Dynamics of Taste Compound Release from Gel Systems

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Submitted in accordance with the requirements for the degree of Doctor of Philosophy

The University of Leeds
School of Food Science and Nutrition

March 2017

The candidate confirms that the work submitted is her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

ACKNOWLEDGEMENTS

I would like to convey my utmost gratitude to Allah s.w.t due to His grace, He has eased my road towards success.

I would also like to express sincere gratitude to my Supervisor Prof Brent Murray for his continuous guidance, patience, motivation and immense knowledge throughout the difficult years. His kindness and concerns are truly appreciate it.

I would also like to convey my utmost gratitude to the rest of the thesis committee for continuous support and knowledge generosity towards Dr Rammile Ettelaie and Dr Laura Laguna Cruanes. The insightful comments, guidance has broaden my knowledge.

I would like to express my sincere thanks towards Ian Hardy for his kind consideration in providing proper training and access on all the laboratory facilities. Without the support it would not be possible to conduct this research.

Not to forget my fellow lab mates for the stimulating discussions, hardships, joy and tears shared, throughout the four years together, Dr Woroud Alsanei, Dr.Tugba Akhtar, Dr. Plearn Nataricha, Dr. Lilynorfeshah Linda Pravinata, Didem Sanver, Phil Bentley, Sandi Darniadi, and Suzaira Bakar.

Close friends who shared the same sleepless nights fighting for success, Siti Fatimah Zakaria, Nurasyikin Hamzah and Ernest Magantig. Those distant friends yet close to the heart, Nooriati Taib, Nadia Razali, Sarahaizad Salleh, Noorul Linda Suraya, Azrin Adrina, Juliet Ooi.

Last but not least, with whom that I shares my deepest fears and euphoria, my family, my mama, Zainoora Hussin (she's would listen even those wordless phone calls only filled with sobs), My papa Che Othman Che Mat, who would watch me from afar. My siblings, Dr. Siti Balqis (who inspired me

in so many ways, Mohd Iryan, Muhammad Izwan, Siti Adlina, Siti Haleeda and Shukri who supported me spiritually throughout the thesis completion.

ABSTRACT

Looking into recent trend on healthy lifestyle, consumers have opted for healthier food product with low sodium and sugar content. However, the reduction of salt and sugar in food products affects the consumer's acceptance. This research aims in gaining a more in depth understanding on the dynamics of taste compounds release mechanism in the oral cavity. There were many studies conducted previously on volatile compounds without any oral processing actions. Furthermore, little study was done on volatile compounds and on samples under submerge condition. The findings of this research may offer small portion of information on the dynamics of food system under submerged condition. An instrumental model measuring flavour release from gel systems was developed. The instrumental setup enabled modelling of unidirectional solute mass transfer from a cylinder of gel into the surrounding buffer (at pH 7). Gels formed from □-carrageenan, alginate and gelatin were compared, due to their wide application in the food industry. Sodium chloride and glucose were chosen as the initial taste compound carrier due to the simplicity and accuracy of recording its release via conductivity measurements and glucometer respectively. In the attempt to mimic certain oral processing conditions, release from gels was studied under a number of controlled conditions: room temperature (ca. 25 ºC) and body temperature (37 ºC), compressed and non-compressed gels. Results showed that release of sodium chloride and glucose were significantly influenced by increasing concentrations of polymer and therefore rigidity of the gels, but the effect of biopolymer types was even more significant. Alginate exhibited the slowest release rate as compared to the other gels, irrespective of gel rigidity. Release rates of sodium chloride or glucose were higher at the higher temperature, but particularly for the gelatin gels, which melted at 37 ºC. Interestingly, compression of the gels did not significantly increase or change on the rate of release of sodium chloride or glucose, so that the differences between the types of gel may be more connected with specific interactions between the gel matrix and the flavour than the ease of

diffusion of the flavour through different gel network structures. Comparing the instrumental data collected, curves agrees with the diffusion theoretical curve which suggest the mechanism governs the release is purely diffusion. Gelatin at higher temperature shows poor fit due to its melting properties. Relatively, faster release in instrumental measurement as compared to theory; this suggests the presence of unbound taste compounds in the gel systems which were readily to diffuse away from the gel matrices. Time-intensity sensory evaluation data revealed the correlation between panellists response with the instrumental analysis. Overall findings showed that the instrumental set up gives reproducible results. Investigation reveals polymer types and temperature plays a significant role in the taste compounds release profile. Understanding the fundamental mechanism lies behind the mechanism or taste compounds release and factors affecting it give the food industry more control over its formulations. Food industry may find ways formulating food product with low sodium and sugar content without jeopardizing the consumer's acceptance.

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ABBREVIATIONS

Gas Chromatography	GC
Mass Spectrometry	MS
Electromagnetic articulography	EMA
Food Drug Administration	FDA
Food Standard Agency	FSA
World Health Organization	WHO
International Organization of the Flavour Industry	IOFI
Texture Profile Analysis	TPA
Monosodium glutamate	MSG
Sodium Chloride	NaCl
κ-carrageenan	κ-C
Mannuronic Guluronnic	MG
Hydrochloric acid	HCl
Hydrogen Potential	pH
Taste receptor cells	TRC
Nucleotide monophosphate	cNMP
Inositol phosphate	IP_3
Time intensity	TI
Maximum Intensity	IMAX
Time to reach maximum	TMAX
Area Under Curve	AUC
Area under decrease angle	IArea
Area under decrease angle	DArea

SYMBOLS

%	Percentage
g	gram
ml	mililiter
mol	moles
mM	milimolar
nm	nanometer
μm	micrometer
mm	millimetre
s	seconds
$\dot{\gamma}$	Shear stress
±	Minus-plus
Δ	Change
μ	Coefficient of friction
A	Area
K	Mechanical strength
R	Rate of release
D	Diffusion coefficient
T	Temperature
De	Deborah number
E	Elastic modulus/Young's modulus
G'	Storage modulus
G''	Loss modulus
F	Force
G	Shear modulus, rigidity
Pa	Pascal

N	Newton
l	Length
p-value	Calculated probability
R^2	Coefficient of determination
t	Observation time
δ	Phase lag
ε	Extensional strain
η	Viscosity
σ	Shear stress
τ	Response time
γ	Strain
κ	kappa
λ	lamda
ι	iota
ϖ	nu
ν	mu
θ	theta

CHAPTER 1

INTRODUCTION, BACKGROUND, AIMS AND OBJECTIVES

1.1 RESEARCH BACKGROUND

Recent trends in healthy living and lifestyle, clean eating (diets designed to have low sodium and sugar content) reflect consumers becoming more health aware and conscious of the labels and ingredients consumed. Due to this trend, the food industry is working hard in meeting the demand of the consumers. Flavour is defined as the combined perception of mouth-feel, texture, taste, and aroma (Baldwin et al., 1998; Hollowood et al., 2002; Stokes et al., 2013). Salt and sugar are essential flavours used widely in the food industry. Salt and sugar are ubiquitous components in almost all food products. The release rate of flavour compounds is highly dependent on food texture and structure, which is usually very intricate and complicated. The complex effect of the food structure leads to the addition of unnecessary high amounts of salt and sugar in the food products. Reduction of these flavours is considered necessary as excessive consumption is closely linked to many adverse health effects (Floury et al., 2009; Mills et al., 2011). Many attempts have been made by industry to reduce salt and sugar, however, reducing the salt and sugar jeopardized the consumer's acceptance of the food products (Floury et al., 2009; Hollowood et al., 2002; Mills et. al., 2011; Renard et al., 2006).

The baseline daily salt consumption established by the Food Standard Agency (FDA) is 6g/day (Mills et al., 2011). Excess intake of dietary salt is estimated to be a leading risk to health worldwide, closely linked to cardiovascular disease and hypertension (Campbell et al., 2012). Sugar is seen by many responsible for the pandemic of obesity and cardiovascular disease and this has become an issue that still needs to be resolved by many dietary bodies. Recommended daily sugar intakes are 6 teaspoons equivalent to 25 g for most women and 9 teaspoons equivalent to 36 g for men (Johnson et al., 2009). Many attempts and campaigns have been conducted among consumers to increase awareness, by dietary advice

bodies as well as industries. In conjunction with the effort displayed, many food companies have launched various food products with lower sodium and sugar content. However, generally consumer acceptance of such products is usually low.

In order to reduce salt and sugar levels in products, the release of the salt and sugar from within the other food components needs to be well understood. The development of an in-vitro mouth model is relatively new. Several attempts have been made by previous researchers in designing an experimental set up that enables instrumental measurement of release flavour release from foods. Emphasis has been made on re-creating mouth conditions that allows the researcher to deduce accurate information on the real flavour release mechanism from the experimental set-up. The methods of design used are divided into two categories 1) the breath exhaled from the mouth is collected and analysed by mass spectrometry (MS) or gas chromatography (GC) 2) a model system is constructed, that attempts to mimic what occurs in the mouth and the effluent from this model system is collected and analysed using MS or GC-MS (Elmore & Langley 2000). Both of the methods have been widely applied. Using human studies is highly dependable on individuals, and the variation among individual varies upon many factors such as mouth size, gender, age and many more. In relation to the previous study, it focuses more on volatile compounds and little research has been conducted on non-volatile taste compounds such as salt and sugar. Furthermore, model designs previously invented have presented some flaws such as listed below:

- Previous studies focus more on the release of volatile compounds under static conditions, whereas the mouths are very dynamic. Experimental designs indicate the measurement of the volatile release in a static condition which cannot act as an actual representation of the real mouth condition which is more dynamic and complex.
- Number of studies performed on purely volatile compounds with the absence of a polymer.

- Not considering samples under submerged conditions as samples are usually coated or submerged in saliva.
- Most studies performed used purely samples, with the absence of any oral processing actions.
- Not altering the pH suitable for mouth conditions.

In overcoming the above disadvantages, vessels model systems need to take into account of several factors such as the:

- Inertness
- Size
- Shape
- Sample introduction
- Agitation of the sample
- Temperature
- Ease of modification and connection to the measuring device

In designing a functional instrumental mouth model which is comparable to the actual human mouth model, it is important to identify the step involved in the oral processing of certain food components. Food oral processing involves a complex set of processes beginning with the ingestion of food until swallowing. The processes are interlinked and dependent on each other in timing and extent. This process divided into six distinct stages by Stokes et al. (2013) which are 1) first bite 2) comminution 3) granulation 4) bolus formation 5) swallow and 6) residue. Mastication is a complex function which is orchestrated by a number of parts including muscles and teeth, lips, cheeks, tongue, hard palate and salivary gland. The tongue plays a major part in initiating the deformation process by pressing the food upward the hard palate (Chen, 2009; Malone et al., 2003; Mills et al., 2011). Normal liquid mouthfuls were reported to be 30 ± 10 g for adult males and 25 ± 8 g for adult females (Mills et al., 2011). The same authors also reported the average weight of banana to fill the oral cavity under a normal eating condition as 18 ± 5 g for adult male and 13 ± 4 g for adult females.

The applications of food colloids and hydrogels in the food industry are extremely wide and have been a part of the consumer's everyday diet with products such as condiments, sauces, dressings, ice creams and many more. In order to comply towards the recommendations from health agencies, nutritionists and boards of various agencies (e.g. FDA, FSA and WHO), many colloidal studies are largely focusing on gaining fundamental understanding of their behaviour leading to the reduction of ingredients such as fat, salts and carbohydrates as well as targeted delivery of nutrients. Due to wide applications of these food materials, this sparks interest in conducting research on the effect of the food material in flavour or taste compounds release. The addition of hydrogels contributes to the complex food microstructure which affects the release of flavours into the oral cavity. The addition of hydrogel in the certain food components will affect the microstructure physical and chemical properties of food component adding up to its complexity. This complexity can lead to the unnecessary excessive addition of the salt, sugar and other flavouring. Complexity can lead to the unnecessary excessive addition of the salt, sugar and other flavouring. Moreover, the complex structure of food gels and colloids is also an interesting tool that could be manipulated in designing healthier food without compromising its organoleptic properties.

1.2 AIMS AND OBJECTIVES

The main objective of the research study is to gain in-depth understanding on the relationship between various factors affecting the dynamic of the food flavour release in gel systems. Previous researchers have listed the possible factors affecting the flavor release profile of a certain flavor component. Factors identified are as follows;

a) Polymer concentration
b) Temperature
c) Compression
d) Physicochemical properties of the polymers
e) Physicochemical properties of the taste components

f) Physical and chemical interaction between the taste compounds and polymer

This research project investigates the release behavior based on the above-listed factors.

Flavour can be considered as comprising of volatile components that are sensed in the nose (aroma) and non-volatile components that are sensed on the tongue (taste) shown in **Figure 1.1**. Extensive studies have been done on the sensation and behaviour of the volatile compounds both in vitro and in vivo. Methods for analysing flavour concentrated on the volatile components because of their importance in overall flavour and because they are more amenable to analysis by instrumental means (e.g. by gas chromatography - mass spectrometry; GC-MS (Taylor & Linforth 1994). However, relatively little research on the detection of the non-volatile taste compounds on the tongue has been done. This was due to the difficulty in designing the chamber/vessel and determining the accurate method of measuring the release of the flavour compound. Also, most research has been conducted in static conditions which cannot be an accurate representation of the flavour release in the mouth as the process is a very dynamic. Most flavour release studies are performed on emulsion samples such as protein-polysaccharide gels (such as whey protein isolate-gellan gums) and gums (gellan, xanthan gum etc.). Little work has been done on pure gel systems such as carrageenan, alginate and gelatin. The selection of the gel types mentioned is due to the extensive application food industry. Furthermore, the selection of hydrocolloids (gels) used in the research studies, was based on the variation on the physical and chemical properties that it offers. Gels with different chemical and physical properties were anticipated to give different taste compounds release profiles.

Upon the completion of this thesis we are hoping to answer the following key research questions:

1) Does the instrumental set up gives reproducible results?
2) Does the listed parameters (polymers concentration, temperature, compression, physicochemical properties of the polymers,

physicochemical properties of the taste components, physical and chemical interaction between the taste compounds and polymer) plays a significant role in the taste release?

3) What are the mechanisms that govern the release of the taste components?
4) Do the instrumental measures give the same results as the sensory evaluation studies? Are there any correlations between the two studies?

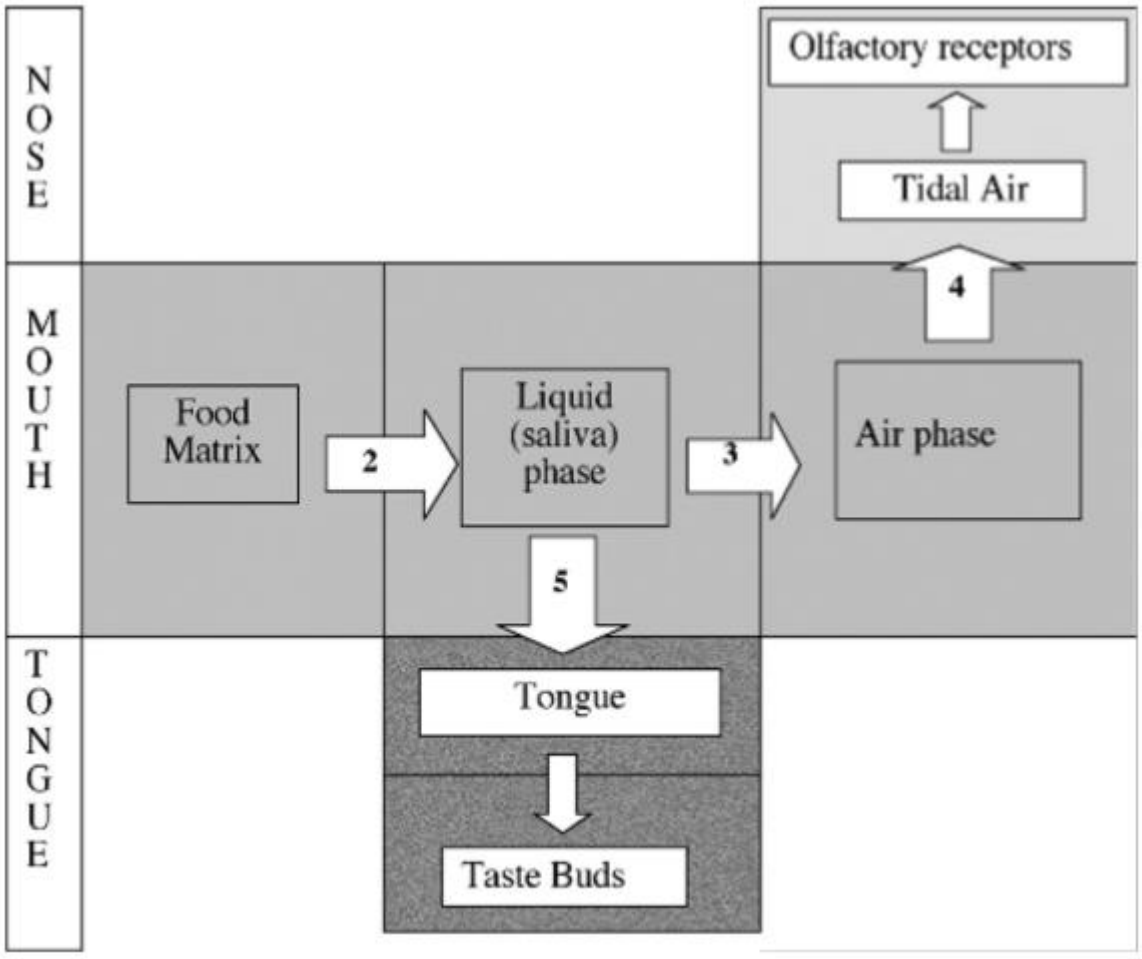


Figure 1.1 Schematic representation of flavour release in vivo and subsequent flavour transport to the receptor of mouth and nose. Adapted from Taylor (2002).

CHAPTER 2

DETAILED SURVEY ON EXISTING LITERATURE

2.1 HYDROCOLLOIDS AND FOOD GELS

The application of hydrocolloids in the food industry is beneficial in the alteration of food texture resulting in the improvement of the quality and shelf-life of the food products. There are many types of colloidal systems such as dispersions, suspensions and network colloids. But this research study focuses on network colloids, where two or more phases exist as an interpenetrating network with elements of the colloidal dimension. A colloid having a liquid dispersion medium, but whose overall properties are solid like, is called a gel (Dickinson, 1992). Hydrocolloids are also defined as heterogeneous group of long chain polymers (Saha & Bhattacharya 2010 ; Milani & Maleki 2012). Hydrocolloid gelation can be either irreversible (single-state) or reversible (Milani & Maleki, 2012; Ahmed, 2013). The colloids used are usually polysaccharide or protein. They are then further characterized by their properties of forming viscous dispersion and/or gels when dispersed in water. Due to their large number of polar groups this increases their affinity for binding to water. They produce a dispersion which is intermediate between a true solution and a suspension that exhibits the property of a colloid. Hydrocolloids are applied as thickening agents and gelling agents causing an increase of the viscosity of the aqueous phase which causes significant changes to the stability of food products. Types of colloids and their application are shown in **Table 2.1** and **2.2.**

Food gels are a high moisture content three dimensional polymeric network that resist flow under stress and more or less retain their direct distinct structural shape. The definition of a gelled material was coined by Ferry (1980) explaining that a gel is a substantially diluted system which resists steady state flow. This includes materials or substances which exhibit solid like properties while a vast excess of solvent is present. Gels consist either of filled networks of interacting particles such as fat crystals in the case

of butter or from cross-linked polymers that form space filling networks such as in the case of boiled egg. The formation of the network is due to different types of interaction between the polymers. These interactions could be covalent reactions or physical interactions between different types of polymers such as the depletion force, Van der Waals forces, electrostatic forces and hydrogen bonding (Renard et al. 2006). Food gel viscoelasticity is defined by the storage modulus (G'), which describes the elastic properties and is larger than the loss modulus (G''), which describes the viscous properties. However G' is relative small (generally $\leq 10^7$ Pa) as compared to true solid material (10^9-10^{11} Pa) (van Vliet et al., 2009).

Table 2.1 Hydrocolloids used as gelling agents adapted and modified from (Banerjee & Bhattacharya, 2012)

Gelling agent	Source	Gelation condition	Application	References
Agar	Red algae (*Gelidium* sp.) or seaweeds (*Sphaerococcus* euchema)	Thermoset (reversible)	Used as laxative, vegetarians gelatin substitute, in jellies and Japanese dessert such as anmitsu	Matsuhashi (1990)
Cereal flour and starch (cooked/instant/gelatinized/modified	Potato, wheat, rice, maize, tapioca	Thermoset (reversible)	Secondary gelling agent, cost effective, rice flour based gels	Boland et al. (2004)
Carageenan (κ, ι, λ, hybrid, blend, refined)	Red seaweed (*Chondrus crispus*)	Thermoset (reversible)	Desserts, gel to immobilize cells/enzymes	Stanley (1990)
Pectin (high-methoxyl, HM and low methoxyl, LM)	Hetero polysaccharide derived from the cell wall of higher terrestrial plants and fruits like citrus peel, guava and apple	Thermoset (reversible)	Jam, jelly, marmalade, jujubes, yogurt	Rolin, Claus and De Vries (1990)
Guar gum	Endosperm of guar gum	Thermoset (reversible)	Pastry fillings, yogurt, liquid cheese products and sweet dessert	Banerjee & Bhattacharya (2012)
Gum arabic	Sap taken from two species of the *Acacia* tree, *Acacia Senegal* and *Acacia seyal*	Thermoset (reversible)	Hard gummy candies, chocolate candies and chewing gums	Banerjee & Bhattacharya (2012)
Xantham gum	Fermentation of glucose or sucrose by *Xanthomonas campestris*	Thermoset (reversible)	Salad dressing and sauces, helps to stabilize the colloidal oil and solid components against creaming by acting as an emulsifier in different foods	Banerjee & Bhattacharya (2012)
Alginate (alginic acid)	Brown seaweeds (*Macrocystis pyrifera*, *Ascophyllum nodosum* and various types of *Laminaria*)	Chemical set (irreversible)	Jellies, gelation with divalent cations, cell immobilization and encapsulation, appetite suppressant	J. Sime (1990)
Konjac mannan	Tubers of Konjac (*Lasioideae*	Thermoset	Gelling, texturing, water	(Banerjee &

	amorphophallus)	(reversible)	binding agent, to provide fat replacement properties in fat-free and low-fat meat meat products	Bhattacharya, 2012)

Table 2.2 Protein use as gelling agents

Gelling agent	Source	Gelling condition	Applications	References
Gelatin (acidic/alkaline)	Animal skin and bones (made by partial hydrolysis of collagen animal connective tissue)	Thermoset (reversible)	Gelling agent in gelatin desserts, jelly, trifles and confectionaries, jam, yogurt, cream cheese and margarine	Jonhnston-Banks (1990)
Whey protein	Acid or sweet dairy whey, separated from casein curd as the soluble fraction during cheese manufacture	Thermoset (reversible)	Gelling agent and thickeners in food industry	Aguilera & Baffico (1997)
Egg protein	Egg	Thermoset (reversible)	Gelling and thickening agent for confectionary products	Woodward (1990)

2.1.1 κ-CARRAGEENAN (κ-C)

Carrageenan plays significant roles in the food industry acting as thickening, gelling and stabilizing agent and is widely utilized in many foods such as sauces, meats and dairy products. The polysaccharides are responsible in modifying and achieving a certain desirable texture in a food components

resulting to the creaminess, smoothness of a certain food products. The combination of carrageenan and starch enables modification and manipulation of certain food structures which lead to 50% reduction of fat content in food. The commercially recognizable carrageenans are the kappa (κ), iota (ι) and lambda (λ). Carrageenan are found in marine red algae of the family Rhodophyceae (Dunstan et al., 2001; Viebke, Borgstrom, & Piculell, 1995). Carrageenan constitutes 30 to 80% of the cell wall of these algae, and their functionality depends on the species, season, and growing conditions. They are composed of linear chains of D-galactopyranosyl units linked via alternated (1→3)-β-D-and (1→4)-α-D-glucoside, in which sugar units have one or two sulfate groups (Hoffmann et al., 1995; Viebke et al., 1995; Rochas et al., 1990). Depending on the amount and position of the SO^{3-} group carrageenan are classified as υ, ϖ, λ, γ, κ, ι, and θ types (**Figure 2.1**).

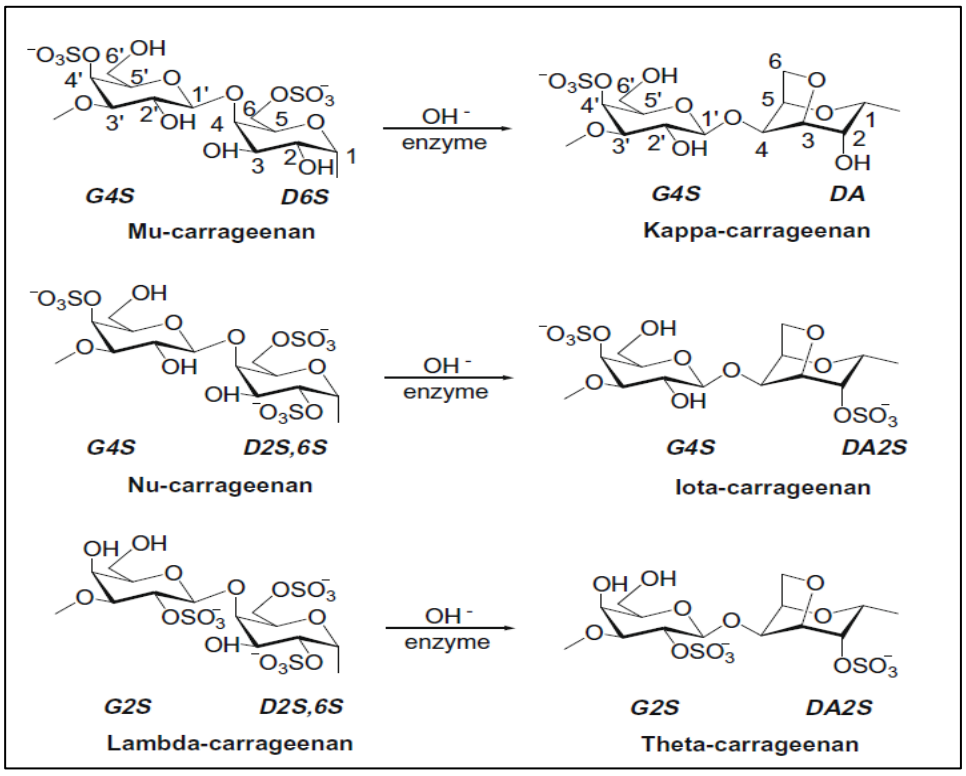


Figure 2.1 Schematic representation of different structure of dimeric units of commercial carrageenan and related structure (Gulrez et al., 2003)

2.1.2 ALGINATE

The extensive application of alginate ranges from food, pharmaceutical and medical purposes. Alginate is utilised in food industries as thickeners and gelling agent, changing physical food structure in achieving desirable texture. The pharmaceutical industry uses alginate as excipients, as an inactive substance that serves as the vehicle or medium for a drug or any active substance. Wide applications of alginate in these industries are due its biocompatibility, low toxicity and low cost (Lee & Mooney, 2012). Alginate is a naturally anionic polymer extracted from various species of brown seaweed such as *Lamanaria hyperborean, Laminaria digitate, Laminaria japonica and Macrocystic pyrifera*. Alginate is located in the cell wall of the algae which act as building block cementing the cells together and giving mechanical properties to the algae. Alginates are unbranched copolymers of (1→4)-linked β-D-mannuronic (M) and α-L-guluronic acid (G) residues. The ratio of these residues β-D-mannuronic (M) and α-L-guluronic acid varies among algal species, the age of the plant and the type of tissues extracted but the ratio is reported to be 2:1 respectively. The uronic acid groups in the acid form (-COOH), named as alginic acid are insoluble in water. The sodium salts of alginic acids (-COONa) or sodium alginates are water soluble. Based on the residues, the three types blocks in alginates have been characterised by partial hydrolysis with HCl; i.e. mannuronic-guluronic (M-G block), mannuronic (M-block) and guluronic (G-block) **Figure 2.3**. The main unique advantage of alginate is its ability to form heat-stable gels that can set at room temperatures.

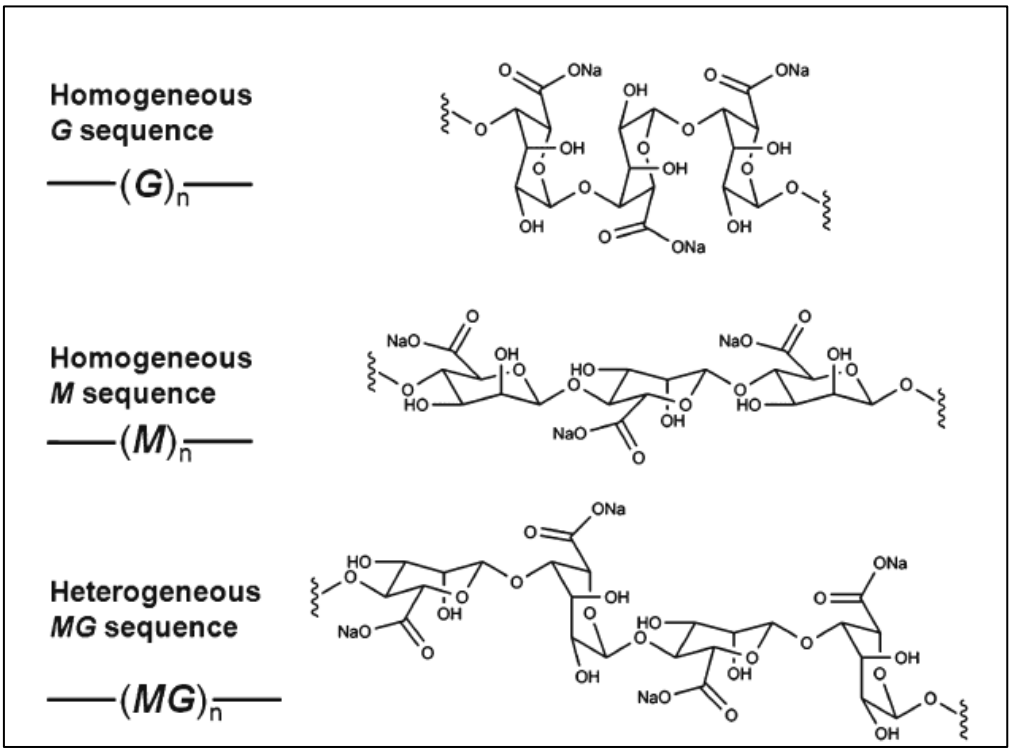


Figure 2.2 Sodium alginate sequences (from top to bottom): homogeneous G sequence, homogeneous M sequence, and heterogeneous MG sequence. M mannuronic acid, G guluronic acid. (Fu et al., 2011)

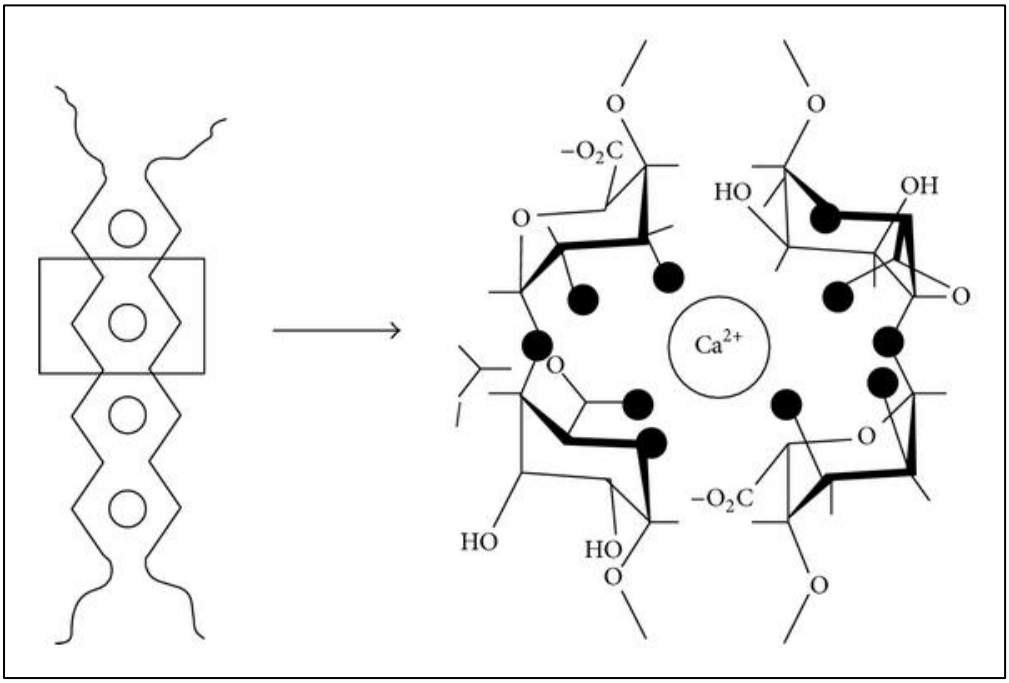


Figure 2.3 Schematic drawing and calcium coordination of the "egg-box" model, as described for the pair of guluronate chains in calcium ALG junction ones. Dark circles represent the oxygen atoms involved in the coordination of the calcium ion. Reproduced from with the permission of the American Chemical Society (Sosnik, 2014).

Since alginate is an anionic polymer, it exhibits unique physical properties via electrostatic interaction. One of the prominent property of aqueous solutions of alginate is their ability to form firm gels on addition of di- and trivalent metal ions such as bivalent alkaline earth metals (Ca^{2+},Sr^{2+},and Ba^{2+}) or trivalent Fe^{3+} and Al^{3+} ions (Montanucci et al., 2015). This is a result of ionic interaction and intramolecular bonding between the carboxylic acid groups located on the polymer backbone and the cations that are present. Alginate mechanism of gelation begins in regions of guluronate monomers with the presence of divalent cations such as Ca^{2+}. In the presence of the divalent ions, one guluronate is linked to a similar region in another molecule. The calcium ionically substitutes the carboxylic site. A second alginate strand can also connect at the calcium ion, forming a link in which the Ca^{2+} ion attaches two alginate strands together. The result is a chain of calcium-linked alginate strands that form solid gel. The divalent calcium fits snuggly into the electronegative cavities which resembles the eggs in an egg box, which is

also the origin of the term “Egg Box” model as shown on **Figure 2.4**. This binds the alginate polymer molecules together by forming junction zones, thus leading to gelation of the solution. Alginic acid is slightly soluble in water and in most organic solvents. It is soluble in alkaline solution. However, sodium alginate dissolves slowly in water forming viscous, colloidal solutions. It is insoluble in alcohol and in hydro-alcoholic solutions. Literature reported the range of the molecular weight that is commercially available is between 32 000 and 400 000 g/mol. The molecular weight of the sugar unit is 222 g/mol.

2.1.3 GELATIN

Gelatin is a type of gelling and thickening agent which is widely applied in in various fields such as the food industry, medical, pharmaceutical and many more. Gelatin is a common thickening and gelling agent which has a very wide application in the food industry. Gelatin is a protein ingredient which derived from collagen that undergoes structural and chemical degradation. The source of gelatin is the white fibrous material in the connective tissues such as skin, tendon, bone and etc of bovine, porcine and fish tissue. The amino acid content sequence varies, but highly consistent in the large amount of proline, hydroxyproline and glycine (**Figure 2.5**). The proline plays a significant role as it promoted the formation of the polyproline II helix, which determines the form of the tropocollagen trimer. The basic molecular units of collagen is the tropocollagen rod, a triple helical structure composed of three separate polypeptide chains (total molecular weight ~ 330 000, persistence length ~ 180 nm) (Murphy, 1991). Gelatin is slightly different from many other hydrocolloids in being made of proteins and being digestible.

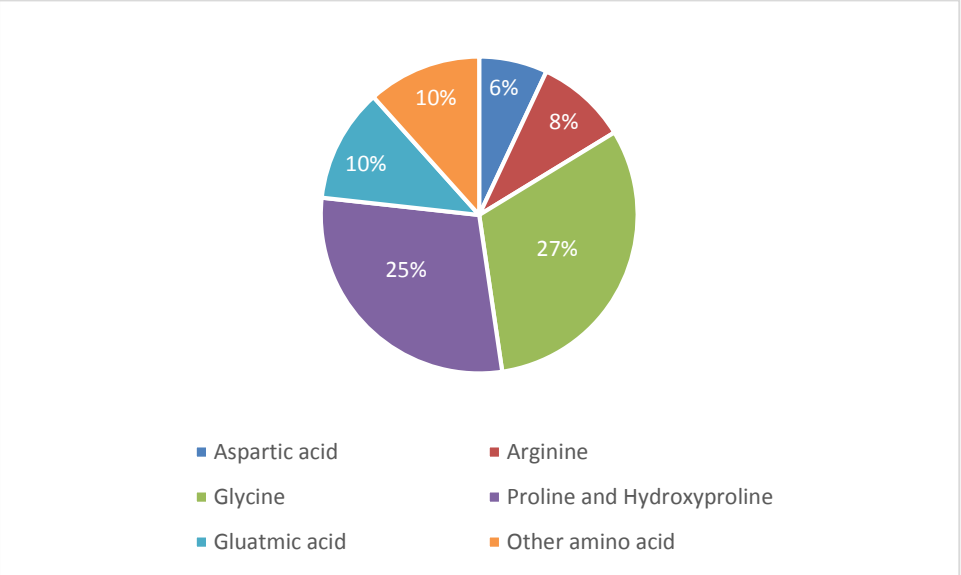


Figure 2.4 Amino acid composition in gelatin.

The properties of gelatin as a typical rigid chain high molecular weight compound are similar to other rigid chain polymer in many various aspects. Specific conditions such as temperature, solvents and temperature allow the manipulations on the gelatin macromolecule which is flexible and allows the gelatin to produce a wide variety of conformations. One of the most prominent characteristics of gelatin is its “melt-in-the-mouth” characteristic. The manipulation of these variables proves the flexibility of gelatin molecules and enables the possibilities of many different varieties of gelatin characteristics. Gelatin produces thermo-reversible gels; the network formation is via hydrogen bonded junctions zones. Aside from that, hydrophobic and ionic also involved in the gelation of gelatin gels. Gelatins are known for their uniqueness with the presence of both acidic and basic functional groups in the gelatin macromolecules. Some other visible peculiarity of gelatin lies in its capacity to form specific triple-stranded helical structure not observed in other synthetic polymers (this structure is formed in solutions at low temperature).The rate of formation of helical structures depends on factors such as the presence of covalent cross bonds, gelatin molecular weight, the presence of amino acids and the gelatin concentration in solutions. Gelatin traits also lie in the specific interaction with water which

is different from other synthetic hydrophilic polymers. This specific trait governs the structural and physicochemical properties of gelatin in the solid state.

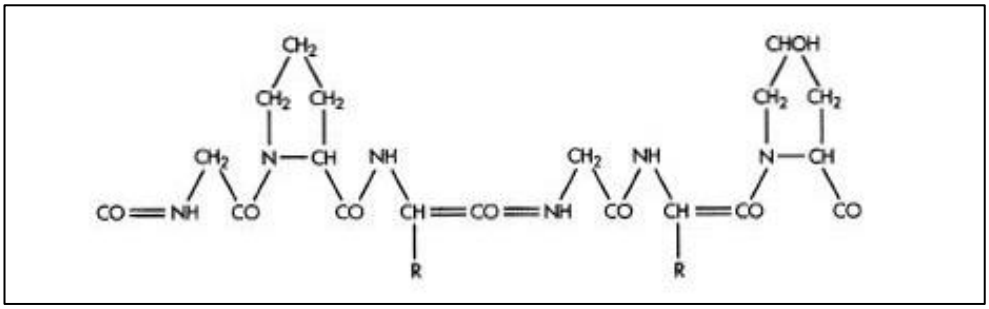


Figure 2.5 The chemical structure of gelatin from Murphy (1991).

One of the most significant characterization properties of gelatin is known as “bloom”, which is a function of the molecular weight of gelatin. The gel strength properties are related to α- and β- chains components in the gelatin. The bloom strength refers to the strength which is also an important property in the food industry. Bloom range determines the gelatin gel strength and divides it into different category. The “bloom” value ranges from 50 to 300. For instance, Type B gelatin with gel strength from 125-250 is commonly utilised for confectionary products. Type A gelatin with the lowest bloom number 70-90 produces weak gels are widely applied in wine and juice refinery. The gelatin melting point is the temperature at which gelatin softens sufficiently to allow the carbon tetrachloride drops to sink through. Melting points of gelatin are highly dependent on the gelatin concentration and maturing temperature.

2.2 FRACTURE MECHANICS IN FOODS

2.2.1 INTRODUCTION

Food texture is associated with all the rheological and structural attributes of a product perceptible by mechanical, tactile, visual and auditory receptors (Ross & Hoye, 2012). Texture and rheology are the key factors in food

acceptability by individuals. Attributes that contribute to the consumer acceptability is the food texture itself as well as flavour compound released during mastication. Past studies have provided useful information in designing food products; which increase acceptability value. Food texture is divided into two components: first, perceived texture via human senses and second, rheology. Perceived texture includes attributes such as mouth-feel, hardness, chewiness, gumminess and adhesiveness. Rheology is defined as the science of deformation and flow. Combinations of these attributes (rheological behaviour and perceived texture) determine the mechanical properties of a food. Mechanical properties are usually associated to the characteristics of the food component with respect to their behaviour during consumption, meal preparation and production. The mechanical properties among food components vary widely. Liquid food such as milk and varieties of beverages flow rapidly under low force stress. Semisolid food such as ketchup, mayonnaise and numbers of desserts flows under higher force stress application. With increasing force they yield and the mechanical behaviour changes from solid-like to liquid-like. Solid product such as candies, breads, chocolate bars and types of cheese does not possess any significant flow behaviour and fracture once a large enough amount of force is applied resulting in fracture and deformation (breakdown).

2.2.2 DEFINITION OF FOOD TEXTURE

Texture is derived from the Latin word *textura* meaning weave, and was initially used to demonstrate the structure, feel and appearance of fabrics. It was not until 1660s that texture was used to describe “the constitution, structure or substance of anything with regards to its constituents, formative elements, according to Oxford English Dictionary. Together with that, various attempts were done to define food texture in some international agreements with the development of international standards ISO 5492 , International Organization for Standardization (1981) which define texture as “All the mechanical, geometrical and surface attributes of a product perceptible by means of mechanical or tactile and where appropriate, visual and auditory

receptors'. One of the earliest definitions of food texture was provided by Szczesniak (1963) as 'sensory manifestation of the structure of food and the manner in which this structure reacts to the forces applied during handling and, in particular, during consumption'. To simplify, texture is a quality attribute that is closely linked to the structural and mechanical properties.

Food material rheological properties in food vary widely as, ranging from thin liquids such as water and wine to hard, solid products such as biscuits and candies. The wide variation of foods exhibits textural complexity as well. According to Szczesniak (2002) since texture is a multi-parameter, there is a large number of words used to define certain textural characteristics or properties such as hardness, adhesiveness, cohesiveness, springiness, gumminess and chewiness.

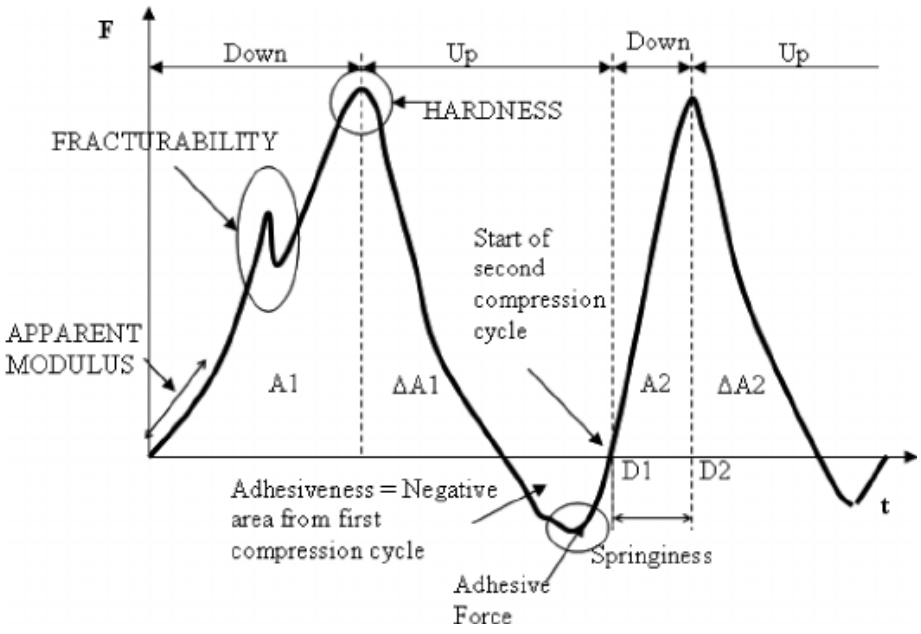


Figure 2.6 Force- time curve obtained from texture profile analysis (TPA) (Szczesniak 2002)

2.2.3 MECHANICAL PROPERTIES AND STRUCTURE OF SOFT SOLIDS

The quality of many food products is highly dependent on its structure and mechanical/rheological properties. Therefore, in the food industry the characterization on the food product mechanical properties is essential.

Mechanical/rheological properties are known to change with storage time. The mechanical or rheological tests conducted and the information obtained can be utilised to monitor food quality and freshness. The complexity of the food structure is seen to play a key role on a flavour release profile. Texture profile analysis (TPA) obtained defines the mechanical terms/properties as shown in **Figure 2.7**. The terms used in TPA apply to food with more solid-like characteristics.

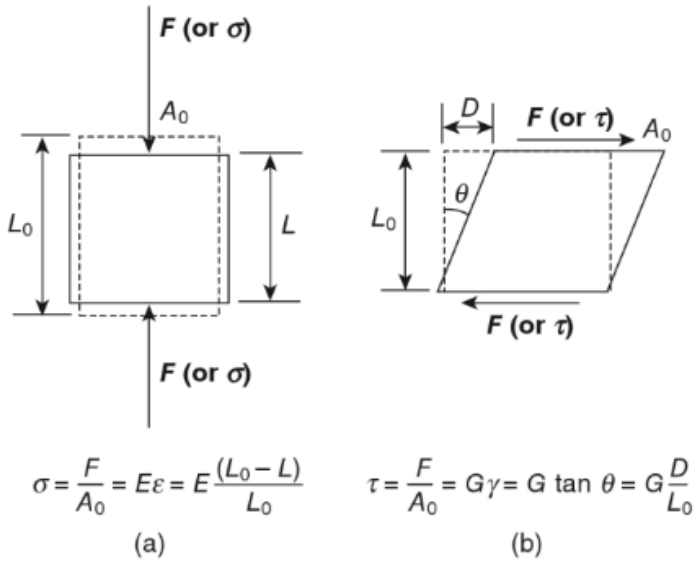


Figure 2.7 Uniaxial compression (a) and shearing b) of a sample or product. Uniaxial compression of a sample with and original length L_0 and area A_0 and the Young's modulus E. (b) Shear stress τ acting on opposite planes causing the distortion of the specimen with the shear modulus G and the area of A_0. Adapted from (Lu 2013).

Common variables in studying and measuring food texture and rheology are Force (*F*), deformation (*D*), and time (*t*).The force deformation relationships of any materials are dependent on time or loading rate. *Stress* is expressed in force per unit of are (N/m^2 or Pa (pascal)), which has the same unit as pressure. Stress is usually accompanied by external factors such as temperature (thermal stress) and humidity (hygroscopic stress). *Strain* is a measurement of deformation at a point on a plane in an object; it measure the unit change of the distortion of the size or shape of an object with respect to its original size or shape and is a dimensionless quantity.

Figure 2.8 exhibits two basic types of stresses, represented by σ, known as the normal stress, that acts in a directional normal (perpendicular) to the plane of the object and the other is the shear stress, τ, tangential to the plane on which the forces act.

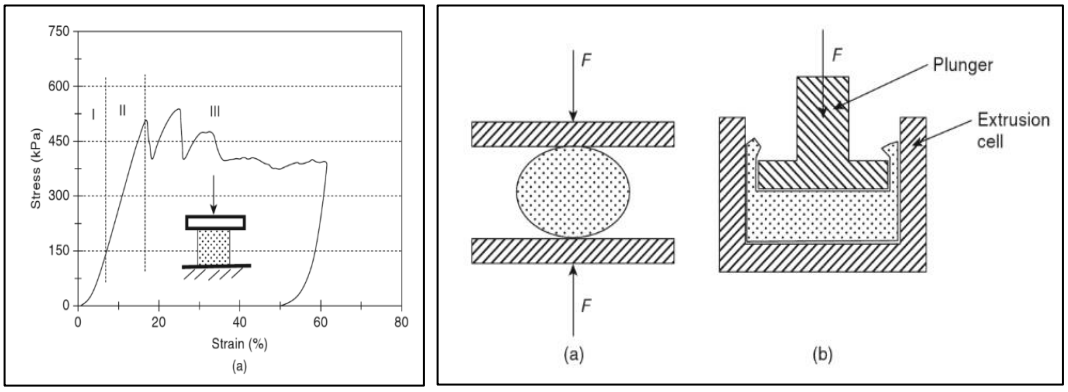


Figure 2.8. Example of Stress-strain (or *F-D*) curves of cylindrical apples tissue specimen under uniaxial compression. The stress-strain curves are approximately categorize into three phases of deformation: elastic, yielding and post yielding. Two types of compression test: (a) the uniaxial compression test between plates and (b) the simple compression-back extrusion test. Adapted from (Lu 2013)

Compression testing is one destructive method widely applied in measuring the basic mechanical properties of a large variety of materials and food product including gels, fruits, vegetables, grains and processed food. Compression tests are often applied on cylindrical specimens excised from food samples, if possible, under uniaxial loading. There are two types of compression performed on samples: uniaxial compression between two plates and a confined compression test, such extrusion. In uniaxial compression, a unidirectional force is applied to the sample and the sample is allowed to expand freely in the other two directions. Continuous force is applied until it breaks or is completely distorted. In contrary to simple compression, compression-extrusion tests are applied to liquids, soft gels, fats and some fresh and processed fruits. Force is applied through a plunger to compress the food in the test cell until it crushes and flows through the gap between the plunger and the cell.

