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ORIGINAL ARTICLE

Fabrication and Characterization of Semi-refined Carrageenan Films Incorporated with TiO_2 Nanoparticles

K.H. Abd Hamid, T. Jayakumar, S. Gunasegaran, N.A. Mohd Azman*

Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang Al-Sultan Abdullah, Lebuhraya Persiaran Tun Khalil Yaakob 26300 Kuantan, Pahang, Malaysia.

ABSTRACT – In this study, a packaging film was developed using semi-refined carrageenan, incorporating varying concentrations of TiO_2 nanoparticles. The aim of this study was to investigate the effect of TiO_2 nanoparticles on the properties of the SRC-based film. The films were prepared through a casting method, and the resulting samples were characterized in terms of their functional, mechanical, and physical properties. The SRC film containing 1 wt% of TiO_2 nanoparticles demonstrated the highest tensile strength. However, with the addition of TiO_2 nanoparticles at any concentrations (1, 3, 5, and 7 wt%), the elongation at break of the SRC film decreased in comparison to the SRC film without TiO_2 nanoparticles. Moreover, as the concentration of TiO_2 nanoparticles increased from 1 to 7 wt%, the moisture content, and water solubility of the SRC films decreased. The FTIR spectra analysis provided valuable information on the interaction between SRC and TiO_2 nanoparticles. The results suggest that incorporating TiO_2 nanoparticles into semi-refined carrageenan films shows promise for developing packaging materials with improved mechanical strength and physical performance.

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INTRODUCTION

Food packaging is one of the most practical ways to ensure food safety and quality, along with extending the shelf life of packaged food. Synthetic packaging materials, such as polyethylene, polypropylene, polystyrene, poly(vinyl chloride), and poly(ethylene terephthalate) are the most widely used non-biodegradable plastic packaging materials in packaging industry [1]. The UN Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP) reported that 70–95 % of plastic waste enters oceans, rivers, and landfills, which leads to environmental consciousness among consumers [2]. As an alternative to non-biodegradable plastic packaging, it is crucial to create green and biodegradable packaging films. In particular, most natural polymers, such as those made from polysaccharides and proteins, have the potential to replace petrochemical-based polymers because they are renewable, biodegradable, abundant, biocompatible, and sustainable [3, 4].

Among the various biopolymers, carrageenan, derived from red seaweed (Rhodophyta), is a nontoxic, biodegradable, and renewable material. Carrageenan has emerged as a suitable biopolymer for food packaging because of its natural gel-forming ability, abundance, and biocompatibility [5]. Carrageenan is divided into two categories based on its purity level: refined carrageenan (RC) and semi-refined carrageenan (SRC). In this regard, the semi-refined process still contains a small amount of cellulose settled in carrageenan, which improves the gelling and binding properties at a lower cost. However, carrageenan is limited by its inherent hydrophilicity and films made from it alone possess poor barrier and functional properties [6]. To overcome these drawbacks, numerous studies have been conducted to improve the functional properties of films by implementing nanoparticles, blended polymers, and/or incorporating active compounds from natural extracts or essential oils [7–10]. Many previous studies have reported the development of biofilms based on carrageenan reinforced with cellulose nanofibers [11], carrageenan/ZnO [12], carrageenan/agar/zinc sulfide [13], carrageenan/orange essential oil [14], and carrageenan/nanoclay [15] for food applications.

Nanoparticulate compounds from metal oxides are at the forefront of the hunt for the functional characteristics of biopolymeric films [16–18]. Among all metal oxides, TiO_2 nanoparticles have been used as nanofillers in the film matrix because of their excellent stability and antimicrobial properties [19]. TiO_2 nanoparticles have many advantages, such as affordability, high stability, photocatalytic activity, ultraviolet absorption, high refractive index, low toxicity, antibacterial activity, and biocompatibility [20]. TiO_2 nanoparticles have been utilized in food packaging to fabricate active packaging films with improved functional properties. Moreover, TiO_2 nanoparticles interact with the film matrix to enhance their physical, barrier, and antimicrobial properties [21]. Therefore, our main focus is to investigate the possibility of TiO_2 nanoparticles to SRC films to develop a packaging material that possesses desirable mechanical and physical properties.

