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Research Article

Development of active packaging films from semirefined carrageenan integrated with rosemary essential oil and TiO_2 nanoparticles

Khadijah Husna Abd Hamid, Tarchiani Jayakumar, Sarmeswari Gunasegaran, and Nurul Aini Mohd Azman*

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

*Corresponding author: ainiazman@umpsa.edu.my

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Abstract

Active packaging films based on semirefined carrageenan (SRC) were fabricated by integrating rosemary essential oil (REO) with varying concentrations of TiO_2 nanoparticles (1, 3, 5, and 7 wt.%) using the solvent casting method. FTIR spectra analysis of the SRC films revealed no significant interactions between the SRC compounds, REO, and TiO_2 nanoparticles (TiO_2NPs). The SRC film with 1 wt.% TiO_2NPs exhibited the highest tensile strength (26.5890 MPa), while the incorporation of 0.5 wt.% REO in the SRC/TiO_2 films enhanced the elongation at break of the SRC films. The presence of TiO_2NPs and REO reduced the moisture content and water solubility of the SRC films. The SRC film with 1 wt% TiO_2NPs displayed lower opacity values; however, the opacity of the films increased with the concentration of TiO_2NPs, indicating their suitability for preventing spoilage in photosensitive foods. The integration of REO in the SRC film showed higher antioxidant activity (22.51%). However, the inclusion of TiO_2NPs in the films reduced the antioxidant activity, possibly due to the nanoparticles acting as nanofillers in the film matrix and immobilising the essential oil release to the film surface.

Keywords: active food packaging, titanium dioxide, rosemary essential oil, mechanical properties, physical properties

Introduction

Packaging holds significant importance as it plays a crucial role in safeguarding food from spoilage. According to statistics from the Food and Agriculture Organization of the United Nations (FAO), approximately one-third of the food produced spoils every year, primarily due to foodborne pathogens [1]. In addition, food waste and loss usually occur in the marketplace during production and distribution, and even by unwitting consumers [2]. The ideal food packaging material should be practical, affordable, and biodegradable to ensure the long-term preservation of food quality [3]. A viable strategy for preventing food spoilage is the formulation of active packaging films containing antimicrobial and antioxidant compounds. Active packaging films effectively guarantee the reliability of packaged food products by preventing food oxidation and microbial growth, which can lead to human illness [4,5]. Currently, many researchers are focused on the production of active packaging films using biodegradable materials, mainly because of the adverse environmental effects caused by the increase in waste disposal from petroleum-based plastic packaging.

Carrageenan is widely utilized and studied due to its biodegradability, biocompatibility, and impressive mechanical properties in the food packaging field [6]. It has been utilized as a film-forming material for packaging products owing to its natural gelling and binding characteristics [7-9]. Abundant in red algae (*Rhodophyta*), carrageenan is a water-soluble polysaccharide [8]. It is categorized into two groups: refined carrageenan and semirefined carrageenan (SRC). Following the semi refining process, a certain amount of seaweed cellulose remains in carrageenan. However, natural biopolymers have several drawbacks that limit their applications in food packaging. Their use in packaging applications is compromised by their poor barrier properties owing to their hydrophilicity and weak mechanical strength. Researchers have recently shown significant interest in incorporating nanoparticles to enhance the quality of packaging materials used for food products [7,11,12]. The favorable interaction between nanoparticles and polymers enhances the properties of nanocomposite-based packaging films [13].

Owing to their strong antibacterial and photocatalytic properties, as well as their ability to scavenge ethylene, metal oxides, such as TiO_2 nanoparticles (TiO_2NPs), are widely used as nanofiller components in food packaging [14]. Hou et al. [15] found that the addition of TiO_2NPs to the film matrix improved the tensile properties and protected the film from visible and UV light frequencies. The UV-filtering property of TiO_2NPs can prevent food spoilage, mainly due to light induction in food packaging systems [16]. Active packaging, however, consists of elements that help maintain the organoleptic properties of food while extending its shelf life by inhibiting microbial development and increasing antioxidant capacity. The addition of antioxidants such as essential oils (EO) can induce antioxidant and antimicrobial properties while improving the physical properties of the films. The main constituents of rosemary essential oil (REO) consist of 1,8-cineole, camphor, α-pinene, and camphene, which is known for its antibacterial and antifungal properties [17]. In addition, REO is highly effective in inhibiting oxidation reactions in food and has a strong antibacterial effect against Pseudomonas spp., a common spoilage bacterium in poultry meat [18].