2.3 FOOD ORAL PROCESSING

2.3.1 FOOD ORAL PROCESSING

Food oral processing allows food intake and metabolism process that delivers energy, distributing essential nutrients throughout the whole body. Understanding the food oral processing is very important in order to investigate the controlling factors that affect the human sensory perception which directly linked to the overall acceptance of a food product. Food oral processing involves many oral operations such as first bite, chewing and mastication, transportation, bolus formation and swallowing (Chen 2009). According to Chen, food enjoyment by the consumers is a combined perception of multi-contributions, including texture, the flavour and taste, and the visual appearance. Oral processing is seen as a bridge between food texture and sensory perception (Stieger & van de Velde 2013). For this section will provide a brief explanation on the fundamentals of oral food processing. According to Stieger & de Velde (2013), food oral processing is a combination of movements that allows the breakdown of food and ensures the food is ready and safe to swallow. The significance of food oral processing was highlighted by Hutchings and Lillford in 1988 where they sketched the dynamic breakdown of different types of food structure from its initial stage to the formation of bolus that is ready to be swallowed. The degree of lubrication and the degree of structure plus the mastication time were visualized as the key parameters, creating the three dimensional oral processing model as shown in **Figure 2.10**.

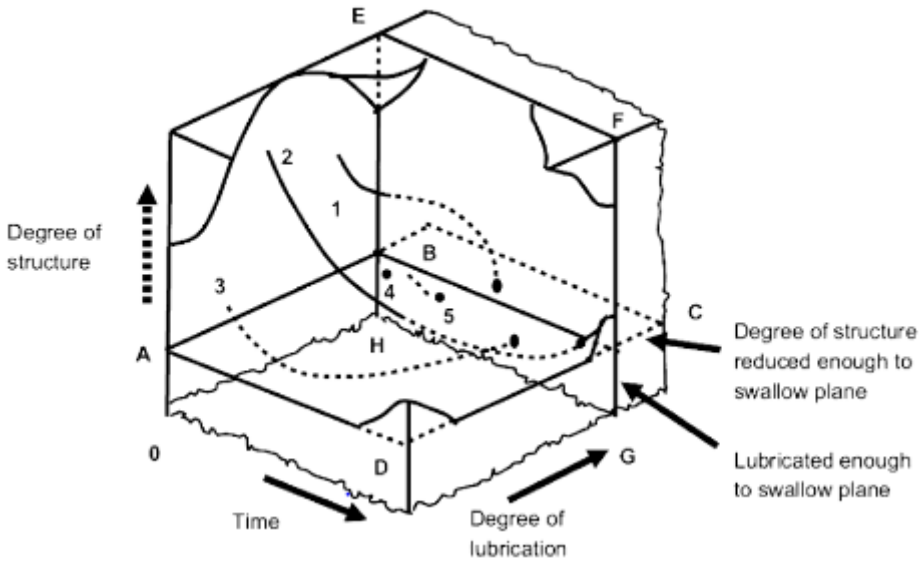


Figure 2.9 Schematic presentation of the dynamic breakdown pathway in different foods according to Hutchings and Lillford (1988). Diagram reported from Chen (2009)

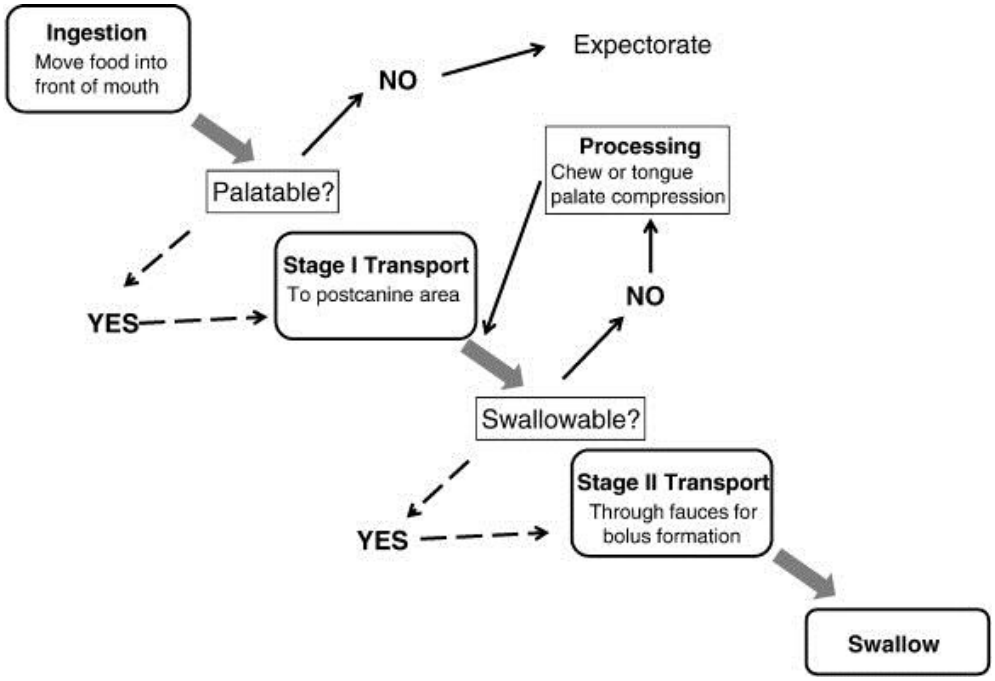


Figure 2.10 Model for Feeding by Pascua et al. (2013)

According to a review by Chen (2009) and Pascua et al. (2013) food oral processing involves serial of decision makings and oral operations as represented by **Figure 2.11**. The review further explained that it is crucial that the process occurs in the right order and is well coordinated. The above model summarize the serial decision making ranging from the grip, first bite,

fracture, size reduction, transportation and swallowing. Decision making in oral processing actions is usually affected by the structure and the physical properties of food. For instance, liquid foods are usually directly transported without size reduction. Food products which undergo size reduction processes undergo further decision making to continue chewing or to transport the food particles for swallowing. Structure breakdown usually continues until fragments reach a critical size particle size ranging from 0.8-3.0 mm**. Figure 2.12** exhibits length scales of some structural elements in food products.

2.3.2 ORAL PHYSIOLOGY

The oral cavity is the main path towards the digestive tract. Mastication plays a significant role in oral processing. The combined function of the teeth, muscles of mastication and salivary glands allows the food to be shredded and broken down for swallowing. The teeth are the hardest tissues and participate in many other various oral activities such as food ingestion, pronunciation of words and many more. The mastication muscles apply the forces needed to allow jaws elevation which enable food to be shredded and broken down between the teeth as the lower and the upper arches comes into contact.

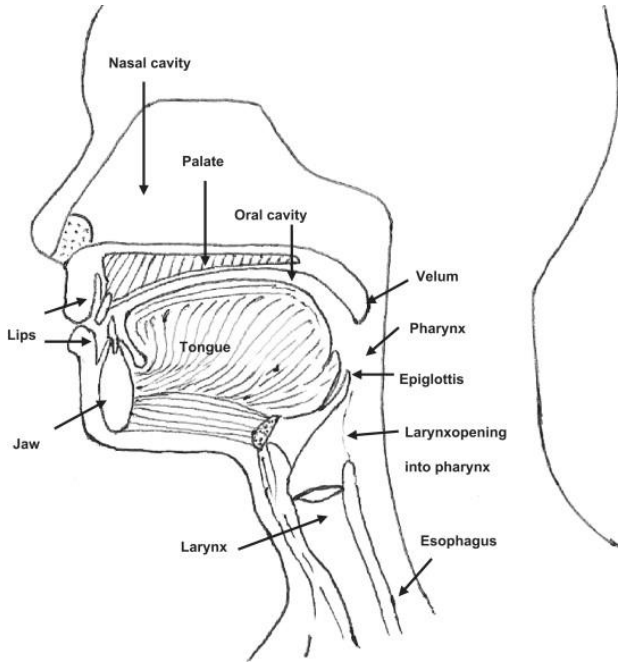


Figure 2.11 An anatomic diagram of oral organs adapted from Chen (2009)

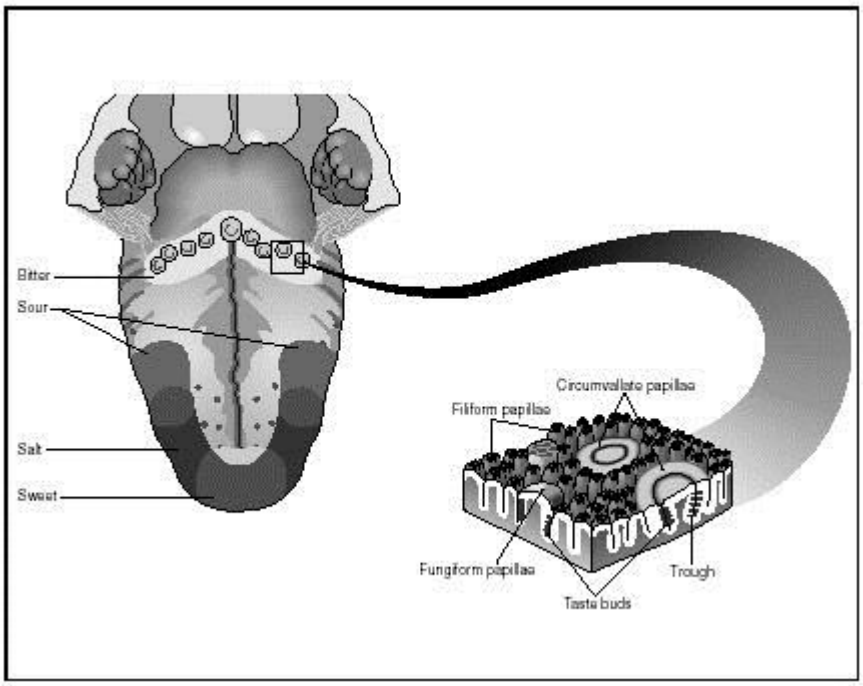


Figure 2.12 The tongue: taste areas and papillae disposition (Engelen, 2014)

The anterior surface of the tongue is covered by a layer of stratified squamous epithelium with variation in the types of papillae and taste buds.

Papillae are categorized into four distinct classes based on their physical shapes, which are the filiform (thread-shaped), fungiform (mushroom-shaped), circumvallate (ringed-circle) and foliate. These papillae are responsible for the taste sensation and have taste buds on the surface, except the filiform. The mechanical modulation and coordination of the tongue is controlled by the extrinsic (muscles with the origin of outside the tongue body) and intrinsic muscles (muscles with the origin and insertion in the tongue).

2.3.3 SALIVA

Saliva plays a multifunctional role in the oral cavity. Saliva coats basically almost parts of the mouth. Saliva is produced by three pairs of major glands, i.e., parotid, submandibular and sublingual glands. Minor salivary glands present in the mucosa of the tongue (Von Ebner glands), cheek, lips and palate. The major salivary glands contribute to the 90% of the secretion with the remaining 10% from the minor glands. This naturally occurring biological fluid is made of water (99.5%), protein (0.3%) and inorganic and trace substance (0.2%). Proteins and peptides identified in the whole saliva compositions, including glycoproteins such as the mucins MCU5B and MUC7, proline-rich glycoprotein, enzymes (e.g., α-amylase, carbonic anhydrase)., immunoglobulins, and a wide range of peptides (cystatins, statherin, histatins, proline-rich protein). The inorganic compounds of saliva contain common electrolyte (sodium, potassium, chloride and bicarbonate) (van Aken et al., 2007). Saliva's pH ranges from 5.6 and 7.6 which is fairly neutral. However, variation of saliva's pH are observed from time to time during a single day in the same person (Chen 2009). Saliva is produced at 0.3 to 7 ml per minute with the average volume 0.5-1.5 litre daily depending on factors such as flow rate, circadian rhythm, types and size of salivary gland, type of stimulus, diet, drugs, age gender and blood type and physiological status. Nearly all parts of the mouth are coated with saliva. Saliva unknowingly plays a significant role in many aspects of food processing. The saliva properties allow it to modulate many functions of

homeostasis during food processing or even at rest. One of the many functions of saliva is to prevent desiccation, abrasion and to reduce stickiness of the mucosal surface preventing one surface sticking to another. Besides that, saliva also prevents intrusion of harmful microorganisms and maintains an optimize condition for taste buds to optimally detect taste compounds. In terms of the function of saliva upon food ingestion, food of solid or semi-solid in structure needs to be broken up to be assessed for its taste and smell, smoothness and rheological measurements and to check the product quality. During the chewing process the also saliva serves to protect the teeth as well preventing it from cracking. Finally saliva coats food particles to make it cohesive and form bolus which allows the food components to be safely swallowed. Saliva also acts as a clearing agent during the post mastication process of any residual food which reduces the availability of sugar and nutrients for microorganism growth that may affect oral and dental health.

2.3.4 TONGUE

Other than speaking and tasting, the tongue is also responsible for manipulating food and enables swallowing. The tongue is a bundle of striated muscles on the floor of the mouth. It is a boneless organ and depends wholly on the extrinsic muscles to anchor it firmly to the surrounding bones. The length of the tongue extends longer than it is visually perceived as the length reaches past the posterior border of the mouth and into the oropharynx. The oral parts are situated mostly in the mouth and the pharyngeal part faces backward to the oropharynx. The dorsum of the tongue takes a form of a convex and is marked by a median sulcus symmetrically divided into halves: an oral part (approximately the anterior two-thirds of the tongue) and a pharyngeal part (approximately the posterior third of the tongue) (Chen, 2009)

2.4 RELATIONSHIP BETWEEN MICROSTRUCTURE, TEXTURE AND SENSORY PERCEPTION

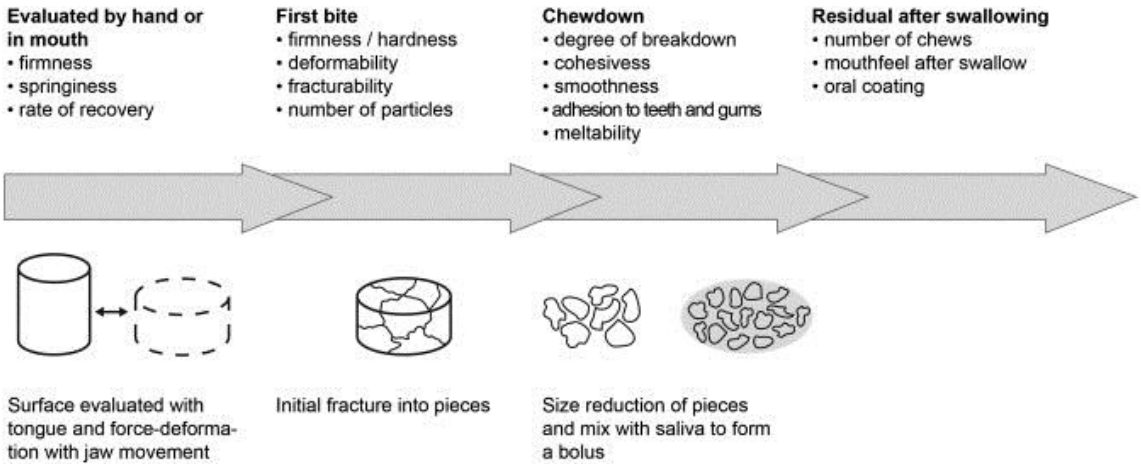


Figure 2.13 Schematic representation of the different stages in the oral processing of soft- and semi-solid foods and the associated sensory attributes by Stieger and van Velde (2013)

This section will further discuss the relationship between microstructure, texture and sensory perception. Before the food is prepared to for a bolus for swallowing the food is processed where the size is reduced under a controlled degree of lubrication. This specific pathway is very important as the sensory inputs are triggered throughout pathways which all together affect the consumer's perception on the food sensory properties. Experts and consumers utilize their sensory attributes in order to recognize or identify the food properties. The identification of the food properties or how it is perceived, were observed to occur in the food oral processing stages where it was further defined or categorized into four different specific stages which are: pre-fracture, first bite, chew down and residual after swallowing. The sub division on the mastication process (pre-fracture, first bite, and oral coating) are summarize based on a review written by Stieger and van Velde (2013).

2.4.1 PRE-FRACTURE

Pre-fracture is where visual appearance plays a role in giving a perception of texture. The visual perception will lead to the consumer's first impression of the food product. For instance, a consumer's visual perception and observations can imply or guess the physical structure of soft or semi-solid food product via whether it is self-supporting or not. This stage creates an expectation of the food product physical characteristics and texture before it is consumed. The next stage of perception development is through the manipulation of the food using cutlery or fingers when placing in the mouth. This stage usually ends with a small pressure applied on the food to cause slight deformation on the food products. This stage is usually closely linked to the rheology parameters measured under small or large deformation.

2.4.2 FIRST BITE

In the first bite stage the food is compressed between tongue and palate or bitten through with the incisors causing total deformation of the food product. The mode of oral processing at this stage relies on the rheological properties of the food such as firmness and the springiness. The transitional stage between palating and chewing during the first bite on soft-solids were reported to occur at Young's modulus of around 16 kPa or at a fracture stress of 12 kPa (Foegeding et al., 2011). Values of the applied force were obtained after a wide application of force on a wide series of mixed polysaccharide, gels, emulsion-filled gels and soft-semi solid food products comprised of yogurt, boiled egg white, desserts, tofu and mozzarella cheese. The term firmness by sensory perception are usually associated to the rheological parameters such as the Young's modulus, stress at fracture and energy to fracture. Firmness in the first chew is highly linked to physiological parameters, such as the activity of the jaw muscles where measurements of the activity can be recorded by the EMG, the vertical amplitude measured with jaw tracking and the duration of the first bite cycle.

2.4.3 CHEW DOWN

In oral processing, chew down is a process that consumed the highest amount of time and is also referred to as the rhythmical chewing phase. Observations had shown that the major change in the food product is the particle size during this stage (Malone et al., 2003; Mills et al., 2011). The reduction in the particle size is describes by the rate of breakdown and the properties of the resulting particles, such as number, size, shape, surface properties. The food particles form a cohesive bolus which is glued together by the saliva. During this process fluids are release from the food product. The term watery, separating and moisture release are usually used to describe the release of fluids during oral processing of the food product. The degree of moisture release is closely linked to the microstructure of the product. For instance, the higher the porosity of the gels, the higher the moisture release. Types of gels such as heterogeneous, bi-continuous or coarse microstructure tend to show high moisture release. The moisture release is believed to be directly proportional to the opening and occlusion duration of the chewing and inversely related to the chewing frequency. It was also discovered that the muscle activity, number of chews and chewing duration has no effect on the moisture release of the food product.

2.4.4 RESIDUAL AFTER SWALLOWING (ORAL COATING)

The residual coating results in the presence of particles or residues adhering to the tongue, teeth and oral tissues despite the clearance after swallowing. Oral coating is defined as a residual film from food covering the oral surfaces after swallowing food or beverages. There are claims mentioning that the oral coating has a significant effect on taster perception and the mouthfeel attributes. However there is still little information that is able to give a clear description on the formation of oral coating. The experimental approach applied in measuring the coating is by measuring and observing the turbidity of oral rinse water. A model study was recently performed using e.g. custard. The studies revealed that the correlation between the turbidity of the oral rinse water and the sensory attributes such as creaminess, fattiness and

stickiness for custard varying in fat content. However, the studies did not quantify the composition or thickness of the oral coating itself.

2.5 MICROSTRUCTURE, TEXTURE AND ORAL PROCESSING

2.5.1 ORAL PROCESSING OF SEMI- AND SOFT-SOLID FOODS

Gaining consumer acceptance is a very important and daunting task in the food manufacturing and processing industry. The challenges are greater when consumers have become more aware and cautious on the health benefits that one food product may or may not offer. The attempt in modifying food formulation is an ongoing process that had been set in motion by the manufacturers in order to meet the consumer demand for healthier food products. The desire to alter food composition poses new challenges to manufacturer in altering the composition (such as reducing the sugar, salt, fat and increase in bioactive compounds) without compromising the food sensory perception and consumer's acceptance. Foods are categorized into four categories based on their physical, rheological and sensory properties: liquids, semi-solids, soft solids and hard solids. These four types of food involves in different mastication mechanisms and their modulation for instance; 1) liquid flow does not require chewing before swallowing (e.g. drinks, beverages, milks) 2) Semi-solid food are compressed or squeezed between tongue and palate (e.g. puddings) 3) Soft solids which requires chewing between the molars but do not elicit crispy sensations (e.g. cheese, processed meat) 4) Hard solids are crispy and require chewing between the molars and produce acoustic sound emission (e.g. crackers, raw vegetables, apples) (Floury et al. 2009; Mills et al. 2011; Pascua et al. 2013; Stieger & van de Velde 2013). The tongue and saliva discussed in previous sections have their main role in processing semi- and soft solid foods. Semi- and soft solid is usually associated to certain texture attributes and subjected to certain oral processing action shown in **Table 2.3**.

Table 2.3 Texture terminology for semisolids and solids (Pascua et al., 2013).

Attribute	Definition /Evaluation	Material/Reference
A. Tongue-Palate compression		
1. Springiness/Rubberiness	The degree or rate which the samples return to its original size, shape after partial compression/Between the tongue and palate/Between teeth/After biting, assessed during first 2-3 chews	Whey protein gel, semisolids and sof-solid foods, cheese, protein gels, processed cheese
2. Compressibility	The degree to which sample deforms or compresses before fracture/ Partial compression between the tongue and the hard palate	Whey protein gels
B. First bite/ first chew		
1. Hardness/Firmness	1) Force require to/Bite completely trough the samples between molars (for solids)/Compress sample between tongue and hard palate during compression (semi-solid)/Compressed sample between fingers until fracture 2) Extent of initial resistance/First bite with incisors 3) Solid, compact sensation; holds until its shape 4) Hardness sensation perceived during mastication	Whey protein gels, mixed whey protein/ K-carrageenan gels, semisolid, soft-solid foods, cheese, caramel, biopolymer gels, mixed whey protein-polysaccharide gels, cream cheese, agarose gel, processed cheese, yogurt
2. Moisture release	Extent to which moisture is release from the samples/First bite with molars	Mixed whey protein/ κ-carrageenan gels, agar gels

3. Deformability/Cohesiveness	The degree of which the sample deforms or compresses before fracture/Bite completely thorugh with the molars	Semisolid and soft-solid foods, agar gel, cheese
C. Mastication (evaluated during or after degree of chewing)		
1. Hardness	Samples falls apart in pieces/Compression between tongue and hard palate	Gelatin gels, polysaccharide gels,
2. Cohesiveness of mass/Mass-forming	Degree which samples holds together in a mass/Compression with tongue against palate at least 5 times	Cream cheese, yogurt, processed cheese, whey protein gels, cheese

2.6 FLAVOUR

Flavours are the most researched area and undergo constant change. Companies allocate a huge fund in this area in an attempt to understanding their function, interaction with food matrix, they are released, etc. Historically, flavour gained vast amount of attention as the literature began to grow rapidly in the early 1970s. The flavour industry has produced numerous flavouring materials. These material are sourced from plants and animals, products of fermentation and enzymology, as well as synthetic chemicals (Reineccius 2006). Flavour is the sum of all the characteristics of any material taken in the mouth, perceived principally by the senses of taste and smell, and also pain and tactile receptors in the mouth, as received and interpreted by the brain (Juteau et al., 2004) . The perception of flavour is a property of flavourings. According to The Code of Practice of the International Organization of the Flavour Industry (IOFI) flavouring is defined as “Concentrated preparations, with or without food adjuncts [Food additives and food ingredients necessary for the production, storage and application of flavourings as far as far as they are nonfictional in the finished food] required in their manufacturer, used to impart flavour with the exception of salt, sweet, or acid tastes”.

2.6.1 TYPES OF FLAVOUR

According to IOFI legislation and code of practice favour are further divided into two distinct categories which are the natural and artificial flavourings. Definitions taken from the chapter in a book by Reineccius (2006).

2.6.1.1 NATURAL FLAVOURINGS

Natural flavourings are defined as follows “The term natural flavours or natural flavourings means essential oil, oleoresin, essence or extractive, protein hydrolysate, distillate, or any product of roasting, heating or enzymolysis, which contain flavouring constituents derived from spice, fruit or fruit juice, vegetables or vegetable juice, edible yeast, herb, bark, bud. Root, leaf or similar plant material, meat, seafood, poultry, eggs, dairy product, or fermentation products, thereof, whose significant function in food flavouring rather than nutritional.

2.6.1.2 ARTIFICIAL FLAVOURINGS

Artificial flavourings are defined a follows “The term artificial flavour or flavourings means any substance, the function of which to impart flavour, which is not derived from spices, fruit or fruit juice, vegetable or vegetable fruit juice, edible yeast, herb, bark, bud, root, leaf or similar plant material. Artificial flavouring usually produced synthetically.

2.6.2 SCIENCE OF TASTE

Tastes are detected by taste buds positioned throughout the oral cavity (tongue, palate, pharynx and larynx). The majority of taste buds are located on the tongue within the papillae. Papillae are the visible bumps scattered on the surface of the tongue. The sensation of taste is initiated by the interaction of the flavour molecules with receptors and ion channels in the microvilli of the taste receptor cells (TRCs) as shown in **Figure 2.15**. Other mechanisms of the taste transduction pathway involve conversion of chemical information

into a cellular second messenger codes (e.g., cyclic nucleotide monophosphates [cNMPs] and inositol triphosphate [P_3]).

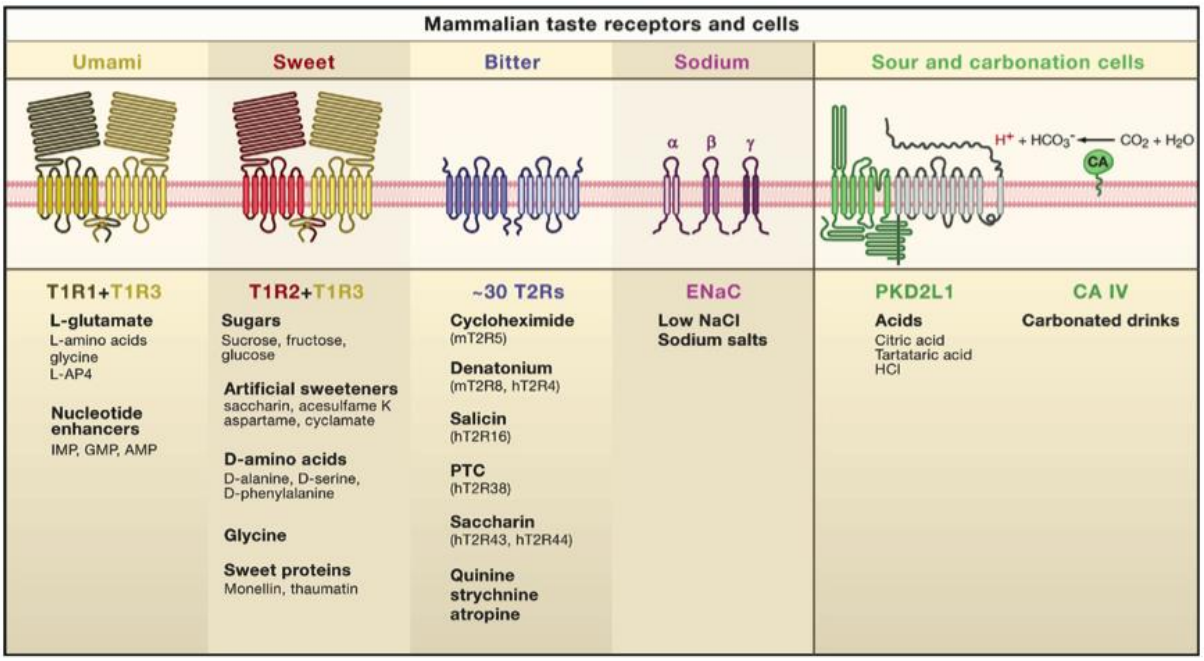


Figure 2.14 Interactions of taste receptors and chemicals responsible for taste sensation (Yarmolinsky et al. 2009)

2.6.3 SALTINESS

The principal stimulus for salty taste is the sodium ion, Na^+, Table salt, NaCl, is the widely used prototypic salty taste compound. Both salt ions are essential nutrients, playing a significant role in maintaining blood volume, blood pressure, regulating body water and in the case of Cl, maintaining the acid/base homeostasis (i.e Cl shift). The detection threshold for NaCl is 1 to 15 mM on average in humans depending on the stimulus volume (Engelen 2012). However, the strength and taste quality is also modified by the anion present. Hence, salt detection is thought to be dependent on the on the cation channels.

2.6.4 SWEETNESS

Most natural ‘sweets’ come from ripe fruits and some vegetables and they also contain a lot of valuable nutrients. Sugar are one of the most common sources of sweetness, but there are many other substances of different molecular structure that are able to evoke the same sensation such as amino acids, peptides, and proteins as well as artificial sweeteners. Due to the diversity in of the sweet tasting substances, it is difficult to give a detection threshold, however, the threshold for sugars have been reported to be in the range around 2-5 mM and 14-22 mM . This may differ among individual, age and gender (Valery et al. 2014).

2.6.5 SOURNESS

Sourness is mainly caused by the acidic condition of certain foods. There is a considerable variation in the degree of sourness in certain acids and this is usually associated with the non-dissociated acid molecules. The threshold for citric acid has been reported to be around 0.5 to 1.5 mM.

2.6.6 BITTERNESS

Bitterness is usually associated with undesirable and unfavourable flavours. The production of the bitter compounds in certain plants is associated as a deterrent or defence mechanism to protect the plants from the ‘predator’. It is believed that the ability to taste bitterness serves to detect noxious compound and prevent the animal for consuming harmful foodstuffs. Bitterness as whole has a lower threshold from activation, to prevent consumption of even small quantities of toxins. For instance, the human threshold for caffeine has been reported to be 1 mM and for quinine only 0.05 mM (Engelen 2012). Aside than that, there are many other bitter compounds from certain amino acids, urea, fatty acids, phenols, amines, esters and salts.

2.6.7 UMAMI

The sensation of umami is conveyed by the L-amino acids, including the amino acid glutamate. Umami is usually associated with the specific taste of monosodium glutamate (MSG) which is utilised as a flavour enhancer for food products. Glutamate imparts the meaty sensation of certain food products which natural occurs in many foods including meat and also dairy, seafood and tomatoes. For adult humans, the detection threshold is about 0.7mM.

2.7 MASS TRANSFER, DIFFUSION AND CONTROLLED RELEASE SYSTEMS

2.7.1 MASS TRANSFER AND DIFFUSION

Mass transfer can be defined as the transfer of material through an interface between two phases, whereas diffusion can be defined in terms of the relative motion of molecules from the centre of a mass mixture, moving at the local velocity of fluids.

The phenomenon of diffusion involves the Brownian motion of molecules in a fluid medium or in other words diffusion is defined as spontaneous net movement of molecules from an area of high concentration to an area of low concentration in a given volume of fluid, down the concentration gradient.

2.7.2 MECHANISM OF DIFFUSION FROM COMPLEX MATRICES

The mechanism of diffusion or mass transport is an important topic that has undergone massive evolution in the past 70 years (Asano 2006). It is also important to highlight that food products are complexed and diffusion is known to be controlled by several important attributes. Through active debates and vigorous studies conducted, diffusion entails several steps depending on the active ingredients and types of polymers utilised as the matrix. The steps are as follows (Vashisht, 2014):

- Surface wetting

- Hydration or swelling of the matrix composition layer
- Disintegration or erosion of the matrix
- Dissolution of the active ingredient to induce molecular diffusion or mobility
- Permeation of the active ingredient in the matrix phase
- Permeation of the active ingredient through the matrix phase into the bulk food phase

The rate controlling steps or the rate of release depend on the matrix material, morphology and physicochemical properties of the active ingredients. An excellent point to understand the different kinetics and release profiles is to focus on the fundamental concepts of various diffusion models such as the zero order diffusion, Fickian diffusion, first order diffusion, Higuchi's diffusion model and case II diffusion. The most common model is Fickian diffusion, since most model designs are dependent on the concentration gradient.

2.7.3 ZERO ORDER OR PSEUDO ZERO ORDER DIFFUSION MODEL

This model represents the hypothetical model of diffusion where diffusion rate is independent of the concentration of the active agent. Increasing the concentration will not speed up the rate of release, nor does the reduction in concentration slows down the diffusion. This is counter-intuitive. In the concept of the zero order models, the hypothesis is that the amount of active loading is infinite. Zero order release diffusion is described as the amount released is directly proportional to time. This model is mathematically written as follows:

$$C \; \alpha \; t$$

$$\frac{dCt}{dt} = k_o$$

Where:

C_t = amount of active agent

t = time

k_o = zero oder constant

By integration the previous equation:

$$(C_t - C_o) = k_o * (t - 0) \tag{2.1}$$

Where:

C_o = represents the initial release at t→0 for a fixed volume in which the release is measured:

$$C_t = C_o + k_o * t \tag{2.2}$$

This equation is called the integrated zero order rate law. A true zero order is often a rare phenomenon because of the short desirable release time, solubility of the active agent in the matrix, surface activity and the desirability for a burst release from the microcapsule. Release shown in **Figure 2.17**.

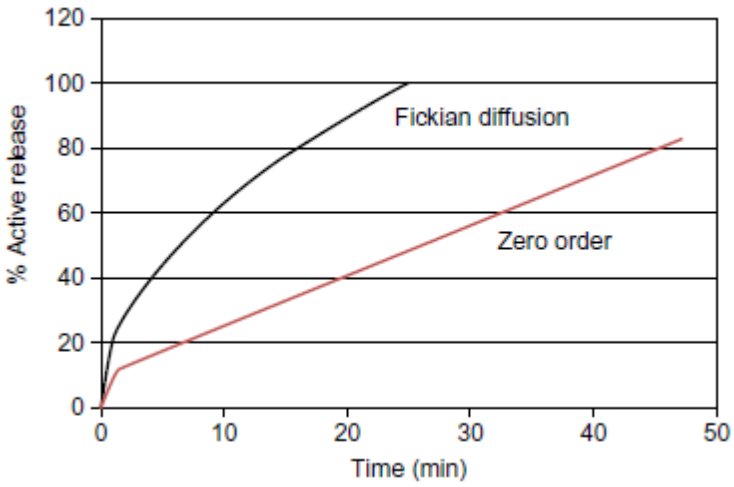


Figure 2.15 Schematic profile for zero order and Fickian diffusion model (Vasisht, 2014)

2.7.4 FICKIAN DIFFUSION MODEL

The Fickian model proposes that the diffusive flux, *J*, goes from the region of high concentration to regions of low concentration, with a magnitude that is proportional to the spatial concentration gradient. In terms of one-

dimensional spherical coordinates relating to microsphere morphology, *Fick's first law* written as:

$$J = \left(\frac{1}{A}\right).\frac{dC}{dt} = -D\,\frac{dC}{dr} \tag{2.3}$$

Where:

J = diffusion flux or mass flow of the active ingredients under the assumption of steady state

D = is the diffusion coefficient

r = radius of the designed capsule

A = surface area of the microcapsule

C = the amount of the active ingredients

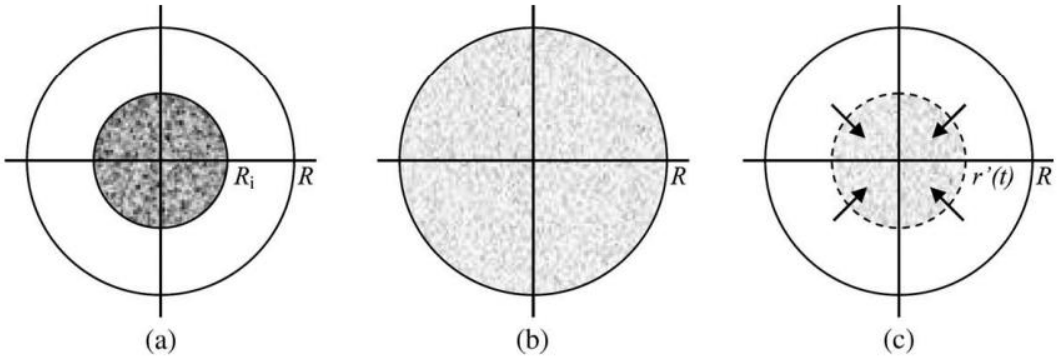


Figure 2.16 Schematic diagram of the cross section sphere loaded with active ingredients of (a) reservoir system (b) dissolved system and (c) dispersed system. In reservoir system, drug is confined by a spherical shell of outer radius R and inner radius R_i; therefore, the drug must diffuse through a polymer layer of thickness ($R-R_i$). In dissolved drug system, drug is dissolved uniformly at loading concentration C_0 in the polymeric matrix. In dispersed drug system, the radius of inner interface between "core" (non-diffusing) and matrix (diffusing) regions, r′(t), shrinks with time. The "core" region is assumed to be at drug loading concentration C_0 (Arifin et al., 2006)

The negative sign signifies the flux is in the opposite direction to that of increasing concentration. It is worthy to emphasise that the equation is consistent only for isotropic media, where the diffusion properties do not change throughout the material. The equations above can further be simplified with respect to the concentration difference between inside and outside of the microcapsule:

$$\frac{dC}{dt} = -D * A * \left(\frac{(\Delta C)}{R}\right) \tag{2.4}$$

Where:

(ΔC) = C_{OM} – C_{IN} (where C_{OM} is the concentration of the active agent on the outside of the microcapsule; C_{IN} is concentration of the active agent on the inside of the microcapsule)

R = the thickness of the microcapsule

Comparison with the zero order diffusion model equation shows that the Fickian diffusion will approximate zero order when:

$$k_o = -DA * \frac{(\Delta C)}{R} \tag{2.5}$$

In essence, for constant release, a pseudo-zero order rule can be applied as a practical approximation. The higher the k_o the faster the rate of diffusion.

2.7.5 DIFFUSION IN FOOD FLAVOUR RELEASE IN THE ORAL CAVITY

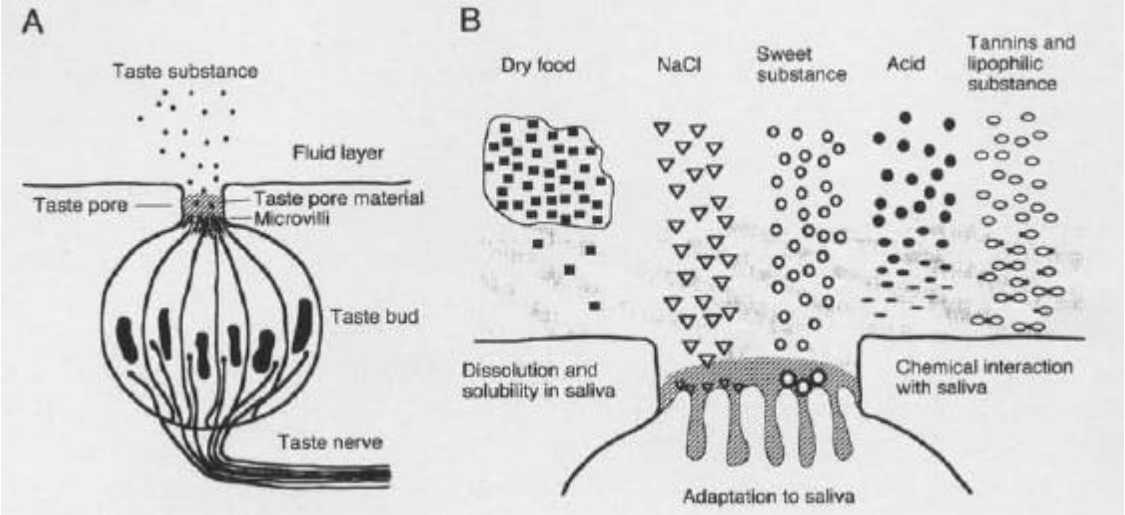


Figure 2.17 Schematic diagram of a taste bud (A) and model of initial events in taste perception (B). (A) Microvilli extend from the apical portion of the taste cells into the taste pore. Taste stimulant must enter and diffuse through the fluid layer to come into contact with the receptor sites on the microvilli. (B) Taste sensitivity is affected by the solubility of the taste substance in saliva and in the taste pore material and by the chemical interaction with various components of saliva, resulting in a decrease or increase of their sensitivity adapted from (Matsuo 2000).

Understanding the taste compound release mechanism inside the mouth may provide useful information on how to manipulate food products and achieving consumer's acceptance towards a food product. Transport of flavour from the product in the mouth involves a complicated process in which mastication, diffusion, and in-stationary convective transport plays an important role. As discussed in previous sections, saliva plays an important role in transferring the taste substance to the chemoreceptor of the tongue. According to Matsuo (2000) the taste substance has to undergo two major steps where the first step is the taste substance must initially pass the through the saliva fluid layer in order to reach the receptor site and this process includes the solubilisation of taste substance with salivary

components. Secondly saliva containing some components may also stimulate the receptor. In other words, where the continuous stimulation with saliva decreases the taste sensitivity to the salivary components (adaptation to saliva), and the responses to the incoming taste compounds are determined by the sensitivity of the saliva adapted receptors. The taste substance comes in many different physical forms and the rate of dissolution of taste substances into saliva differs significantly depending on the physical properties of food. For instance, taste stimulants in an aqueous solution are more readily dissolved in saliva rather than those in solid form as depicted in **Figure 2.20**. Taste response is highly dependent on the diffusion of the taste stimulating ions and molecules into the peri-receptor material. A taste solution flowing constantly over the surface of the tongue is separated from the taste receptors by a distance of 10 μm and taste substance must diffuse across this layer. Delivery of the taste stimulus in a stream of taste solution flowing over the tongue surface (involves convection) and the other is the diffusion of the taste stimulus across the peri-receptor layer that is undisturbed by the convective force of the stream of the taste solution.

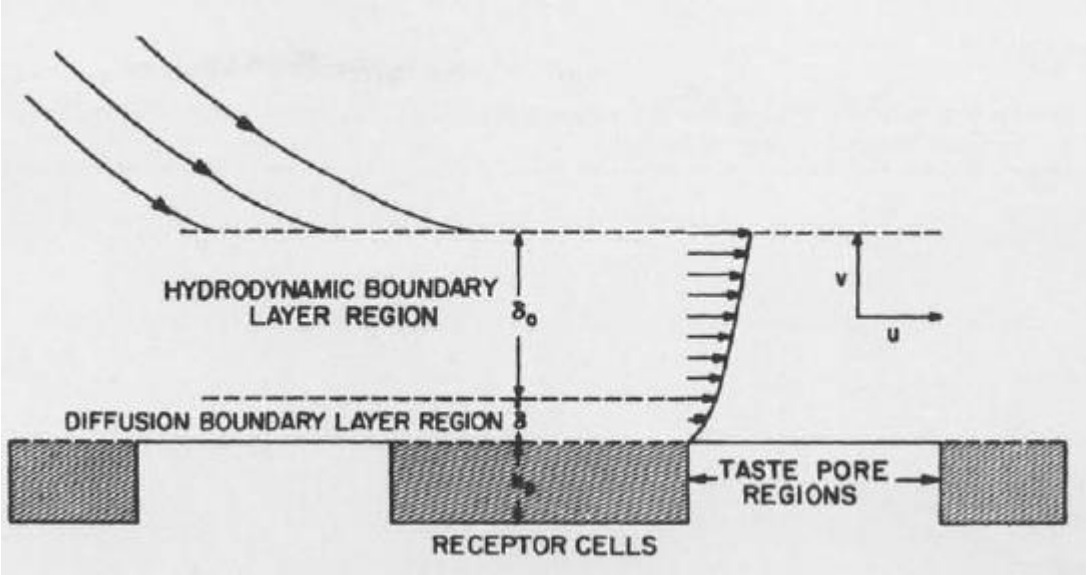


Figure 2.18 Theoretical model of taste stimulus transport from a flowing source to the receptor cells within the taste pore. The diffusion boundary layer thickness varies with stimulus flow rate. The hydrodynamic boundary layer, the fluid velocity changes rapidly and is zero at the surface (Matsuo 2000)

As shown in **Figure 2.21**, the stimulus is conveyed by a fluid stream which is initially vertical to the lingual surface but is subsequently deflected parallel to it. The streams enter and displace part of the fluid layer overlying the tongue surface. The fluid layer immediately in contact with the tongue surface is less susceptible to displacement because of the “no slip” boundary condition. Near the surface of the tongue, where the distance from the lingual surface is less than 20 µm, the vertical component of the taste stream (v) is virtually zero and the taste stimulus is transfer solely by diffusion.

Aside from understanding how taste compound is released, it is essential to understand the condition of the specific taste compounds inside the food. Taste compounds such as salt or sugar might have a specific chemical or physical interaction with the food component before it is fractured and released into the mouth and react with the specific taste buds. In order to understand the mechanism in detail it is important to know the different types and aspects of controlled release systems. Controlled release can achieve specific benefits such as follows (usually defined in drug delivery):

a) Maintenance of optimum therapeutic drug concentration in the blood with minimum fluctuation
b) Predictable and reproducible release rates for extended duration
c) Enhancement of activity duration for short half-life drug
d) Elimination of side effects, frequent dosing, and waste of drug
e) Optimized therapy and better patient compliance

These benefits are focused on the effectiveness of delivery to the designated target. The aim in applying similar concepts on to food ingredients (taste compounds) is to give consumers the most satisfaction while minimizing the food ingredients concentration (preferably the taste compounds).

2.7.6 TYPES MICROCAPSULE OR MICROSPHERE TYPE

In modelling the release of taste compound/flavour, the food industry has been looking into encapsulation models from drug in pharmaceutical research studies. Pharmaceutical research studies have provided many examples on controlled release designs and varieties of microencapsulation models which is easily adaptable for many food models. These examples allow the flavour/taste compound release study to be design and manipulated in such manner that it is useful for flavour/taste compound release study. Morphological positioning of the active ingredients, contained in either a microcapsule with a distinct matrix wall around the active ingredient, or in a uniform microsphere morphology may significantly impact the stability and release of active ingredients. In addition, the morphology of the active ingredients is important whether they exist as small discrete droplets or particles that are dispersed in the matrix material. **Figure 2.22** shows the different structural configurations of microencapsulated systems and presents how the active ingredient is distributed in the matrix polymer. Ideally, both microcapsule and microsphere morphologies must be free of defects, pin holes, or high curvature to provide enhanced stability. The presence of defects can cause oxidative or hydrolytic degradation over longer periods of time.

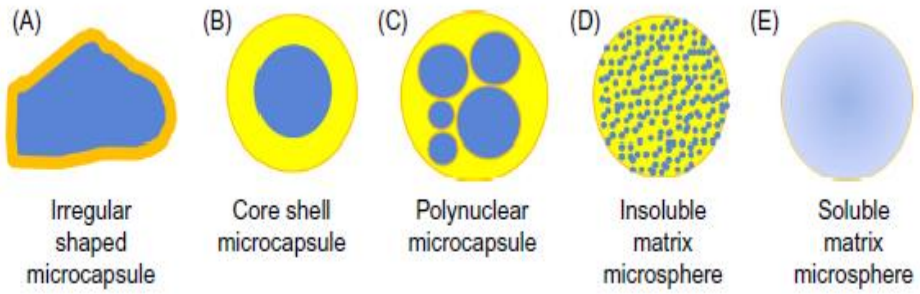


Figure 2.19 Microcapsule (A, B and C) versus microsphere (D and E) morphology. (Vasisht, 2014)

2.7.7 CONTROLLED RELEASE SYSTEMS

A controlled release system is typically defined as a drug/particle delivery system that delivers drug into a systemic circulation at a predetermined rate. The objective in designing a controlled release system is to release the active agent in a predetermined, predictable and reproducible fashion. Most of the drug release systems are purely diffusion controlled with constant diffusion coefficients assumed. There are different types of controlled release system that are quite distinct including (**Figure 2.23**) :

a) Reservoir devices consisting of a drug depot, which is surrounded by a release rate controlling barrier of membrane (usually a polymer base)
b) Monolithic systems also called as a one blocked system, because there is no local separation between the drug reservoir and a release rate controlling barrier.

