



Fabrication, characterization, and anti-free radical performance of edible packaging–chitosan film synthesized from shrimp shell incorporated with ginger essential oil

Rawdah M. Al-Ali¹ · Sawsan A. Al-Hilifi¹ · Marwan M.A. Rashed²

Received: 4 January 2021 / Accepted: 3 March 2021

© The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2021

Abstract

This study was aimed to investigate the properties of macromolecule chitosan composite film extracted from shrimp shells combined with ginger essential oil (GEO). Shrimp shells were employed to produce chitin. Their properties were measured as an effective food coating. The tensile strength decreased significantly with increased GEO concentrations compared to the control sample 31.12, 32.34, and 35.12 Map for both control and GEO concentrations of 0.1, 0.2 and 0.3%, respectively. Furthermore, the percentage of elongation increases with concentrations of GEO from 18.10 to 19.87% for each film 0.1 and 0.3%, respectively. Thermogravimetric analysis showed that GEO reduced the weight of chitosan-based film incorporating GEO loss at high levels of temperature. Composite films were characterized by their high ability scavenging hydroxyl and superoxide radicals. The findings of the current study showed that chitosan-based film incorporating GEO is a promising source for preparing bioactive films and that its use as anti-free radicals can be highly effective in the food, pharmaceutical, and cosmetic industries.

Keywords Macromolecule chitosan · Shrimp shells · Ginger essential oil · Edible film thermogravimetric analysis · Antioxidant bioactive components

Introduction

Considerable challenges facing companies producing long-term processed food, the most important of which is the loss of food quality characteristics during storage and handling as a result of microbial and physicochemical contaminations [1]. These changes usually lead to significant losses in stored food. Recently, interest in the fabricating and utilization of edible and biodegradable macromolecule films (EBMFs) has increased through employing different types of biodegradable polymers. Such biodegradable polymers are widely

used in the food and pharmaceutical industries due to their unique preservation properties, Generally Recognized as Safe (GRAS), and their ability to biodegrade [2, 3].

Sheets of the EBMFs are known as thin sheets commonly prepared using safe ingredients for human health and the environment. Generally, EBMFs are classified as GRAS and can be directly consumed as well. Kouhi et al. [4] reported that EBMFs refer to all polymers that can be consumed by human beings or animals without causing any adverse effects on their health. Edible EBMFs can be produced from various sources such as plants, cereals, fruits, vegetables, meat, and marine products. The concept of innovative packaging in the food industry was called active packaging [5]. Preparation of active packages based on orientated polypropylene (OPP) or low-density polyethylene and thymol will improve mechanical properties such as increased elongation at break and decreased tensile strength [6]. The incorporation of essential oils improves the biofilm values and their barrier properties [7].

Chitosan (CH) is one of the most important natural polysaccharides characterized by its biodegradability and safety, as it is widely used in the food industries [8]. Chemically,

✉ Sawsan A. Al-Hilifi
sawsanali701@gmail.com

Rawdah M. Al-Ali
rawdahmalali@gmail.com

¹ Department of Food Science, College of Agriculture, University of Basrah, Basrah, Iraq

² School of Biological and Food Engineering, Suzhou University, Bianhe Middle Road 49, Yongqiao, Suzhou 234000, Anhui Province, China

CH (β -(1,4)-2-amino-2-deoxy-D-glucopyranose) is a biopolymer derived from deacetylation chitin [9], which is the most common compound in nature after cellulose, found in the skeletal and external structure of shrimp, lobster, snails, and another marine source [10]. The process of preparing chitosan consists of the following steps: demineralization, deproteinization, discoloration, and deacetylation [11]. Several studies have indicated that chitosan is nontoxic, biocompatibility, and biodegradability and possess antioxidant and antimicrobial characteristics [12]. Compounds were characterized as aromatic rings linked with one or more hydroxyl groups [13].

Ginger is one of the most important spices widely used in food preservation not only for its pungent taste and distinctive aroma that the consumer prefers but also for its bioactivity such as chemopreventive potential, antioxidant, and antimicrobial [14]. Ginger essential oil (GEO) contains various bioactive compounds such as zingiberene, farnesene, curcumin, gingerols, shogaol, and paradol [15]. Chitosan-based film incorporating GEO have demonstrated a significant biological activity through their ability to scavenging free radicals and thus prevent the intracellular oxidative process [16].

Natural and synthetic antioxidants are widely used in food [17], cosmetics, and dietary supplements. Moreover, many of these compounds are already incorporated into the pharmaceutical industries as medicines for Alzheimer's and cancer diseases [15–18].

Various types of essential oils (EOs) have shown high bioactivity as antioxidants [19–21], antimicrobial [22], and anticancer [23], some of which are widely used in the food, pharmaceutical, and cosmetic industries. However, the problem facing the manufacturers is the instability of these EOs in their current state, which has led the researchers to look for efficient techniques to preserve and protect the effective compounds of these EOs. Accordingly, this study is prepared to investigate the thermomechanical and antioxidant properties of GEOs fabricated using a biodegradable chitosan film prepared from shrimp wastes to extend the shelf-life of food, which would benefit producers and the wider food industry.

Materials and methods

Materials

Shrimp shells were obtained from the local markets of Basrah city, Iraq. Shrimp shells were washed carefully using distilled water and dried at 50 °C for 12 h, then ground and packed in polyethylene bags and kept frozen at -18 ± 2 °C until use. All chemical materials used in this experiment were purchased from Sigma (Germany), namely: NaOH; Na₂SO₄; HCl; Acetic acid.

Extraction of GEOs

Ginger rhizomes (GRs) (*Zingiber officinale*) were collected from the local markets in Basrah city, Iraq. Then, GRs have been thoroughly washed, peeled, and cut into small pieces before being dried in an air oven at 40 ± 2 °C overnight. The essential oil was extracted using a Clevenger-type hydrodistillation apparatus (Germany). 100 g of GRs with 500 mL of distilled water was transferred into a round-flask at 90 °C for 3 h. The water residue in the extracted EO was removed using Na₂SO₄ and then preserved at 4 °C until use.

GC and GCMS analysis of the chemical constituents of GEO

The analysis of chemical compounds was performed to determine the volatile compounds of the GEOs. The method described by Abdullahi et al. [24] was used with a slight modification to analyze volatile constituents using the QP-2010 GCMS system and GC-2010 (Shimadzu Co., Kyoto, Japan) fitted with a capillary silica column DB-5 (0.25 nm, 0.25 m film thickness, 30 m). The oven temperature program was set as follows: the initial temperature was set at 40 °C for 1 min, then it was increased to 150 °C (time), followed by the increase to 250 °C for (time). The total GC running time was 35 (mins). GC was equipped with a mass spectrometric detector in the Electron Impact Ionization mode with an electron energy voltage of 70 eV.

The detector was set in intervals at a mass scanning range of 50–600 m/z. Both ion source temperature and interface temperature were set at 200 °C and 250 °C, respectively. The GC-MS was programmed to perform a 1 L splitless injection with an injection temperature of 250 °C. Helium was used as a carrier gas at a flow rate of 0.8 mL/min.

The obscured volatile compounds of the GEOs were identified by comparing mass spectral data of samples with those from Wiley 7 (Wiley, New York, NY, USA) library and NIST 08 lib mass spectral databases (National Institute of Standards and Technology, Gaithersburg, MD, USA). The concentration (%) of volatile compounds was expressed based on the total peak area.

