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Development and characterization of semi-refined carrageenan (SRC) films from *Eucheuma cottonii* incorporated with glycerol and α-tocopherol for active food packaging application

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Development and characterization of semi-refined carrageenan (SRC) films from *Eucheuma cottonii* incorporated with glycerol and α-tocopherol for active food packaging application

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Abstract. This works focuses on the development of biodegradable active films packaging using all natural compounds with the aim of contributing sustainable film not only by reducing the plastic waste to environment but also as a potential substitute of synthetic preservative in food. Active film packaging was formulated using semi-refined carrageenan (SRC) biopolymer extracted from *Eucheuma cottonii* plasticized with glycerol (G) and incorporated with different concentrations of α-tocopherol (Tp) at 0.1, 0.2, 0.3 and 0.4% v/v as natural antioxidants. Opacity, water solubility and mechanical properties of the resultant film were analysed whereas the migration behaviour of antioxidant films into food simulant during 30 days storages were determined using total phenolic content and DPPH assay. The addition of Tp in SRC+G film decreased the tensile strength but increased the value of elongation at break significantly ($p<0.05$). Opacity and water solubility were improved with increasing concentration of Tp ($p<0.05$). The highest and prolonged release of antioxidant to food simulant was determined by SRC+G+Tp0.4% through 30 day storage with total phenolic content value of 2 mg GAE/ L sample and 88.59% inhibition for DPPH assay. Hence, the new formulation of SRC+G with tocopherol could be an alternative degradable active packaging that might reduce the need of adding antioxidants directly into food products and also prolong the food shelf life.

1. Introduction

The development of biodegradable film from natural sources is becoming important nowadays as it is considered as an alternative to the petrochemical derived plastic that is not safe for the environment. Many researchers have focused on the development of edible and/or biodegradable films made from natural and renewable polymers such as polysaccharides, protein and lipids [1–2] whereby biopolymer from agro-resources showed potentially good film-forming properties [3]. Many natural biopolymers are not only edible and degradable but also possess biocompatibility properties with other functional materials that offer many advantages in food packaging industries.

Carrageenan is a natural polysaccharide polymer obtained from the extraction of red seaweed species from Rhodophyceae family. Previous studies reported that carrageenan is one of the potential biopolymers that has the ability to form a strong gel and provides efficient barrier against gas, lipids and oils [3-4]. The presence of 3,6-anhydrobridges compound in kappa (κ) and iota (ι) carrageenans demonstrating the potential as a film forming ability and the κ-carrageenan having strong properties in

forming hard, strong and brittle gels are widely found in *Eucheuma cottonii* species [5]. In industrial process of producing carrageenan, the process involves two distinct types of carrageenan; 1) semi-refined carrageenan and 2) refined carrageenan. Semi-refined carrageenan (SRC) is available at cheaper cost compared to refined carrageenan where it also has excellent binding properties in film-forming solution [6].

Polymer blending with active compound is one of the innovations to obtain new film material containing desired functional properties that offers specific protection for food. Active film packaging is normally derived from natural polymer coated with active compounds such as antioxidant for the purposes of extending food shelf life as well as improving safety and sensorial properties in the food packaging. Various natural antioxidants such as α-tocopherol [7] and phenolic compounds [8] have been used in food films and coating systems. Medina-Jaramillo et al. [9] reported that natural extract from green tea that was blended into starch films demonstrated good film forming properties and exhibited high antioxidant activity in food simulant. Other than that, active film developed from herbs such as lavender, oregano and bearberry leaves successfully showed their antioxidant and antimicrobial properties in food protection by previous studies [10–11].

Vitamin E or known as α-tocopherol is a nontoxic natural antioxidant possessing many pharmacological benefits to human health including anti-cancer and reduces the risk of degenerative diseases such as cardiovascular diseases [12]. Many researches have been conducted to investigate the potential use of the α-tocopherol as antioxidant coating in packaging since the compound is an excellent stabilizer and shows high solubility during polymer processing [13-14]. Furthermore, Shojaee-Aliabadi et al. [4] showed that the addition of active and hydrophobic compounds of α-tocopherol not only gives the protective effect in food, but also improves the mechanical and barrier properties in the development of biodegradable films.

