Understanding the Cooking of Food in a Domestic Microwave Oven

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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 2018

The candidate confirms that the work submitted is her own and that appropriate credit has been given where reference has been made to the work of others.

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Acknowledgements

I would firstly like to thank my supervisor Prof. Megan Povey for encouraging me to begin a PhD. Without your support, endless patience and guidance this thesis wouldn't be what it is today.

I would also like to thank Sandra Hill, Nik Watson, Caroline Orfila, Mel Holmes, Bernd Koehler, Pam Hume, Nagamani Koganti, Rob Toleman and Fred Nightingale from the University of Nottingham, Leeds and McCain Foods for all your insights into the world of potatoes and microwaves. A special mention for Steve Haldenby who spent tireless hours helping me make kgs of chips at a time and for teaching me what makes the ultimate chip!

This thesis would not be possible without the technical insight and assistance from Miles Ratcliffe and Ian Hardy. You helped me think of unique ways around the problems I had during the method development stage and I cannot thank you enough. Thanks also to Taryn Beasley and Algy Kazlauciunas.

I am indebted to my fantastic friends for putting up with my obsession with chips for so long and always being on hand to lend advice and support, or to just distract me during the less enjoyable times; Julia, Heather, Oscar, Sam, Helen, Ellie x2, Chris, Danny, Vicky, Gowri, Georgina, Leah and Emma I thank you all!

Lastly I thank my wonderful family. I feel truly blessed to have you! To nan and grandad for showing me hard work pays off! To mum and dad for your pep talks and always being there to celebrate or commiserate! To Hollie, my best friend and sister for your hugs and willingness to play boardgames! To Neil, for your unwavering support and for eating so many chips without complaint! To Laine, Andy, Ciaran, Sue, Orla, Cormac, Aoife, Dearbhla and Saoirse for always being there and making me smile. To Mary for cheering me up with Fat Rascals and Slarm and the rest of the O'Briens/Pattens for their kindness. To Arlo my therapy dog even though you didn't know it. I couldn't have done it without you all so thank you!

Abstract

Since its creation in 1945, the microwave has become a popular method of cooking food on both domestic and commercial scales. Despite its popularity, manufacturers have increasingly struggled to provide food products with desirable textural attributes similar to those achieved via conventional oven cooking. A prime example of this is in the potato industry where it is difficult to maintain crispy/crunchy textures of microwaved products due to moisture migration from the centre of the potato to the surface. Microwave heating primarily relies on dielectric heating with heating occurring via dipolar polarisation and ionic conduction. Previous research in this area has identified water as the main driving factor of dielectric activity due to its polar nature. In terms of this thesis, research has been conducted with the aim of understanding the science required to produce a potato chip product within the microwave oven which is able to maintain a moisture rich soft centre with a low moisture crispy exterior.

The research has concluded that creation of crisp products within a microwave environment is multifactorial and strongly depends on storage time, selection of potato part and coating constituents, as well as where in the production process a coating is applied (pre fryer, post fryer or post freezer). Further investigation has also shown the importance of water and highlighted that water content alone is not an indicator of dielectric activity, but rather the ratio of free:bound water within the food product and how moisture moves throughout the product as a function of time. It has been found that addition of a polar and ion rich coating can improve product crispness of the base product although not to the same degree as deep fat frying and conventional heating. However, it must be noted that during the first 8 weeks of storage the product constantly alters in terms of moisture content, dielectric activity, acoustic activity, mechanical force measurement, recon loss and ratio of bound:free water with particular reference made to the role of moisture and sodium chloride as a ‘chemical oscillator’. This indicates that the manufacturer should not sell their product until at least 8 weeks after production if they require a high efficacy for their product. Whilst the end product produced was not as crisp as required, the research is promising with further work being required in terms of coating formulation to improve the end product crispness of potato based products within the microwave. Further work is required within the area of moisture migration due to the complex nature of the product involved.

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List of Abbreviations

MTP – Market Transformation Programme

NHS – National Health Service

AED – Acoustic Envelope Detector

SPL – Sound Pressure Level

JND – Just Noticeable Difference

SPDR – Split Post Dielectric Resonator

SLT – Slotted Line Technique

MDC – Maxwell Displacement Current

ESR – Equivalent Series Resistance

MH – Microwave Heating

NaCl – Sodium Chloride

w/w – Moisture on a wet weight basis

W? – Week followed by Number

W?m?c? – Week followed by number, measurement and number, chip and number

C?/F? – Control/Fresh Sample Followed by Number

PO2 – Polynomial Order 2

PO3 – Polynomial Order 3

PCA – Principal Component Analysis

PC? – Principal Component followed by number

TGA – Thermogravimetric Analysis

DSC – Differential Scanning Calorimetry

CMC– Carboxymethylcellulose

LBG – Locust Bean Gum

XG – Xanthan Gum

HPMC/MC – Hydroxypropylmethylcellulose/ methylcellulose

Tg – Glass Transition of Starch

Tm – Melting Point

Chapter 1
Introduction

1.1 Problem Statement

Domestic microwave heating is a fast and efficient method for the heating of foodstuffs and since its creation in 1945 by Percy Spencer (Spencer, 1945) has gained in popularity with 86% microwave ownership levels in the UK being recorded in 2005, predicted to rise to 90% by 2020 (MTP, 2006). The Market Transformation Programme report (MTP) has also indicated that microwave owners use microwave ovens twice a day thus indicating it is an accepted and often utilised method for the convenient cooking of foods. However, despite this high level of market saturation, microwave heating remains poorly understood and has been associated with non-uniform cooking issues which can result in lower quality food products. Therefore, it is of interest to characterise certain food types in terms of dielectric properties in order to understand how a product will be affected on application of microwave heating.

A leading microwaveable meal provider wishes to improve the texture of one of their potato based products whilst understanding the following areas;

1) Can accurate data be acquired on the dielectric activity of food which will allow for it to be modelled in a microwave oven?
2) Can the storage, dielectric and physical properties of the base uncoated product be understood in order to determine requirements for a coating to promote crispness?
3) Can a coating be developed which improves the product in terms of crispness?

As such the format of this thesis shall firstly observe an understanding of the base uncoated product and secondly shall observe the development of a coating to promote product crispness and the learnings gained during its application and on storage.

1.2 Definition of Crispness

The texture of a food product is paramount to consumer acceptance. Currently microwave heating does not lend itself to the development of crisp outer textures. The food system undergoing investigation is very different in that it requires a moisture rich soft and fluffy interior and a crisp outer skin with very little moisture present. The challenge therefore is to allow these two contradicting textures to be produced under the same processing conditions. In the literature crispness is defined in terms of its physical, acoustic and sensory properties.

1.2.1 Physical definition of product crispness

(Jowitt, 1974) distinguished two forms of crispness;

1) Crispness in fruits and vegetables such as apples, lettuce and celery
2) Crispness in porous dried foods such as potato chips and crackers

On referencing crispness in fruits and vegetables he noted crisp textures as 'a tendency to yield suddenly with a characteristic sound when subjected to an applied force.' Whereas in porous foods such as crackers he used the term brittle. (Vickers and Bourne, 1976) agree with this definition but refer to them as wet crisp foods (fruit and vegetables) and dry crisp foods (crackers). (Duizer, 2001) described wet crisp foods as those that contain fluid in their cells and dry crisp foods as those containing only air which, whilst physically different, produce the same crisp sensation. (Dijksterhuis et al., 2007) observed that factors such as flavour, odour, sight and taste contributed to product crispness with particular attention paid to the texture and sound of a foodstuff. (Vincent, 1998) acknowledges the complexity of the crispness sensation and attempts to quantify it in terms of a single mechanical parameter. This was the rate at which 'the force applied by…the closing muscles (of the jaw) drops when the material fractures.' According to (Vincent, 1998) 'crispness may be associated with a rapid drop in force.' He also argues that at the microstructure failure point, further fracture propagation occurs before being inhibited, therefore classifying crisp products as brittle in nature. (Varela et al., 2006) classifies crispness and crunchiness as two separate parameters which are both 'directly related to the mechanical and fracture properties of solid food materials.' (Chen et al., 2005) states that whilst crispness is a difficult parameter to measure, all crisp foods are 'mechanically brittle and acoustically noisy.'

(Varela et al., 2006) discusses the physical aspect of crispness in further detail. On discussing almonds they also discuss the microstructure of crisp foods and state that 'fracture in food materials starts in inhomogeneities.' They also discuss how the crack then propagates until coming into the presence of a 'crack stopper' such as air pockets or other food constituents such as starch granules. (Varela et al., 2006) argues that having a non-homogenous product is vital for the development of crisp textures. The role of crack stoppers has also been highlighted as important by (Vincent, 1998).

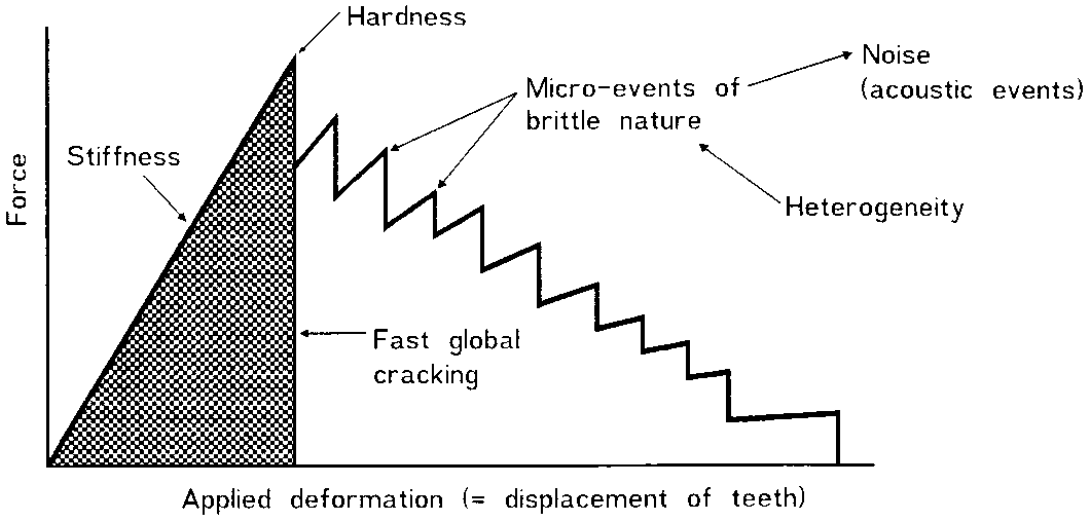


Figure 1-1 Typical Force Displacement Curve (Vincent, 1998)

The main method used to measure product crispness mechanically is the force displacement curve. Figure 1-1 shows a typical force curve for the first bite of a crisp/brittle foodstuff as it is broken on application of the jaw muscles applying increasing force. (Vincent, 1998) states that the initial increase in force is due to the stiffness of the object being tested as well as factors such as the 'thickness of the sample, density and shape.' The point at which the max force is achieved is identified as the products 'hardness' with a higher max force being linked to a harder product. However, (Vincent, 1998) did advise caution regarding the hardness, as if the product is a different size, density or shape 'it can register as harder because of its structure…not because the material is different.' (Mohamed, 1980) observed a poor correlation between product hardness and product crispness. The area which regards crispness is found at the first major failure point as this is synonymous with microstructural breakdown. According to (Vincent, 1998) when a material is brittle 'the fracture will travel quickly' and so results in a sudden force drop on a force displacement curve. With crisp, brittle foods this deformation was observed to become inhibited but propagate again on application of further force. It is during this time point that acoustic events are expected to be observed. It would be expected that crisp brittle products will have acoustic events grouped together at certain stages through the force displacement curve with further acoustic events grouped together as and when fracture propagation occurs. Finally (Vincent, 1998) gave consideration to the frequency of force failures (deformation) in the product microstructure on application of force. (Bourne, 2002) discusses the use of force profile curves to provide indications of the texture and/or quality of a food product. Although he does state that this is geometry dependent.

The main issue with mechanical measurements is that the biting speed of humans may be much higher than the speeds set by the probe. (Meullenet et al., 2002) found the biting

velocity of humans when eating cheese is nearer to 20 mm/s. Whilst this study only utilised 7 test subjects, even if not completely accurate, the biting velocity is still much higher than the speed of the probes used during the (Chen et al., 2005) and (Varela et al., 2006) work. (Flavel et al., 2002) observed the human biting speed to be even higher at 50 mm/s. However, slower test speeds are required during experimentation as otherwise important mechanical data may be missed. A compromise therefore needs to be reached.

There are plenty of instances in which a texture analyser is used with a probe attachment to measure the texture of a food product. (Luyten and Van Vliet, 2006, Luyten et al., 1992, Chen et al., 2005, Vickers, 1987, Vickers, 1988, Varela et al., 2006, Alvarez et al., 2000) However, there is not a universal probe attachment which can absolutely differentiate between the effect of biting down with human incisor, molar or different chewing behaviour of individuals at the same time. As such mechanical measurements are an approximation of mouthfeel and texture. (Luyten and Van Vliet, 2006) used a wedge with a wedge angle of 30^{o} and a probe speed of 40mm/min to represent biting with the front teeth. (Chen et al., 2005) used a three point bend testing rig at speeds of 0.01 mm/s, 0.1 mm/s and 1 mm/s. (Alvarez et al., 2000) used a Volodkevich jaw probe attachment at 0.1 mm/s. (Varela et al., 2007) also used a Volodkevich jaw attachment with a test speed of 1 mm/s. (Varela et al., 2007) state that the Volodkevich jaw simulates the action of an incisor tooth biting through the sample. As the tooth bites through a sample this is known as a penetrative test. The area of a force curve using this test can be associated with shearing forces and is thus related to toughness, hardness or rigidity. Other methods for determining the texture of bitten foods observe ways of measuring the biting force. (Duizer and Winger, 2006) discussed methods such as the sound transmission system in which an accelerometer attached to the chin of test subjects detects vibrations produced during biting with greater vibrations correlated with higher forces produced between the mandible and maxillae. (Duizer and Winger, 2006) utilised a strain gauge placed between two plates that are compressed by the teeth.

1.2.2 Acoustic definition of product crispness

(Kuttruff, 2007) states that 'the generation, propagation and perception of sound is connected with mechanical vibrations or oscillations.' Sound can be viewed as a longitudinal wave where particles present within a medium (the substance that transports a wave from one place to another) vibrate in a direction parallel to the movement of the wave before reverting back to their original position.

(Rossing, 2007) highlights four ways in which sounds can be produced;

1) Vibrating bodies (vibrations displace air and cause local air pressure to fluctuate)
2) Changing airflow

3) Time-dependent heat sources (caused by rapid heating e.g. explosion produces a bang due to expansion of air caused by rapid heating)
4) Supersonic flow (shock waves produced when air is forced to flow faster than the speed of sound)

(Rossing, 2007) also highlights that not all sound can be heard by humans with the frequency range of human hearing being denoted as 20-20000 Hz. (McCain, 2013) have stated that the main consumers of their products are students and the elderly. This is of importance as only young people are likely to hear frequencies up to 20000 Hz. Middle aged people are able to hear frequencies up to 8000- 15000 Hz with the elderly having a lower upper hearing range than those in middle age.

$$intensity\ ratio\ in\ dB = 10log_{10}\left(\frac{I}{10^{-12}\frac{W}{m^2}}\right)$$

Equation 1-1 Intensity of Sound in dB (Chesnutt, 2017a)

The general consensus is to report sound using the decibel scale. (Chesnutt, 2017a) states that 'perceived loudness of sound is related to the sound intensity of the sound wave that hits your ear.' The intensity is a measure of how much energy passes through a certain area every second. This is not a linear relationship as for the perceived sound to double, the intensity of the sound would have to increase by a factor of 10. As such the decibel range has been used to measure the perceived sound as it uses the log function. It is calculated by using equation 1-1 whereby I is the intensity (W/m^2) and 10^{-12} W/m^2 is the lowest threshold of human hearing. In terms of decibel range, from the loudest to softest sound humans can perceive, the range given is 120 dB. (Rossing, 2007) discusses the SPL (Sound Pressure Level) which refers to where in this 120 dB range a sound is perceived and states that 0 dB is the equivalent threshold of hearing at 1000 Hz/1kHz. (Chesnutt, 2017b) describes the SPL as the logarithmic relationship between the sound pressure of a sound relative to a reference pressure of $2x10^{-5}$ Pa, the threshold of human hearing. Equation 1-2 describes this relationship with p denoting the sound pressure of the sound wave and p_o denoting the reference sound pressure.

$$L_P = 20\ log_{10}\left(\frac{p}{p_0}\right)\ dB$$

Equation 1-2 Calculating the Sound Pressure Level (SPL)

The upper limit of hearing is the point at which pain or tingling is felt within the ears and has been defined as 115-140 dB dependent on individuals. The greatest sensitivity to sound is within the range 3500-4000 Hz due to the resonance of the ear canals. As pitch is related to the perception of frequency, crisp foods are expected to produce sounds of higher pitch than crunchy foods.

(Vickers, 1984) discusses the differences between crisp and crunchy textures in relation to sound. He suggested that crisp and crunchy textures can be differentiated in terms of frequency, with crisp products producing higher frequencies and pitches whilst lower frequencies and pitches result in crunchier products. However, he failed to quantify what these thresholds would be. (Duizer, 2001) discusses the different mechanism by which dry and wet crispy foods produce sound. Wet crisp foods are composed of turgid cell walls which when broken cause the contents to expand rapidly resulting in a sound pressure wave. Dry crisp foods contain air filled cavities which are surrounded by brittle walls. On application of continuous force the walls firstly bend then break. The remaining cell wall and fragments connected to the main matrix snap back into place. This causes vibrations and a sound wave to be produced. Sounds can be produced by rupturing one or more cells.

(Duizer, 2001) determined that humans can perceive the sound on breaking crisp structures in three main ways;

1) Air conducted sounds to the ear
2) Bone conducted sounds via the mandible
3) Sound conducted through the soft tissue of the cheeks and tongue

Two main approaches for defining acoustics in crisp textures have been recognised. According to (Chen et al., 2005) the two methods are as follows;

1) measure the perception of air conducted sounds and how they contribute to the identity of a crisp texture
2) measuring the sounds produced on application of force to the foodstuff and correlating to force deformation measurements

(Duizer, 2001) agrees with this approach. (Edmister and Vickers, 1985) enlisted 20 volunteers to consume 16 food products. The food products chosen varied in terms of wet crisp foods/dry crisp foods and thickness. Changes were also made in terms of orientation of samples during consumption and whether several samples of the same foodstuff were stacked or served individually. During consumption, test subjects were taught to bite through the samples once with the incisors and chew twice with the molars. On biting subjects were asked to determine whether they were biting through a wet crisp food or a dry crisp food. The author of this paper also consumed the foodstuff in the same way with a

Bruel and Kjaer microphone above the opening of the ear canal. The 20 volunteers also performed separate tests with a Bruel and Kjaer microphone. The sensory perception of auditory sounds had the highest correlation with the log of the number of acoustic events x mean height of the peaks. It was also determined that dry crisp foods are viewed as crispier than wet crisp foods indicating that lack of moisture is a driving factor for improved product crispness.

To measure acoustics (Chen et al., 2005) and (Varela et al., 2006) utilised an Acoustic Envelope Detector (AED). The AED functions by integrating all the frequencies within the band pass range and generates a voltage proportional to the Sound Pressure Level. The SPL provides a decibel scale which can then be related to human hearing. (Barrett et al., 1992) has utilised Fast Fourier transform (FFT) in order to understand acoustic frequencies of crisp foods. According to (Duizer, 2001) FFT is used to decompose amplitude time plots of the sound waves produced on biting to determine amplitudes, frequencies and phases of the sinusoidal sound waves. Based on this (Duizer, 2001) has classified crisp frequencies as being in the range of up to 12kHz with potato crisps producing crisp frequencies of 3-6 kHz. They also state that crunchier products produce frequencies of 1.25 – 2 kHz.

Whilst focus for measuring acoustics has been given to air conducted acoustic sounds, sound can also be conducted via bone (Kapur, 1971). According to the manufacturer (McCain, 2013), the main consumers of their products are the elderly and student populations. Every 10 years the NHS conduct an adult dental health survey (NHS, 2009). They determined that 19% of all adults in the UK wore dentures with <5% incidence in people aged 16-44 years old rising to 45% in 65-74 year olds and >70% in those 75 years and older. (Kapur, 1971) investigated the effect of dentures on sound conduction through bone. It had been previously observed that denture wearers chewed foodstuffs in random patterns whilst those with natural teeth had a preferential way of chewing food. It was determined using frequency spectrographic analysis that louder sounds were observed in people with natural teeth and that the presence of dentures inhibited sound conduction. However, on application of dental adhesive, denture wearers performed similarly to those with natural teeth. Regardless of denture/non-denture wearers, crispness could still be detected as a texture. Finally (Kapur, 1971) determined that different parts of the bone of the head (forehead, mastoid, mandible) resulted in different sound conduction with the mandible producing sounds that were 2.5 times higher than either the forehead or mastoid in terms of amplitude. As the mandible is heavily involved in the chewing of foods, it is not unreasonable to suggest that bone conducted sounds could contribute to acceptance of certain textures over others. Crisp wafers produced sounds 2.2 times louder than non-crisp wafers. Whilst denture wearers could distinguish crispy textures they still present with randomised chewing which could affect the results observed by (Vickers, 1984) particularly

as one of the main groups of consumers (elderly) have a high incidence of denture wear. (Chen et al., 2005) references the dampening effect/attenuation of the soft tissues present in the human mouth and the loss of energy as the sound waves propagate through the mouth. Therefore as acoustic events are recorded via machinery, the values may not translate on consumption via the mouth. (Duizer, 2001) observed that when the dampening effect is absent, the differences in crushing sounds between food products is larger.