Although various studies on carrageenan/metal oxide nanoparticles or carrageenan/EO films have been reported, the combined effects of TiO_2NPs and REO in SRC-based packaging films remain unexplored. In this context, the synthesis and characterization of SRC film integrated with REO and varying concentrations of TiO_2NPs were carried out. The FTIR spectra of the SRC films were evaluated, and their mechanical and physical properties were examined. Finally, SRC films integrated with REO and TiO_2NPs were analyzed for antioxidant activity using DPPH scavenging activity.

Materials and Methods

Materials

The materials employed in this study included semirefined carrageenan sourced from CV Simpul Agro Globalindo, Indonesia. TiO_2 nanoparticles (particle size of 20–25 nm, 99.7% purity), DPPH (2,2-diphenyl-1-picrylhydrazyl) and food grade glycerol (99.5% purity) were supplied from Sigma-Aldrich, USA. Rosemary essential oil was obtained from a local store in Pahang, Malaysia.

Preparation of SRC-based film

SRC-based films were fabricated using a solvent casting technique with slight modifications [19]. The SRC (2%, w/v) was gradually added to pure water at 80 °C with continuous stirring. Prior to mixing with the SRC film solution, TiO_2 powder was suspended in pure water and sonicated for 30 minutes using an ultrasonic probe (Shanghai KUDOS Ultrasonic Instrument Co., Ltd.). Furthermore, SRC/REO/TiO_2 films were prepared with varying TiO_2NP concentrations (1, 3, 5, and 7 wt.% based on SRC), along with the addition of 0.5% REO. Glycerol (40 wt.% based on SRC) was introduced to all film-forming solutions as a plasticizer. The SRC/REO film, excluding TiO_2NPs, was also prepared as a control film. Following the cooling of the SRC film-forming solution to 50 °C, 80 mL of the solution was cast on a plate measuring 20 cm × 25 cm. The various films developed are outlined in the **Table 1**.

Fourier transform infrared (FTIR)

The FTIR spectrum of the film sample was recorded with an attenuated total reflection (ATR) part (Nicolet iS5 spectrometer, Thermo Fisher Scientific, United States). The FTIR spectra were determined in the wavelength region from 600 to 4000 cm^{-1} using OMNIC software.

Mechanical properties

Film thickness was measured with a precision of 0.001 mm using a Vernier caliper. The tensile strength (TS) and elongation at break (EB) of the film samples were measured following the ASTM D882 method (ASTM International) [20] using a universal testing machine (AG-X plus, Japan). Uniform film strips (10×1.5 cm^2) were vertically stretched at a constant speed of 50 mm/min.

Water solubility (WS)

The film samples (2×2 cm^2) were dried in an oven at 100 °C to a constant weight, W_0 [21]. The film samples were placed in 30 mL distilled water for 24 h at room temperature. Subsequently, the undissolved film samples were dried at 100 °C to a constant weight, W_f. The W_S was calculated using the following equation:

$$\mathrm{WS}(\%) = \frac{\mathrm{W_0} - \mathrm{W_f}}{\mathrm{W_0}} \times 100 \qquad \text{(Eq. 1)}$$

Table 1. Film formulation

Sample	TiO_2 (wt.%)	REO (wt.%)
SRC/REO	–	0.5
SRC/TiO_2 1%	1	–
SRC/REO/TiO_2 1%	1	0.5
SRC/REO/TiO_2 3%	3	0.5
SRC/REO/TiO_2 5%	5	0.5
SRC/REO/TiO_2 7%	7	0.5

Moisture content (MC)

The film samples were determined by measuring the weight loss of the films (2 × 2 cm^2) before W_1 and after drying them in an oven at 100 °C for 24 h, W_2 [21]. MC was calculated using the provided equation:

$$\mathrm{MC}(\%) = \frac{\mathrm{W_1} - \mathrm{W_2}}{\mathrm{W_1}} \times 100 \qquad \text{(Eq. 2)}$$

Opacity

A UV-visible spectrophotometer (U-1800, Japan) was used to measure the opacity of the films at a wavelength of 600 nm, with an empty plastic cuvette serving as the reference [14]. The opacity of the films was calculated using the following equation:

$$\mathrm{Opacity} = \frac{\mathrm{Abs_{600}}}{\mathrm{d}} \times 100 \qquad \text{(Eq. 3)}$$

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

Antioxidant activity

The film samples (50 mg) were mixed with 10 ml of 0.1 mM DPPH solution [22]. After incubating the films for 30 min, absorbance was measured at 517 nm using a UV-visible spectrophotometer (U-1800, Japan). The results were expressed as % DPPH scavenging activity using the provided equation 4.