Preparation of chitosan

The method was followed according to Trung et al. [25] with a slight modification described by Resmi et al. [26]. The chitosan was prepared from a 7.5 g of shrimp shell that was treated with HCl 1 N at a ratio of 1:3 (W: V). To remove the mineral salts, the mixture was washed with deionized distilled water four times. Then, the acidic mixture of shrimp shell was treated with NaOH 1 N at a ratio of 1:4 (W: V) to remove the protein. In a subsequent step, the mixture was filtered and washed with deionized distilled water four times to get the chitin.

The chitosan was prepared by removing the acetyl group (CH_3CO) from chitin treated with NaOH 70% at 85 °C for 12 h. The obtained chitosan was rinsed with deionized distilled water several times to completely remove NaOH, after which it was placed in Petri dishes to be dried at 50 °C. Chitosan was ground into a fine powder that was kept at a low temperature in light-permeable containers until the next analysis.

Preparation of the films

Chitosan-based film incorporating GEO were prepared according to Ojagh et al. [27] with a slight modification. Briefly, 1% of CH dissolved with acetic acid (1%) and glycerol (1%). To prepare the bioactive CH film (CHF), GEOs was added to the CH solution at four concentrations (0, 0.1, 0.2, and 0.3%) under continued magnetic stirring for 30 min. 250 mL of CH solution was put in the Petri dishes to dry at 50 °C in a sterilized oven. The obtained dried films were collected and put in sealed polyethylene bags for further analysis.

$$\text{Hydroxyl Radical Scavenging} = \left[\left(\% = \frac{(\text{Absorbance of sample} - \text{absorbance of the control})}{\text{Absorbance of blank} - \text{absorbance of control}} \times 100 \right) \right] \quad (1)$$

Characterization of film

Film thickness

The average thickness of the film was measured using a micrometer with an accuracy of 0.001 mm. The determents were done in 5 random points for each film [28].

$$\text{Superoxide Radical Scavenging \%} = \left(\frac{(\text{Absorbent of sample} - \text{absorbance of the control})}{\text{Absorbent of sample}} \times 100 \right) \quad (2)$$

Tensile strength (TS) and percentage elongation at break (E)

The tensile strength (TS) and elongation rate (E) to cut the films were conducted using a texture analyzer (Zwick Rolle BTi-FR 25TN. D12, Germany) according to the ASTM Standard Method D882-91 as described by Ferreira et al. [29]. Films were cut in the strips form with a diameter 70 mm length and 20 mm wide at several film tapes to ensure that they are well fixed between the handles of the device. Crossheads speed was 50 mm/min until breaking, the cutting

speed was 200 mm/min, and the speed of the device was 5 mm/min. The tensile strength and elongation were calculation through the stress-strain curves.

Thermogravimetric analysis (TGA)

Thermal stability and degradation of CHF were measured using a TGA Q50V20.13 Build 39 apparatus. The sample was heated by a rate of 10 °C/min from 10–700 °C under the nitrogen atmosphere of 20 °C/min [30].

Scavenging hydroxyl peroxide

The susceptibility of the film with hydroxyl radical scavenging was tested according to Nie et al. [31] with some modifications. Mixing of 50 µL of the sample with 50 µL of 1,10-Phenanthroline at a concentration of 3 mM dissolved in 0.1 M phosphate buffer with PH 7.4 and 50 µL of ferrous sulphate 5 mM and to start the reaction 50 mM of 0.01% hydrogen peroxide was added, mixed the solution at 37 °C for 1 h. The absorbance was then measured at 536 nm and the following equation has applied the scavenging of the hydroxyl radical.

Superoxide anion radical scavenging

Superoxide anion radical scavenging was carried out according to Kumar et al. [32] with some modifications. Briefly, 80 µL of film solution with 80 µL of Tris-HCL at a concentration of 50 mM and PH 8.3 which content 1 mM EDTA-2Na add to it 40 µL from 1.5 mM pyrogallol that solvent in 10 mM HCL. Absorption was measured at 420 nm. The control was added by buffer solution instead of sample and the radical scavenging was calculated according to the following equation:

Statistical analysis

Statistical experiments were designed for data using a complete randomized design. The results were analyzed using (SPSS version 13.0, 2009). The significance of the difference between mean values was assessed using the Least significant difference L.S.D rang test at a significance level of $P < 0.05$.

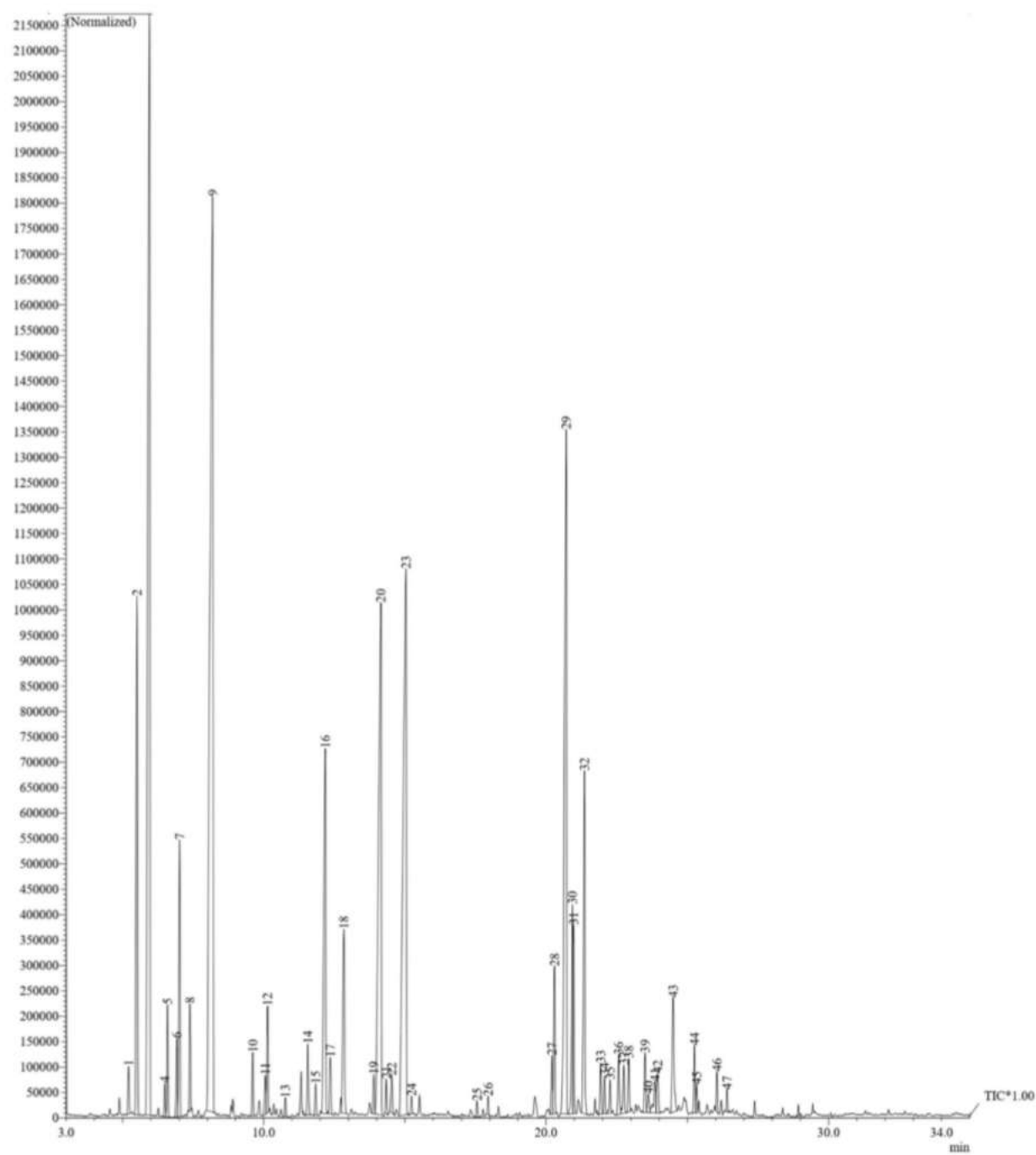


Fig. 1 Chromatogram of total ion current plot of ginger essential oil from GC-MS analysis

