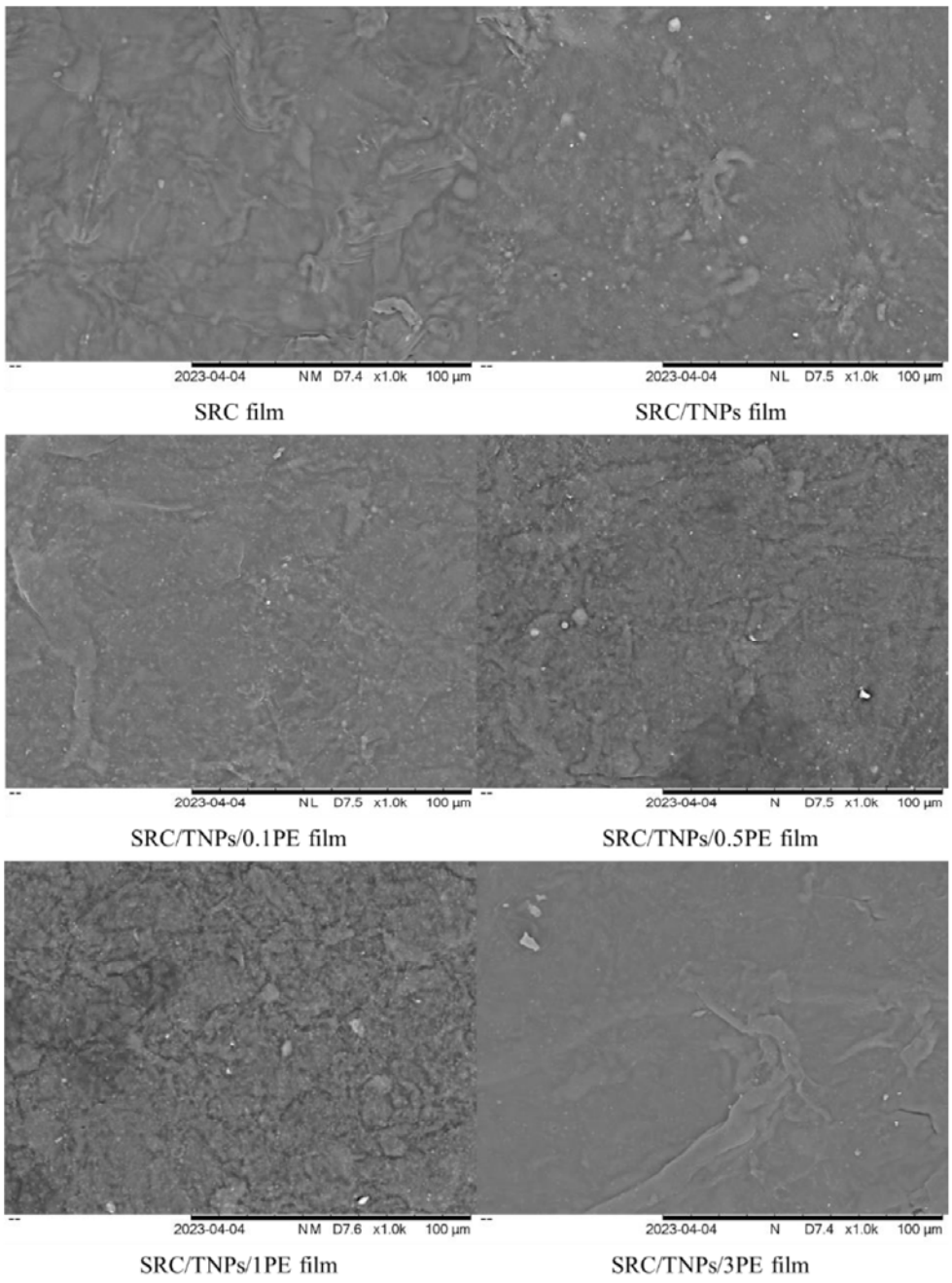

Figure 2: Surface morphology of SRC films with TNPs and varying concentrations of cinnamaldehyde PE.