On private communication (Povey, 2013) discussed the importance of sound attenuation further. The intensity of sound waves decrease as a function of distance from its original source. However, natural materials can also cause sound waves to weaken via scattering and absorption. Scattering is defined as the reflection of sound in directions alternate to the original direction of the sound wave e.g. an echo. Absorption is defined as the conversion of sound energy into alternate energy forms. Sound attenuation is the sum of this absorption and scattering phenomena. (Povey, 2013) states that at lower frequencies sound attenuation occurs at a lower rate than at higher frequencies. Lower frequencies , are therefore, able to travel through air more easily than higher frequencies meaning that crisp and crunchy textures are perceived differently. (Povey, 2013) also discussed that sound travels faster in solids than in liquids and faster in liquids than in gases due to particle arrangement.

1.2.3 Sensory definition of product crispness

(Bourne, 2002) states that the perception of crispness varies between individuals and between countries making it a difficult parameter to define. (Duizer, 2001) states that the perception of crispness is at its maximum at the initial bite and decreases as a function of time. (Szczesniak and Kahn, 1971) conducted a study of 150 respondents and determined an appreciation of the texture of a foodstuff is often subconscious and is only noticed when a certain texture is absent. Texture ‘symbolises the state of the food’ indicating whether that foodstuff is fit for consumption, particularly in the case of product freshness. They also discussed the link between sight and texture whereby ‘visual appearance of the food triggers certain mental assumptions about texture’. Flavour was also a contributing factor with less flavoursome foods denoting an increased awareness of texture. Texture is, therefore, complex and is influenced by many factors. In terms of crispness the authors described it as ‘tooth centered’ and synonymous with ‘freshness and wholesomeness’. On the other hand, sogginess is a texture linked with ‘something that has gone wrong’ making it a less desirable food choice. However, this study focussed only on North American subjects and so it is unknown if other cultures would respond differently. The sample size was also small. (Szczesniak, 2002) discussed sensory understanding further when they interviewed 200 consumers asking them to give examples of crisp foods. As opposed to the English language where the words crisp, crunchy and brittle are used to define this textural parameter, the

Japanese and Chinese languages express crispness in >20 ways with saku-saku relating directly to the texture of celery in the Japanese language. This study used an even number of male and female respondents as a function of age; 18-30 years, 31-50 years and 51 +. However, this study was conducted with only North Americans. On referring to crisp foods, lettuce was the most popular answer (13%) among both men and women with crackers, celery and potato chips also scoring highly in terms of frequency. Potato chips were mentioned with a frequency of 7.6% for men and 7.7% for women. They found that both wet crisp foods and dry crisp/brittle foods were mentioned indicating that human beings recognise both types of crisp texture as crisp. (Szczesniak, 2002) was also able to split the crisp foods mentioned into three further groups;

1) Raw fruits and vegetables such as lettuce, celery, apple
2) Farinaceous products such as crackers, toast and pretzels
3) Fried products such as bacon, chicken and French fries

On referencing crispness the terms fresh, crunchy and crackly were frequently used by males with consideration also given to the 'sound it makes when you bite into it'. Women referred to crispness as something that cracks/breaks easily in the mouth. They also defined crispness as 'the amount of resistance the food gives the teeth in chewing' implying a mechanical role in the description of crisp textures.

The final area of interest concerns the Weber-Fechner Law. This is a set of laws which observes the noticeable threshold of human perception. (Salkind, 2010) discusses the Weber Law in relation to the just noticeable difference (JND). In terms of two weights the just noticeable difference is described as the smallest difference in weight noticed between the two samples reliably. It is found that the JND increases as a function of the magnitude of the difference. He notes that the JND for human senses in relation to taste, sight, touch and sound is a constant fraction of the size of the standard stimulus. This is expressed as ;

$$k = \mathrm{JND}/S$$

Equation 1-3 Weber Law

Where k is the Weber fraction constant and S is the value of the stimulus. (Salkind, 2010) states that Fechner's Law relates to the relationship between the intensity of a stimulus and the perceived magnitude. To achieve this Fechner assumed that the JND is a constant fraction of the stimulus (Weber's Law) and that the JND is the basic unit of perceived magnitude so that all JND are equal. This is expressed as;

$$\mathrm{P} = k\log I$$

Equation 1-4 Perceived Magnitude

where P = the perceived magnitude, *k* is the Weber fraction constant and *I* is the stimulus intensity. This means that the JND is referred to as a magnitude when the log of each measurement is taken. A log of 1, therefore, represents a tenfold increase in perception.

1.2.4 Relationship between physical measurements of crispness and acoustic measurements

As discussed previously, acoustic response occurs on microstructural breakdown. As such, when performing mechanical tests on a crisp texture it is prudent to also measure the acoustic response. (Chen et al., 2005) utilised a force displacement curve and an acoustic envelope detector from Stable Microsystems Ltd to measure the sound profile produced on application of the probe. They measured 6 types of biscuits using a three point bend probe attached to a Stable Microsystems Ltd. TA-XT Texture Analyser. They used test speeds of 0.01, 0.1 and 1 mm/s. The highest test speed of 1 mm/s produced the best acoustic signal followed by 0.01mm/s and 0.001mm/s indicating that probe speed is important in terms of acoustic signal measurement. At a test speed of 0.01mm/s, during the force profile curve labelled as stiffness by (Vincent, 1998), there were very few acoustic events and whilst deformation is occurring no significant microstructural breakdown occurred. (Chen et al., 2005) determined that when the force profile is jagged microstructural breakdown is occurring with acoustic events 'bunching' around larger mechanical breakdowns. (Chen et al., 2005) believe this is due to stress building up until the material fractures and subsequent propagation of the crack. This causes further cracks in the structure and the release of energy in the form of sound. However, as this energy dwindles, further deformation is required to cause further acoustic events to occur which is why there are periods of no acoustic events and compression of the food product by the probe before further microstructural breakdowns occur. Finally (Chen et al., 2005) analysed the force data in more detail. They suggest that acoustic events are 'not necessarily linked to a drop in compression force' as sound waves are due to a release of energy as the microstructure suddenly breaks down over a short period of time. The force displacement curve observes the energy inputted into the food product. As such raw force displacement data was smoothed using an 11 point Savitzky-Golay smoothing technique in an attempt to minimise digitisation noise and maximise time resolution and the 2^{nd} derivative was taken. The 2^{nd} derivative of a force displacement curve will show the rate of energy release as the microstructure fails. They determined that the 2^{nd} derivative and the acoustic data are correlated except for a lag caused by smoothing of the data. Whilst for crisp foods the relationship between the force curves and acoustic data can be observed without further analysis, for softer foods it is recommended that the 2^{nd} derivative be observed as force drops may not occur in a short enough space of time. Finally they used a sensory panel to

observe perception of crispness from highly crisp (1) to least crisp (5). They were then asked to bite into each biscuit and the sound was recorded using a microphone.

(Varela et al., 2006) quantified crispness by using 'passive acoustic and mechanical measures of sensory crispness' on roasted almonds. To achieve this they utilised a Stable Microsystems TA-XT texture analyser with P/40 cylinder for compression tests. Attached to this was an acoustic envelope detector and the probe speed was set at 1 mm/s. This speed was selected based on preliminary tests where effective mechanical and acoustic measurements could be made. The presence of acoustic bursts/groupings around crack failure events on the force displacement curves was found. By using 2nd derivatives they were able to correlate the acoustic profile and the force plots with each other. In terms of correlation with the sensory data (Varela et al., 2006) also took the logarithm of the negative values of the 2nd derivative. They stated their reasons for this as being;

1) In terms of sensory perception humans respond to stimulus logarithmically (Weber-Fechner law)
2) The 2nd derivative is a measure of the rate of change in elastic energy as the sample is put under stress. Positive values are associated with energy storage and negative values with energy release.

As energy release is what gives rise to acoustics signals, it is of more interest to observe negative values than positive values. Due to the large amount of data generated Principal Component Analysis (PCA) was also performed. PCA is a form of multidimensional scaling whereby variables are linearly transformed in an orthogonal nature to reduce the number of overall variables which can then be plotted. A principal component is a combination of the original starting variables with the number of principal components produced equal to the number of starting variables. As each principal component is perpendicular to the previous principal component they can never be correlated with other principal components. The number of principal components considered varies amongst sample sets with either a scree plot used to determine the elbow plot or by selecting principal components based on a threshold of 75-100% of the data variances being explained. PCA is a useful tool for dealing with large amounts of data and to show variance between samples. It can also be used to determine correlations between variables which may not readily be expected to influence one another.

1.2.5 Methods for Measuring Product Crispness

Type of Test	Equipment Used	Factors Measured	Product Tested	References
Mechanical	Texture Analyser, Three Point Bend Test	Force displacement curves, 2nd derivatives	Biscuits	(Chen et al., 2005)
	Texture Analyser P/40 cylinder	Force Displacement Curve, Linear distance, PCA, 2nd derivative	Almonds	(Varela et al., 2006)
	Texture Analyser, Volodkevich Jaw	Force displacement curve, maximum force, number of positive peaks, number of negative peaks, area of the force displacement curve	Potato fries , Apples	(Alvarez et al., 2000, Varela et al., 2007)
Air conducted sounds	Acoustic envelope detector, Texture Analyser and Probe	Number of acoustic events	Biscuits, Almonds, Bread	(Chen et al., 2005, Varela et al., 2006, Marzec et al., 2007)
	Panel chewing foods, Shure Pe54 series 2 microphone, Bruel and Kjael FFT signal analyser	Frequency	Potato chips, tortilla chips	(Lee et al., 1988)

	Oscilloscope, sensory panel, Bruel and Kjael microphone and Scotch Branch 227 tape	Mean Height of Peaks	Toast, biscuits, almonds, shredded wheat, crisps, flatbread, water chestnuts, radish, carrots, parsnips	(Edmister and Vickers, 1985)
	Oscilloscope, sensory panel, Bruel and Kjael microphone and Scotch Branch 227 tape	Log of acoustic events x mean height of peaks	As above	(Edmister and Vickers, 1985)
	Instron Universal Testing Machine, two parallel plates	Fast Fourier Transform, stress-strain graphs, fractal analysis	Corn-rice extrudate, corn meal extrudate at different relative humidities	(Barrett et al., 1992)
Sensory	5 point scale (most crisp to least crisp)	Acoustic recordings	Biscuits	(Chen et al., 2005)
Bone Conducted Acoustics	Earphones, 0.0005 inch stainless steel needle mounted on a phonograph cartridge to pick up vibrations	Noise intensity, amplitude, frequency	Vanilla wafers at two different moisture contents	(Kapur, 1971)

Table 1-1 Overview of Methods Used to Measure Product Crispness

1.3 The Potato

1.3.1 Potato Structure

The potato crop are tubers formed from swollen stolons which are attached to the stems of potato plants (Pringle et al., 2009). Most potato varieties have stems which will develop underground stems called stolons of which there are three types;

1) Main stolons arising from a main stem
2) Lateral stolons present at the axils between the main stem and the main stolon
3) Branch stolons presenting as branches coming from the main stolons

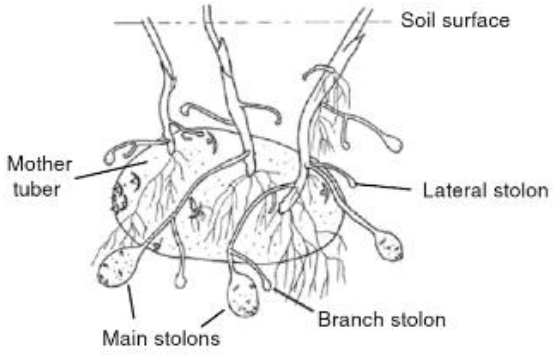


Figure 1-2 Types of Stolon (Pringle et al., 2009)

Potatoes act as storage organs storing starch which the plant is able to break down to use as a sugar source. Stolon formation occurs 14-30 days after the plant becomes visible above the surface of the soil.

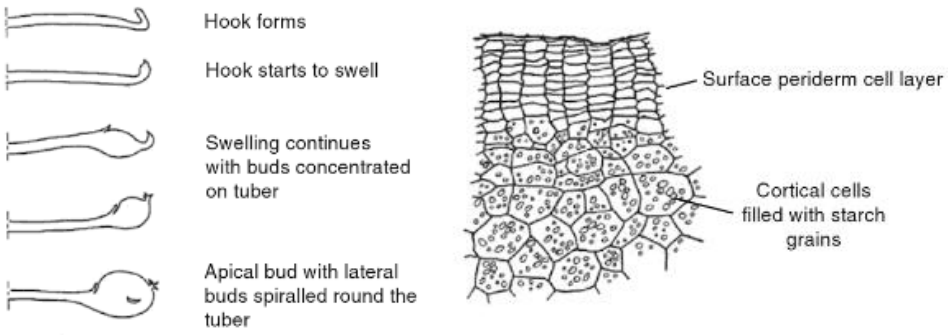


Figure 1-3 Development of Potato Tuber (Pringle et al., 2009)

After stolons have formed the stolon tips begin to swell and tuber development begins. The tuber develops as shown in Figure 1-3 towards the right of the Figure. New cells are created via cell division with starch being deposited after being converted from translocated sugars. The tuber periderm of the skin is then formed via 'the laying down of stacked periderm cells with the deposition of suberin within and under these cells to form a protective barrier against disease and water loss.' (Pringle et al., 2009). Suberin is hydrophobic which could impact moisture migration within the potato. Dry matter accumulation and tuber expansion occurs over the potato season. However, if the potato goes into stress through factors such as colder temperatures this process can be reversed with starch breaking down into sugar once again. The resultant potato tuber will have a scar at one end where it was attached to the stolon of the potato plant with a bud/rose present at the other end.

According to (Pringle et al., 2009) potato planting occurs earliest in January/February in the south west and at latest in May/June in Ireland and Scotland.

(Arthur, 1888) defined the structure of the potato as early as 1888. On slicing a potato lengthwise and staining it with iodine he was able to observe the presence of channels with the rest of the structure being dominated by starch.

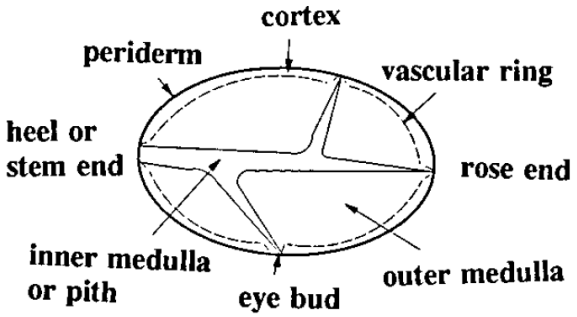


Figure 1-4 Cross Section of the Potato (Arthur, 1888)

(Olsson, 1989) describes the cross section of a potato tuber with the channels being identified as the inner medulla and pith. (Reeve et al., 1969a) agrees with this representation. (Ahmed et al., 2009) states that the potato tuber contains 13-37% dry matter with starch being the main component of the dry matter. They also state that potato starch contains 20-23% amylose and 77%-80% amylopectin.

Secondary plant metabolites also exist within the potato structure. (Deshpande et al., 1984) discusses the presence of polyphenolic compounds in potato varieties where their oxidation function is used for protection against invading pathogens. Chlorogenic acid constitutes 90% of the polyphenolic compounds present in the potato structure (Friedman, 1997). However, (Reeve et al., 1969b) state that 50% of the polyphenols present are contained within the cortex and peel. As the current manufacturer product uses peeled

potatoes the impact of polyphenols will be reduced. The concentration of polyphenols decrease as a function of the distance from the outer peel towards the centre of the potato. This is of interest due to the structure of chlorogenic acid. Chlorogenic acid contains hydroxyl groups (OH) which are able to form hydrogen bonds with water molecules thus limiting their ability to interact with the microwave field. Whilst 50% of the polyphenols are removed there is still chlorogenic acid present that could impact the ability of water within the potato from interacting with the electromagnetic field and thus affect product heating.

On private communication with (Orfila, 2015) the importance of the cell walls of potatoes was also considered. (Orfila, 2015) observed that cell walls are 1 to 2 μm thick and that water is the main component. It behaves like a strong gel composed mainly of a hydrated pectin matrix. The cell wall is permeable to water and objects that are less than 40 kDa have the ability to diffuse through the cell wall. Water was also determined to move between cells as opposed to through cells. This is because the plasma membrane is impermeable to water due to the presence of lipids and so water has to travel via specific channels. (Orfila, 2015) also discussed other components of cell walls such as aribinose and galactose which are water soluble and bind to water thus strengthening the cell wall. Acetyl groups make pectin more hydrophobic ensuring it binds to cellulose and suppresses gelation. In the potato, pectin breaks down after reaching temperatures of 68^{o}C to 70^{o}C and after this occurs water is able to reach the starch present in the potato cells.

1.3.3 How processing affects potato based products

1.3.3.1 Harvest Time

The first consideration is whether to select early, middle or end of harvest potato varieties. (Pringle et al., 2009) states that late harvest crops tend to have more disease than early harvested crops. However, he also notes that early harvested crops produce more heat during storage than late crops and, therefore, need adequate ventilation to prevent subsurface ventilation. Harvest selection of potato varieties could be vitally important for the development of crisp coatings as, if not stored correctly, early harvested potatoes could impact the amount of water present in the system.

1.3.3.2 Blanching

A method widely used in the food industry during processing of potato based products is blanching. Blanching involves submerging the product in hot water which sometimes contains other components before fast cooling after a few minutes to prevent further cooking of the sample. Blanching has a multipurpose in that it; increases the water content of potato cells by 10% due to the formation of holes in the plasma membrane, removes air from potato cell tissue, increases the leaching of built up sugars by 2% to prevent a

detrimental level of Maillard browning on frying, aids gelatinisation of starch due to increased water content and finally inactivates enzymes in plant tissue, most notably polyphenol oxidase known for its colour changing properties. However, according to (Orfila, 2015) not all enzymes become deactivated as at temperatures above 50 ºC the enzyme pectinmethylesterase (PME) becomes active. This can cause issues for blanching as it exposes acidic groups (methyl groups from methyl esters) that can bind to calcium and form strong gels thus toughening the texture. However, PME becomes deactivated again at temperatures exceeding 70 ºC.

1.3.3.3 Frying

The product under investigation incorporates a frying step as depicted in Figure 1-5. (Hubbard and Farkas, 2000) refer to this as immersion frying which is defined as 'the immersion of a food product in edible oil or fat heated above the boiling point of water.' (Mallikarjunan et al., 2010) discusses the phenomena of the frying process. During deep fat frying there is simultaneous heat, moisture and fat transfer between the food stuff and the oil. Frying temperatures are within the region of 175- 205 ºC resulting in moisture loss and evaporation at the surface of the product and the formation of a crust on the foodstuff outer layer, According to (McCain, 2013) when coatings are present, low temperature frying results in water migrating through the batter unimpeded whilst high temperature frying results in the batter being sealed thus resisting water loss. Because the batter is sealed water finds the weakest point and forces through resulting in blow off, fractures in the coating and crumbs/debris left within the oil. (Mallikarjunan et al., 2010) observed hardening of the surface locks moisture inside the product, resulting in a relatively moist interior and dry exterior. Therefore coatings can be labelled as a 'barrier to mass transfer during frying.' (Mallikarjunan et al., 2010) highlighted that during frying and moisture loss there is an increase in fat uptake from the oil. (Ziaiifar et al., 2008, Ziaiifar et al., 2009, Carrascal, 2015) agree with this description of the frying process.

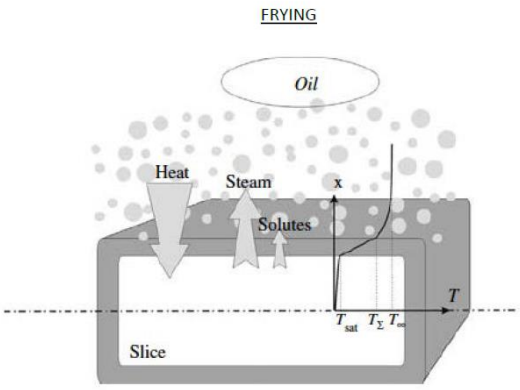


Figure 1-5 The Frying Process (Carrascal, 2015)

(Kalogianni and Smith, 2013) investigated the effects of frying on French fry properties. They found that the most significant changes to the product are during the first 1- 2 minutes of frying. They also determined that the ratio of crust:core continued to increase after the first frying period although this did not translate into an increased crust thickness due to crust shrinkage. The inner core of the French fry reached 100 ^{o}C but did not exceed it indicating that most of the dehydration occurs at the surface layer. Finally no difference was observed when using palm oil to olive oil and oil uptake was independent of water removal and thickness of the outer crust.

1.3.3.4 Freezing

According to (McCain, 2013) freezing has the largest effect on the end product properties than any other processing stage including frying due to its transformative nature. They state that fast freezing results in firmer textures. (Orfila, 2015) states that freezing supresses starch retrogradation but that osmotic dehydration on storage of the product in the freezer does impact the product quality. Issues with product quality of frozen product also relate to freeze/thawing cycles on product transport due to the development of ice crystals.

1.4 Dielectrics and electromagnetism in relation to microwave heating

Microwave heating occurs due to the presence of electromagnetic waves which are created via interactions between electric and magnetic fields. A brief understanding of the two shall be given before understanding microwave heating in more detail.

1.4.1 Electric Field

The electric field is caused by the presence of electric charges with neutrons having no charge, protons having a positive charge and electrons bearing a negative charge. Like charges repel and opposite charges attract each other. Each electric charge has a field around it and its behaviour depends on the charge. Positive charges cause the electric field to direct away from the positive charge origin and a negative charge directs the electric field inwards (Maxwell'sEquations, 2012). The magnitude of an electric field decreases as a function of distance. In the presence of multiple charges the electric field is said to be equal to the sum of the electric field from each individual charge. It can be measured in Newtons/Coulomb or Volts/Meter. The permittivity is a measure of how well atoms and molecules within an electric field are able to interact with the electric field (Metaxas and Meredith, 2008). For an electric charge to be labelled a current the charge has to move. There are two types of current; AC and DC. AC is labelled as alternating current and is described as the movement of electrical charge through a medium that changes direction periodically. DC is labelled as direct current and is described as the movement of electrical charge in one constant

direction. (Metaxas and Meredith, 2008) discuss the electric field in terms of the frequency. They state that the higher the frequency the smaller an electric field required to cause a specific dissipation rate in terms of dielectric heating.