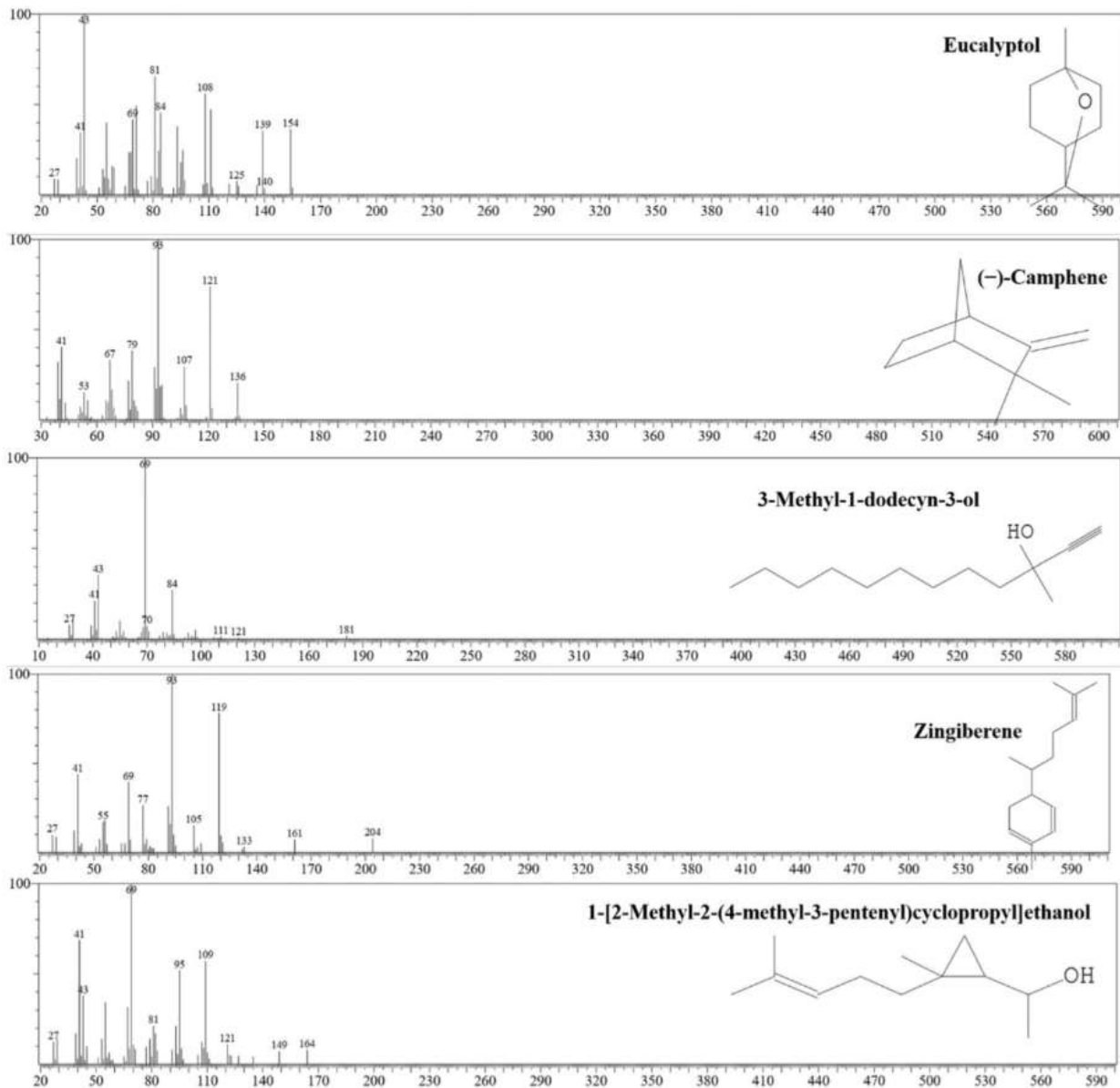


Fig. 2 Mass spectra of the main compounds of ginger essential oil

Results and discussion

Essential oil yield

The GEO yield (%) extract using Clevenger is 3.82%. As the heat increases the speed of movement of the atoms between them, and this led to the destruction of the cells that contain the oil and the release of the largest amount of oil in the water.

Chemical composition of GEOs

The results of the GC-MS analysis (Table 1) showed the concentration (%) of the chemical components of the GEOs. More than 39 volatile compounds have been identified, including five main compounds that achieved a concentration higher than 5%. Figure 1 showed the main compounds identified in GEOs, which are listed in ascending order of concentration as follows: Eucalyptol (19.36%), (–)—Camphene (15.07%), 3-Methyl-1-dodecyn-3-ol (11.52%), Zingiberene (9.58%),

Table 1 Chemical composition of ginger essential oil constituents using GC/GC-MS analysis

Peak No.	RT	Compound	Concentration %	Formula
1	05.210	1 S-.alpha.-Pinene	0.38	C ₁₀ H ₁₆
2	05.510	.alpha.-Pinene	4.69	C ₁₀ H ₁₆
3	05.925	(-)-Camphene	15.07	C ₁₀ H ₁₆
4	06.590	Bicyclo[3.1.1]heptane, 6,6-dimethyl-2-meth	0.77	C ₁₀ H ₁₆
5	06.917	2-Oxabicyclo[2.2.2]octan-6-ol, 1,3,3-trimethyl	0.57	C ₁₀ H ₁₈ O ₂
6	07.018	.beta.-Myrcene	2.03	C ₁₀ H ₁₆
7	07.383	.alpha.-Phellandrene	0.69	C ₁₀ H ₁₆
8	08.191	Eucalyptol	19.36	C ₁₀ H ₁₈ O
9	09.614	(+)-4-Carene	0.43	C ₁₀ H ₁₆
10	10.058	Naphthalene, 1,2,3,4,4a,5,8,8a-octahydro-4a	0.37	C ₁₁ H ₁₈
11	10.139	1,6-Octadien-3-ol, 3,7-dimethyl-	0.78	C ₁₀ H ₁₈ O
12	11.564	7-Octenal, 3,7-dimethyl-	0.61	C ₁₀ H ₁₈ O
13	11.838	Santolina epoxide	0.26	C ₁₀ H ₁₆ O
14	12.181	Bicyclo[2.2.1]heptan-2-ol, 1,7,7-trimethyl-,	4.47	C ₁₂ H ₂₀ O ₂
15	12.358	Bicyclo[3.1.0]hexan-2-ol, 2-methyl-5-(1-me	0.58	C ₁₀ H ₁₈ O
16	12.840	3-Cyclohexene-1-methanol, .alpha.,.alpha.,4	1.97	C ₁₀ H ₁₈ O
17	13.893	6-Octen-1-ol, 3,7-dimethyl-	0.35	C ₁₀ H ₂₀ O
18	14.149	Cyclopropanemethanol, .alpha.,2-dimethyl-2	9.18	C ₁₂ H ₂₂ O
19	14.534	2,6-Octadien-1-ol, 3,7-dimethyl-, (E)-	0.36	C ₁₀ H ₁₈ O
20	15.038	3-Methyl-1-dodecyn-3-ol	11.52	C ₁₃ H ₂₄ O
21	20.205	1,6-Cyclodecadiene, 1-methyl-5-methylene-	0.50	C ₁₅ H ₂₄
22	20.296	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4 met	1.25	C ₁₅ H ₂₂
23	20.708	α -Zingiberene	9.58	C ₁₅ H ₂₄
24	20.930	.alpha.-Farnesene	1.81	C ₁₅ H ₂₄
25	20.971	Cyclohexene, 1-methyl-4-(5-methyl-1-meth	1.21	C ₁₅ H ₂₄
27	21.357	Cyclohexene, 3-(1,5-dimethyl-4-hexenyl)-6-	3.31	C ₁₅ H ₂₄
28	21.933	3,7-Cyclodecadiene-1-methanol, .alpha.,alp	0.45	C ₁₅ H ₂₆ O
29	22.067	Epiglobulol	0.30	C ₁₅ H ₂₆ O
30	22.265	1,6,10-Dodecatrien-3-ol, 3,7,11-trimethyl-, (0.29	C ₁₅ H ₂₆ O
31	22.570	1 H-Cycloprop[e]azulen-7-ol, decahydro-1,1	0.59	C ₁₅ H ₂₄ O
32	22.749	(-)-Globulol	0.48	C ₁₅ H ₂₆ O
33	22.927	Epiglobulol	0.45	C ₁₅ H ₂₆ O
34	23.505	1,6,10-Dodecatrien-3-ol, 3,7,11-trimethyl-, (0.54	C ₁₅ H ₂₆ O
35	23.854	6-(3-Hydroxy-but-1-enyl)-1,5,5-trimethyl-7	0.46	C ₁₃ H ₂₂ O ₃
36	23.949	4-(2,2-Dimethyl-6-methylenecyclohexyl)but	0.48	C ₁₃ H ₂₂ O
37	24.494	2-Naphthalenemethanol, decahydro-.alpha.,	1.42	C ₁₅ H ₂₆ O
38	25.251	6-Octen-1-yn-3-ol, 3,7-dimethyl-	0.57	C ₁₀ H ₁₆ O
39	26.046	Spiro[2.7]dec-4-ene, 1,1,5,6,6,9,9-heptamet	0.29	C ₁₈ H ₃₀