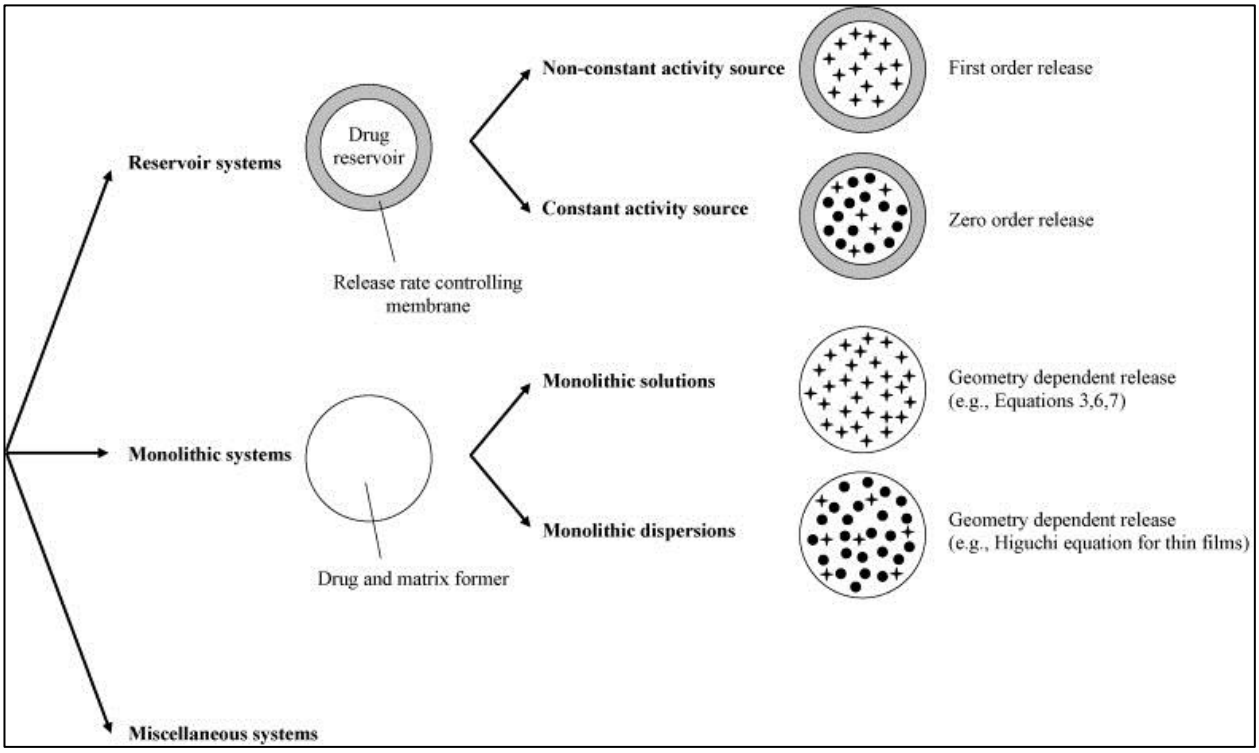


Figure 2.20 Classification system for primary diffusion controlled drug delivery system. Stars represent individual drug molecules, black circles drug crystals and/or amorphous aggregates. Only spherical dosage forms are illustrated, but the classification system is applicable to any types of geometry taken from Siepmann and Siepmann 2008

2.7.7.1 FACTORS AFFECTING RELEASE OF FLAVOURS

In the microencapsulation studies is comparable to studies of the dynamics of food flavour release, gelling agents are commonly utilised as flavour delivery vehicles. Then there are several main factors that affect the release of the active ingredient or flavour into the surroundings, as follows (factors were listed by Vasisht (2014) in a book section entitle Factors and mechanisms in microencapsulation):

2.7.7.1.1 Molecular Weight of the Active Agent

Typical active food ingredients have molecular weights that are less than 500 Da. Referring to the small molecular dimension of many food compounds, it is assumed that these molecules can easily travel through the tortuosity of

the matrix polymer interstitial spaces or through the polar heads of the phospholipids in the case of a liposome. As the molecular size increases, the diffusion decreases exponentially. This means that larger molecules, such as proteins and peptides, may require more time to diffuse into the outer surroundings.

2.7.7.1.2 Functional Moieties and Surface Charge

In biological transport, glucose in known to enter cells much faster than other sugars, facilitated by a carrier protein specific for glucose and this phenomenon is known as facilitated diffusion. Their application in the pharmaceutical drug industry is widely known, but its application in the food industry is rare. In contrast, the ionic surface charge on the active ingredient can play a significant role in inhibiting the rate of diffusion by electrovalent binding to the matrix polymer moieties. Changing the ionic properties often results in a change in solubility of the active ingredient in the matrix phase. Thermodynamics also affects microcapsule stability and release. Thermodynamic properties such as concentration, temperature, solubility, and interfacial properties are all key factors contributing to the performance and stability of the microcapsule.

2.7.7.1.3 Concentration of Active Ingredients

The nature of any controlled released system involves the movement of the active ingredients from highly concentrated region to the less concentrated region. As the concentration gradient between the inside of the matrix decreases as compared to the surrounding food outside, the rate of diffusion decreases. This is important from two standpoints. First, because the initial concentration gradient in a matrix is high, this consider as contributing to the burst effect resulting to the release of the active ingredients. Also, as the concentration gradient decreases, the driving force associated with release decreases and, therefore, such a system exhibits a first order release.

2.7.7.1.4 Temperature

In most cases, increase in temperature causes molecules to move faster, therefore enhancing diffusion. The temperature also allows the matrix to undergo entropic relaxation from a metastable state to an equilibrium state. As the density increases, the molecule undergoes fewer collisions; this allows for faster diffusion. Similarly, lowering the temperature will lower the diffusion rate by lowering the energy of each particle. As a result, microcapsules stored at room temperatures or under refrigeration offer greater stability than those kept at elevated temperatures. Polymer matrices can undergo phase transitions with respect to temperature, thus changing from a crystalline to an amorphous state, glassy to rubbery state, or solid to molten state, and sol to gel state. In each of the phases transition states, the product release profiles differ. Obviously, the selection of the matrix material therefore becomes a key factor in microencapsulation design.

2.8 SENSORY EVALUATIONS

2.8.1 INTRODUCTION

Sensory evaluation has experienced rapid developments during the second half of the twentieth century alongside the massive developments and expansion of processed food and consumer's product industries. Sensory evaluation aims accurately measure human responses to food and minimize the potential biasing effects of brand identity and other information that influence the consumer's perception. Sensory evaluation are defined as a scientific method to evoke, measure, analyse and interpret those responses to product as perceived through the senses of sight, smell, touch, taste and hearing. Sensory evaluations have become an essential stage in the industry, deemed to be necessary to avoid any product failure that is launched in the market. The importance of the human preferences has brought the researcher to look into the key factors affecting human perceptions on a certain food products. This is actually a complicated process involving many different factors. Like any other analytical test

procedure sensory evaluations is concerned with precision, accuracy sensitivity and avoiding any false positive. Aside from gaining understanding of human preferences, many sensory studies are conducted in conjunction with the instrumental analysis that is conducted in the laboratory. The development of designing instruments in mimicking the human oral conditions is under rapid development. Bridging instrumental studies with sensory evaluations allows a more accurate prediction from the instrumental analysis to sensory evaluation.

2.8.2 BASIC SENSORY REQUIREMENTS

An important factor in designing a sensory analysis is to define the aims and the objectives of the research project. A clear objective enables the researcher to accurately design the sensory evaluation; extracting the right information and addressing the research questions (Kilcast 1999). The panellists are the main contributors to the sensory analysis. The number of subjects, their level of expertise (trained or untrained) and any special circumstances (infant, adult, elderly, etc.) are important factors that should be considered when designing the test.

The validation of the data obtained usually requires appropriate statistical analysis, which is essential for data interpretation.

Alongside these essential elements of a well-designed approach, selecting the sensory test methodology is also critical. The success and feasibility of the achieving objectives depend to a great degree on the method chosen. There are three main classes of sensory tests:

1. Discrimination/difference tests,
2. Descriptive tests, and
3. Hedonic/affective tests (Kilcast 1999).

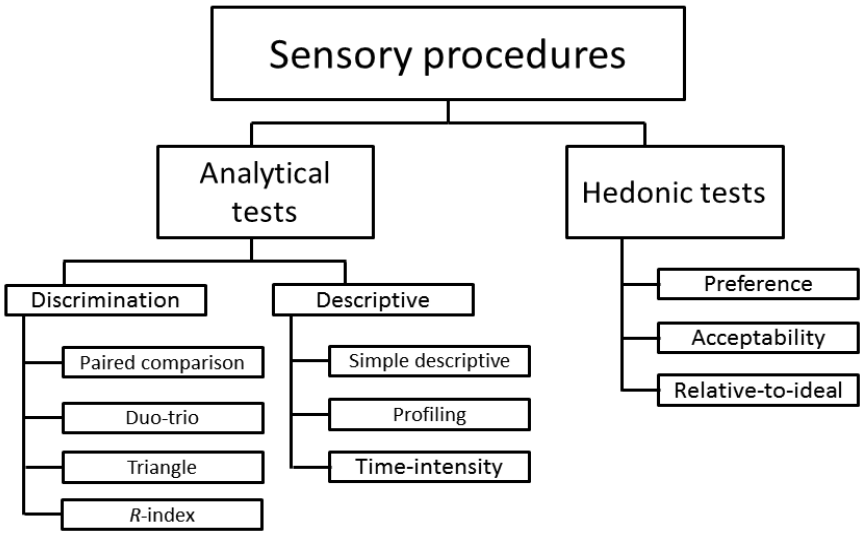


Figure 2.21 Main classification of sensory testing procedures (Kilcast 1999).

The nature of the human perception system is designed towards detecting change. Most sensory methods listed in the **Figure 2.24** focus on static judgements. However descriptive analysis is a class of methods adapted to measuring perceived change in stimulations by food since appreciation of the food flavour is highly dependent on the timely release of the taste substance. Flavour release is a process generally not happening at a constant rate but changes due to many factors such as the physical properties of the food texture and the chemical interactions between the flavour molecules with the polymer. Once the taste molecules reach the receptors, the neural response will begin the initiation of the psychological processes.

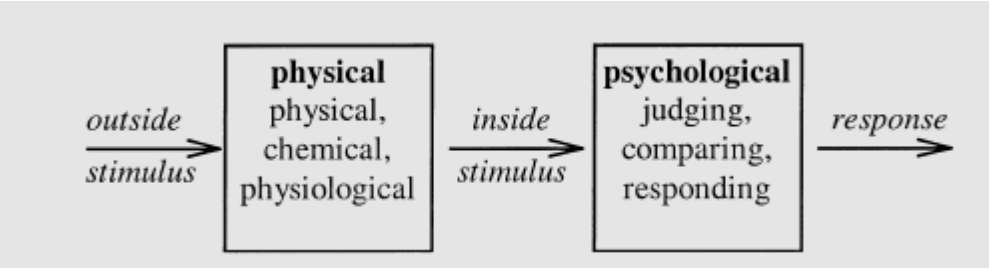


Figure 2.22 Illustration on the physical and psychological processes involved in the time-intensity sensory evaluations.

2.8.3 TIME INTENSITY METHODOLOGY FOR SENSORY EVALUATION

Time intensity (TI) sensory evaluation method uses a modified and extension of the classical scaling method providing temporal information of the perceived sensations. By having the panellist continuously monitor their perceived sensations, from onset through extinction; one is able to quantify the continuous perceptual changes that occur in the specified attribute. For a period of 40 years, TI quantification has undergone many evolutions as food scientists and psychophysicists have attempted to record the human response. Sjostrom and Jellinek were among the first few researchers who attempted to quantify temporal response, by recording the perceived bitterness of beer at 1s interval on a scorecard, using a clock to indicate time. TI curves were constructed by plotting the x-y coordinates on graph paper. They found that the experienced panellists were able to rate two different attributes simultaneously. The greatest improvement was when Larson-Powers and Pangborn (1978) utilizes a moving chart recorder equipped with foot pedal, for TI evaluations. Panellists initiated the chart recorder with the food pedal and moved the pen according to the perceived intensity. More recently, computerized TI systems have been commercially available (Compusense, 1991; OP&P 1991) greatly enhancing the ease and TI data availability, collection and data processing. With the computerised sensory system, each booth is installed with a computer, monitor and mouse. The panellist indicates his/her response by manipulating the mouse. Booths are networked to a mother computer.

2.8.4 INTERPRETATIONS AND ANALYSIS OF TI CURVES

Data obtained from every TI sensory evaluations is in the forms a curve. As a result, interpretations are limited to quantifying key parameters from the curves. Universally, common information and data extracted from these curves include maximum intensity, time-to-maximum intensity and total time. More or less common parameters such as plateau time, lag time, highest intensity before expectoration/ingestion, time of half maximum, decline time

and time for taste to linger. Some researchers extended manipulation of the curve by reporting the area under the curves. Based on this basic principle, many studies were conducted and further modified to gain more meaningful information from the curve**. Table 2.4** compiles a list of terminologies and parameters that are derived from the TI curves.

Table 2.4 Parameters for time intensity evaluation (Cliff & Heymann, 1993).

Parameters	Alias	Abbreviation
Maximum intensity	Initial intensity	I_{max}
	Height to max. intensity	I_i
	Max. perceived intensity	HTMAX
	Maximum intensity	$(I)_{max}$
		MAX
		T_{max}
Time-to-maximum intensity	Time to max	TTM
	Onset time	TMAX
	Appearance time	T_0
	TIME to MAX	AT
Total time	Persistence time	T_{tot}
	Time	T_p
	Persistence	T
	Finish time	P
	Extinction time	T_{end}
	Total duration	ET
		DUR
Plateau time	Protraction of max. int.	T_{plat}
		T_i
Lag time	Start time	T_{lag}
	Reaction time	T_{start}
		T_r
Expectoration	Highest intensity before	HIBE

	expectoration Highest intensity before ingestion	HIBI
Recording time	Total recorded time Total elapsed time	RT T_S
Time of ½ maximum	Time of ½ max (decay) Time of ½ max (onset)	$t_{1/2}$ T_{hdec} T_{hmax} T_{dec}
Decline time after maximum time	Time of taste linger	T_l IT
Maximum intensity-time area	Total amplitude Total gustatory resp. Total intensity Area under curve	TGR STIP AUC
Rate of increase	Max. rate of absorption Maximum intensity rate Rate of onset Slope rising Max. rate onset	M_{ads} MIR RATE MAX ONSET M_{onset}
Rate of decrease	Max. rate of desorption Rate of decay Slope tailing Max. rate decay	M_{des} DECAY M_{decay}
Area before-maximum time		A H_{area}
Area after-maximum time		B OH_{area}
After taste	Area after max./area before max.	B/A Ratio AT

2.8.5 RELATING INSTRUMENTAL ANALYSIS AND SENSORY EVALUATIONS

Food oral processing studies have developed rapidly in recent years. Many instrumental designs have been tested to mimic the actual human oral conditions. Instrumental texture measurements are reliable and robust and can represent defined physical characteristics in standard units. The case for sensory perception of texture is far more complicated. A human is the 'instrument' of the sensory tests, and human texture perception is governed by psychophysical phenomena with their nonlinear characteristics (Rosenthal 1999). Many attempts have been made to close the gap between the two and reducing possible variance between instrumental designs and human sensory studies. If somehow the instruments were to able give an identical response to that of the perceived human response, this would give an upper hand for the industry to predict the response of the consumers.

2.8.6 ATTEMPTS IN MODELLING

There have been numerous approaches using various combinations of instrumental and techniques in the attempt to understand the mechanisms involved in oral processing. One method of understanding the oral processing of semi-solid food is via observing the oral movement. Oral movements were observed in semi-solid foods with various physical structure attributes such as thickness, creaminess, etc. (Stieger & van Velde, 2013; Prinz et al., 2007). Specific oral movements can be recorded via ultrasonic echo-sonography measurements of jaw movements, known as jaw tracking, and force during chewing and biting. These measurements have demonstrated that the oral movement varies significantly depending on the attributes of the semi-solid. Other method includes such as electromyography which measures the electrical activities of masticatory muscles. Videofluorography has also been utilized in observing tongue and soft tissues movements (Pascua et al. 2013). Other methods include real-time MRI, video fluoroscopy, video-rate confocal endoscopy, electromyography and oral pressure sensoring. Electromagnetic

articulography (EMA) has been applied in determining the spatial displacement of the jaw during the consumption of solid food differing in texture properties (Stieger & van de Velde 2013). The development of an in-vitro mouth model is relatively new. Previous researchers have designed experimental set ups that enable one to instrumentally measure release flavour compounds from foods. The methods used are divided into two categories 1) the breath exhale from the mouth is collected and analysed by mass spectrometry (MS) or gas chromatography (Brattoli et al. 2013) 2) a model system in constructed that attempts to mimic what occurs in the mouth and effluent from this model system is collected and analysed using MS or GC/MS (Elmore & Langley 2000). Both of the methods have been widely applied and there are advantages and disadvantages of both methods. In overcoming the disadvantages, vessels have to be designed to take into account several factors such as the inertness, size, shape, sample introduction, agitation of the sample, temperature, ease of modification and connection to the measuring device. Other flavour release research conducted focuses on the volatile compound released from gels (Bayarri et al., 2003; Déléris et al., 2010; Druaux & Voilley, 1997; T. Mills et al., 2011). The experimental designs indicate that the measurement of the volatile release in static conditions cannot accurately represent the real mouth condition which is more dynamic and complex.

CHAPTER 3

MATERIALS AND METHODS

3.1 INSTRUMENTS AND MATERIALS

Experiments were carried out using commercially available food grade biopolymers: κ - carrageenan (Kelcogel, United Kingdom), 250 bloom bovine skin gelatin (Sigma, United Kingdom) and high viscosity sodium alginate (Alfa Aesar, United Kingdom). Taste components used were sodium chloride (NaCl, Sigma, United Kingdom) and glucose (Amresco, Unites States of America). Phosphate buffer (0.05M) prepared using Potassium Phosphate monobasic (KH_2PO_4, Sigma, United Kingdom), Sodium Phosphate monobasic (Na_2HPO_4, ACROS Organics, United Kingdom) and sodium azide (Sigma, United Kingdom) and sodium hydroxide pellets (1 M, Sigma, United Kingdom). Calcium chloride ($CaCl_3$, Sigma United, Kingdom) and dialysis membrane diameter of 21.3 mm 14000 molecular weight cut off (Fisher Scientific, United States of America) for the preparation of alginate gels. All samples concentrations are percentage weight concentration (w/w). All were prepared as per manufacturer instructions outlined in the next section. The different formulations are presented in the **Table 3.1**. The conductivity meter model is ORION STAR A215 pH/Conductivity BT meter (purchased from ThermoScientific, United Kingdom. The ACCU-Chek Aviva glucometer (Roche, United Kingdom) used in the glucose release assay purchased from Superdrug, United Kingdom. Texture Analyser (TA.XT plus, Stable Micro Systems-SMS, United Kingdom) were utilised both in the determination of the gels mechanical properties and flavour release assay. Microscope utilised for microscopy study was the Celestron Digital LCD microscope (California, United States of America) and Zeiss LSM 8800 (Carl Zeiss, Oberkochen, Germany).

Table 3.1 Polymer formulations used in the study.

Gel type	Polymer	NaCl	Glucose	Condition
	Concentration (wt. %)			
κ - Carrageenan (κ-c)	2.0 1.6 1.2 0.8	2.0	10.0	Non-compressed & Compressed
Alginate	2.0 3.0	2.0	10.0	Non-compressed & Compressed
Gelatin	8.0 6.0 4.0	2.0	10.0	Non-compressed & Compressed

3.2 METHODS

3.2.1 PHOSPHATE BUFFER PREPARATION

Phosphate buffer was prepared with the addition of 0.05 mol dm^{-3} monopotassium phosphate (KH_2PO_4), sodium phosphate dibasic (Na_2HPO_4), 0.05 mol dm^{-3} sodium chloride) NaCl, sodium azide (0.02 wt.%) were added as a bactericide agent. The pH was adjusted by adding either sodium hydroxide (1M, NaOH) or hydrochloric acid (1 M, HCl). The pH for the experiments was adjusted to pH 7.

3.2.2 GEL PREPARATIONS

3.2.2.1 κ-C AND GELATIN

Gelatin samples were made by adding dry gelatin and sodium chloride or glucose (0.3 mol dm^{-3} and 0.55 mol dm^{-3} respectively) to a beaker with phosphate buffer (to make the total sample weight of 100 g. The beaker was then covered, stirred (magnetic stirrer set at 100 rpm) and heated to approximately 60 °C and left to dissolve for 30 min. The samples were then poured into petri dishes, covered with parafilm and chilled at 4 °C for 24 h. Gels were then taken out and cut using a cylindrical cutter to form small cylinders (10 mm height, 20 mm diameter). κ-carrageenan samples were prepared in a similar way however heated at 70 °C. κ-carrageenan gels were allowed to set on its own without the addition of potassium chloride (KCl). Samples were then set and stored as with gelatin.

3.2.2.2 ALGINATE

Sodium alginate (high viscosity sodium alginate) gels, were chemically set by the addition of Ca^{2+} ions. Sodium alginate solutions with the desired alginate concentration were made up by heating a total of sample weight of 100g of sodium alginate in a phosphate buffer with 2% of sodium chloride to 50 °C. The solutions were stirred until the solutions fully dissolved. The solutions were then poured into a 21.3 mm diameter dialysis membrane, which was then sealed and immersed in a water bath containing 1% (0.068 mol dm^{-3}) calcium chloride for 8 hours.

3.2.3 MECHANICAL PROPERTIES OF GELS

The uni-axial test was performed with a Texture Analyser (TA.XT plus, Stable Micro Systems-SMS) on cylindrical gel pieces (20mm diameter and 10 mm height). A 40 mm probe was used at room temperature, at a constant deformation speed of 2mm/s and to a 5mm distance. Uniaxial compression tests were performed with 3 gel samples per variant prepared. The averaged value of the compression fracture force, fracture strain and Young's modulus

were calculated. Alginate gels were compressed at the rate of 2mm/s to 7mm distance (as there were no signs of damage at 5mm distance).

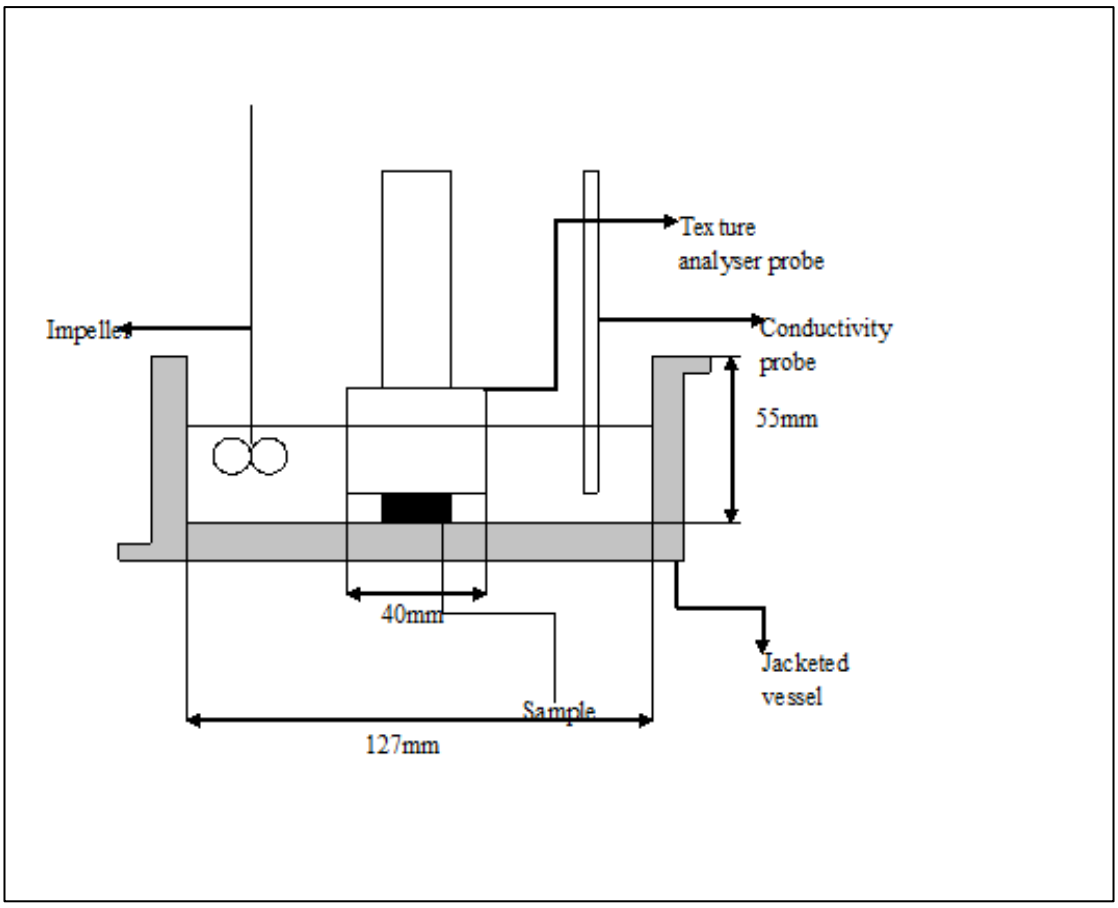


Figure 3.1 Vessel diagram for the experimental setup used in this study.

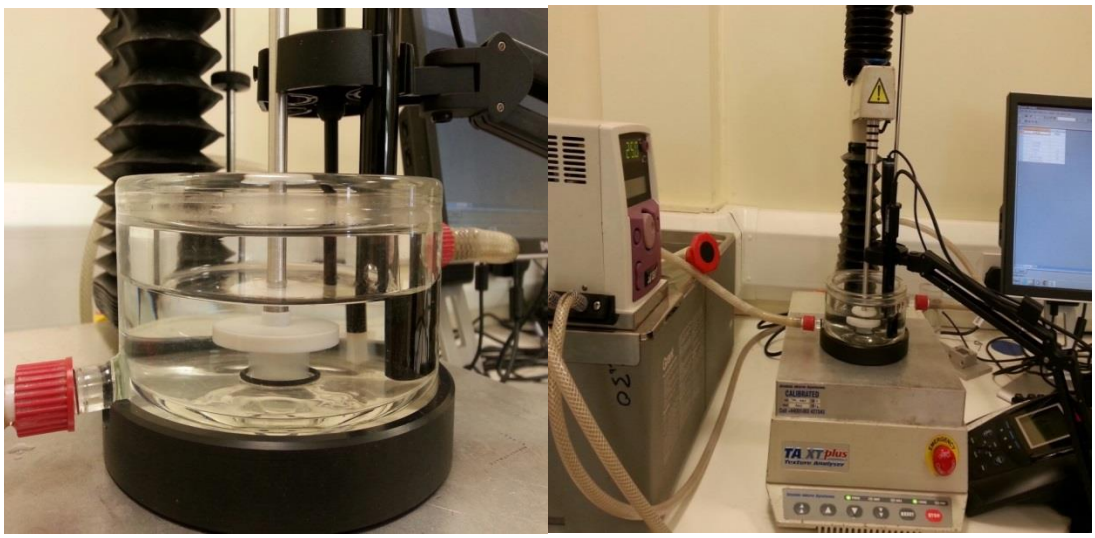


Figure 3.2 The actual experimental setups attached to the texture analyser.

3.2.4 SALT RELEASE EXPERIMENTS

The salt (sodium chloride) release profile from a gel system to a surrounding volume of phosphate were observed. The vessel shown in **Figure 3.1** and **3.2** was set up by filling in 200 ml of phosphate buffer and allowed to equilibrate at a certain temperature (25 ° C and 37 ° C) while stirring to ensure the uniformity of the environment. The conductivity probe was then inserted into the vessel and set to record every 10 seconds for an hour. Experiments were carried out for both 25 ^{o}C and 37 ^{o}C. NaCl release from the structures was continuously recorded by inserting the probe into the main body of the chamber filled with phosphate buffer. Maximum expected conductivity was calculated from calibration curves that have been previously plotted. Consequently, results have been normalized and presented as a fraction of total release. Methods derived from Mills et al. (2010) with slight modification. The concentration of sodium chloride calculated from the calibration curve of conductivity vs sodium chloride concentration.

3.2.5 GLUCOSE RELEASE EXPERIMENTS

In designing the glucose release experiments, the initial step was to ensure the reproducibility of the glucometer utilised (**Figure 3.3**). Serial dilutions of

glucose a solution were prepared (ranging from 0.2 mmol/L to 1 mmol/L). These tests were repeated three times with the same concentration and three different batches to ensure reproducibility and validity of the whole measuring method. Results obtained have proven to be accurate and the reproducibility of the glucometer allows it to be utilised as the measuring device for the experimental set-up. The glucose release profile from gel matrix to surrounding volume of phosphate was observed. Samples of each gel were moulded into cylindrical segments (20 mm in diameter, approximately 10 mm in height). These were covered and placed in the fridge (4 °C). The vessel was set up by filling in 200 ml of phosphate buffer and allowed to equilibrate at a certain temperature (25 °C and 37 °C) while stirring to ensure the uniformity of the environment. The glucose monitor with a glucose strip was then inserted into the vessel and set to record every interval of 5 minutes for 30 minutes. Experiments were carried out for both 25 ^{o}C and 37 ^{o}C. Consequently, results have been normalized and presented as a fraction of total release.

Figure 3.3 Glucometer used in the study for glucose release measurements.

3.2.6 RELEASE EXPERIMENTS WITH APPLIED FORCE

Compressions were applied to the gel samples in order to mimic some oral processing at constant rate 2mm/s to a 2mm distance whilst NaCl or glucose release was being measured. Samples were fixed within the vessel by lowering the compression arm to contact point. 200ml of phosphate buffer was then added and the sample was held in its compressed position for a duration of 10 minutes (for salt release assay) and 30 minutes (for glucose release assay). Conductivity and glucose concentrations were recorded as per initial experiments.

3.2.7 CHARACTERIZATION OF HYDROGEL MORPHOLOGY VIA MICROSCOPY

3.2.7.1 CELESTRON DIGITAL LIGHT MICROSCOPE

The microstructure of the gels was observed and imaged with Celestron LCD digital microscope. Each gel was placed onto a glass slide then covered with a coverslip. Still images were captured for each gel type from various areas. Gels were then sliced to obtained cross-sectional images. The microstructure was observed under 4x and 10x magnification (100µm graticule). The microstructure and porosity of the gels were then determined to allow qualitative microstructure comparisons to be done among the gels in the research.

3.2.7.2 CONFOCAL LASER SCANNING MICROSCOPY (CLSM)

CLSM on gels was performed using the Zeiss LSM 880 confocal scanning microscope (Zeiss,Germany). The confocal was used with Ar/ArKr (488, 514 nm) and He/Ne (543, 633 nm) laser sources. Laser excitation of the fluorescent samples was at 488 nm (≈ 49% intensity of laser) for Acridine Orange (AO). A 10x objective with numerical aperture 0.5 was used to obtained images at 1024 x 1024 pixel resolution. 0.5 wt.% of AO were dissolved with Milipore water and the solution was stored in the dark when

not being used. During preparation of gel sample, solutions was constantly stirred and once cooled, 30 μl of the prepared dye were then added. Alginate was stained only after the gels were set with calcium chloride solution.

3.2.7.3 SCANNING ELECTRON MICROSCOPY (SEM)

The morphology and microstructure of the gels with sodium chloride and glucose were observed using scanning electron microscope (FEI Quanta 200F FEG ESEM, USA). Gel systems with the dimension of 20mm diameter and 5mm in width were then sliced thinly. Gel thins was then frozen using a blast freezer (Valera, United Kingdom) at -30 ° C for 3 hours before transferring it to the freeze drier (Christ alpha 1-4, Biopharma, United Kingdom). The samples were freeze-dried for 24 hours at -55 ° C under 0.4Mbar of pressure. The samples were then coated with platinum using a Cressington sputter coater (Cressington, United Kingdom). The microstructure of the hydrogels was observed at x50 and x100 magnification using 3.00 kV. The diameters of the pores were measured using SEM software by authorised staff Martin Fuller.

3.2.8 TIME-I NTENSITY SENSORY EVALUATION

3.2.8.1 INTRODUCTION

The time-intensity evaluation was carefully designed to be as closely in as possible to that of the instrumental assay, to allow their direct comparison. The conditions are tabulated in **Table 3.2**. Samples presented were κ-carrageenan, alginate and gelatin gels. To avoid exhaustion on the panellists' ability to taste, rather than using all the concentrations utilised in the instrumental assay, only two concentrations (high and low polymer concentration), and two different conditions (non-compressed and compressed) were assessed. Trained panellists were presented with 12 samples. Each session lasted for a total of 30 minutes.

3.2.8.2 TRAINING OF PANELLISTS

Ten panellists consisting of ten women and two men were selected among the PhD students from the School of Food Science and Nutrition and were trained with respect to the TI (time intensity) methodology. The training was run on three steps.

1. Introducing the method to the panellists
2. Familiarisation of the panellist with the computer system (Compusense Inc. 1996)
3. Threshold test
4. Training panellists using the real product

The time intensity test was designed according to the conditions of the instrumental assay. The test designed comprise of two tasks. The first task required the participant to record their perception of the flavour intensity by simply placing the gel in the mouth. The second task required the participant to apply pressure to a new gel piece by pushing the gel with the tongue towards the palate of the mouth without fracturing the gel, if possible.

3.2.8.3 METHOD INTRODUCTION

The first step of the training consisted of a short talk presenting the aims and objective of the research. Panellists were shown the instrumental setup of the research to provide the clear insights on the relevance of the sensory studies in relation to the instrumental assay. The panellists were also introduced to the computer system. General questions about the experiments and the procedures were answered.

3.2.8.4 THRESHOLD TEST

Thresholds are the limits of sensory capabilities. A threshold study was used as an initial screening method before finalising the participants who decided to participate in the time intensity study. This step is deemed to be important

as this method determines the panellist ability to taste and sensitivity to the level of the saltiness and sweetness used in this time intensity study of the level the saltiness and sweetness. A triangle test was used for this simple threshold test, where the panellists were presented with the combination of three gel samples. Panellists were then instructed to choose the odd sample from the three gels presented (salty or sweet) from left to right. Samples were offered simultaneously with three possible random combinations (ABB, BAB and BBA). Panellists were requested to choose the odd sample out of every combination.

3.2.8.5 TRAINING WITH THE REAL PRODUCT

During the training, panellists were presented with the gel and were required to place the gel and holding it in the mouth for sixty seconds. As the panellists were holding it in the mouth they were required to identify the intensity of the flavour over sixty seconds. The level of the flavour intensity was measured using the Compusense (Compusense Inc., Canada). Following this, the panellists were introduced to the time intensity attribute test. The test consisted of a horizontal scale originating at zero point in the bottom of the left hand corner of the computer monitor. The line was 60 pixels in length. Anchors on lines were displayed as not salty to extremely salty, not sweet and extremely sweet. The participants moved a cursor along the scale depending on the intensity of the flavour in the mouth. Panellists were instructed to begin recording the perception at the moment the gel was placed inside the mouth.

3.2.8.6 TIME - INTENSITY PROCEDURE

All training sessions and testing sessions were conducted using Compusense stations. All ten panellists were trained according to the procedures listed above. During the training and testing, panellists were provided with a cylinder of the gels (20mm in diameter; 10 mm in height). The polymers utilised are listed in the **Table 3.2**. The table indicates the lists

of polymers utilised in this time intensity sensory studies. Samples were randomly labelled with sets of three digit numbers. As mentioned above the time intensity tests were divided into two main tasks, placing the gel in the mouth without manipulating it and second task require for the participant to apply a little pressure to the gel. At the beginning of each session, the trained panellist was again briefed on the objectives of the study. Aside from samples, panellists are presented with a glass of water and plain cracker. Plain crackers were consumed to cleanse the panellist taste bud and the water allows the panellist to cleanse the oral cavity in between each sample.

Data were collected at an interval of sixty seconds; data were collected at every 0.1 second to ensure refined analysis of fastest change in flavour perception. Panellist tasted a total of 12 samples each session. There were a total of four sessions, where the sessions were categorised into two sections; perceived saltiness and perceived sweetness. Each of the perceived flavour intensity tests were repeated twice, resulting into a total of four sessions. Samples were presented randomly using three digit codes design by the Compusense software.

Table 3.2 Lists of polymers, flavour and set conditions for the sensory research

Gel type	Polymer	NaCl	Glucose	Condition
	Concentration (wt. %)			
Kappa Carrageenan (κ-c)	2.0 0.8	2.0	10.0	Non-compressed & Compressed
Alginate	2.0 3.0	2.0	10.0	Non-compressed & Compressed
Gelatin	8.0 4.0	2.0	10.0	Non-compressed & Compressed

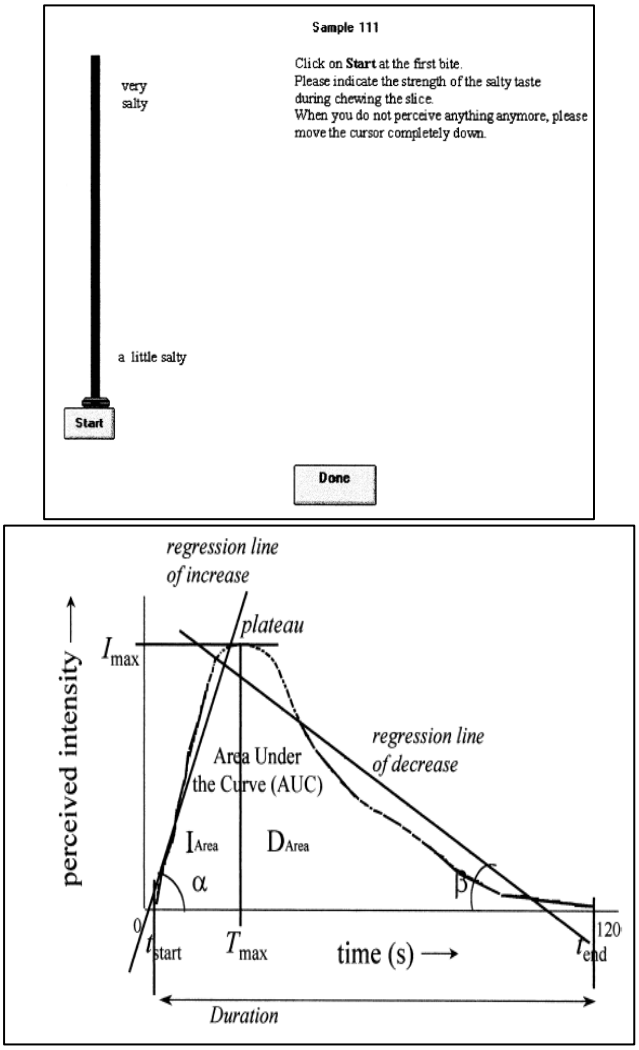


Figure 3.4 Examples of computer screen for TI evaluations of saltiness (Peyvieux & Dijksterhuis, 2001).

Table 3.3. Time-intensity parameters and their definition (Peyvieux & Dijksterhuis, 2001).

PARAMETER	ABBREVIATION	DEFINITION
Maximum intensity	*IMAX*	The maximum intensity (up to 60 pixels) of each samples
Time to maximum	*TMAX*	The time (in seconds) reaching maximum intensity
Increase angle	*α*	The angle of increase to maximum intensity. This can be interpreted to be the rate of onset of sweetness sample
Increase area	*IArea*	The area under the increase portion of the curve.
Decrease angle	*β*	The angle of decrease from maximum intensity. This can be interpreted to be the rate of decrease of the perception Can be simple termed as the 'aftertaste'
Decrease area	*DArea*	The area under the decreasing portion
Area Under the Curve	*AUC*	The total area under the time-intensity curve

3.2.8.7 STATISTICAL ANALYSIS

Using the Compusense 5.0 software (Compusense Inc., Guelph, Ont., Canada), the parameters were extracted from the thirteen individual time-intensity curves based on the flavour intensity perceived by the panellists; IMAX, TMAX, α, IArea, β, DArea and AUC the salty and sweetness and under different condition (non-compressed and compressed). All measurements were done in duplicate. The data were statistically analysed using SPSS version 22.0 for windows (SPSS Inc., Illinois, USA).

The extracted data from all thirteen individuals were subjected to one-way ANOVA with Tukey's HSD post hoc test ($p < 0.05$ denoting significance) descriptive analysis of variance to compare between all individual samples with all the time-intensity parameters (IMAX, TMAX, *α, IArea, β, DArea and AUC)*. Conditions were then further divided into three major categorical conditions which are concentrations, pressure (non-compressed and compressed) and biopolymers (polymer types). In studying the effects of the conditions (concentration, pressure and biopolymers) on the flavour intensity perceived by the panellists, data were then subjected to multivariate analysis. Contingent on the significant differences of the samples we further inquire on the difference on the intensity perceived by the panellist on the two different flavour (saltiness and sweetness). Thus, the repeated measure values for all obtained from previous analyses were subjected to t-test analysis to see the difference between the intensity level for salt (NaCl) and sugar (glucose). The data were statistically analysed using SPSS version 22.0 for windows (SPSS Inc., Illinois, USA).

Principal Component Analysis (PCA) was performed between parameters obtained from the instrumental analysis and time-intensity sensory evaluation. PCA is an explanatory data analysis useful for making predictive models. The results of PCA discusses the factor scores (the transformed variables values corresponding to a particular data points), and loadings (the weight of by which each standardize original variable should be multiplied to get the component score). PCA analysis was performed using the XLStat 2016 (Microsoft, United Kingdom).

CHAPTER 4

TEXTURE AND TASTE COMPOUND RELEASE FROM MODEL GELS

4.1 INTRODUCTION

Several authors have used different gels or gel-like consistency foods (semi solid or soft solid) as model foods looking into quantifying sugar and salt release behaviour (Bayarri et al., 2004; Floury et al., 2009; Holm et al., 2009; Kohyama et al., 2016; Rodrigues et al., 2014; Yang et al., 2015). Due to the limitations of the previous work, this experimental was design to quantify the release of the flavour in an efficient and simple manner. The instrumental measurement model as displayed in previous chapter was carefully designed to allow the mimicking certain oral processing actions. The experimental setup designed in order to be able to consider the unidirectional solute mass transfers from the gel to the phosphate buffer surrounding it. Sodium chloride and glucose were chosen as taste compounds due to the simplicity in recording.

During the optimization of the method, the instrumental set-up was proven to be highly accurate and reproducible. That selection of hydrocolloids (gels) used in the research studies, was based on the variation on the physical and chemical properties that it offers. Gels with different chemical and physical properties were anticipated to give different taste compound release profiles. Before the selection of hydrocolloids was finalise, preliminary tests were done on wide arrays of hydrocolloids (gels), ranging from commercial gel (Dr. Oetker), high methoxylated pectin, κ-carrageenan, alginate and gelatin (type B; medium strength). After final selection was decided upon the simplicity of the preparation, easy handling, the ability to retain its shape under submerge condition. The final concentration presented

in **Table 3.1** was within the suitable range where the mechanical strength of it is not too fragile or rigid to handle.

Regulating the surrounding at pH 7 is an attempt to create a close approximation of the actual mouth condition as the pH in the mouth is reported to be neutral (Chen et al. 2011). Impeller was also inserted to ensure the uniformity the flavour through the buffer solution. Many previous researches have suggested that flavour retention and suspension in the food matrix are highly dependent on the type of food ingredients and on the physicochemical properties of the flavour compounds and that this retention induces noticeable decrease in flavour perception (Guichard 2015; Juteau et al. 2004). This section will look into factors affecting flavour release such as polymer type, polymer concentration, microstructure and temperature. The instrumental data collected from the experiments will further be compared to that of the actual human saltiness and sweetness perception. If the instrumental agrees with the actual human sensory study, this might help the food industry develop and manipulate food formulations to provide healthier alternatives to the consumers. The instrumental set-up is anticipated to become a predictive model for the human perception of the food products that are tested.

4.2 AIM AND OBJECTIVES

Aim of this study is to optimise the instrumental measure that enables the measurement of taste compound release from gel systems. The objective of this section is to observe the effect of the listed parameters on the taste compound release profile:

- Polymer types
- Polymers concentration
- Polymer mechanical strength
- Polymer microstructure
- Temperature
- Compression

This chapter aims to answer key questions; whether these parameters plays any significant role on the taste compound release profiles.

4.3 RESULT AND DISCUSSION

4.3.1 TEXTURE/MECHANICAL PROPERTIES OF GELS WITH ADDITION OF SODIUM CHLORIDE AND GLUCOSE

The gel physical and mechanical properties was known to be one of the factors affecting the release of flavour (Holm et al. 2009; Buettner & Schieberle 2000; Hons 2002; Ferry et al. 2006; de Roos 2003). The first step of this research was to perform mechanical testing on all the gels utilised in the research. The results were then analyse and compare with the percentage of flavour release which will be discussed in the next section

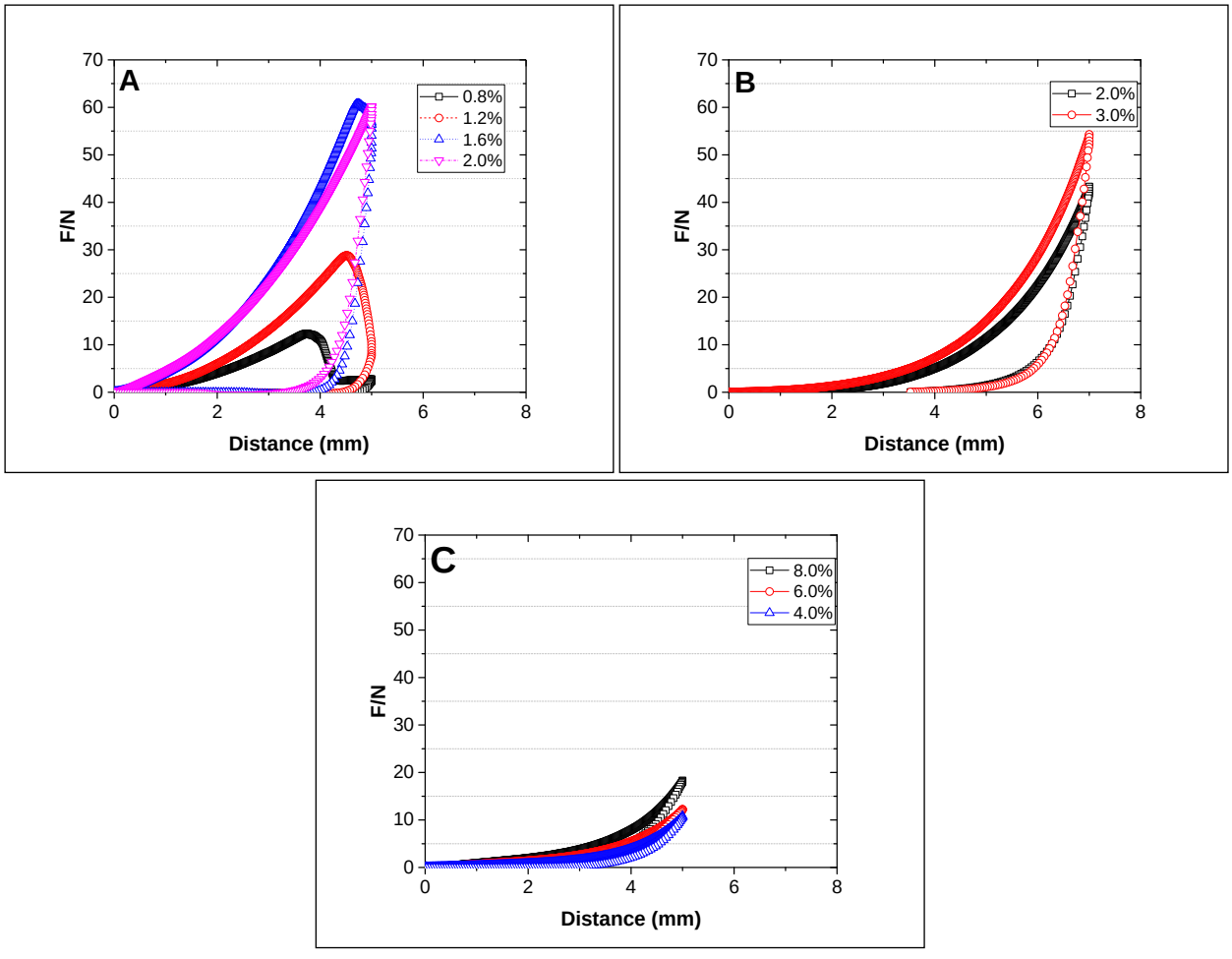


Figure 4.1 Force (N) against distance (mm) curve for compression of cylinder with the addition for NaCl of κ-c (A), alginate (B) and gelatin (C) gels at different concentration. Tests were performed at a constant rate of 2mm/s to 5 mm distance compression. Alginate compressed at constant rate of 2mm/s to 7 mm distance.