Nevertheless, the addition of plasticizers within the production of plastic film products is not new. Incorporating plasticizer into the active film packaging is able to modify the polymer properties and allow the mass transport of the active agents to the foods. Vieira et al. [3] reported that several properties of the film are improved including increasing flexibility of film and decreasing the glass transition temperature by adding plasticizer. Currently, focus is on natural plasticizers such as glycerol, sorbitol, sunflower oil and linseed oil as substitutes to the synthetic plasticizers due to their low toxicity and migration, and they have been widely used to prepare edible film.

A recent study found that SRC blended with glycerol has good potential to be used as an alternative polysaccharide material for the production of edible biodegradable packaging films with improved mechanical and barrier properties [6]. However, the formulation of SRC with glycerol (G) and α-tocopherol (Tp) as new functional material in active packaging film has not been fully developed. In addition, the mechanical properties, opacity, solubility of film in water and antioxidant release of active packaging film from SRC + G + Tp have been not fully documented. Hence, this research aims to develop and characterize SRC based film with enhanced functional properties by adding glycerol (0.9% v/v) and different concentrations of α-tocopherol (0.1, 0.2, 0.3 and 0.4%, v/v) for potential use as active packaging in food.

2. Materials and Methods

2.1. Materials

Semi-refined carrageenan (SRC) was extracted from *Eucheuma cottonii* seaweed obtained from Sabah, Malaysia. Food grade glycerol, 2,2-diphenyl-1-picrylhydrazyl (DPPH), sodium chloride, folin & ciocalteu's phenol reagent and α-tocopherol were purchased from Sigma Aldrich (England).

2.2. Preparation of semi-refined carrageenan (SRC) from Eucheuma Cottonii seaweed

SRC film was prepared according to the established method of Mustapha et al. [24]. *Eucheuma cottonii* seaweed was cleaned under running tap water to remove debris and dried under sunlight for 8 h. Extraction process was prepared by adding 150 g of dried seaweed into 1.0M KOH solution at 80°C for 2 h and soaked in water for 12 h. Then, the neutralised seaweeds were dried at 50°C for 24 h using a laboratory oven (MEMMERT, EQP004, Schwabach, Germany). Finally, the SRC samples were

ground at mesh 0.5 mm using laboratory grinder (Retsch, ZM 200, Haan, Germany) and stored in the dessicator (25°C) for further analyses.

2.3. Preparation of SRC films

SRC based films were prepared according to the method of Farhan et al. [6] with slight modifications. SRC film solution was prepared by dissolving 2 g of SRC in distilled water (2% w/w) under continuous stirring and the solution was heated at 70 °C for 10 min using hot plate magnetic stirrer. After dissolution, plasticizer glycerol was added at 0.9% v/v into the solution. The film-forming solution was heated again and maintained for ± 10 min prior to the addition of antioxidant α-tocopherol at different concentrations (0.1%, 0.2%, 0.3%, and 0.4% v/v) under continuous stirring. Adequate amount of SRC film forming solutions were casted on casting plates and dried using laboratory oven at 40 °C and 30% relative humidity (RH) for 24 hr. The films was then cooled in room temperature and RH for 30hr prior to experimental use.

2.4. Mechanical properties of films

Tensile strength (TS) and elongation at break (EAB) of the film samples were measured according to ASTM D882 method [16] 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 with a crosshead speed set at 50 mm/min. Tested film strips were equilibrated at 25 °C and 50% relative humidity (RH) in desiccators for 48 h prior to testing. TS of the films were calculated using the following equation:

$$TS(MPa) = \frac{F_{\max}}{\phi} \tag{1}$$

where F_{max} is the maximum load and Φ is the cross-sectional area. EAB of the films was calculated using the following equation:

$$EAB(\%) = (\frac{\Delta_1}{l_0}) \times 100 \tag{2}$$

where Δ_1 is the film extension and l_0 is the initial length of the film sample.