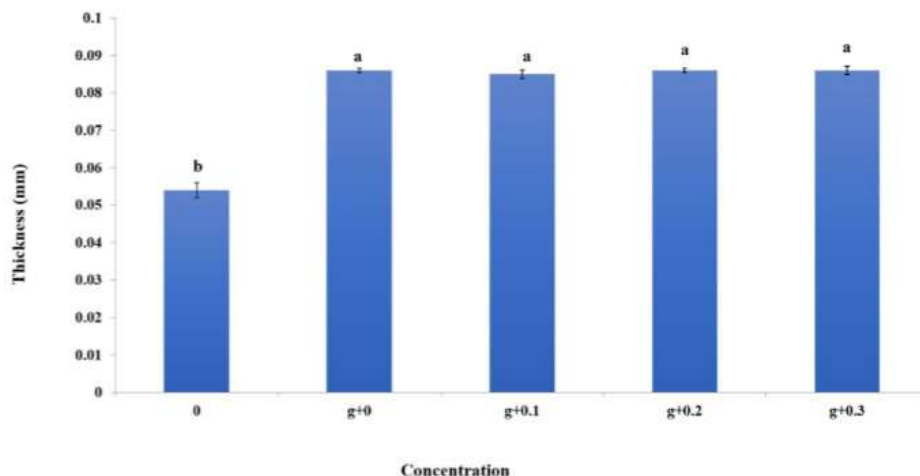
and 1-[2-Methyl-2-(4-methyl-3-pentenyl)cyclopropyl]ethanol (9.18%). Figure 2 shows the effective compounds of GEOs. The results of the main chemical constituents of GEOs obtained from the current work are consistent with those reported in the previous studies with normal variations in the concentrations (%) due to differences in the growth environment, harvest season, and extraction method used. In this regard, Abdullahi et al. [24] reported that the concentrations of each Eucalyptol, (-)-Camphenein, and α -Zingiberene in the GEOs were 5.05, 5.34, and 18.56%, respectively. Reis et al.

[15] found that the concentrations of the α -Zingiberene and Eucalyptol were about 25.2–24.2% and 9–6.5%, respectively.

Thickness of films

The film thickness measurement is one of the most important parameters since film thickness values can change as major components change. Furthermore, the film thickness values are related to mechanical properties that influence its applications in the manufacturing uses in the

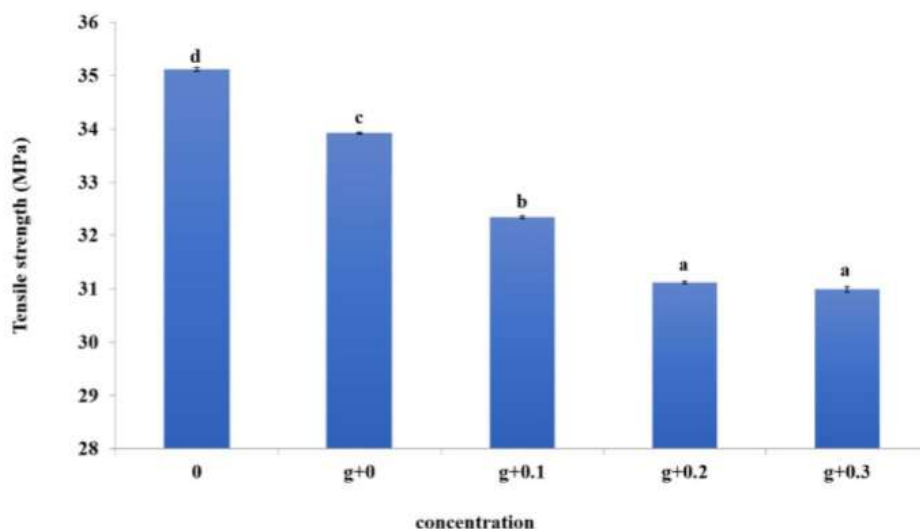
Fig. 3 The thickness properties of chitosan-based film incorporating GEO with ginger essential oil (0) chitosan; (g+0) chitosan with glycerol; (g+0.1) chitosan with glycerol and essential oil 0.1; (g+0.2) chitosan with glycerol and essential oil 0.2; (g+0.3) chitosan with glycerol and essential oil. Different small letters indicate significant differences ($p \leq 0.05$)



products to be packaged. The film samples added GEOs has shown a smooth appearance with no noticeable cracks or pores on the surface. Figure 3 shows the thickness of films prepared using chitosan and glycerol at different concentrations of GEO (0.1, 0.2 and 0.3%). There was no significant difference ($P \leq 0.05$) in the average thickness of the edible films (0.054, 0.085, 0.086, and 0.086 mm) in A, B, C, and D treatments, respectively. Haghighi et al. [33] found an increase in the thickness of the films prepared from chitosan-gelatin when adding different types of EOs, as the thickness of films (21.66–33.41 μm) were higher compared to the control sample. Wu et al. [34] noticed that there were no significant differences were observed in the thickness of the apple puree films when increasing the concentrations of allspice, clove, and

cinnamon EOs from 0 to 3%. This may be attributed to the added amounts of EOs is lower compared to the rest of the other components within the film composition, and thus, the distributing and dispersing of the essential oil droplets within the component's matrix become more fluid and smoother. Filho et al. [35] reported that the thickness of the film prepared using chitosan combined with *Citrus limonia* essential oil has increased with the increase in the concentration of essential oil addition, which could be attributed to an increase in the number of molecules with an increase in the concentration of essential oil, increasing in the film's free volume. Lyn and Hanani [36] noticed the thickness of the chitosan-based film incorporating GEO has increased significantly at higher concentrations of the lemongrass essential oil.