Results and Discussion

FTIR spectra

Figure 1 illustrates the functional group properties of SRC films integrated with REO and varying concentrations of TiONPs. The stretching vibration of the –OH group was observed between the peaks at 3200 – 3500 cm^{-1}, corresponding to the polysaccharide polymer of carrageenan in the FTIR spectra [9]. The vibration at ~1640 cm^{-1} is due to the –CH and CH_2 deformation vibrations in the CH_2OH of polysaccharide polymers [23]. It has been suggested that the C–H stretching vibrations of the alkane groups in carrageenan are responsible for the peak at 2920 cm^{-1} [24]. The C–O–C bonds of carrageenan (3,6-dehydrogenated galactose repeating units) are associated with the peak at 920 cm^{-1}, while the C–O–S bonds (galactose 4-sulphate repeating units) are associated with the peak at 844 cm^{-1} [23]. The slight changes observed in the intensity and peaks of certain functional groups, such as –OH stretching and C–H stretching, indicate the interaction between REO, TiO_2NPs, and SRC. (3)

Roy & Rhim [25] previously observed similar alterations in peak intensity and shifts in peak positions, which were attributed to the physical interactions between melanin nanoparticles and the agar substance. However, upon comparing the spectra of all SRC films, no additional peaks or obvious shifts of the characteristic peaks were observed. In general, the functional group of the SRC/REO film and the SRC/TiO_2NPs film with REO or without REO, remained unchanged, indicating that the integration of REO or TiO_2NPs into the SRC film did not change the structure of the SRC film.

$$\text{DPPH scavenging activity (\%)} = [(\mathrm{Abs_{control}} - \mathrm{Abs_{sample}})/\mathrm{A_{control}}] \times 100 \qquad \text{(Eq. 4)}$$

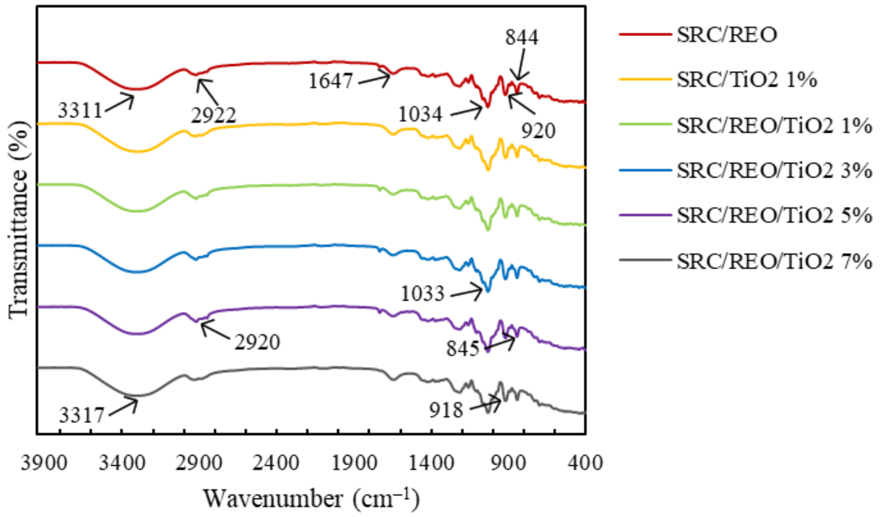

Figure 1. FTIR spectra of SRC/REO, SRC/TiO_2NPs, and SRC films with REO and varying concentrations of TiO_2NPs

Mechanical properties of the films

Mechanical properties such as tensile strength (TS) and elongation at break (EB) are used to determine the flexibility, rigidity, and strength of the films for packaging purposes. A previous study showed that the SRC film plasticized with 0.9 wt.% glycerol possesses good TS (57.20 MPa) in contrast to the conventional plastic packaging low density polyethylene (LDPE) (19-44 MPa) [21,26]. **Figure 2** illustrates the TS and EB of SRC films containing REO with varying concentrations of TiO_2NPs. According to the results, SRC film with REO showed a lower TS of 16.41 MPa, whereas the inclusion of 1 wt.% TiO_2NPs increased the TS of the SRC film to 26.59 MPa. Overall, the incorporation of TiO_2NPs resulted in a higher TS of the SRC films than that of SRC films without TiO_2NPs. This may be ascribed to the homogenous dispersion of nanoparticles, which possess a large specific surface area, enhancing their interaction within the film matrices [27]. Moreover, upon the inclusion of REO in the SRC/TiO_2 film, the TS of the films decreased slightly, with values ranging from 18.58 MPa to 22.86 MPa. The addition of REO to SRC films can disrupt the polymer–nanoparticle–EO interaction and form a discontinuous structure in the film matrices [28]. Additionally, the interaction affects the stiffness and strength of the films as the intermolecular forces of the polymer network decrease, thereby reducing the TS value of the SRC films [29,30].