The main objective of this study was to prepare semi-refined carrageenan-based packaging film incorporated with TiO_2 nanoparticles. In this regard, the synthesis and characterization of semi-refined carrageenan-based packaging films were carried out. The functional, physical and mechanical properties of carrageenan-based films were examined.

*CORRESPONDING AUTHOR | N.A. Mohd Azman | ainiazman@ump.edu.my

MATERIALS AND METHODS

Materials

The materials used in this study are semi-refined carrageenan obtained from CV Simpul Agro Globalindo, Indonesia, while TiO_2 nanoparticles (anatase, particle size of 20–25 nm, 99.7 % purity), and food grade glycerol were supplied by Sigma-Aldrich, USA.

Preparation of SRC-based film

SRC-based films were prepared by a solution casting method using water as the solvent [22]. The SRC film-forming solution was prepared by gradually dissolving SRC (2.0% w/v) in pure water at 80 °C with continuous stirring. SRC/TiO_2 films were prepared by the addition of TiO_2 nanoparticles at different concentrations (1, 3, 5, and 7 wt%, based on dry weight SRC). The TiO_2 powder was first suspended in pure water and sonicated in an ultrasonic probe (Shanghai KUDOS Ultrasonic Instrument Co., Ltd.) for 30 min before mixing with the SRC film solution. According to EFSA, TiO_2 up to a dose of 1000 mg/kg per day of EOGRT had no adverse effects [20]. Glycerol (30 wt%, based on dry weight SRC) was added to all the film-forming solutions as a plasticizer. The neat SRC film was prepared without the addition of TiO_2 nanoparticles. The SRC film-forming solution was then cooled to 50 °C and 80 mL of the solution was cast on a casting plate (20 cm × 25 cm). The film-forming solution was dried in a laboratory oven at 40 °C for 24 h. The films were conditioned at 25 °C and 50 ± 5% relative humidity (RH), which was controlled using a humidity probe (CS215-L, Campbell Scientific, United States) in a desiccator with an adequate amount of desiccant prior to further analyses. The developed films are listed in Table 1.

Table 1. Film samples

Sample	SRC (g)	TiO_2 (wt%)
SRC	2	-
SRC/TiO_2 1%	2	1
SRC/TiO_2 3%	2	3
SRC/TiO_2 5%	2	5
SRC/TiO_2 7%	2	7

Fourier transform infrared (FTIR)

FTIR spectrum of the film sample was recorded on a Nicolet iS5 spectrometer (Thermo Fisher Scientific Inc., Massachusetts, MA) equipped with an attenuated total reflection (ATR) part. The FTIR spectra were determined in a wavelength region from 700 to 4000 cm^{-1} using OMNIC software.

Mechanical properties

Mechanical properties of the film samples were measured according to the ASTM D882 standard method [24] using a universal testing machine (AG-Xplus Series, Shimadzu, Japan). The film samples were uniformly cut (10 cm × 1.5 cm) and clamped between tensile grips at a crosshead speed of 50 mm/min. The film strips were equilibrated at 25 °C and 50 ± 5% relative humidity (RH) in desiccators for 48 h prior to testing. The tensile strength values of the films were calculated using the following equation.

$$TS(MPa) = \frac{F_{max}}{\Phi} \quad (1)$$

where F_{max} is the maximum load and Φ is the cross-sectional area of the film.
The elongation at break values of the films were calculated using the following equation:

$$EB(\%) = \frac{\Delta l}{l_0} \times 100 \quad (2)$$

where Δl is the film extension and l_0 is the initial length of the film sample. Each sample and measurement were carried out in triplicate.

Film thickness

The film thickness was measured using a micrometer (Mitutoyo Co, Tokyo, Japan) with a precision of 0.001 mm. The average of five random measurement positions was used to measure the thickness and TS of film samples.

Water solubility

The water solubility (WS) of the films was determined according to the method described by Abd Hamid et al. [25]. The film samples were cut uniformly (2 cm × 2 cm) and dried at 100 °C in a laboratory oven for 24 h. Subsequently, the samples were weighed to the nearest 0.0001 g to determine their initial dry weights. Each film sample was placed in 30 mL of distilled water in 50 mL screw-capped centrifuge tubes. The tubes were incubated at room temperature with

constant shaking at 25 °C for 24 h. The undissolved film samples were then filtered using Whatman No. 1 filter paper and dried at 100 °C for 24 h to determine their final dry weights. The solubility of the films in water was calculated as a percentage, using the following equation:

$$WS(\%) = \frac{W_0 - W_f}{W_0} \times 100 \quad (3)$$

where W_0 is the initial dry weight of the film and W_f is the final weight of the dried undissolved film. Each sample and measurement were carried out in triplicate.