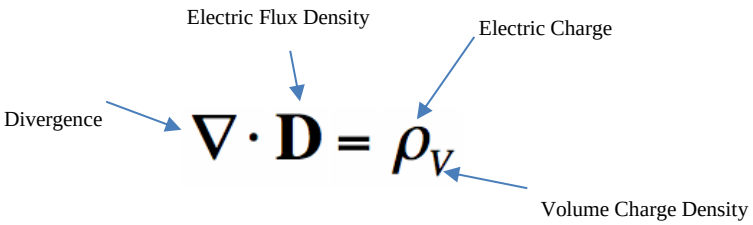
1.4.2 Magnetic Field

The electric current causes the existence of the magnetic field. Whilst the electric field either directs itself towards a negative charge or away from a positive charge, the magnetic field moves perpendicular to the electric field in a circular motion around the electric current. The magnetic field is directly proportional to the electric current. The units for the magnetic field are Amps/Meter.

1.4.3 Maxwell's Equations

The laws of electromagnetism describe how both electric fields and magnetic fields behave in nature, that they are co-dependent on each other when a charge is moving and that according to (Feynman, 2014) the two fields are 'not interconnected' and are in fact 'distinct' from each other when charges and currents are static. The four equations can also be split with Gauss Law and Faraday's Law focussing on the electric field and Gauss Law for magnetism and the Ampere Maxwell Law observing the magnetic field.

1.4.3.1 Gauss Law

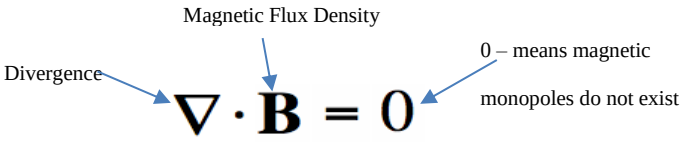


Equation 1-5 Gauss Law (Maxwell'sEquations, 2012)

The first law, Gauss Law (Equation 1-5), states that like charges repel one another whilst charges of opposing signs attract each other. It also states that the amount of charge within a given volume is equal to the electric flux (**D**) leaving the surface of a volume (**S**). (Feynman, 2014) observes that 'electric charge gives rise to a diverging electric field' and as divergence is a measure of how a vector flows outwards from a surface (in this case the chip surface) surrounding a specific point in space and time, the electric flux (**D**) can be directly compared to the electric field (**E**) if the permittivity of the medium under an electric field is also considered. The final observation of Gauss Law is that electric charge acts as either a source of electric fields or as a 'sink' and that if divergence is positive, more fields are

produced around the selected point than are taken in by the surface. If the divergence is negative the field becomes diminished and propagation cannot occur.

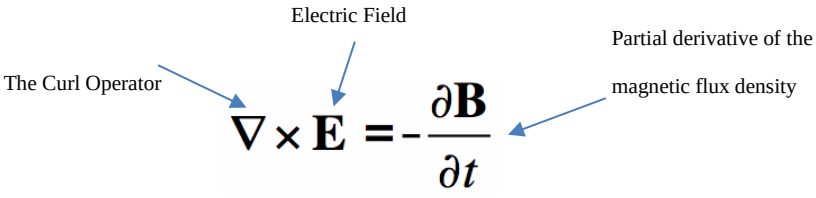
1.4.3.2 Gauss Law for magnetism



Equation 1-6 Gauss Law for Magnetism (Maxwell'sEquations, 2012)

Like the electric field and electric flux density can be related in Gauss' first law, the magnetic flux density and magnetic field can be related in Gauss' law for magnetism (Equation 1-6). They can be related via the permeability. This law states that the divergence of the magnetic flux density/magnetic field is equal to 0. In Gauss first law, the divergence of the electric flux density/electric field is equal to the electric charge density. The reason the magnetic flux density is 0 is because as of 2018 evidence of magnetic monopoles (a magnet with only one pole) has not been found. Therefore, Gauss law of magnetism indicates that magnetic fields enter and leave a volume equally. They are also able to flow in a circular manner as fields that flow in a circular manner have no divergence. They are not able to act as a sink or an initial source of fields as this would require the existence of magnetically charged particles. Thus it is said that magnetic and electric fields are only co-dependent if a charge is moving and when the charge is static the fields remain separate from each other.

1.4.3.3 Faraday's Law

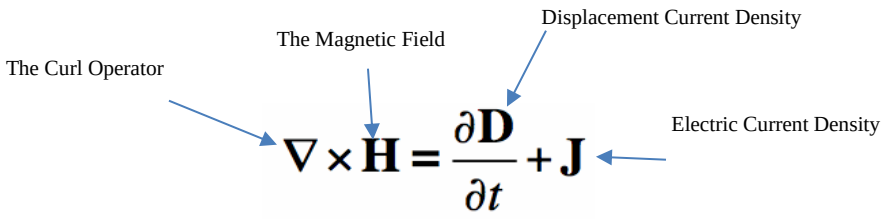


Equation 1-7 Faraday's Law (Maxwell'sEquations, 2012)

Faraday determined that electric currents give rise to magnetic fields and that a changing magnetic field around a loop causes an electric current to be produced. He also determined that magnetic fields which change with time causes the production of an electric field which rotates around it. Finally he determined that a rotating electric field results in the production of a magnetic field which alters over time. Faraday was able to identify that electric fields can be produced in two ways; from an electric current which is flowing or stationary and

from a magnetic field which is changing over time. This is expressed mathematically in Equation 1-7.

1.4.3.4 Ampere- Maxwell Law



Equation 1-8 Ampere-Maxwell Law (Maxwell'sEquations, 2012)

Ampere determined that a flowing electric current causes a magnetic field to be produced which in turn rotates around that current. Maxwell determined a second way in which a circulating magnetic field can be produced. By inserting the displacement current density portion of the equation he was able to state that an electric field which changes over time also gives rise to a magnetic field which encircles the electric field. This is given mathematically in Equation 1-8.

1.4.4 The microwave and the electromagnetic wave

According to (Fay, 2007) microwave frequencies are from 300MHz to 1GHz at the lower end to upwards of 100GHz at the upper limit.

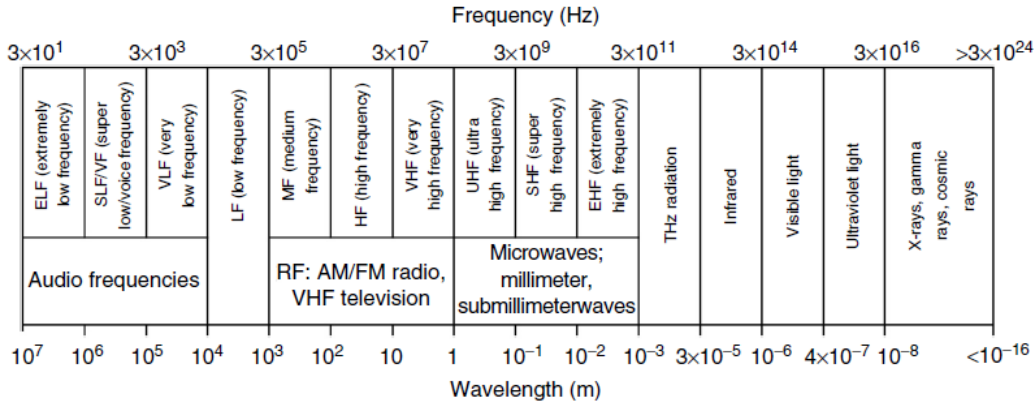


Figure 1-6 The Electromagnetic Spectrum (Fay, 2007)

Figure 1-6 encompasses the entire microwave frequency 'from audio frequencies through cosmic rays.' (Fay, 2007). The wavelength and frequency are inversely proportional ensuring that radio waves have the lowest frequency and largest wavelengths with x-rays/gamma rays having the highest frequency but lowest wavelength. (Meredith and Metaxas, 1979) agree with this although state an absolute microwave limit of between 300 MHz and 300 GHz with the wavelength at these frequencies between 1 cm and 1 m.

(Maxwell, 1954) observed that at these frequencies electromagnetic waves are able to radiate through a perfect vacuum and requires no medium in order to transfer energy from one object to another. As such microwave heating is a form of radiation. (Maxwell, 1954) observed that electromagnetic waves have two components;

1) An electric field (**E**)
2) A magnetic field (**B**)

When a charge in a medium alters its position in space, it produces a corresponding field which also alters its position in space. As a result a wave is produced, otherwise known as the electromagnetic wave. Electromagnetic waves are characterised by the wavelength and the frequency and so can be related by Equation 1-9.

$$c = f\lambda$$

Equation 1-9 Electromagnetic Wave Speed

where c is the speed of light in the medium (m/s), f is the frequency of the wave (Hz) and λ is the wavelength of the wave (m). (Metaxas and Meredith, 2008) state that 'electromagnetic energy propagates through free unbounded space at 3 x 10^8 metres/second irrespective of frequency.' This means that the electromagnetic wave will always travel at the speed of light.

The domestic microwave oven operates at the frequency 2450 MHz (2.45GHz) with a wavelength of 12.24 cm. The wavelength presents issues with heating of its own. (Meredith, 1998) suggests that if a medium is dielectric, the wave velocity will decrease on entering the material and so will be slower than the speed of light and may be determined by dielectric factors described in section 1.4.5. This means that the wavelength will shorten even though the frequency is still 2.45 GHz. This has implications for the uniform heating of foodstuffs. (Hammack, 2012) suggests the wavelength is another reason for non-uniform heating apart from non-homogeneity of the foodstuff. In a typical microwave of 38.1 cm in size three crests and troughs can exist. The wave is at its highest energy state during its peak and troughs (anti-nodes) whilst returning to its lowest energy state at the node. Due to this non-uniform distribution, many manufacturers incorporate turn-tables to ensure energy is spread evenly across the product being heated. (Metaxas and Meredith, 2008) discuss how this electromagnetic wave is able to heat foodstuffs. Microwave energy penetrates into a medium and produces a volumetrically distributed heat source. Further complicating this area is the issue of penetration depth. The penetration depth refers to the distance when the

electromagnetic field penetrates into a food and diminishes to 1/e intensity (Bradshaw et al., 1998).

$$D_p = \frac{1}{2\alpha}$$

Equation 1-10 Penetration Depth

Equation 1-10 describes the penetration depth with α denoting the attenuation/reduction of the electromagnetic wave power/interims of power. This is because when an electromagnetic wave enters the medium some of the energy is absorbed and converted into heat. The penetration depth translates to an electromagnetic wave with 37% of the intensity of the wave observed at the surface of the foodstuff. (Chaplin, 2014) states that the penetration depth in a transparent liquid is infinite but that in a reflective material is 0 and this explains how materials such as metals are able to reflect electromagnetic waves. (Chaplin, 2014) also states that at 2.45 GHz, most energy is absorbed by water. (Metaxas and Meredith, 2008) state that the penetration depth increases inversely with frequency. This presents an issue as at the 2.45 GHz frequency, the penetration depths are often smaller than the size of the material being heated and as such can result in non-uniform heating of foodstuffs.

The time dependent electromagnetic field can heat foodstuffs in one of two ways. The first is caused by dipole rotation of polar materials in response to the changing electric field. For water this occurs at a rate of 2.45 billion times a second. This fact, along with the 'inability of this polarisation to follow extremely rapid reversals of the electric field' allows friction to be generated thus causing heating of the foodstuff. This rotation is caused by the change in polarity of the electromagnetic field within the microwave cavity as a function of time. Electromagnetic waves are also able to interact with dissociated ions in the form of ionic conduction. Charged ionic particles oscillate under the influence of the electric force of microwaves which create the electric current. The electric current faces internal resistance due to collisions of charged species with neighbouring molecules/atoms. As a result the food stuff will heat due to ionic conduction. (Metaxas, 1996) The difference between ionic conduction and dipolar polarisation has also been noted by (Gabriel et al., 1998). They state that dipolar polarisation occurs from 'the finite displacement of charges or rotation of dipoles in an electric field.' Ionic conduction is referred to as 'translational motion of the charges when an electric field is applied.'

Evidence has also been found that another form of microwave heating exists, interfacial polarisation which is a combination of ionic conduction and dipolar polarisation (Anwar et al., 2015). At different points through the wave form the dipoles are reorienting themselves

to return to their original state (Pitchai, 2011). In their original state there is no lag between the dipole and the electromagnetic field, no heating occurs.

1.4.5 Dielectric Heating

As dielectric heating of foods is a relatively new concept, understanding how different ingredients interact in the microwave field will be paramount in terms of future product development and optimisation of the microwave process. Different terms are often used to discuss dielectric heating.

1.4.5.1 Permittivity and Permeability

The absolute permittivity refers to how the electromagnetic field affects and is subsequently affected by the addition of a component or foodstuff in response to an applied electric field. (Gabriel et al., 1998) refers to the absolute permittivity of a material, ε, as a property which 'describes the charge storing ability of the medium' irrespective of sample dimension whilst the relative permittivity (dielectric constant) is the permittivity of the material relative to that of free space/a vacuum. In other words it is a measure of how able charged molecules within a medium are able to resist an external electric field before aligning with said electric field. It is also related to a material's ability to transmit/permit an electric field. (Chaplin, 2014) describes the complex permittivity as the ability of a material to be polarised by an external electric field. Permeability is related to the magnetic field in that it is a measure of the orientation of bound magnetic particles and thus explains how easily a magnetic field can travel through a medium.

1.4.5.2 Dielectric Constant and Dielectric Loss Factor

$$\frac{\varepsilon(\omega)}{\varepsilon_0} = \varepsilon_{r(\omega)} = \varepsilon_{r(\omega)} * = \ \varepsilon_r'(\omega) - \ \varepsilon_r''(\omega)$$

Equation 1-11 Dielectric Parameter Relationship

Equation 1-11 observes the dielectric parameter relationship whereby the absolute permittivity (ε) relative to the permittivity of free space (ε_0=*8.854X10*$^{-12}$ [*F/m*] – Farads) is equivalent to the relative permittivity (ε_r). The relative permittivity is further separated into a real part and an imaginary part and is typically referred to as complex permittivity (ε_{r*}). The real part is denoted as the dielectric constant/factor (ε'_r) and observes how much energy is stored within the material, whilst the imaginary part is the dielectric loss factor/loss factor (ε''_r). This observes how much energy is lost or dissipated from the sample in the form of heat. In most cases $_r$ is not included as it is assumed that the data is relative to that of free space/a vacuum. The relative permittivity for lossy materials (Equation 1-12) is denoted as;

$$\varepsilon_r(\omega) = \varepsilon'_r(\omega) - \frac{i\sigma}{\omega\varepsilon_o}$$

Equation 1-12 Relative Permittivity

where ω indicates the angular frequency (rate of change of a sinusoid wave) σ indicates the dielectric conductivity which considers all the dissipative effects of the material and can refer to energy losses associated with the dispersion of ε' (dielectric constant).

1.4.5.3 Maxwell displacement current theory, Tan δ, the Q Factor and Relaxation Time

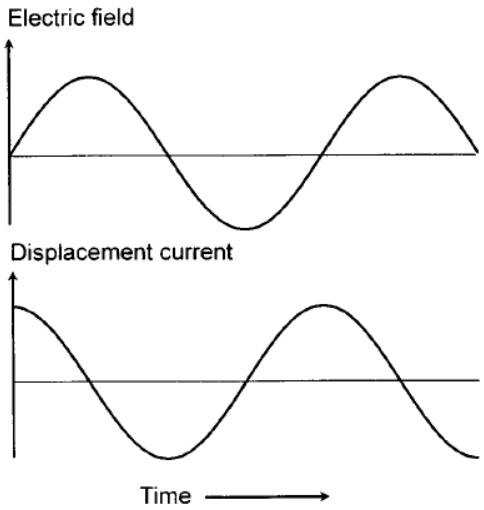


Figure 1-7 Sinusoidal Electric Field on Application to an Ideal Dielectric Solution and the Out of Phase Displacement Current Induced (Gabriel et al., 1998)

(Gabriel et al., 1998) discusses the Maxwell displacement current theory (MDC). This is a measure of the lag between reorientation of molecules on application of the electromagnetic wave and is considered as equivalent to an electric current. In an ideal dielectric liquid at lower frequencies there will be no lag between the orientation of molecules and the alternating voltage, therefore, the MDC is 90^o out of phase with the oscillating electric field. This is observed in Figure 1-7. In these ideal cases a dielectric material is able to follow the changing electric field and so no heating occurs. This is depicted in example a) of Figure 1-8.

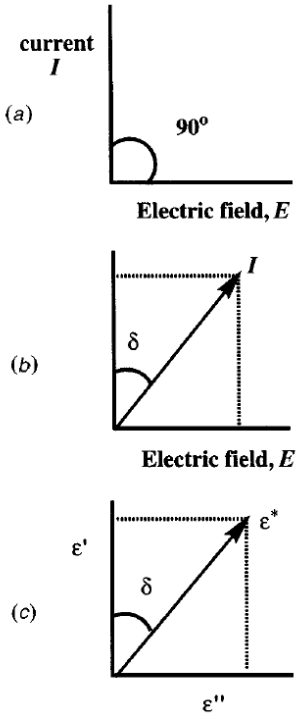


Figure 1-8 Phase diagrams to understand dielectrics (Gabriel et al., 1998)

a) an ideal dielectric where energy is transmitted without loss; (b) phase displacement; (c) relationship between ε′ and ε′′

This is not an issue for dielectric liquids in the microwave frequencies as the frequency is high enough for a lag to exist and this resultant phase displacement/loss angle is called δ and in combination with the current (*I*) and sin function in phase with the voltage, these losses are known as the dielectric loss factor. Example b) of Figure 1-8 shows this relationship. The final example c) observes the relationship between the dielectric constant and the loss. (Gabriel et al., 1998) states that where the loss angle δ differs significantly from the usual 90° out of phase displacement, the material acts as not only a dielectric material but also as a conductor. From observing phase diagram c) it can be seen that $\varepsilon'/\varepsilon''$ (dielectric constant/dielectric loss) is equal to the tan δ. (Peng et al., 2010) state that the tan δ is used to signify the ratio between the amount of energy stored per cycle to the amount of energy lost per cycle. As a result the tan δ is used to 'indicate the efficiency of conversion of microwave energy into thermal energy within the dielectrics' – the amount of energy dissipated in the form of heat. Tan δ increases in proportion with conductivity and inversely with the frequency or real permittivity. Tan δ is also known as the dissipation factor (**D**), loss tangent and the Df. The Q factor is the reciprocal of the tan δ and so can be used as a measure of energy dissipation. The higher the dielectric loss factor or energy dissipation in relation to the amount of energy stored, the lower the Q factor.

A final parameter used to define materials within the microwave environment is the relaxation time. (Gabriel et al., 1998) defines this as the time it takes for polar/ionic molecules to return to a randomised orientation after the external electric field has been removed. At low frequencies dipole rotation can follow the field easily meaning the dielectric constant will be high and the dielectric loss factor will be low. As the frequency increases the dielectric loss factor also increases. There is a frequency at which the frequency is optimal and is described as the frequency at which the dipoles are rotating as quickly as possible ensuring the highest possible dielectric constant and loss is observed. However, if the frequency increases beyond this point the dipolar molecules can no longer follow the electric field and so dipolar heating cannot occur.

1.4.6 Microwave Heating Process

According to (Meredith, 1998) the standard microwave frequency used is 2450 MHz/ 2.45 GHz, principally because this aims to minimise 'interference with communication services' (Hammack, 2012). During the time of its invention, the Federal Communications Commission only allowed frequencies in the electromagnetic range of 2450 MHz and 915 MHz to be tested. It was determined that 915 MHz provides a penetration depth 5 times that of 2450 MHz with a wavelength of 32.8cm produced against the 12.2 cm wavelength produced by 2450 MHz microwaves. 915 MHz microwave ovens produced more desirable cooking results. To achieve effective heating at 915 MHz, a much larger microwave would be required in the region of four feet (Hammack, 2012). For this reason 2450 MHz became the industry standard as it was intended for small scale domestic use.

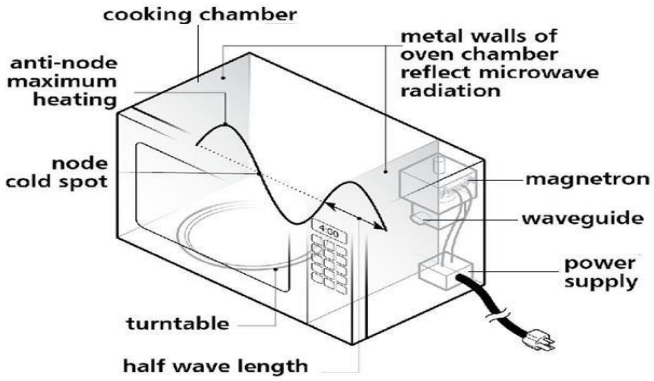


Figure 1-9 Domestic Microwave Oven Mechanics (Hammack, 2012)

Three components are required to heat food; a waveguide, a magnetron and a cavity in which to contain the food and microwaves as shown in figure 1-9. The cavity is usually lined with metal to prevent microwave leakage. (Hammack, 2012) observed the mechanics of the microwave oven. The vacuum tube or magnetron 'produces electromagnetic radiation that heats the food.'

The magnetron is able to generate electromagnetic waves because it contains positive and negative electrodes present in the vacuum tube. This tube is surrounded by two magnets to allow for the creation of a magnetic field. On applying a high voltage across the two electrodes, the electrons move from the cathode towards the anode which is usually copper. The presence of the magnets provide a magnetic field 'perpendicular to the path of the current' (Hammack, 2012). As the electrons approach the anode, the magnets cause them to alter their path and return to the cathode. As a voltage is still being provided across the electrodes the electrons are once again sent to the anode only to be returned to the cathode.

