RHEOLOGICAL BEHAVIOR OF KAPPA AND IOTA SEMI-REFINED CARRAGEENAN MIXTURE

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ABSTRACT

SRC (Semi Refined Carrageenan) is a more cost effective product from the red seaweed. *Kappaphycus alvarezii* and *Eucheuma denticulatum* are the major two species being focus in the present study for its excellent sources of kappa-(κ) and iota-(ι)carrageenan respectively. An experiment was conducted to study the viscoelasticity of SRC as compare to refined carrageenan (RC) and the effect of different κ- and ι-carrageenan ratio. The Fourier Transform Infrared Spectroscopy – Attenuated Total Reflectance (FTIR-ATR) analysis provide evidence that critical functional group of κ- and ι-carrageenan was no altered during the purification process by alcohol precipitation method. Six mixtures of different κ/ι ratio were formulated 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 for RC and SRC respectively. The viscoelasticity measurements consist of temperature dependence, mechanical spectra and stress dependence analysis. Results showed that the mixtures of the κ- and ι-carrageenan had two-step gelation behavior in the cooling cycle while this effect was absent in the heating cycle. In all viscoelasticity measurement, superior dynamic moduli (G′) and loss shear modulus (G″) was observed in the RC. However, at lower G′ and G″ values, SRC possessed a highly identical rheological behavior observed in RC. SRC showed good potential in food application with significantly lower cost compare to RC.

SIFAT REOLOGI PERCAMPURAN KARAGENAN KAPPA DAN IOTA SEPARA TULEN

ABSTRAK

SRC (Karagenan Separa Tulen) merupakan antara produk daripada rumpai laut merah yang lebih kos efektif. Kappaphycus alvarezii dan Eucheuma denticulatum adalah sumber yang baik untuk kappa-(κ) dan iota-(ι)karagenan yang menjadi tumpuan dalam penyelidikan ini. Suatu eksperimen telah dijalankan untuk menyelidik perbandingan antara SRC dan karagenan tulen (RC) dalam aspek 'viscoelasticity' dan kesan pencampuran κ- and ι-karagenan dalam nisbah yang berlainan. Analisis 'Fourier Transform Infrared Spectroscopy –Attenuated Total Reflectance' (FTIR-ATR) membuktikan bahawa kumpulan berfungsi yang penting dalam κ- and ι-karagenan adalah tidak terolah semasa proses penulenan dengan menggunakan kaedah pengendapan alcohol. Enam campuran dengan nisbah κ/ι yang berlainan iaitu 0.0, 0.1, 0.2, 0.3, 0.4 dan 0.5 telah disediakan untuk kedua-dua RC dan SRC. Antara pengukuran 'viscoelasticity' yang dijalankan adalah pergantungan suhu, spectrum mekanik, dan pergantungan tekanan. Keputusan menunjukkan bahawa semua percampuran κ- and ι-karagenan mempunyai ciri-ciri pengelan dua-peringkat dalam kitaran penyejukan tetapi kesan ini adalah tidak nyata dalam kitaran pemanasan. Dalam semua pengukuran 'viscoelasticity', RC menunjukkan nilai modulus dinamik (G') dan modulus ricih hilang yang jauh lebih tinggi daripada SRC. Namun demikian, SRC menunjukan ciri-ciri rheologi yang amat sama seperti RC tetapi pada nilai G' dan G" yang lebih rendah. SRC menunjukan potensi yang tinggi dalam aplikasi produk makanan dengan kos yang lebih rendah berbanding dengan RC.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AMF	Acid-modified Flour
ANOVA	Analysis of Variances
AOAC	Association of Official Analytical Chemist
ARC	Alternatively Refined Carrageenan
ATR	Attenuated Total Reflectance
CC	Cooling cycle
DA	C-O bond of 3,6-anyhydrogalactose
DA2S	Sulphate ester at the 2-position of the anhydro-D-galactose
DNA	Deoxyribonuclei Acid
DSC	Differential Scanning Calorimetry
FAO	Food and Agriculture Organization
FTIR	Fourier Transform Infrared Spectroscopy
G4S	C-O-SO_3 on the C4
GRAS	Generally Regarded As Safe
HC	Heating cycle
HSD	Honestly Significant Differences
IUPAC	International Union of Pure and Applied Chemistry
KOH	Potassium Hydroxide
LBG	Locust Bean Gum
LKIM	Malaysia Fisheries Development Department
LVR	Linear Viscoelasticity Region
NMR	Nuclear Magnetic Resonance
PES	Processed *Euchema* seaweed
PNG	Philippines Natural Grade
PVC	Polyvinyl chloride
RC	Refined Carrageenan
SAOT	Small amplitude oscillatory testing
SPSS	Statistical Package of Social Sciences
SRC	Semi-refined Carrageenan
TPA	Texture Profile Analysis
USD	United State Dollar
W/W	Weight over weight
WHO	World Health Organization