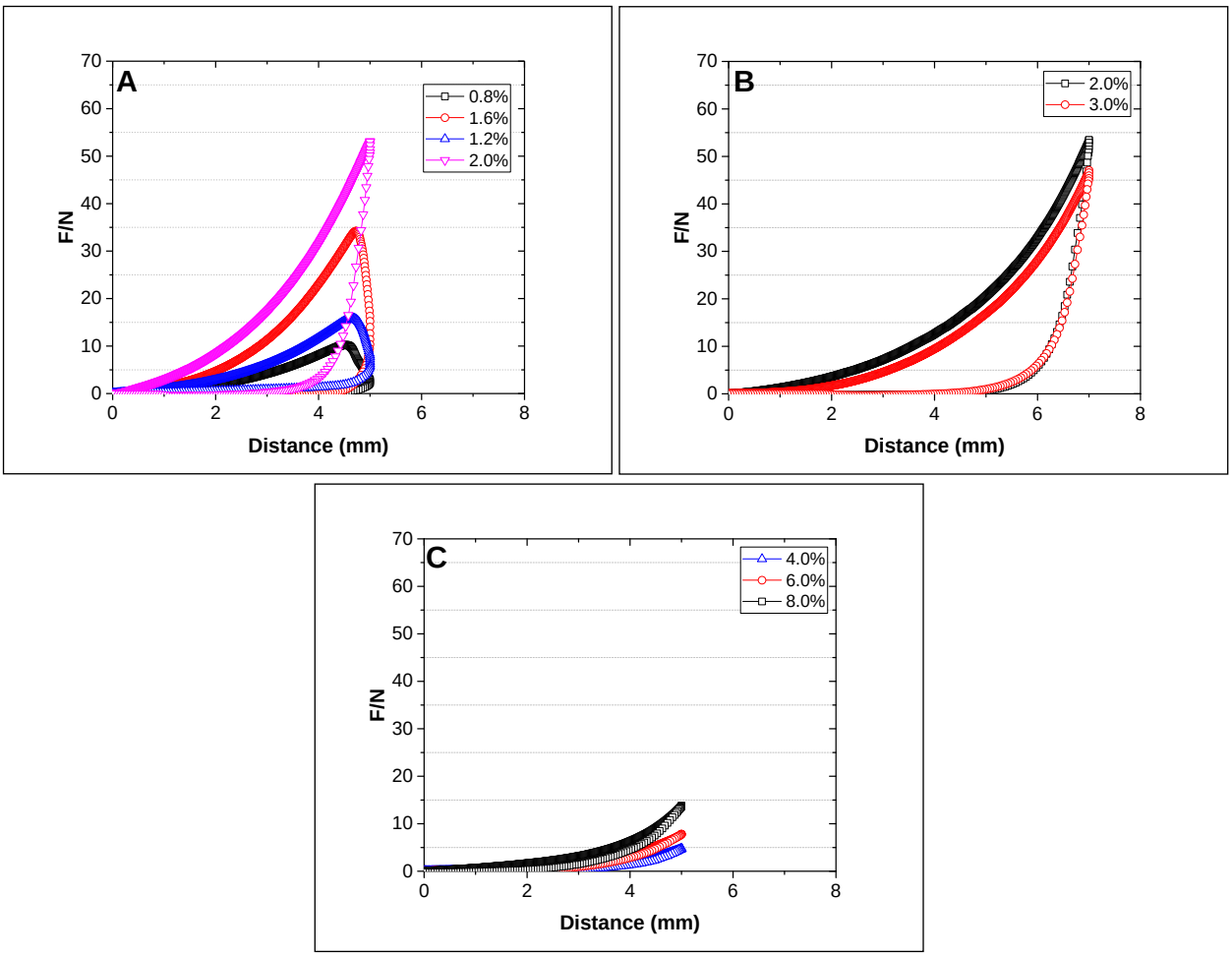


Figure 4.2 Compression fracture force (N) against distance (mm) curve for compression of cylinder with the addition for glucose of κ-C (A), alginate (B) and gelatin (C) gels at different concentration. Tests were performed at a constant rate of 2mm/s to 5 mm distance compression. Alginate compressed at constant rate of 2mm/s to 7 mm distance.

Figure 4.1 and **4.2** shows the compression curves and demonstrate the mechanical strength of the κ-carrageenan, alginate and gelatin gels at their respective concentrations with the addition of NaCl and glucose. There was no evidence of fracture as results shows smooth line. However, the peak of the all the curves indicate the hardness/firmness of the gel. This point indicates that damage and deformation have occurred. Alginate was compressed at a greater distance (7 mm) as at 5mm distance compression the alginate gels were still intact. **Table 4.1** shows the hardness of the gels at 5 mm distance compression.

Table 4.1 Hardness (F = N; maximum peak) of gels compressed to 5mm distance.

Samples	Concentration (%)	Hardness (N)	
		NaCl	Glucose
κ-C	0.8	2.73 ± 0.15	2.82 ± 0.26
κ-C	1.2	10.07 ± 0.32	7.68 ± 1.46
κ-C	1.6	50.37 ± 2.17	15.22 ± 0.97
κ-C	2.0	60.28 ± 0.12	53.11 ± 2.36
Alginate	2.0	11.40 ±3.67	16.87 ± 7.28
Alginate	3.0	15.09 ± 6.54	20.56 ± 6.35
Gelatin	4.0	10.67 ± 0.43	4.38 ± 0.46
Gelatin	6.0	12.23 ± 0.38	7.77 ± 0.48
Gelatin	8.0	18.24 ± 0.36	20.56 ±1.64

The increment of gel concentration makes stronger gels. The application of higher forces was needed to cause fracture of the gel. Overall, gel mechanical strength was weakened with the addition of glucose. At 5mm compression of the κ-c gave the highest compression force and gelatin the lowest. Previous studies have shown that κ-carrageenan is able to form strong gels and stable gels at low concentration (Brenner et al., 2014; Garrec et al., 2013; Madene et al., 2006; Tecante & Núñez, 2012). This property has

contributed to the wide application of κ-c in the food industry. Alginate is also known to form very strong and sturdy gels. Extensive applications of alginate especially in the medical and pharmaceutical industries is also due to its property as a strong gel which with can withstand extreme conditions such of pH and temperature and with low toxicity (Lee & Mooney, 2013; Masuelli & Illanes, 2014; Sosnik, 2014; Vicini et al., 2015). The application of gelatin is often to increase the viscosity of fluids or semi/ soft solids such as cakes and confectionaries as compared to the other two gels used here (Saha & Bhattacharya 2010; Banerjee & Bhattacharya 2012).

4.3.2 MICROSTRUCTURE OF GEL SYSTEM (LIGHT, CONFOCAL AND CANNING ELECTRON MICRSOCOPE)

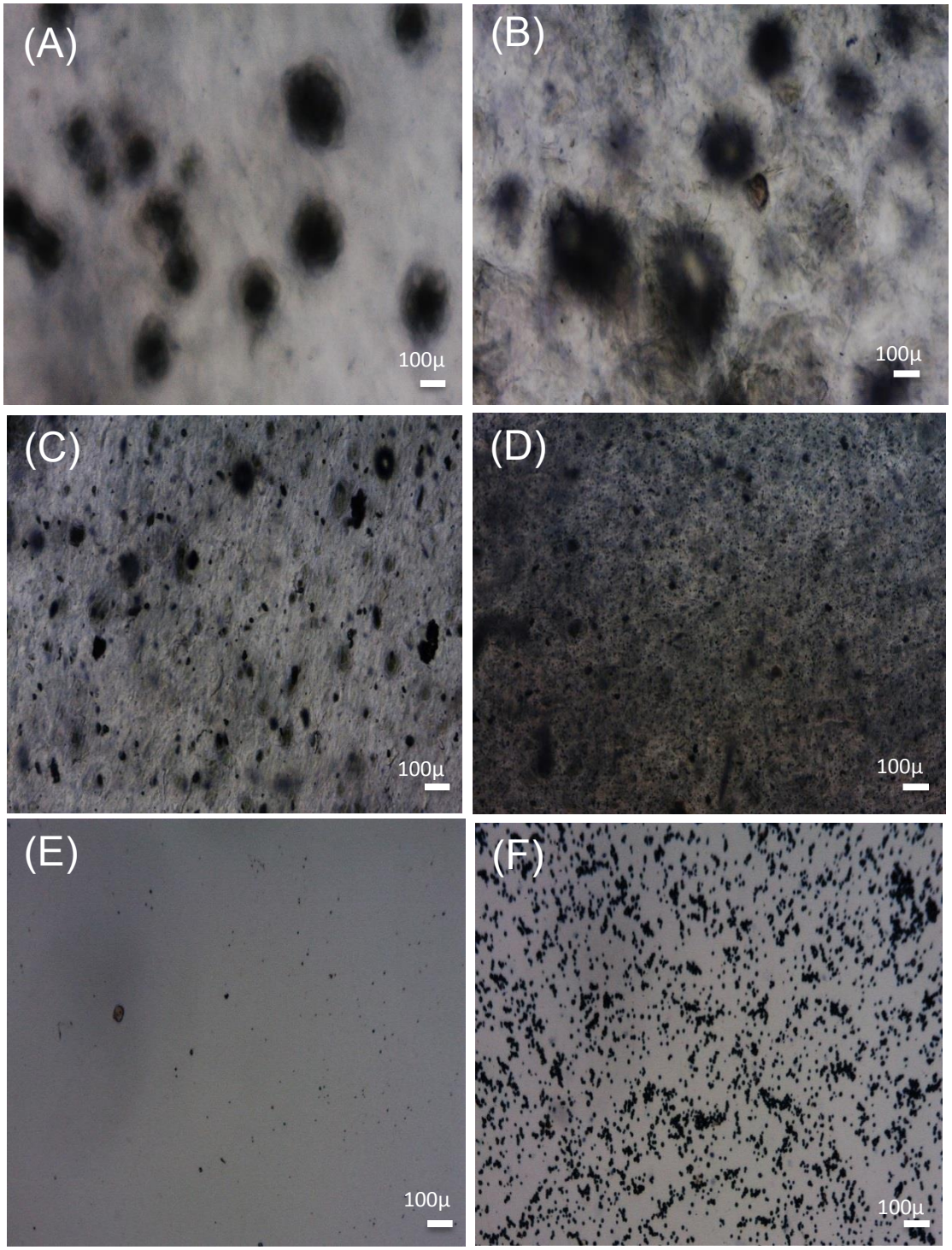


Figure 4.3 Representative light microscope micrographs of gel systems with the addition of both sodium chloride and glucose A) 2% κ–C + NaCl B) 2% κ–C + glucose C) 2% alginate + NaCl D) 2% alginate + glucose E) 6% gelatin + NaCl F) 6% gelatin + glucose. Dark regions are pores. In gelatin (F) dark region are bubbles. The size bar = 100 μm.

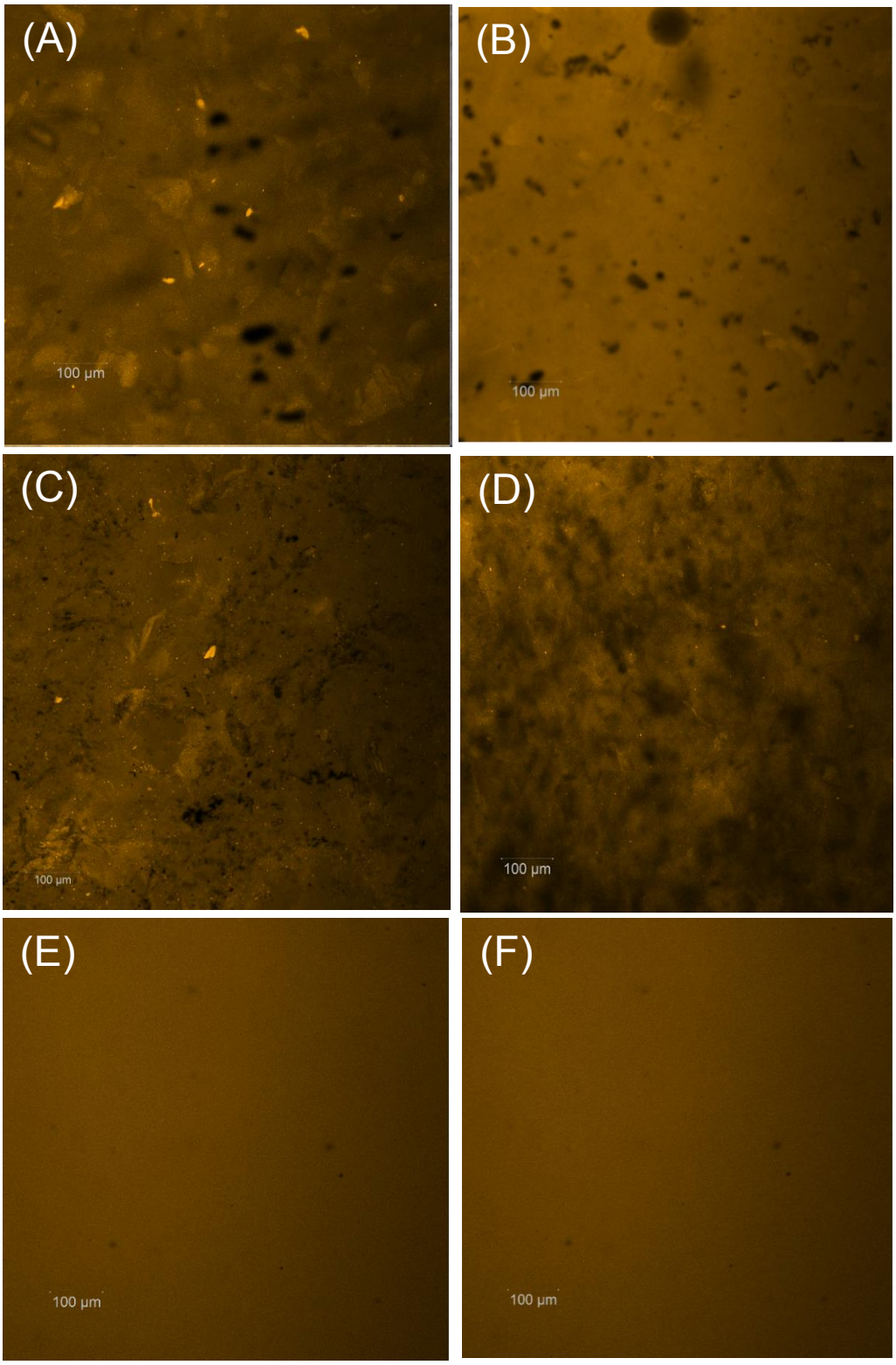


Figure 4.4 Representative micrographs of gel systems with the addition of both sodium chloride and glucose A) 2% κ–C + NaCl B) 2% κ–C + glucose C) 2% alginate + NaCl D) 2% alginate + glucose E) 6% gelatin + NaCl F) 6% gelatin + glucose. Dark regions are pores. The size bar = 100 µm.

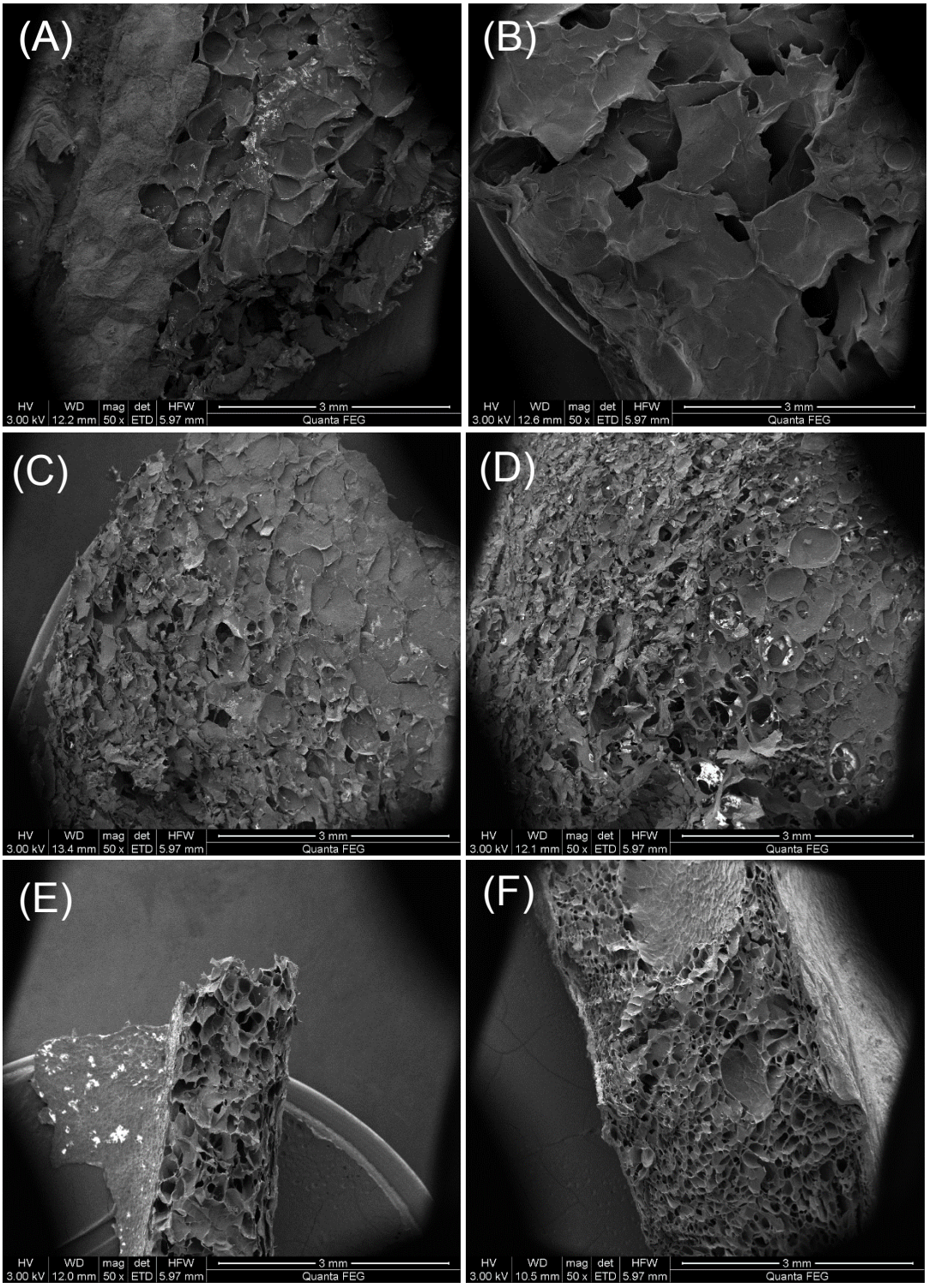


Figure 4.5 Representative micrographs of gel systems with the addition of both sodium chloride and glucose A) 2% κ–C + NaCl B) 2% κ–C + glucose C) 2% alginate + NaCl D) 2% alginate + glucose E) 6% gelatin + NaCl F) 6% gelatin + glucose. Dark regions are pores. The size bar = 3 mm.

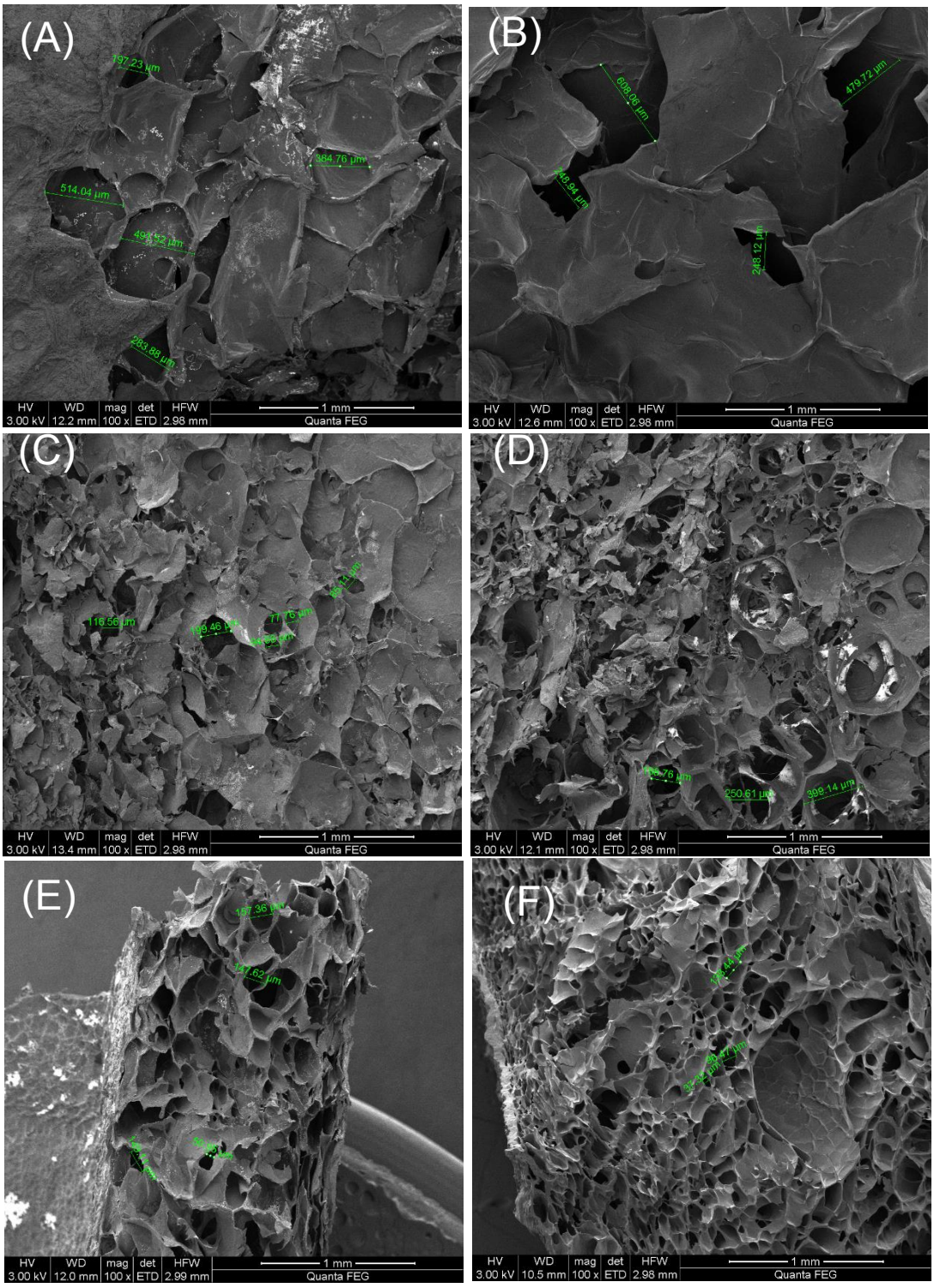


Figure 4.6 Representative micrographs of gel systems with the addition of both sodium chloride and glucose A) 2% κ–C + NaCl B) 2% κ–C + glucose C) 2% alginate + NaCl D) 2% alginate + glucose E) 6% gelatin + NaCl F) 6% gelatin + glucose. Dark regions are pores. The size bar = 1 mm.

Figures 4.3 to **4.6** are the micrographs for κ-carrageenan, alginate and gelatin gels. The gel physical microstructure was captured from three different types of microscopes and the micrographs show close resemblance among another. The formation of pores by different gel systems varies in size. Based on the overall observations, both κ-carrageenan and alginate gels were shown to be porous gels. However, κ-carrageenan gels have larger pores as compared to alginate. Gelatin exhibit smooth surface in **Figure 4.3** and **4.4,** this suggests gelatin gels to have finer pores and channel size. A closer observation can be seen in **Figure 4.5 (50x magnification) and 4.6 (100x magnification)** and the measurements scale insert for the pores can be seen in **Figure 4.6.** It was worthy to mention, the addition of NaCl and glucose seems to have an effect on the pore size of the gels. Both sodium chloride and glucose are well known gel cross-linkers which are responsible in formation and packing of the gel network (Hollingworth, 2010; Lee & Mooney, 2012; Mahdavinia et al., 2014; Smidsrød & Haug, 1967). The addition of NaCl produce gels with finer pores as compared to gels with the addition of glucose. However, for gelatin gels with the addition of both taste compounds does not show any striking differences in the pore size. Gelatin gels have finer pores and channel size as compared to other two gels. The differences in the pore size for κ-carrageenan and alginate is believed to be affected by the mechanism of gelation and polymer packing. The physical arrangement of these junction zones within the network can be affected by various parameters like temperature, presence of ions and inherent structure of hydrocolloid (Doi, 2009; Otake et al., 1990; Saha & Bhattacharya, 2010). The size of the ions in salt is very fine which allows the ions to meander or move in between the polymer chains to create a more closely packed structure as illustrated in **Figure 4.7**. It is also know the addition of salt to the polymer will reduce the electrostatic repulsion pushing the network to be closer to one another. For alginate gels, the egg box model is known to offer a very effective close polymer packing which leads to a more dense network. In contrast, the sugars which have larger

molecular size, created a more loosely packed network, mechanism shown in **Figure 4.8**.

In relation to the previous section, this further explains the formation of stronger gels for κ-carrageenan and alginate gels with the addition of NaCl as compared to glucose. The effect of the mechanical and physical microstructure on the flavour release will be further discussed in the next section.

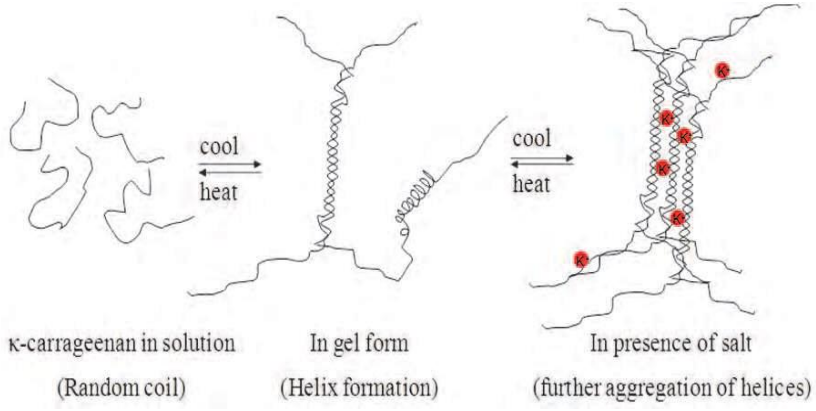


Figure 4.7 Gel formation due to aggregation of helix upon cooling a hot solution of carrageenan (Gulrez et al., 2003)

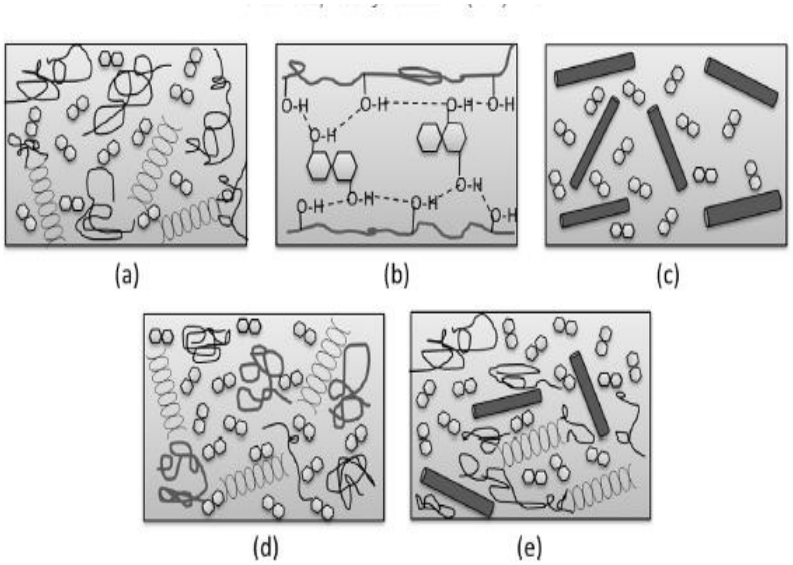


Figure 4.8 Schematic illustration to show the impact of the sugar molecules in the hydrocolloid solution of a) agarose, b) alginate, c) xanthan d) agarose alginate mixture and e) agarose-xanthan mixture. Hexagonal symbols represent the sugar molecules thin lines and helices the agarose and thick lines the alginate polymers. In the agarose solution, the sugar molecules hinder the diffusion of polymer chains and double helices. In the alginate solution, the sugar molecules act as linker between the polymer chains, and

in the xanthan solution the sugar molecules reduce the electrostatic repulsion. In the agarose-alginate mixture, the mobility of the agarose polymers is limited by the less flexible alginate coils additionally. For agarose-xanthan mixtures, free sugar molecules as well as xanthan rods hinder the agarose network formation. (Russ et al., 2014).

4.3.3 SALT AND GLUCOSE RELEASE FROM MODEL GELS

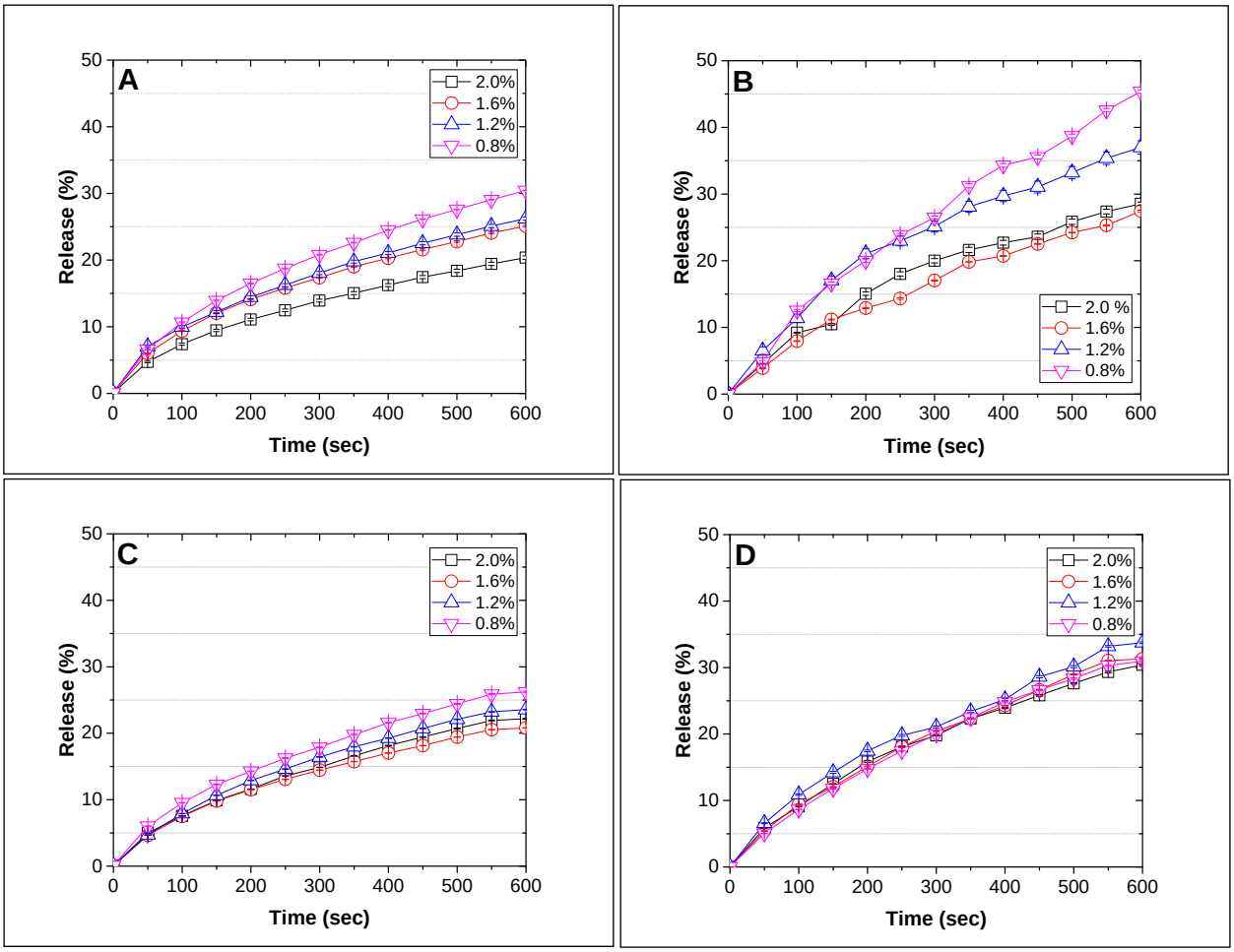


Figure 4.9 NaCl release over time into 200 ml of phosphate buffer from compressed cylinder of κ-carrageenan gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C), at 37 ºC (D) compressed by constant amount (2mm).

Figure 4.9 shows salt release of κ-carrageenan under ambient/room temperature and at 37 **º**C as well as under applied pressure. Overall, the trends show under almost all conditions, release is faster for gels with lower

polymer concentration. However, there was no significant difference ($p > 0.05$) on the overall effect of concentration on the release of NaCl. Results also revealed to be significantly ($p<0.05$) faster release at higher temperature. Pressure applied causes not much significant change, just slightly slowing down the release.

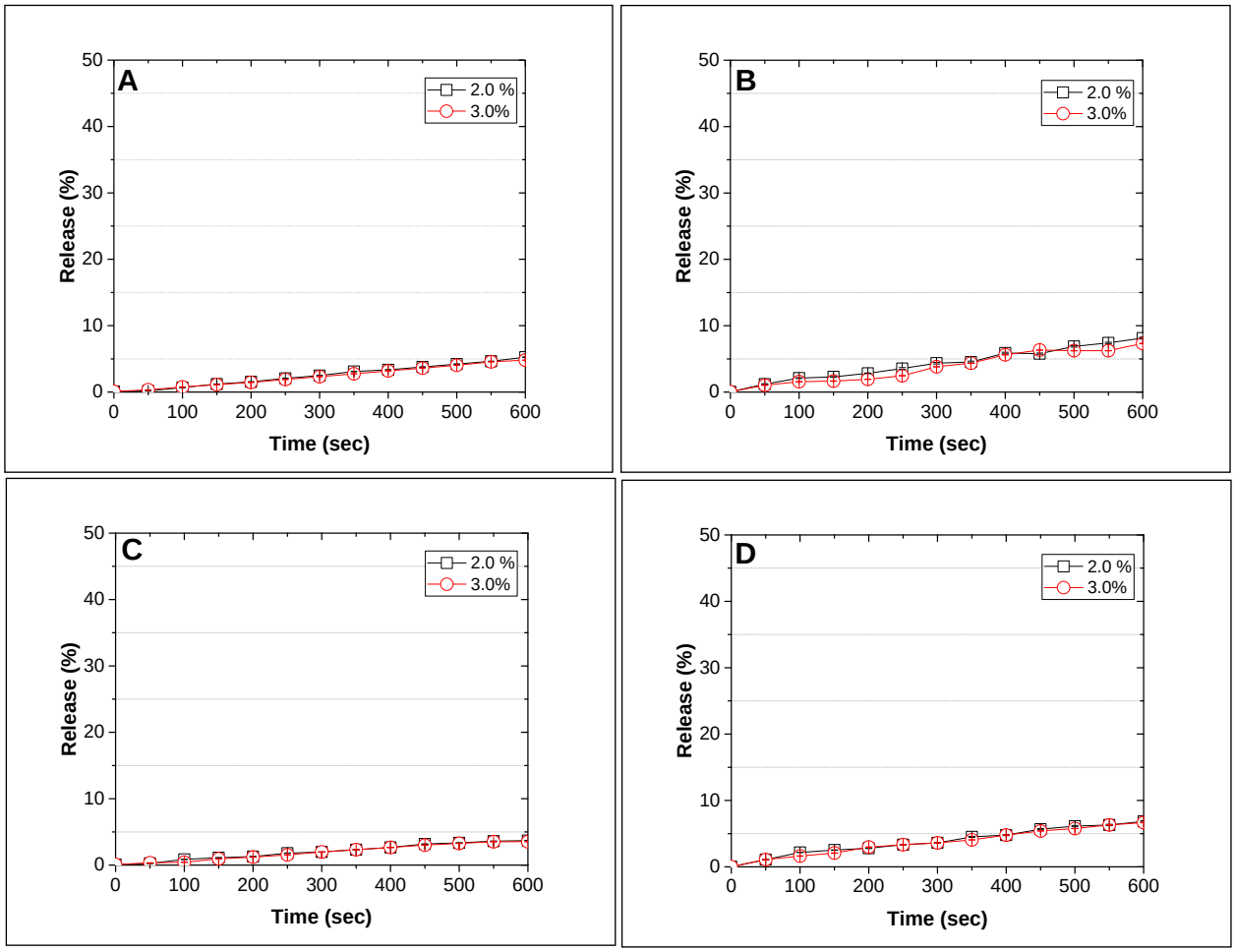


Figure 4.10 NaCl release over time into 200 ml of phosphate buffer from compressed cylinders of alginate gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C), at 37 ºC (D) compressed by constant amount (2mm).

Figure 4.10 shows the salt release of alginate gels under similar condition as the κ-carrageenan gels. Release of NaCl from alginate gels was observed to be significantly lower ($p<0.05$) as compared to salt release from κ-

carrageenan. Unlike κ-carrageenan gels, concentrations seem to have no effect on the release of the salt. The release of salt at both polymer concentrations under all condition was observed to be almost similar. The release was observed to be slightly faster at higher temperature (37 ºC). Compression again showed no evident change, only a slight reduction in the salt release.

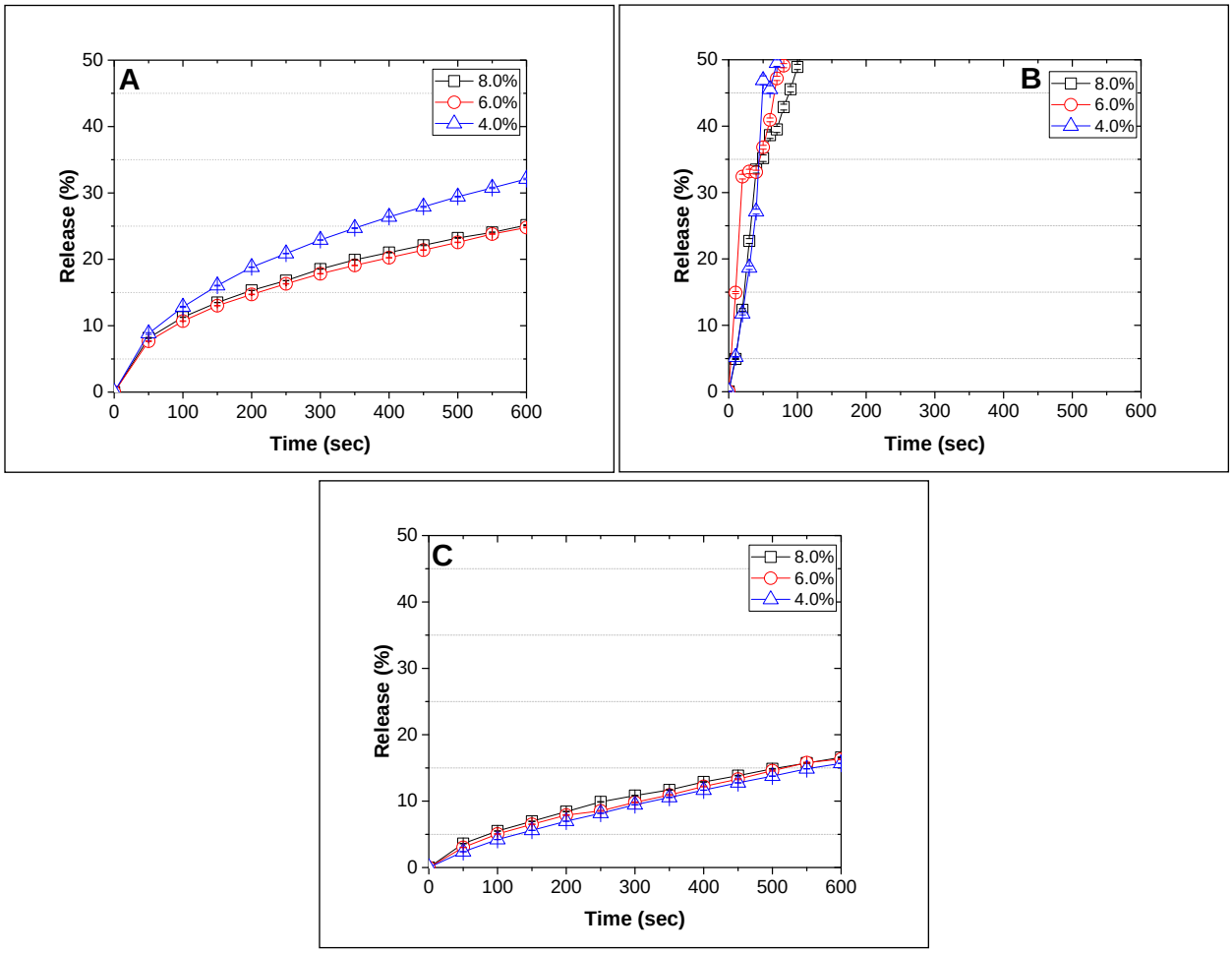


Figure 4.11 NaCl release over time into 200 ml of phosphate buffer from compressed cylinders of gelatin gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C), at 37 ºC (D) compressed by constant amount (2 mm).

Figure 4.11 shows results of NaCl release from gelatin gel. At room temperature, faster release was observed in gelatin gels at lower concentration. However, under applied pressure, under all concentration it was observed that the release rate was similar. Like other gels, the application of pressure was seen to slow down the NaCl release as well. Rapid release was observed for gelatin gels at 37 ºC**.** The release was recorded almost under two minutes. Due to the rapid melting of gelatin gels at 37 ºC, it was impossible to perform the experiments of the gelatin gels under compression.

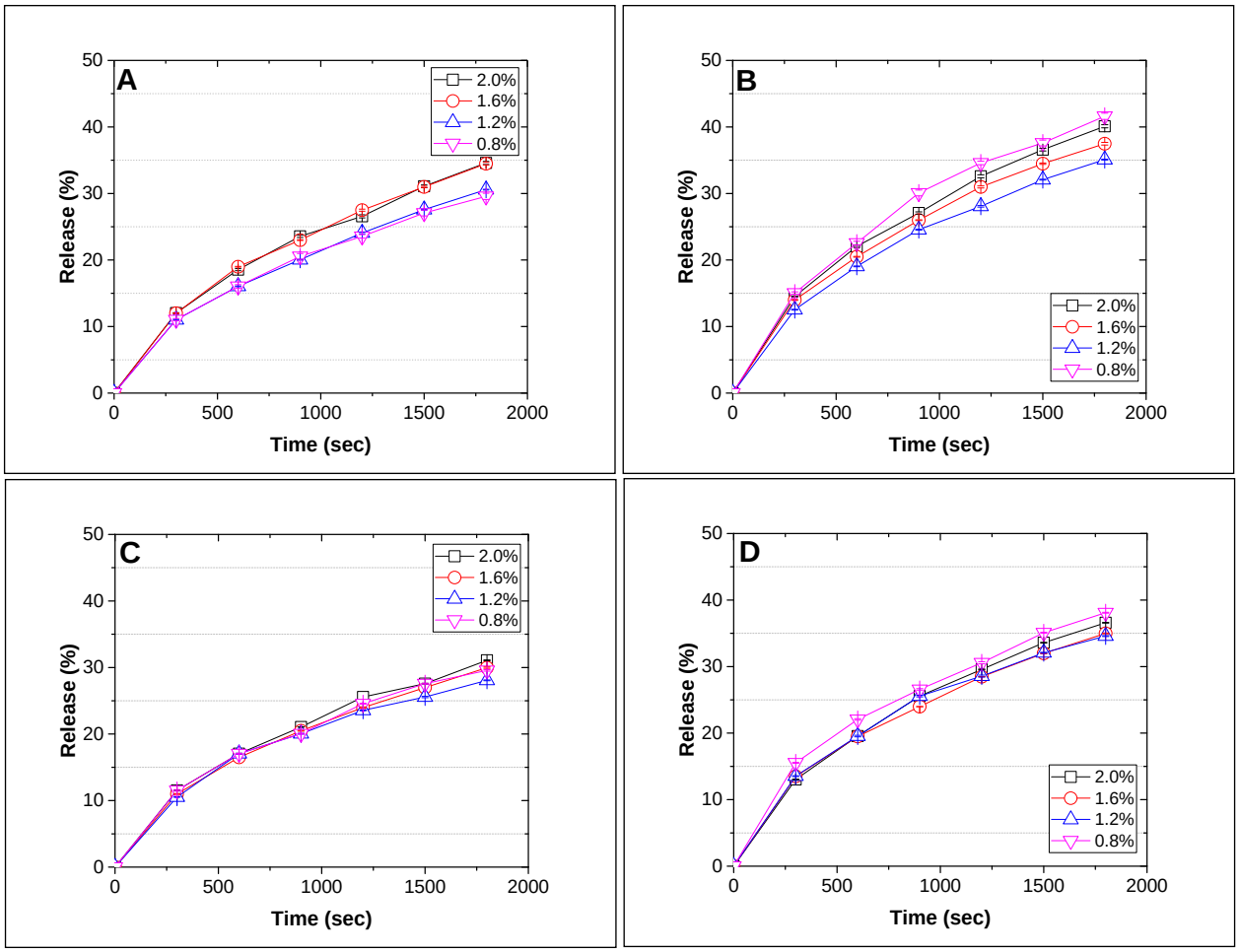


Figure 4.12 Glucose release over time into 200 ml of phosphate buffer from compressed cylinders of κ-carrageenan gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C), at 37 ºC (D) compressed by constant amount (2mm).

Similar conditions were applied for the glucose release test. **Figure 4.12** shows glucose release for κ-carrageenan gels. In contrary to the salt release, overall, gel concentration does not seem to affect the release of glucose. Similar to salt release, the compression of the gel does not cause any significant change on the glucose release. However, it was evident that higher temperature leads to faster glucose release.

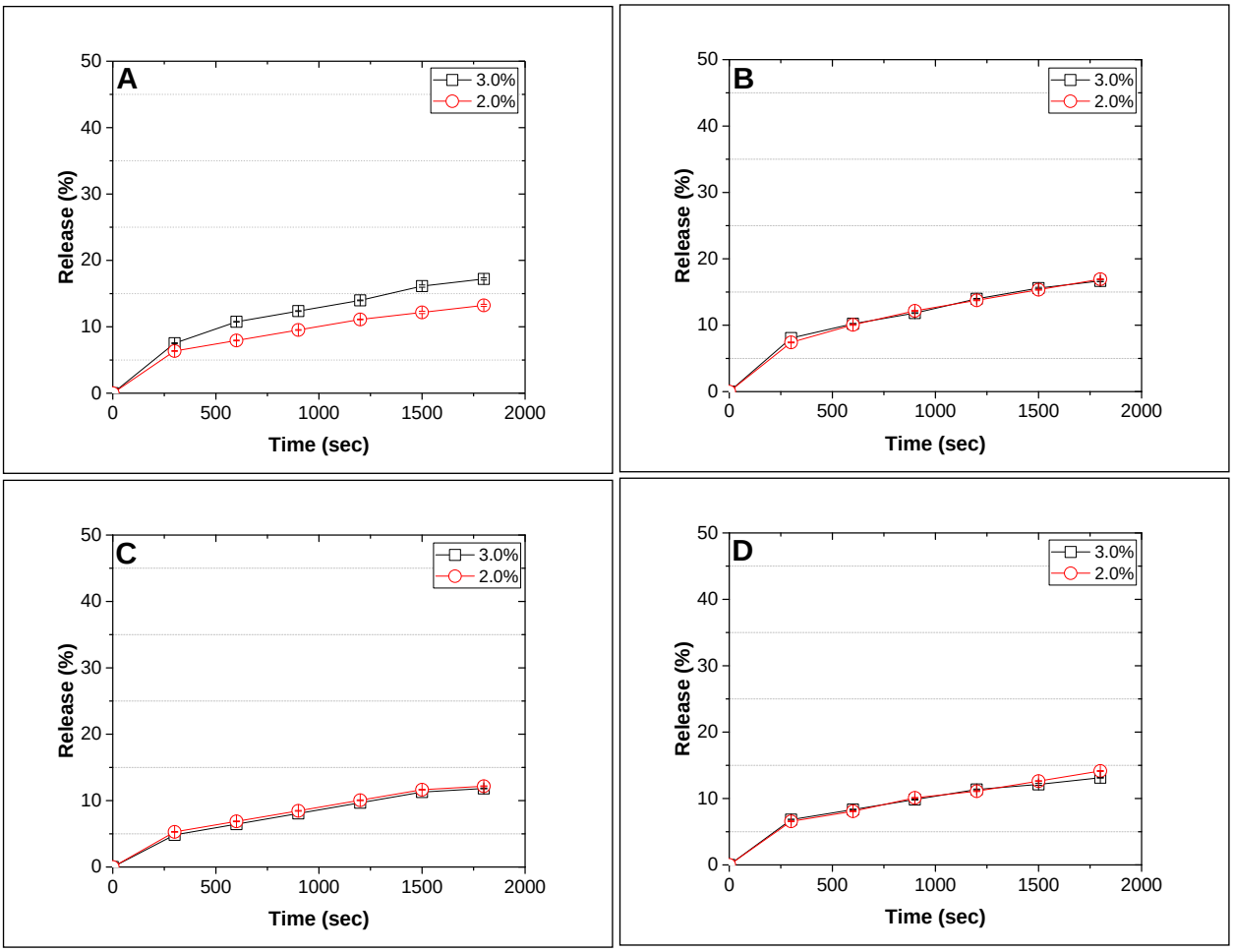


Figure 4.13 Glucose release over time into 200 ml of phosphate buffer from compressed cylinders of alginate gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C), at 37 ºC (D) compressed by constant amount (2mm).

Glucose release from alginate gels displayed in **Figure 4.13** shows similar resemblance on their trends of release. Concentration does not seem to have any effect on the release of glucose. Furthermore, the release of glucose for the alginate gels is significantly slow ($p < 0.05$). The increment in temperature was seen to have no effect on the release. Interestingly, temperature increment seems to have no effect on the glucose release.