Fig. 4 The tensile strength (MPa) properties of chitosan-based film incorporating GEO with ginger essential oil (0) chitosan; (g+0) chitosan with glycerol; (g+0.1) chitosan with glycerol and essential oil 0.1; (g+0.2) chitosan with glycerol and essential oil 0.2; (g+0.3) chitosan with glycerol and essential oil. Different small letters indicate significant differences ($p \leq 0.05$)



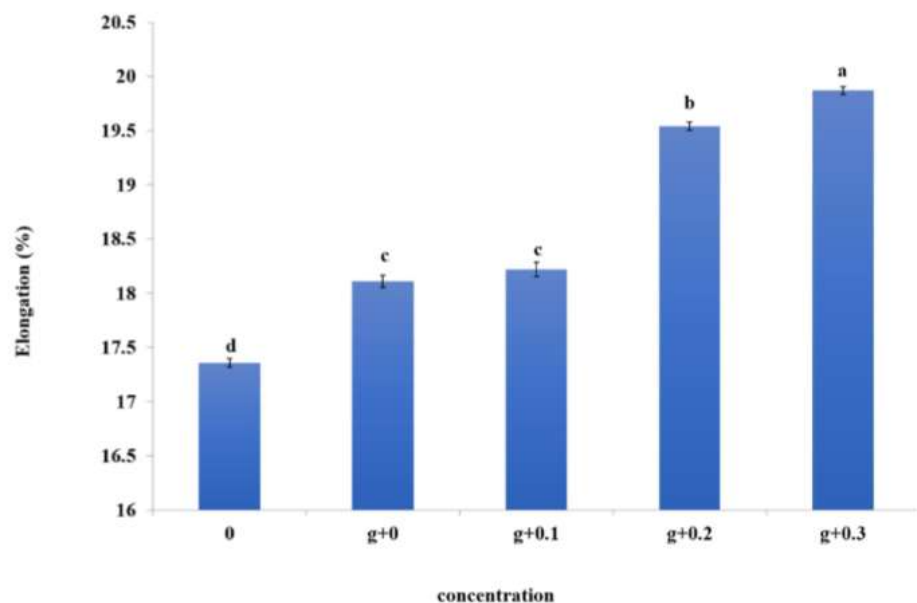
Tensile strength (TS)

The Tensile strength characteristics were considered as a very important matter for the fabricating of bioactive films due to their role in maintaining the safety aspects of the packaged food during handling processes [37, 38]. Figure 4 showed that the tensile strengths of the control treatment were at 35.12 and 33.92 MPa. In the current investigation, the films were affected by increasing concentrations of GEO. Increasing the concentration of GEO (0.1, 0.2, and 0.3%, with glycerol) added to chitosan films decreased the values of tensile strength. This is due to the strong interaction between chitosan and GEO producing a cross-linking effect, as well as decreasing the molecular mobility and free volume of the polymer. The lowest tensile strength value (30.99 MPa) was achieved in chitosan film at a concentration of 0.3% GEO with glycerol. This tensile strength value (30.99 MPa) showed a significant difference ($P \leq 0.05$) compared to the tensile strength values of the control treatment (35.12 MPa), chitosan with glycerol (33.92 MPa), chitosan with GEO at a concentration of 0.1% (32.34 MPa), and chitosan with GEO at a concentration of 0.2% (31.12 MPa). These results were consistent with those reported by Haghghi et al. [33], as they demonstrated that tensile strength values decreased with increasing concentrations of cinnamon and pink clove oils. Several studies have shown that tensile strength decreases within increasing concentrations of EOs [39].

Elongation (E)

Bioactive polymer films possess distinctive properties as they act as a barrier that protects packaging products from the surrounding environmental deterioration conditions [4]. The elongation percentage is an estimate of the stretchability of the film before breaking, and it is the maximum change in the length of the film, which depended on the intermolecular forces of the film, the mechanical properties of the films are largely related to the distribution and density of intra- and intermolecular interactions, which depend on the arrangements and orientation of the chains in the polymer network [40]. Figure 5 showed a significant difference ($P \leq 0.05$) observed in the elongation values by adding glycerol and increasing the concentration of GEO in the films. The elongation values have increased from 18.10 to 19.87% when the concentration of GEOs increased from 0.1 to 0.3%. In agreement with the current results, Šuput et al. [41] found that the elongation values increased from 38 to 52% and from 32 to 61% for the samples black cumin and oregano oils, respectively. The addition of essential oils significantly contributed to increasing the elongation of chitosan films and this characteristic increased with increasing oil concentrations [42, 43]. Besides, Noshirvani et al. [44] found that the elongation of chitosan-carboxymethyl cellulose films increased by increasing ginger and cinnamon oils. However, Benavides et al. [45] found that the elongation values of gelatin films were significantly affected by adding cinnamon hydrosol. The GEO added to the chitosan films can act as a film plasticizer that increases their plasticity and stretchability before breaking [46]. Chitosan is a good

Fig. 5 The elongation properties of chitosan-based film incorporating GEO with ginger essential oil (0) chitosan; (g+0) chitosan with glycerol; (g+0.1) chitosan with glycerol and essential oil 0.1; (g+0.2) chitosan with glycerol and essential oil 0.2; (g+0.3) chitosan with glycerol and essential oil. Different small letters indicate significant differences ($p \leq 0.05$)