LIST OF SYMBOLS

$(CH_3)_4N^+$	Tetramethylammonium ion
°C	Degree Celsius
Ca^{2+}	Calcium ion
cP	CentiPoises
Cs^+	Cesium ion
E	Young Modulus
G′	Dynamic Storage
G″	Loss Shear Modulus
K^+	Potassium ion
K0E10	0.0 κ/ι ratio
K2E8	0.1 κ/ι ratio
K4E6	0.2 κ/ι ratio
K6E4	0.3 κ/ι ratio
K8E2	0.4 κ/ι ratio
K10E0	0.5 κ/ι ratio
Li^+	Lithium ion
mm	millimeter
mms^{-1}	millimeter per second
N.m	Newton meter
Na^+	Sodium ion
NH_4^+	Ammonium ion
Pa	Pascal
rad/s	Radian per second
rad/s	radius per second
Rb^+	Rubidium ion
T_g	Gelling temperature
T_m	Melting temperature
ι	iota
κ	kappa
λ	lambda
μ	mu
ν	nu

CHAPTER 1

INTRODUCTION

1.1 Introduction

Carrageenan is one of the important hydrocolloids in food industry after gelatin and starch (Van de Velde and Ruiter, 2002). Carrageenan is extracted majorly from the specific species of red seaweed, *Rhodophyta* (Van de Velde *et al.*, 2002). Three major types of carrageenan have been identified by differences on the number and position of sulphate groups which are iota (ι)-, kappa (κ)- and lambda (λ)-carrageenan respectively (Van de Velde *et al.*, 2001; Van de Velde, 2008). According to Pereira *et al.* (2009), carrageenan is a natural ingredient and is generally regarded as safe (GRAS). Carrageenan has a great potential in the food application worldwide as it has the outstanding physical functional properties in food system such as binding, stabilizing, thickening, gelling, and apply extensively to enhance the viscosity and texture of food (Campo *et al.*, 2009; Lee *et al.*, 2008). The food application of carrageenan ranges from frozen desserts, chocolate milk, cottage cheese, whipped cream, instant products, yogurt, jellies, meats and sauces to pet foods (Van de Velde and Ruiter, 2005). Non-food application of carrageenan also covers the industry such as pharmaceutical, printing, textile formulations and cosmetics (Imeson, 2000).

Semi-refined carrageenan (SRC) is another type of product from red seaweed. SRC is also known as Philippines Natural Grade (PNG), alternatively refined carrageenan (ARC), alkali-modified flour (AMF) and processed *Euchema* seaweed (PES) which is the regulatory name (Van de Velde and Ruiter, 2005). Philippines and Indonesia are the major harvest areas for this *Eucheuma* seaweed (*Eucheuma cottonii* and *Eucheuma denticulatum*) which is subjected to a more cost- effective process that excludes the extraction of carrageenan in a dilute solution. SRC is different from the traditionally refined carrageenan (RC) in the acid-insoluble matter content namely 8% to 15% in SRC and 2% in RC respectively. The major component of the acid-insoluble matter is the cellulose from the algae cell wall (Van de Velde and Ruiter, 2005). Insoluble particle will cause turbidity in the sol and gels system of SRC (Gunning *et al.*, 1998). The heavy metal content by Atomic Absorption Spectrometry (AAS) of SRC is higher compared to RC (Imeson, 2000). SRC is suitable for product in which the clarity does not make a significant impact (McHugh, 2003).