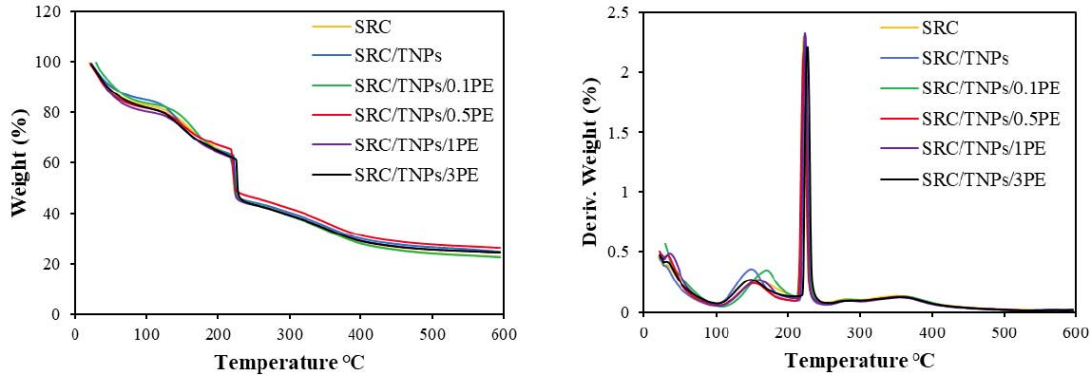

Figure 3: Thermal profile (**a**) TGA and (**b**) DTG of SRC films with TNPs and varying concentrations of cinnamaldehyde PE.

of 0.5% cinnamaldehyde PE possessed the highest TS and E with values of 21.86 MPa and 34.22%, respectively, in the SRC film. Furthermore, the SRC film with TNPs and 0.5% cinnamaldehyde PE showed a smooth surface morphology as compared to the other SRC films. The moisture content and water solubility of the films improved with the addition of TNPs and cinnamaldehyde PE at any concentration. The thermal stability of the films marginally increased with the incorporation of cinnamaldehyde PE at 0.5%. Hence, this study integrated that the addition of TNPs and cinnamaldehyde PE enhanced the mechanical, physical, and thermal properties of the SRC films, which presenting favorable attributes to support the preservation of packaged food as an eco-friendly alternative to non-degradable packaging materials.

ACKNOWLEDGEMENT

This study received financial support from Universiti Malaysia Pahang Al-Sultan Abdulah through an internal university grant (No. RDU233020 and PGRS 220316).

REFERENCES

[1] Maraz KM, Karmaker N, Meem RA, Khan RA. Development of Biodegradable Packaging Materials from Bio-Based Raw Materials. J Res Updates Polym Sci 2019; 20(8): 66-84. https://doi.org/10.6000/1929-5995.2019.08.09

[2] Basavegowda N, Baek KH. Advances in Functional Biopolymer-Based Nanocomposites for Active Food Packaging Applications. Polymers (Basel) 2021; 13(23): 4198. https://doi.org/10.3390/polym13234198

[3] Wullandari P, Sedayu BB, Novianto TD, Prasetyo AW. Characteristic of semi refined and refined carrageenan flours used in the making of biofilm (bioplastic). In: IOP Conf Ser Earth Environ Sci. IOP Publishing Ltd; 2021. https://doi:10.1088/1755-1315/733/1/012112

[4] Aga MB, Dar AH, Nayik GA, Panesar PS, Allai F, Khan SA, *et al*. Recent insights into carrageenan-based bio-nanocomposite polymers in food applications: A review. Int J Biol Macromol 2021; 192: 197-209. https://doi.org/10.1016/j.ijbiomac.2021.09.212

[5] Yahaya WAW, Chik SMST, Azman NAM, Nor AM, Abd. Hamid KH, Ajit A. Mechanical properties and antioxidant activity of carrageenan-cellulose nanofiber incorporated butylated hydroxyanisole as active food packaging. Mater Today Proc. 2023. https://doi.org/10.1016/j.matpr.2023.08.180

[6] Kim YH, Kim HJ, Yoon KS, Rhim JW. Cellulose nanofiber/deacetylated quaternary chitosan composite packaging film for growth inhibition of Listeria monocytogenes in raw salmon. Food Packag Shelf Life 2023; 35: 101040.