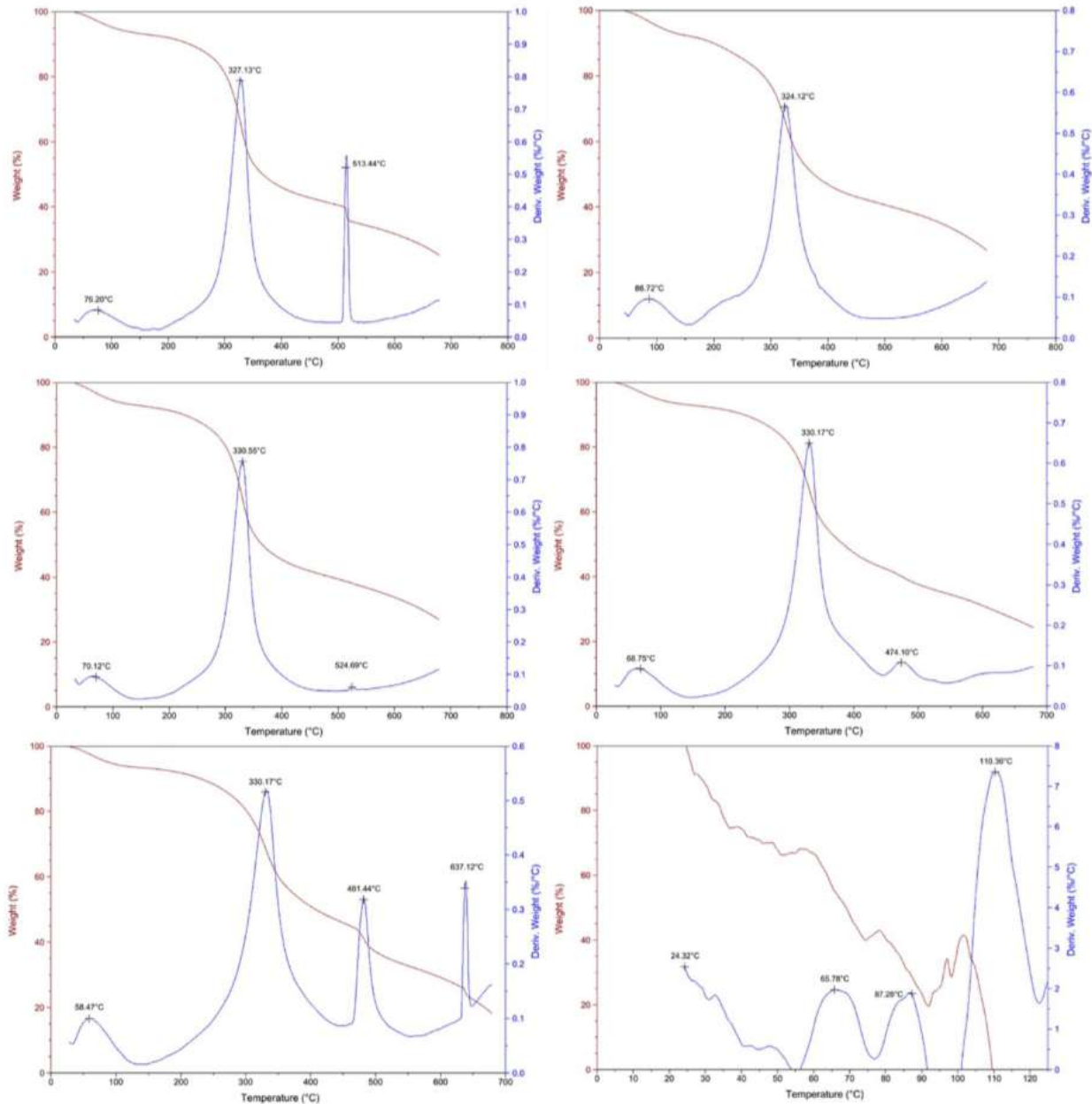


Fig. 6 Thermo gravimetric analysis curve of ginger essential oil composite films **a** chitosan; **b** chitosan+g; **c** chitosan+g+0.1; **d** chitosan+g+0.2; **e** chitosan+g+0.3

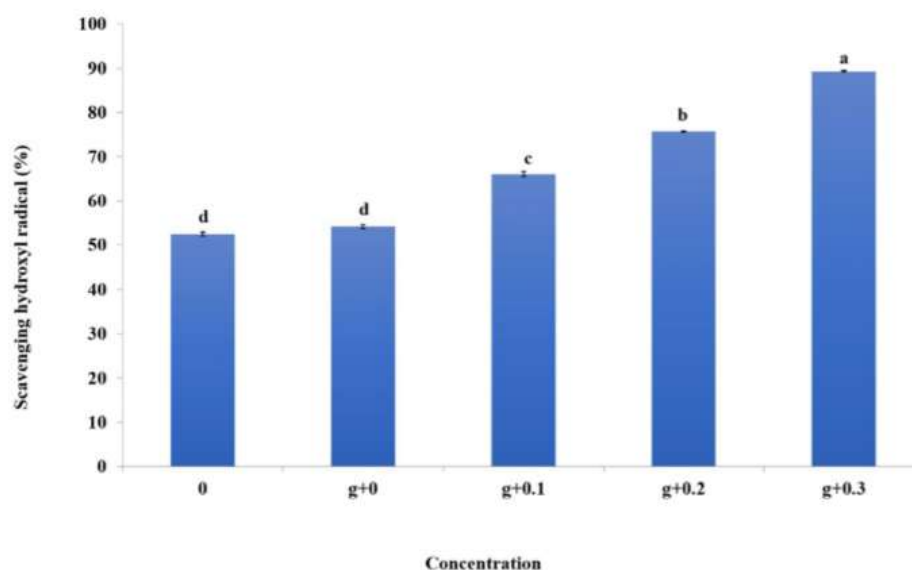
and favorable alternative to synthetic polymers because it is bioactive, biodegradable, water-soluble, and has good film properties [34, 47].

Thermogravimetric analysis TAG

Thermogravimetric test (TGA) for chitosan-based film incorporating GEO showed in Fig. 6. In this experiment,

the weights of all the films were taken 5 mg. The TGA data for films showed three and four steps in weight loss one at (20–100 °C) total weight loss at 76.20, 70.12, 58.47, and 24.32 °C were 7, 5, 3, and 9% respectively. The first step corresponds to the loss of adsorbed moisture and residual solvent and changes related to the position and/ or area position are connected to physical and molecular variation created by interaction materials used to get the film [48].

Fig. 7 The scavenging hydroxyl radical properties of chitosan-based film incorporating GEO with ginger essential oil (0) chitosan; (g+0) chitosan with glycerol; (g+0.1) chitosan with glycerol and essential oil 0.1; (g+0.2) chitosan with glycerol and essential oil 0.2; (g+0.3) chitosan with glycerol and essential oil. Different small letters indicate significant differences ($p \leq 0.05$)

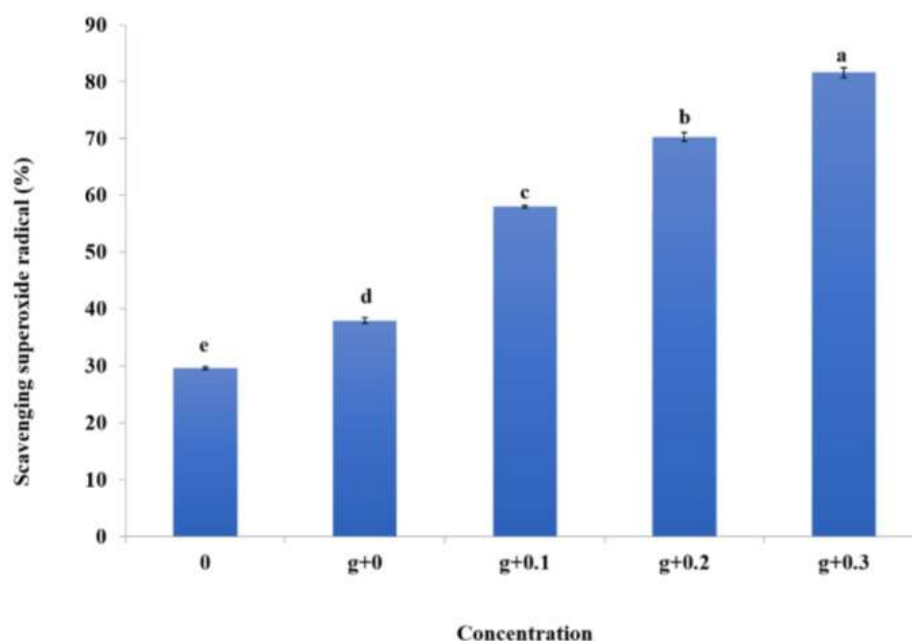


Secondly, important weight loss is due to the loss of hydrogen bonds between the neighboring molecules of chitosan chains [46–50]. The third and fourth steps occur between 300 and 400 °C were related to the breaking of the main chain and decomposition of respectively, on the other hand, the weight loss of GEOs is mainly between 300 and 400 °C, while over 500 °C GEOs is completely decomposed, this was supported by Souza et al. [51]; Zhang et al. [52]. The GEOs appears to have stabilized the chitosan films.