2.5. Solubility in water

Solubility of films in water were determined according to the method described by Farhan et al. [6] with slight modifications. The film samples were cut uniformly (2 cm × 2 cm) and dried at 100°C in a laboratory oven for 24 h and weighted to determine their initial dry weight. Each film samples were placed with 30 ml of distilled water and immersed into laboratory water bath (Memmert Waterbath, WNE14, Tokyo, Japan) under constant shaking at 25°C for 24 h. After that, undissolved film samples were filtered using Whatman No. 1 filter paper and the samples were dried at 100°C for 24 h to determine their final dry weight. The solubility of films in water was calculated as a percentage (WS %) using the following equation:

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

where W_0 is the initial dry weight of the film and W_f is the final weight of the dried undissolved film.

2.6. Opacity measurement

The opacity of the film samples was performed as described by Shojaee-Aliabadi et al. [4]. The opacity of the films was evaluated using UV-visible spectrophotometer (HITACHI, U-1800, Tokyo, Japan) at an absorbance of 600 nm. The films (3 x 0.3 cm^2) were placed on the plastic cuvette. The opacity of the films was calculated using the following equation:

$$Opacity(OP) = \frac{Abs600}{\gamma} \quad (4)$$

where Abs600 is the value of absorbance at 600 nm and γ is the thickness of film (mm).

2.7. Determination of antioxidant activity

2.7.1. Migration test. A study on the release of the active compounds from the films was carried out by determining the specific migration from polymer into food simulant (90% ethanol) as reported by López De Dicastillo et al. [17]. Film samples (2 x 3 cm^2) were placed in separate 30 mL amber glass vials and added with 10 ml of 90% ethanol. The vials were hermetically sealed with open-top cap and stored at room temperature and protected by light for 30 days storage period. The migration of α-Tocopherol in the simulants was analysed to determine their 1) total phenolic content (TPC) and 2) antioxidant activity.

2.7.2. Determination of TPC and antioxidant activity. Total phenolic content and antioxidant activity was measured using Folin-Ciocalteu method and DPPH scavenging activity respectively and these assays was performed according to previous study [18]. Folin-Ciocalteu method: The final concentration (v/v) for the mixture was prepared with 10 µL samples (90% ethanol of food simulant), 50 µL 10% Folin reagent and 150 µL 7% sodium carbonate solution and diluted with 790 µL MiliQ water. Absorbance at 765 nm was measured using UV-visible spectrophotometer. The results were expressed as mg of Gallic acid equivalents/L sample (mg GAE/ L sample). DPPH assay: A solution of 0.6 mM DPPH dissolved in ethanol appropriate dilutions were made to allow the fall in DPPH concentration to be in the range of 10-90 % (v/v). One aliquot (0.025 ml) of the diluted ethanol solution (90% ethanol of food simulant) was mixed with 0.975 ml of 0.6 mM DPPH. The solution was added to the plastic cuvette and the absorbance was measured at 585 nm using UV-visible spectrophotometer after 4 h. The results were expressed as % inhibition of DPPH radical.

2.8. Statistical Analysis

Statistical analysis was performed using one-way analysis of variance (ANOVA) using SPSS statistical software version 17.0 (SPSS Inc., Chicago, IL, USA). Bonferroni's test was used to determine significant differences at $p < 0.05$ level. Each sample was measured in triplicate and the average standard deviation for each sample was less than 5%.

3. Results and Discussion

3.1. Mechanical properties of SRC based films

Tensile strength (TS) and elongation at break (EAB) assays are to measure the ability of film resistance breakage when used as packaging materials. The value of TS indicated the sustainability of the film when applied with the maximum tensile stress. Table 1 showed the value of TS (MPa) and EAB (%) of SRC based films. SRC-control exhibited lowest TS value compared to SRC+G film and SRC+G film demonstrated the highest TS value compared to all samples with value of 58.20 MPa ($p<0.05$). This was supported by Farhan et al. [6] who revealed the adding glycerol as plasticizer improved the mechanical properties of SRC based film. They pronounced that the increase of TS value of SRC+G film could be attributed to the strong polymer-plasticizer interaction form via hydrogen bonding between SRC matrix chains and glycerol molecules [6]. Meanwhile, the incorporation of α-tocopherol with SRC+G experienced a slight decrease of TS value inversely with the concentration of α-tocopherol ($p<0.05$). These results indicated that the addition of antioxidant α-tocopherol affected the TS value of SRC films might be due to the interaction that modifies the chains between polymeric