In the world total production of carrageenan, food industry is accounted for 70% to 80% of the total amount which is estimated at 45,000 metric tonnes per year. Dairy industry is responsible for 45% of total consumption of the carrageenan production whereas 30% is for the meat and meat derivatives industry (McHugh, 2003). In year 2009, total market estimation for carrageenan is USD 527 million (Bixler and Porse, 2010). Despite the growth in carrageenan market, substitution and extension of seaweed hydrocolloids ingredient by the lower-cost hydrocolloids ingredients are observed due to higher price of hydrocolloids. SRC having advantage of requiring lower processing cost than the standard RC purification. SRC could be cost-effectively sold at two-third of the price of traditional RC. From year 1999 to 2009, compound growth rate of SRC is slightly more than 4% if the pet food industry is excluded (Bixler and Porse, 2010).

According to Bixler *et al.* (2001), nearly pure κ-carrageenan with less than 10% of iota carrageenan can be extracted from *Eucheuma cottonii* (*Kappaphycus alvarezii*), and nearly pure iota carrageenan with less than 15% kappa carrageenan can be extracted from the *Eucheuma spinosum* (*Eucheuma denticulatum*). κ-carrageenan is sulfated gelling polysaccharides consisting of an alternating β-D-galactopyranosyl-4-sulpahate and α-D-3,6-anhydrogalactopyranosyl residues (Stanley, 1990). In the presence of specific cations, κ-carrageenan forms a brittle gel upon cooling and has a stable viscosity over wide pH range (Whistler and BeMiller, 1997). κ-carrageenan has the affinity for monovalent ions as the following sequence: $Rb^+ > Cs^+ > K^+ > NH_4^+ > (CH_3)_4N^+ > Na^+ > Li^+$ (Rochas and Rinaudo, 1980). The ability of κ-carrageenan to form parallel double helix three-dimensional network enables the formation of strong gels (Morris *et al.*, 1980). ι-carrageenan is a gelling polysaccharide with the IUPAC name of (1→4)-3,6-anhydro-2-*O*-sulfonato-α-D-galactopyranosyl-(1→3)-4-*O*-sulfonato-β-D-galactopyranan (Ridout *et al.*, 1996). Gel of ι-carrageenan is clear, elastic and indicates the syneresis and hysteresis resistance (Janaswamy and Chandrasekaran, 2001). Gelation of ι-carrageenan is favored in the presence of calcium ions (Ca^{2+}) due to the cross-link formation which promoting the effect of ions (Morris and Chilvers, 1981; Tako and Nakamura, 1986; Tako *et al.*, 1987). κ-carrageenan and ι-carrageenan are the gel forming carrageenans with the highly distinctive characteristics in nature.

The two major components of rheological properties of food are textural and viscoelasticity properties of food. Textural studies and evaluation are essential in food product development and for optimizing the processing parameters (Meullenet, 1997). In food texture research, both sensory evaluation and instrumental measurement are applied. Texture Profile Analysis (TPA) is initially developed by Szczesniak *et al.* (1963) for General Foods Texturometer. Excellent correlation between texture parameters identified by General Foods group and sensory ratings was shown (Szczesniak *et al.*, 1963). An adaptation had been made on the Instron, TA.XT2 Texture Analyzer and some other universal testing machines to perform a modified TPA (Bourne, 1968; Bourne, 1974). Salt and ion effects on the texture and rheological properties of carrageenan have been studied extensively (Morris *et al.*, 1980; Watase and Nishinari, 1982[a]; Watase and Nishinari, 1982[b] ;Morris and Chilvers, 1983; Watase and Nishinari, 1990; Hermansson *et al.*, 1991; Núñez-Santiago *et al.*, 2010; Thrimawithana *et al.*, 2010). Rheological studies on the effect of aggregation of κ-carrageenan also have been studied (Chronakis *et al.*, 1996). Nishinari *et al.* (1995) had studied the rheological properties of gel-sol transition in κ-carrageenan and agarose system in the presence of sugars. Rheological properties of κ- and ι-carrageenan indicated the significant differences which possessed the distinctive application and potential in the food industry respectively (Piculell, 2006). However, there is very little research on textural and viscoelasticity properties of SRC. This study is therefore aimed at studying the effect of different κ- and ι-carrageenan mixture on textural and viscoelasticity properties of SRC.