Besides, the EB values of the SRC films with REO and varying concentrations of TiO_2NPs are presented in **Figure 2**. The results expressed that SRC/REO/TiO_2 1% film exhibited the highest EB (28.10%) among all the SRC films. The SRC/TiO_2 1% film displayed a lower percentage of EB, with a value of 16.43%. This observation could be ascribed to the inherent rigidity of the TiO_2NPs within the film matrix [27]. Furthermore, the EB of the SRC films improved with the inclusion of REO, which could be attributed to the plasticization effects of the oil, which increased the mobility and flexibility of the polymer chains [29]. This result aligns with the observations of Shahrampour and Razavi [26], who noted that incorporating REO nanoemulsions (ranging from 0.5 to 4 wt.%) increased the EB of root gum film. Additionally, similar trends were observed in active packaging film made from chitosan, with an improvement in EB and a decrease in TS value upon incorporation of Santalum album EO [30]. Hence, the incorporation of REO and TiO_2NPs can influence the molecular interactions between the particles within the polymer matrices, consequently affecting the mechanical strength of the packaging films.

Physical properties of the films

The water solubility (WS) of a film determines its integrity when encountering water. In particular, the WS of films reflects their ability to decompose as biodegradable packaging materials. **Table 2** shows that the highest WS was observed in the SRC/TiO_2 1% film (88.65%), and the inclusion of REO slightly decreased the WS of the SRC/TiO_2 film, with values ranging from 77.08 to 85.39%. The reduction in WS was ascribed to the intermolecular interaction between REO and SRC in the polymeric chain. In general, the hydrophilic nature and presence of sulphate and hydroxyl groups in the carrageenan polymer can be attributed to the improved WS of the film [31]. This interaction reduces the number of free hydroxyl groups, leading to the formation of hydrogen bonds with water [26]. In a study conducted by Sripahco et al. [31], it was observed that the WS of nanocellulose gellan gum with Anethum graveolens EO exhibited similar behavior. The decrease in WS is likely attributable to the nature of the oil as a hydrophobic substance in the polymer matrix, thereby reducing the overall hydrophilicity of the film.

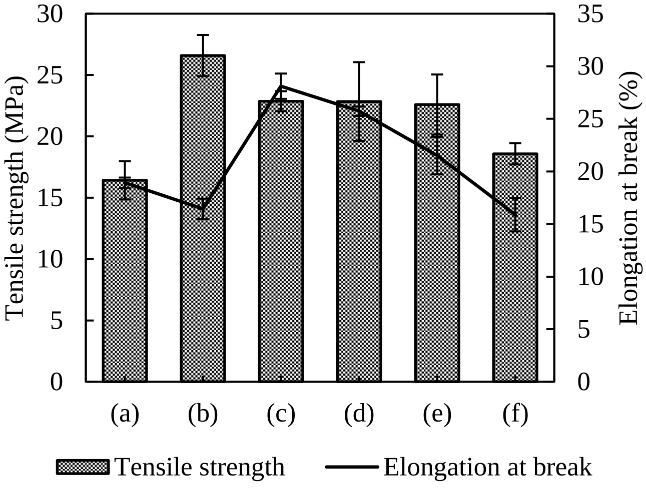

Figure 2. Mechanical properties of (a) SRC/REO, (b) SRC/TiO_2 1%, (c) SRC/REO/TiO_2 1%, (d) SRC/REO/TiO_2 3%, (e) SRC/REO/TiO_2 5%, and (f) SRC/REO/TiO_2 7% film

The moisture content (MC) of the SRC film decreased with the incorporation of TiO_2NPs and REO (Table 2). Compared to the SRC film with REO, the incorporation of 1 wt% TiO_2NPs slightly reduced the MC of the films. The incorporation of TiO_2NPs may enhance and limit the motion of the network arrangement of the film, leading to a decrease in the weight loss of water components in the polymer matrices [33]. Riahi et al. [34] also showed that the MC of gelatin/grapefruit seed extract film slightly decreased with the incorporation of 0.5 wt% of TiO_2NPs.