[7] https://doi.org/10.1016/j.fpsl.2023.101040

[8] Ezati P, Rhim JW, Molaei R, Priyadarshi R, Han S. Cellulose nanofiber-based coating film integrated with nitrogen-functionalized carbon dots for active packaging applications of fresh fruit. Postharvest Biol Technol 2022; 186: 111845. https://doi.org/10.1016/j.postharvbio.2022.111845

[9] Sripahco T, Khruengsai S, Pripdeevech P. Biodegradable antifungal films from nanocellulose-gellan gum incorporated with Anethum graveolens essential oil for bread packaging. Int J Biol Macromol 2023; 243: 125244. https://doi.org/10.1016/j.ijbiomac.2023.125244

[10] Ahmadi A, Ahmadi P, Sani MA, Ehsani A, Ghanbarzadeh B. Functional biocompatible nanocomposite films consisting of selenium and zinc oxide nanoparticles embedded in gelatin/cellulose nanofiber matrices. Int J Biol Macromol 2021; 175: 87-97. https://doi.org/10.1016/j.ijbiomac.2021.01.135

[11] Ardebilchi Marand S, Almasi H, Ardebilchi Marand N. Chitosan-based nanocomposite films incorporated with NiO nanoparticles: Physicochemical, photocatalytic and antimicrobial properties. Int J Biol Macromol 2021; 190: 667-78. https://doi.org/10.1016/j.ijbiomac.2021.09.024

[12] Wu M, Zhou Z, Yang J, Zhang M, Cai F, Lu P. ZnO nanoparticles stabilized oregano essential oil Pickering emulsion for functional cellulose nanofibrils packaging films with antimicrobial and antioxidant activity. Int J Biol Macromol 2021; 190: 433-40. https://doi.org/10.1016/j.ijbiomac.2021.08.210

[13] Zhang W, Rhim JW. Titanium dioxide (TiO2) for the manufacture of multifunctional active food packaging films. Food Packag Shelf Life 2022; 31: 100806. https://doi.org/10.1016/j.fpsl.2021.100806

[14] Alizadeh Sani M, Maleki M, Eghbaljoo-Gharehgheshlaghi H, Khezerlou A, Mohammadian E, Liu Q, *et al*. Titanium dioxide nanoparticles as multifunctional surface-active materials for smart/active nanocomposite packaging films. Adv Coll Int Sci 2022; 300: 102593. https://doi.org/10.1016/j.cis.2021.102593

[15] Sharma S, Byrne M, Perera KY, Duffy B, Jaiswal AK, Jaiswal S. Active film packaging based on bio-nanocomposite TiO2 and cinnamon essential oil for enhanced preservation of cheese quality. Food Chem 2023; 405: 134798. https://doi.org/10.1016/j.foodchem.2022.134798

[16] Arezoo E, Mohammadreza E, Maryam M, Abdorreza MN. The synergistic effects of cinnamon essential oil and nano TiO2 on antimicrobial and functional properties of sago starch films. Int J Biol Macromol 2020; 157: 743-51. https://doi.org/10.1016/j.ijbiomac.2019.11.244

[17] Riahi Z, Priyadarshi R, Rhim JW, Bagheri R. Gelatin-based functional films integrated with grapefruit seed extract and TiO2 for active food packaging applications. Food Hydrocoll 2021; 112. https://doi.org/10.1016/j.foodhyd.2020.106314

[18] Liu Z, Du M, Liu H, Zhang K, Xu X, Liu K, *et al*. Chitosan films incorporating litchi peel extract and titanium dioxide nanoparticles and their application as coatings on watercored apples. Prog Org Coat 2021; 151: 106103. https://doi.org/10.1016/j.porgcoat.2020.106103