Moisture content

The moisture content (MC) of the films was determined according to the method described by Abd Hamid et al. [25]. The MC of the film samples was determined by measuring the weight loss of the films (2 cm × 2 cm) before and after drying in a laboratory oven at 100 °C for 24 h. The MC was calculated as a percentage according to the following equation:

$$MC(\%) = \frac{W_{wet} - W_{dry}}{W_{wet}} \times 100 \quad (4)$$

where W is the weight of the film. Each sample and measurement was carried out in triplicate.

RESULTS AND DISCUSSION

FTIR spectra

The FTIR spectra of the carrageenan-based films are shown in Figure 1. The peak at ~3311 cm^{-1} in the FTIR spectra was attributed to the –OH stretching vibration of carrageenan [14]. The vibration at ~1640 cm^{-1} was attributed to the –CH and CH_2 deformation-vibration in CH_2OH, and the peaks also corresponded to the –NH group, a typical amide I, which is present in carrageenan polymer [25, 26]. The absorption bands at ~2935 cm^{-1} were attributed to the C–H stretching vibrations of the alkane groups in carrageenan [13]. The peaks at 918 cm^{-1} were associated with C–O–C (3,6-dehydrated galactose repeated unit) bonds, whereas the peaks at 844 cm^{-1} were associated with C–O–S (galactose-4-sulfate repetitive unit) bonds of carrageenan [26]. The minor changes in the intensity and peaks of certain functional groups show the interaction between TiO_2 nanoparticles and the SRC compound. Roy and Rhim [10] observed that the alterations in peak intensity and shifts in peak positions could be attributed to the physical interactions occurring between the melanin nanoparticles and the agar substance. However, compared to the spectrum of the neat SRC film, the spectra of the SRC/TiO_2 films showed no additional peaks and no obvious shifts of the characteristic peaks. A similar observation was reported in a previous study that investigated carrageenan/agar-based functional films incorporating zinc sulfide nanoparticles [13].

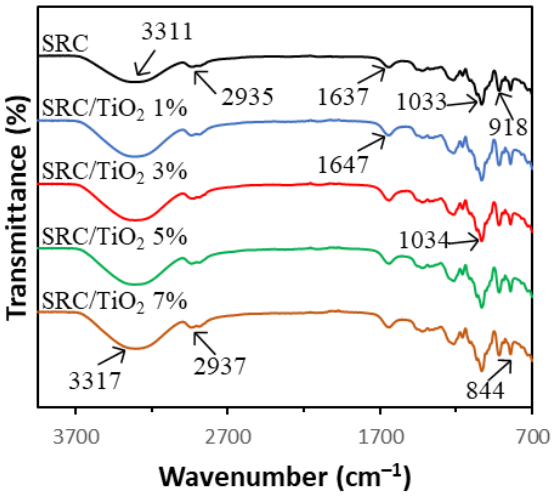

Figure 1. FTIR spectra of SRC film and SRC films incorporated with different concentrations of TiO_2 nanoparticles (1, 3, 5, 7 wt%).

Mechanical properties of SRC-based films

The mechanical properties of SRC films containing various amounts of TiO_2 nanoparticles are summarized in Figure 2. The tensile srength (TS) and elongation at break (EB) of the films varied according to the TiO_2 nanoparticle contents.

The neat SRC film exhibited the lowest TS of 19.7218 MPa, whereas the SRC/TiO_2 1% film showed the highest TS of 26.5890 MPa. The TS values of SRC/TiO_2 3%, SRC/TiO_2 5% and SRC/TiO_2 7% were 20.3508, 20.4548, and 20.8610 MPa, respectively. The decrease in TS could be attributed to heterogeneous TiO_2 dispersion in the polymeric matrix; such heterogeneity may have worked as a stress concentrator, reducing the TS of the films [16]. An increase in the TiO_2 content caused a decrease in the TS value due to the agglomeration of TiO_2 nanoparticles at higher concentrations, leading to a reduction in the film's rigidity [27]. In contrast, the increased TS of the SRC/TiO_2 1% film could be attributed to the homogenous dispersion of TiO_2 in the biopolymeric matrix [28].