1.2 Objectives

1) To study the viscoelasticity properties of κ- and ι-RC and SRC.

2) To study the effect of κ- and ι-SRC ratio in specific combination on viscoelasticity of RC and SRC system.

CHAPTER 2

LITERATURE REVIEWS

2.1 Carrageenan

Carrageenan is a polymer with linear, sulphated galactan which is build up from alternating disaccharide with repeating units of 3-linked β-D-galactopyranose (G units) and 4-linked α-D-galactopyranose (D units) or 4-linked 3, 6- anhydro α-D-galactopyranose (DA units) (Van de Velde, 2008; Van de Velde *et al.*, 2001). The degree of sulfatation varies from 15% to 40% (Van de Velde and Ruiter, 2005). According to Blakemore and Harpell (2010), the major species of *Rhodophyceae* (red seaweed) used in the commercial production of carrageenan include *Kappaphycus alvarezii* (*Eucheuma Cottonii*) and *Eucheuma denticulatum* (*Eucheuma spinosum*). Indonesia, Philippines and East Africa are the major cultivar areas for these tropical species of gelling carrageenans (Blakemore and Harpell, 2010). The diversity of the carrageenan is one of the most prominent features of carrageenan. Great diversity of carrageenan is due to the differences in algal source and the method of preparation, as well as non-gelling or gelling samples. Variations in the primary structure of carrageenan determine the unique gelling abilities of carrageenan-containing units that have the ability to form ordered helical structures.

Depending on the type of carrageenan, high sensitivity of aqueous carrageenan to the composition of aqueous environment especially ionic content is observed. By manipulating the quantity and type of salt added to carrageenan, properties such as thermal stability, elasticity, optical clarity, and yield stress of carrageenan gel can be altered. Gelling carrageenan is extremely versatile due to the diversity of the chemical structure and the profound influence of the environment (Guiseley *et al.*, 1980; Witt, 1985; Bixler, 1996). A wide spectrum of rheological profile, gel texture and properties, synergy interactions with other food gums and protein and molecular charge densities are observed in different types of carrageenan which lead to a great potential in various applications (Blakemore and Harpell, 2010).

Κ-carrageenan contain approximately 22% and 33% of ester sulphate and 3,6-anhydrogalactose respectively and ι-carrageenan contain 32% and 26% respectively. In contrast, ester sulphate present in λ-carrageenan are approximately 37% and 3,6-anhydrogalactose are present in little quantity or usually absent. Danish agar or furcellaran contains 16–20% ester sulphate. Agars are distinctive from carrageenan by having the low ester sulphate (1.5% to 2.5%) compare to high ester sulphate levels in carrageenans. Therefore, carrageenan is best defined as 'polygalactan extracts from *Rhodophyceae* with ester sulphate content of 18–40% and alternate *α*-(1,3) and *β*-(1,4) glycosidic linkages' for food applications (Blakemore and Harpell, 2010).

Commercially, several species in *Gigartina* family of seaweeds also contains continuum of molecular structures for kappa carrageenan or more specifically to the amount of 2-sulphate associated with the 3,6-anhydrogalactose moiety of the idealised structure (Falshaw *et al.*, 2001). The 3,6-anhydrogalactose-2-sulphate content are approximately zero for *Kappaphycus alvarezii* and icreased to about 5–10% for *C. crispus*, 10–15% for *Gigartina stellata*, 20–25% for *Gigartina chamisoi*, 30–40% for *Gigartina radula* and *Mastocarpus crispata* and 45–55% for *Gigartina skottsbergii* and close to 100% for *Eucheuma spinosum* (Blakemore and Harpell, 2010). Protein reactivity and reduction of water gel strength is significantly improved and enhanced by the increase in ester sulphate (Blakemore and Harpell, 2010). 'Kappa-2'-carrageenans are defined as κ-carrageenans with 3,6-anhydrogalactose-2-sulphate contents between about 30% and about 55% (Bixler *et al.*, 2001).