Scavenging of Hydroxyl radical

The results indicate in Fig. 7 the scavenging of hydroxyl radical activity of the chitosan-based film incorporating GEO. Free radicle scavenging ability has increased significantly ($P \leq 0.05$) with an increase in the concentration of GEOs it has a g+0.3% highest ability compared to other concentrations. Melo et al. [53] reported an increase in antioxidant properties when adding mango seed oil to films. The results of this study agreed with Martínez et al. [54], while noticed that chitosan film containing *Mentha*

Fig. 8 The scavenging superoxide radical properties of chitosan-based film incorporating GEO with ginger essential oil (0) chitosan; (g+0) chitosan with glycerol; (g+0.1) chitosan with glycerol and essential oil 0.1; (g+0.2) chitosan with glycerol and essential oil 0.2; (g+0.3) chitosan with glycerol and essential oil. Different small letters indicate significant differences ($p \leq 0.05$)



spicata essential oil with grape seed extracts higher free radical scavenging activity compared with a film without essential oil. Yahaya et al. [55] observed that the films stored for 14 days at 4 °C and added five Malaysian herbs showed the ability to scavenge free radicals. Several investigations show that the relationship between the total phenolic content of essential oil and extracts incorporated into the biodegradable films and antioxidant activities was positive [56–58].

Scavenging of superoxide radical

The superoxide may be a comparatively weak oxidizer, however, it decomposes to create stronger reactive species, such as hydroxyl and oxygen radicals that initiate lipid peroxidation. The superoxide radical may also be a zwitterionic radical and it might react with the free radical and amino groups in chitosan thereby resulting in a scavenging impact. Chitosan has a compact structure attributable to the unit chemical element bonding due to that the scavenging impact is comparatively less in untreated chitosan [59]. Superoxide radical scavenging activity of Chitosan-based film incorporating GEO was investigated (Fig. 8). As the concentration of GEOs increased from 0.1 to 0.3%, the superoxide anion radical scavenging activity of all chitosan-based film incorporating GEO increased. The chitosan-based film incorporating GEO exhibited an increased significantly ($P \leq 0.05$) higher increase rate, reaching a clearance rate of 81.57%. The superoxide anion radical scavenging activity of chitosan-based film incorporating GEO increased indicating super oxygen-anion radical scavenging ability is powerfully concentration-dependent. This scavenging ability is considerably higher for chitosan-essential oil than that for chitosan. Adding GEOs to chitosan films reinforces the clearance rate of superoxide anion radical. Besides, the amino groups in chitosan will react with free radicals to create the most stable macro radicals [60, 61]. The GEO contains many active compounds such as zingiberene, ar-curcumin, camphene, broneol that contribute to increasing the antioxidant effectiveness and the ability to scavenging free radicals Noshirvani et al. [44]. Ballester-Costa et al. [62] noticed an increase in antioxidant activity in the chitosan films with the addition of pomegranate extract peel and cinnamon essential oil.

Conclusions

In sum, the findings of the current work showed that ginger essential oil (GEOs) has a unique chemical composition with high biological activity. The use of GEOs as an ingredient in the fabrication of bioactive chitosan films stabilized chitosan film thickness and tensile strength at

acceptable levels. Besides, GEOs significantly contributed to increasing the elongation of chitosan-based film incorporating GEO and this characteristic increased with increasing GEO concentrations (0.1–0.3%). According to the thermogravimetric analysis, GEOs has reduced the weight loss of chitosan films at high levels of temperature. Chitosan-based film incorporating GEO possess high ability scavenging hydroxyl and superoxide radicals. This work concluded that GEO-based biodegradable chitosan film synthesized from shrimp shell composite is a promising source for preparing bioactive films and that its use as anti-free radicals can be highly effective in the food, pharmaceutical, and cosmetic industries.

Author contributions RMA-A: Conceptualization, Investigation, Software, Data curation. SAAH: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Data curation, Formal analysis, and Supervision. MMAR: Review, Writing, and Editing.

Funding This work did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Declarations

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Research involving human and/or animal participants This article does not contain any studies with human participants performed by any of the authors.

References

1. R. Suhag, N. Kumar, A. Trajkovska, A. Upadhyay, *Food Res. Int.* **136**, 109582 (2020)
2. S. Kumar, A. Mukherjee, J. Dutta, *Trends Food Sci. Technol.* **97**, 196 (2020)
3. S. Yadav, G.K. Mehrotra, P.K. Dutta, *Food Chem.* **334**, 127605 (2021)
4. M. Kouhi, M.P. Prabhakaran, S. Ramakrishna, *Trends Food Sci. Technol.* **103**, 248 (2020)
5. A.G. Ponce, S.I. Roura, C.E. del Valle, M.R. Moreira, *Postharvest Biol. Technol.* **49**, 294 (2008)
6. D. Mousavian, A. Mohammadi Nafchi, L. Nouri, A. Abedinia, *J. Food Meas. Charact.* (2020)
7. M.M. Marvizadeh, A. Tajik, V. Moosavian, N. Oladzadabbasabadi, A. Mohammadi Nafchi, *J. Chem. Health Risks* (2020). <https://doi.org/10.22034/jchr.2020.1900584.1135>
8. M. Esmaili, P. Ariaii, L.R. Nasirae, M.Y. Pour, *J. Food Meas. Charact.* **15**, 341–352 (2020)
9. S. Lekjing, *MESC* **111**, 192 (2016)
10. M.M. Jaworska, D. Antos, A. Górak, *React. Funct. Polym.* **152**, 104606 (2020)
11. R. Priyadarshi, J.W. Rhim, *Innov. Food Sci. Emerg. Technol.* **62**, 102346 (2020)