matrix of SRC with plasticizer and α-tocopherol and formed discontinuities between polymeric structure [1]. The presence of phenolic compound in α-tocopherol weakened the intermolecular interactions between SRC and glycerol resulted to the decrease of TS value. Therefore, the addition of active compounds can decrease the film strength. Martins et al. [7] also proved in their study where the TS value of chitosan based films decreased when the films incorporated with α-tocopherol compared to control film. Although many authors found similar effect on films with Tp incorporation, however the substantial decrease of TS in the active film did not cause much changes and able to use as packaging or coating systems in foods. Biopolymer films with an appropriate concentration plasticizer can be classified as having good mechanical properties under the range of 10–100 MPa of TS and EAB >10% [19]. EAB showed the maximum value of the film allowed to stretch. On the contrary, film with glycerol and addition of α-tocopherol increased the value of EAB % significantly ($p<0.05$) with increase in Tp concentration (Table 1). SRC+G+Tp0.4% film significantly demonstrated the highest value of EAB with 20% value compared to all film produced ($p<0.05$). The results showed that SRC+G with incorporation of Tp (at any concentration) exhibited good flexibility and stretch ability by presenting higher value of EAB % compared to SRC-control film ($p<0.05$). In addition, EAB value of SRC+G film was higher when compared to SRC-control film, and these results convinced that plasticizer was added to polymer to increase the flexibility of film [6]. Theoretically, film with antioxidant addition decreased the TS which would lead to the increase in EAB %, the intermolecular interaction between SRC and glycerol molecules as weakened by α-tocopherol may increase the polymer mobility. Thus, good synergic effect and compatibility SRC polymer with plasticizer and α-tocopherol can increase the mobility of polymeric structure and produce stretchable films. Ma et al. [20] found similar finding on the effect of blending curcumin as antioxidant, where tara gum acted as plasticizer with PVA film on decreasing the TS value and increasing the EAB%. To the best of our knowledge, this is the first report of SRC blending with glycerol and α-tocopherol assessed using TS and EAB%.

3.2. Opacity and solubility of films

The transparency values of all films are presented in Table 1. The lower opacity values indicate the greater transparency of the film, making the film attributes more attractive and clear. The SRC-control film showed highest non-transparency value ($p<0.05$) while adding glycerol reduced the opacity value significantly ($p<0.05$). Similar observation of OP applied to bioplastics made from 2% (w/w) SRC plasticized with glycerol was reported by Farhan et al. [6]. Opacity value increased with the increasing concentration of Tp blended with SRC+G film. These results found that Tp incorporation caused a film reduce in transparency when compared to SRC+G film. The addition of Tp resulted in decreasing of light transmission might be due to the light-scattering induced by the oily droplets of Tp in the film matrix. Consequently, light-scattering event is depending on the particle size of the dispersed phase, where the intensity of the light-scattering is affected by the amount of droplets added in solution [4]. The similar behaviour of films incorporated with oily materials was observed by others literature [4,10]. Film morphology affected the transparency and opacity traits, whereby, the presence of glycerol in films did not permit the SRC polymer to crystalize due to the action of glycerol that interferes with the ice formation by interposing itself within the water hydrogen-bond network. This was achieved by keeping

Table 1. Mechanical properties, opacity and water solubility of SRC based films.

Film Types	Mechanical Properties		Opacity	Water Solubility (%)
	TS (MPa)	EAB (%)		
SRC-control	46.63±2.88^{a}	6.54±0.27^{a}	9.03±0.25^{a}	83.40±2.05^{a}
SRC+G	58.20±2.76^{a}	14.5±0.27^{b}	6.24±0.14^{b}	74.59±1.92^{a}
SRC+G+Tp0.1%	43.88±1.17^{b}	14.7±1.70^{c}	6.88±0.13^{a}	58.61±1.68^{b}
SRC+G+Tp0.2%	42.87±0.24^{c}	16.2±1.84^{d}	8.39±0.47^{a}	52.18±3.62^{c}

SRC+G+Tp0.3%	39.33±0.13^{d}	17.7±1.70^{e}	8.70±0.60^{a}	49.69±2.46^{d}
SRC+G+Tp0.4%	38.23±1.54^{e}	20.0±0.63^{f}	8.05±1.46^{a}	48.65±2.45^{e}

the film material amorphous that permit to light pass through. Furthermore, the crystallinity observed may be attributed by the polysaccharide present in the SRC as a barrier to light, resulting in the increase of the opacity. Thus, incorporation glycerol in the SRC film has a profound impact on light transmittance and transparency of films.