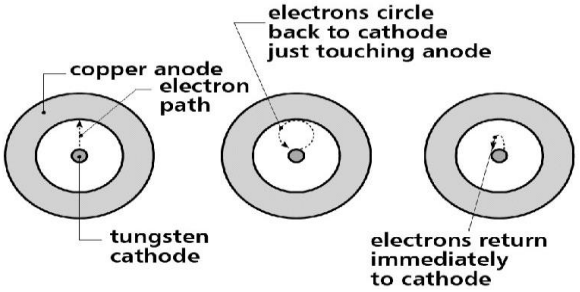


Figure 1-10 Method in which Magnetron Generates Electric Field (Hammack, 2012)

In a magnetron small cavities are created across the anode surface and as the electrons pass over these cavities they resonate. This is because the cavities allow the electrons to store and transfer energy between the electric and magnetic states. Figure 1-10 observes how the magnetron generates an electric field. The wave is directed into the chamber/cavity via a waveguide. The walls of the cavity are coated with metal to reflect radiation back and forth across the space. This causes standing waves to be produced which heat the food stuff as they oscillate.

1.4.6.1 Differences between microwave heating and conventional oven heating

The main difference between microwave heating and conventional oven heating is that microwave heating occurs via electromagnetic radiation (Maxwell, 1954) and conventional oven heating occurs via surface heating with further heating occurring due to thermal conduction and diffusion. Conventional heating is also considered as a process which is heated externally whilst microwave heating generates heating internally. (Gabriel et al., 1998) states that microwave heating can lead to 'higher heating rates than those achieved conventionally.' However, they stipulate that this is only the case where the material being heated has dielectric activity.

1.4.7 Dielectric Materials and Means of Measurement

According to (Gabriel et al., 1998) a dielectric material is one which contains either permanent or induced dipoles which when placed between two electrodes act as a capacitor. This means that charges are able to be stored within the material. As discussed in section

1.4.4, microwave heating (MH) can occur via dipolar polarisation, ionic conduction or a combination of the two. The interaction between the electromagnetic field and the foodstuff within the microwave can be affected by other factors which only adds to the complexity of this field. Some factors affecting the heating of foods include;

- Food Composition
- Meal Components, e.g. coatings
- Packaging Materials
- Food Geometry
- Location in the oven
- Individual microwave oven
- Time of day in which the microwave oven is used
- Age of the microwave oven
- Moisture Content and Ratio of Bound:Unbound Water

1.4.7.1 Dielectric properties of potato based products and their interaction within the microwave environment

(Pace et al., 1968) observed the dielectric properties of raw potatoes and potato chips at 300 MHz (0.3 GHz), 1000 MHz (1 GHz) and 3000 MHz (3 GHz) and at three different moisture contents in the case of the potato chips. All measurements were made at 25ºC. Dielectric measurements were made using the precision slotted line technique (SLT). Whilst SLT is accurate it is extremely labour intensive and require manual calculations to provide useable data. Damage occurs if not handled with care when the probe is moved. Using the SLT they determined that as moisture content decreased the dielectric effect also decreased in the potato chips. They also found that as the frequency increased so did the dielectric constant and loss. The moisture ranges of the samples differed from 1.25% to 15.3% and at higher moisture contents, the dielectric loss factor was higher at the highest frequency 3000 MHz than at 1000 MHz. For the lowest moisture contents e.g. 1.25% the opposite was found to be true. The dielectric loss increased as a function of temperature except where moisture contents were 3% and below where the effect no longer occurred and in effect the opposite occurred. (Pace et al., 1968) theorise this is due to the ratio of lipid:moisture in the product samples and how that ratio alters as the moisture content decreases/increases. Very thin samples of potato (0.050 in) were used to make the dielectric measurements and as such may not be truly representative of the dielectric properties in the whole potato. (Ahmed et al., 2009) looked at the dielectric properties of potato flour -water dispersions and commercial potato purees at the frequency range 500 – 2500 MHz (0.5 – 2.5 GHz) using an open ended coaxial probe technique attached to a network analyser. This was performed as a

function of temperature (20-75°C). The effect of sodium chloride addition was also considered at a steady concentration of 15% on a wet weight basis. They determined that the dielectric constant decreased with increased temperature and frequency and increased with NaCl concentration. The dielectric loss factor was found to increase with frequency and NaCl concentration with temperature having a mixed effect. There was a change in the dielectric constant and loss above 70°C which the authors attribute to starch gelatinisation. The coaxial probe technique is limited due to issues such as air gaps and so the data produced may not be fully representative.

1.4.7.2 Dielectric Properties of Other Foodstuffs in Literature

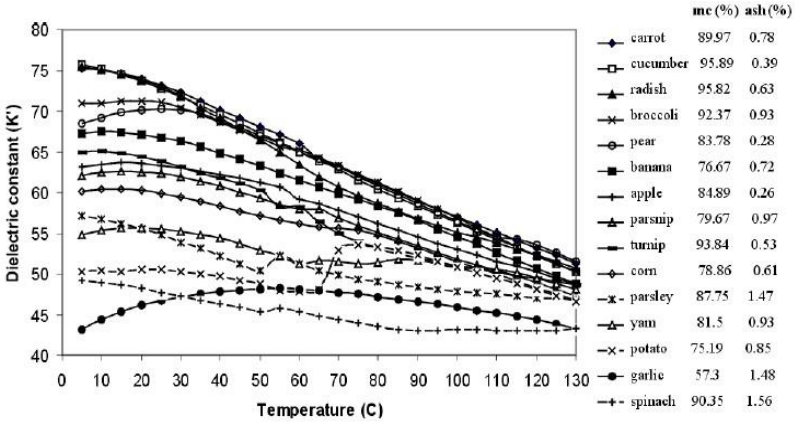


Figure 1-11 Dielectric Constant of 15 Fruit and Vegetables (Sipahioglu and Barringer, 2003)

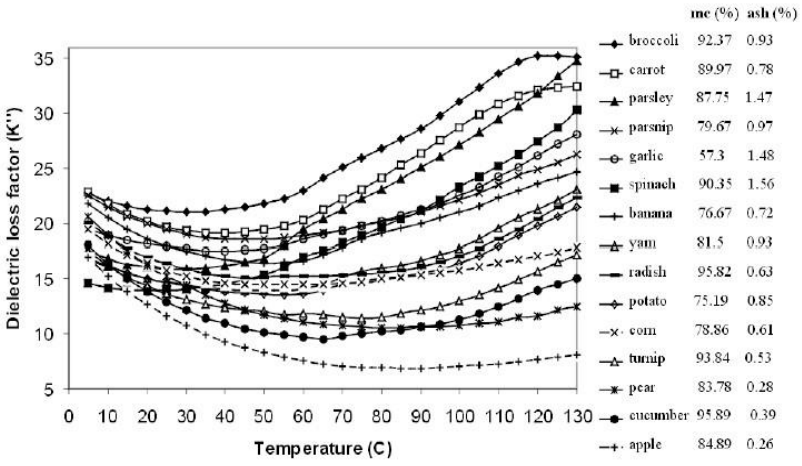


Figure 1-12 Dielectric Loss of 15 Fruit and Vegetables (Sipahioglu and Barringer, 2003)

Figures 1-11 and 1-12 show the dielectric constant and loss of 15 fruit and vegetables. The work performed by (Sipahioglu and Barringer, 2003) suggests that the dielectric constant decreased as temperature increased. This was expected as most of the water in

fruit and vegetables is free. As the moisture content increased so did the dielectric constant. However, it was found that the constant of garlic increased up to 55ºC whereas the other samples tended to decrease as temperature increased. In terms of dielectric loss it was found that the loss was reduced at temperatures below 34ºC. Above this temperature it was found that both fruits and vegetables increased their dielectric loss factor as temperature increased. In simple terms the loss first decreased then increased as the temperature increased. (Sosa-Morales et al., 2010) has also provided dielectric data for different foods such as walnuts and almonds.

1.4.7.3 Methods used in this thesis and the literature for dielectric measurement

Two methods have been used in this thesis to measure dielectric activity and these are the Split Post Dielectric Resonator and a novel cavity built by Sylatech Ltd. Both are connected to a network analyser.

Network Analyser

According to (AgilentTechnologies, 2006) a network analyser consists of a signal source, receiver and display. It is used to measure swept high frequency stimulus response measurements from 300 kHz to 110 GHz. The network analyser emits a signal at a single frequency which is picked up by a receiver that is tuned to that single frequency. The receiver is able to detect the reflected signal from the food material within the receiver and records the magnitude and phase data at that frequency. The network analyser repeats this process at different frequencies to measure reflectance and transmission measurements as a function of the frequency. A main limitation with this test method is that it is difficult and costly to characterise products across the whole microwave range as products that perform well at low frequencies may not perform well at higher frequencies and vice versa. As such a calibration is performed across the whole microwave range to eliminate systematic error caused by the machinery. This is problematic as it ensures that random errors due to noise or the environment (temperature, humidity etc.) cannot be removed and so care must be taken by the investigator to ensure that the machinery is set up correctly every time. A network analyser measures the Q Factor and insertion loss as a function of frequency. The insertion loss is measured using equation 1-13;

$$Insertion\ Loss\ (dB) = 10 * Log(\frac{Po}{Pi})$$

Equation 1-13 Insertion Loss

with P_o denoting the power out and P_i denoting the power in. There are 3 main causes of a change in the insertion loss and these are reflected losses, dielectric losses and copper losses.

Split Post Dielectric Resonator

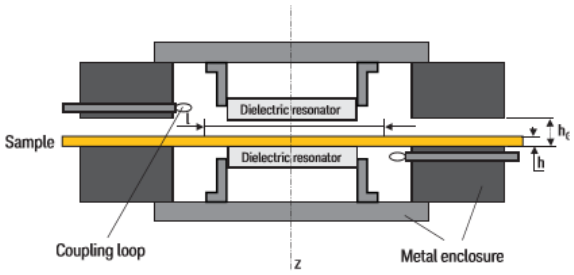


Figure 1-13 Cross Section of Split Post Dielectric Resonator (AgilentTechnologies, 2015)

Figure 1-13 shows a cross section of a Split Post Dielectric Resonator. According to (AgilentTechnologies, 2015) the Split Post Dielectric Resonator (SPDR) consists of a pair of thin dielectric resonators connected to a coil on either side of the resonator. This allows for the creation of an electromagnetic field between the air gap of the two resonators as well as within the cavity region ensuring that dielectric readings can be generated for materials placed within the metal cavity. The SPDR is connected to a vector network analyser of type PNA Network Analyser with installed 85071E software. The electric field produced remains continuous meaning that air gaps between the sample and the top of the resonator do not impact the dielectric measurement. The SPDR is operated at the resonant frequency of 2.69 GHz, ensuring that for this cavity, 2.69 GHz is the frequency at which charged particles in this cavity are most likely to vibrate.

For samples to be measured accurately only samples with a maximum thickness of 3.5mm and minimum size of 70 x 70 mm in length can be inserted. This limits the samples that can be tested using this piece of equipment.

A main limitation of this method is that the SPDR is set at a frequency of 2.69 GHz as opposed to the microwave frequency of 2.45 GHz and, as such, may give slightly different readings to the dielectric readings observed at 2.45 GHz. This is not too much of an issue due to the nature of dielectric materials. According to (AgilentTechnologies, 2006) both dipolar polarisation and ionic conduction methods of dielectric heating have characteristic cut off frequencies and that before these frequencies the dielectric measurements should remain fairly similar as lossy materials are non-dispersive. Thus if an effect is observed at 2.69 GHz it would also occur at the microwave frequency of 2.45 GHz. (AgilentTechnologies, 2006) state that the cut off frequency for water is 22 GHz and as water is a driving factor for dielectric activity in foodstuffs the dielectric activity would not be expected to be too dissimilar between the two frequencies. Smaller events may be lost at

2.69 GHz meaning that the dielectric activity recorded at 2.69 GHz would potentially be even stronger at 2.45 GHz.

Agilent Technologies have provided a computer program into which the Q factor, frequency and thickness of sample is inserted when the cavity is empty and when the cavity is filled with a sample. By doing this the dielectric constant (real part of permittivity), dielectric loss and the tan δ can be calculated.

Novel Cavity method

Currently commercial resonant cavities do not provide resonant cavities large enough to measure large product samples. On consultation with McCain Foods, Sylatech Ltd. developed a resonant cavity operating at 2.45 GHz with the dimensions of a domestic microwave oven. The inner cavity measures 36 cm in diameter, in keeping with industrial microwave ovens which measure 36cm ± 1cm dependent on microwave manufacturer and whether a turn table is present. Figure 1-14 shows the novel cavity attached to a PNA network analyser.

The cavity is connected to a vector network analyser of type PNA Network Analyser with installed 85071E software with its resonant frequency being 2.45 GHz.

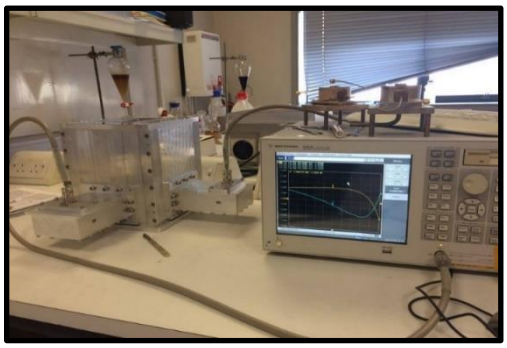


Figure 1-14 Novel Cavity Attached to a PNA Network Analyser Operating at 2.45 GHz Frequency

The main advantage of using this method as opposed to previous dielectric methods is that the whole 100 g sample set can be measured at the same time. The product is non-homogenous and so by measuring the whole sample set at a time this reduces errors due to accidental sampling of only certain types of chip e.g. chips produced from the pith of a potato.

A further advantage is that this method can measure products as a function of temperature. For some experiments the cavity is placed in a Genlab OV general purpose oven made from stainless steel and containing a built in fan. It has internal dimensions of (H x W x D) 45 x 49 x 46 cm and external dimensions of 58 x 85 x 48 cm. The oven can be used to heat frozen products and the change in dielectrics detected by the network analyser meaning that

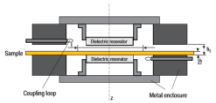
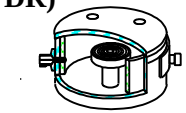
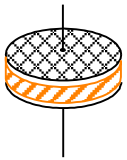
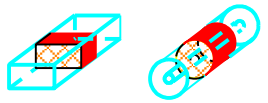
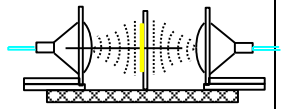
changes across the whole heating process can be detected. However, there is a limitation in that the product is heated conventionally rather than using a microwave. This is because if microwaves were present, they would interfere with the dielectric measurements of the product being measured.

On making dielectric measurements, the Q Factor, insertion loss and frequency were recorded both empty and with sample present as a function of time.

An overview of methods used to measure the dielectric activity of materials is found in table 1-2.

Table 1-2 A Summary of Methods measuring the dielectric activity of materials

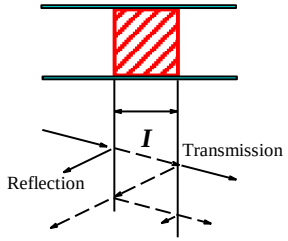
(Begley, 2015, AgilentTechnologies, 2006, KeysightTechnologies, 2017)

	Split Post Dielectric Resonator (SPDR) 	**Single Post Dielectric Resonator (SiPDR)** 	**Parallel Plate** 	**Open ended Co Axial Probe**	**Transmission Line (waveguide, coaxial)** 	**Transmission Free Space** 
Frequency	Single	Single	Low (up to 30 MHz)	Broad band	Broad band (if using coaxial fixtures) Banded (if using waveguide)	Broad band (if using coaxial) Banded (if using waveguide)
Dielectric measurement observed	ε_r (Permittivity) μ_r (Permeability)	Surface Resistance (R)	ε_r	ε_r	ε_r, μ_r	ε_r, μ_r

High Temperature Range				✓		✓
Low loss	✓	✓				
High loss		✓		✓		
Restriction in Geometry	✓	✓	✓	✓	✓	✓
Materials Suitability	Solid	Solid	Solid	Solid, Liquid, Powder (best for liquids and semi solids)	Solid, Liquid	Solid, Liquid
Sample Size/ Geometry	Small flat disk/sheet	Thin Layer	Very small thin sheet samples	Large enough to appear infinite	Smooth flat faces	Thin, flat parallel faced materials
Accuracy	High (Superior to transmission methods)	High	High	Low to moderate	Moderate	Moderate
Sources of Error	Sample Thickness,	Sample needs to be flat. Accuracy is	Measurement errors likely when	Homogenous materials	Difficult to manufacture, Samples needs to be;	System scales with frequency but with

	Random errors cannot be eliminated so care must be taken, Issues with measuring conductive materials. Materials may be too conductive for measurements to be made	stated as ± 2%. Does not give permittivity and permeability and extra work required to calculate these parameters making it less user friendly	measuring low dielectric loss materials The permittivity will alter over frequency, temperature etc. and measurement errors are more pronounced at higher frequencies Sample needs to be flat and have no air gaps	required, cable stability, air gaps, sample thickness needs to be high enough to appear infinite to probe, not suitable for magnetic materials, , Limited ε_r accuracy and tan δ low loss resolution	1) Smooth 2) Flat 3) Homogenous 4) Have no air gaps 5) Fill entire cross section System scales with frequency so sample size determines frequency limits. At frequencies <5GHz waveguides are large and so a large sample filling the cross section is needed. Sample length is an issue <1GHz and >75GHz.	free space samples are required to be larger so at low frequencies can be difficult to generate samples large enough. Higher frequencies are no longer an issue as smaller sample sizes needed. Sample must be far enough away from the antennae to generate accurate results. ($2d^2/I$ with d= largest dimension of the antenna) Data can only be calculated for

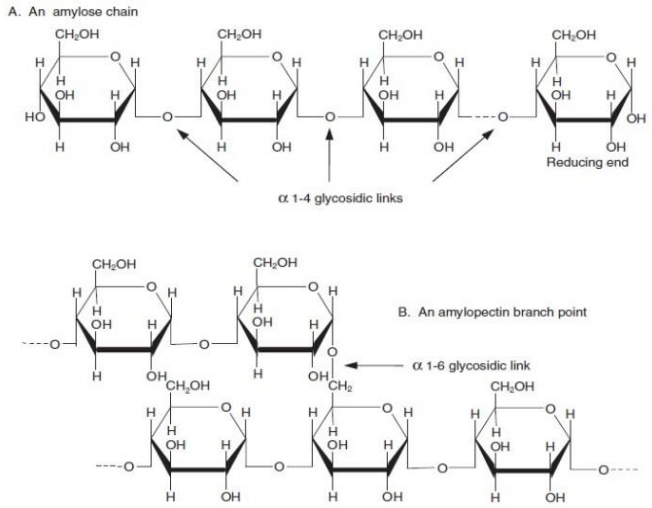
						wavelengths of 20 - 360 λ
Positive Aspects	Affordable, small sample size possible, highly accurate at a particular frequency, easy to operate	Resonator can have air gaps which does not impede dielectric measurement due to cylindrical geometry Q factor and dielectric losses starts off larger meaning very sensitive measurements of losses possible	Has high accuracy	High temperature range (-40 to 200°C), Non destructive, Simple and Convenient	Can measure magnetic materials Can measure broadband and banded frequencies	Overcomes difficulties of transmission line technique as sample no longer needs to fit within a waveguide/coaxial tube. Sample is isolated from rest of equipment meaning that samples could be heated in e.g. an oven and measurements still be made if microwave windows were present on oven

						allowing for energy radiating from antennae to reach the sample.
Brief Description	SPDR is connected to a vector network analyser. The resonant frequency and Q factor of the empty cavity is recorded. Sample is then inserted into cavity and the frequency and Q factor are again recorded. Thickness of sample recorded. Data converted to constant and loss. Minimum sample size depends on frequency.	SiPDR connected to vector network analyser. Measures surface impedance of samples by taking the Q factor and frequency of the empty cavity and the Q factor and frequency of the filled cavity. Agilent Technologies provide software which converts to surface resistance.	Material is placed between a parallel plate (two electrodes) capacitor and permittivity calculated from the area of the plate, thickness of sample. Capacitance measured using impedance analyser. Material stimulated with an AC source and the actual voltage across the material is measured.	Cut off section of transmission line. Probe immersed and pressed to flat surface of material causing fields to change. Reflected signal measured and related to dielectric constant.	Material placed within enclosed transmission line of a rectangular waveguide connected to a network analyser. The permittivity and permeability are calculated from the reflected and transmitted signal. 	Variation of transmission line technique. Contains two antennae facing each other with a sample holder placed between them connected to a network analyser. The permittivity and permeability are calculated from the reflected and transmitted signal.

1.5 What is Starch?

According to (Coultate, 2008) starch is a polysaccharide primarily used by plants as an energy storage method (figure 1-15 A). Starch ranges in both shape and size from 2 to 100 µm dependent on their botanical source. Starch consists of linear glucose units linked together (α 1-4) called amylose and glucose units linked together (α 1-4) and at (α 1-6) in a branched format called amylopectin. Amylose is not strictly linear and can have some branching although not to the extent of the amylopectin constituent of starch. In amylose it is believed branching occurs at 'only one per several thousand glucose units' (Blanshard and Mitchell, 1979). According to (Banks and Greenwood, 1975) all properties of a starch granule are related to the presence and ratio of amylose:amylopectin and how these components are subsequently organised; in short both its 'chemical constitution and physical constitution' play a role. It has also been well documented that starch is semi crystalline.