[19] Fonseca J de M, Valencia GA, Soares LS, Dotto MER, Campos CEM, Moreira R de FPM, *et al*. Hydroxypropyl methylcellulose-TiO2 and gelatin-TiO2 nanocomposite films: Physicochemical and structural properties. Int J Biol Macromol 2020; 151: 944-56. https://doi.org/10.1016/j.ijbiomac.2019.11.082

[20] Abdalla G, Mussagy CU, Sant'Ana Pegorin Brasil G, Scontri M, da Silva Sasaki JC, Su Y, *et al*. Eco-sustainable coatings based on chitosan, pectin, and lemon essential oil nanoemulsion and their effect on strawberry preservation. Int J Biol Macromol 2023; 249: 126016. https://doi.org/10.1016/j.ijbiomac.2023.126016

[21] Yan C, Li N, Zhang Y, Wei Y. Enrichment of cinnamaldehyde from Cinnamomum cassia by electroosmotic coupled particle-assisted solvent flotation. J Chromatogr A 2023; 1710: 464411. https://doi.org/10.1016/j.chroma.2023.464411

[22] Sharma S, Barkauskaite S, Jaiswal AK, Jaiswal S. Essential oils as additives in active food packaging. Food Chem 2021; 343: 128403. https://doi.org/10.1016/j.foodchem.2020.128403

[23] Atarés L, Chiralt A. Essential oils as additives in biodegradable films and coatings for active food packaging. Trends Food Sci Technol 2016; 48: 51-62. https://doi.org/10.1016/j.tifs.2015.12.001

[24] Roy S, Rhim JW. Gelatin/agar-based functional film integrated with Pickering emulsion of clove essential oil stabilized with nanocellulose for active packaging applications. Colloids Surf A Physicochem Eng Asp 2021; 627. https://doi.org/10.1016/j.colsurfa.2021.127220

[25] Niroula A, Gamot TD, Ooi CW, Dhital S. Biomolecule-based pickering food emulsions: Intrinsic components of food matrix, recent trends and prospects. Food Hydrocoll 2021; 112: 106303. https://doi.org/10.1016/j.foodhyd.2020.106303

[26] Almasi H, Azizi S, Amjadi S. Development and characterization of pectin films activated by nanoemulsion and Pickering emulsion stabilized marjoram (Origanum majorana L.) essential oil. Food Hydrocoll 2020; 99: 105338. https://doi.org/10.1016/j.foodhyd.2019.105338

[27] Yang S, Ban Z, Jin L, Chen C, Li L, Yi G, *et al*. Polyvinyl alcohol films incorporated with clove essential oil emulsions stabilized by soy protein isolate-derived amyloid fibrils: Fabrication, characterization, and its application for active packaging. Food Chem 2024; 440: 138245. https://doi.org/10.1016/j.foodchem.2023.138245

[28] Abd Hamid KH, Jayakumar T, Gunasegaran S, Mohd Azman NA. Fabrication and Characterization of Semi-refined Carrageenan Films Incorporated with TiO2 Nanoparticles. J Chem Eng Ind Biotechnol 2023; 9: 1-7. https://doi.org/10.15282/jceib.v9i1.9466

[29] Wan Yahaya WA, Raja Ahmad RN, Mohd Azman NA. Characterization of Semi-Refined Carrageenan Reinforced with Cellulose Nanofiber Incorporated α -Tocopherol for Active Food Packaging Applications. Materials Sci Forum 2020; 1007: 154-9. https://doi.org/10.4028/www.scientific.net/MSF.1007.154

[30] Xu Y, Chu Y, Feng X, Gao C, Wu D, Cheng W, *et al*. Effects of zein stabilized clove essential oil Pickering emulsion on the structure and properties of chitosan-based edible films. Int J Biol Macromol 2020; 156: 111-9. https://doi.org/10.1016/j.ijbiomac.2020.04.027

[31] Abd Hamid KH, Wan Yahaya WA, Mohd Saupy NAZ, Almajano MP, Mohd Azman NA. Semi-refined carrageenan film incorporated with α -tocopherol: Application in food model. J Food Process Preserv 2019; 43(5): e13937. https://doi.org/10.1111/jfpp.13937