Values are given as mean ± standard deviation. Different letters in the same column indicate significantly different ($p<0.05$) when analysed by Bonferroni's Test. Film solubility is used an indicator to measure film integrity, water resistance and biodegradability of films when used as packaging materials. The solubility of films was improved with the addition of plasticizer and α-tocopherol as shown in Table 1. The result demonstrated that the incorporation of α-tocopherol (at any concentration) in SRC based film significantly decreased ($p<0.05$) the solubility of films in water compared to the SRC-control film. α-tocopherol is hydrophobic in nature due to the present of aliphatic group and lower number of O-H bonds in α-tocopherol makes the film less soluble [21]. Meanwhile, control SRC film dissolved almost completely during the analysis due to the hydrophilic nature of carrageenan. Cerqueira et al. [21] has proven in their study that incorporating oil into the carrageenan lead to significant decrease ($p<0.05$) of the film solubility. This was due to the interaction between the hydroxyl groups of carrageenan chain and plant oil component decreased the availability of hydroxyl groups, thereby reducing the polysaccharides-water interactions and decreasing solubility of film in water [4]. Solubility affects the potential of biodegradable films to protect food products from moisture and contamination in the present of water. However, water solubility may be required in the consumption of food products such as prepackaged products ready for cooking. Therefore, the solubility of films is depending on the application and intended use, whereby the solubility of water also can be considered as indicator for film biodegradability. Thus, adding antioxidant, Tp enhanced the water resistance and integrity of film during contact with water.

3.3. Antioxidant activity of SRC based films incorporated with α-tocopherol

Food simulant of 90% ethanol was used and recommended according to the Commission Regulation (EU) No. 10/2011 that was assigned for food with a lipophilic character [17]. The migration of α-Tocopherol into food simulants was measured by total phenolic content (TPC) and DPPH assay and the release test was performed for 30 days. The idea was to demonstrate the possible practical application of the produced active films in the food packaging field [22]. Overall migration tests with food simulants were carried out and the results are shown in Figure 1 and Figure 2. SRC-control film with or without glycerol showed no polyphenol content whilst all films coated with α-tocopherol showed increased TPC value proportionally to the concentration of α-tocopherol ($p<0.05$). SRC+G+Tp0.4% exhibited the highest release of TPC through 30 day storages compared to all samples with value of 3.5 mg GAE/ L sample ($p<0.05$). Meanwhile, the release test of TPC showed a decline at 20 day storages onwards. These results indicated that the declining behaviour may be due to the longer storage time that affected the degradation polyphenol compounds in α-tocopherol. The degradation of polyphenol was caused by many factors, one of them was the constant release of Tp that began to oxidize the remaining Tp dissolved in 90% ethanol. Similar effect was observed by Jamshidian et al. [23] for which the release of PLA film containing TBHQ in ethanol 95% began to oxidize PLA film with TBHQ throughout storage time.

Figure 2 demonstrated migration study measured using DPPH assays of produced films through 30 days storages. Overall, the films with Tp (at any concentration) displayed increment of percentage inhibition of DPPH radicals ($p<0.05$) whereas the SRC-control and SRC+G displayed no significant difference until 30 days' storages ($p>0.05$). SRC+G+Tp0.4% film experienced highest radical scavenging activity of DPPH with value reaching 80% ($p<0.05$) at 20 days' storages due to the high content of α-tocopherol in the film. Moreover, the release trend of total phenolic contents (Figure 1) was correlated with DPPH scavenging activity to all samples. According to Rafiquzzaman et al. [24], alkaline treated carrageenan exhibited marginally antioxidant activities measured by various assays including DPPH radical while glycerol showed no study on the antioxidant activities towards DPPH

radical. Chemical composition of active compounds, the interaction between polymer and active compounds, and the medium conditions may be the factors that influenced the release behaviour of active components from films to food simulant. After 30 day storages, all film still remained intact, and the polymer signals and film traits remained similar as produced observed visually.