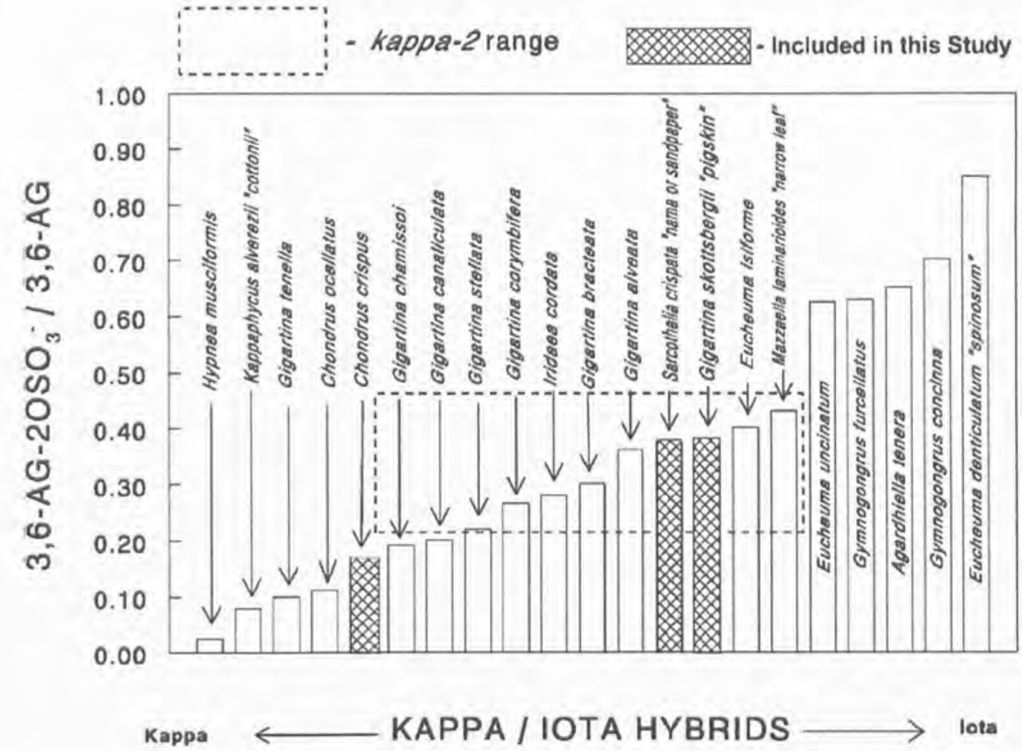

Figure 2.1 3,6-Anhydrogalactose-2-sulfate content of gelling fractions of carrageenophytes

Source: Bixler *et al.* (2001)

Commercial applications of carrageenan are used as gelling, thickening, and stabilizing agents, particularly in food products such as frozen desserts, chocolate milk, cottage cheese, whipped cream, instant products, yogurt, meat, jellies, pet foods, and sauces (Van de Velde and Ruiter, 2005). Application of carrageenan in the food system enables the improvement of texture, viscosity, stability and palatability of food product. Carrageenan also shows its significant application in the non-food industry such as pharmaceutical, printing and textile formulations as well as cosmetics (Imeson, 2000). Functional properties of carrageenan in non-food application incldue absorbing body fluid in wound dressing formulation, stabilizing toothpaste and giving soft skin and silky hair in hand lotion and shampoo as it interacts with human carotene. Persistence viscoelasticity, high robustness, good compatibility and most importantly sustained-release formulations make carrageenan a great ingredient for tablet excipients (Bhardwaj *et al.*, 2000).

Extensive applications and functional rheological properties of the carrageenan indicate its significance in wide range of industry.