[32] Wan Yahaya WA, Azman NAM, Adam F, Subramaniam SD, Abd Hamid KH, Almajano MP. Exploring the Potential of Seaweed Derivatives for the Development of Biodegradable Plastics: A Comparative Study. Polymers (Basel) 2023; 15(13): 2884. https://doi.org/10.3390/polym15132884

[33] Mehraie A, Khanzadi S, Hashemi M, Azizzadeh M. New coating containing chitosan and Hyssopus officinalis essential oil (emulsion and nanoemulsion) to protect shrimp (Litopenaeus vannamei) against chemical, microbial and sensory changes. Food Chem X 2023; 19: 100801. https://doi.org/10.1016/j.fochx.2023.100801

[34] Otoni CG, Avena-Bustillos RJ, Olsen CW, Bilbao-Sáinz C, McHugh TH. Mechanical and water barrier properties of isolated soy protein composite edible films as affected by carvacrol and cinnamaldehyde micro and nanoemulsions. Food Hydrocoll 2016; 57: 72-79. https://doi.org/10.1016/j.foodhyd.2016.01.012

[35] Saedi S, Shokri M, Priyadarshi R, Rhim JW. Silver ion loaded 3-aminopropyl trimethoxysilane -modified Fe3O4 nanoparticles for the fabrication of carrageenan-based active packaging films. Colloids Surf B Biointerfaces 2021; 208: 112085. https://doi.org/10.1016/j.colsurfb.2021.112085

[36] Farhan A, Hani NM. Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol. Food Hydrocoll 2017; 64: 48-58. https://doi.org/10.1016/j.foodhyd.2016.10.034

[37] Farhan A, Hani NM. Active edible films based on semi-refined κ-carrageenan: Antioxidant and color properties and application in chicken breast packaging. Food Packag Shelf Life 2020; 24: 100476. https://doi.org/10.1016/j.fpsl.2020.100476

[38] Yong H, Liu J, Kan J, Liu J. Active/intelligent packaging films developed by immobilizing anthocyanins from purple sweetpotato and purple cabbage in locust bean gum, chitosan and κ -carrageenan-based matrices. Int J Biol Macromol 2022; 211: 238-48. https://doi.org/10.1016/j.ijbiomac.2022.05.046

[39] Kanmani P, Rhim JW. Development and characterization of carrageenan/grapefruit seed extract composite films for active packaging. Int J Biol Macromol 2014; 68: 258-66. https://doi.org/10.1016/j.ijbiomac.2014.05.011

[40] Razali MH, Ismail NA, Mat Amin KA. Titanium dioxide nanotubes incorporated gellan gum bio-nanocomposite film for wound healing: Effect of TiO2 nanotubes concentration. Int J Biol Macromol 2020; 153: 1117-35. https://doi.org/10.1016/j.ijbiomac.2019.10.242

[41] Candra A, Tsai HC, Saragi IR, Hu CC, Yu WT, Krishnamoorthi R, *et al*. Fabrication and characterization of hybrid eco-friendly high methoxyl pectin/gelatin/ TiO2/curcumin (PGTC) nanocomposite biofilms for salmon fillet packaging. Int J Biol Macromol 2023; 232: 123423. https://doi.org/10.1016/j.ijbiomac.2023.123423

[42] Basumatary IB, Mukherjee A, Kumar S. Chitosan-based composite films containing eugenol nanoemulsion, ZnO nanoparticles and Aloe vera gel for active food packaging. Int J Biol Macromol 2023; 242: 124826. https://doi.org/10.1016/j.ijbiomac.2023.124826

[43] Perera KY, Sharma S, Duffy B, Pathania S, Jaiswal AK, Jaiswal S. An active biodegradable layer-by-layer film based on chitosan-alginate-TiO2 for the enhanced shelf life of tomatoes. Food Packag Shelf Life 2022; 34: 100971. https://doi.org/10.1016/j.fpsl.2022.100971

[44] Zhao R, Guan W, Zhou X, Lao M, Cai L. The physiochemical and preservation properties of anthocyanidin/chitosan nanocomposite-based edible films containing cinnamon-perilla essential oil pickering nanoemulsions. LWT 2022; 153: 112506. https://doi.org/10.1016/j.lwt.2021.112506