Film appearance, thickness and opacity of the films

The SRC films blended with REO and/or TiO_2NPs exhibited smooth surfaces and were easily peeled off from the casting plate. The addition of TiO_2NPs slightly decreased the transparency of the developed films with increasing concentrations of TiO_2NPs (**Figure 3**). In contrast, compared to the SRC/TiO_2 1% film, the REO-integrated SRC film has greater clarity.

The thickness of the SRC films in this study ranged from 0.095 to 0.105 mm (Table 2). As the amount of TiO_2NPs in the film matrix increased, the solid content of the film increased as well, resulting in a greater thickness of the SRC films. Similarly, Rong et al. [35] demonstrated that as the concentration of TiO_2NPs increased, the thickness of hyacinth bean starch/*Mesona chinensis Benth* polysaccharide films increased. The transparency or opacity of a film is a key element that influences consumer consent for packaging packaged food products. Table 2 illustrates the opacity of SRC films with REO and varying concentrations of TiO_2NPs. The opacity value of the SRC film with REO is significantly higher than that of the SRC film with 1 wt% of TiO_2. This is likely due to the presence of large lipid molecules during film drying, which could be responsible for the heterogeneity and roughness observed on the surfaces of the film samples. In general, the opacity of the SRC films increased with increasing concentration of TiO_2NPs, ranging from 8.02 to 18.47 mm^{-1}. This aligns with a previous study that observed an increase in film opacity for chitosan/cassava starch-based packaging films, incorporating TiO_2NPs at concentrations of 0.25% and 1%, compared to the control film without TiO_2 [36]. Furthermore, increasing the incorporation of TiO_2NPs from 0.1 to 0.3 wt.% resulted in reduced visibility of the chitosan/alginate film in food products [37]. Riahi et al. [34] demonstrated that the inclusion of TiO_2NPs decreased the light transmission of the active packaging film and prevented the passage of visible and UV light. Therefore, SRC films incorporated with TiO_2NPs can serve as packaging films to protect light-sensitive foods from spoilage and extend their shelf lives.

Antioxidant activity of the films

The DPPH scavenging activity was used to measure the antioxidant properties of the SRC films. The antioxidant activity of pure REO was 51.62% (**Figure 4**), demonstrating the antioxidant ability of the EO for use in active packaging films. According to Alizadeh-Sani et al. [38], the antioxidant properties of rosemary oil are commonly associated with the existence of polyphenolic compounds like carnosoic acid, carnosol,

Table 2. Thickness, moisture content, water solubility, and opacity of SRC/REO, SRC/TiO_2NPs, and SRC films with REO and varying concentrations of TiO_2NPs

Sample	Thickness (mm)	Moisture Content (%)	Water Solubility (%)	Opacity (mm^{-1})
SRC/REO	0.095 ± 0.0032	33.46 ± 0.52	80.42 ± 4.38	4.05 ± 0.89
SRC/TiO_2 1%	0.100 ± 0.0071	25.10 ± 1.67	88.65 ± 2.90	2.38 ± 1.26
SRC/REO/TiO_2 1%	0.105 ± 0.0087	24.74 ± 0.26	77.08 ± 0.76	8.02 ± 0.40
SRC/REO/TiO_2 3%	0.102 ± 0.0056	26.39 ± 0.21	83.03 ± 1.40	11.50 ± 1.09
SRC/REO/TiO_2 5%	0.101 ± 0.0042	22.81 ± 0.04	80.22 ± 1.94	15.03 ± 0.63
SRC/REO/TiO_2 7%	0.102 ± 0.0038	26.07 ± 0.81	85.39 ± 0.36	18.47 ± 0.67

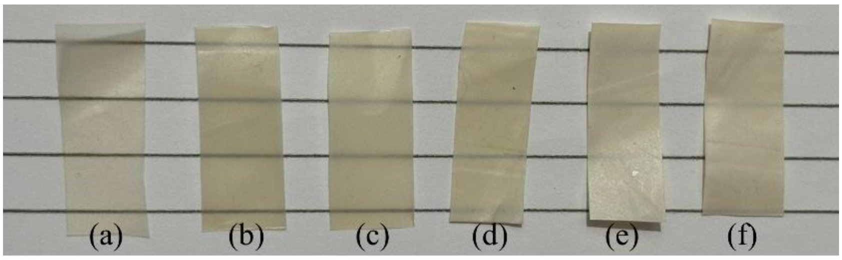

Figure 3. The image of (a) SRC/REO, (b) SRC/TiO_2 1%, (c) SRC/REO/TiO_2 1%, (d) SRC/REO/TiO_2 3%, (e) SRC/REO/TiO_2 5%, and (f) SRC/REO/TiO_2 7% film