A



B

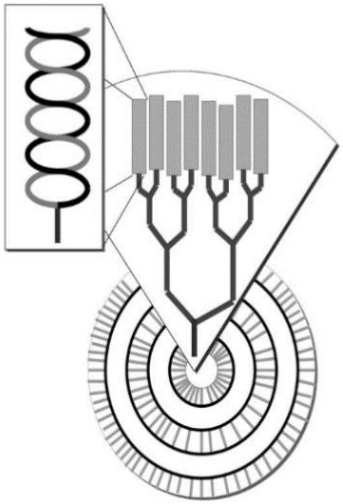


Figure 1-15A) The Structure of Amylose and Amylopectin (Coultate, 2008) B) Structure of a Native Waxy Starch Granule (Van der Sman and Meinders, 2011)

(Van der Sman and Meinders, 2011) observe the structure of a native waxy starch granule in figure 1-15 B. Alternating regions of crystalline double helices of branched amylopectin and amorphous regions (starting branches of amylopectin) are observed. In native starch granules containing amylose, the amylose is contained within the amorphous regions due to its largely linear nature. Previous work performed by the sponsor (Sponsor, 2013) has highlighted significant differences in branching, ratio of amylose:amylopectin and particle size and shape across different botanical sources of starch which could affect how the different starches interact within the microwave field. Different botanical sources of starch lose their structure in a process called gelatinisation at different temperatures. According to (Banks and Greenwood, 1975) gelatinisation is the point at which irreversible changes occur

to the starch granule on application of water and heat. (Van der Sman and Meinders, 2011) consider gelatinisation as a ‘single melting transition of a semi-crystalline polymer’ although they agree that this is a simplistic view. Contradicting evidence appears in the literature regarding whether altering the physical form of the starch via gelatinisation has an impact on the dielectric constant and loss factor (Ryynanen et al., 1996, Miller et al., 1991). Differences have also been seen in the literature in relation to botanical source and dielectric behaviour. (Ndife et al., 1998) observed the properties of six different starch species at 2.45 GHz. They found significant differences existed between starch types and found that more efficient heating occurred in corn, wheat and rice due to their higher dielectric loss factors or energy dissipation. For all the starches tested they did show that as the moisture content increases so does the dielectric constant and loss. It was also shown that dielectric measurements were also dependent on temperature. (Ahmed et al., 2007) measured the dielectric properties of Indian Basmati rice slurries over the frequency range 500-2500 MHz and observed that frequency did not generally affect energy storage (dielectric constant) but did increase the dielectric loss factor on increasing the frequency to 2.45 GHz. At gelatinisation temperature the dielectric properties of the rice slurry differed. However, (Ryynanen et al., 1996) found no difference in dielectric properties between native and gelatinised starch samples.

(Van der Sman and Meinders, 2011) have also described gelatinisation as a phase transition at which transformation of the ‘native semi-crystalline starch granule to a polymer solution in the rubbery state’ occurs. It involves multiple phase transitions. Within each starch granule, the double helices of amylopectin undergo ordering similar to that of liquid crystals which can temporarily increase the order of crystallinity. The double helices of amylopectin unwind (known as melting). Finally the starch granule swells and amylose leaches out. The resultant structure of gelatinised starch granules is amorphous. Due to a range of starch granule sizes being present within each native starch, granules will swell at different rates and so gelatinisation occurs for the same starch over a temperature range. Different methods have been used to gelatinise starch. (Buckow et al., 2009) used pressure temperature phase diagrams of maize starches with different amylose contents. 1.5 ml of each starch was held in water baths ranging from 50 ^{o}C to 100 ^{o}C until the desired temperature was reached. To check gelatinisation had occurred, starch granules were analysed using a microscope equipped with a polarisation filter. (Francisco and Sivik, 2002) used a more novel approach to achieve gelatinisation of cassava, potato and wheat starches. Starch samples mixed with water at 28% (w/w) were placed in high pressure containers and carbon dioxide or nitrogen was added. The starch was then gelatinised in a temperature controlled water bath for a period of 20 minutes.

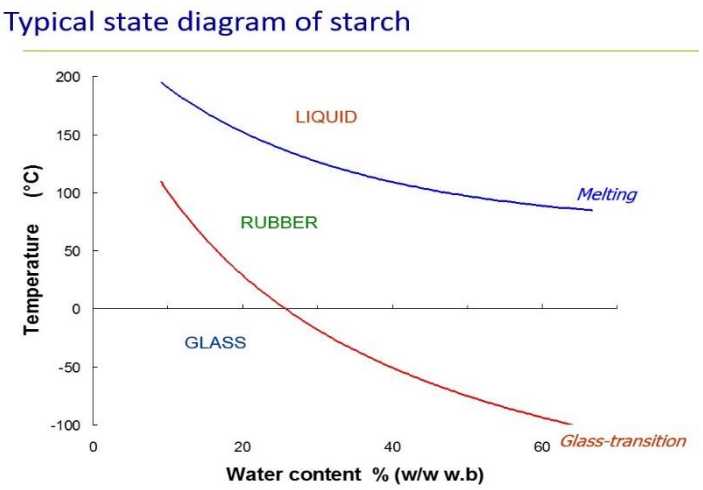


Figure 1-16 Typical State Diagram of Starch (Hill, 2014)

According to (Blanshard and Lillford, 1993) starch will always attempt to return to its lowest energy state. Despite the crystalline structure of native starch being disrupted during gelatinisation, over time recrystallization of the starch will occur through the reordering of the amylose constituent of starch, albeit not to the same degree of order as before. Reordering will also occur in amylopectin albeit at a slower rate. This is known as retrogradation. This is because starch is at its lowest energy state in the crystalline form, although, starch must have mobility in order for successful crystal reformation. Figure 1-16 observes a state diagram for starch. On observing a starch alternating between two different phases two numbers are used; the melting point (Tm) of the starch (covering a range of temperatures across different starches) and the glass transition temperature (Tg). According to (Chung et al., 2002) the glass transition refers to the temperature at which the material presents rubbery as opposed to brittle behaviours on addition of temperature or suitable plasticisers. If a material is moving from a glassy state to a rubbery state, the boundary line between these states is the glass transition state. (Van der Sman and Meinders, 2011) suggest that the Tg is not simple and that there is no general consensus as to whether glass transition should be measured at the beginning, during or after transition has occurred. At the transition, two phases exist together in the water-starch system and so during freezing for example amorphous water starch/ice can coexist with crystalline water/ice.

The glassy state refers to a ‘material formed by cooling from the normal liquid state which shows no discontinuous change at any temperature at any time, but has become more rigid through a progressive increase in viscosity’ (Blanshard and Lillford, 1993). To achieve a rubbery state the starch liquid which has become amorphous as the result of heating and subsequent gelatinisation must be cooled. If the starch is further cooled (supercooled) then the starch is in the glassy state and ‘no crystallisation occurs in the supercooled state.’

1.6 Importance of polar and ionic materials and their interaction with water

The moisture content of materials undergoing the microwave process is a driving factor behind dipolar polarisation. (Ahmed et al., 2007, Sipahioglu and Barringer, 2003, Roebuck et al., 1972, Ryynanen et al., 1996). The state of the water is of fundamental importance as to whether it can interact with the electromagnetic field (Henry et al., 2003, Trabelsi and Nelson, 2006). As such, it is important to classify the different types of water to understand how complex food systems will interact within the microwave. Also of importance are how specific ionic compounds interact in the microwave in terms of ionic conduction.

1.6.1 Definition of bound and free water

Water is a molecule composed of two hydrogen molecules and one oxygen molecule in which each hydrogen molecule is covalently bound to the central oxygen molecule. Two of the six outer shell electrons are used to form this covalent bond leaving four electrons which organise themselves into two non-bonding pairs as far away as possible due to like charges repelling. This results in a tetrahedral structure. Overall the water molecule contains a neutral charge although due to the way in which the hydrogen and oxygen molecules are bonded, the hydrogen atoms have a partial positive charge whilst the oxygen has a partial negative charge. In terms of dielectrics water can be classified in one of two ways;

1) Phase state of the water
2) Ability to interact with the electromagnetic field

Water exists in three different phase states. (Marechal, 2007) refers to these as water vapour, ice and liquid water and quantifies them in terms of their ability to hydrogen bond. In water vapour at ambient pressures (Marechal, 2007) states that a very small proportion of water molecules establish hydrogen bonds on other water molecules. This is not the case if the water is in the form of ice. In these cases water molecules form four hydrogen bonds per water molecule thus ensuring ice particles have limited rotational properties. (Marechal, 2007) calls ice a ‘unique species’ as the hydrogen molecules are equal to the number of covalent bonds. This is also true for liquid water, although in ice the structure is more highly ordered. In ice the two hydrogen atoms from each H_2O molecule create two hydrogen bonds between neighbouring water molecules whilst two acceptor sites on the same molecule allow a hydrogen bond to be created from another hydrogen molecule producing a tetrahedral arrangement. To achieve this shape the hydrogen bonds are slightly distorted. Hydrogen bonds can be further distorted on application of pressure to ice causing ice to adapt its hydrogen bond network to minimise the strain. (Marechal, 2007) refers to water in

ice format as exceptional in that the effects of Van der Waals forces become negligible due to the water molecules efficiency at creating and accepting hydrogen bonds.

In liquid water two theories have been discussed; the continuum model/random network model and the mixture model (Jeffrey, 1997). The continuum model/random network model proposes that there is a continuous network of hydrogen bonds in a tetrahedral shape in which the hydrogen bonds are flexible and able to bend. Although it is also argued within this theory that the hydrogen bonds break as opposed to bend. Mixture models of liquid water have been shown to be more diverse with some preferring the flickering cluster model (Frank and Wen, 1957) in which there are clusters of water molecules amongst lone water molecules. The commonly accepted arrangement is that in liquid water, molecules form one large cluster which is grouped closer together than the molecules in ice thus explaining why ice has a lower density than liquid water.

(Gabriel et al., 1998) states water present within liquid and gas states are able to respond to field reversals occurring at frequencies as low as 10^6 Hz with the microwave frequency residing at around 10^9 Hz. In ice, 'molecular rotations are generally restricted and therefore reorientation in an electric field does not generally contribute to the dielectric constant.' (Chaplin, 2014) agrees and states that ice is able to rotate in the kHz frequency (higher than the microwave frequency) also stating that ice is 40 times less effective in terms of dielectric heating than liquid water or gas. (Jeffrey, 1997) references water as having 'a high dielectric constant associated with the distortion or breaking of hydrogen bonds.'

Water is vital in the promotion of dielectric heating and there are different forms - 'free and bound water.' Free water is water that is free to interact within the electromagnetic field and bound water is water that is restricted or unable to interact within the microwave frequencies of 300 MHz to 300 GHz. (Chaplin, 2014, Henry et al., 2003). (Gabriel et al., 1998) refers to bound water when discussing hydrogen bonding. They observe the interaction between carbohydrates/alcohol and water as a function of dielectric properties. As both carbohydrates and alcohols have hydroxyl groups, they are able to hydrogen bond to the water and restrict water molecules from rotating on application of the electromagnetic field. On studying a range of alcohol-water solutions at 2.45 GHz a significant decrease in relaxation time occurred when the hydrocarbon chain contained a double bond or phenyl ring adjacent to CH_2OH fragments. A decreased relaxation time means improved dielectric heating. Whilst overall hydrogen bonding to water molecules can restrict H_2O rotation on application of the wave, if in the presence of double bonds/phenyl rings, this effect appears to be negated. (Gabriel et al., 1998) theorise that this is due to localised rotational processes being observed within the water molecule.

1.6.1.1 Hydrogen Bonding : A definition

(Marechal, 2007) states the hydrogen bond occurs between molecular groups which contain hydrogen (H) atoms covalently linked to an electronegative atom commonly either an oxygen or nitrogen group. This same hydrogen atom forms an electrostatic link with another electronegative atom within the same or a different molecule. The polar group containing the H atom is known as the donor whilst the O or N group is referred to as the acceptor.

1.6.1.2 Bound and Free Water in Literature

The moisture content of materials undergoing the microwave process are a driving factor behind dielectric storage and loss. (Henry et al., 2003) investigated the differences in free and bound water in tomato, pimento and melon seeds. They proposed free and bound water have different dielectric properties and that alive and dead seeds have different amounts of free and bound water ensuring viability could be determined. (Chaplin, 2014) discusses the impact of free and bound water in terms of frequency and states that free water can rotate in the GHz frequency (microwave frequency), if bound will rotate in the MHz frequency (short radio wave frequency) and in the form of ice will rotate within the kHz frequency (long radio wave frequency). This has implications for the product as it is placed within the microwave in a frozen state and so microwaves at frequency 2450 MHz/2.45 GHz will not be as effective at causing ice to rotate and heat the foodstuff. Understanding bound and free water may prove useful in the future as other components within a food matrix can interact with water and dictate whether water is bound or free.

There is a natural moisture level present in each botanical source of starch prior to being modified. It is currently theorised that this natural moisture content is bound into the starch matrix via hydrogen bonding, so will not have a strong dielectric effect on application of the electromagnetic wave. Whether additional water added is bound within starch matrices or left free to interact with the microwave field is important. (Pethrick and Song, 2013) state the structure of the starch itself can impact on if water is bound or free within the matrix.

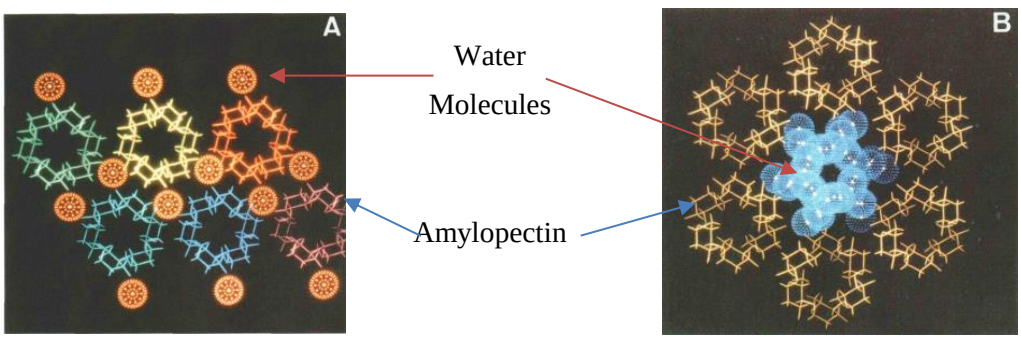


Figure 1-17 Location of Moisture in A) Type A Polymorphs and B) Type B Polymorphs (Buleon et al., 1997)

On describing starch structure, branched starch chains pack together to form 3 types of crystals: A, B and C - a mixture of A and B. (Pethrick and Song, 2013) state if starch contains amylose in its A or B polymorph then there are 'no internally bound water molecules.' B polymorphs contain more moisture in the gaps between the amylose than polymorph A which could impact on dielectric measurement. (Buleon et al., 1997) also found that the arrangement in amylopectin also differs dependent on polymorph type as shown in figure 1-17. According to (McCain, 2013) A type polymorphs are usually found in cereals whilst B type polymorphs are typically found in tubers. (Sipahioglu and Barringer, 2003) found that the higher the amount of free water in fruits and vegetables, the higher the dielectric constant. This indicates it is not purely the amount of water present in a food that governs its dielectric response but rather how much of that water is free to interact within the electromagnetic field. It is not known whether different botanical sources have different water binding capabilities which would prevent dipole rotation.

(Orfila, 2015) states potatoes contain components such as aribinose and galactose which are able to bind to water thus reducing its ability to rotate on application of the field.

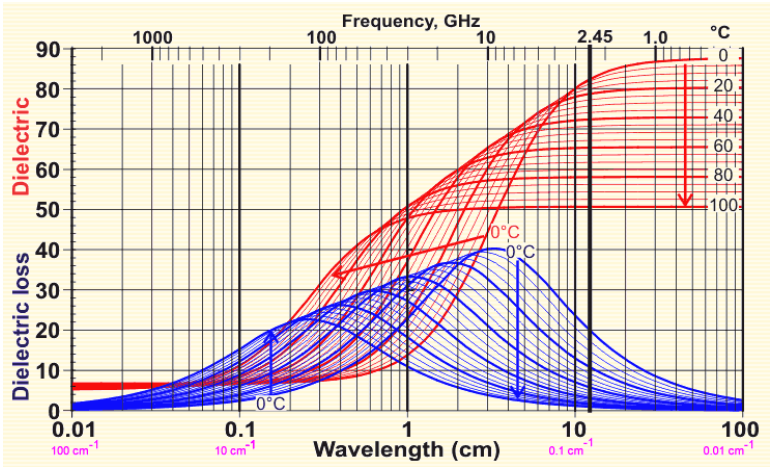


Figure 1-18 Dielectric Constant (red lines) and Dielectric Loss (blue lines) of Liquid Pure Water as a Function of Frequency, Wavelength and Temperature (Chaplin, 2014)

(Chaplin, 2014) observes the dielectric activity of liquid pure water as a function of frequency, wavelength and temperature in figure 1-18. As the temperature increases, the strength of hydrogen bonds decrease resulting in decreased permittivity/dielectric constant. At higher frequencies the water molecules oscillate more readily and so results in less friction and a decreased dielectric loss factor (blue line). At shorter wavelengths the dielectric constant remains fairly stable regardless of the temperature. At shorter wavelengths the dielectric loss factor increases as a function of temperature until a wavelength of 0.2 cm at which point the loss factor decreases as the temperature increases. Most of the dielectric loss is observed between the microwave frequency of 1-300 GHz and

0.0817 cm to 12.24 cm wavelength. The maximum dielectric loss factor is at a frequency higher than 2.45 GHz. (Chaplin, 2014) states this is beneficial as the microwaves are not absorbed by the first layer of water it encounters and so may penetrate the foodstuff further resulting in more uniform heating.

1.6.1.3 Absorption Vs Adsorption

According to (Verma, 2017) absorption occurs when the molecules of a substance e.g. water are uniformly distributed throughout the bulk of the material e.g. starch. Adsorption is referred to as the molecules of one substance being present at higher concentrations at the surface of the other material and so does not enter the bulk material. It is instead described as a surface phenomenon.

1.6.1.4 Dry Basis Vs Wet Basis

When reporting moisture measurements one of two terms are usually presented; wet basis and dry basis. Table 1-3 explains the difference between the two terms.

Solid Material contributing to whole Sample (g)	Water contributing to whole sample (g)	Dry Basis Reporting (%)	Wet Basis Reporting (%)
100	100	100	50

Table 1-3 Dry Basis Vs Wet Basis Reporting

1.6.1.5 Drying Behaviour in relation to moisture

During drying there are 3 regions; the constant rate, falling rate and horizontal plateau (Onwude et al., 2016);

Constant Rate: Linear reduction in moisture content over time (surface moisture removal) which is limited by rate of heat transfer

Falling Rate: The saturated surface region retreats and the drying rate is not as steep during removal of moisture from the centre of the product and is limited by mass transfer

2nd Falling Rate /Horizontal Plateau: Once a horizontal plateau has been reached for a significant period of time the sample and medium are said to be in equilibrium.

This behaviour can be extracted from data by plotting the data graphically and observing the R^2 value. A regression line can be used to determine the relationship between a dependent (y) and independent variable (x). The equation of this line can be calculated in the form $y = mx+c$. The R^2 value (coefficient of determination) measures the degree of linear association between two variables (Schroeder et al., 1986) and describes how well the data gathered fits

to the regression line with R^2 values closer to 1 indicating a closer fit. It is the proportion of the variance in the dependent variable that is predictable from the independent variable with values closer to 1 (100%) providing a model in which all of the variability of the data around the mean is explained. In drying behaviours the constant rate is linear in relation to time and the falling rate is not (Onwude et al., 2016). Therefore the R^2 value can be used to determine when the sample has left the constant rate and entered the falling rate. A horizontal plateau can be observed visually and it is at this point that the sample is said to be in equilibrium and successful drying has occurred.

(Altan and Maskan, 2005) compared the drying time and drying characteristics of macaroni dried by microwaves at different powers and conventional hot air. As the power output of a microwave increased, the drying rate also increased. However, they only observed microwave powers of 70, 210, 350 and 490 W. (Wang and Sheng, 2006) observed microwave drying in peaches determining that drying rate increases as the power of the microwave increased at the same moisture content.

According to (Menczel and Prime, 2009), thermogravimetric analysis (TGA) analysis involves measuring the mass of a material as a function of temperature whereby the sample is subjected to a controlled temperature program in a controlled atmosphere. As a result, TGA can be used to measure the drying behaviours of specific sample types. To determine whether typical drying behaviour is being observed the R^2 association can be applied.

1.6.1.6 Heat Flow and Transfer

According to (Menczel and Prime, 2009) there are three forms of heat flow;

1) Conduction (occurs via diffusion as atoms/molecules transfer vibrational energy to their neighbours)
2) Convection (heat transferred from a solid surface to a flowing material)
3) Radiation (energy radiated from the surface of the system in the form of electromagnetic energy; no medium is required and transfer takes place between solid surfaces. The intensity and frequency relies on the surface temperature with a positive correlation being observed)

Latent heat is the amount of heat absorbed or emitted by a material during a phase transition and is referred to as latent as a temperature change of the material is not observed despite an increase in enthalpy (ΔH).

1.6.1.6.1 How heat flow in DSC can be used to determine product characteristics

'Differential Scanning Calorimetry' is a technique in which the heat flow rate difference into a substance and a reference is measured as a function of temperature, while the sample is subjected to a controlled temperature program' (Menczel and Prime, 2009). The amount

of heat inserted into the sample to ensure equilibrium with the reference sample, is measured. Negative numbers are associated with an endothermic reaction - heat flowing into the sample. Positive numbers are associated with an exothermic reaction - heat leaving the system. According to the 2nd law of thermodynamics heat is a form of energy flowing from higher temperatures to lower temperatures and so heat flow can be defined as a process in which two thermodynamic systems exchange energy.

DSC can be used to observe the type of structure e.g. amorphous, semi-crystalline, thermoplastic, thermoset and the state of the material e.g. incomplete cure, incomplete crystallisation, volatile, multiple polymers/monomers or multiple crystal morphologies within the same sample set.

1.6.2 Effect of sodium chloride on the dielectric factor

According to (Keiko, 2003) ionic conduction has a much stronger effect than dipolar polarisation in terms of heat producing ability. (Anwar et al., 2015) refers to ionic conduction as dissolved charged particles (ions) which oscillate backwards and forwards under the influence of the electric force of microwaves, producing an electric current. This electric current faces internal resistance due to neighbouring charged particle collisions causing the sample to heat up.