In this study, SRC+G+Tp0.4% seems to be reasonably attractive as active film development, indicates the sustainable release kinetics of antioxidant in the food simulants during 30 day storage time. Engagement of α-tocopherol as active compounds in active packaging films was not new, since Sun et al. [14] demonstrated synergic effect α-tocopherol with LDPE film whereas Byun et al. [13] suggested addition of α-tocopherol gives dramatic increase on the antioxidant activity in PLA films development. The migration behaviour of SRC+G+Tp film into food simulant can be considered suitable for application in food packaging field. To our knowledge, no scientific work have been carried out so far on synergic of antioxidant release from α-tocopherol incorporated with SRC-film plasticised with glycerol.

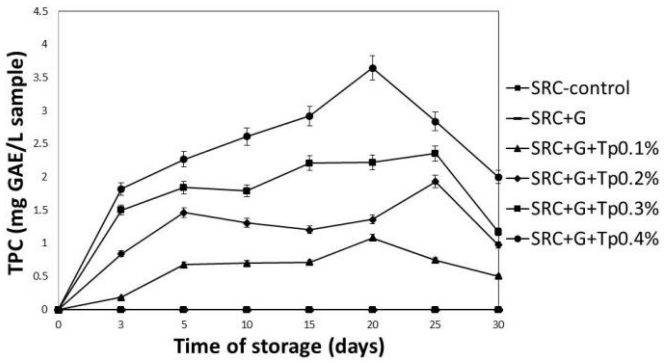

Figure 1. Changes in TPC values (mg GAE/ L sample) of produced film during 30 days storage at 25 ± 1 °C.

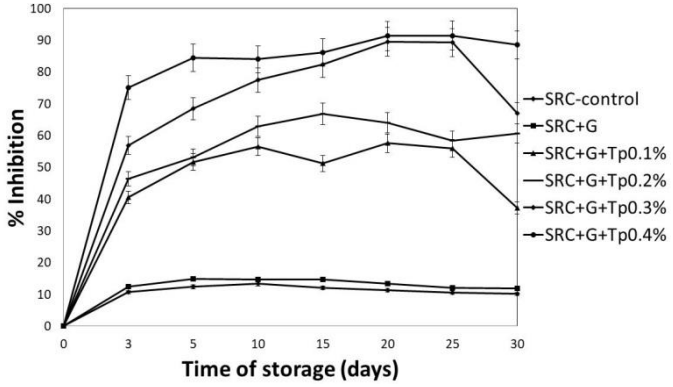

Figure 2. Changes in DPPH values (% inhibition) of produced films during 30 days storage at 4 ± 1 °C.

4. Conclusion

Incorporation of α-tocopherol in SRC plasticized with glycerol reduced slightly the tensile strength but the elongation and stretch ability of the produced film increased significantly. The solubility of film and opacity of the treated film improved significantly. The addition of α-tocopherol into SRC+G+0.4%Tp showed high antioxidant activity release to food simulant through 30 days storages may use in the food packaging application for extending shelf-life and retarding the oxidation process. In conclusion, the formulation of SRC incorporated with α-tocopherol might be an alternative

degradable packaging not only that it can prolong shelf life but can also avoid synthetic preservative in contact direct with foods.