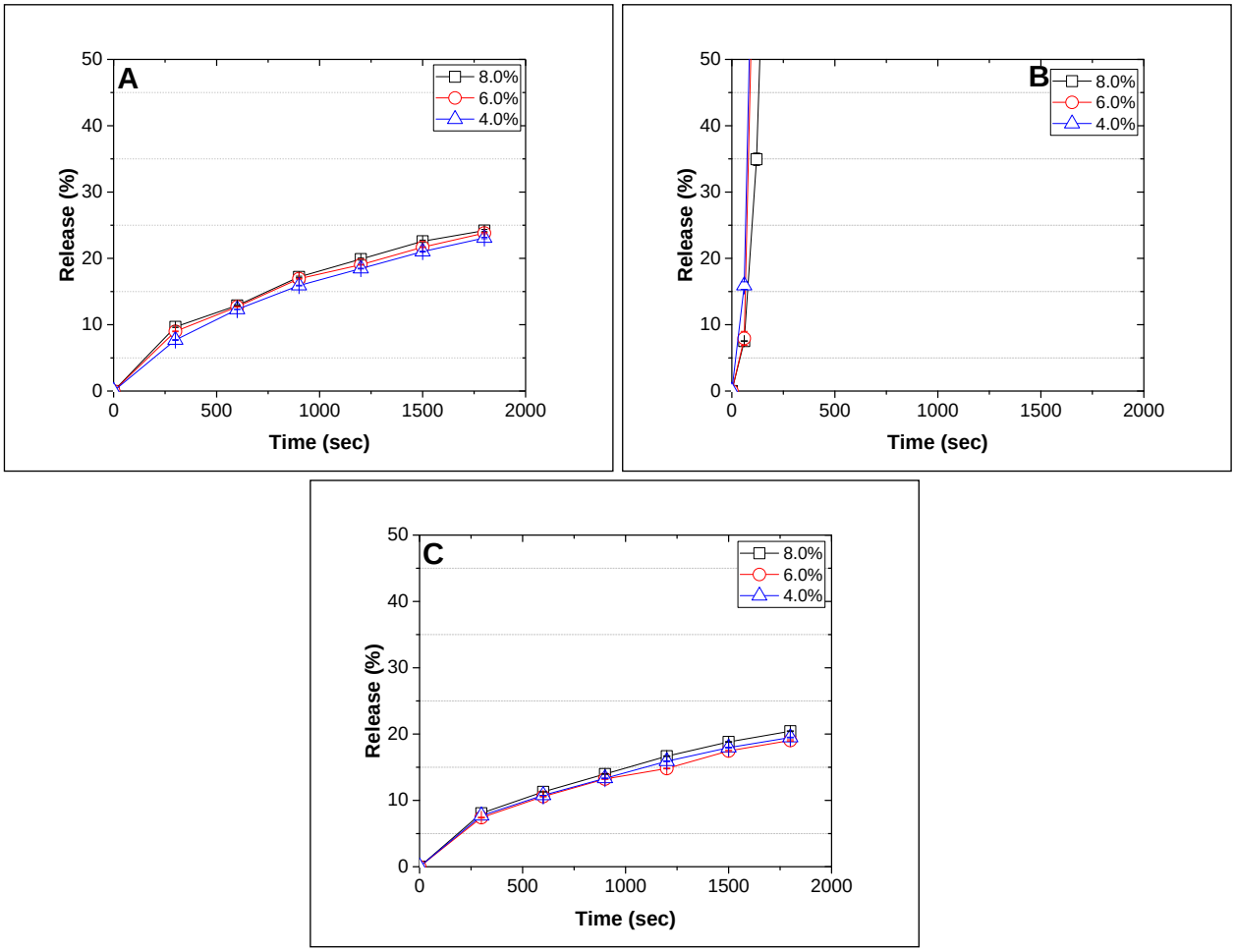


Figure 4.14 Glucose release over time into 200 ml of phosphate buffer from compressed cylinders of gelatin gels at room temperature (A), at 37 ºC (B) (non-compressed) and room temperature (C) compressed by constant amount (2mm).

Figure 4.14 shows glucose for gelatin gels. There is no significant difference ($p > 0.05$) in the release at different gel concentrations. There was also no significant difference at room temperature and under compression ($p > 0.05$). Besides that, compression was observed not to have any major effect on the release of glucose from the gelatin gel. Again, the melting properties rapid release glucose release was observed at higher temperature.

In order to make a more thorough observation on the relationship of mechanical properties release percentage with the, the mechanical curves and release curves were further analysed. A detail discussion on these relationships will further be discussed in the next section.

4.3.4 COMPARATIVE STUDY ON SODIUM AND GLUCOSE RELEASE PROFILE

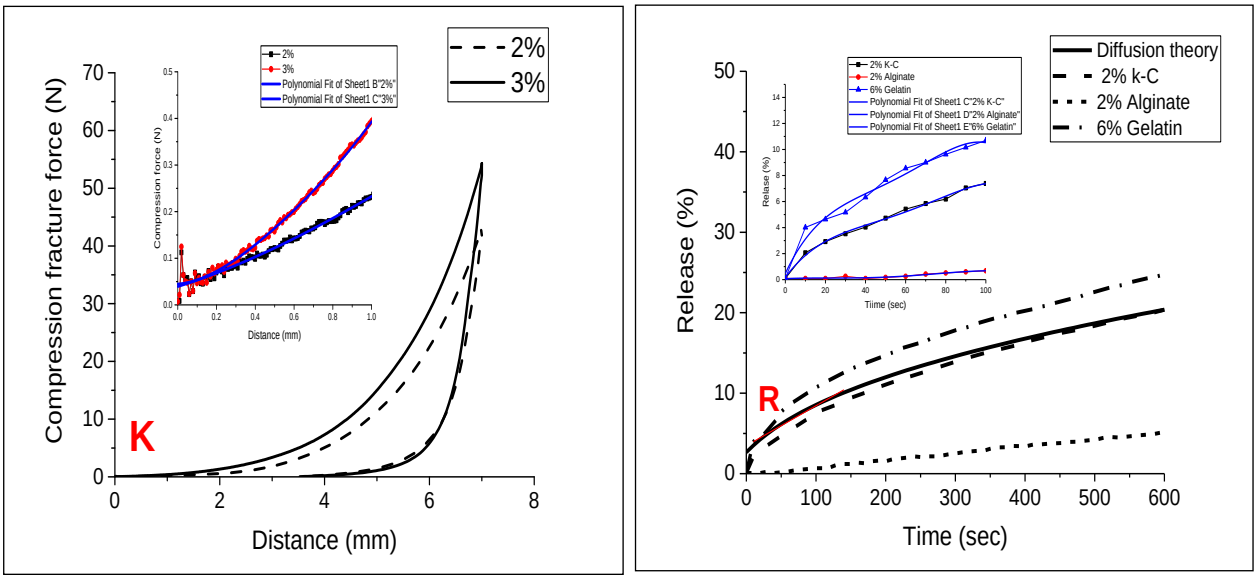


Figure 4.15 Calculation gradient initial gradient for both release and compression fracture curves. Initial gradient for mechanical strength at distance 0.1-1 mm and the initial gradient for taste compound release from 0-100 seconds.

The release experiments can be performed for long period of time. However, in the oral processing, the mastication process in oral cavity is a rapid process lasted for only seconds (Chen, 2009; Mills et al., 2011 & Stieger & van Velde, 2011). The initial gradient of the release curve therefore gives meaningful results as the initial seconds of release represent the flavour release behaviour in the mouth. The gradient of the initial force versus distance (at 0.1 – 1 mm) and initial release rate (at 0-100 secs) were measured are done to simplify on the relationship between mechanical properties and rate release of taste compounds. An illustration of the fit was done of the initial gradient are shown in **Figure 4.15**. The small figure insert is an example of the polynomial fitting done on each mechanical and release curve. **K (N mm^{-1})** represents the mechanical gel strength or stiffness, best fit of the data over the firm 0.1-1.0 mm at 1.0 mm. **R (%/s)** represents the release rate of taste compound best fit at 100 seconds.

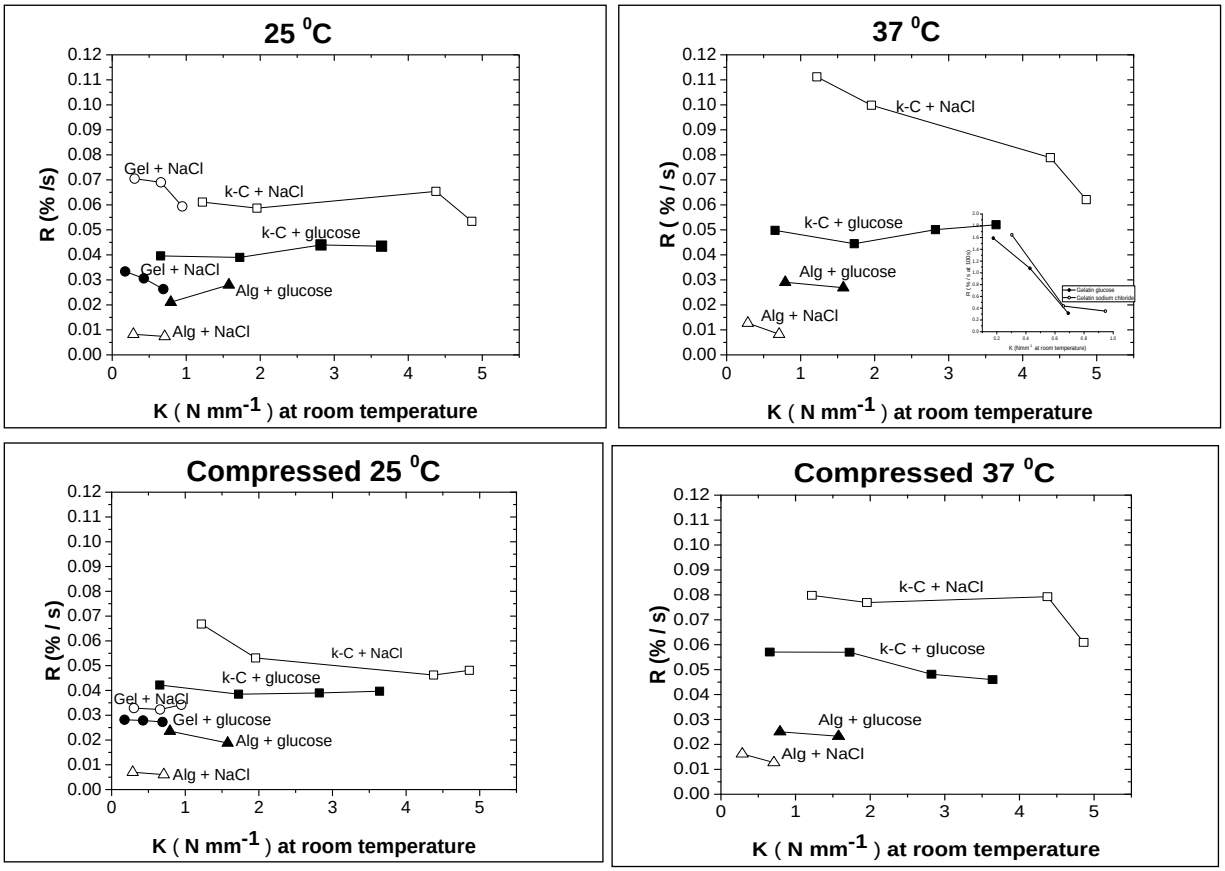


Figure 4.16 R (%/s) over K (N mm^{-1}) for all gels with the addition of sodium chloride and glucose room temperature.

Figure 4.16 shows at 25 **º**C irrespective of gel stiffness **K**, κ-carrageenan gave the most rapid release of both NaCl and glucose, probably due to the larger porosity of the κ-carrageenan gels which has been discussed in earlier section. Alginate gave lowest release rate of both NaCl and glucose, release of NaCl being particularly low, whereas for κ-c and gelatin, release of NaCl was faster than for glucose for gels of the same **K**. This probably points to the some physical binding of NaCl to the negatively charge alginate. Network, plus possibly a finer gel network based on the microscopy results. The affinity of the NaCl κ-c and alginate towards sodium ions might explain the difference rate of release from κ-c and alginate gels. Based on a review written by Tecante et al. (2005) and Rochas (1982) listed the affinity of κ-carrageenan towards monovalent ions in decreasing order such as follows:

$Rb+ > Cs+ > K+ > NH_4 + > (CH_3)_4N+ > Na+ > Li+$

The low affinity towards NaCl makes sodium ions to be easily disassociated from the polymer and into the surrounding buffer. A study conducted by Smidsrod and Haug (1967) on ion pairs formed with potassium and sodium ions by different polymers inclusive of alginate and carrageenan shows, alginate exhibited higher affinity towards sodium ions as compared to carrageenan.

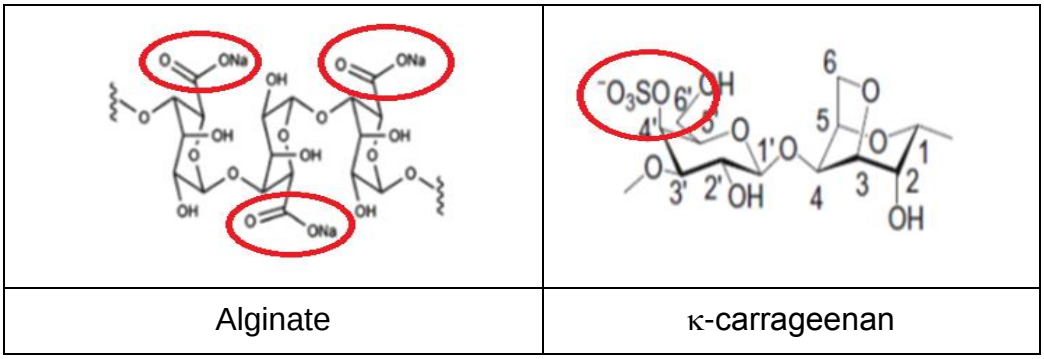


Figure 4.17 The negative net charge for per sugar unit of alginate and κ-carrageenan circles in red.

Figure 4.17 shows the net charge in sugar unit for both alginate and κ-carrageenan. The diagram might also help in explaining high affinity of sodium chloride towards alginate as compared to κ-carrageenan. The number of negative net charge in alginate is higher due to the presence of the carboxyl group (COO^-) in each of the sugar unit as compared to the κ-carrageenan. There is only one negatively charged sulphated group in one sugar unit of κ-carrageenan. This negatively charge provides electrostatic attraction towards the NaCl ions. The higher the negative net charge in the polymer the more strongly the taste compound will be bound to it.

At body temperature (37 ºC) κ-c with NaCl gels were weaker and showed faster release of both NaCl and glucose, but particularly NaCl. The increment in temperature in a solution's temperature resulted to changes in polymers structure and an increase in the mobility of the ions in solution. An increment in temperature may assist in disassociating ions from polymers matrix all together allowing the ions to be released into the surrounding matrix. The increment in temperature is usually linked in reducing viscosity of

solution and polymers. Temperature provides energy later absorbed inciting ions mobility and movement. High mobility ions and low viscous polymers create spaces for ions and glucose molecules movement in leaving the gel matrix and into the surrounding. Gel stiffness did not decrease as much at 37 **º**C for alginate, and release rates of glucose and NaCl increased only slightly but particularly for NaCl which remained very low. Gelatin gels melted at 37 **º**C resulting to the extremely rapid release. Only κ-c gels shows strong dependence on **K** at both at 25 and 37 **º**C, where release rates **R** decreased with increasing ok **K**.

For the compressed gels at 25 and 37 **º**C, the trends NaCl were more or less the same except that NaCl release rate were lower for κ-c gels even though the stiffness were more or less the same for uncompressed gels. This point to some sort of change in NaCl binding or porosity on compression even though **K** is not affected. Release rates for alginate and gelatin gels are not so much affected by compression, only slight reductions were observed. At 37 **º**C, again, κ-c gels showed the most significant increase in **R** compared to gels at 25 **º**C. Release rate of alginate gels again remained very low. Gelatin gels again melted at 37 **º**C so **R** versus **K** plots presented in the small insert. Aside than alginate, rate of glucose release was observed to be slower, as this might be due to larger molecular size as compared to NaCl ions. The presence of 10% glucose in buffers was seen to affect buffer's viscosity which may contribute to the slower release of glucose.

4.3.5 SUMMARY

Initial findings of this section suggest that different polymers exhibit different release profiles. The effect of polymer concentration was roughly observed to have striking effect on κ-carrageenan. Temperature was also observed to play a significant role resulting to a faster taste compounds release. The initial gel mechanical strength and instrumental measure of taste compound release allows a more detailed observation to be performed by calculating the initial gradient at a specified point. The result suggested that irrespective to the gel stiffness, κ-carrageenan gave the most rapid flavour release

followed by gelatin and alginate. This is believed to be affected by gel porosity, where release rate decrease as **K** increases. In alginate gels the release of glucose was observed to be faster than NaCl. This suggest some sort of binding of NaCl to the negatively charge alginate. It also provided that the negative net charge per sugar molecules unit of alginate is higher than κ-carrageenan which explains the strong binding of NaCl towards alginate as compared to κ-carrageenan. Due to this alginate was observed to have very slow release as compared to κ-carrageenan. In general, at higher temperature release rates increases for all gels except for alginate gels. Besides that, κ-carrageenan shows strong dependence on **K** (stiffness), specifically at body temperature 37 **º**C, where release rates **R** decreased with increasing **K.** The rapid release observed in gelatin gels was due to their melting property. Compression does not cause any significant change in release rate, only slight reduction was observed in all gels. The compression is known to have no effect on the gel stiffness; however, internal structural change might cause the increase in contact of the taste compounds towards the gel polymer and hinder the flavour to be released from the gel matrix. Previous studies on taste compound release profile have suggested the mechanism governs the release are diffusion. This chapter has provided information on the release profile of taste compounds in different polymers, which further leads to an inquiry whether the mechanism of the instrumental measure is simply diffusion or maybe the release is controlled by some other unique mechanism. In order to answer the research question, a mathematical model based on the diffusion theory needs to be initiated. The next section is dedicated into discussing the theoretical consideration and mathematical modelling of the instrumental measures.

CHAPTER 5

KINETIC OF TASTE COMPOUND RELEASE IN GEL SYSTEMS: EXPERIMENTAL STUDIES AND MATHEMATICAL MODELLING

5.1 INTRODUCTION

The majority of interactions of real food systems are far too complicated and very difficult to model it in a complete form. Mathematical modelling involves translating a simple model system into mathematical equations. Models can be useful in testing various assumptions about the factors controlling flavour release. There has been past research studying the behaviour of flavour release from the food matrices.

5.2 AIMS AND OBJECTIVE

The aim is to design a simple mathematical diffusion model based on the instrumental design used this research. The objective of this study is to attempt in proving that the mechanism that governs the release of the taste compound is diffusion. This chapter also investigates the degree of variation between the experimental releases with the theoretical release.

5.3 THEORETICAL CONSIDERATIONS

In this section, the flavour release mechanisms from gel systems are discussed from a theoretical point of view. The process of the flavour transfer to the solution surrounding the cylindrical piece involves the process of diffusion. Why diffusion? The main principle in various mass transfers both physical and biological phenomenon is diffusion. Diffusion is defined as the movement of a fluid from an area of higher concentration to an area of lower concentration (Vashisht, 2014). Wide arrange of work that has been done flavour compounds (volatile and non-volatile) described the mechanism that

lied behind their release are diffusion (Hendrickx et al., 1987; de Roos et al., 2003; Bayyari et al., 2004; Boland et al., 2004; Floury et al., 2009; Buettner et al., 2000; Kohyama et al, 2010). We are assuming the mechanism in this instrumental set up as it does involved the movement of taste compound against the concentration gradient.

In modelling the simple diffusion of this gel system and vessel, the several of factors that is has been taken into accounts are as follows:

1) The dimension of the gel systems
2) The volume vessel surrounding the gel system
3) The viscosity of the buffer with the presence of taste compound
4) Diffusion coefficient value of the taste compound at 25 °C

The gel is confined in the chamber in between the probe surface and the bottom surface of the chamber, so it is assumed there is no diffusion from the top and bottom of the cylinder. Throughout the diffusion process, we also assume that the volume of the gel remains constant. Due to its porous nature water can migrate through the gel matrix to the outer medium surrounding the gel.

At short time, the concentration of solutes in surrounding medium remains zero; compared to that in the cylinder. So that we can take C (ρ_o, t) = 0, where ρ_o is the radius of the cylindrical gel. It is assumed that the diffusion coefficient, D, inside the gel remains constant and independent of solute concentration. Based on these listed assumptions, we need solve the diffusion equation:

$$D\nabla^2 C = \frac{\partial C}{\partial t} \quad (1) \qquad (5.1)$$

Where,

C= Concentration at time

t = time

∇ = vector differential operator

Expressing this is in cylindrical co-ordinates and corresponding to the gel geometry, the above equation becomes

$$\left(\frac{D}{r}\frac{\partial}{\partial r}\right)\left(r\frac{\partial C}{\partial r}\right)=\frac{\partial C}{\partial t} \tag{5.2}$$

Where r is the radial direction (distance) away from the centre of cylinder. Equation (5.2) can furthermore be written as

$$\frac{\partial C^2}{\partial r^2}+\frac{1}{r}\frac{\partial C}{\partial r}=\frac{1}{D}\frac{\partial C}{\partial t} \tag{5.3}$$

To solve the above equation, we use method of variable separation that is substituting

$$C\ (r,t)=\ \varepsilon\ (t)\ \theta(r)$$

Giving the solution

$$\varepsilon(t)=\ e^{-D\beta i^2 t} \tag{5.4}$$

We have chosen to be negative, the term $(-\beta i^2)$, since we expect the transient to decay away and reach a steady state. The equation can be further evolved and to arrive at equation (5.5).

$$y^2 * \frac{\partial^2\theta}{\partial y^2}+y*\frac{\partial\theta}{\partial y}+y^2\theta=0 \tag{5.5}$$

The above equation is known as a Bessel equation of zero order which has the solution

$$\theta(\beta ir)=\ \theta(y)=J_o(y)=J_o(\beta ir) \tag{5.6}$$

The function $J_o(y)$ is the Bessel function of zero order. Combining (5.6) and (5.4) then,

$$C(r,t)=\ \lambda_i J_o(\beta ir)e^{-D\beta i^2 t} \tag{5.7}$$

where λ_i is a constant determined by initial boundary conditions. We know that the boundary conditions requires $C(\rho_o,t)=0$ at all times, t. This means that βi can only take up certain values such that

$$J_o(\beta i\rho_o)=0$$

In other words $\beta i \rho_o$ has to be the root of the Bessel function of zero order $J_o(y)$, as depicted in **Figure 5.1**.

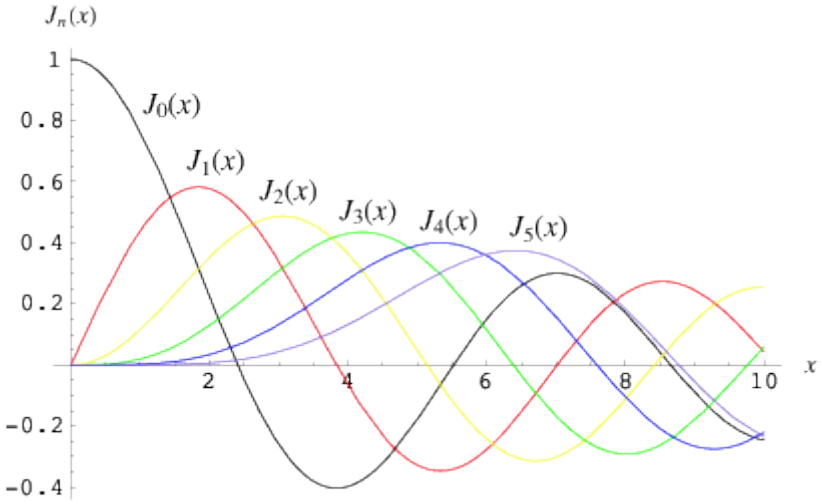


Figure 5.1 Bessel function curves.

Where the first root of $J_o(y)$ is denoted as x_1, second root as x_2, third root as x_3 , etc. Then

$$\beta i = \frac{x_1}{\rho_o}.\frac{x_2}{\rho_o}, \ldots\ldots\ldots\ldots \beta_l = \frac{x_l}{\rho_o}$$

for any value for βi given by above we have the appropriate boundary conditions. Hence, more generally, the solution to the diffusion equation for such a cylindrical geometry can be written as

$$C(r,t) = \sum_{i=1}^{\infty} \lambda_i J_o\left(x_1 \frac{r}{\rho_o}\right) \exp\left(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t\right) \qquad (5.8)$$

We now need to determine the coefficient λ_i, which is a constant and independent of *t* and *r*, and determined by initial profile of $C(r,t)$ at time t=0. To calculate λ_i we make use of some useful properties of $J_o(x)$, in particular completeness and orthogonality. The first means that any function $f(r)$ defined in range of 0 to ρ_o such that $f(\rho_o) = 0$ can be written as a superposition of functions $J_o\left(x_i \frac{r}{\rho_o}\right)$, that is

$$f(r) = \sum_{i=1}^{\infty} \lambda_i J_o(x_i \frac{r}{\rho_o}) \tag{5.9}$$

Secondly that the functions $J_o(x_i \frac{r}{\rho_o})$ for different i are orthogonal such that,

$$\int_0^{\rho_o} r\, J_o\left(x_i \frac{r}{\rho_o}\right) J_o\left(x_j \frac{r}{\rho_o}\right) dr = \frac{\rho_o^2}{2} J_{i^2}\ \ (\beta_i \rho_o)\delta_{ij} \tag{5.10}$$

Where $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$.

At time $t = 0$, we have $C(r, 0) = C_o$, the initial concentration of the solute in the gel. Using these equations (5.9) and (5.10), we can now express the coefficients λ_i in equation (5.8),

$$\lambda_i = (\int_0^{\rho_o} r J_o(x_i \frac{r}{\rho_o}) C_o dr)/(\frac{\rho_o^2}{2} J_1^2(x_i)) \tag{5.11}$$

So,

$$\lambda_i = (\left(\frac{C_o \rho_o^2}{x_i}\right) J_1(x_i))/(\ (\frac{\rho_o^2}{2} J_1^2(x_i)) = \frac{2C_o}{x_i J_1(x_i)} \tag{5.12}$$

This then gives the general solution to the problem, namely $C(r, t)$ as

$$C(r, t) = 2C_o \sum_{i=1}^{\infty} \frac{1}{x_i J_1(x_i)} J_o\left(x_i \frac{r}{\rho_o}\right) \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t) \tag{5.13}$$

It is useful to define normalised values of $C(r, t)$ by using the following scaling for each quantity. Take the unit of r to be the ρ_o so that in the new units, the radius of the cylinder is always 1. Take the time unit to be $= \frac{\rho_o^2}{D}$, to solve for diffusion across the cylinder, and the units of C as $C_o$the initial concentration of solute in the gel. Finally, we are interested in the amount of solute, $x(t)$, that still remains in the gel after time t (or conversely the amount that has been released). This can be obtained by integrating the concentration, as given by (5.13) throughout the cylindrical gel. Then

$$X(t) = LC_o 2\pi \int_0^{\rho_o} rC(r, t) dr \tag{5.14}$$

Where L is the length of the cylinder

$$X(t) = 4\pi LC_o \int_o^{\rho_o} \sum_{i=1}^{\infty} r \frac{J_o(x_i r)}{x_i J_1(x_1)} \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t)\, dr \tag{5.15}$$

To obtain the integral, we do the integration one by one for each term of the summation in (5.15). Note that we can make a change of variable $q = \frac{x_i r}{\rho_o}$

$$\begin{aligned}
&\int_o^{\rho_o} r \frac{J_o(x_i r)}{x_i J_1(x_1)} \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t)\, dr \\
&= \frac{\rho_o^2}{x_i^2} \int_0^{x_i} \frac{q J_o(q)}{x_i J_1(x_i)} \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t)\, dq \\
&= \frac{\rho_o^2 \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t}{x_i^3 J_1(x_i)} [q J_1\,(q)]_0^{x_i} \\
&= \frac{\rho_o^2}{x_i^2} \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t
\end{aligned} \tag{5.16}$$

Where we have used the fact that

$$\int_0^{x_i} q J_o(q) dq = [q J_1\,(q)]_0^{x_i} = q\, J_1(x_i)$$

Using equation (5.16) for every term of the sum in (5.15), we get

$$X(t) = 4\pi LC_o \sum_{i=1}^{\infty} \frac{1}{x_i^2} \exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t) \tag{5.17}$$

Note that at time t=0

$$X(0) = 4\pi LC_o \sum_{i=1}^{\infty} \frac{1}{x_i^2} \tag{5.18}$$

It is a property of the Bessel function of the zero order $J_o(x)$ that sum of square of its solutions, $x_1, x_2 \ldots x_n$.. is $\frac{1}{4}$

$$\sum_{i=1}^{\infty} \frac{1}{x_i^2} = \frac{1}{4}$$

So equation (5.18) simply reduces to

$$X(0) = \pi \rho_o^2 L C_o \tag{5.19}$$

Also note that at sufficiently long times, $t \gg \frac{D}{\rho_o^2}$, all the terms in (5.17) will be much smaller than the first (higher terms decay more rapidly than the first one). Therefore, equation (5.17) can be simplified to

$$X(t) \simeq \frac{1}{x_i^2} (\exp(-\left(\frac{D}{\rho_o^2}\right) x_i^2 t) \tag{5.20}$$

$$for\ t \gg \frac{\rho_o^2}{D}$$

5.4 RESULTS AND DISCUSSION

It is worthy to mention that the theoretical diffusion values obtained for both flavours took into consideration of the buffer viscosity with the presence of 2% sodium chloride and 10% of glucose. There is no significant effect on the viscosity of water with the addition of 2% sodium chloride. It also important to mention that this diffusion model was only done solely based only on basic information of theoretical/literature diffusion coefficient values, buffer viscosities values based on the presence of both taste compounds and the geometry of both the chamber/vessel and gels systems. Other condition was not taken into account.

There is a slight difference on the viscosity of buffer in 10% glucose. The diffusion coefficient for sodium chloride is twice the value of glucose. Viscosity specification and diffusion coefficient for NaCl and glucose is shown in **Table 5.1**. The differences in the viscosity may have an affect on the release of the taste compound which will be discussed in the later section of this chapter.

Table 5.1 Literature values for viscosity **(η)** and diffusion coefficient (D) for NaCl and glucose in water and the viscosities of these solution (Handbook of Chemistry and Physics).

Compounds	Viscosity (η) (**kg m^{-1} s^{-1}**)	Diffusion coefficient (**D**) (x **10^{-5}cm^{2}s^{-1}**)
Water	1.010	-
Sodium chloride (2%)	1.034	1.483
Glucose (10%)	1.327	0.512

Further comparison on the effects of gel concentration, temperature and applied pressure will be discussed in depth in the next section. The final mathematical equation (5.20) allows the calculation of taste compound remained in the gel systems. Slight modification to this equation, were able to calculate the amount of solutes in the surrounding buffer a certain point of time. This equation enables the development of the theoretical diffusion curve shown in the next section. In the next section we will also put together the theoretical diffusion curve with the experimental curve that we obtained from the previous chapter.

5.4.1 COMPARISON OF EXPERIMENTAL RELEASE CURVES WITH DIFFUSION THEORY

In the beginning of this section, diffusion theoretical curve and the experimental curves obtained from previous (**Chapter 4**) are plotted together. All of the experimental data will later be fitted to make sure it overlaps theoretical curves perfectly. If the experimental curve is shown to superimpose perfectly after the fitting, this indicates that the mechanism involve in the release is diffusion. This will also allow for us to draw a more conclusive summary for this modelling work.

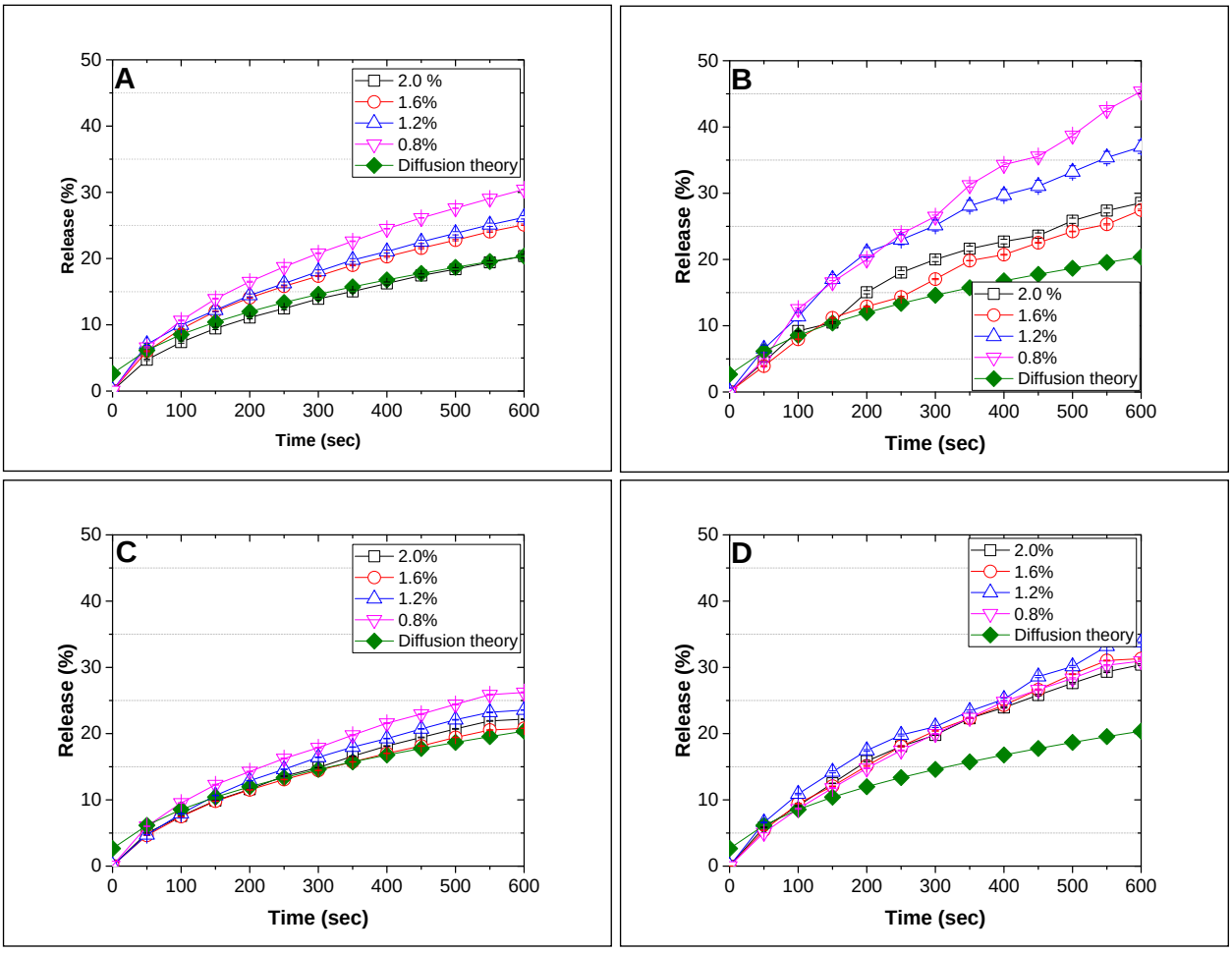


Figure 5.2 Experimental release (%) over time (sec) for κ-carrageenan gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

Figure 5.2 shows the experimental release for NaCl together with the theoretical release for κ-carrageenan gels. The form or shape of the experimental curves seems to plot closer to the predicted theoretical release rates. Rough observation shows the experimental curves seems to show some resemblance to the theoretical curve. This shows the mechanism involves in flavour release is pure diffusion. However, κ-carrageenan gels irrespective of concentration and under all conditions (non-compressed or compressed; room temperature or body temperature), shows slightly faster release than predicted rates. Also significant differences compared to the theoretical rates are experimental data for release a higher temperature. The origin of this discrepancy probably lies in the values of the diffusion coefficient assumed, which may not be completely accurate under these conditions.

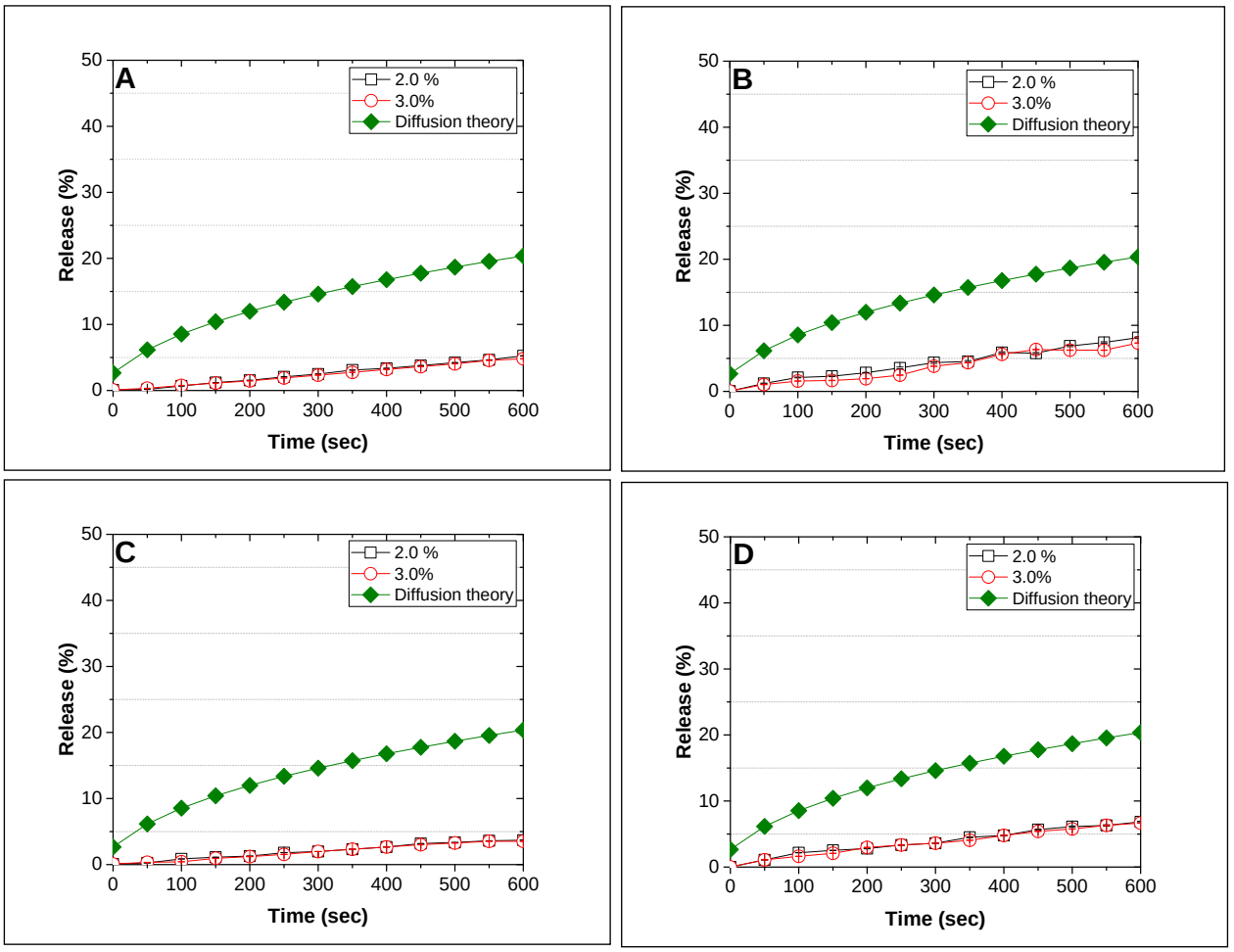


Figure 5.3 Experimental release (%) over time (sec) for alginate gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

In contrary to κ-carrageenan gels, experimental release for NaCl in all alginate gels (**Figure 5.3),** the release was observed to be very low as compared to theoretical release. The experimental release of flavour from alginate gels is significantly lower than predicted release rates. As discussed in previous section, this might be due to the dense microstructure and binding mechanism of NaCl with the alginate polymer network. We will discuss more in the later section of this chapter.

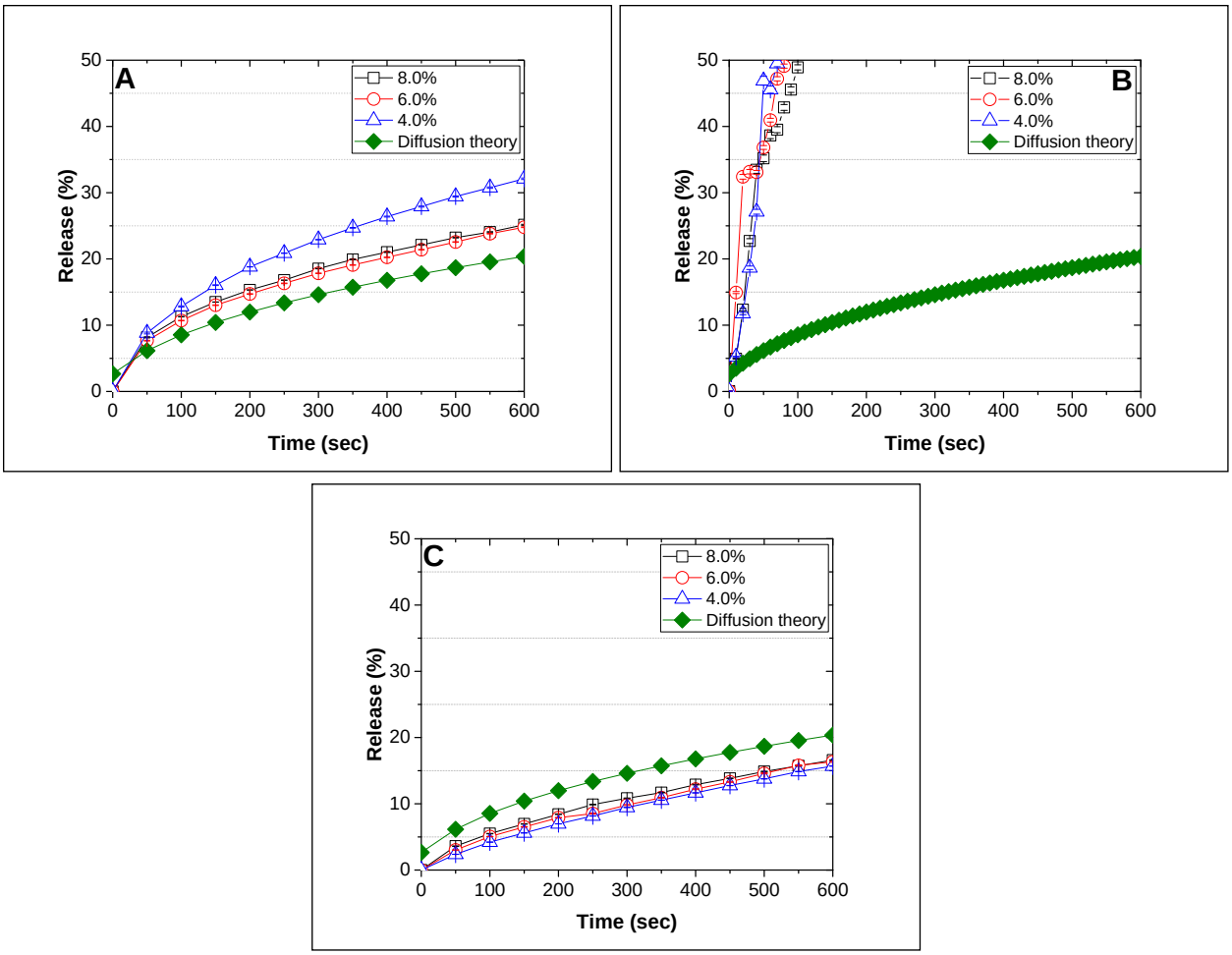


Figure 5.4 Experimental release (%) over time (sec) for gelatin gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

Experimental release for NaCl from gelatin gels almost agrees with the theoretical release rates. This again indicated the mechanism of release is probably pure diffusion. Applied force causes slight reduction in the release rate, as the experimental release observed to be slightly lower that the theoretical release. Due to the gelatin melting and degradation property at 37 °C, the experimental curves do not agree with the theoretical release rate.

Figure 5.5 to 5.7 shows similar data to **Figure 5.3 to 5.5** but for release of glucose.

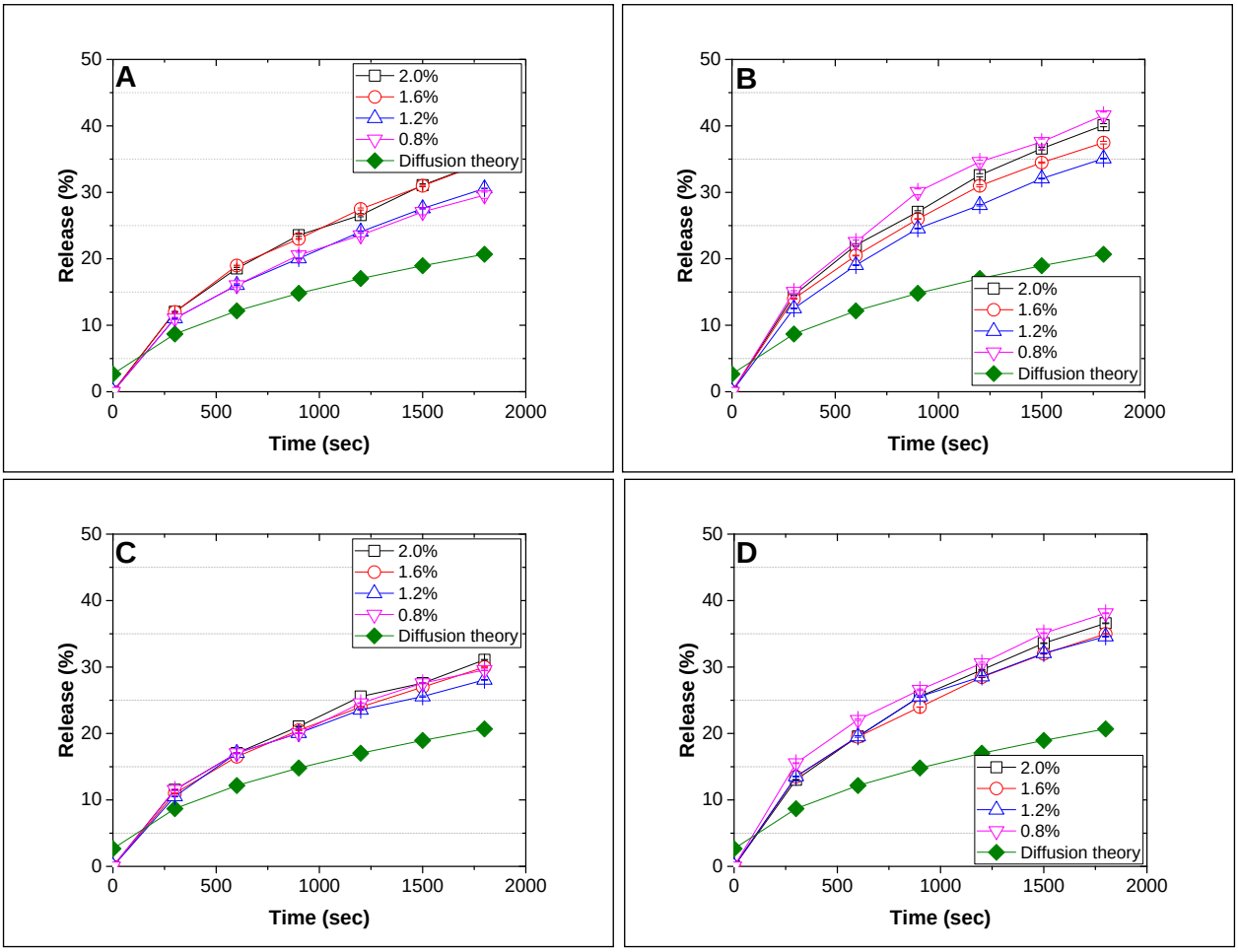


Figure 5.5 Experimental release (%) over time (sec) for κ-carrageenan gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

Experimental release of glucose for κ-carrageenan gels shows agreement with the theoretical curve also experimental rates are again slightly faster. The mechanism of release is probably still pure diffusion. Glucose experimental release shows similar trend with the NaCl release, irrespective of gel concentration and all conditions, experimental release is faster than the predicted release.