(Gabriel et al., 1998) discuss the mechanism of aqueous solutions of ions. Both ionic conduction and dipolar polarisation occurs in these systems. As the concentration of ions increase, the loss factor occurring due to ionic conduction is stronger than the dielectric loss factor of dipolar polarisation. This results in an overall increase of the loss factor. However, if the sodium chloride concentration is too high, the contribution of dipolar polarisation will be reduced as the water becomes bound by sodium chloride and is therefore not free to interact within the electromagnetic field.

The promotion of dielectric heating in the presence of sodium chloride (NaCl) is only possible if the NaCl is in a moisture rich environment. When dry, NaCl is unable to dissociate, so does not possess a charge, leaving it unable to interact with the microwave field. (Glover et al., 2013) found that when dry NaCl was placed on potato spheres, the electromagnetic wave penetrates the sample heating the interior. However, when the NaCl coating is dissociated the coating ‘acts like a shield to the microwave energy thus preventing heating internally.’ Due to this screening effect if the concentration of NaCl is increased within the same volume of water, a concentration will be reached in which not all the NaCl is able to dissociate and so will no longer contribute to dielectric heating.

(Ahmed et al., 2007) looked at the effects of adding NaCl and butter to basmati rice slurries as a function of dielectric properties. They found that adding NaCl, an ionised material, to

the rice slurries caused a decrease in dielectric constant but an increase in the dielectric loss factor. On addition of butter there was a 30-35% decrease in the dielectric constant at 70-80ºC. (Bircan and Barringer, 1998) looked at starch-NaCl interactions observing that addition of NaCl caused a decrease in dielectric constant, possibly due to NaCl binding to water and preventing polarisation. As the starch concentration increased the dielectric loss decreased despite NaCl being present. This suggests that NaCl could interact with the starch. One theory was there was now less NaCl per starch quantity in the amount of sample measured which could account for the difference in dielectric measurement. (Miller et al., 1991) observed that starches containing a higher amount of phosphates (potato starch and chemically modified) gave a higher dielectric loss factor than starches not containing phosphates. This suggests that ionisable materials have an effect on the dielectric properties.

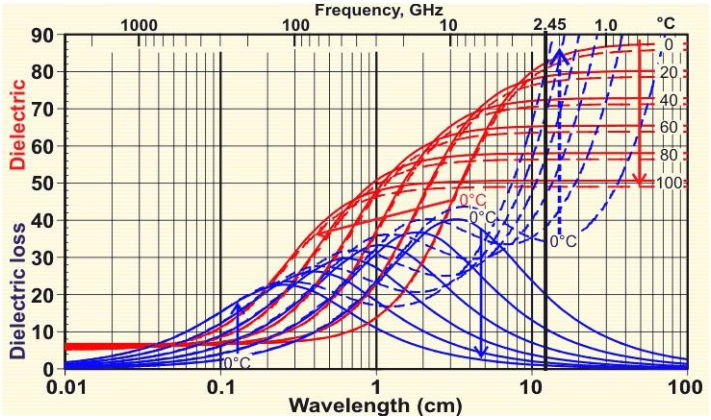


Figure 1-19 Dielectric Constant (red lines) and Dielectric Loss (blue lines) of Dilute Sodium Chloride Solution (dashed lines) and Pure Water (solid lines) as a Function of Frequency, Wavelength and Temperature (Chaplin, 2014)

(Chaplin, 2014) states that NaCl decreases the natural structuring of the water in a similar manner to increased temperature and so reduces the dielectric permittivity. This is dependent on the NaCl concentration and the hydration of the individual molecules once they have become dissociated in solution. Figure 1-19 observes the effect of a dilute NaCl solution and a pure water solution as a function of wavelength, temperature and frequency. In terms of wavelength, at higher frequencies and shorter wavelengths the dielectric constant of pure water and dilute NaCl solution remains stable regardless of temperature. As the wavelength and frequency increase and decreases respectively a difference is observed in temperature with both the pure water and NaCl solutions observing decreasing dielectric constant as the temperature increases. After the microwave frequency of 2.45 GHz the dielectric constant plateaus with no further increases in dielectric constant. The presence of NaCl depresses the dielectric constant. Pure water solutions report higher dielectric constants than dilute NaCl solutions at the same wavelength, frequency and temperatures.

The relationship between the loss factor of pure water solutions and salty solutions as a function of wavelength, frequency and temperature alter more drastically. At lower wavelengths and higher frequencies the dielectric loss factor is similar for both pure water and salty solutions although as the temperature increases the loss factor increases in both solution sets. The solutions begin to differ at a wavelength of 0.3 cm via a decrease in loss factor. At a wavelength of 1 cm (the lower limit of the microwave frequency) the NaCl solution begins to increase its dielectric loss factor whilst pure water continues to experience decreasing loss factor as a function of wavelength and frequency. At the microwave frequency of 2.45 GHz the NaCl solution has a much increased dielectric loss factor than pure water although the exact difference has not been determined. The dielectric loss factor increased as the temperature increased for NaCl solutions but decreased as the temperature increased for pure water solutions. (Chaplin, 2014) therefore suggests that NaCl may be able to improve heating within the microwave environment as whilst water becomes less able to absorb microwave energy as a function of a decreased frequency and increased wavelength, NaCl solutions increase their dielectric loss factors at the domestic microwave frequencies.

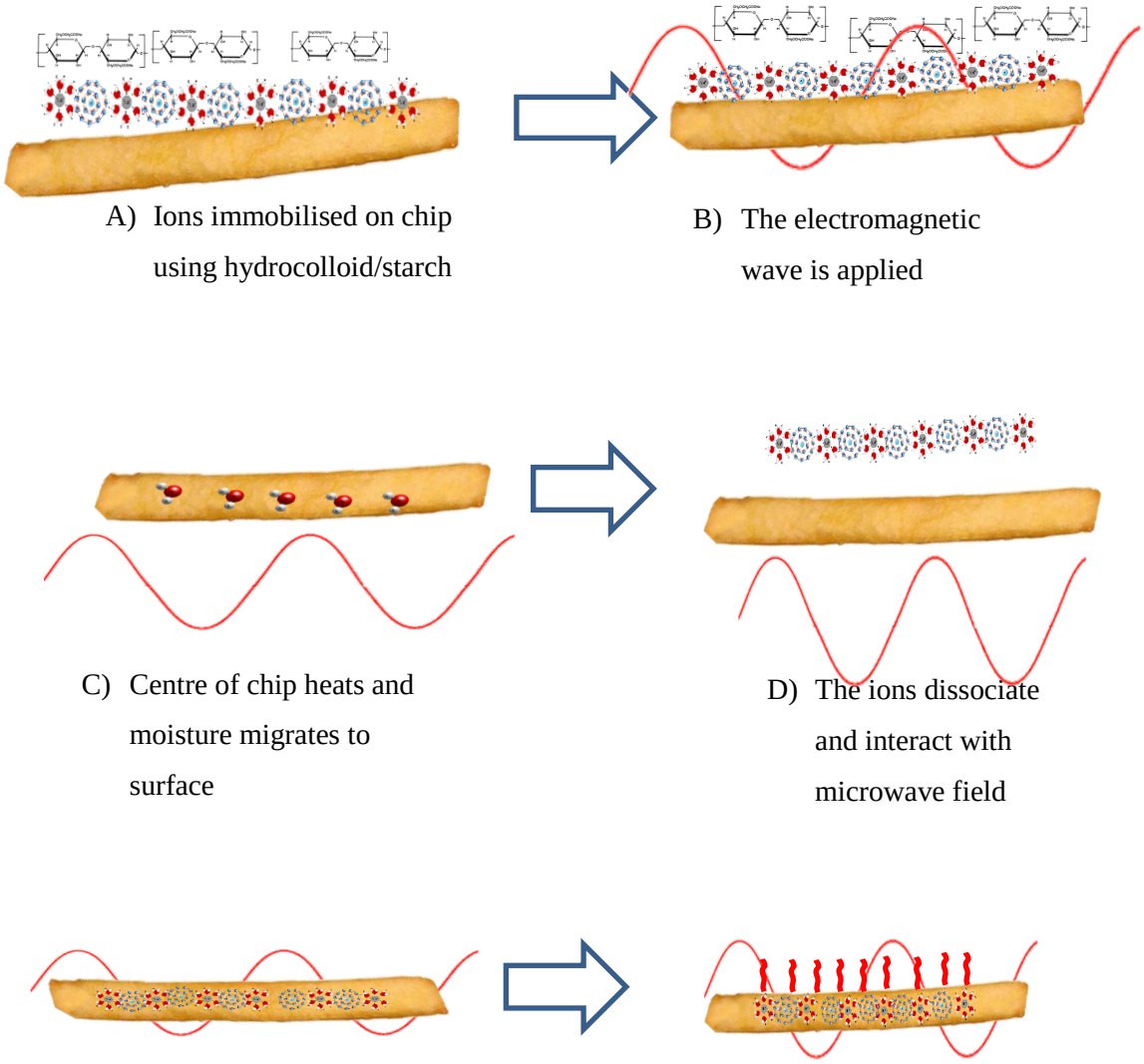
1.6.3 Method to Measure Content of Ions (Atomic Absorbance Spectroscopy)

AAS is ‘an analytical technique in which a sample is vaporized and the nonexcited atoms absorb electromagnetic radiation at characteristic wavelengths’(Rennie and Law, 2016). It consists of a hollow cathode lamp, nebulizer, air/acetylene flame, and an optical system. The sample is drawn into the nebuliser which allows for a fine mist to be created. The flame causes the solvent to evaporate, leaving free atoms and ions. A light (hollow cathode lamp) is shone through the base of the flame which allows ions to become excited. (Kirk and Sawyer, 1991) state that the hollow cathode lamp is specific for measuring a certain element. They operate at specific wavelengths and only atoms which resonate at these wavelengths will absorb and become excited allowing for measurements to be made for individual ion types. AAS measures the absorbance of these wavelengths by calculating the difference between the transmitted wavelength and the wavelength reaching the detector.

1.7 Self-Limiting Systems

Based on the work conducted by (Albert et al., 2009a, Albert et al., 2009b, Chaplin, 2015, Glover et al., 2013), the idea of a self-limiting theory was proposed. The theory was to provide a surface coating where initially sodium chloride ions are dry and only become active when moisture migrates from the centre of the product to the surface thus causing dissociation. Due to the higher dielectric activity at the surface of the product due to the dissociation of the ions, the surface temperature would increase causing moisture to evaporate from the surface at a faster rate. This in turn would cause the NaCl to revert back

to its inert state as the moisture evaporates and allow for the development of a crisp outer texture. To immobilise the sodium chloride onto the surface of the product a method was required. Therefore starches and hydrocolloids were both examined in terms of their abilities to act as a coating. Figure 1-20 observes the self-limiting theory.



A) Ions immobilised on chip using hydrocolloid/starch

B) The electromagnetic wave is applied

C) Centre of chip heats and moisture migrates to surface

D) The ions dissociate and interact with microwave field

E) The ions and water cause surface temperature to increase and the ions return to dried state due to evaporation

F) Dried ions no longer interact, surface becomes dry due to further evaporation, water starts to migrate to surface but not before end of microwave heating period allowing surface to remain crisp

Figure 1-20 Self – Limiting Theory

1.8 Coating Systems

1.8.1 Coating methods observed in conventional cooking

(Glover et al., 2013) found that coating potato spheres with NaCl resulted in an improved product. (Albert et al., 2014) were interested in improving the sensory properties of breaded chicken nuggets in the microwave for fast food purposes. The product initially underwent deep fat frying where the oil exceeded 100 ^{o}C allowing the coating to become dehydrated and so give crisp textures. On freezing and subsequent microwaving for reheating purposes, moisture from the chicken migrated to the surface and caused the coating to become 'soggy'. (Albert et al., 2014) attributed this to temperatures within the microwave not reaching above 100 ^{o}C meaning that condensation could occur. (Albert et al., 2014) hypothesised that the number of coatings may improve the texture and therefore observed chicken nuggets that were twice coated (egg-breadcrumbs-egg-breadcrumbs) against once coated nuggets (egg-breadcrumbs). Differences between using egg or commercial batter as the binder with both one coating and two coating applications were observed. A trained sensory panel alongside a texture analyser and moisture analysis highlighted that the introduction of a commercial batter/egg binder and a double/single coating did not significantly improve the texture within the microwave environment. (Singh and Singh, 1999) observed the effects of adding coatings to popcorn to aid in the popping process during microwaving. Adding NaCl contributed to a higher loss factor particularly if the concentration was increased in the absence of oil which agrees with (Chaplin, 2014). (Singh and Singh, 1999) also found that oil resulted in a low dielectric constant and loss. The popping of corn varied with concentration of the ingredients used as coatings and whilst hydrogenated oil, butter and NaCl did have an effect on the dielectric properties, sodium bicarbonate did not interact with the electromagnetic field at all.

(Albert et al., 2009a) looked at the effect of different coatings on improving microwaveable fish nuggets. They suggest a batter/coating is useful in acting as 'a barrier against moisture loss, protecting the natural juices of the food substrates during freezing or reheating.' (Albert et al., 2009a) have hypothesised that adding dextrins (dry heated unmodified starch) to the batter could improve their performance as previous work has indicated strong links between dextrin use and improved textures of microwaved foods. For this experiment, two white corn dextrins were used, with one having a solubility of 97% and the other a solubility of 60%. The dextrins were incorporated into a batter containing 'wheat flour (11%), wheat flour (11.18%), sodium chloride (5.5%), monosodium glutamate (0.6%), sodium pyrophosphate (1.78%) and sodium bicarbonate (1.32%). On testing they found that the samples containing dextrins had a smaller significant difference in terms of colour than deep fat fried nuggets that were not frozen and reheated in the microwave. This suggests

that the dextrins aided in giving a darker appearance, not surprising due to the Maillard reaction. Texture analysis using a texture analyser gave a different force profile for products that were microwaved to those that were deep fried indicating a difference in texture. On sensory testing, nuggets containing dextrins and in susceptor packaging were viewed positively for crispness although these products were also more oily in nature.

1.8.2 Starch based coatings

Different botanical sources of starch may have dielectric properties which could contribute to surface heating. Characterising these starches in terms of dielectric properties will determine if they are suitable for the development of a coating which promotes crispness.

1.8.3 Hydrocolloids

1.8.3.1 What are Hydrocolloids?

According to (Wüstenberg, 2014) hydrocolloids 'are macromolecular hydrophilic substances.' They are 'a range of polysaccharides and proteins' used for many different functions including emulsification, gelling, and thickening (Phillips and Williams, 2009). They have the ability to thicken or gel in aqueous solutions (Xue and Ngadi, 2007). Not every hydrocolloid interacts in the same way as some hydrocolloids are water soluble whilst others are 'only able to swell in water' (Wüstenberg, 2014). Hydrocolloids which are able to swell in water shall be investigated as this will be more beneficial in preventing water migration as it will provide a physical barrier between the inner core and outer crust when considering French fry formulation.

1.8.3.2 Current uses in the Food Industry

Whilst there are many hydrocolloids used in the food industry they are primarily used for their rheological properties. (Phillips and Williams, 2009) provide examples of where they are used in table 1-4.

Product	Purpose	Hydrocolloid
Baked Beans Hoi-Sin Sauce	Thickener	Modified Corn Starch
Sweet and Sour Sauce	Thickener	Guar Gum
Sunny Delight Drink	Emulsifier	Carboxymethylcellulose
Light Mayonnaise	Fat replacers enhancing viscosity	Guar Gum Xanthan Gum
Mousse	Stabiliser	Pectin
Bramley Apple Pies	Gelling agent	Modified Maize Starch Sodium Alginate
Fruit Pie Bars	Gelling Agent	Gellan Gum, Pectin

Table 1-4 Uses of Hydrocolloids in the Food Industry

(Galus and Kadzinska, 2015) observe how emulsion based edible hydrocolloid films are used within the food industry. They looked at the meat, fruit, vegetable, cheese and baking industries. Whilst these areas are not directly related to microwave or frying, the reason some hydrocolloids have been used is of interest. Pea protein is used in Brussel sprouts as it improves retention of vitamin C and polyphenols. Vitamin C is water soluble and so indicates that pea protein is able to form a barrier that prevents leaching of the vitamin. A physical barrier is required as part of the self-limiting theory to prevent too much moisture leaving the centre of the product. Whey protein isolate has also been shown to reduce water loss in cheese.

Research is primarily focussed on the rheological benefits of hydrocolloids. (Xue and Ngadi, 2007) observed the rheological properties of batters containing different hydrocolloids and flours. Batters were created using either wheat, corn or rice flours coupled with either methylcellulose (0.5%, 1%, 1.5%) or xanthan gum (0.2%). During their work they define batter as being either adhesive or tempura with adhesive batters providing a layer between the product and an outer ‘breading layer’ and tempura batters being chemically leavened forming a crispy and light texture. During batter preparation 2.5% NaCl was also added to each batter. By using a texture analyser with a stress/strain rheometer attachment, it was found xanthan gum increased shear thinning of the batter with increasing concentration in all flour types. Xanthan gum showed a greater shear thinning behaviour than methylcellulose. Methylcellulose showed shear thinning behaviour at 1% and above but had a similar viscosity to the control batter at the lower concentration.

Research has also been concerned with finding ways of strengthening gels. This is of interest as a potential way to create and sustain a physical barrier between the inner core and outer skin. (Ulbrich et al., 2015) characterised acid thinned wheat, potato and pea starches in relation to gel properties. Acid thinning increased gel strength possibly because the negative effect of amylopectin branches is reduced due to molecular degradation in amorphous regions where the branching occurs. A reduced gel strength was evident where there is a reduced molar mass of amylose. A higher percentage of short chains gives gel strength and the acid hydrolysis causes cleaving of polysaccharides, allowing a higher percentage of short chains.

1.8.3.3 Other industrial uses

Hydrocolloids are not just used within the food industry but within many other sectors due to their versatility. This is no more apparent than in the pharmaceutical industry. (Karrout et al., 2015) looked at a variety of advanced drug delivery systems. One such discussion revolved around the successful use of hydroxypropylmethylcellulose (HPMC) coating and an outer gastro resistant film to allow a time dependent drug release.

1.8.3.4 Application of barrier layers e.g. sodium and hydrocolloid layers

(Albert et al., 2009a) looked at the effect of adding a predust prior to adding a batter. The product they were interested in was a frozen hake nugget. They defined a predust as a fine dry substance that is dusted onto the moist surface of the hake prior to a further coating being applied with the aim of preventing slips, gaps or too thin a layer of batter being formed. This research looked at using different hydrocolloids as the pre dust because hydrocolloids are able to 'develop wet adhesive properties at various degrees of hydration.' HPMC (hydroxypropylmethylcellulose), xanthan gum and oxidised starch were investigated in terms of deep frying, conventional oven and microwave heating. Fish was predusted with each hydrocolloid then put in batter for 1 min and cooked for 30 seconds at 190 ^{o}C and stored at -18 ^{o}C for 2 weeks and then cooked straight from frozen using each of the three methods highlighted above. (Albert et al., 2009a) discovered that oxidised starch provided the best adhesion regardless of cooking method. For microwave heating, all samples with a hydrocolloid adhesion performed better than when no hydrocolloid predust was applied.

(Salvador et al., 2005) looked at batter coatings for fried seafood without a pre-fry step. The addition of wheat starch, modified cornstarch, dextrin, dried egg and gluten among others were considered. Dextrin gave the best crisp texture due to the highest degree of crispiness and flakiness. Gluten gave a lower end oil uptake than other ingredients and the control. The hydrocolloids had no impact on the colour of the product. The proteins increased water retention so it may be of interest to incorporate these into the end batter.

(Jia et al., 2014) looked at improving hydrocolloid characteristics in angel food cake by modifying the thermal and physical properties of frozen batter. This research did not consider batters in a microwave environment, although microchips are frozen prior to being reheated and so the effect of freezing on hydrocolloid functionality must be considered. CMC (carboxymethylcellulose), LBG (locust bean gum) and XG (xanthan gum) were tested. The frozen batter was stored at -18^{o}C for 1,2 and 4 weeks prior to experimentation or was entered into a freeze thaw cycle to observe refreezing effects. Thawing was achieved by placing in a fridge for 10 hours at 6^{o}C. The cycles were as follows;

1) 1 week frozen storage and thawed
2) 1 week frozen, thawed, 1 week frozen, thawed
3) 1 week frozen, thawed, 1 week frozen, thawed, 2 week frozen, thawed.

(Jia et al., 2014) discovered that freeze thawing the batter resulted in a higher ice melting enthalpy in all samples. Frozen storage 'led to the formation and growth of ice crystals and freeze thawing accelerated the growth of ice crystals.' Addition of hydrocolloids, regardless of type, inhibited ice formation and growth in the batter. 1% CMC was most effective at preventing ice recrystallization. It was also able to retain gas more successfully during frozen storage which could aid in preservation of crispy batters in the microchip product. (Carrascal, 2015) found that addition of carbon dioxide to tempura batter resulted in a crispier product on reheating in a conventional oven through the creation of air bubbles.

1.8.3.5 Functional Properties of Hydrocolloids- Charges

The hydrocolloids are primarily going to be used to provide a physical barrier for water migration whilst the NaCl is believed to interact with the microwave to cause surface drying due to being charged when dissociated. However, (Chaplin, 2015) has discussed hydrocolloids having charges which could be beneficial for this project. He refers to hydrocolloids as 'hydrophilic polymers of vegetable, animal, microbial or synthetic origin that generally contain many hydroxyl groups and may be polyelectrolytes.' According to (Chaplin, 2015) alginate, CMC, carrageenan, gum arabic, pectin and XG are all polyelectrolytes. 'Charged groups ensure strong hydration' which is important in terms of water binding ability. Counter ions and co ions (meaning they have the same charge as the polyelectrolyte) make the hydrocolloid behaviour even more complex.