The addition of TiO_2 nanoparticles led to a reduction in EB, as shown in Figure 2. The lack of significant interactions between the TiO_2 nanoparticles and the polymers in the SRC/TiO_2 films may be attributed to the weaker interface bond resulting from the agglomeration of nanostructures at higher concentrations [18]. The interaction also prevented the smooth sliding of polymer chains, leading to a decrease in the EB of the SRC/TiO_2 films. Similar observations reported a decrease in EB upon addition of TiO_2 nanoparticles (1 – 5 wt%) in carboxymethyl cellulose-based films [27]. Moreover, the EB of gelatin/grapefruit extract films decreased with the addition of TiO_2 nanoparticles at 0.5 wt%, but gradually increased when the concentration of TiO_2 nanoparticles increased above 0.5 wt% [22]. Consequently, the films with TiO_2 nanoparticles affect the molecular interaction between the particles in the film matrix, which affects the mechanical performance of the packaging films.

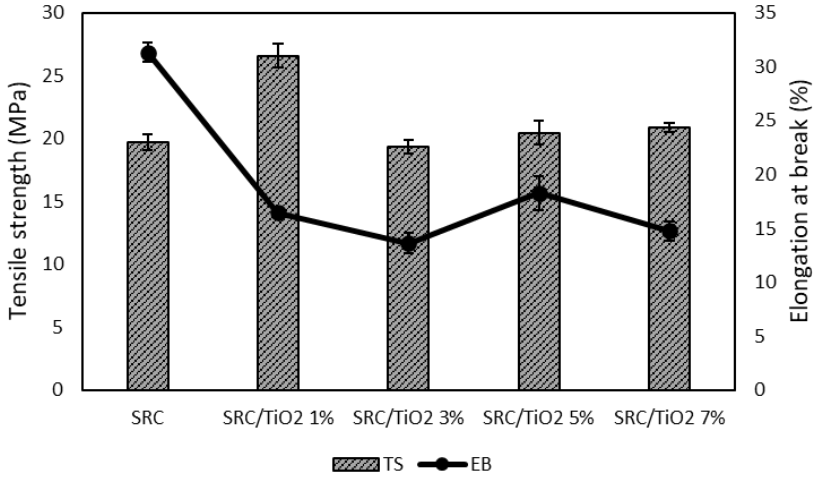

Figure 2. Mechanical properties of SRC film and SRC films incorporated with different concentrations of TiO_2 nanoparticles (1, 3, 5, 7 wt%).

Physical properties of SRC films

The packaging films with a certain degree of transparency help the consumer to check the quality of the products before buying. Figure 3 shows the appearance of the SRC films incorporated with TiO_2 nanoparticles. The films were viewed under ambient light and their overall appearance, color and transparency were evaluated. Overall, the films produced were homogeneous and smooth, had uniform color over the entire film surface, and were easy to peel from the casting plate. However, it was found that the addition of TiO_2 nanoparticles affected the appearance of the film. As the concentration of TiO_2 nanoparticles increased from 1–7 wt%, the films became whiter and less transparent. This was attributed to the light scattering properties of TiO_2, which reduced the light transmission of the film [29]. In some packaging applications, this property can be very helpful in preventing lipid oxidation and food spoilage, which are normally caused by light and UV radiation.

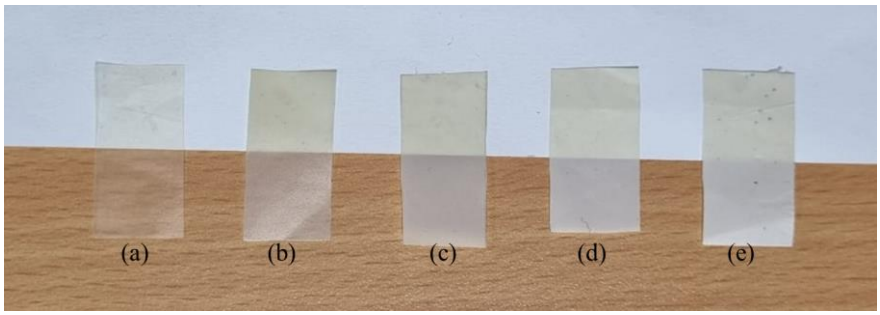

Figure 3. The appearance of (a) SRC; (b) SRC/TiO_2 1%; (c) SRC/TiO_2 3%; (d) SRC/TiO_2 5%; and SRC/TiO_2 7% films.