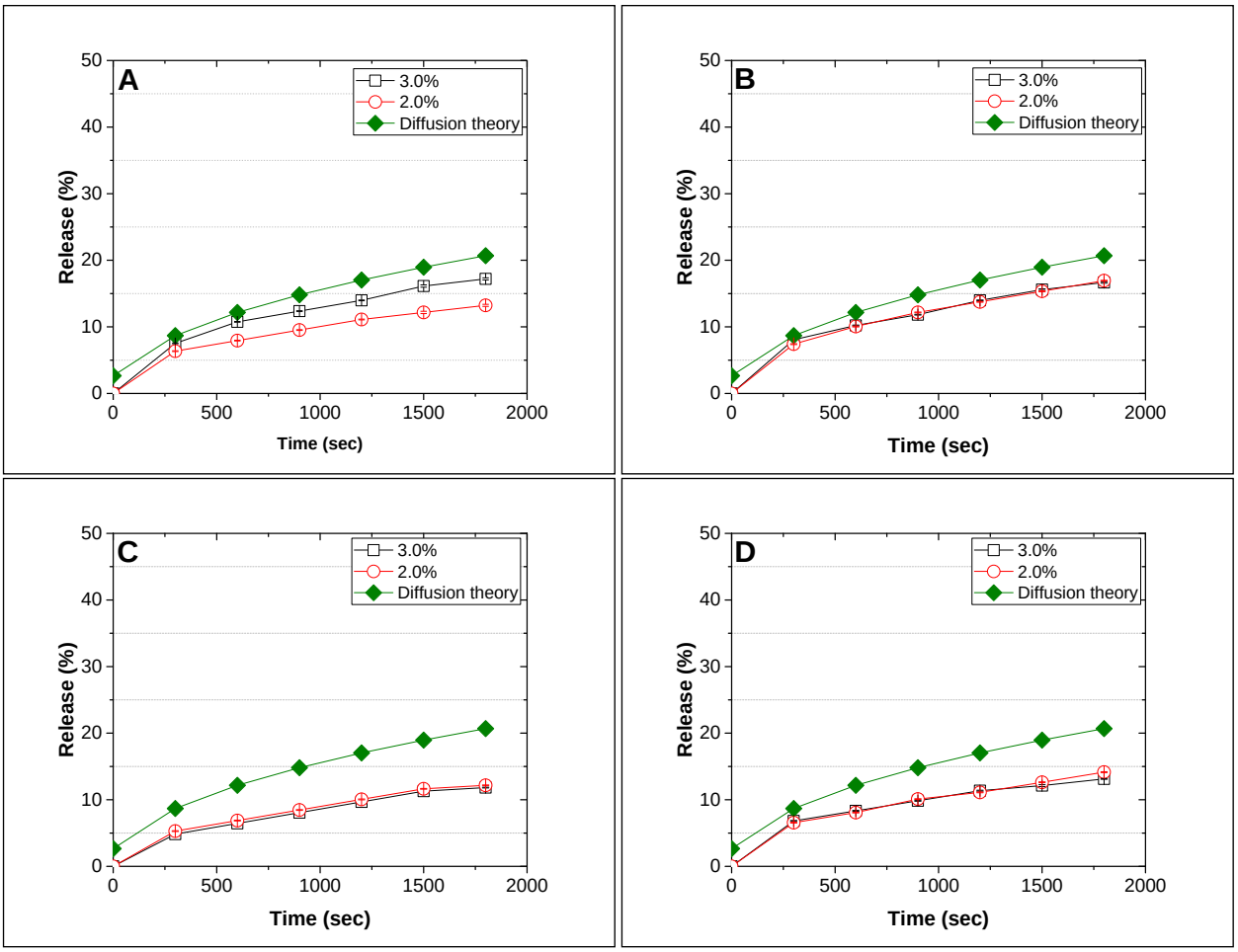


Figure 5.6 Experimental release (%) over time (sec) for alginate gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

In contrary to the experimental release for NaCl, glucose release seems to be closer to theoretical release curves. This again indicated that the release is probably governed by mainly diffusion. Again, similar to the NaCl experimental release, glucose release from alginate gels irrespective of gel concentration and under all condition is slightly lower release compared to theoretical curves. This is maybe due to the gel microstructure and some sort of binding between the taste compounds with alginate polymer.

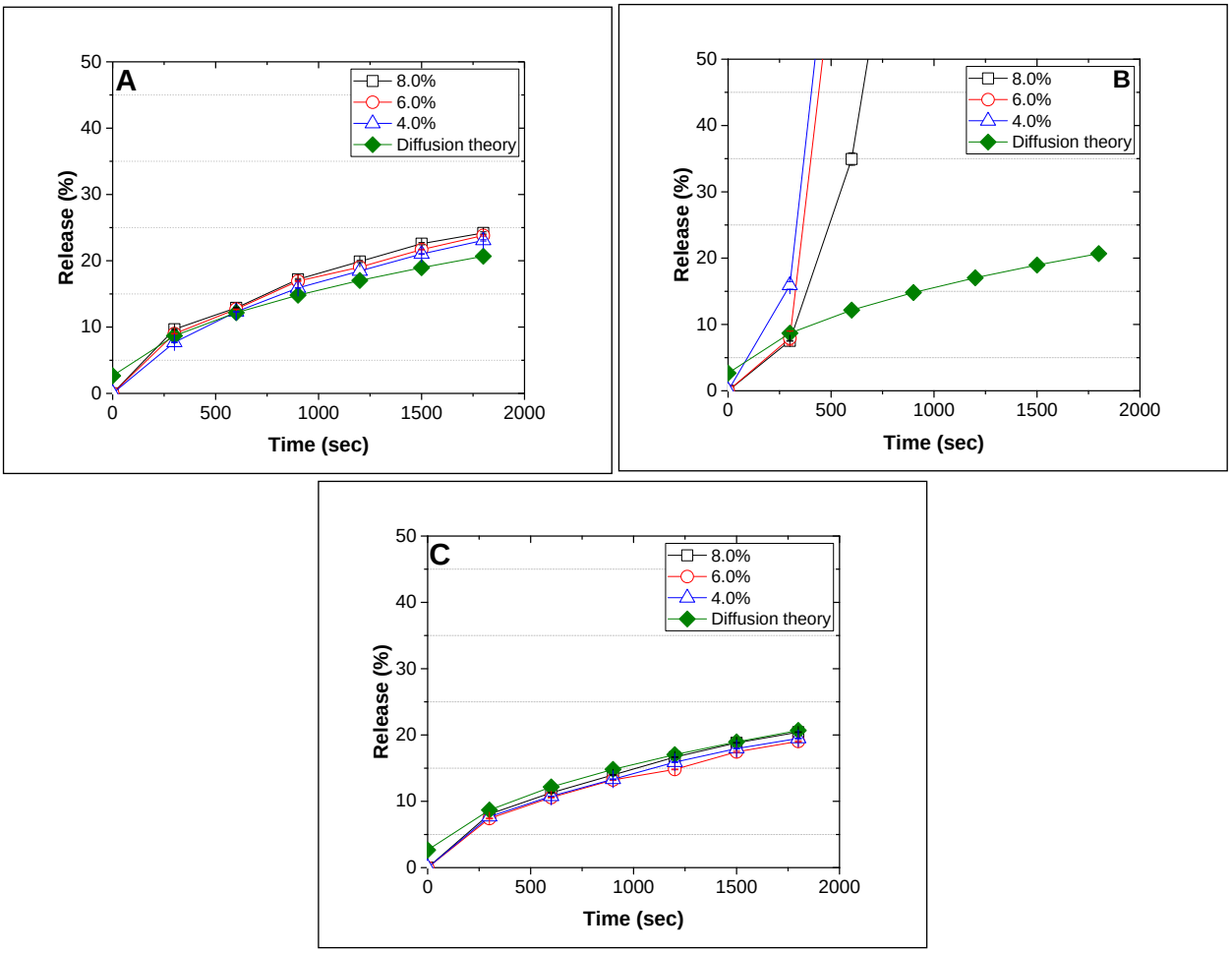


Figure 5.7 Experimental release (%) over time (sec) for gelatin gels for sodium chloride room temperature (A) and 37 °C (B) and compressed at room temperature (C) and 37 °C (D) plus theoretical release rates based on literature diffusion coefficients and viscosity.

The glucose experimental curves from gelatin gels for all concentration and under all conditions were observed to overlap theoretical release curve which shows the release of glucose is pure diffusion. Again, at higher temperature, the experimental curves do not agree with the theory due their melting property at body temperature.

Previously mentioned, that all of the experimental curve were fitted in order for it to superimpose the theoretical curve perfectly. In overlapping the experimental curve over the theoretical curve, the time is factored with the a certain value of α. In order to summarise all this results more succinctly a

value of α was calculated which gives the best agreement between the instrumental theory measurements over the first 100 seconds where:

$$\alpha = \frac{Experimental\ rate}{Theoretical\ rate}$$

So is $\alpha > 1$, the measured diffusion is faster than diffusion theory predicts or $\alpha<1$ diffusion on slower than the theory predicts. α can also be defined as a form factor which explains the relationship of the diffusion coefficient of the flavour with presence and absence of the gel network and could also be written as:

$$\alpha = \frac{D_o}{D_g}$$

Where D_o is diffusion coefficient flavour with the absence of the polymers gel network and D_g is diffusion coefficient in the presence of the polymer gel network.

The fitted work in obtaining the value of α is not shown, however, the value of α obtained from the fitting work is reported. All experimental data was able to fit the theoretical data perfectly. This confirms that the mechanism involved on the release of taste compounds is diffusion. The α for all polymer concentration and under all condition is displayed in **Table 5.2** expressed the diffusion coefficient value of the flavour for all polymer concentration and under all conditions.

It is important to highlight, plotting of the diffusion theoretical curves with the experimental curves might show a dramatic differences. However the calculation of α shown in **Table 5.2** indicates the experimental release rate does not fall not far from the α cut off value which is 1. The only significant differences were observed in alginate gels by average is twenty times slower that the predicted release for NaCl release. In the case of gelatin gels dramatic differences (15 times faster) were due to its melting properties at 37 °C.

Table 5.2 Comparisons of α for sodium chloride and glucose in different gel polymer concentrations.

Polymer	**Concentration (%)**	**Sodium chloride (NaCl)**				**Glucose**			
Temperature/Conditions		**25 °C non compress**	**25 °C Compress**	**37 °C non compress**	**37 °C compress**	**25 °C non compress**	**25 °C compress**	**37 °C non compress**	**37 °C compress**
κ-c	0.8	2.00	1.50	2.60	1.80	2.00	2.00	3.10	3.00
κ-c	1.2	1.50	1.25	2.60	2.00	2.00	1.80	2.80	2.50
κ-c	1.6	1.50	1.00	1.50	1.90	2.20	2.00	3.00	2.50
κ-c	2.0	1.00	1.00	2.00	1.85	2.20	2.00	3.00	2.50
Alginate	2.0	0.05	0.03	0.12	0.10	0.45	0.35	0.60	0.45
Alginate	3.0	0.05	0.03	0.098	0.09	0.70	0.30	0.70	0.40
Gelatin	4.0	2.40	0.50	16.00	-	1.15	0.90	3.00	-
Gelatin	6.0	1.50	0.59	15.00	-	1.30	0.80	1.00	-
Gelatin	8.0	1.70	0.65	13.00	-	1.40	1.00	1.00	-

Notes: (-) Experiments were unable to perform to the melting property of gelatin.

Based on the **α** value from **Table 5.2**, comparison to the theoretical rate if release, the order of release in increasing order based on polymer types is as followed:

Alginate < Gelatin < κ-c

Many previous research suggested the contribution factors of the flavour release are dependent on the polymer viscosity and concentration (Buettner & Schieberle, 2000; de Roos, 2003; Ferry et al., 2006; Holm et al, 2009; Hons, 2002). Concentration was observed to play no significant role in the release for alginate and gelatin gels, however, in κ-carrageenan, concentration is observed to play a small role in the release rate. Higher α was observed at lower polymer concentration Studies done on volatile and non-volatile compounds with similar instrumentals set up suggested that concentration does play a key role in the release of flavour (Hendrickx et al., 1987; de Roos et al., 2003; Bayyari et al., 2004; Boland et al., 2004; Floury et al., 2009; Buettner et al., 2000; Kohyama et al, 2010). However, because the range of polymer concentration is very small in this research study, we were not able to see much difference in the release rate. Even a study done by Hendrickx et al. (1987) in observing the diffusion of glucose release from carrageenan and gelatin gels, using small range of polymer concentration, they could not see any profound differences in the release rate. There were even small fluctuations in the in release rate of the taste compound among different polymer concentrations. This could be observed in **Figure 5.8**.

Temperature was observed to have an effect on the value of α in all polymers. Overall, increment of temperature was observed to cause escalation in the taste compound release rate. Dramatic difference in the rate of release for gelatin is due to its melting properties. Based on **Chapter 4**, higher temperature may cause the pore size to slightly expand reducing the possible contact of the taste compound with the polymer. Conductivity of an ion or molecules is dependent on several factors such as concentration, mobility of ions, valence of ions and temperature. The increment in a solution's temperature leads to changes in polymers structure and an

increase in the mobility of the ions in solution. High mobility ions and low viscous polymers create spaces for salt ions and glucose molecules movement in leaving the gel matrix and into the surrounding. Hydrogel are known to be thermo-responsive and application of heat might result to structure change causing expansion or swelling (Bromberg et al. 1987; Cai & Suo 2011; Ahmed 2013). Such intrinsic change allows the sodium chloride ions and glucose to leave the matrix more readily. Sodium alginate is not a thermo-responsive gel, however, application of heat to sodium alginate lead to decrease in viscosity suggesting structural changes. This structural change explains the higher release rate of sodium chloride at higher temperature.

Compression was anticipated to cause a burst in taste release, however the opposite was observed. Compression was observed to lower the α value for all polymers. Previous chapter have discussed on the effect of compression reduce the pore size of the gels which increases contact of the taste components with the gel polymers. According to Mills et al. (2011) in their attempt to quantify salt release in gel system, they observed that compression does not give any major effect on the salt release. They further mentioned that was because the gel system, unless compress to fracture, the internal structure remains the same, hence, not much difference was in the release upon compression. The release will only increase dramatically upon fracture as this creates wider surface area for possible diffusion.

The measured release for NaCl and glucose from κ-carrageenan gels was faster than diffusion theory predicts. Any affinity of Na^+Cl^- for the gel would slow down release. So if it is faster, it means it is repelled from the gel. The molecular weight of each sugar units is 444 g/mol. Considering the average molecular weight of κ-carrageenan one can roughly calculate the number of sulphate groups (SO^{3-}). This gives a molar ratio of sulphate to Na^+ and Cl^- 1:120. There is therefore a huge access of Na^+ over SO^{3-} and so if any significant binding occurred this would have very little effect on the concentration of Na^+Cl^- free to diffuse out of the gel. Alginate shows completely different behaviour. The release was observed to 20-30 times

slower than the predicted theory. Smidsrod and Haug (1967) reported that the tendency of the Na^+ to bind to alginate is two times higher than that of κ-carrageenan (see **Table 5.3**).

Table 5.3 Ion Pairs formed with potassium and sodium ions, given as percent of total amount of anionic groups o th polymer (approximately 0.01N) (Smidsrod and Haug, 1967)

	Potassium	**Sodium**
Dextran sulfate	81.5	77.5
Carrageenan	**38.5**	**36.5**
Carboxymethydextran	73.8	68.5
Alginate	**58.8**	**53.5**

The molecular weight of each alginate sugar units is 222 g/mol. Again, considering the average molecular weight of alginate one can roughly calculate the number of carboxyl groups (COO^-). This gives a molar ratio of COO^- to Na^+ and Cl^- 1:20. Thus Na^+ is more likely to be bound to alginate. As highlighted in earlier section the gel pores diameter might be a factor in release of NaCl from the gel system. In **Chapter 4** (**section 4.2.2**), κ-carrageenan displayed bigger and wider pores. In alginate the size of the pores seemed a lot finer. The finer pores in alginate increase the surface contact area with the Na^+ ions. In relation to polymer microstructures, taste compounds mobility will somehow slow in denser and finer pore channels. It will take sometime for the travel from the inner matrix of the gel system to the outer surroundings.

Similar to NaCl release, glucose release was faster than the theoretical diffusion values. Glucose molecules are able to bind to uncharged polymers via hydrogen bonding. The concentration of glucose (10%) far exceeded the concentration of polysaccharide used, so that the significant binding to any available uncharged polymer sugar residues suitable for hydrogen bonding would not significantly affect glucose available for diffusion. Furthermore, the concentration of glucose (10%) resulting in a solution with slightly higher viscosity, shown in **Table 5.1,** may explain the slightly slower release of glucose in κ-carrageenan and gelatin gels.

The release of NaCl was observed to be faster than that of glucose for the same κ-carrageenan gels. In contrast, release of glucose from alginate gel was again slower than theory, though not as slow as NaCl, which again suggest some binding to the network.

For all the systems except for alginate, at higher temperature, the diffusion values were seen to be significantly higher than predicted. As has been previously discussed, temperature weakens the gel structure and aids the dissociation of flavour molecules from the polymer network and release to the surrounding solution.

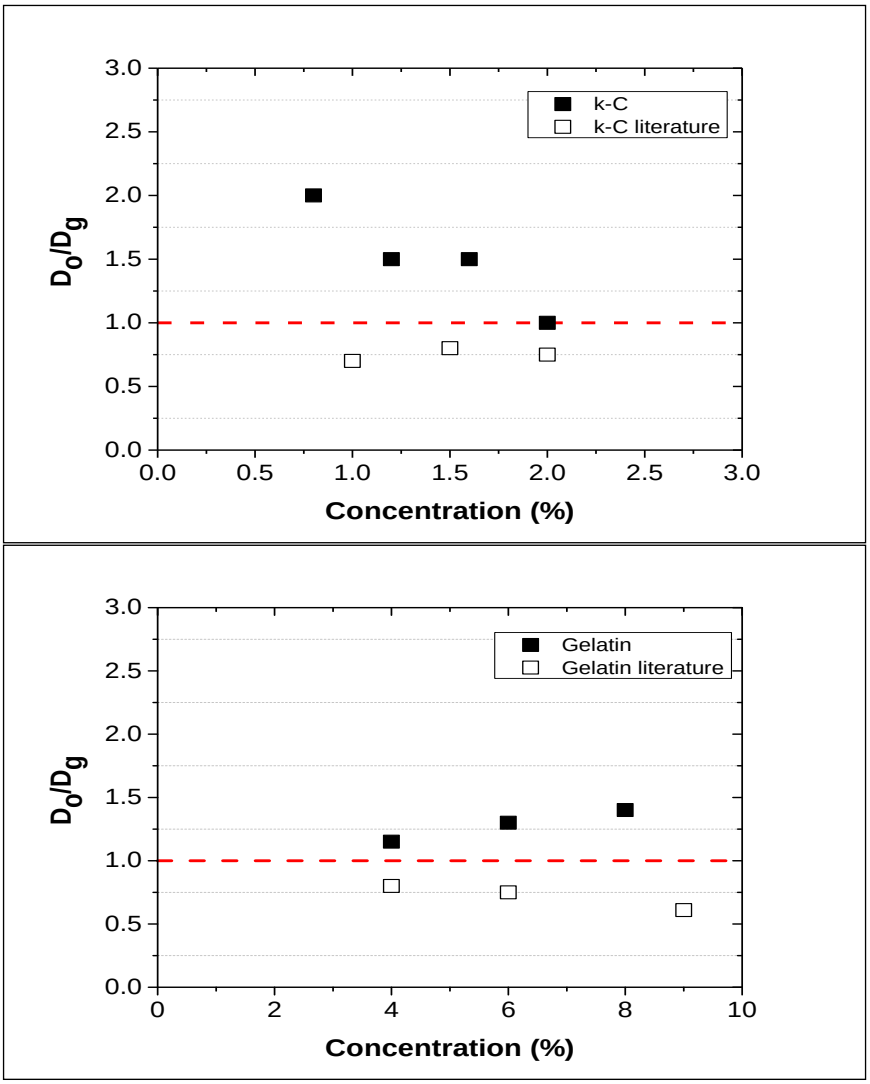


Figure 5.8 Graphs showing comparisons of $\frac{Do}{Dg}$, Where (□) obtained from study by Hendrickx et al., 1987) (■) is from the experimental data for glucose release.

Figure 5.8 shows comparison of the $\alpha = \frac{D_o}{D_g}$ one of the literature value obtained with the experimental data of diffusion coefficient in κ-carrageenan and gelatin gels from study conducted by Hendrickx et al., (1987). Interestingly, it shows striking resemblance for gelatin gels which shows that diffusion value of the experimental data is very close to the predicted release. For κ-carrageenan, the data shows a close clustering between the literature studies with the experimental data. Furthermore, κ-carrageenan shows that at 2% gel concentration, the release is close to the predicted value.

5.5 SUMMARY

Findings have proven that the mechanism of release of the taste compound from the gels is diffusion. The mathematical modelling only takes into account all the basic condition of the instrumental measures such as the dimension of the cylinder, volume of the vessel, buffer's viscosities and diffusion coefficient values of both taste compounds. Instrumental measures of taste compound release were observed to be faster than the theoretical diffusion for κ-carrageenan gels. This is associated to the unbound taste compounds present in the gel matrix. Polymer types were shown to play significant role in taste compounds release. Different polymers types exhibit differences in their microstructural properties (i.e polymer network, pore size). This undoubtedly has an effect in the release of the polymer to the outer surroundings. For both taste compounds release were evidently slow in alginate gels. Alginate in previous chapter has shown to have finer pores as compared to other gels. The ones with finer pores exhibited slowest release as compares to gel with bigger pores. Furthermore, alginate gels are known to have higher affinity toward sodium chloride as compare to the other two gels. Increase in temperature was seen to affect the release of the release of the taste compounds. Release was observed to be extremely fast in gelatin gels as the melting point of this gel is quite low. Compression causes slight decrease in the release which shows in the collapsing of the curves towards the diffusion theoretical curves. Release of glucose for all gels is slower than

sodium chloride. The difference in buffer's viscosities with concentration of taste compounds respectively may affect the slow release of glucose. The addition of glucose altered the viscosity of the buffer; making it slightly viscous, resulting in the slow release of this flavour. In contrary, alginate gels shows slower release of sodium chloride as compare to the glucose and again this is associated to the polymers affinity towards the sodium chloride and its morphology. The affinity of the flavour molecules differs significantly due to the chemical interactions formed between the molecules and types of polymers. The instrumental set up was designed to represent the human mouth model. In order to increase the reliability of certain mouth model, it needs to be coupled with sensory evaluation. In the next step, time-intensity sensory evaluation will be performed on panellist. The data collected from the instrumental measures and sensory evaluation will be subjected to analysis to see whether if there is any correlation. This will be further discussed in the next chapter.

CHAPTER 6

TIME-INTENSITY SENSORY EVALUATION

6.1 INTRODUCTION

Food oral processing involves a complex set of processes beginning with the ingestion of food until swallowing. The processes are interlinked and dependent on each other in timing and extent. This process is divided into four distinct stages which are 1) Initial ingestion and oral preparation (bolus formation) phase. 2) Transport of bolus to the pharynx. 3) Expulsion of bolus from the oral cavity. 4) Propulsion of bolus down the oesophagus and finally stomach. Mastication is a complex function which is orchestrated by a number of parts including muscles and teeth, lips, cheeks, tongue, hard palate and salivary gland. The tongue plays a major role in initiating the deformation process by pressing the food upward the hard palate (Malone et al. 2003; Mills 2011; Chen 2009).

The mimicking of oral processing applied on gels in this research is based on the oral processing mechanism suitable for soft solids. Based on the literature provided, soft solids are usually handled or masticated by compressing it using the tongue and the hard palette. No chewing was involved in the sensory evaluation here. The methods for the time-intensity evaluation were designed to match as closely as possible instrumental measurements of flavour release. Sensory evaluation is also conducted to develop health products for a specific group of people. In creating healthy product alternatives flavours of the food product are often compromised. Designing an instrumental measure that enables one to predict behaviour of the food inside the mouth will provide useful information; which will further contribute in the development of healthier and nutritious food products, whilst possibly avoiding lengthy and expensive sensory profiling.

6.2 AIMS AND OBJECTIVES

The aim of this research is to observe the human perception on different polymer types with the presence of different taste compounds. The time-

intensity evaluation was designed to closely resemble the instrumental set up. Objective of the study is to observe the effects of polymer concentration and compression on the human intensity perceptions. Study was also conducted in finding correlations between both instrumental measure and sensory evaluations. This chapter aims in answering the question on the reliability of the instruments measure by looking into comparison on the release rates with the human taste intensity perception.

6.3 RESULT AND DISCUSSION

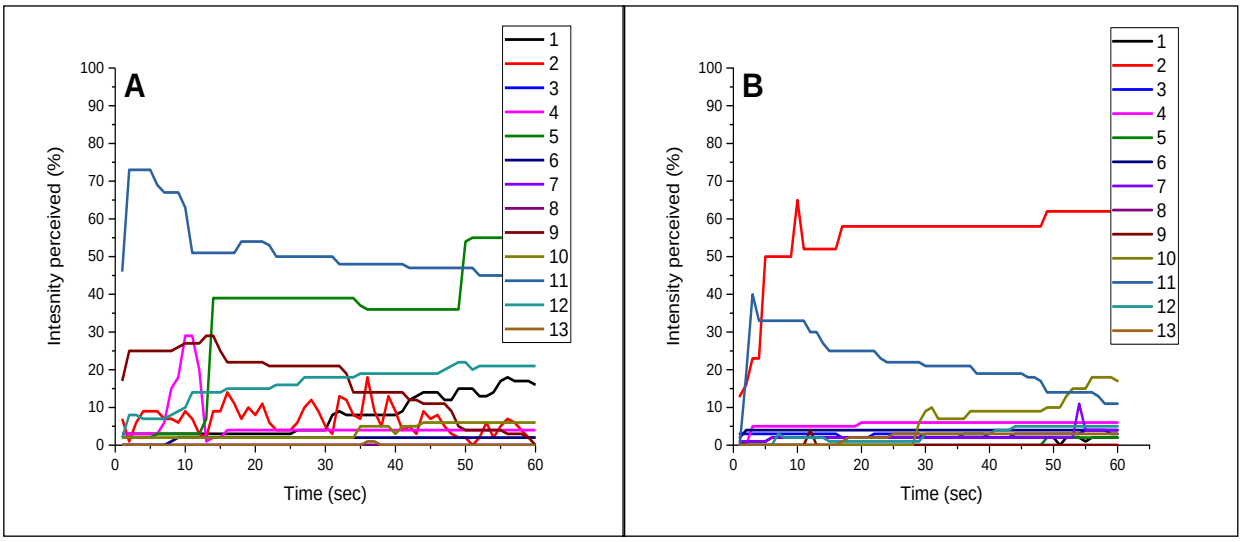


Figure 6.1 Examples on the time-intensity evaluation curve collected from a total of 13 panellists in one of the sensory session for A) sodium chloride and B) glucose. Parameter such as MAX, IMAX, AUC, α, IArea, β and DArea are extracted from the curve provided by the Compusense software.

The examples of the time intensity curves were taken from one of the test for both gels with the addition of sodium chloride and glucose. The curves are examples from κ–c which is one of the gel systems. The time intensity parameter which is later analyse are extracted from the graph collected from a total of four sessions (two sessions for sodium release and two for glucose release) attended by the panellists. All the parameters extracted have been described previously in the **Method** section.

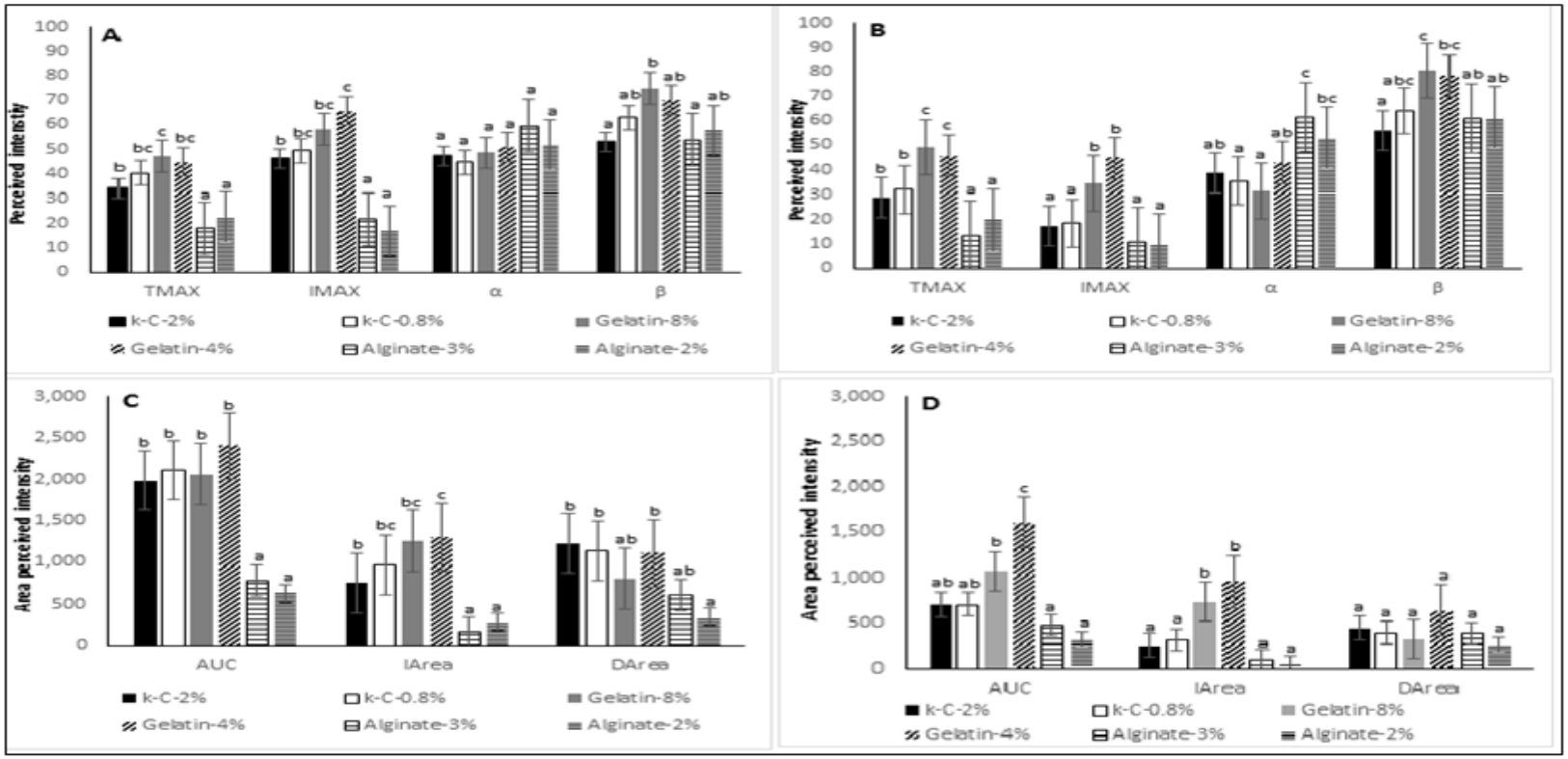


Figure 6.2 Values of the time-intensity parameters obtained for κ-c (κ-carrageenan), gelatin or alginate gels with salt (A and C) and sugar (B and D). Values represent sample means of n = 11. Values means do not share common letter differs significantly according to the Tukey test ($p<0.05$). k-C= κ-carrageenan; TMAX=Time to maximum; IMAX= Intensity at maximum; AUC=Area under curve; α= Increase angle; IArea= Increase area; β= Decrease angle; DArea= Decrease area. TMAX expressed in seconds, IMAX values represent mean intensity units (NONE = 0 and EXTREME = 60), α and β are expressed as intensity units/ second. Areas for AUC, IArea and DArea expressed as intensity units x time.

Initial analysis was done using one-way ANOVA for all the time intensity parameter by samples. From **Figure 6.2**, significant difference was observed among the samples for both salt and sugar. Results suggested IMAX (Maximum intensity) experience in salt are in the following order.

Gelatin > κ-carrageenan > Alginate

Observation on TMAX shows that gelatin exhibits longer time to reach maximum as well as the most intense flavour experience by the panellist. The melting temperature of gelatin which is 37 ºC results to the morphological/structural changes in the oral cavity leading to the intense flavour perceived by the panellists.

Both κ-carrageenan and alginate gels retained their shape under the human temperature as it is known that both polymers have higher heat resistance compared to that of gelatin. Significant differences in the flavour intensity perceived between κ-carrageenan and alginate were observed. However in the sugar sensory evaluation there is no significant difference in the IMAX for κ-carrageenan and alginate.

Further comparison shows significant difference these two polymers for the Area under the curve. Higher AUC (area under curve) indicates the intensity level experienced by the panellists. In this instance, κ-carrageenan has a higher AUC as compared to alginate. Alginate in both salt and sugar were seen to show the lowest AUC score. This might suggest the polymer structure or the interaction of the flavour compound which causes the difference in the intensity perceived by the panellist. The sensory findings were seen to match the instrumental analysis results. Which will be further discusses in later part of this section.

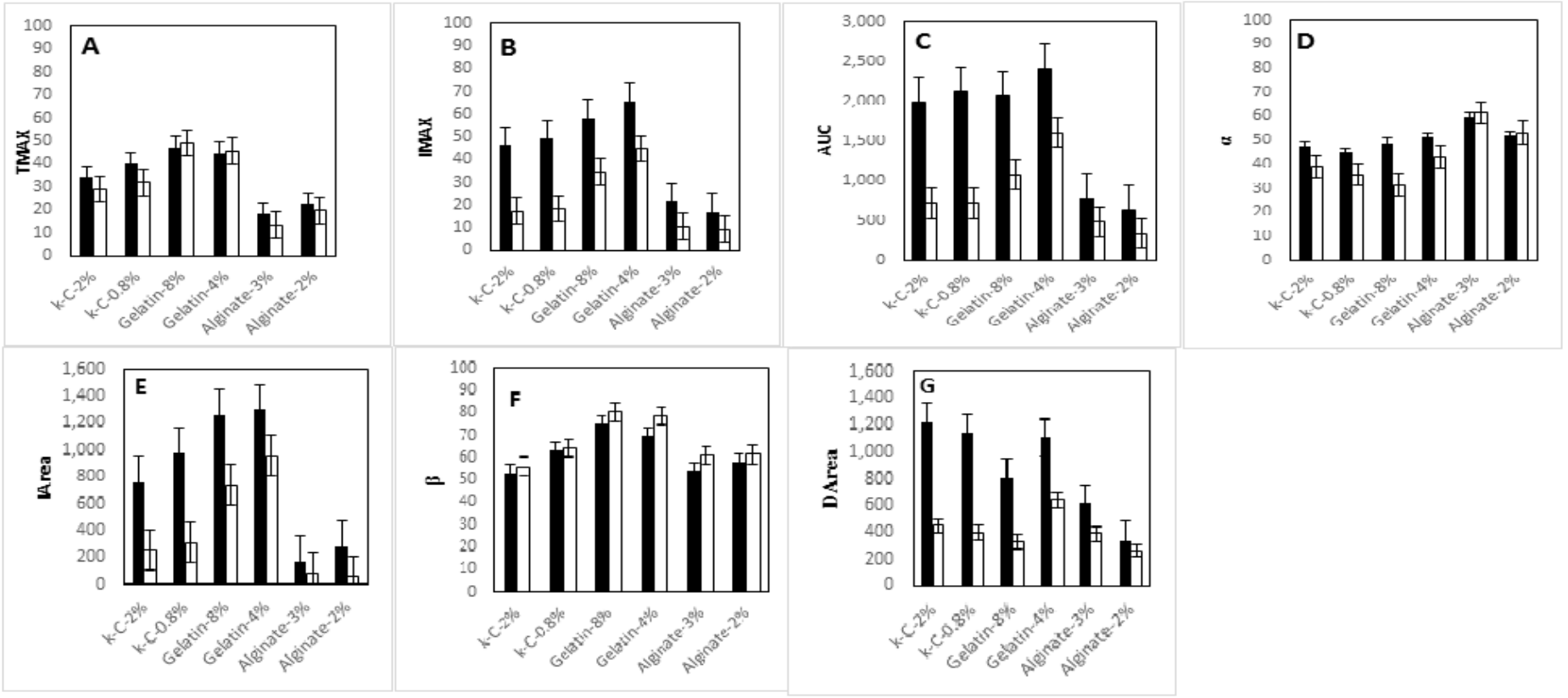


Figure 6.3 Values with significant difference ($p<0.05$) based on the T-test analysis for the time-intensity curve obtained for κ-c (κ-carrageenan), gelatin or alginate gels at different concentration with the addition of salt (■) and sugar (□). A) TMAX B) IMAX C) AUC D) Increase angle (α) F) Decrease angle (β) G) DArea. TMAX expressed in seconds, IMAX values represent mean intensity units (NONE = 0 and EXTREME = 60), α and β are expressed as intensity units/ second. Areas for AUC, IArea and DArea expressed as intensity units x time.

Figure 6.3 compares the same data but from the two different flavours (salt and sugar). T-test analysis was performed on the parameters and results suggested significant differences for all parameters. Parameters show salt to exhibit a higher level of intensity as compared to sugar. Profound differences were seen on parameters such as IMAX, AUC and IArea. The reported reference detection threshold for sodium chloride ranges from 1 to 15 mM depending on the stimulus volume relative to sugar detection threshold has wider detection range which is from 2-5mM or 14-22 mM (Engelen 2012). Sensitivity towards salt is higher than to sugar.

6.3.1 MULTIVARIATE ANALYSIS ON DIFFERENT CONDITIONS ON THE PERCEIVED INTENSITY

The time-intensity sensory evaluation was designed to enable observation on the effect of pressure (compressed and non-compressed), polymer concentration and type of polymers/materials (biopolymers) on the intensity profile of the flavour throughout time perceived by the trained panellists. Panellists were given specific instructions in handling the samples in achieving the effects desired. Results of the effect of pressure, concentration and biopolymers types through multivariate analyses are tabulated in **Table 6.1** and **6.2.**

Table 6.1 ANOVA of time intensity parameters for salt in function of: (A) conditions (pressure with tongue or not pressure, materials (gels ingredients: KC, alginate and gelatin), concentration (high or low) and interactions between them (B).

	Pressure		Biopolymers		Concentration	
	F	Sig.	F	Sig.	F	Sig.
TMAX	2.12	0.15	**36.23**	**0.00**	1.17	0.28
IMAX	2.01	0.16	**42.33**	**0.00**	0.27	0.60
AUC	1.17	0.28	**24.89**	**0.00**	0.31	0.58
α	0.04	0.84	1.95	0.15	0.46	0.50
IArea	**7.63**	**0.01**	**50.14**	**0.00**	2.04	0.16
β	0.01	0.91	**6.72**	**0.00**	0.58	0.45
DArea	0.04	0.85	**6.57**	**0.00**	0.01	0.92

	Pressure * Biopolymers		Pressure * Concentration		Bioplymers * Concentration		Pressure * Biopolymers * Concentration	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.
TMAX	0.35	0.71	0.31	0.58	1.04	0.36	0.62	0.54
IMAX	0.10	0.90	0.12	0.73	0.84	0.43	0.04	0.97
AUC	0.02	0.98	0.00	0.98	0.55	0.58	0.15	0.86
α	0.16	0.85	0.09	0.77	0.53	0.59	0.58	0.56
IArea	0.37	0.69	0.00	0.97	0.36	0.70	0.70	0.50
β	1.31	0.27	0.07	0.79	1.17	0.31	**4.25**	**0.02**
DArea	0.19	0.83	0.00	0.99	1.10	0.34	0.09	0.91

Significant p values (5% level; $p<0.05$) are highlighted in bold.

Table 6.2 ANOVA of time intensity parameters for sugar in function of: (A) conditions (pressure with tongue or not pressure, materials (gels ingredients: KC, alginate and gelatin), concentration (high or low) and interactions between them (B).

	Pressure		Biopolymers		Concentration	
	F	Sig.	F	Sig.	F	Sig.
TMAX	1.54	0.22	**67.12**	**0.00**	0.81	0.37
IMAX	1.91	0.17	**48.47**	**0.00**	1.74	0.19
AUC	1.35	0.25	**28.97**	**0.00**	1.56	0.21
α	0.16	0.69	**15.31**	**0.00**	0.00	0.99
IArea	1.03	0.31	**70.16**	**0.00**	2.30	0.13
β	2.16	0.14	**10.94**	**0.00**	0.35	0.56
DArea	0.56	0.46	1.23	0.30	0.28	0.60

	Pressure * Biopolymers		Pressure * Concentration		Biopolymers * Concentration		Pressure * Biopolymers * Concentration	
	F	Sig.	F	Sig.	F	Sig.	F	Sig.
TMAX	0.08	0.92	0.29	0.59	1.72	0.18	0.32	0.73
IMAX	0.15	0.86	0.09	0.76	1.88	0.16	0.14	0.87
AUC	0.04	0.96	0.07	0.79	**4.14**	**0.02**	0.21	0.81
α	0.04	0.96	0.02	0.90	3.05	0.05	0.15	0.86
IArea	0.55	0.58	1.11	0.29	1.72	0.18	0.55	0.58
β	0.16	0.85	0.52	0.47	0.62	0.54	0.08	0.92
D_{Area}	0.08	0.92	0.14	0.71	2.64	0.08	0.28	0.75

Significant p values (5% level; $p<0.05$) are highlighted in bold.

After obtaining information from the one-way ANOVA analyses, multivariate analysis was then applied to the data in order to obtain more information on the effects concentration, pressure (compressed and non-compressed) and biopolymer materials as an independent variables. Data were then further analysed to observe the interaction between the different effects/conditions on the intensity profile perceived by the panellists. Outcomes of analyses on the conditions as independent variable proposed; for both salt and sugar, the application of compression and changes in concentration show no significant difference on the level of intensity perceived by the panellists. Result shows biopolymer type to be the main driving factor on the intensity level perceived by the panellist. Significant values were seen in almost all time-intensity parameters except for the DArea for salt and increase angle (α) for sugar.

For salt flavoured gels, data analysis shows a significant interaction between all the combined conditions (Bioplymers*Concentration*Pressure) to have a significant effect on the decrease angle (β).

Results also deduced that the combined conditions of material and concentration were seen to have a significant positive effect on the area under the curve (AUC) for the flavoured sugar gels.

6.3.2 ANALYSIS ON THE EFFECTS OF MATERIALS ON THE TIME-INTENSITY PARAMETERS

Multivariate analysis revealed biopolymer type had the greatest influence in the level of intensity perceived by the panellist. Biopolymer type data were then further analysed to investigate their impact on the all the time-intensity parameters. Results are presented in **Figure 6.4**. Significant differences were observed in all the parameters apart from than the decrease area (β) for both salt and sugar. The greatest IMAX values were displayed by gelatin followed by κ-carrageenan and alginate. The initial analysis (instrumental measures) on gel samples revealed the similar results. The change in the gelatin morphology in the human oral cavity contributes the high level intensity perceived by the panellist, previously discussed.

T-test analysis was then performed on the data to compare the two flavours. Significant differences were observed on the all of the parameters between salt and sugar. Salt shows the higher values in all parameters. This shows that the detection level or salt threshold is very low in all panellist as compared to sugar.

The sensory evaluations findings generally agree with the results from the instrumental assay. Data collected from the instrumental assay at both room temperature and 37 º C exhibited gelatin to have the fastest release profile, followed by κ-carrageenan and alginate. Instrumental data collected demonstrated that the amount of release for both salt and sugar within 60 seconds is below the detection threshold for the average human. This also further elucidates the extreme low level of intensity perceived by panellist in alginate gels.

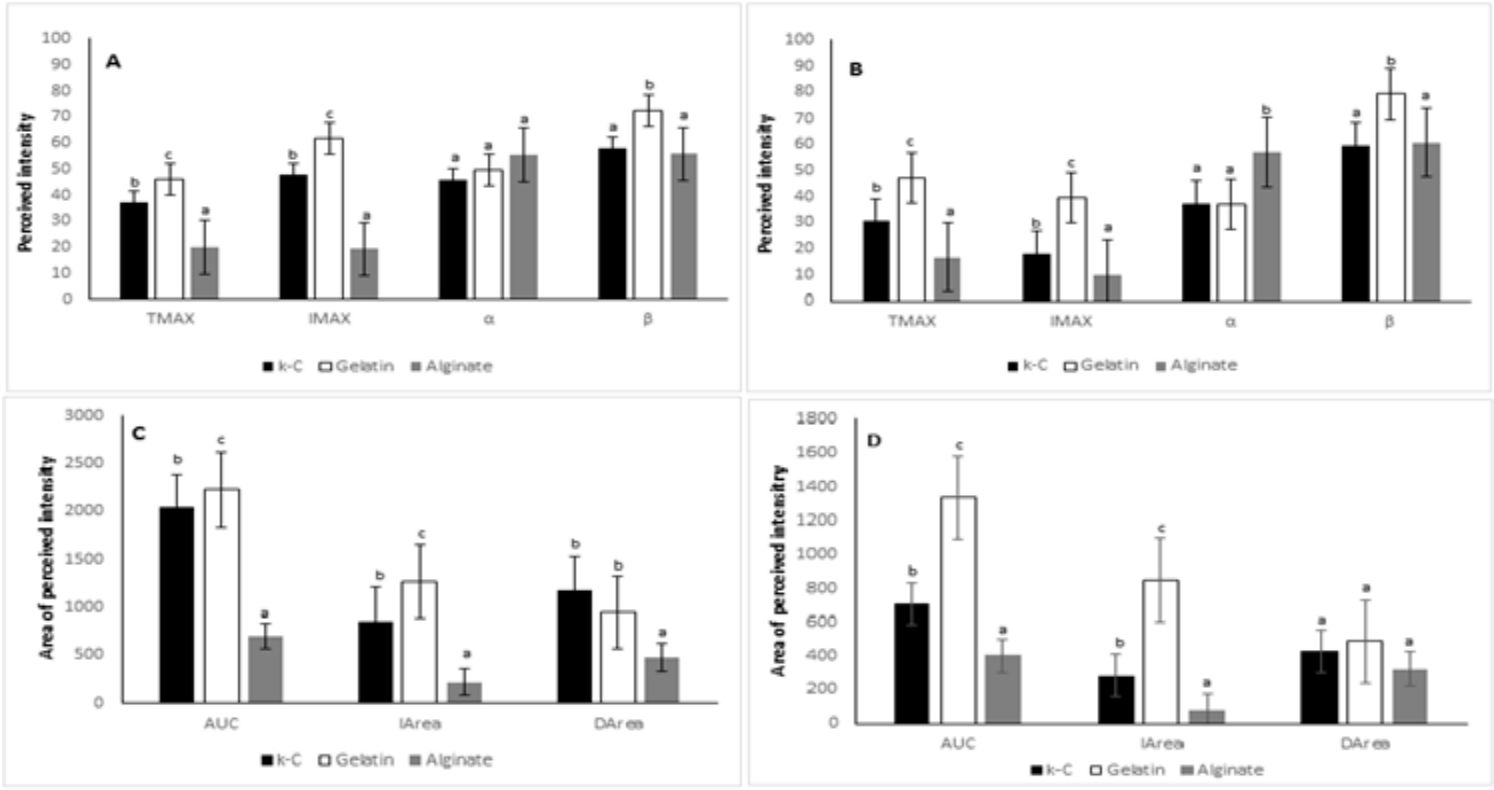


Figure 6.4 Values of the time-intensity parameters obtained for κ-c (κ-carrageenan), gelatin or alginate gels with salt (A and C) and sugar (B and D). Values represent sample means of n= 11. Values means do not share common letter differs significantly according to the Tukey test ($p<0.05$). k-C= κ-carrageenan; TMAX=Time to maximum; IMAX= Intensity at maximum; AUC=Area under curve; α= Increase angle; lArea= Increase area; β= Decrease angle; DArea= Decrease area. TMAX expressed in seconds, IMAX values represent mean intensity units (NONE = 0 and EXTREME = 60), α and β are expressed as intensity units/ second. Areas for AUC, lArea and DArea expressed as intensity units x time.

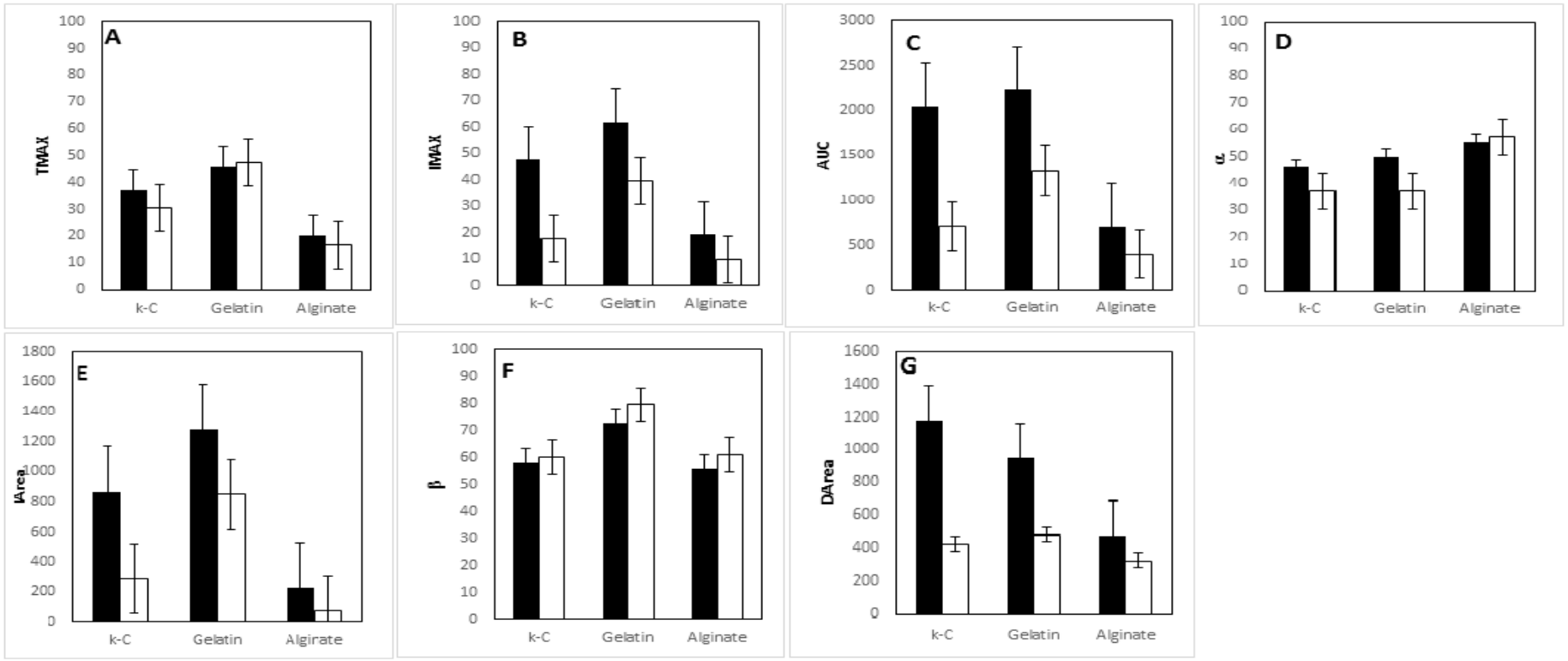


Figure 6.5 Values with significant difference ($p<0.05$) based on the T-test analysis for the time-intensity curve obtained for κ-c (κ-carrageenan), gelatin or alginate gels with the addition of salt (■) and sugar (□). A) TMAX B) IMAX C) AUC D) Increase angle (α) E) IArea F) Decrease angle (β) G) DArea. TMAX expressed in seconds, IMAX values represent mean intensity units (NONE = 0 and EXTREME = 60), α and β are expressed as intensity units/ second. Areas for AUC, IArea and DArea expressed as intensity units x time.