12. L.E. Abugoch, C. Tapia, M.C. Villamán, M. Yazdani-Pedram, M. Díaz-Dosque, *Food Hydrocoll.* **25**, 879 (2011)
13. M.S. Brewer, *Compr. Rev. Food Sci. Food Saf.* **10**, 221 (2011)
14. Z. Ban, J. Zhang, L. Li, Z. Luo, Y. Wang, Q. Yuan, B. Zhou, H. Liu, *Food Chem.* **306**, 125628 (2020)
15. N. dos Santos Reis, N.B. de Santana, I.M. de Carvalho Tavares, O.A. Lessa, L.R. dos Santos, N.E. Pereira, G.A. Soares, R.A. Oliveira, J.R. Oliveira, M. Franco, *Ind. Crops Prod.* **146**, 112210 (2020)
16. R.E. Kenari, Z.R. Amiri, A. Motamedzadegan, J.M. Milani, J. Farmani, R. Farahmandfar, *J. Food Meas. Charact.* **14**, 2828 (2020)
17. M.M.A. Rashed, Q. Tong, M.H. Abdelhai, M.A.A. Gasmalla, J.B. Ndayishimiye, L. Chen, F. Ren, *Ultrason. Sonochem.* **29**, 39 (2016)
18. O. Taofiq, A.M. González-Paramás, M.F. Barreiro, I.C.F.R. Ferreira, D.J. McPhee, *Molecules* **22**, 281 (2017)
19. M.M.A. Rashed, A.A. Mahdi, A.D.S. Ghaleb, F.R. Zhang, D. YongHua, W. Qin, Z. WanHai, *Int. J. Biol. Macromol.* **151**, 702 (2020)
20. M.M.A. Rashed, A.D.S. Ghaleb, J. Li, A. Nagi, Y. Hua-Wei, Z. Wen-You, Q. Tong, *ACS Sustain. Chem. Eng.* **6**, 1639 (2018)
21. M.M.A. Rashed, C. Zhang, A.D.S. Ghaleb, J.P. Li, A. Nagi, H. Majeed, A.M. Bakry, J. Haider, Z. Xu, Q. Tong, *Ind. Crops Prod.* **136**, 66 (2019)
22. M.M.A. Rashed, Q. Tong, A. Nagi, J.P. Li, N.U. Khan, L. Chen, A. Rotail, A.M. Bakry, *Ind. Crops Prod.* **100**, 236 (2017)
23. M. Grajzer, B. Wiatrak, T. Gębarowski, A. Matkowski, H. Grajeta, E. Rój, A. Kulma, A. Prescha, *Food Chem.* **335**, 127649 (2020)
24. A. Abdullahi, A. Khairulmazmi, S. Yasmeen, I.S. Ismail, A. Norhayu, M.R. Sulaiman, O.H. Ahmed, M.R. Ismail, *Arab. J. Chem.* **13**, 2012 (2020)
25. T.S. Trung, L.H. Tram, N. Van Tan, N. Van Hoa, N.C. Minh, P.T. Loc, W.F. Stevens, *Carbohydr. Res.* **489**, 107913 (2020)
26. R. Resmi, J. Yoonus, B. Beena, *Materials Today: Proceedings* (Elsevier, Amsterdam, 2020).
27. S.M. Ojagh, M. Rezaei, S.H. Razavi, S.M.H. Hosseini, *Food Chem.* **122**, 161 (2010)
28. I. Leceta, P. Guerrero, I. Ibarburu, M.T. Dueñas, K. De La Caba, *J. Food Eng.* **116**, 889 (2013)
29. A.R.V. Ferreira, C.A.V. Torres, F. Freitas, C. Sevrin, C. Grandfils, M.A.M. Reis, V.D. Alves, I.M. Coelho, *Carbohydr. Polym.* **147**, 8 (2016)
30. T. Hemalatha, T. UmaMaheswari, R. Senthil, G. Krithiga, K. Anbukkarasi, *J. Food Meas. Charact.* **11**, 2160 (2017)
31. J.Y. Nie, R. Li, Z.T. Jiang, Y. Wang, J. Tan, S.H. Tang, Y. Zhang, *Ind. Crops Prod.* **144**, 112060 (2020)
32. V. Kumar, C.S. Mathela, M. Kumar, G. Tewari, *Med. Drug Discov.* **1**, 100004 (2019)
33. H. Haghghi, S. Biard, F. Bigi, R. De Leo, E. Bedin, F. Pfeifer, H.W. Siesler, F. Licciardello, A. Pulvirenti, *Food Hydrocoll.* **95**, 33 (2019)
34. J. Wu, S. Ge, H. Liu, S. Wang, S. Chen, J. Wang, J. Li, Q. Zhang, *Food Packag. Shelf Life* **2**, 7 (2014)
35. J.G. de Oliveira Filho, I.P.B. de Deus, A.C.F. Valadares, C.C. Fernandes, E.B.B. Estevam, M.B. Egea, *Coll. Interfaces* **4**, 18 (2020)
36. F. Han Lyn, Z.A. Nur Hanani, *J. Packag. Technol. Res.* **4**, 33 (2020)
37. B. Rohini, S. Padma Ishwarya, R. Rajasekharan, A.K. VijayaKumar, *Polym. Test.* **87**, 106465 (2020)
38. K. Sadeghi, M. Shahedi, *J. Food Meas. Charact.* **10**, 137 (2016)
39. F.T. Sarcaoglu, S. Turhan, *Food Packag. Shelf Life* **25**, 100527 (2020)
40. M. Gursoy, I. Sargin, M. Mujtaba, B. Akyuz, S. Ilk, L. Akyuz, M. Kaya, Y.S. Cakmak, A.M. Salaberria, J. Labidi, N. Erdem, *Int. J. Biol. Macromol.* **114**, 1224 (2018)
41. D.Z. Šuput, V.L. Lazić, L.L. Pezo, L.B. Lević, J.M. Gubić, N.M. Hromiš, B.V. Šojić, *Rom. Biotechnol. Lett.* **18**, 8160 (2013)
42. S. Remya, C.O. Mohan, J. Bindu, G.K. Sivaraman, G. Venkateshwarlu, C.N. Ravishankar, *J. Food Sci. Technol.* **53**, 685 (2016)
43. R. Bagheri, P. Ariaii, A. Motamedzadegan, *J. Food Meas. Charact.* (2020). <https://doi.org/10.1007/s11694-020-00738-0>
44. N. Noshirvani, B. Ghanbarzadeh, C. Gardrat, M.R. Rezaei, M. Hashemi, C. Le Coz, V. Coma, *Food Hydrocoll.* **70**, 36 (2017)
45. S. Benavides, R. Villalobos-Carvajal, J.E. Reyes, *J. Food Eng.* **110**, 232 (2012)
46. V.G.L. Souza, C. Rodrigues, L. Ferreira, J.R.A. Pires, M.P. Duarte, I. Coelho, A.L. Fernando, *Ind. Crops Prod.* **140**, 111563 (2019)
47. T.S. Sazanova, K.V. Otvagina, I.V. Vorotyntsev, *Polym. Test.* **68**, 350 (2018)
48. E.A. El-Hefian, M.M. Nasef, A.H. Yahaya, *E-J. Chem.* **8**, 91 (2011)
49. J.F.B. Barata, R.J.B. Pinto, V.I.R.C. Vaz Serra, A.J.D. Silvestre, T. Trindade, M.G.P.M.S. Neves, J.A.S. Cavaleiro, S. Daina, P. Sadocco, C.S.R. Freire, *Biomacromolecules* **17**, 1395 (2016)
50. M.A.V. Junca, C. Valencia, E.F. López, J. Delgado-Ospina, P.A. Zapata, M. Solano, C.D. Grande Tovar, *Biomolecules* **9**, 458 (2019)
51. V.G.L. Souza, J.R.A. Pires, C. Rodrigues, P.F. Rodrigues, A. Lopes, R.J. Silva, J. Caldeira, M.P. Duarte, F.B. Fernandes, I.M. Coelho, A.L. Fernando, *Coatings* **9**, 1 (2019)
52. H. Zhang, J. Jung, Y. Zhao, *Food Hydrocoll.* **69**, 164 (2017)
53. P.E.F. Melo, A.P.M. Silva, F.P. Marques, P.R.V. Ribeiro, M. de Sá Souza Filho, E.S. Brito, J.R. Lima, H.M.C. Azeredo, *Food Hydrocoll.* **95**, 487 (2019)
54. K. Martínez, M. Ortiz, A. Albis, C.G.G. Castañeda, M.E. Valencia, C.D.G. Tovar, *Biomolecules* **8**, E155 (2018)
55. W.A.W. Yahaya, M.P. Almajano, N.A. Yazid, N.A.M. Azman, *Antioxidants* **8**, 204 (2019)
56. M. Jouki, S.A. Mortazavi, F.T. Yazdi, A. Koocheki, *Carbohydr. Polym.* **99**, 537 (2014)
57. F. Roysanpour, J. Tavakoli, F. Beigmohammadi, S. Alaei, *J. Food Meas. Charact.* (2020)
58. D. Kilinc, B. Ocak, Ö. Özdestan-Ocak, *J. Food Meas. Charact.* **15**, 795–806 (2020)
59. J. Zhang, W. Tan, Q. Li, F. Dong, Z. Guo, *Mar. Drugs* **18**, 1 (2020)
60. C. Wu, L. Wang, Y. Hu, S. Chen, D. Liu, X. Ye, *RSC Adv.* **6**, 20892 (2016)
61. Y. Li, C. Wu, T. Wu, C. Yuan, Y. Hu, *Food Sci. Nutr.* **7**, 1131 (2019)
62. C. Ballester-Costa, E. Sendra, J. Fernández-López, M. Viuda-Martos, *J. Food Sci. Technol.* **53**, 3374 (2016)

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.