The thickness of the SRC films significantly increased, whereas the moisture content and water solubility decreased with the addition of TiO_2 nanoparticles into the film matrix (Table 2). The thickness of SRC-based films was measured using vernier caliper. As the composition of TiO_2 nanoparticles in the film matrix increased, more complex matrices were generated, thereby increasing the thickness of the films. Chen et al. [30] also reported that the addition of nano–TiO_2/CuO increased the thickness of gellan gum-based packaging film as the concentration of CuO increased from 0.2 – 0.6 wt%.

The WS (%) of a film determines its integrity when it comes into contact with water. In particular, the water solubility of the film reflects its ability to decompose when utilized in packaging materials. According to the results in Table 2, the solubility of the film decreased significantly after the addition of TiO_2 nanoparticles. The neat SRC film had the highest solubility compared to the other films, which could be attributed to the abundance of hydrophilic groups in the SRC molecules, particularly –OH and $–NH_2$ [31]. The reduction in the solubility of the composite films can be attributed to the compact structures and strong bonds formed by interactions between TiO_2 and the SRC polymer matrix. In addition, the incorporation of TiO_2 into the film matrix can mix with the composite substrate to produce a tight network structure, preventing water molecules from entering the film [32].

The results presented in Table 2 show the MC of SRC-based films for this study. MC is an important parameter for packaging products because biopolymer-based films generally tend to be sensitive to moisture. Moreover, the reduction of MC is essential for such materials in the packaging sector in the future. The addition of TiO_2 nanoparticles to the film matrix reduced the MC of SRC-based films by about 25% compared to the neat SRC film. However, the results showed that no significant differences were observed between the film samples with TiO_2 nanoparticles. This result is consistent with a previous study that reported a decrease in MC when TiO_2 nanoparticles (4 % w/w) were added to sago starch film, ranging from 12.96 % to 8.04 % [33]. Moreover, the void volume occupied by water molecules in the film matrix decreased as the TiO_2 content in the gelatin/TiO_2 nanocomposite film increased from 0 to 1 wt% [34]. Therefore, the incorporation of TiO_2 nanoparticles may result in the enhancement and limitation of the motion of the network structure of the film, which could lead to a decrease in the weight loss of water molecules in the film matrix [35].

Table 2. Thickness, moisture content, and water solubility of SRC film and SRC films incorporated with different concentrations of TiO_2 nanoparticles (1, 3, 5, 7 wt%).

Sample	Thickness (mm)	Moisture content (%)	Water solubility (%)
SRC	0.095 ± 0.0010	35.05 ± 0.43	91.27 ± 3.02
SRC/TiO_2 1%	0.100 ± 0.0071	25.10 ± 1.67	88.65 ± 2.90
SRC/TiO_2 3%	0.105 ± 0.0056	26.70 ± 0.26	81.30 ± 1.59
SRC/TiO_2 5%	0.104 ± 0.0034	24.90 ± 0.26	84.40 ± 0.91
SRC/TiO_2 7%	0.100 ± 0.0041	24.80 ± 0.97	86.30 ± 1.05

CONCLUSION

In conclusion, the incorporation of TiO_2 nanoparticles into semi-refined carrageenan-based packaging films yielded several remarkable results. FTIR analysis revealed the interaction between TiO_2 nanoparticles and the SRC compound. The addition of TiO_2 nanoparticles led to a significant improvement in the tensile strength of SRC films, with the SRC/TiO_2 1% film demonstrating the highest tensile strength at 26.5890 MPa. However, the elongation at break of SRC films decreased with the addition of 1% to 7 wt% of TiO_2 nanoparticles. Furthermore, as the concentration of TiO_2 nanoparticles increased, the moisture content percentage in the films decreased from 35% to 24% compared to the SRC film without TiO_2 nanoparticles. Additionally, the SRC/TiO_2 films exhibited reduced water solubility, with the SRC/TiO_2 3% film showing the lowest water solubility at 81.30%. These improvements indicate that the incorporation of TiO_2 nanoparticles effectively enhances the functionality and performance of semi-refined carrageenan films for packaging applications.

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