6.3.3 RELATING INSTRUMENTAL ASSAY AND SENSORY EVALUATIONS

One of the main objectives of the research is to do a comparative study between the instrumental assay and sensory evaluation. Data gathered from both instrumental assay and the sensory evaluations were subjected to the bivariate Pearson correlation analysis. Pearson analysis is an analysis that produces a sample correlation coefficient, r, which measures the strength and direction of linear relationships between pairs of continuous variables. Results of Pearson analysis for both salt and sugar is displayed in **Table 6.3** and **6.4**. By extension, the Pearson Correlation factor evaluates whether there is statistical evidence for a linear relationship among the same pairs of variables in the population, represented by a population correlation coefficient, ρ ("rho"). The Pearson Correlation is a parametric measure. In salt flavour gels, strong correlation was seen between release rate at room temperature (25 º C) and 37 º C with TMAX, IMAX and AUC. The parameters listed are responsible in explaining the intensity level perceived by the panellist. The findings suggest a significant direct relationship which explained in increase in the rate of release will lead to increase of the parameters listed. It is worthy mentioning the higher the release rate, the higher level of intensity will be perceived by the panellists. The application of pressure on the gel were at room temperature was seen to have an effect on the AUC, however, no direct relationship is seen on the parameters on the application of force at 37 º C.

Pearson analysis shows no direct relationship between the time-intensity parameters and instrumental assay at room temperature for sugar flavoured gels. But there is a definite direct relationship between the AUC and DArea at 37 ºC. The application of force seems to have no effect on the parameters for both room temperature and 37 ºC. Based on the two previous chapter (**Chapter 4 and 5**), instrumental measure shows that the applied force or compression resulting in a reduction in the taste compound release rate. It was suggested that, even there where no major deformation was

observed, there might be some intrinsic structural changes inside the gels. The application of pressure might reduce the polymer pore sizes which increase the contact of taste compound to the polymer, all together retarding the release of the taste compound. Again study conducted by Mills et al. (2011) in their attempt to quantify salt release in gel system, they have observed that compression does not give any major effect on the salt release. They further mentioned that was because the gel system, unless compress to fracture, the internal structure remains the same, hence, not much difference was in the release upon compression. The release will only increase dramatically when fracture as this increase the surface are for possible diffusion. But note there is a strong inverse relationship between the compression fracture force (hardness) and the aftertaste. The inverse relationship explains the stronger the gel strength resulting to a lower aftertaste.

The lack in correlations between the instrumental assay and the sensory evaluation might be due to proper training received by the panellists. A more comprehensive training should be done to reduce the variations between panellists.

Table 6.3 Pearson correlation coefficients between sensory and instrumental data for salt.

b) Salt		a) Salt							Instrumental study						
		TMAX	**IMAX**	**AUC**	**α**	**IArea**	**β**	**DArea**	**Rate of release 25ºC**	**Rate of release 37ºC**	**Rate of release comp 25ºC**	**Rate of release comp37ºC**	**Gradient force vs distance**	**Force (Hardness)**	**Elastic modulus**
Sensory evaluation	TMAX	1.00	**0.959****	**0.932****	-0.70	0.994**	.828*	0.65	**0.831***	**0.901***	0.75	-0.01	0.05	-0.73	0.08
	IMAX		1.00	**0.976****	-0.57	0.977**	0.73	0.77	**0.880***	**0.935****	0.75	0.00	0.13	-0.65	0.16
	AUC			1.00	-0.68	**.939****	0.60	**0.879***	**0.933****	**0.857***	**0.870***	0.22	0.27	-0.57	0.31
	α				1.00	-0.64	-0.34	-0.61	-0.67	-0.40	-0.86	-0.58	-0.38	0.40	-0.38
	IArea					1.00	**0.833***	0.66	**0.844***	**0.941****	0.72	-0.06	0.02	-0.74	0.05
	β						1.00	0.16	0.52	**0.840***	0.29	-0.50	-0.46	-0.88	-0.43
	DArea							1.00	**0.865***	0.56	**0.903***	0.57	0.57	-0.22	0.60
Instrumental study	Rate of release 25ºC								1.00	0.81	**0.848***	0.31	0.12	-0.67	0.15
	Rate of release 37ºC									1.00	0.51	-0.28	-0.19	-0.79	-0.16
	Rate of release comp 25ºC										1.00	0.65	0.53	-0.34	0.55
	Rate of release comp 37ºC											1.00	0.71	0.29	0.71
	Gradient force vs distance												1.00	0.60	**0.998****
	Compression fracture force													1.00	0.57
	Elastic modulus														1.00

Values in bold are significant (p<0.05)

Table 6.4 Pearson correlation coefficients between sensory and instrumental data for sugar.

	b) Sugar	Sensory evaluation							Instrumental study						
		TMAX	**IMAX**	**AUC**	**α**	**Iarea**	**β**	**Darea**	**Rate of release 25ºC**	**Rate of release 37ºC**	**Rate of release comp 25ºC**	**Rate of release comp 37ºC**	**Gradient force vs distance**	**Force (Hardness)**	**Elastic modulus**
Sensory evaluation	TMAX	1.00	**0.917****	**0.86***	-0.82	**0.931****	**0.852***	0.42	-0.21	0.52	0.23	-0.75	-0.31	-0.78	-0.31
	IMAX		1.00	**0.98****	-0.55	**0.999****	**0.889***	0.67	-0.25	0.79	0.05	-0.67	-0.45	-0.77	-0.45
	AUC			1.00	-0.50	**0.977****	0.81	0.79	-0.17	**0.854***	0.07	-0.58	-0.41	-0.74	-0.41
	α				1.00	-0.58	-0.45	-0.14	-0.04	-0.07	-0.55	0.55	-0.05	0.57	-0.05
	IArea					1.00	**0.902***	0.65	-0.27	0.77	0.07	-0.67	-0.46	-0.79	-0.46
	β						1.00	0.33	-0.58	0.58	0.01	-0.62	-0.69	**-0.822***	-0.69
	DArea							1.00	0.18	**0.867***	0.06	-0.17	-0.17	-0.41	-0.17
Instrumental study	Rate of release 25ºC								1.00	0.06	0.10	-0.15	0.71	0.38	0.71
	Rate of release37ºC									1.00	-0.09	-0.46	-0.41	-0.55	-0.41
	Rate of release comp 25ºC										1.00	0.14	-0.22	-0.54	-0.22
	Rate of release comp 37ºC											1.00	0.01	0.40	0.01
	Gradient force vs distance												1.00	0.76	**1.00****
	Compression fracture force													1.00	0.76
	Elastic modulus														1.00

Values in bold are significant (p<0.05)

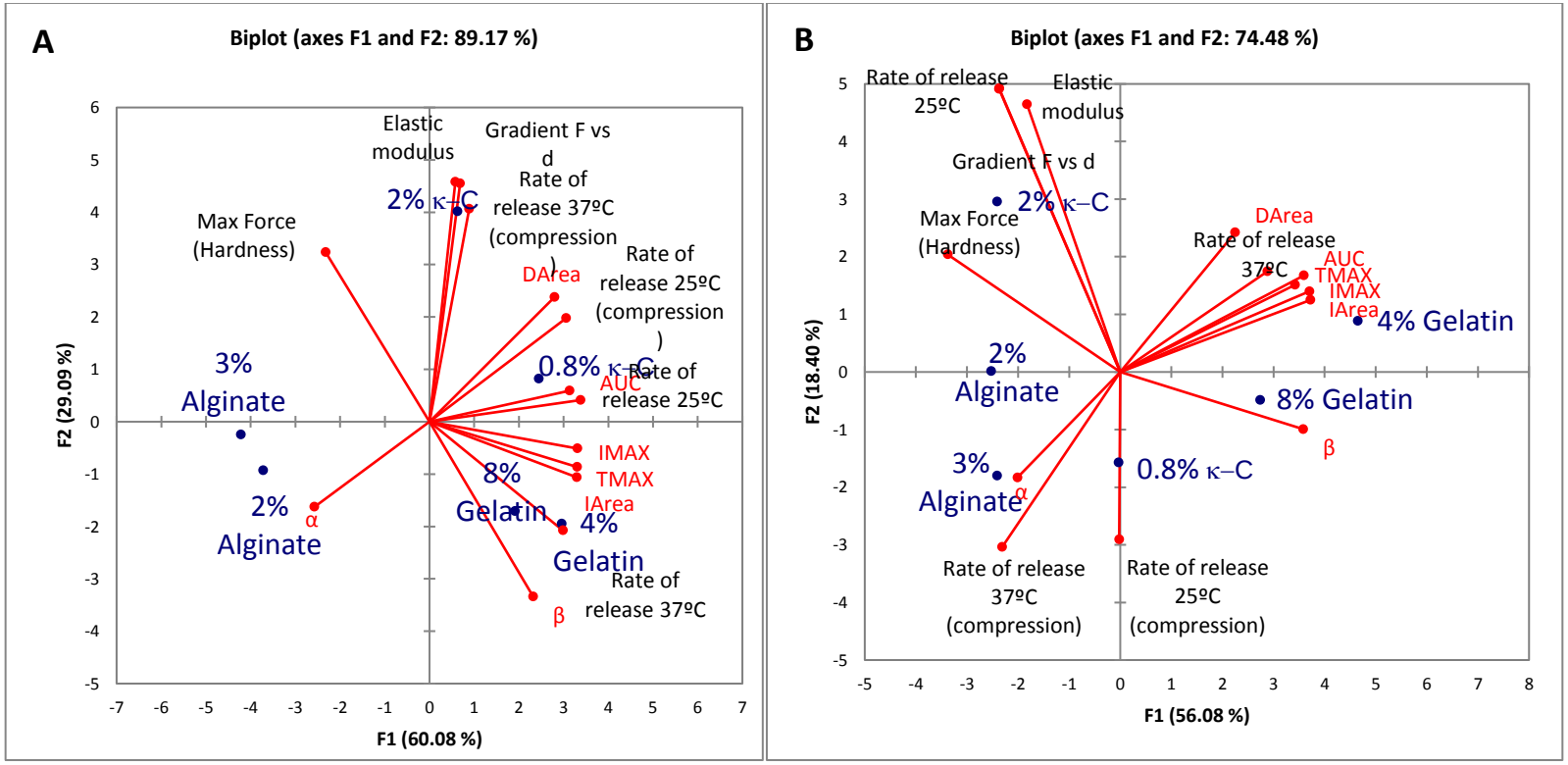


Figure 6.6 Principal Component Analysis of the time intensity parameter from sensory evaluations and mechanical properties from the instrumental analysis for salt (A) and sugar (B).

A Principal Component Analysis was done to describe the relationship between the instrumental data and time-intensity sensory evaluation parameters depicted in **Figure 6.7**. The cov-PCA (covariance- PCA) also allowed distinguishing the weight of each descriptor towards the types of gel utilised in the research. For salt and sugar flavoured gels, axis 1 (representing 60.08% and 56.08% of variability respectively), separates κ-carrageenan, gelatin and alginate. Distribution for the both of instrumental data sets suggests 2% κ-carrageenan to be a very rigid and highly elastic material as compared to the other gels. Instrumental salt release profiles show that 2% κ-carrageenan to have the fastest release profile at 37 º C under compressed condition. However, the instrumental analysis in sugar shows 2% κ-carrageenan exhibited the highest release profile at room temperature under the non-compressed condition. 0.8% κ-carrageenan exhibited the fastest release profile at room temperature (ca. 25 º C) under compressed conditions. Gelatin at 4% concentration showed the fastest release rate at 37 º C for both salt and sugar. The clustering of the time-intensity parameters (IMAX, TMAX, IArea) infers the highest intensity level perceived by panellist. Similar pattern of clustering on the time intensity data were seen in the sugar flavour gels.

In relating instrumental study with sensory evaluation for the salt flavour gels corresponding to axis 2 (representing 29.09% and 18.40 respectively), compression fracture force shows in inverse relationship with that of the (IMAX, TMAX, IArea and β). In other words, more rigid of gels reduced the intensity level perceived. In contrast to the sugar flavoured gels, none of the instrumental analysis seems to have any relation to that of the sensory data except the inverse relationship between the maximum forces (hardness) with aftertaste (β) i.e., as the rigidity of the gel increased aftertaste decreased

6.4 SUMMARY

This part of the study contributes a better understanding on the effects of several factors on the flavour intensity perceived by the panellist. The time-intensity sensory evaluation was designed to resemble conditions that of the

instrumental assay. Salty and sweetness perception were shown to be significantly different in all samples. The highest intensity of saltiness and sweetness were shown in gelatin, because the gelatin gels melted at 37 º C. κ-carrageenan and alginate were resistant to any morphological changes in the oral cavity. The two gels showed lower intensity perceive of saltiness and sweetness. However, alginate exhibited the lowest intensity. There were also significant differences in the levels of intensity of saltiness and sweetness. As an independent variable, biopolymer type was seen to play a significant role in level intensity. Interestingly, applied pressure (compressed condition) and concentration were seen to have no obvious effect on the perceived intensity when analysed independently for both salt and sugar. According to Mills et al. (2011) applied pressure or compression without fracture does not change the structure of a gel system. This might explains why application of force does not lead to any increment in the panellist perception. However, for saltiness, analyses on the combined conditions (biopolymers*pressure*concentration) shows significant effect on the decrease angle (β; aftertaste). In the sweetness perception, the combined conditions of biopolymer types and concentration (biopolymer* concentration) were seen to have significant effect on area under curve (AUC). Finally, in relating the instrumental measurements and time-intensity sensory evaluation, data gathered for two studies were subjected to Pearson correlation analysis and Principal Component Analysis. Pearson correlation analysis conducted on the salt flavour gels revealed a direct relationship on the time intensity parameters TMAX, IMAX, AUC, IArea, DArea and β for both room temperature and at 37 ºC. For sugar flavoured gels only a few time-intensity parameters showed a direct relationship with the release rate at 37 ºC. Negative/inverse relationship is observed between the β (aftertaste) with compression fracture force. Principal component analysis revealed an inverse relationship between maximum force (hardness) with IMAX, TMAX, IArea and β for salt release. Compression fraction force (hardness) was also seen to have an inverse relationship with β (aftertaste) for sugar flavoured gels. Overall, findings revealed in the time-intensity sensory evaluations seemed to agree to the data obtained from the instrumental analysis.

CHAPTER 7

CONCLUSION, LIMITATIONS AND FUTURE WORK

7.1 SUMMARY OF THE THESIS AND IMPLICATIONS OF THE FINDINGS

The research findings for the entire project have achieved the main aims and fulfilled all the research objectives. This research shows the potential usefulness of a simple instrumental measurement of flavour release in different gel systems. The gel systems used have very wide applications in the food industry. The instrument gave reproducible results.

In **Chapter 4**, series of preliminary test were performed in optimising methods in quantifying the taste compounds release. The preliminary test has shown to provide accurate reproducible results. In this section findings show that polymer concentration and temperature played significant roles in the flavour release profile. An inverse relationship was observed between polymer concentration and the release rate specifically for k-c. Higher temperature (37 ºC) gave faster release than lower temperature (25 ºC). High temperature aids flavour release polymer via internal structural changes and the increases taste compounds mobility. Morphological changes at higher temperature (37 ºC) for gelatin gels resulted rapid flavour release. Compression was observed not to have any significant impact on the release of taste compounds, although release recedes slightly possibly due to internal structural changes might reduce the pore size and increase contacts between the taste compounds and retarding its release.

Mathematical modelling in **Chapter 5** suggested that the principal mechanism involved in the release of the taste compounds is diffusion. However, at 37 ºC degradation/melting is the mechanism involved for gelatin gels. The calculated diffusion coefficients were seen to be slightly higher than the theoretical diffusion coefficients in some cases. This could be due to

errors in the diffusion coefficients used under these conditions. As mentioned at the beginning of the chapter, theoretical considerations that were taken into accounts were the gel dimension, volume of the vessel, buffer viscosities and the literature diffusion values of each taste compounds. Alginate gave much lower release than predicted by theory, in agreement with its much higher affinity for NaCl and glucose. In general, release of salt was faster than sugar probably due to its lower molecular size and lower tendency for binding to the gel matrix. Also, the presence of 10% glucose in the buffer solution increase its viscosity, thus the movement of the glucose molecules into the surroundings will be affected as the buffer is slightly more viscous.

A final part **Chapter 6** of the study compared the instrumental measurements with the time-intensity sensory evaluation. The results collected from the time-intensity revealed the level of intensity experience in salt and glucose are in the following order.

Gelatin > k-carrageenan > Alginate

Correlations between instrumental analysis and time-intensity sensory evaluations were observed in certain parameters. There were no correlations observed in between the time-intensity parameters with instrumental compressed result. Based on overall observations, sensory results does shows agreement with the instrumental analysis.

7.1 RESEARCH LIMITATIONS

During the initial optimisation stage in **Chapter 4**, instrumental set up was designed with the attempt to closely mimic the actual human oral processing. However, the design of this instrumental measure only allows the mimicking certain oral processing action. The compression on the sample could only bear a resemblance to the action of tongue movement toward the upper mouth palate. The release measurement was conducted without the absence of fracture using the teeth and saliva. Repeated compression was not able to be conducted as it was very difficult to measure the release of fractured sample without the presence of noise. This research finding only offers little information on the effect of compression on sample and taste compounds

release. It is known in previous studies, the fracture of samples causes faster release, however, due to limitations of the instrumental set up, an elaborated work on compression was not able to be done. Future work might involve in a more detailed optimisation which allows quantifying of release in fractured samples. In certain polymers we might not see any profound effect on the release of taste compounds. Furthermore, only one concentration of taste compounds was used. Using wide range of concentration may allow us to deduce a more conclusive summary on the taste compounds release.

In **Chapter 5**, only simple mathematical modelling was attempted in order to understand the mechanism that governs the taste compounds release. Only basic theoretical was taken into account (gel dimension, volume of the vessel, buffer viscosities and the literature diffusion values if each taste compounds). Little disagreement between the instrumental curves and theoretical curve were observed because to readily existing error. Future work could be done on the mathematical modelling and taking into account into many more factors such as polymer concentration, polymer swelling or degradation properties, temperature and many more. This will improve the agreement between the theoretical and instrumental measures.

Limitation on time intensity evaluation (**Chapter 6**) is similar to the instrumental measures. The sensory evaluations were conducted without involving any oral processing actions except for compression. The repeated compression and biting were not involved. There were also wide variations on the time-intensity curves between the panellists, which reflected insufficient training of panellists for the sensory evaluations. In making valid comparison and finding correlation between the instrumental measures and sensory evaluation, sensory evaluation was designed to closely resemble one another. The time intensity evaluation was done with the absence many oral processing actions which allows little information to be deduce. Methods could be re-evaluated and re-designed in order to produce more accurate results and hoping to give more solid conclusive information on dynamics of oral processing actions on taste compounds release.

7.2 RECOMMENDATIONS AND FUTURE WORK

The instrumental mouth model used in this research has been shown to be applicable to mimic some of the oral processing actions. This model could further be optimised to give a closer resemblance on the actual oral cavity conditions. Further work could be performed using the actual saliva or synthetic saliva instead of buffer. Saliva contains certain enzymes that aid the breakdown of certain foods entering the oral cavity (although the gels here are not degraded by the enzymes, others, such as starch would be). It is also known that saliva is shear thinning fluid and this property may play significant role in the release of taste compounds. A wide variations both polymer and taste compound concentration may also be conducted to see a profound effects on the taste release profiles.

The model could further be optimised in measuring both volatile and non-volatile compounds at the same time. Tests and similar analysis could be performed on a wide range on food materials under submerged condition.

The accuracy and reproducibility of the results gained from the model may assist the food industry with the development of more healthy foods, allowing the prediction on the consumer's oral assessment of the food product avoiding much sensory evaluation that is costly and time consuming. However, oral processing is complex. Chewing was excluded in this study, for example due to its complexity. Thus, sensory analysis will still be necessary until such instrumental models become more sophisticated.

REFERENCES

Aguilera, J.M. & Baffico, P. (1997). Structure-mechanical properties of heat-induced whey protein/cassava starch gels. *Journal of Food Science*, 62, pp.0–1048.

Aguilera, J. M., & Kinsella, J. E. (1991). Compression Strength of Dairy Gels and Microstructural Interpretation. *Journal of Food Science*, *56*, 1224–1228.

Aguilera, J. M., & Stanley, D. W. (1993). The Microstructure Of Food Protein Assemblies. *Food Reviews International*, *9*, 527–550.

Ahmed, E. M. (2013). Hydrogel: Preparation, characterization, and applications. *Journal of Advanced Research*, *6*(2), 105–121.

Akhtar, M., Chan, P., Safriani, N., Murray, B., & Clayton, G. (2011). Concentration of Apple Juice Using Spinning Disc Reactor Technology. *Journal of Food Processing & Technology*, *02*(02).

Akinshina, A., Ettelaie, R., Dickinson, E., & Smyth, G. (2008). Interactions between adsorbed layers of alphaS1-casein with covalently bound side chains: a self-consistent field study. *Biomacromolecules*, *9*(11), 3188–200.

Aldrich, J. (1962). The Effect of Selected Anions of Potassium Salts on the Gel Strength of Carrageenan in the Kappa Fraction, *Department of Foods and Nutrition, Michigan State University,* 795-800.

Arabie, P., & Moskowitz, H. R. (1971). The effects of viscosity upon perceived sweetness. *Perception & Psychophysics*, *9*(5), 410–412.

Arancibia, C., Costell, E., & Bayarri, S. (2013). Impact of Structural Differences on Perceived Sweetness in Semisolid Dairy Matrices. *Journal of Texture Studies*, *44*(5), 346–356.

Arifin, D. Y., Lee, L. Y., & Wang, C. H. (2006). Mathematical modeling and simulation of drug release from microspheres: Implications to drug delivery systems. *Advanced Drug Delivery Reviews*, *58*(12-13), 1274–325.

Asano, K. (2006). Mass Transfer: From Fundamnetals to Modern Industrial Applications. Darmstadt: Wiley-VCH.

Atarés, L., Marshall, L. J., Akhtar, M., & Murray, B. S. (2012). Structure and oxidative stability of oil in water emulsions as affected by rutin and

homogenization procedure. *Food Chemistry*, *134*(3), 1418–1424.

Baek, I., Linforth, R. S. T., Blake, A., & Taylor, A. J. (1999). Sensory Perception is Related to the Rate of Change of Volatile Concentration In-nose during Eating of Model Gels. *Chemical Senses*, *24*(2), 155–160.

Bajaj, I. B., Survase, S. A., Saudagar, P. S., & Singhal, R. S. (2007). Gellan Gum : Fermentative Production , Downstream Processing and Applications, *45*(4), 341–354.

Baldwin, E. A., Scott, J. W, Einstein, M. A., Malundo, T.M. M. , Carr, B.T., Shewfelt, R.L., & Tandon, K. S. (1998). Relationship between Sensory and Instrumental Analysis for Tomato Flavor. *Journal of the American Society for Horticultural Science*, *125*(5), 906–915.

Banerjee, S., & Bhattacharya, S. (2012). Food gels: gelling process and new applications. *Critical Reviews in Food Science and Nutrition*, *52*(4), 334–46.

Bat, A., Amerongen, I. A. Van, Groat, R. D., Hoekstra, N. L., & Agterof, W. G. M. (1996). Large Deformation Rheology of Gelatin Gels, *4*, 189–227.

Bayarri, S., Durán, L., & Costell, E. (2004). Influence of sweeteners on the viscoelasticity of hydrocolloids gelled systems. *Food Hydrocolloids*, *18*(4), 611–619.

Bayarri, S., Rivas, I., Izquierdo, L., & Costell, E. (2007). Influence of texture on the temporal perception of sweetness of gelled systems. *Food Research International*, *40*(7), 900–908.

BeMiller, J. N. (2011). Pasting, paste, and gel properties of starch–hydrocolloid combinations. *Carbohydrate Polymers*, *86*(2), 386–423.

Boland, A. A., Bhur, K., Giannouli, P & van Ruth, S. M. (2004). Influence of gelatin, starch, pectin and artificial saliva on the release of 11 flavour compounds from model gel systems. *Food Chemistry*, *86*(3), 401–411.

Bongaerts, K., Reynaers, H., Zanetti, F., & Paoletti, S. (1999). On the Molar Mass of κ -Carrageenan in the Course of Conformational Transition from the Disordered to the Fundamental Ordered Form. *Macromolecules*, *32*, 675–682.

Bot, A., Van Amerongen, I. A., Groot, R. D., Hoekstra, N. L., & Agterof, W. G. M. (1996). Large Deformation Rheology of Gelatin Gels. *Polymer Gels and Networks*, *4*(3), 189–227.

Boudhrioua, N., Bonazzi, C., & Daudin, J. D. (2003). Moisture And Salt Transfers During Constant Temperature Drying Of Gelatin Gels : Effects

Of, *81*(October).

Brannon-peppas, L.(1993). Controlled Release in the Food and Cosmetics Industries, *In Polymeric Delivery System,* 42–52.

Brattoli, M., Cisternino, E., Rosario Dambruoso, P., de Gennaro, G., Giungato, P., Mazzone, A., &Tutino, M. (2013). Gas chromatography analysis with olfactometric detection (GC-O) as a useful methodology for chemical characterization of odorous compounds. *Sensors,13*(12), 16759–16800.

Brenner, T., Tuvikene, R., Parker, A., Matsukawa, S., & Nishinari, K. (2014). Rheology and structure of mixed kappa-carrageenan/iota-carrageenan gels. *Food Hydrocolloids*, *39*, 272–279.

Bromberg, L., Rudman, A., & El'tsefon, B. (1987). Effect of temperature on structure and transport properties of hydrogels based on regenerated cellulose. *Polymer Science USSR*, 29(8), 1669–1675.

Brostow, W., & Hagg Lobland, H. E. (2009). Brittleness of materials: implications for composites and a relation to impact strength. *Journal of Materials Science*, *45*(1), 242–250.

Brostow, W., & Hagg Lobland, H. E. (2010). Brittleness of materials: Implications for composites and a relation to impact strength. *Journal of Materials Science*, *45*(1), 242–250.

Buettner, A., & Schieberle, P. (2000). Influence of mastication on the concentrations of aroma volatiles - some aspects of flavour release and fl avour perception, *71*, 347–354.

Buettner, K. M., Rinciog, C. I., & Mylon, S. E. (2010). Aggregation kinetics of cerium oxide nanoparticles in monovalent and divalent electrolytes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *366*(1-3), 74–79.

Bures, C. D., & Peppas, N.(2006). Glucose-Responsive Hydrogels. *Biomedical Engineering*, 1–11.

Burey, P., Bhandari, B. R., Howes, T., & Gidley, M. J. (2008). Hydrocolloid gel particles: formation, characterization, and application. *Critical Reviews in Food Science and Nutrition*, *4*, 361–377.

Busch, J. L. H. C., Tournier, C., Knoop, J. E., Kooyman, G., & Smit, G. (2009). Temporal contrast of salt delivery in mouth increases salt perception. *Chemical Senses*, *34*(4), 341–348.

Cai, S., & Suo, Z. (2011). Mechanics and chemical thermodynamics of phase

transition in temperature-sensitive hydrogels. *Journal of the Mechanics and Physics of Solids*, *59*(11), 2259–2278.

Calvert, P. (2009). Hydrogels for soft machines. *Advanced Materials*, *21*(7), 743–756.

Campbell, N. R. C., Johnson, J. A., & Campbell, T. S. (2012). Sodium consumption: An individual's choice? *International Journal of Hypertension*, 14–17.

Campo, V. L., Kawano, D. F., da Silva, D. B., & Carvalho, I. (2009). Carrageenans: Biological properties, chemical modifications and structural analysis - A review. *Carbohydrate Polymers*, *77*(2), 167–180.

Chaudhari, N., & Roper, S. D. (2010). The cell biology of taste. *Journal of Cell Biology*, *190*(3), 285–296.

Chen, J. (2009). Food oral processing—A review. *Food Hydrocolloids*, *23*(1), 1–25.

Chen, J., Gaikwad, V., Holmes, M., Murray, B., Povey, M., Wang, Y., & Zhang, Y. (2011). Development of a simple model device for in vitro gastric digestion investigation. *Food & Function*, *2*(3-4), 174–82.

Clarke, S. F., & Foster, J. R. (2012). A history of blood glucose meters and their role in self-monitoring of diabetes mellitus. *British Journal of Biomedical Science*, *69*(2), 83–93.

Cliff, M., & Heymann, H. (1993). Development and use of time-intensity methodology for sensory evaluation: A review. *Food Research International*, *26*(5), 375–385.

de Roos, K. B. (2003). Effect of texture and microstructure on flavour retention and release. *International Dairy Journal*, *13*(8), 593–605.

Déléris, I., Andriot, I., Gobet, M., Moreau, C., Souchon, I., & Guichard, E. (2010). Determination of aroma compound diffusion in model food systems: Comparison of macroscopic and microscopic methodologies. *Journal of Food Engineering*, *100*(3), 557–566.

Déléris, I., Atlan, S., Souchon, I., Marin, M., & Tréléa, I. C. (2008). An experimental device to determine the apparent diffusivities of aroma compounds. *Journal of Food Engineering*, *85*(2), 232–242.

Déléris, I., Saint-Eve, A., Dakowski, F., Sémon, E., Le Quéré, J. L., Guillemin, H., & Souchon, I. (2011). The dynamics of aroma release during consumption of candies of different structures, and relationship with temporal perception. *Food Chemistry*, *127*(4), 1615–1624.

Déléris, I., Zouid, I., Souchon, I., & Tréléa, I. C. (2009). Calculation of apparent diffusion coefficients of aroma compounds in dairy emulsions based on fat content and physicochemical properties in each phase. *Journal of Food Engineering*, *94*(3-4), 205–214.

Dickinson, E., Ettelaie, R., Murray, B. S., & Du, Z. (2002). Kinetics of disproportionation of air bubbles beneath a planar air-water interface stabilized by food proteins. *Journal of Colloid and Interface Science*, *252*(1), 202–13.

Dijksterhuis, G. B., & Piggott, J. R. (2001). Dynamic methods of sensory analysis. *Trend in Food Science & Technology*, *11*, 284–290.

Doi, M. (2009). Gel dynamics. *Journal of the Physical Society of Japan*, *78*(5), 1–19.

Doublier, J. (2006). and 7 Gums Hydrocolloids : Functional Aspects, 233–272.

Druaux, C., & Voilley, A. (1997). Effect of food composition and microstructure on volatile flavour release, *8*(November), 364–368.

Dubois, M., Gilles, K. A., Hamilton, J. K., Rebers, P. A., & Smith, F. (1956). Colorimetric Method for Determination of Sugars and Related Substances. *Analytical Chemistry*, *28*(3), 350–356.

Duizer, L.M., Gullet, E. A., & Finlay, C. J. (1993). Time – Intensity Methods for Beef Tender ness Perception. *Journal of Food Science*.58(5). 943-947.

Dunstan, D. E., Chen, Y., Liao, M., Salvatore, R., Boger, D. V, & Prica, M. (2001). Structure and rheology of the k -carrageenan / locust bean gum gels. *Food Hyfrocolloids, 15*, 475–484.

Elmore, J. S., & Langley, K. R. (2000). Novel Vessel for the Measurement of Dynamic Flavor Release in Real Time from Liquid Foods, 44 , 3560–3563.

Engelen, L. (2012). Oral Receptors. In J. Chen & L. Engelen (Eds.), *Food Oral Processing: Fundamentals of Eating and Sensory Perception* (pp. 15–38). West Sussex, United Kingdom: Wiley-Blackwell.

Erkstrom, L. G. (1985). Molecular-Weight-Distribution And Kappa-Carrageenan On Hydrolysis and The Behaviour on Hydrolysis. *Carbohydrate Research*, *135*, 283–289.

Ettelaie, R., Tasker, A., Chen, J., & Alevisopoulos, S. (2013). Kinetics of food biopolymer film dehydration: Experimental studies and mathematical

modeling. *Industrial and Engineering Chemistry Research*, *52*(22), 7391–7402.

Fabre, M., Aubry, V., & Guichard, E. (2002). Comparison of different methods: Static and dynamic headspace and solid-phase microextraction for the measurement of interactions between milk proteins and flavor compounds with an application to emulsions. *Journal of Agricultural and Food Chemistry*, *50*(6), 1497–1501.

Fell, C. J. ., & Hutchison, H. P. (1971). Diffusion Coefficients for Sodium and Potassium Chlorides in Water. *Journal of Chemical and Engineering Data*, *16*(4), 427–429.

Ferry, a.-L., Hort, J., Mitchell, J. R., Cook, D. J., Lagarrigue, S., & Valles Pamies, B. (2006). Viscosity and flavour perception: Why is starch different from hydrocolloids? *Food Hydrocolloids*, *20*(6), 855–862.

Finney, M., & Meullenet, J. F. (2005). And Individual Crosshead Speed Instrumental Imitative Tests For Predicting Sensory Hardness Of Gelatin Gels, *20*, 114–129.

Firoozmand, H., Murray, B. S., & Dickinson, E. (2012). Microstructure and elastic modulus of mixed gels of gelatin+oxidized starch: Effect of pH. *Food Hydrocolloids*, *26*(1), 286–292.

Floury, J., Rouaud, O., Le Poullennec, M., & Famelart, M. H. (2009). Reducing salt level in food: Part 2. Modelling salt diffusion in model cheese systems with regards to their composition. *LWT - Food Science and Technology*, *42*(10), 1621–1628.

Foegeding, E. a., Daubert, C. R., Drake, M. a., Essick, G., Trulsson, M., Vinyard, C. J., & Van De Velde, F. (2011). a Comprehensive Approach To Understanding Textural Properties of Semi- and Soft-Solid Foods. *Journal of Texture Studies*, *42*(2), 103–129.

Fu, J., & Rao, M. A. (1999). The influence of sucrose and sorbitol on gel – sol transition of low-methoxyl pectin + Ca 2+ gels. *Food Hydrocolloids*, *13*, 371–380.

Fu, J. T., & Rao, M. A. (2001). Rheology and structure development during gelation of low-methoxyl pectin gels: the effect of sucrose. *Food Hydrocolloids*, *15*(1), 93–100.

Fu, S., Thacker, A., Sperger, D. M., Boni, R. L., Buckner, I. S., Velankar, S., & Block, L. H. (2011). Relevance of rheological properties of sodium alginate in solution to calcium alginate gel properties. *AAPS PharmSciTech*, *12*(2), 453–460.

Garrec, D. A., Guthrie, B., & Norton, I. T. (2013). Kappa carrageenan fluid gel material properties. Part 1: Rheology. *Food Hydrocolloids*, *33*(1), 151–159.

Gibbon, B. C., Wang, X., & Larkins, B. A. (2003). Altered starch structure is associated with endosperm modification in Quality Protein Maize. *Proceedings of the National Academy of Sciences of the United States of America*, *100*(26), 15329–34.

Gidley, M. J. (2013). Hydrocolloids in the digestive tract and related health implications. *Current Opinion in Colloid & Interface Science*, *18*(4), 371–378.

Gilbert, C. C. (2008). Designing your sensory test for simple and effective statistical analysis, 15–16.

Gilbertson, T. A., Damak, S., & Margolskee, R. F. (2000). The molecular physiology of taste transduction. *Current Opinion in Neurobiology*, *10*(4), 519–527.

Guggenheim, E. A. (1954). The diffusion coefficient of sodium chloride. *Transactions of the Faraday Society*, *50*, 1048.

Guichard, E. (2002). Interactions between flavor compounds and food ingredients and their influence on flavor perception. *Food Reviews International*, *18*(1), 49–70.

Guichard, E. (2015). *Flavour Development, Analysis and Perception in Food and Beverages*. *Flavour Development, Analysis and Perception in Food and Beverages*. Elsevier.

Gulrez, S. K. H., Al-Assaf, S., & Phillips, G. O. (2003). Hydrogels : Methods of Preparation , Characterisation and Applications. *Progress in Molecular and Environmental Bioengineering*, *51*, 117 – 150.

Han, X., Xu, S. Z., Dong, W. R., Wu, Z., Wang, R. H., & Chen, Z. X. (2014). Influence of carboxymethyl cellulose and sodium alginate on sweetness intensity of Aspartame. *Food Chemistry*, *164*, 278–285.

Haug, A., & Smidsrød, O. (1970). Selectivity of Some Anionic Polymers for Divalent Metal Ions. *Acta Chemica Scand*inavica, 24, 843-854.

He, J. S., Azuma, N., Hagiwara, T., & Kanno, C. (2006). Effects of sugars on the cross-linking formation and phase separation of high-pressure induced gel of whey protein from bovine milk. *Bioscience, Biotechnology, and Biochemistry*, *70*(3), 615–25.

Hendrickx, M., Abeele, C. Vanden, Engels, C., & Tobback, P. (1986).

Diffusion of glucose in carrageenan gels. *Journal of Food Science*, *51*(6), 1544–1546.

Hendrickx, M., Ooms, C., Engels, C., Van Pottelbergh, E., & Tobback, P. (1987). Obstruction effect of carrageenan and gelatin on the diffusion of glucose. *Journal of Food Science*, *52*(4), 1113–4.

Hoffmann, R., Russell, A., & Gidley, M. (1995). Molecular weight distribution of carrageenans: Characterisation of commercial stabilisers and effect of cation depletion on depolymerisation. *Gums and Stabilisers for the Food Industry*, *8*, 137–150.

Hollingworth, C. S. (2010). *Food Hydrocolloids Characteristics, Properties and Structure*. Nova Science Publisher.

Hollowood, T. A., Linforth, R. S. T., Taylor, A. J., Campus, S. B., & Le, L. (2002). The Effect of Viscosity on the Perception of Flavour, *Chem Senses*, *27*, 583–591.

Holm, K., Wendin, K., & Hermansson, A.-M. (2009). Sweetness and texture perceptions in structured gelatin gels with embedded sugar rich domains. *Food Hydrocolloids*, *23*(8), 2388–2393.

Holway, A., & Hurvich, L. (1937). Differential gustatory sensitivity to salt. *The American Journal of Psychology*, *49*(1), 37–48.

Hombreiro-Pérez, M., Siepmann, J., Zinutti, C., Lamprecht, a, Ubrich, N., Hoffman, M., &Maincent, P. (2003). Non-degradable microparticles containing a hydrophilic and/or a lipophilic drug: preparation, characterization and drug release modeling. *Journal of Controlled Release,*, *88*(3), 413–28.

Hons, T. A. H. (2002). Taste-Aroma-Matrix Interactions Determine Flavour Perception By, *University of Nottingham,*Thesis.

Hutchings, J. B., & Lillford, P. J. (1988). Discussion Paper - The Philosophy Of The Breakdown Path, *Unilever Research, 19*, 103-115

Ikeda, S., Morris, V. J., & Nishinari, K. (2001). Microstructure of Aggregated and Nonaggregated K -Carrageenan Helices Visualized by Atomic Force Microscopy, *Biomacromolecules, 2* 1331–1337.

Itamunoala, G. F. (1987). Effective diffusion coefficients in calcium alginate gel. *Biotechnol. Prog.*, *3*(2), 115–120.

International Standards Organization (1981). Sensory analysis vocabulary, *4*, 5492.

Janes, K. A, Calvo, P., & Alonso, M. J. (2001). Polysaccharide colloidal particles as delivery systems for macromolecules. *Advanced Drug Delivery Reviews*, *47*(1), 83–97.

Jin, L., & Seright, R. S. (2000). Rheology of Gels Used For Conformance Control in Fractures. *Proceedings of SPE/DOE Improved Oil Recovery Symposium*, 1–8.

John D. Ferry. (1980). *Viscoelastic properties of polymer solutions Vol: 41*. New York / London / Sydney / Toronto (1970): John Wiley & Sons, INC.

Johnson, R. K., Appel, L. J., Brands, M., Howard, B. V., Lefevre, M., Lustig, R. H., & Wylie-Rosett, J. (2009). Dietary sugars intake and cardiovascular health a scientific statement from the american heart association. *Circulation*, *120*(11), 1011–1020.

Jones, G. M. J. (2004). Rheological Properties Of Gelatin , Carrageenan And Locust Bean Gum Mixtures, *University of Nottingham.*Thesis.

Jones, O. G., Lesmes, U., Dubin, P., & McClements, D. J. (2010). Effect of polysaccharide charge on formation and properties of biopolymer nanoparticles created by heat treatment of β-lactoglobulin–pectin complexes. *Food Hydrocolloids*, *24*(4), 374–383.

Jonhnston-Banks, F. A. (1990). Gelatine. In P. Harris (Ed.), *Food Gels* (pp. 233–290). England: Elsevier Ltd.

June, R. (1993). Polymer-Controlled Drug Delivery Systems, (5), 537–542.

Juteau, a, Cayot, N., Chabanet, C., Doublier, J. , & Guichard, E. (2004). Flavour release from polysaccharide gels. *Trends in Food Science & Technology*, *15*(7-8), 394–402.

Kalur, G. C., Frounfelker, B. D., Cipriano, B. H., Norman, A. I., & Raghavan, S. R. (2005). Viscosity increase with temperature in cationic surfactant solutions due to the growth of wormlike micelles. *Langmuir : The ACS Journal of Surfaces and Colloids*, *21*(24), 10998–1004.

Karim, A. A., & Bhat, R. (2008). Gelatin alternatives for the food industry: recent developments, challenges and prospects. *Trends in Food Science Technology*, *19*, 644–656. http://doi.org/10.1016/j.tifs.2008.08.001

Karnes, H. T. (1990). Thomas Karnes School of Pharmacy Virginia Commonwealth University Richmond, VA 23298, *80*(2), 7997.

Kasapis, S., Al-Marhoobi, I. M., Deszczynski, M., Mitchell, J. R., & Abeysekera, R. (2003). Gelatin vs polysaccharide in mixture with sugar.

Biomacromolecules, *4*(5), 1142–1149.

Kheadr, E. E., Vuillemard, J ., & El-Deeb, S . (2003). Impact of liposome-encapsulated enzyme cocktails on cheddar cheese ripening. *Food Research International*, *36*(3), 241–252.

Koç, H., Vinyard, C. J., Essick, G. K., & Foegeding, E. A. (2013). Food oral processing: conversion of food structure to textural perception. *Annual Review of Food Science and Technology*, *4*, 237–66.

Kohyama, K., Hayakawa, F., Kazami, Y., & Nishinari, K. (2016). Sucrose release from agar gels and sensory perceived sweetness. *Food Hydrocolloids*, *60*, 405–414.

Koliandris, A. (2008). Relationship between texture of gels and flavour release.*University of Nottingham,* Thesis.

Krogstad, D. V, Lynd, N. A., Choi, S., Spruell, J. M., Hawker, C. J., Kramer, E. J., & Tirrell, M. V. (2013). Effects of Polymer and Salt Concentration on the Structure and Properties of Triblock Copolymer Coacervate Hydrogels. *America Chemical Society, 46, 1512-1518.*

Langton, M., Astrdm, A., & Hermansson, A. (1996). Texture As A Reflection Of Microstructure, *Food Qualtiy and Preferences, 7*(3), 185–191.

Lao, L. L., Peppas, N. a, Boey, F. Y. C., & Venkatraman, S. S. (2011). Modeling of drug release from bulk-degrading polymers. *International Journal of Pharmaceutics*, *418*(1), 28–41.

Larson-Powers, N., & Pangborn, R. M. (1978). Paired Comparison and Time-Intensity Measurements of the Sensory Properties of Beverages and Gelatins Containing Sucrose or Synthetic Sweeteners. *Journal of Food Science*, *43*(1), 41–46.

Lauverjat, C., Loubens, C. De, Déléris, I., Tréléa, I. C., & Souchon, I. (2009). Rapid determination of partition and diffusion properties for salt and aroma compounds in complex food matrices. *Journal of Food Engineering*, *93*(4), 407–415.

Lawless, H., & Heymann, H. (2010). Introduction. In H. Lawless & H. Heymann (Eds.), *Sensory evaluation of food: principles and practices*, Springer .

Lee, K. Y., & Mooney, D. J. (2012). Alginate: Properties and biomedical applications. *Progress in Polymer Science (Oxford)*, *37*(1), 106–126.

Leloup, V. M., Colonna, P., Ring, S. G., Roberts, K., & Wells, B. (1992). Microstructure of amylose gels. *Carbohydrate Polymers*, *18*(3), 189–

197.

Lemaitre, J., & Chaboche, J.L. (1990). Elements Of The Physical Mechanisms Of Deformation And Fracture. *Mechanics Of Solid Materials*.

Leo, A., Hansch, C., Elkins, D., Law, A. H., & Behavior, B. N. (1971). Partition coefficients and their uses, *71*(6).

Leo, W. J., McLoughlin, A. J., & Malone, D. M. (1990). Effects of sterilization treatments on some properties of alginate solutions and gels. *Biotechnology Progress*, *6*(1), 51–3.

Lević, S., Pajić Lijaković, I., Dorević, V., Rac, V., Rakić, V., Šolević Knudsen, T., … Nedović, V. (2015). Characterization of sodium alginate/d-limonene emulsions and respective calcium alginate/d-limonene beads produced by electrostatic extrusion. *Food Hydrocolloids*, *45*, 111–123.

Li, L., Ni, R., Shao, Y., & Mao, S. (2014). Carrageenan and its applications in drug delivery. *Carbohydrate Polymers*, *103*(1), 1–11.

Lide, D.R., Ed (2003) CRC Handbook of Chemistry and Physics, 84th Ed., CRC Press: Boca Raton.

Lorén, N., Nydén, M., & Hermansson, A. M. (2009). Determination of local diffusion properties in heterogeneous biomaterials. *Advances in Colloid and Interface Science*, *150*(1), 5–15.

Lu, R. (2013). Principles of solid food texture analysis. In D. Kilcast (Ed.), *Instrumental Assessment of Food Sensory Quality: A Practical Guide* (pp. 103–124). Woodhead Pub.

Lucas, P. W., & Luke, D. A. (1983). Methods for analysing the breakdown of food in human mastication. *Archives of Oral Biology*, *28*(9), 813–9. Retrieved from

Lukasik, K. V., & Ludescher, R. D. (2006). Molecular mobility in water and glycerol plasticized cold- and hot-cast gelatin films. *Food Hydrocolloids*, *20*(1), 96–105.

Madene, A., Jacquot, M., Scher, J., & Desobry, S. (2006). Flavour encapsulation and controlled release - a review. *International Journal of Food Science and Technology*, *41*(1), 1–21.

Mahdavinia, G. R., Iravani, S., Zoroufi, S., & Hosseinzadeh, H. (2014). Magnetic and K+-cross-linked kappa-carrageenan nanocomposite beads and adsorption of crystal violet. *Iranian Polymer Journal*, *23*(5), 335–344.

Malone, M. E ., Appelqvist, I. A. M., & Norton, I. T. (2003). Oral behaviour of food hydrocolloids and emulsions. Part 1. Lubrication and deposition considerations. *Food Hydrocolloids*, *17*(6), 763–773.

Malone, M. E., Appelqvist, I. A. M., & Norton, I. T. (2003). Oral behaviour of food hydrocolloids and emulsions. Part 2. Taste and aroma release. *Food Hydrocolloids*, *17*(6), 775–784.

Mandala, I. G. (2012). Viscoelastic Properties of Starch and Non-Starch Thickeners in Simple Mixtures or Model Food.

Manju, S., Antony, M., & Sreenivasan, K. (2010). Synthesis and evaluation of a hydrogel that binds glucose and releases ciprofloxacin. *Journal of Materials Science*, *45*(15), 4006–4012.

Mao, R., Tang, J., & Swanson, B. G. (2000). Texture properties of high and low acyl mixed gellan gels. *Carbohydrate Polymers*, *41*(4), 331–338.