(Vlachy, 2008) states that polyelectrolytes are 'polymers consisting of monomers having groups which ionize in water' and are not limited to hydrocolloids but may also be structures such as DNA. They also appear in many different shapes such as chain like in the case of DNA, globular or micelles and colloids. The fact that polyelectrolytes become

ionisable in water is important as it suggests polyelectrolyte hydrocolloids will also be able to create heating within a microwave environment and so promoting surface drying as well as providing a physical barrier. If the correct hydrocolloid could be found that provides desirable surface heating and defence against water migration this could even negate the need for NaCl in the coating. (Chaplin, 2015) states that hydrocolloid ionisation abilities are different. This is because a proportion of the counter ions present in polyelectrolyte hydrocolloids remain 'tightly associated' with the polyelectrolyte and so are trapped within its electric field. This reduces activity and mobility and if dilution occurs, the difference between different hydrocolloids increases.

1.8.3.6 Functional Properties of Hydrocolloids- Water Binding Ability

The hydrocolloid chosen needs to be able to bind enough water to allow dissociation and interaction within the microwave field as well as the ability to hold on to that water and prevent moisture migration from the core to the surface.

(Torres et al., 2012) looked at the water adsorption isotherms of CMC, guar, LBG, tragacanth and XG. The moisture content of the hydrocolloids increased with increasing water activity at every temperature measured and also decreased when the temperature increased at constant water activity. They found that different hydrocolloids had a different ability to attract and hold water. CMC performed the best with guar gum the worst in terms of water binding ability. (Torres et al., 2012) attribute this to the 'presence of acid and ionic units in the chemical structures of the higher water binding hydrocolloids.'

Chapter 2
Final Materials and Methods

As the research focusses on investigating the uncoated base product and the development of a coating and it subsequent application; the methods section shall be separated into two parts. As many of the methods needed to be developed by the investigator chapter 3 is dedicated to understanding how the final methods outlined below were determined.

2.1 Final methods for understanding the dielectric, physical and chemical properties of the base product

2.1.1 Frozen Storage of Base Product Methods

McCain microchips were provided for 8 weeks. As observed in table 2-1 during the first week 420 boxes of microchips were delivered. These are referred to as the control samples. Control samples were kept in a domestic freezer at -18 ^{o}C for 8 weeks. Every week up to 30 boxes would be removed for use in sensory panels and acoustic and mechanical testing. Every other week 60 boxes would be provided 2 days before each sensory panel. These products are referred to as the fresh samples.

w/c (week commencing)	19-Oct	26-Oct	02-Nov	09-Nov	16-Nov	23-Nov	30-Nov	07-Dec
Practical number	1	2	3	4	5	6	7	8
Number of boxes for shelf life & testing CONTROL	**420**	-	-	-	-	-	-	-
Number of boxes for shelf life & testing FRESH	-	**60**	**60**	**60**	**60**	**60**	**60**	**60**
Taste Panel	✓	✓	✓	✓	✓	✓	✓	✓
Texture Analysis on frozen and cooked products	✓	✓	✓	✓	✓	✓	✓	✓
Recon Loss	✓	✓	✓	✓	✓	✓	✓	✓

Table 2-1 Delivery Schedule of Control and Fresh Chips and the Tests Performed

2.1.1.1 Acoustic and Mechanical Method

For this series of experiments the AED was broken and measurements were not possible. Only mechanical measurements could be taken.

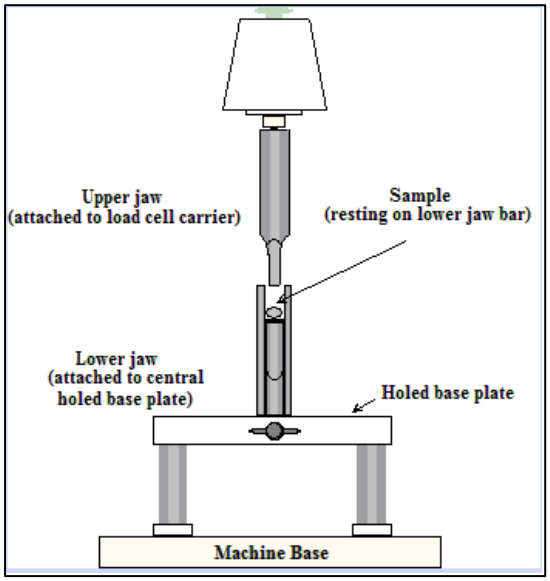


Figure 2-1 Volodkevich Jaw Testing Apparatus (StableMicroSystemsApplicationStudies, 2016)

Mechanical measurements were made using a Volodkevich jaw probe attachment connected to a Stable Microsystems Texture Analyser with a 30 kg load cell (StableMicroSystemsApplicationStudies, 2016). A return to start test was selected with a probe speed of 1 mm/s for 5 mm adopted. This was due to the product thickness being recorded as 5mm. The equipment used is observed in figure 2-1.

Measurements were taken on samples in the following conditions;

1) Frozen Control products
2) Cooked Fresh products
3) Cooked Control products

Samples used for the frozen storage investigation were from boxes given to the sensory panel with one chip being taken from the first 6 boxes given to sensory panellists. For the first 2 weeks mechanical and acoustic data was generated 3 times a week. After this 2 week period samples were only tested once a week for their acoustic and mechanical properties. Mechanical data was generated by the investigator and sensory panels were conducted by (Beasley, 2015). Cooked samples were heated in a Daewoo 700 W microwave oven (model number KOR-6L 155L) for 2 minutes 40 seconds and left to rest for 1 minute.

2.1.1.2 Sensory Panel

Acceptability Test

Instructions: Please evaluate the given sample on the following attributes:

1. OVERALL how would you rate this sample?

Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like or Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

2. How would you rate the TEXTURE of this sample?

Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like or Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

3. How would you rate the COLOUR of this sample?

Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like or Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

4. How would you rate the FLAVOUR of this sample?

Dislike Extremely	Dislike Very Much	Dislike Moderately	Dislike Slightly	Neither Like or Dislike	Like Slightly	Like Moderately	Like Very Much	Like Extremely

Figure 2-2 Sensory Panel Questionnaire Acceptability Test for Frozen Storage Experiment (Beasley, 2015)

Figure 2-2 observes the sensory questionnaire completed by panellists during the investigation. Once a week for 8 weeks and after 7 months an uncoated microchip product was tested against a fresh uncoated microchip product to investigate the effect of storage on end product satisfaction. Untrained panellists were asked to rate each product using a 9 point hedonic scale from dislike extremely (1) to like extremely (9). An average score over 5 indicated more like ratings whilst an average score under 5 indicated more dislike ratings.

During week 1 there was only one product called the control sample. For the remaining investigation fresh and control products were provided as discussed in section 2.1.1. Four different attributes were considered; overall rating, texture, colour and flavour. All samples were given a code to prevent panellists from knowing which product was fresh and which was control. Further to this panellists were asked to write down any words they would use to describe the product. All data collected was anonymised with panellists referred to by number.

2.1.2 Dielectric Properties of the Base Product Methods

2.1.2.1 Measurement of Microchip Inner using SPDR

2.1.2.1.1 Dielectric Equipment

A Split Post Dielectric Resonator was attached to an E5071CEP ENA series Network Analyser from Agilent Technologies and operated at the frequency 2.69 GHz. Before any tests were performed the network analyser was left running for 90 minutes as per the operating procedure. An overview of how this machinery carries out its function is provided in section 1.4.7.3.

2.1.2.1.2 Sample Preparation

Figure 2-3 Preparation of Uncoated Microchip Inner (Outer Layer Removed) for Insertion into SPDR

Frozen microchips from the same batch had their outer layer removed using a potato peeler. They were placed on cling-film and allowed to thaw for 10 minutes so that they could be moulded together. The cling-film was placed over the chips and a rolling pin was applied to mould the chips into one complete slab measuring 70mm x 70mm. Clingfilm was used to retain sample and to prevent moisture from leaving the sample. Samples that were frozen when measured were placed within a domestic freezer at -18 ^{o}C ±2 ^{o}C overnight. Prior to testing in the SPDR the samples were inserted into vacuum bags of 90 mm x 90 mm and sealed using a Model J-V002 vacuum sealer provided by the Food Machinery Company Limited. Prior to each experimental session the Q factor of the empty SPDR cavity and empty vacuum bag was recorded before the sample was inserted into the bag. The sample in the bag was then inserted into the cavity at which point the altered Q factor was recorded. The Q factor of the sample minus the Q factor of the vacuum bag was inputted into a

computer program provided by Agilent Technologies which allowed for the dielectric constant and dielectric loss to be calculated.

2.1.2.2 Measurement of 100 g uncoated microchip product

A custom built cavity to represent the dimensions of a microwave cavity was attached to an Agilent Technologies Network Analyser and operated at the frequency 2.45 GHz. The frequency, Q factor and insertion loss were recorded for all samples tested. Testing conditions differed dependent on the sample being tested.

2.1.2.2.1 Ambient Measurement

Experiments were performed in a laboratory with no special soundproofing or temperature control measures. The measurements were conducted at 22 ± 2 ^{o}C. Prior to tests being conducted the Q factor, insertion loss and frequency were recorded. Samples were inserted into the cavity with the lid fitted tightly within 5 seconds. The changing Q Factor, insertion loss and frequency were recorded every 1 minute for 45 minutes.

2.1.2.2.2 Temperature Dependent Measurement

The cavity was placed in a Genlab OV general purpose oven made from stainless steel and containing a built in fan. It has internal dimensions of (H x W x D) 45 x 49 x 46 cm and external dimensions of 58 x 85 x 48 cm. The oven was preheated to 180 ^{o}C for 30 minutes. Prior to sample being inserted into the cavity the Q factor, insertion loss and frequency were recorded. Samples were placed in the cavity and the cavity lid tightly sealed. The oven door was closed. The Q factor, insertion loss and frequency was recorded at different time intervals dependent on the experiment.

Measurement Method A

The Q factor, insertion loss and frequency of the samples was recorded every minute for 30 minutes.

Measurement Method B

The Q factor, insertion loss and frequency was recorded every 15 seconds for 45 minutes.

2.1.3 Ionic Component Determination Methods

The (AOAC, 1980) and (Kirk and Sawyer, 1991) provided the method for ashing. 2 g of raw Innovator potatoes (Sample A) and 2 g of the fried and frozen product with the outer skin removed (Sample B) were ashed. Six platinum dishes were rinsed with deionised water and placed in a furnace at 500 ^{o}C before being placed in a desiccator and cooled for 30 minutes. The plates were weighed accurately using an analytical balance to 4 decimal places with 2 g of Sample A and Sample B added to three platinum dishes each. Samples were burned using

a Bunsen burner in a fume cupboard before being transferred to a furnace at 500ºC. Samples were burned until smoke was no longer produced from the sample. The samples were kept in the furnace for 4 hours. After this time no carbon material was present. Samples were placed in a desiccator for 30 minutes and subsequently weighed once cool. Before the samples could be used 1cm^3 of hydrochloric acid was added to each sample. After 10 minutes, 10cm^3 of deionised water was added to each sample dish and left for 15 minutes. Each sample was then transferred to a 100cm^3 volumetric flask and brought to volume with deionised water via performing washings on the platinum dish containing the sample. This enables all dissolved ions to be kept in solution. In total 6 standard solutions were created; 3 for the innovator potato and 3 for the microchip product. Figure 2-4 depicts how the samples were prepared prior to AAS measurement.

Figure 2-4 Sample Preparation of Raw Innovator Potato and Microchips Inner Layer for AAS

2.1.3.1 Standards Preparation

Standards of each ion needed to be created so that the ions present in the sample could be measured. The concentrations produced are observed in table 2-2.

Ion Type	Concentrations µg/ml	Dilution Factor
Sodium	1, 2, 3, 4, 5	0
Magnesium	0.1, 0.2, 0.3, 0.4	0
Manganese	1, 2, 3, 4, 5	0
Zinc	0.4, 0.8, 1.2, 1.6	0
Potassium	1, 2, 3, 4, 5	50
Calcium	1, 2, 3, 4, 5	50
Copper	1, 2, 3, 4, 5	0
Iron	1, 2, 3, 4, 5	0
Phosphate	873, 1746, 2619, 3492, 4365	2.5, 2

Table 2-2 Concentration of Ions Produced and Dilution Factor from Source Required to Achieve Final Concentration

Further dilutions of the phosphate standard had to occur as the absorbance reading of the samples was too low for the concentration to be calculated from standard curves. According to (Kirk and Sawyer, 1991) if absorbances are >1 for the standard curves then further dilution is required. In terms of the 6 samples tested a dilution of 100 occurred as 1cm^3 of the 100cm^3 sample bulk was created to allow testing to occur for each ion. This has been factored into calculations for the concentration of ions in the solution. 10% lanthium chloride was added to the sample when measuring calcium to prevent phosphate from interfering with the release of calcium ions.

2.1.3.2 AAS Measurement Procedure

The samples were measured using a Pye Unicam SP9 Atomic Aborbance Spectrophotometer by diluting the standard sample down and acidifying as explained in section 2.1.3 and 2.1.3.1. For each element measured a series of standards was created and the absorbance measured. The sample was then diluted by a factor of 100 and the absorbances of all 6 samples measured for each ion with the hallow cathode lamp being changed for each ion group to be tested. Standard curves were produced for all ions. Figure 2-5 shows an example standard curve produced for zinc.

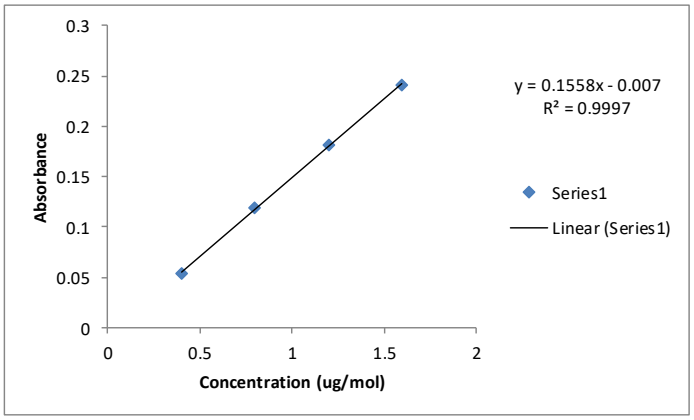


Figure 2-5 Standard Curve Produced for Zinc

The absorbance of the sample was measured against a standard curve to determine the concentration of the sample in relation to the standards. Equation 2-1 was used to determine the ion content in mg/100 g of sample whilst considering dilutions of both the sample and standards made during the preparation process.

$$\frac{Mean\ Concentration\ Calculated\ (\mu g) * 100}{Mean\ Concentration\ After\ Sample\ Correction\ (\mu g) * Dilution\ Factor}$$

$$Mean\ Concentration\ After\ Dilution\ Factor\ (\mu g)/1000000$$

$$Mean\ Concentration\ (g)/Mean\ Sample\ Weight\ (g)*\ 100$$

$$Sample\ Concentration * 1000 = mg/100g$$

Equation 2-1 Determining Ion Content in mg/100g of Sample

In the case of sodium chloride the values for sodium were multiplied by 2.5 to give sodium chloride values as this is a known conversion factor (Kirk and Sawyer, 1991).

2.2 Final methods for understanding the underlying principles required for the creation of a coating which promotes product crispiness

2.2.1 Dielectric Activity of Starch Powders Method

2.2.1.1 Dielectric Equipment

A Split Post Dielectric Resonator was attached to an E5071CEP ENA series Network Analyser from Agilent Technologies and operated at the frequency 2.69GHz. Before any tests were performed the network analyser was left running for 90 minutes as per the operating procedure. An overview of how this machinery carries out its function is provided in section 1.4.7.3.

2.2.1.2 Sample Preparation

An empty vacuum bag measuring 90 x 90 mm was measured in the SPDR with the Q factor and thickness of sample recorded. 2.5 g of every powder tested using the SPDR were placed in each empty vacuum bag. To avoid powder compromising the seal the sample was measured to be only 70 x 70 mm. Each powder was flattened using a metal ruler and paint roller and then sealed using a Model J-V002 vacuum sealer provided by the Food Machinery Company Limited. A 1kg weight was applied to each vacuum bag on sealing to ensure it remained in place. Prior to each experimental session the Q factor of the empty SPDR cavity and empty vacuum bag was recorded before each powder was inserted into the cavity. The resultant Q factor for the empty vacuum bags and vacuum bags filled with sample was inputted alongside the sample thickness into a computer program provided by Agilent Technologies which allowed for the dielectric constant and dielectric loss to be calculated. The dielectric constant and loss of the empty vacuum bag was subtracted from the vacuum bag filled with starch so that only the effect of the starch was observed. As the two dielectric factors are a ratio of the permittivity and use the same base units (Farads/metre) they are considered dimensionless. Different powders were produced for use in the SPDR and these are considered overleaf.

2.2.1.2.1 Native Starch Preparation

Ten native starches used by the manufacturer which form components of their batters were delivered for use in the SPDR. Each type of starch was given a unique code so the identity of each starch could remain confidential. Table 2-3 shows the native moisture contents of the 10 native starches.

Name of Coded Starch	Native Moisture Content (%)
MU56	11
YG10	10.5
DW69	11
OV12	12
YF61	11
NU06	11
YE60	12
K457	12
PJ46	14
BA75	18

Table 2-3 Native Moisture Content of the 10 Coded Starches

2.2.1.2.2 Moisture Measurement

Prior to measuring samples in the SPDR the starting moisture of each starch powder was determined. The method followed was provided by the (AOAC, 1980). 30 stainless steel pans with lids and glass rods were placed in an oven at 105 ^{o}C for 30 minutes. They were placed in a desiccator for 30 minutes and left to cool. The pans, lids and glass rod were weighed prior to the addition of 2 g of each starch sample. Three repeat 2 g measurements of each starch were placed into each steel pan resulting in a total sample size of 30. Each 2 g of starch was weighed accurately. Sand was added to each pan in the quantity of 2.5 g to prevent clumping issues. The samples were placed in the oven at 105 ^{o}C with lids beneath each pan and left overnight. Samples were transferred to a desiccator and the lids were placed on top of each steel pan. The samples were left to cool before being weighed to 4 decimal places. Equation 2-2 was applied to determine the moisture of each starch.

$$\frac{Total\ Weight - Weight\ After\ Oven}{Total\ Weight - (Total\ Weight - Weight\ of\ Sample)}\ x\ 100$$

Equation 2-2 Dry Weight Basis Moisture Calculation

2.2.1.2.3 Creation of Saturated Solutions & Moisture Isotherms

As moisture is believed to be a driving factor for dielectric activity within the microwave the moisture contents of all 10 native starches were altered.

Relative Humidity	Salt Required	Preparation Condition
0% RH	Phosphorous Pentoxide	Dry powder due to violent reaction with water
33% RH	Magnesium Chloride	Make supersaturated solution
75% RH	Sodium Chloride	Make supersaturated solution
95% RH	Potassium Nitrate	Make supersaturated solution
100% RH	Distilled Water	Make supersaturated solution

Table 2-4 Salts Used to Achieve Different Relative Humidity Conditions and Preparation Conditions

Table 2-4 shows the different salts used to alter the moisture contents of the 10 starches. According to (Greenspan, 1977) different salts are able to provide different relative humidities when present in a saturated solution. A saturated solution is referred to as a solution that contains as much solute as can be dissolved in the solvent at the temperature of the solution. As the production of a saturated solution is dependent on the temperature of the solution, solubility curves for the different salts was considered.

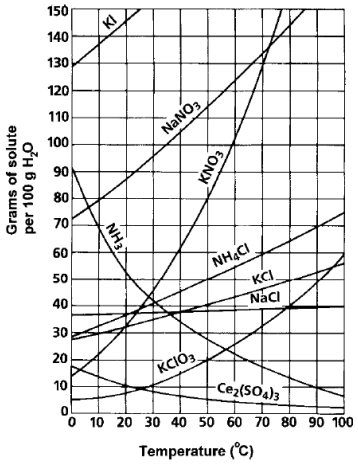


Figure 2-6 Solubility Curves of Salts (CheggStudy, 2017)

Unfortunately the solubility curves for magnesium chloride could not be determined so by observing (Greenspan, 1977) the amount of magnesium chloride was determined. A fully saturated salt solution was required and the samples were being stored at ambient so the remaining salt solutions were prepared at temperatures of 40 ^{o}C to ensure the salt solutions were saturated. Salt was added until salt crystals could be physically observed and the sample said to be supersaturated. Saturated salt solutions were made of 150 ml using the preparation condition highlighted in table 2-4. On creation of the saturated solutions, sodium chloride, magnesium chloride and potassium nitrate was added until the solution was supersaturated and the salt crystals no longer dissolved. Each 150 ml salt solution was placed in a separate desiccator with vacuum grease applied to the lid of each desiccator prior to sealing. Six desiccators were allocated to phosphorous pentoxide with 150 g of dry phosphorous pentoxide being deposited in the bottom of each one. This was because the starting moisture of the starches was different and so a preliminary stage was required to reduce the moisture contents to a similar level before the starches were placed in the five different relative humidity conditions.

Preliminary Starch preparation

Three 50 g weights of each of the 10 native starches were measured using a 4 point scale and placed in stainless steel pans before being deposited in the phosphorous pentoxide desiccators . Small holes were placed throughout each powder sample to ensure that the surface did not develop a crust preventing further moisture loss thus allowing absorption to occur as opposed to adsorption. Samples were weighed after 10 days and the moisture content was determined using the equation 2-2. After 10 days the three samples were mixed together to provide a more homogenous sample set.

Starch preparation using different relative humidities

30 g of each native starch was weighed using a 4 point scale and placed in a stainless steel pan which was also weighed prior to sample being added. Starches were weighed at 0, 2, 6, 24, 72, 120, 240 etc. hours until the weight of each starch reached an equilibrium. Figure 2-7 shows the effect of placing sample BA75 in different relative humidity conditions. As can be observed the change in weight is negative at 0% RH and positive at 100% RH thus showing that the test methodology functioned as predicted. However, for all samples the highest positive change in samples weight occurred at 95% RH meaning that more moisture was inserted into the sample at this RH instead of 100% RH. This could be because the saturation point of the starches has been reached and so excess moisture is not taken up by the starches.