2.2 Semi-Refined Carrageenan (SRC)

SRC is also known as Philippines Natural Grade (PNG), alternatively refined carrageenan (ARC), alkali-modified flour (AMF) and processed *Euchema* seaweed (PES) which is the regulatory name (Van de Velde and Ruiter, 2005). The European Commission and the FAO/WHO Codex Alimentarius require the ingredient label of Carrageenan or E-407 and PES or E-407a (Bixler and Porse, 2010). In nature, the biosynthetic precursors known as µ- (mu, D6S-G4S) and ν- (nu, D2S6S-G4S) carrageenan are present and known to reduce the gelation ability of carrageenan (Rees, 1969; Bellion *et al.*, 1983; Van de Velde *et al.*, 2002). Therefore, the hot alkali treatment will initiate the cyclization of the 3,6 anhydro rings which allowed the carrageenan to take on the helical conformation in sol-gel transition and thus improve the performance for industrial application (Rees, 1969; Lawson and Rees, 1970; Jouanneau *et al.*, 2010). In order to obtain SRC, raw seaweed from *Euchema cottonii* and *Eucheuma spinosum* are subjected to hot alkali (KOH) treatment for few hours (Figure 2.1). During the process, sea salt, colour bodies, DNA, lipids, protein and impurities are extracted by the alkali. The seaweed is washed and subjected to sundrying or fluid bed drying before subject to milling to produce SRC.

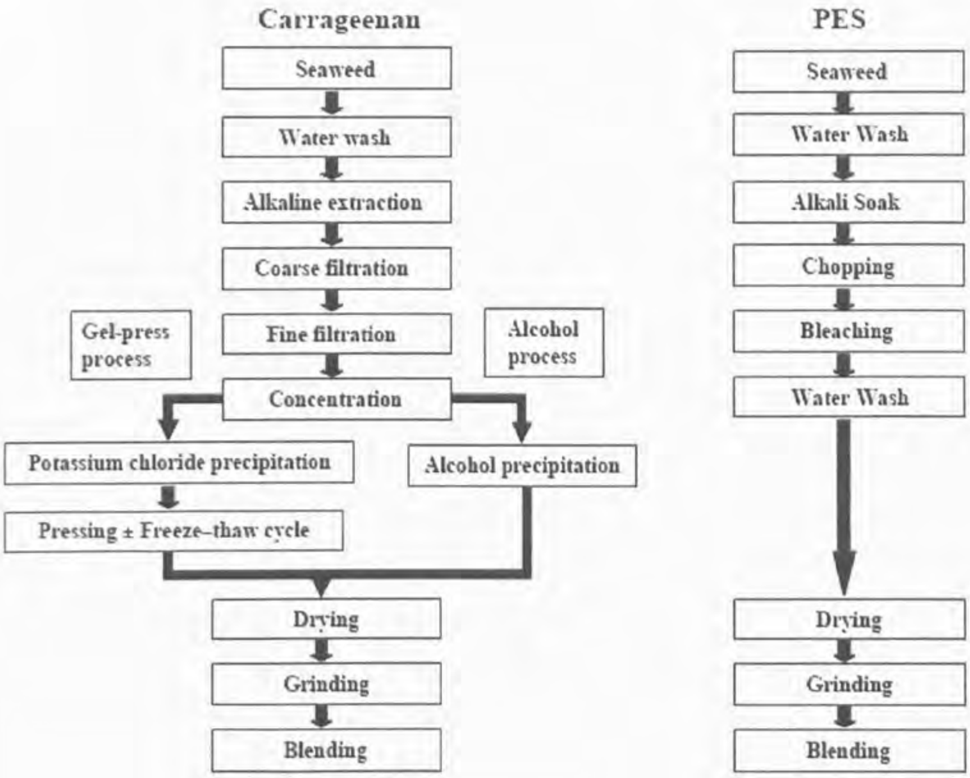

Figure 2.2 Manufacturing process for carrageenan and SRC or PES.
Source: Blakemore and Harpell (2010)

Generally, SRC is different from RC due to the absence of alcohol or salt precipitation at the final stages of purification. This had made SRC profitably sold at approximately two-third the price of RC due to the lower capital cost in the processing. According to Hoffmann *et al.* (1995), further refining of solubilized carrageenan by isopropyl alcohol precipitation, gel pressing or freeze-drying resulted in only minor differences in chemical composition. Hot solution viscosity and gelation properties in the presence of potassium chloride show no significant differences in gelling behaviour between alkali treated weed and the different carrageenan isolates but a higher solution viscosity for the alkali treated weed. κ-carrageenan is the water soluble component in the SRC and shows no significant differences in gelling behavior compared to RC. Compare to RC, SRC has a slightly higher molecular mass of κ-carrageenan (Hoffmann *et al.*, 1995).