rosmarinic acid, and other active constituents such as myrcene, camphor, and α-pinene. Nonetheless, the DPPH scavenging activity of REO-integrated SRC film is 22.51%, which can be attributed to the minimal use of REO (0.5 wt%) in the film formulation. On the contrary, the integration of TiO_2NPs into SRC film did not enhance the antioxidant properties of the film, with a DPPH scavenging activity of 9.29%, indicating that this inorganic substance was not an effective radical scavenger. Researchers reported that the DPPH of chitosan films containing *Santalum album* EO increased (7.34% to 23.69%) as the EO concentration increased from 0.5 to 2 wt.% [30]. In addition, as shown in Figure 4, the DPPH values decreased with increasing concentration of TiO_2NPs in the SRC films. The introduction of TiO_2NPs did not significantly affect the antioxidant activity of the SRC films. This result indicates that the excessive amount of nanoparticles used in the film formulation immobilized the EO molecules and reduced the release rate of the EO on the film surface. A previous study showed a similar trend in antioxidant activity as the content of TiO_2NPs increased in the gelatin/grapefruit seed extract [34]. The study suggests that the adsorption of the extract on the surface of TiO_2 prevents the active compounds from freely interacting with free radical oxidation. The phenolic components of antioxidant compounds play a crucial role in preventing rancidity caused by oxidation in foods [39]. Therefore, this study advocates that the synergistic effect of REO and TiO_2NPs in the SRC films can contribute to the interaction between the active compounds and oxidizing free radicals on the film surface.

Conclusion

SRC films were prepared by integrating 0.5 wt.% REO and varying concentrations of TiO_2NPs (1, 3, 5, and 7 wt.%). Compared to the SRC/REO film (16.4183 MPa), the introduction of 1 wt.% TiO_2NPs enhanced the tensile strength of the film to 26.5890 MPa. The inclusion of TiO_2NPs in the SRC/REO films reduced their moisture content and water solubility. Furthermore, the opacity of the films increased as the concentration of TiO_2NPs increased, limiting the passage of visible and UV light radiation. The antioxidant activity of the SRC film containing REO was higher, with a value of 22.51%. However, the inclusion of TiO_2NPs inhibited the antioxidant activity of the SRC/REO films and resulted in a lower DPPH value. This could be attributed to the restraining of the interaction between the compounds with free radical oxidation when the TiO_2NPs were added to the films. Therefore, this study suggests that the incorporation of REO and TiO_2NPs into polymer matrices can improve the functional properties of SRC films for active food packaging applications.

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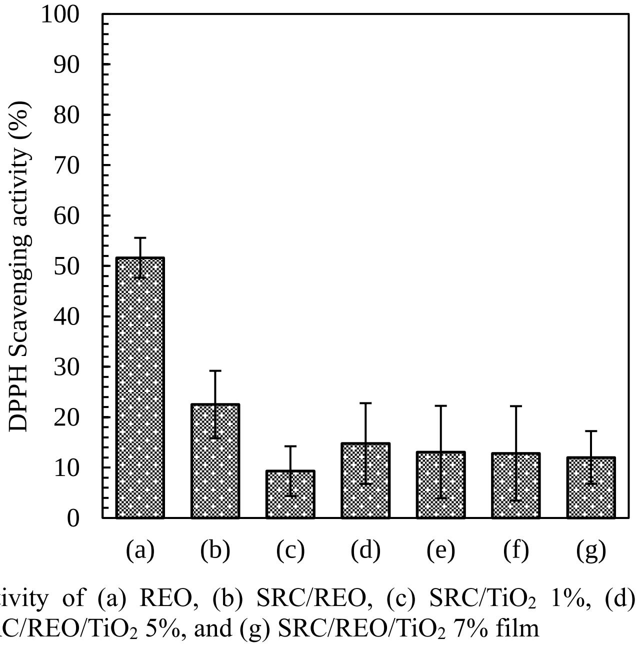

Figure 4. Antioxidant activity of (a) REO, (b) SRC/REO, (c) SRC/TiO_2 1%, (d) SRC/REO/TiO_2 1%, (e) SRC/REO/TiO_2 3%, (f) SRC/REO/TiO_2 5%, and (g) SRC/REO/TiO_2 7% film

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