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References

[1] Shen Z and Kamdem D P 2015 Development and characterization of biodegradable chitosan films containing two essential oils *Int. J. Biol. Macromol.* **74** 289–296
[2] Ma W, Tang C, Yin S W, Yang X Q, Wang Q, Liu F and Wei Z H 2012 Characterization of gelatin-based edible films incorporated with olive oil *Food Res. Int* **49** 572–579
[3] Vieira M G A, Da Silva M A, Dos Santos L O and Beppu M M 2011 Natural-based plasticizers and biopolymer films: A review *Eur. Polym. J.* **47** 254–263
[4] Shojaee-Aliabadi S, Hosseini H, Mohammadifar M A, Mohammadi A, Ghasemlou M, Hosseini S M and Khaksar R 2014 Characterization of κ-carrageenan films incorporated plant essential oils with improved antimicrobial activity *Carbohydr. Polym.* **101** 582–591
[5] Zia K M, Tabasum S, Nasif M, Sultan N, Aslam N, Noreen A and Zuber M 2017 A review on synthesis, properties and applications of natural polymer based carrageenan blends and composites *Int. J. Biol. Macromol.* **96** 282-301
[6] Farhan A and Hani N M 2017 Characterization of edible packaging films based on semi-refined kappa-carrageenan plasticized with glycerol and sorbitol *Food Hydrocoll.* **64** 48–58
[7] Martins J T, Cerqueira M A and Vicente A A 2012 Influence of α-tocopherol on physicochemical properties of chitosan-based films *Food Hydrocoll.* **27** 220–227
[8] Azman, N A M, Skowyra M, Muhammad K, Gallego MG, Almajano M P 2017 Evaluation of the antioxidant activity of Betula pendula leaves extract and its effects on model foods. *Pharm. Biol.* **55** 912-919
[9] Medina-Jaramillo C, Ochoa-Yepes O, Bernal C and Famá L 2017 Active and smart biodegradable packaging based on starch and natural extracts *Carbohydr. Polym.* **176** 187–194
[10] Atarés L and Chiralt A 2016 Essential oils as additives in biodegradable films and coatings for active food packaging *Trends Food Sci. Technol.* **48** 51–62
[11] Martucci J F, Gende L B, Neira L M and Ruseckaite R A 2015 Oregano and lavender essential oils as antioxidant and antimicrobial additives of biogenic gelatin films *Ind. Crops Prod.* **71** 205–213
[12] Jiang Q 2017 Natural Forms of Vitamin E as Effective Agents for Cancer Prevention and Therapy *Adv. Nutr.* **8** 850–867
[13] Byun Y, Kim Y T and Whiteside S 2010 Characterization of an antioxidant polylactic acid (PLA) film prepared with a-tocopherol, BHT and polyethylene glycol using film cast extruder *J. Food Eng.* **100** 239–244
[14] Sun L N, Lu L X, Qiu X L and Tang Y L 2017 Development of low-density polyethylene antioxidant active films containing α-tocopherol loaded with MCM-41(Mobil Composition of Matter No. 41) mesoporous silica *Food Control* **71** 193–199
[15] Normah O and Nazarifah I 2003 Production of semi-refined carrageenan from locally available red seaweed Eucheuma cottonii on a laboratory scale *J. Trop. Agric. Fd. Sc.* **31** 207–213
[16] ASTM D882 2000 Standard test method for tensile properties of thin plastic sheeting method D882-00 (Philadelphia: American Sociaty for Testing and Materials)
[17] López De Dicastillo C, Ares Pernas A, Castro López M D M, López Vilariño J M and González Rodríguez M V 2013 Enhancing the release of the antioxidant tocopherol from polypropylene films by incorporating the natural plasticizers lecithin, olive oil, or sunflower oil *J. Agric. Food Chem.* **61** 11848–11857
[18] Azman N, Segovia F, Martínez-Farré X, Gil E and Almajano M 2014 Screening of Antioxidant Activity of Gentian Lutea Root and Its Application in Oil-in-Water Emulsions *Antioxidants*

3 455–471
[19] Hun J H and Cennadios A 2005 *Innovative in Food Packaging* p 241–262
[20] Ma Q, Ren Y and Wang L 2017 Investigation of antioxidant activity and release kinetics of curcumin from tara gum/ polyvinyl alcohol active film *Food Hydrocoll.* **70** 286–292
[21] Cerqueira M A, Souza B W S, Teixeira J A and Vicente A A 2012 Effect of glycerol and corn oil on physicochemical properties of polysaccharide films - A comparative study *Food Hydrocoll.* **27** 175–184
[22] Yang W, Fortunati E, Dominici F, Giovanale G, Mazzaglia A, Balestra G M, Kenny J M and Puglia D 2016 Effect of cellulose and lignin on disintegration, antimicrobial and antioxidant properties of PLA active films *Int. J. Biol. Macromol.* **89** 360–368
[23] Jamshidian M, Tehrany E A and Desobry S 2012 Release of synthetic phenolic antioxidants from extruded poly lactic acid (PLA) film *Food Control* **28** 445–455
[24] Rafiquzzaman S M, Ahmed R, Lee J M, Noh G, Jo G and Kong I S 2016 Improved methods for isolation of carrageenan from Hypnea musciformis and its antioxidant activity *J. Appl. Phycol.* **28** 1265–1274