SRC has a wide application in wet pet food, meat, dairy and other non-food application such as tooth paste and cosmetic product. SRC is more cost competitive than RC but has weaker solubility than RC at lower temperature (60°C) due to presence of cellulosic and cause reduced clarity in gel (Bixler and Porse, 2010). Solid state NMR, X-ray diffraction and atomic force microscopy had been deployed to study the insoluble component of cellulose I, normally present in algae cell walls (Phillips, 1996; Gunning *et al.*, 1998). Tanaka *et al.* (1996) had studied the effects of this insoluble component on the gelation mechanism. Differential scanning calorimetry (DSC) is also used to study the effect of the insoluble component on the interaction with water (Takigami *et al.*, 2000).

2.3 Market Analysis of Carrageenan

The market for carrageenan is subjected to many factors due to the wide application of carrageenan and diverse variety of carrageenan sources. The primary market for the seaweed hydrocolloids is the food industry where carrageenan is applied as the texturizing agent and stabilizer. The major sale of carrageenan in year 2009 goes to meat (18,500 tonnes) and dairy (14,000 tonnes) out of total sales of 45,000 tonnes for food grade carrageenan. This is mainly due to the special reactivity between carrageenan with protein. Carrageenan also has advantage of application of non-food products such as cosmetics, toothpaste, and tablet excipients in pharmaceutical industry. The growth rate of seaweed hydrocolloids is approximately 1% to 3% per year from 1999 to 2009. However, the growth of seaweed hydrocolloids has been facing a threat from the increment of prices to offset cost and create significant impact on the sales especially the markets of hydrocolloids when it is subjected to substitution or extension by the less expensive ingredients (Bixler and Porse, 2010).

The emerging of low cost producer in Asia such as China has introduced a competitive environment in the hydrocolloids ingredients market which causing a higher cost in the production that is impossible to pass along to food manufacturers. In late 2008 to 2009, the carrageenan producers have finally increased the price because they cannot afford to absorb the high production cost without price increment. The price of carrageenan has been increased from USD 710/dry ton to USD 2,342 from year 2000 to 2008 and finally declined to USD 1,400/dry ton at December 2009. The major factor causing the increase in prices is due to the higher seaweed, chemical and energy costs in the processing. Seaweed shortages have significant impact on the prices of dominant carrageenan-bearing seaweeds which are *Kappaphycus alvarezii* (160,000 tonnes) and *Eucheuma denticulatum* (23,000 tonnes) at year of 2009. Factors limiting seaweed production are observed in the dominant producers (Indonesia and Philippines) of tropical seaweed species. The major factor is global warming which causes a rise in water temperature and heavy raining. As a result, debilitating tropical seaweed disease 'ice-ice' outbreak, exhausted seed stock materials being planted ad depletion of nutrients at cultivar area is observed (Bixler and Porse, 2010). Poorer carrageenan quality happens due to a high demand of carrageenan which leads to immature harvesting of seaweed. Besides, unreliable information on the production statistics and relevant market intelligence circulating among the suppliers and buyers have led to price instability in real time (Bixler and Porse, 2010).

The compound growth rate of SRC is approximately more than 4% from 1999 to 2009 if the declined SRC application in pet food is to be excluded. SRC has shown the greatest growth in the carrageenan market share (22% to 41%) compared to the alcohol carrageenan (32% to 23%) and gel-pressed carrageenan (20% to 26%) from 1999 to 2009. Benefits from substantial cost saving by applying lower cost form of carrageenan has driven food manufacturer to the application of SRC. The rheological properties of SRC which is almost similar to the RC have made the substitution possible in processed meat and less sophisticated dairy industry. The low cost advantage of SRC has exerted the significant impact on the sale of RC (alcohol carrageenan and gel-pressed carrageenan). A better cost structure can be formed through the blending of SRC and RC as a functional blend for food application (Bixler and Porse, 2010).

By observing the chaotic market trend in the unstable supply and price of carrageenan, Malaysia, particularly Sabah as a strategic location for seaweed cultivation has a great potential to be an emerging supplier for carrageenan.

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