[45] Dash KK, Ali NA, 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. Int J Biol Macromol 2019; 139: 449-58. https://doi.org/10.1016/j.ijbiomac.2019.07.193

[46] Roy S, Rhim JW. 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 2021; 193: 2038-46. https://doi.org/10.1016/j.ijbiomac.2021.11.03

[47] Fan S, Wang D, Wen X, Li X, Fang F, Richel A, *et al*. Incorporation of cinnamon essential oil-loaded Pickering emulsion for improving antimicrobial properties and control release of chitosan/gelatin films. Food Hydrocoll 2023; 138: 108438. https://doi.org/10.1016/j.foodhyd.2022.108438

[48] Shen Y, Ni ZJ, Thakur K, Zhang JG, Hu F, Wei ZJ. Preparation and characterization of clove essential oil loaded

nanoemulsion and pickering emulsion activated pullulan-gelatin based edible film. Int J Biol Macromol 2021; 181: 528-39.
https://doi.org/10.1016/j.ijbiomac.2021.03.133

[49] Li Y, Jiang Y, Liu F, Ren F, Zhao G, Leng X. Fabrication and characterization of TiO2/whey protein isolate nanocomposite film. Food Hydrocoll 2011; 25(5): 1098-104.
https://doi.org/10.1016/j.foodhyd.2010.10.006

[50] Fasihi H, Fazilati M, Hashemi M, Noshirvani N. Novel carboxymethyl cellulose-polyvinyl alcohol blend films stabilized by Pickering emulsion incorporation method. Carbohydr Polym 2017; 167: 79-89.
https://doi.org/10.1016/j.carbpol.2017.03.017

[51] Zhao R, Guan W, Zheng P, Tian F, Zhang Z, Sun Z, *et al*. Development of edible composite film based on chitosan nanoparticles and their application in packaging of fresh red sea bream fillets. Food Control 2022; 132: 108545.
https://doi.org/10.1016/j.foodcont.2021.108545

[52] Hasheminya SM, Dehghannya J. Development and characterization of novel edible films based on Cordia dichotoma gum incorporated with Salvia mirzayanii essential oil nanoemulsion. Carbohydr Polym 2021; 257: 117606.
https://doi.org/10.1016/j.carbpol.2020.117606

[53] Pereda M, Amica G, Marcovich NE. Development and characterization of edible chitosan/olive oil emulsion films. Carbohydr Polym 2012; 87(2): 1318-25.
https://doi.org/10.1016/j.carbpol.2011.09.019

[54] Liu J, Song F, Chen R, Deng G, Chao Y, Yang Z, *et al*. Effect of cellulose nanocrystal-stabilized cinnamon essential oil Pickering emulsions on structure and properties of chitosan composite films. Carbohydr Polym 2022; 275: 118704.
https://doi.org/10.1016/j.carbpol.2021.118704

[55] Alizadeh Sani M, Tavassoli M, Salim SA, Azizi-lalabadi M, McClements DJ. Development of green halochromic smart and active packaging materials: TiO2 nanoparticle- and anthocyanin-loaded gelatin/κ-carrageenan films. Food Hydrocoll 2022; 124: 107324.
https://doi.org/10.1016/j.foodhyd.2021.107324

[56] Kim S, Baek SK, Song K Bin. Physical and antioxidant properties of alginate films prepared from Sargassum fulvellum with black chokeberry extract. Food Packag Shelf Life 2018; 18: 157-63.
https://doi.org/10.1016/j.fpsl.2018.11.008

[57] Han Y, Zhou M, McClements DJ, Liu F, Cheng C, Xiong J, *et al*. Investigation of a novel smart and active packaging materials: Nanoparticle-filled carrageenan-based composite films. Carbohydr Polym 2023; 301: 120331.
https://doi.org/10.1016/j.carbpol.2022.120331

Received on 02-01-2024 Accepted on 24-01-2024 Published on 02-02-2024

https://doi.org/10.6000/1929-5995.2024.13.01