Martins, J. T., Cerqueira, M. a., Bourbon, A. I., Pinheiro, A. C., Souza, B. W. S., & Vicente, A. a. (2012). Synergistic effects between κ-carrageenan and locust bean gum on physicochemical properties of edible films made thereof. *Food Hydrocolloids*, *29*(2), 280–289.

Masuelli, M. A., & Illanes, C. O. (2014). Review of the characterization of sodium alginate by intrinsic viscosity measurements . Comparative analysis between conventional and single point methods. *International Journal of BioMaterials Science and Engineering*, *1*(1), 1–11.

Matsuhashi, T. (1990). Agar. In P. Harris (Ed.), *Food Gels* (pp. 1–52). England: Elsevier B.V.

Matsuo, R. (2000). Role of Saliva in the Maintenance of Taste Sensitivity. *Critical Reviews in Oral Biology & Medicine*, *11*(2), 216–229.

Mese, H., & Matsuo, R. (2007). Salivary secretion, taste and hyposalivation. *Journal of Oral Rehabilitation*, *34*(10), 711–23.

Milani, J., & Maleki, G. (2012). Hydrocolloids in Food Industry. *Food Industrial Processes–Methods and Equipments,*, 17–38.

Mills, T., Spyropoulos, F., Norton, I. T., & Bakalis, S. (2011). Development of an in-vitro mouth model to quantify salt release from gels. *Food Hydrocolloids*, *25*(1), 107–113.

Montanucci, P., Terenzi, S., Santi, C., Pennoni, I., Bini, V., Pescara, T., … Calafiore, R. (2014). Insights in Behavior of Variably Formulated Alginate-Based Microcapsules for Cell Transplantation, *2015*.

Morris, E. R., Rees, D. A., & Robinson, G. (1980). Cation-specific aggregation of carrageenan helices: Domain model of polymer gel structure. *Journal of Molecular Biology*, *138*(2), 349–362.

Mouritsen, O. G. (2015). The science of taste. *Flavour*, *4*(1), 18.

Murphy, S. P., & Johnson, R. K. (2003). The scientific basis of recent US guidance on sugars intake 1 – 4. *The Chemical Journal of Clinical Nutrition, 78, 827-833*.

Murray, B. S., Durga, K., Yusoff, A., & Stoyanov, S. D. (2011). Stabilization of foams and emulsions by mixtures of surface active food-grade particles and proteins. *Food Hydrocolloids*, *25*(4), 627–638.

Murray, B. S., & Phisarnchananan, N. (2014). The effect of nanoparticles on the phase separation of waxy corn starch+locust bean gum or guar gum. *Food Hydrocolloids*, *42*, 92–99.

Murray, J. M., Delahunty, C. M., & Baxter, I. A. (2001). Descriptive sensory analysis : past , present and future, *34*, 461–471.

Necas, J., & Bartosikova, L. (2013). Carrageenan : a review, *Veterinarni Medicina, 58*(4), 187–205.

Nguyen, A., & Luong, J. H. T. (1986). Diffusion in K-Carrageenan Gel Beads. *Biotechnology and Bioengineering*, *XXVIII*, 1261–1267.

Okay, O. (2010). Hydrogel Sensors and Actuators, *6*, 1–15.

Olthoff, L.W., van der Bilt, A., Bosman, F. & Kleizen, H. H. (1984). Distribution Of Particle Sizes In Food Comminuted by Human Mastication, *Archs Oral Biology, 29*(11), 899–903.

Otake, K., Inomata, H., Konno, M., & Saito, S. (1990). Thermal analysis of the volume phase transition with N-isopropylacrylamide gels. *Macromolecules*, *23*, 283–289.

Pangborn, R. M., Trabue, I. M., & Szczesniak, A. S. (1973). Effect of Hydrocolloids on Oral Viscosity and Basic Taste Intensities. *Journal of Texture Studies*, *4*(2), 224–241.

Panouillé, M., Saint-Eve, A., de Loubens, C., Déléris, I., & Souchon, I. (2011). Understanding of the influence of composition, structure and texture on salty perception in model dairy products. *Food Hydrocolloids*, *25*(4), 716–723.

Pascua, Y., Koç, H., & Foegeding, E. A. (2013). Food structure: Roles of mechanical properties and oral processing in determining sensory

texture of soft materials. *Current Opinion in Colloid & Interface Science*, *18*(4), 324–333.

Perception, S., To, I. N. R., Of, T. C., & Gels, H. (1972). Sweetness perception i n relation to. *Journal of Texture Studies*, *3*, 173–185.

Peyvieux, C., & Dijksterhuis, G. (2001). Training a sensory panel for TI: A case study. *Food Quality and Preference*, *12*(1), 19–28.

Piculell, L. (2016). Gelling Carrageenans. In A. M. Stephen & G. O. Phillips (Eds.), *Food Polysaccahrides and Their Applications* (pp. 238–276). CRC Press.

Pothakamury, U. R., & Barbosa-gnovas, G. V. (1995). Fundamental aspects of controlled release in foods, *Trends in Food Science & Technology, 61*, 397–406.

Prinz, J. F., Janssen, a. M., & de Wijk, R. a. (2007). In vitro simulation of the oral processing of semi-solid foods. *Food Hydrocolloids*, *21*(3), 397–401.

Puppo, M. C., & Añón, M. C. (1999). Rheological properties of acidic soybean protein gels: Salt addition effect. *Food Hydrocolloids*, *13*(2), 167–176.

Rabe, S. (2004). Volatile Release from Liquids: A Comparison of In Vivo APCI-MS, In-mouth Headspace Trapping and In vitro Mouth Model Data. *Chemical Senses*, *29*(2), 163–173.

Rao, M. A. (1998). Dynamic rheology of structure development in low-methoxyl pectin + Ca^{2++} sugar gels. *Food Hydrocolloids*, *12*, 357–363.

Reineccius, G. (2006). *Flavour Chemistry and Technology* (2nd ed.). CRC Press.

Renard, D., van de Velde, F., & Visschers, R. W. (2006). The gap between food gel structure, texture and perception. *Food Hydrocolloids*, *20*(4), 423–431.

Rice, J. R. (2010). Solid mechanics, *School of Engineering and Applied Sciences*, *Cambridge University.*

Rindlav-westling, A., Stadingb, M., & Gatenholma, P. (1998). Carbohydrate Polymers Structure , mechanical and barrier properties of amylose and amylopectin films, *36*, 217–224.

Roca, E., Guillard, V., Broyart, B., Guilbert, S., & Gontard, N. (2008). Effective moisture diffusivity modelling versus food structure and hygroscopicity. *Food Chemistry*, *106*(4), 1428–1437.

Rochas, C., Rinaudo, M., & Landry, S. (1990). Role of the molecular weight

on the mechanical properties of kappa carrageenan gels. *Carbohydrate Polymers*, *12*(3), 255–266.

Rodrigues, J. F., Gonçalves, C. S., Pereira, R. C., Carneiro, J. D. S., & Pinheiro, A. C. M. (2014). Utilization of temporal dominance of sensations and time intensity methodology for development of low-sodium Mozzarella cheese using a mixture of salts. *Journal of Dairy Science*, *97*(8), 4733–44.

Rolin, Claus and De Vries, J. (1990). Pectin. In P. Harris (Ed.), *Food Gels* (pp. 401–434). England: Elsevier Ltd.

Rosenthal, A. J. (1999). *Food Texture Measurement and Perception*. Maryland, USA: ASPEN.

Ross F., C., & Hoye Jr., C. L. (2012). Breaking and Mastication of Solid Foods. In Chen, J. & Engelen, L. (Eds.), *Food Oral Processing: Fundamentals of Eating and Sensory Perception* (pp. 95–108). Wiley.

Ross-Murphy, S. B. (1992). Structure and rheology of gelatin gels: recent progress. *Polymer*, *33*(12), 2622–2627.

Roylance, D. (2001). Introduction to Fracture Mechanics, 1–17.

Rubert, M., Monjo, M., Lyngstadaas, S. P., & Ramis, J. M. (2012). Effect of alginate hydrogel containing polyproline-rich peptides on osteoblast differentiation. *Biomedical Materials*, *7*(5), 055003.

Russ, N., Zielbauer, B. I., & Vilgis, T. A. (2014). Impact of sucrose and trehalose on different agarose-hydrocolloid systems. *Food Hydrocolloids*, *41*, 44–52.

Sagalowicz, L., & Leser, M. E. (2010). Delivery systems for liquid food products. *Current Opinion in Colloid & Interface Science*, *15*(1-2), 61–72.

Saha, D., & Bhattacharya, S. (2010). Hydrocolloids as thickening and gelling agents in food: a critical review. *Journal of Food Science and Technology*, *47*(6), 587–97.

Salles, C., Chagnon, M. C., Feron, G., Guichard, E., Laboure, H., Morzel, M., & Yven, C. (2011). In-mouth mechanisms leading to flavor release and perception. *Critical Reviews in Food Science and Nutrition*, *51*(1), 67–90.

Sartori, C. (1997). the Characterisation of Alginate Systems for Biomedical Applications, *Brunel University,* Thesis.

Schramm, G. (1994). A Practical Approach to Rheology and Rheometry. *Rheology*, 291.

Shilpa, A., Agrawal, S. S., & Ray, A. R. (2003). Controlled Delivery of Drugs from Alginate Matrix. *Journal of Macromolecular Science, Part C: Polymer Reviews*, *43*(2), 187–221.

Siepmann, J., & Siepmann, F. (2008). Mathematical modeling of drug delivery. *International Journal of Pharmaceutics*, *364*(2), 328–43.

Sime, W. J. (1990). Alginates. In H. Peter (Ed.), *Food Gels* (pp. 53–78). England: Elsevier Ltd.

Sinko, P. (1993). Polymeric Delivery Systems, *America Chemical Society 520*, 18–41.

Slomkowski, S., Alemán, J. V., Gilbert, R. G., Hess, M., Horie, K., Jones, R. G., & Stepto, R. F. T. (2011). Terminology of polymers and polymerization processes in dispersed systems (IUPAC Recommendations 2011). *Pure and Applied Chemistry*, *83*(12), 2229–2259.

Slootmaekers, D., van Dijk, J. A, Varkevisser, F. A, van Treslong, C. J., & Reynaers, H. (1991). Molecular characterisation of kappa- and lambda-carrageenan by gel permeation chromatography, light scattering, sedimentation analysis and osmometry. *Biophysical Chemistry*, *41*(1), 51–9. Retrieved from

Smidsrød, O., & Haug, A. (1967). Precipitation of acidic polysaccharides by salts in ethanol – water mixtures. *Journal of Polymer Science Part C: Polymer Symposia*, *16*(3), 1587–1598.

Song, K., Li, L., Li, R., Lim, M., Liu, P., & Liu, T. (2014). Preparation, mass diffusion, and biocompatibility analysis of porous-channel controlled calcium-alginate-gelatin hybrid microbeads for in vitro culture of NSCs. *Applied Biochemistry and Biotechnology*, *173*(3), 838–850.

Sosnik, A. (2014). Alginate Particles as Platform for Drug Delivery by the Oral Route: State-of-the-Art. *ISRN Pharmaceutics*, *2014*, 926157.

Sriamornsak, P. (1999). Effect of calcium concentration, hardening agent and drying condition on release characteristics of oral proteins from calcium pectinate gel beads. *European Journal of Pharmaceutical Sciences*, *8*(3), 221–227.

Stanley, N. F. (1990). Carrageenans. In H. Peter (Ed.), *Food Gels* (pp. 79–120). England: Elsevier Ltd.

Stieger, M. (2011). Texture-taste interactions: Enhancement of taste intensity by structural modifications of the food matrix. *Procedia Food Science*, *1*, 521–527.

Stieger, M. (2015). Food Hydrocolloids Dynamic texture perception and oral processing of semi-solid food gels : Part 1 : Comparison between QDA , progressive pro fi ling and TDS. *Food Hydrocolloids*, *43*, 207–217.

Stieger, M., & van de Velde, F. (2013). Microstructure, texture and oral processing: New ways to reduce sugar and salt in foods. *Current Opinion in Colloid & Interface Science*, *18*(4), 334–348.

Stokes, J. R., Boehm, M. W., & Baier, S. K. (2013). Oral processing, texture and mouthfeel: From rheology to tribology and beyond. *Current Opinion in Colloid & Interface Science*, *18*(4), 349–359.

Szczesniak, A. S. (2002). Texture is a sensory property. *Food Quality and Preference*, *13*(4), 215–225.

Szczesniak, A. S., & Kleyn, D. H. (1963). Consumer awareness of texture and other food attributes. *Journal of Food Technology*, (27), 74–77.

Tabata, Y., & Ikada, Y. (1998). Protein release from gelatin matrices. *Advanced Drug Delivery Reviews*, *31*(3), 287–301.

Tang, Q., McCarthy, O. J., & Munro, P. A. (2009). Oscillatory rheological study of the effects of pH and salts on gel development in heated whey protein concentrate solutions. *Journal of Dairy Research*, *62*(03), 469.

Taylor, A. J. (1998). Physical chemistry of flavour. *International Journal of Food Science & Technology*, *33*(1), 53–62.

Taylor, A. J. (2002). Release and Transport of Flavors In Vivo : Perceptual Considerations. *Comprehensive Review in Food Science and Food Safety, 1*, 45–57.

Taylor, A. J., & Linforth, R. S. T. (1994). Flavour release in the mouth, *Trends in Food Science and Technology, 7*, 601–605.

Tecante, A., & Núñez, C. (2012). Solution Properties of κ-Carrageenan and Its Interaction with Other Polysaccharides in Aqueous Media. *Rheology*, 241–264.

Teff, K. L. (1996). Physiological effects of flavour perception. *Trends in Food Science and Technology*, *7*(12), 448–452.

Thrimawithana, T. R., Young, S., Dunstan, D. E., & Alany, R. G. (2010). Texture and rheological characterization of kappa and iota carrageenan

in the presence of counter ions. *Carbohydrate Polymers*, *82*(1), 69–77.

Uhrich, K. E., Cannizzaro, S. M., Langer, R. S., & Shakesheff, K. M. (1999). Polymeric systems for controlled drug release. *Chemical Reviews*, *99*(11), 3181–98.

Valery, P., Danielle, J., & Julie, R. R. (2014). Individual Differences Among Children in Sucrose Detection Thresholds, 3–12

van Aken, G. a., Vingerhoeds, M. H., & de Hoog, E. H. A. (2007). Food colloids under oral conditions. *Current Opinion in Colloid & Interface Science*, *12*(4-5), 251–262.

van den Berg, L., Rosenberg, Y., van Boekel, M. a. J. S., Rosenberg, M., & van de Velde, F. (2009). Microstructural features of composite whey protein/polysaccharide gels characterized at different length scales. *Food Hydrocolloids*, *23*(5), 1288–1298.

van Vliet, T. (2014). *Rheology and Fracture Mechanics of Foods*. London: CRC Press.

van Vliet, T., van Aken, G. a, de Jongh, H. H. J., & Hamer, R. J. (2009). Colloidal aspects of texture perception. *Advances in Colloid and Interface Science*, *150*(1), 27–40.

Varzakas, T. H., Leach, G. C., Israilides, C. J., & Arapoglou, D. (2005). Theoretical and experimental approaches towards the determination of solute effective diffusivities in foods. *Enzyme and Microbial Technology*, *37*(1), 29–41.

Vasisht, N. (2014). Factors and Mechanisms in Micorencapsulation. In A. Goankar, N. Vasisht, A. Khare, & R. Sobel (Eds.), *Microencapsulation in the Food Industry: A Practical Implementation Guide* (pp. 173–180). Academic Press.

Vicini, S., Castellano, M., Mauri, M., & Marsano, E. (2015). Gelling process for sodium alginate: New technical approach by using calcium rich micro-spheres. *Carbohydrate Polymers*, *134*, 767–74.

Viebke, C., Borgstrom, J., & Piculell, L. (1995). Characterisation of kappa- and iota-carrageenan coils and helices by MALLS/GPC. *Carbohydrate Polymers*, *27*(2), 145–154.

Vilgis, T. a. (2013). Texture, taste and aroma: multi-scale materials and the gastrophysics of food. *Flavour*, *2*(1), 12.

Vincent, J. (2012). Basic Elasticity and Viscoelasticity. *Structural Biomaterials*, 1–28.

Wedlock, D. J., Fasihuddin, B. A., & Phillips, G. O. (1986). Comparison of molecular weight determination of sodium alginate by sedimentation-diffusion and light scattering. *International Journal of Biological Macromolecules*, *8*(1), 57–61.

Wilkinson, C., & Minekus, M. (2001). From food structure to texture, *11*(2000), 442–450.

Wold, S., Esbensen, K., & Geladi, P. (1987). Principal component analysis. *Chemometrics and Intelligent Laboratory Systems*, *2*(1-3), 37–52.

Woodward, S. A. (1990). Egg Protein Gels. In H. Petter (Ed.), *Food Gels* (pp. 175–200). England: Elsevier Ltd.

Wu, P., & Imai, M. (2012). Novel Biopolymer Composite Membrane Involved with Selective Mass Transfer and Excellent Water Permeability. *Advancing Desalination*, 57–81.

Yada, R. Y. (2004). *Proteins in Food Processing*. Woodhead Pub. Retrieved from

Yang, K., Wang, Z., Brenner, T., Kikuzaki, H., Fang, Y., & Nishinari, K. (2015). Sucrose release from agar gels: Effects of dissolution order and the network inhomogeneity. *Food Hydrocolloids*, *43*, 100–106.

Yarmolinsky, D. A., Zuker, C. S., & Ryba, N. J. P. (2009). Common sense about taste: From mammmals to insects. *Cell*, *139*(2), 234–244.

Young, S., Wong, M., Tabata, Y., & Mikos, A. G. (2005). Gelatin as a delivery vehicle for the controlled release of bioactive molecules. *Journal of Controlled Release*, *109*(1-3), 256–274.

Yven, C., Bonnet, L., Cormier, D., Monier, S., & Mioche, L. (2006). Impaired mastication modifies the dynamics of bolus formation. *European Journal of Oral Sciences*, *114*(3), 184–90.

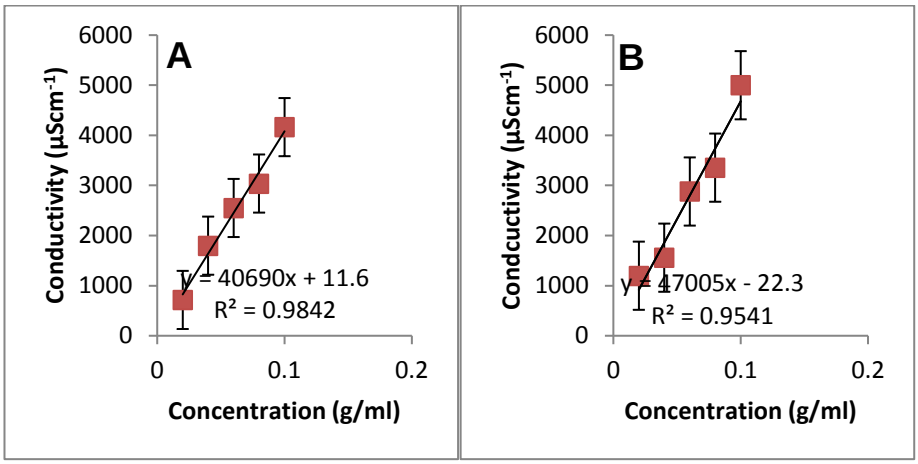
Yven, C., Patarin, J., Magnin, A., Labouré, H., Repoux, M., Guichard, E., & Feron, G. (2012). Consequences of Individual Chewing Strategies on Bolus Rheological Properties At the Swallowing Threshold. *Journal of Texture Studies*, *43*(4), 309–318.

Zhang, Y., Ouyang, H., Chwee, T. L., Ramakrishna, S., & Huang, Z. M. (2005). Electrospinning of gelatin fibers and gelatin/PCL composite fibrous scaffolds. *Journal of Biomedical Materials Research - Part B Applied Biomaterials*, *72*(1), 156–165.

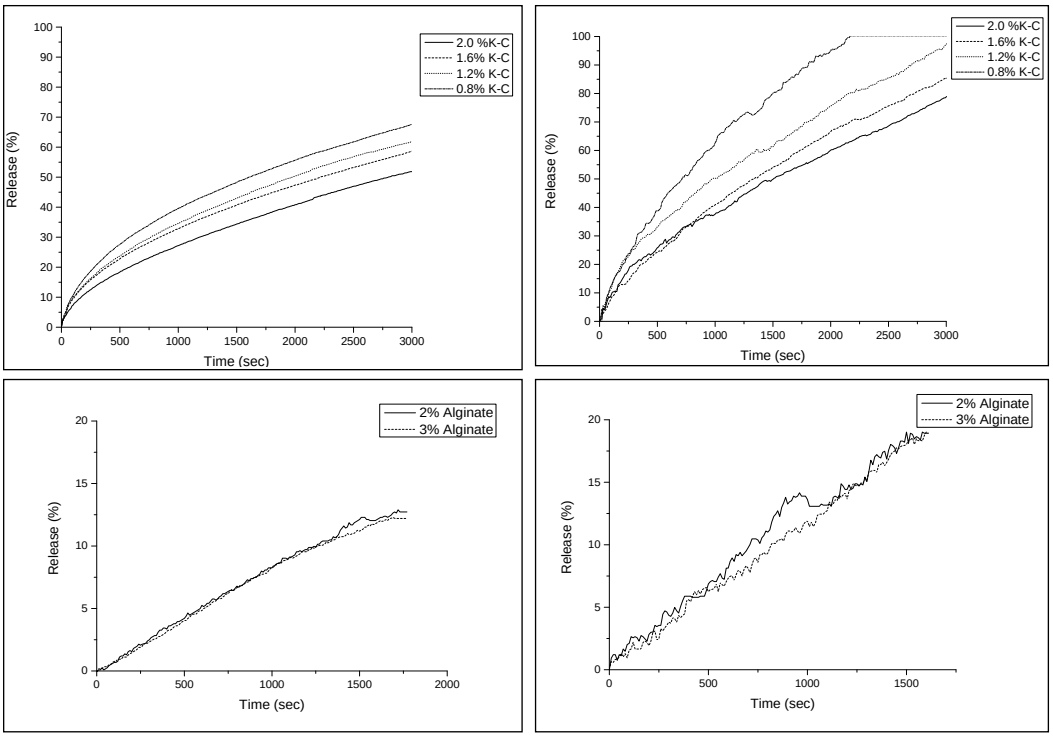
APPENDICES

Appendix 1

DATA IN RELATIONS TO THE INSTRUMENTAL MEASUREMENTS



Calibration curve conductivity over salt concentration 25 ˚C and 37 °C.



NaCl release over time into 200 ml of phosphate buffer from compressed 3 g cylinders of gels at room temperature (A), at 37 º C (B) (non-compressed) and room temperature (C), at 37 º C (D) (compressed). Gel compressed at constant rate of 2mm/s

Appendix 2

THEORETICAL CONSIDERATIONS AND COMPLETE MATHEMATICAL MODELLING EQUATIONS

In this section, the flavour release mechanism for gel systems, as applied to the polysaccharide and protein polymer was discussed in earlier section, is considered from a theoretical point of view. The flavour from within the body of the gel cylinder, the process of the flavour transfer to the outer surrounding involves the process of diffusion. Diffusion equation chosen based on the cylindrical shape of the gel. The gel is confined in chamber in between the probe and the bottom surface of the chamber which assumes there a no diffusion of from the top and bottom of the cylinder. Throughout the diffusion process, we also agreed that the volume of the gel remains constant. The diffusion mechanism in the polymer due to its porous layers allows the water can migrate through living the gel matrix to the outer surrounding.

Concentration of solute in surrounding medium remains small at all time, compared to that in the cylinder. So that we can take C (ρ_o, t) = 0, where ρ_o is the radius of the cylindrical gel. Diffusion coefficient, D, inside the gel remains constant and in are independent of solvent concentration etc. Based on the listed assumptions, we need solve the diffusion equation:

$$D\nabla^2 C = \frac{\partial C}{\partial t} \dots\dots\dots (1)$$

Expressing this is the cylindrical co-ordinates and using the symmetry of the problem, the above equation becomes

$$\left(\frac{D}{r}\frac{\partial}{\partial r}\right)\left(r\frac{\partial C}{\partial r}\right) = \frac{\partial C}{\partial t} \dots\dots\dots (2)$$

Where r is the radial direction (distance) away from the centre of cylinder. Equation (2) can furthermore be written as

$$\frac{\partial C^2}{\partial r^2} + \frac{1}{r}\frac{\partial C}{\partial r} = \frac{1}{D}\frac{\partial C}{\partial t} \dots \dots \dots (3)$$

To solve the above equation, we use method of variable separation that is substituting

$$C\ (r, t) = \ \varepsilon\ (t)\ \theta(r)$$

Upon substituting in equation (3) and dividing by $\varepsilon\ (t)\ \theta(r)$ we have,

$$\frac{\frac{\partial \theta^2}{\partial r^2} + \frac{1}{r}\frac{\partial \theta}{\partial r}}{\theta(r)} = \frac{1}{D\varepsilon(t)}\frac{\partial \varepsilon}{\partial t} \dots \dots \dots (4)$$

Since the right hand side of the equation only depends on *r*, and the left hand side of the equation depends on *t*, it follows that the both sides of the equation (4) must be equal to a constant. Thus,

$$\frac{1}{D\varepsilon(t)}\frac{\partial \varepsilon}{\partial t} = \ -\beta i^2$$

Giving solution

$$\varepsilon(t) = \ e^{-D\beta i^2 t} \dots \dots \dots (5)$$

e have chosen to be negative, $(-\beta i^2)$, since we expect the transient to decay away and reach a steady state. If the constant was chosen to be positive, transients will grow exponentially, which is not expected in this problem. Also from equation (4) we have

$$\frac{\partial^2}{\partial r^2} + \frac{1}{r} * \frac{\partial \theta}{\partial r} = -\beta i^2 \theta$$

Which multiplies by r^2, gives

$$r^2 * \frac{\partial^2 \theta}{\partial r^2} + r * \frac{\partial \theta}{\partial r} + \beta i^2 r^2 \theta \ldots\ldots\ldots (6)$$

A change of variable, $\beta i r = y$ turns equation (6) into

$$y^2 * \frac{\partial^2 \theta}{\partial y^2} + y * \frac{\partial \theta}{\partial y} + y^2 \theta = 0 \ldots\ldots\ldots (7)$$

The above equation is known as a Bessel equation of zero order which has solution

$$\theta(\beta i r) = \theta(y) = J_o(y) = J_o(\beta i r) \ldots\ldots\ldots (8)$$

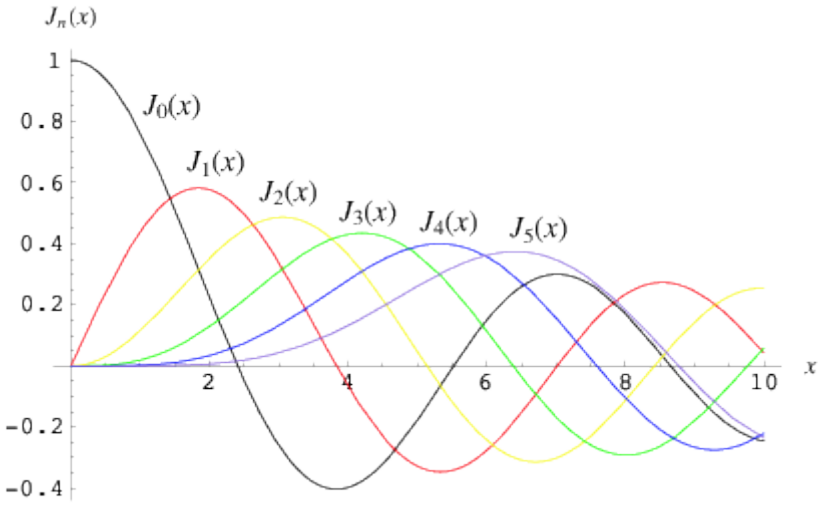
The function $J_o(y)$ is the Bessel function of zero order combining (8) and (5) then

$$C(r, t) = \lambda_i J_o(\beta i r) e^{-D\beta i^2 t} \ldots\ldots\ldots (9)$$

Where λ_i is a constant to be determined by initial boundary conditions. Now we know that the boundary conditions requires $C(\rho_o, t) = 0$ at all times, t. This means that βi can only take up certain values such that

$$J_o(\beta i \rho_o) = 0$$

In other words $\beta i \rho_o$has to be the root of the Bessel function of zero order $J_o(y)$



Let us denote the first root of $J_o(y)$ as x_1, second root as x_2, third root as x_3 and so on then

$$\beta i = \frac{x_1}{\rho_o}.\frac{x_2}{\rho_o}, \ldots\ldots\ldots\ldots.\beta_l = \frac{x_l}{\rho_o}$$

Any value for βi given by above, satisfies equation (6), we have the appropriate boundary conditions. Hence, more generally, the solution to the diffusion equation for such a cylindrical geometry can be written as

$$C(r,t) = \sum_{i=1}^{\infty} \lambda_i J_o(x_1 \frac{r}{\rho_o})\, e^{-D/\rho_o^2 x_i t} \ldots\ldots\ldots (10)$$

We now need to determine the coefficientsλ_i, which are constants and independent of *t* and *r*, and determined by initial profile of $C(r,t)$ at time t=0. Calculate λ_i we make use of some useful properties of $J_o(x)$, in particular completeness and orthogonality. The first of the means that any function $f(r)$ define in range of 0 to ρ_o such that $f(\rho_o) = 0$ can be written as a superposition of functions $J_o(x_i \frac{r}{\rho_o})$ that is

$$f(r) = \sum_{i=1}^{\infty} \lambda_i J_o(x_i \frac{r}{\rho_o}) \ldots\ldots\ldots (11)$$

Secondly that the functions $J_o(x_i \frac{r}{\rho_o})$ for different i are orthogonal such that,

$$\int_0^{\rho_o} r\, J_o\left(x_i \frac{r}{\rho_o}\right) J_o\left(x_j \frac{r}{\rho_o}\right) dr = \frac{\rho_o^2}{2} J_{i^2}\ \ (\beta_i \rho_o)\delta_{ij} \ldots\ldots\ldots (12)$$

Where $\delta_{ij} = 0$ if $i \neq j$ and $\delta_{ij} = 1$ if $i = j$.

At time $t = 0$, we have $C(r, 0) = C_o$, the initial concentration of the solute in the gel-Using this equations (11) and (12), we can now work on the coefficients λ_i in equation 10

$$\lambda_i = (\int_0^{\rho_o} r J_o(\, x_i \frac{r}{\rho_o}) C_o dr)/(\frac{\rho_o^2}{2} J_1^2(x_i)) \ldots\ldots\ldots (13)$$

$$C_o \int_0^{\rho_o} r\, J_o\left(x_i \frac{r}{\rho_o}\right) dr = \frac{C_o \rho_o^2}{x_i} J_1(x_i)$$

So,

$$\lambda_i = (\left(\frac{C_o \rho_o^2}{x_i}\right) J_1(x_i))/(\ (\frac{\rho_o^2}{2} J_1^2(x_i)) = \frac{2C_o}{x_i J_1(x_i)} \ldots\ldots\ldots (14)$$

Thus then gives the solution to the problem, namely $C(r, t)$ as

$$C(r, t) = 2C_o \sum_{i=1}^{\infty} \frac{1}{x_i J_1(x_i)} J_o\left(x_i \frac{r}{\rho_o}\right) e^{-\frac{D}{\rho_o^2 x_i t}} \ldots\ldots\ldots (15)$$

It is useful to define normalised value of $C(r, t)$ by using the following scales for each quantity. Take the unit of *r* to be the ρ_o-so that in the new units, the radius of the cylinder is always 1. Take the unit to be $= \frac{\rho_o^2}{D}$, natural time to solve for diffusion across the cylinder, and the units of C as $C_o$the initial

concentration of solute in the gel. Then, equation (15)in these new units, can be more conveniently written as

$$C(r,t) = 2\sum_{i=1}^{\infty} \frac{J_o(x_i r)}{x_1 J_1(x_1)} J_o\left(x_i \frac{r}{\rho_o}\right) e^{[-x_i^2 t]} \dots\dots\dots (16)$$

Finally, we are interested in the amount of solute, $x(t)$, that still remains in the gel after time t (or conversely the amount that has been release). This can be obtained by integrating the concentration, as given by (15) throughout the cylindrical gel. Then

$$X(t) = LC_o 2\pi \int_0^{\rho_o} rC(r,t)dr \dots\dots\dots (17)$$

Where L is the length of the cylinder

$$X(t) = 4\pi LC_o \int_o^{\rho_o} \sum_{i=1}^{\infty} r \frac{J_o(x_i r)}{x_i J_1(x_1)} e^{-D/\rho_o^2 x_i t} dr \dots\dots\dots (18)$$

Now to perform the integral we do the integration one by one for each term of the summation in (18). Note that we can make a change of variable $q = \frac{x_i r}{\rho_o}$

$$\int_o^{\rho_o} r \frac{J_o(x_i r)}{x_i J_1(x_1)} e^{-D/\rho_o^2 x_i t} dr$$

$$= \frac{\rho_o^2}{x_i^2} \int_0^{x_i} \frac{q J_o(q)}{x_i J_1(x_i)} e^{-D/\rho_o^2 x_i t} dq$$

$$= \frac{\rho_o^2 e^{-\frac{D}{\rho_o^2 x_i t}}}{x_i^3 J_1(x_i)} [q J_1(q)]_0^{x_i}$$

$$= \frac{\rho_o^2}{x_i^2} e^{-D/\rho_o^2 x_i^2 t} \dots\dots\dots (19)$$

Where we have used the fact that

$$\int_0^{x_i} qJ_o(q)dq = [qJ_1\,(q)]_0^{x_i} = q\,J_1(x_i)$$

Using equation (19) for every term of the sum in 18 we get

$$X(t) = 4\pi LC_o \sum_{i=1}^{\infty} \frac{1}{x_i^2} e^{-D/\rho_o^2 x_i^2 t} \ldots\ldots\ldots (20)$$

Note that at time t=0

$$X(0) = 4\pi LC_o \sum_{i=1}^{\infty} \frac{1}{x_i^2} \ldots\ldots\ldots (21)$$

It is a property of the Bessel function of the zero order $J_o(x)$ that sum of square of its solutions, $x_1, x_2 \ldots x_n$.. is $\frac{1}{4}$

$$\sum_{i=1}^{\infty} \frac{1}{x_i^2} = \frac{1}{4}$$

So equation (21) simply reduces to

$$X(0) = \pi\rho_o^2 LC_o \ldots\ldots\ldots (22)$$

Which is exactly as one expects. Also note that at sufficiently long times, $t \gg \frac{D}{\rho_o^2}$, all the terms in (20) will be much smaller than the first (higher terms decay more rapidly than the first one). Therefore, equation (20) can be simplified to

$$X(t) \simeq \frac{1}{x_i^2} e^{-\frac{D}{\rho_o^2 x_i^2}} \ldots\ldots\ldots (23)$$

$$for\ t \gg \frac{D}{\rho_o^2}$$

Appendix 3

Fitted Diffusion coefficients (cm / sec) x 10^{-5} for sodium chloride and glucose in different gel polymer concentrations. [Assumed diffusion coefficient with the absence of polymer 1.48 x 10^{-5} cm/sec (sodium chloride) and 0.518 x 10^{-5} cm/sec (glucose)].

Polymer	**Concentration (%)**	**Sodium chloride (NaCl)**				**Glucose**			
Temperature/Conditions		**25 °C non compress**	**25 °C Compress**	**37 °C non compress**	**37 °C compress**	**25 °C non compress**	**25 °C compress**	**37 °C non compress**	**37 °C compress**
κ-c	0.8	2.96	2.22	3.84	2.66	1.02	1.02	1.58	1.53
κ-c	1.2	2.22	1.85	3.84	2.96	1.02	0.92	1.43	1.28
κ-c	1.6	2.22	1.48	2.22	2.81	1.12	1.02	1.53	1.28
κ-c	2.0	1.48	1.48	2.96	2.73	1.12	1.02	1.53	1.28
Alginate	2.0	0.074	0.004	0.17	0.15	0.23	0.17	0.30	0.23
Alginate	3.0	0.074	0.004	0.14	0.13	0.35	0.15	0.35	0.20
Gelatin	4.0	3.55	0.74	23.70	-	0.60	0.46	6.66	-
Gelatin	6.0	2.22	0.87	22.20	-	0.67	0.41	6.66	-
Gelatin	8.0	2.51	0.96	19.20	-	0.71	0.51	6.66	-

Notes: (-) Experiments were unable to perform to the melting property of gelatin.

Appendix 4

ETHICAL APPROVAL AND RELATED DOCUMENTS

Performance, Governance and Operations
Research & Innovation Service
Charles Thackrah Building
101 Clarendon Road
Leeds LS2 9LJ Tel: 0113 343 4873
Email: ResearchEthics@leeds.ac.uk

UNIVERSITY OF LEEDS

Siti Fairuz Che Othman
PhD Student
School of Food Science and Nutrition
University of Leeds
Leeds, LS2 9JT

MaPS and Engineering joint Faculty Research Ethics Committee (MEEC FREC)

University of Leeds

26 May 2017

Dear Siti Fairuz Che Othman

Title of study	**The dynamic of flavour release from food gels systems**
Ethics reference	**MEEC 14-036**

I am pleased to inform you that the application listed above has been reviewed by the MaPS and Engineering joint Faculty Research Ethics Committee (MEEC FREC) and following receipt of your response to the Committee's initial comments, I can confirm a favourable ethical opinion as of the date of this letter. The following documentation was considered:

Document	Version	Date
MEEC 14-036 Ethical_Review_Form_V3.doc	4	06/08/15
MEEC 14-036 ethical approval signature from SV.png	2	06/08/15
MEEC 14-036 New recruitment form.docx	2	06/08/15

MEEC 14-036 participant information sheet.docx	4	06/08/15
MEEC 14-036 Annex I Consent form.docx	3	06/08/15
MEEC 14-036 Sensory Evaluation of Flavour Release (questionnaires).docx	1	06/08/15
MEEC 14-036 Examples of questionnaires in sensory booth 10-06-2014 (new).docx	1	26/06/15
MEEC 14-036 Annex V Recruitment questionnaire students.doc	1	10/06/15
MEEC 14-036 Annex II Email sample recruiting.docx	2	10/06/15
MEEC 14-036 Examples of questionnaires in sensory booth 10-06-2014.docx	2	10/06/15

The committee made the following comments:

- The committee suggests you consider archiving the research data. Further guidance is available via http://ris.leeds.ac.uk/ResearchDataManagement.

Please notify the committee if you intend to make any amendments to the original research as submitted at date of this approval, including changes to recruitment methodology. All changes must receive ethical approval prior to implementation. The amendment form is available at http://ris.leeds.ac.uk/EthicsAmendment.

Please note: You are expected to keep a record of all your approved documentation, as well as documents such as sample consent forms, and other documents relating to the study. This should be kept in your study file, which should be readily available for audit purposes. You will be given a two week notice period if your project is to be audited. There is a checklist listing examples of documents to be kept which is available at http://ris.leeds.ac.uk/EthicsAudits.

We welcome feedback on your experience of the ethical review process and suggestions for improvement. Please email any comments to ResearchEthics@leeds.ac.uk.

Yours sincerely
Jennifer Blaikie
Senior Research Ethics Administrator, Research & Innovation Service
On behalf of Professor Gary Williamson, Chair, MEEC FREC

CC: Student's supervisor(s)

UNIVERSITY OF LEEDS

Title: The dynamics of food flavour release from gel systems

You are being invited to take part in a research project. Before you decide it is important for you to understand why the research is being done and what will it involve. Please take time to read the following information carefully. For any inquiries, feel free to ask me and I will try my best to attend to any of your question regarding the research. Take time to decide whether or not you wish to take part in the research. You are here today as a respond to the invitation email that was sent throughout the university. Before proceeding to next step, you will be given a consent form. You may withdraw at any time if you were to find this sensory session uncomfortable. If the participant is agree to proceed, the participant will be asked to read through the consent form and sign it.

Aims:

The research aims is to gain an understanding on the effects of food texture on the release rate and the flavour intensity. According to previous researches done, there is a relation between the texture and the release profiles of the certain food flavour. It is believed that as the gel concentration increase, the flavour intensity decreases and opposite condition is observes at lower concentration gels. The participants will asked to gives the intensity profile of the flavour for different gel concentrations.

Methodolgy:

If participants agree to proceed, you will be given a few sets of gel to taste and score the intensity of the flavour (salt and sweet).

The gels that were prepared in this sensory study are as follows:

1. Kappa Carrageenan

2. Alginate
3. Bovine gelatin

The flavour used for the sensory study is as follows:

1. Saltiness using the table salt
2. Sweetness using sugar

The session is was predicted to last for 20-30 minutes.

It is important to highlight that all the gel system and flavourings that are used in this study is food grade and safe to be consumed. However, please note that the gelatin comes from an animal source might not be suitable for vegetarian.

Participants should understand that their name will not be linked with the research materials, and will not be identified or identifiable in the report or reports that will result from this research.

Participants who proceed will agree for the data collected to be utilised in future research.

Once participant has completed the sensory test, the participants will be given and voucher worth £5 as appreciation on their participation.

Your participation is highly appreciated and is hopes to help strengthen and support this research studies

Thank you.

Dynamic Sensory Evaluation of Flavour Release (Human perception)
(Session 1)

- **Personal information:**

Name: **Age:** **Gender:**

Female Male

Weight (kg): **Height (cm):** **Ethnicity:**

Occupation:

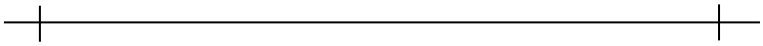
Weekly activity:

Date: _ / _ / ___

Other:

- **Task 1 Texture perception (elasticity) on gel (Panellist will be asked to feel the gel and rank the gel as weak gel or strong gel)**

- **Task description: Panellist is required to apply a little pressure on the gel and rank the gel according to the scale below (Extremely weak gel – Extremely strong gel)**

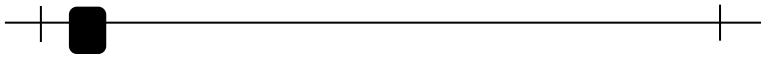


Weak Gel Strong Gel

- **Task 2(a) Perception of flavour intensity over time (Panellist will be asked to rank the flavour intensity in the mouth without applying any force to the gel)**

- **Task description: Panellist is asked to place the gel into the mouth for a period of 2 minutes and rank the gel saltiness according to the scale below. (Not salty – Extremely salty)**

- **Question: Please evaluate the perceived changes in saltiness for gel number……. by moving the black bar on the scale. Please press the 'START' button one you place the gel inside the mouth. Then 'DONE' after the two minutes is up.**

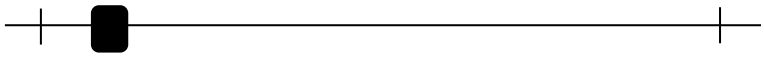


Not salty Extremely salty

- **Task 2(b) Perception of flavour intensity over time (Panellist will be asked to rank the flavour intensity in the mouth applying little force to the gel)**

- **Task description: Panellist is asked to place the gel into the mouth for a period of 2 – 3 minutes and rank the gel saltiness according to the scale below. (Not salty – Extremely salty).**

- **Question: Please evaluate the perceived changes in saltiness for gel number……. by moving the black bar on the scale. Please press the 'START' button one you place the gel inside the mouth. Then 'DONE' after the two minutes is up.**



Not salty Extremely salty

Dynamic Sensory Evaluation of Flavour Release (Human perception)
(Session 2)

- **Personal information:**

Name: **Age:** **Gender:**

Female Male

Weight (kg): **Height (cm):** **Ethnicity:**

Occupation:

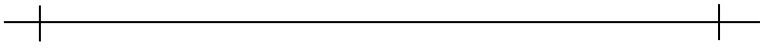
Weekly activity:

Date: _ / _ / ___

Other:

- **Task 1 Texture perception (elasticity) on gel (Panellist will be asked to feel the gel and rank the gel as weak gel or strong gel)**

- **Task description: Panellist is required to apply a little pressure on the gel and rank the gel according to the scale below (Extremely weak gel – Extremely strong gel)**



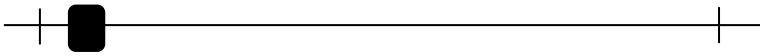
Extremely weak Gel

Extremely strong Gel

- **Task 2(a) Perception of flavour intensity over time (Panellist will be asked to rank the flavour intensity in the mouth without applying any force to the gel)**

- **Task description: Panellist is asked to place the gel into the mouth for a period of 2 – 3 minutes and rank the gel sweetness according to the scale below. (Not sweet – Extremely sweet)**

- **Question: Please evaluate the perceived changes in sweetness for gel number……. by moving the black bar on the scale. Please press the 'START' button one you place the gel inside the mouth. Then 'DONE' after the two minutes is up.**
-

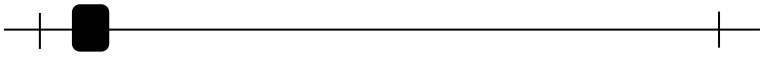


Not sweet Extremely sweet

- **Task 2(b) Perception of flavour intensity over time (Panellist will be asked to rank the flavour intensity in the mouth applying little force to the gel)**

- **Task description: Panellist is asked to place the gel into the mouth for a period of 2 – 3 minutes and rank the gel sweetness according to the scale below. (Not sweet – Extremely sweet)**

- **Question: Please evaluate the perceived changes in sweetness for gel number……. by moving the black bar on the scale. Please press the 'START' button one you place the gel inside the mouth. Then 'DONE' after the two minutes is up.**

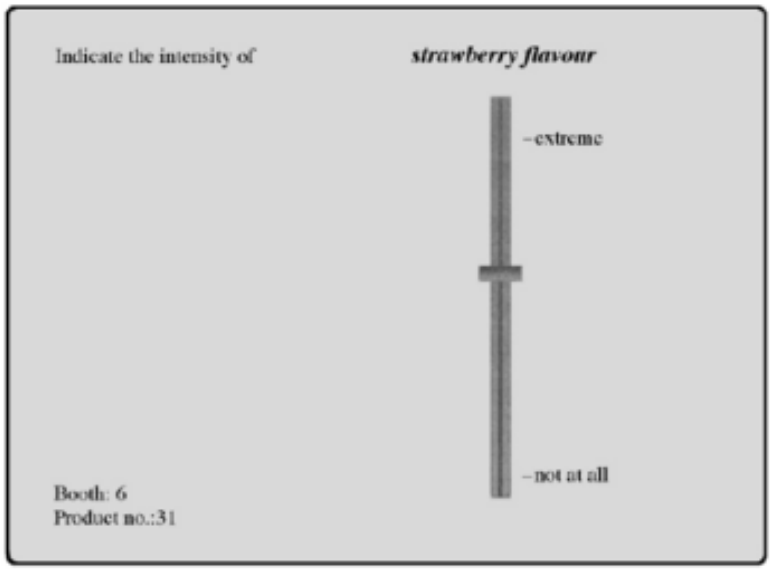


Not sweet Extremely sweet

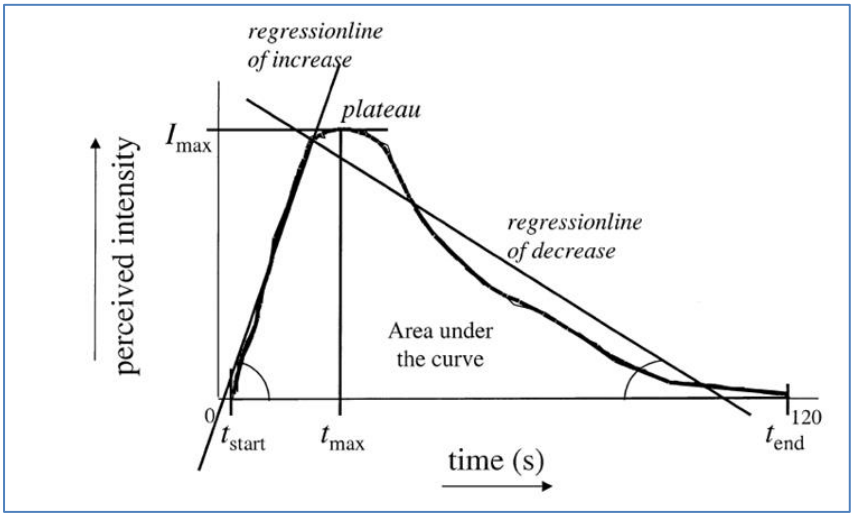
Table 0.1. Lists of polymers, flavour and set conditions for the sensory research

Polymer type	Polymer	NaCl	Glucose	Condition
	Concentration (%)			
Kappa Carrageenan	2.0 1.6 1.2 0.8	2.0	10	Non-compressed & Compressed
Alginate	2 3	2.0	10	Non-compressed & Compressed
Gelatin	8.0 6.0 4.0	2.0	10	Non-compressed & Compressed

**Panellist will taste a total of 36 samples (two sessions). Samples will be randomly labelled with sets of numbers. The conditions were designed according to the instrumental analyses performed. Similarity in the test condition allows comparison to be made between the instrumental and perceived human perception. This will allows a more accurate conclusion to be deduced from the entire research design.



Example of the actual scale in the Compusense Software.



Sample of the graph of result derived from the data obtained from Compusense