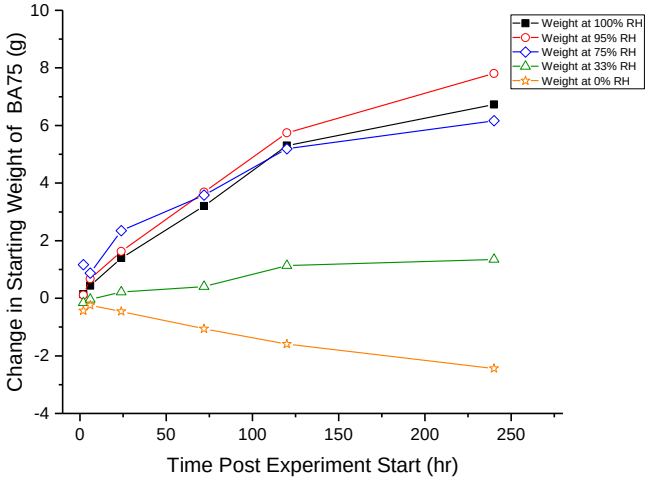


Figure 2-7 Change in Weight of Sample BA75 as a Function of Time and Relative Humidity (100% RH, 95% RH, 75% RH, 33% RH, 0%RH)

The R^2 function was used to determine when a sample had reached a plateau. The reasons for this are outlined in section 1.6.1.5. Once the starches had reached equilibrium they were measured in the SPDR using the method indicated in section. 2.2.1.2. Ten repeats of each native starch at each relative humidity was produced. Figure 2-8 shows how the constant rate and falling rate were determined with linear fits denoting constant rates and non-linear behaviours denoting falling rates.

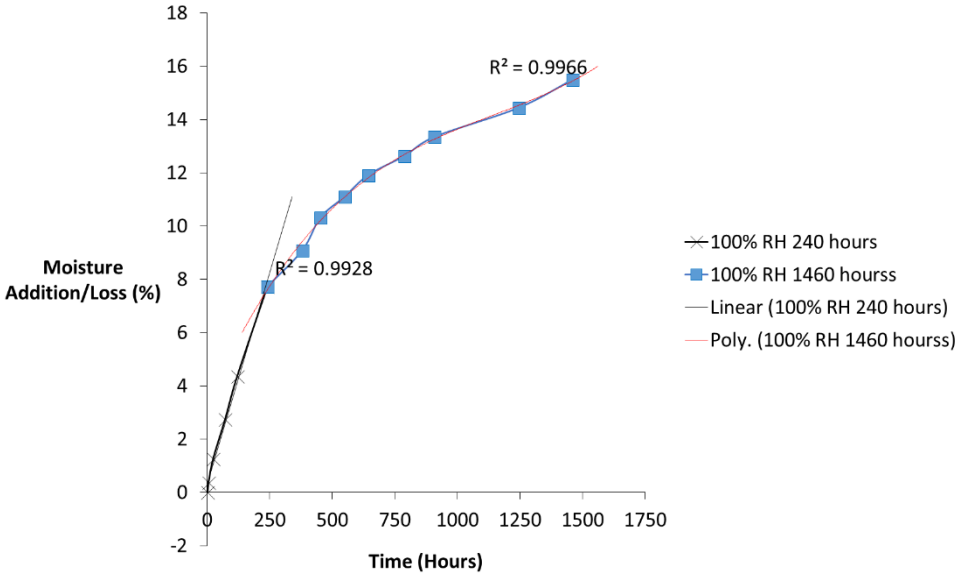


Figure 2-8 Moisture Added to Sample YE60 as a Function of Time on Storage at a 100% RH condition

First R^2 value is constant rate (linear fit), Second R^2 value indicates falling rate (non-linear polynomial fit)

2.2.1.2.4 Gelatinised Starch Samples

10 native starches were sent by McCain Foods for investigation of their dielectric properties. Three batches of each starch were produced of 500 g each. Native starch samples were heated at 105ºC using a heated stirrer plate.

$$\frac{15\ x\ total\ weight\ of\ sample(g)}{100 - moisture\ content\ of\ starch}$$

Equation 2-3 Equation to Achieve 15% Starch Solids

Distilled water was added to each starch dependent on their starting moisture to achieve a total solids of 15% by using equation 2-3. The values for these can be found in Table 2-5. Any moisture that evaporated on heating of the starch was then added on a weight basis to the gelatinised starch. Each 500 g batch of starch was placed on aluminium foils measuring 28 cm x 28 cm and subsequently heated in the oven at 105 ºC until the samples had dried.

Starch ID	Amount of Starch Required (g)	Amount of Water Required (ml)	Starting Moisture of Starches (%)
K457	84.87	415.13	11.63
MU56	84.19	415.81	10.92
PJ46	87.06	412.94	13.85
BA75	91.74	408.26	18.25
YG10	83.81	416.19	10.51
YE60	84.93	415.07	11.69
OV12	85.64	414.36	12.42
YF61	83.95	416.05	10.66
NU06	84.64	415.36	11.39
DW69	84.22	415.78	10.95

Table 2-5 Amounts of Starch and Water Required to Produce Samples with 15% Solids Content as a Function of each Starches Native Moisture Content

A powder from each of the samples was produced by using a ball mill. Each 1.5 kg of gelatinised starch films were placed in the ball mill and rotated at 30 rpm for 2 hours. This resulted in a fine starch powder being produced. The starch powders were then sieved to

separate the particle sizes. The most abundant particles produced were collected and investigated in the SPDR using the sample preparation observed in section 2.2.1.2.

2.2.1.2.5 Statistical Analysis

34 Three, Two and One Factor ANOVAs were performed. The full list of each test may be found in section 5.1.5. All One and Two Factor ANOVA tests were performed using Microsoft Excel. A further Three Factor ANOVA analysis was performed using SPSS Version 22 to observe the three way interaction between the Starch Type, Relative Humidity and Starch Processing Method.

2.2.2 Initial Coating Methods

2.2.2.1 Coating Production and Application Method

Coatings were applied to the product during different stages in the process; pre fryer, post fryer and post freezer. Pre and post fry coating applications were conducted at the McCain factory. All coatings were created by adding 10% sunflower oil to the % of CMC required in the total solution. This was mixed manually until a smooth paste was formed. Water from the factory in Scarborough for the pre and post fryer coatings and deionised water at the University of Leeds was added rapidly to the pastes formed. The mix was shear mixed via a Silverson shear mixer operating at 1200 rpm for 10 minutes. For coatings requiring NaCl this was added to the mix after the first shear mixing stage and underwent further shear mixing for 5 minutes at 1200 rpm. The CMC used to create the coatings was Clear + Stable CRT 30 CMC provided by Dow.

2.2.2.1.1 Pre and Post Fryer Application Method

Name of Solution	CMC Type	CMC (%)	Sodium Chloride (%)
A	CRT30	2	0
B	CRT30	2	2
C	CRT30	2	4
D	CRT30	3.5	0
E	CRT30	3.5	2
F	CRT30	3.5	4
G (control)	-	0	2 (+10% oil)
H (control)	-	0	4 (+ 10% oil)

Table 2-6 Trial Plan for Pre and Post Fry Applications

Table 2-6 gives the trial plan for pre and post fry applications. Two control samples were produced containing 2% and 4% (0.3422 mol/L and 0.6844 mol/L) NaCl, 10% sunflower oil and water. Coatings were applied on line in the McCain Foods factory and then placed in a freezer at -40^{o}C. 500 g of each product was produced. The product the coatings were applied to was uncoated microchips of 0.5 inch thickness. The products were transported to the University of Leeds where they were stored in a domestic freezer at -18±2 ^{o}C. Samples were tested after being stored for 4 weeks.

2.2.2.1.2 Post Freezer Application Method

Products were produced in the same way as pre and post fry coating applications with the exception that no coating was added to the product before it was placed in a domestic freezer at -18±2 ^{o}C . These products were then sent to the University of Leeds for the coating to be applied post freezing. As well as products produced in the pilot plant shop bought McCain Home Frys were acquired and coated with the CMC/sodium chloride coating at the same time as the uncoated microchip base product. Deionised water was used to create the post freezer coatings. After the products were coated they were placed in a

Frulinox model no. BF05SET ABB BF051 blast freezer for 25 minutes at -40ºC and then transferred into a domestic freezer at -18±2 ºC. Samples were tested after being stored for 4 weeks. The age of the Home Fry product before being coated could not be ascertained.

2.2.2.2 Acoustic and Mechanical Method

A Volodkevich jaw probe attachment was connected to a Stable Microsystems Texture Analyser with a 30 kg load cell (Figure 2-9). An acoustic envelope detector (AED) was also attached to a Bruel and Kjael free field microphone with a diameter of 8mm positioned 1 cm away from the Volodkevich jaw probe at a 45º angle (Figure 2-9). The gain of the acoustic envelope detector was set to 2 and a filter was applied to eradicate background noise below 1 kHz. 1 kHz was set as the limit 'due to the preponderance of environmental noises' below 1 kHz (Chen et al., 2005). The data acquisition rate was 500 points per second. The probe was positioned 1 cm above the sample being tested but data was not recorded until a trigger force of 0.049 N was detected. The test speed used was 0.1 mm/s. Each test was conducted over a distance of 7.5 mm. One sample at a time was measured for its top height, bottom height and width before the chip was placed in the Volodkevich jaw attachment and the test started. Prior to measurement 3 chips were heated for 2 minutes 40 seconds according to manufacturer instructions.

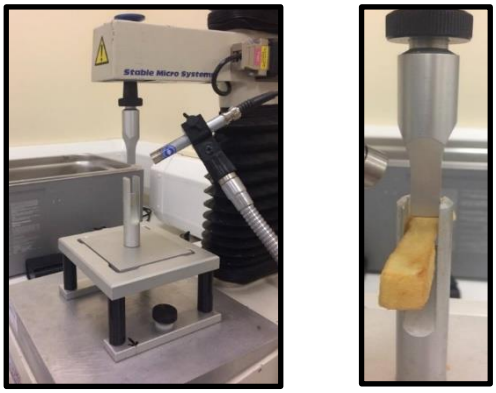


Figure 2-9 Volodkevich Jaw Attachment Piercing a Chip with Acoustic Envelope Detector Recording the Sound Produced

2.2.3 First 8 week Study

Due to time constraints only the below samples were produced;

1) Uncoated microchip product using Maris Piper potatoes and cut to 0.5 inch
2) 2% CMC 4% sodium chloride product using Maris Piper potatoes cut to 0.5 inch

Coatings were created using the method in section 2.2.2. All coatings were applied in the McCain Foods pilot plant during the pre fry, post fry and post freeze application and so used water provided by the pilot plant. The fry loss (difference in weight of product entering the fryer and exiting the fryer as a %), the dry loss (difference in weight of product entering the

dryer and exiting the dryer as a %) and the pick-up (difference in weight of product without a coating and with a coating as a %) were recorded for all three application stages. After product was coated it was placed in a blast freezer for 30 minutes at -40 ^{o}C and then transferred to a domestic freezer at -18 ^{o}C. Samples were transported to the University of Leeds 4 days after production and tested every week for 8 weeks. Samples were placed in one 9kg capacity plastic bag each and stored in cardboard boxes.

2.2.3.1 Recon Loss

The Recon Loss was a method given to the investigator by McCain Foods. The product was weighed before entering the microwave and weighed after cooking in the microwave both immediately and after 1 minute standing time as per manufacturer instruction. The microwave used throughout experimentations was a Daewoo 700 W microwave oven with model number KOR-6L 155L. Samples were heated for 2 minutes 40 seconds and for 4 minutes. The weights recorded for each sample were inserted into equation 2-4;

$$\frac{sw - ew}{sw} \; x \; 100$$

Equation 2-4 Recon Loss

where sw denotes the starting weight and ew denotes the end weight. Both are measured in grams. The % highlights the total moisture loss from the sample.

2.2.3.2 Acoustic and Mechanical Method

The acoustic and mechanical method used was the same base method found in section 2.2.2.2. 100 g of product was heated in a McCain microwave container for 4 minutes cooking time before 3 chips from each 100 g box were taken for acoustic and mechanical measurement. The experiment was also repeated with a 2 minute 40 seconds cook time as per manufacturer guidelines.

2.2.3.3 Variables extracted for further statistical analysis (PCA)

To present the acoustic and mechanical data the number of acoustic peaks has been counted. To present the mechanical data a range of variables have been calculated. These can be found in table 2-7.

Variable	Definition	Units
Area	The area under the force displacement curve. It is the sum of all Y axis data values divided by the number of points of data	N/s

	and multiplied by the sum of the X axis value differences.	
Number of Positive Peaks	The number of positive peaks present on the force displacement curve	n/a
Number of Negative Troughs	The number of negative troughs present on the force displacement curve	n/a
Average Gradient	Average gradient of force displacement curve	N/s
Average Drop Off	The average drop recorded between each positive peak and subsequent negative trough	N
Linear Distance	The length at which all points of the curve have joined together	No allocated units as is based on the data present on the x and y (in this case Time and Force so N/s)
Force at Failure	The force reading at first major microstructural failure	N
% through the chip at first failure	The % through the chip at which the first major microstructural breakdown occurs	%
Change in Force at Failure	The difference in force as the first microstructural breakdown occurs	N
Chip Width	Width of chip	cm
Chip Top Length	The longest length of the chip	cm

Chip Bottom Length	The shortest length of the chip	cm
Number of Acoustic events	Number of acoustic events recorded by the AED	n/a
Number of 2nd Derivative troughs	Number of negative troughs recorded across the testing window when taking the 2nd derivative	Ns^{-2}

Table 2-7 Mechanical Variables Extracted from Volodkevich Jaw and Acoustic AED Data Inserted Into Principal Component Analysis (PCA)

The length of the chip was taken twice with a top and a bottom length. This is because the chips are not equal rectangles due to the cutting process and instead have a shape reflecting a trapezium. According to (StableMicroSystemsApplicationStudies, 2016) the linear distance is useful in understanding crispiness as a crispier product tends to have a lot of fluctuations between positive peaks and negative troughs and so would result in a longer linear distance being produced. Once the variables had been calculated using the Stable Microsystems Exponent Software the variables were then inputted into Origin Lab Pro 2016 Software and a Principal Component Analysis (PCA) was conducted to determine where the variation in the samples was occurring. This was to better determine what differences existed between the samples.

The Recon Loss Data has not been subjected to statistical analysis as only one repeat each week could be performed. Experiments performed during the second 8 week study aim to provide a replicate of the data measured during the first 8 week study.

2.2.4 Second 8 week study

Coatings were produced using the method stated in section 2.2.2. All samples produced were created using water from the Scarborough pilot plant and no deionised water was used. Samples produced were;

1) Uncoated microchip product using Maris Piper potatoes and cut to 0.5 inch
2) 2% CMC 0% sodium chloride product using Maris Piper potatoes cut to 0.5 inch
3) 2% CMC 4% sodium chloride product using Maris Piper potatoes cut to 0.5 inch

15 kg of each coating was produced. Coatings were applied to the product in a pre fryer application only. The fry loss, dry loss and pick-up were all recorded. All products produced were placed in a blast freezer for 30 minutes at -40 ^{o}C before being transferred to a freezer at -18^{o}C. 6 kg of each product was produced. On transferring to the domestic freezer 3 kg of

each sample was placed into a Ziploc 9 kg capacity bag and sealed. Each bag measured 33 cm x 38.1 cm. Each of the two bags containing the same samples were labelled as either ‘experiment’ or ‘keep intact’ and placed in a McCain cardboard box. Each of the 3 cardboard boxes containing the samples were delivered to the University of Leeds 3 days after production.

2.2.4.1 Effect of Storage

Figure 2-10 Method for Storage of Samples During 2nd 8 Week Study

Figure 2-10 provides a visual depiction of the storage method of the samples produced. Only the bag of each sample labelled ‘experiment’ was used over the 8 week testing period. To investigate the risk of moisture evaporation on storage from opening and closing the bag, both the ‘experiment’ bag and the ‘keep intact’ labelled bag were opened for the same amount of time whilst sample was taken from the ‘experiment’ bag to be used during the investigation.

Figure 2-11 Weighting Technique For Samples Used in 2nd 8 Week Study

Figure 2-11 observes the measuring technique for measuring the sample weight during testing and storage. Both bags were weighed before and after sample was taken from the ‘experiment’ bag for each of the two coatings and control sample. This study of the effects of storage on moisture loss was conducted over an 8 week period.

2.2.4.2 Acoustic and Mechanical Method

The acoustic and mechanical method used during the creation of a crispier product work was the same base method as found in section 2.2.2. However, during these tests the test speed was set at 1mm/s. The reasons for this are explained in section 3.2.1.2.

2.2.4.3 Recon Loss

The method for Recon Loss used for the results in section 5.5.3.2 is the same method outlined in section 2.2.3.1 with the exception that the product was heated for 4 minutes only and not for 2 minutes 40 seconds.

2.2.4.4 DSC

Figure 2-12 Insertion of Sample into DSC Q20 Model with Inert Nitrogen Flow

A Ta Instruments DSC Q20 model with inert nitrogen flow was used to perform the Differential Scanning Calorimetry (DSC) analysis (Figure 2-12). The sample pans were not perforated and so were not sealed prior to undergoing experimentation. Products tested were those found in section 2.2.4. Due to the small sample size (10 mg) the outer skin of the product and the inner part of the product were tested separately for each of the three samples over the course of 8 weeks. The samples were stored in a domestic freezer at -18^{o}C and the top layer was removed by a Weck-Prep blade provided by Quorum Technologies and placed in a desiccator. Due to issues highlighted in section 3.2.2 the sample was not weighed and was inserted into the DSC. The DSC heated the sample from its starting temperature of -10 ^{o}C at an increase of 5 ^{o}C a minute until a temperature of 110 ^{o}C was reached for the first two weeks of testing. After the 2nd week of testing, the samples were heated at an increase of 5 ^{o}C a minute up to 150 ^{o}C due to interesting results gathered in the first two weeks. As the potato is non-homogenous only sample from the centre of each chip (in terms of length) was used in order to reduce natural variation. All DSC tests were started within 3 minutes of removing the sample from the freezer. All DSC data was collected with the assistance of Algy Kazlauciunas. For each sample the heat flow and the temperature were observed. Resultant data was analysed by Origin Pro to extract variables suitable for insertion into PCA analysis.

2.2.4.5 TGA

Figure 2-13 Insertion of Sample into Ta Instruments TGA Q50 Model with Inert Nitrogen Flow

A Ta Instruments TGA Q50 model with inert nitrogen flow was used to perform Thermogravimetric Analysis (TGA) (Figure 2-13). All samples tested were those found in section 2.2.4. Due to small sample size the outer skin of the product and interior of the product were tested separately. All samples were stored in the freezer until testing. Chips were then removed from the freezer and a Weck-Prep blade provided by Quorum Technologies was applied to the surface of the product to remove the top layer. The interior product was collected only from the middle of each chip (in terms of length). Collected sample was placed in a desiccator prior to insertion into the TGA. Due to issues highlighted in section 3.2.2 the sample was not weighed prior to each test beginning. All TGA tests started within 3 minutes of samples being removed from the freezer. The TGA heated the sample by 50^0C per minute for 2 minutes. After this point the sample was then held at this temperature for a further 2 minutes. This test time was chosen for comparison with recon loss values and to reflect the heating of the product in the microwave. The drying behaviour of the samples was ascertained by applying the coefficient of determination and regression fit to the data samples.

2.2.4.6 Dielectric measurement

The dielectric method used in section 5.5.3.7 is the same method outlined in section 2.1.2.2. For the first 2 weeks of the 8 week study measurement method A (section 2.1.2.2.2) was used. Due to the findings from the first 2 weeks it was decided that measurement method B would be used for the remaining 6 weeks of the study.

2.2.4.7 Moisture Measurement

The moisture measurement method can be found in section 2.2.1.2.2. The only exception is that sand was not added as there were no clumping issues with the potato based product. The longest chips were selected for measurement to try and reduce natural variability. The outer layer of the potato was removed from the inner part of the chip by applying a Weck-Prep blade provided by Quorum Technologies.

2.2.4.8 Variables extracted for further statistical analysis (PCA)

A PCA was chosen to observe the interaction between the variables tested. Mechanical and Acoustic Variables stated in table 2-7 were inputted into the PCA. Table 2-8 shows the remaining variables extracted from the raw data sets that were inputted into the PCA.

Variable	Definition	Unit
Max Acoustic Signal	Maximum sound level recorded across product testing	dB(SPL)
Recon Loss	Change in sample weight before and after heated in microwave for 4 minutes	%
Time at which Ice Melting ends	Subtracted from TGA data by R^2 function	min
Time at which Constant Rate Starts	Subtracted from TGA data by R^2 function	min
Time at which Falling Rate Begins	Subtracted from TGA data by R^2 function	min
Moisture Content	Moisture Content of sample measured gravimetrically	%
Slope at which ice is heating but not melting	Extracted from DSC. Provides the amount of change occurring in the heat flow relative to the temperature	n/a
Intercept at which ice is heating but not melting	Extracted from DSC. Point at which regression line will cross y axis (heat flow)	mW/^{o}C
Area under the peak at which ice is melting	Extracted from DSC and observes the energy required to cause the subsequent phase change	mW/^{o}C

Temperature at which heat flow is maximum at the peak when ice is melting	Peak temperature at which phase change occurs. Extracted from DSC	^{o}C
Onset Temperature of Ice Melting	Extracted from DSC	^{o}C
End Temperature of Ice Melting	Extracted from DSC	^{o}C
Area under the peak during bound water release/unknown mechanism e(Peak 2)	Extracted from DSC and observes the energy required to cause the subsequent phase change	J/min
Temperature at which heat flow is maximum at peak 2	Extracted from DSC. Related to moisture migration within the sample.	^{o}C
Onset Temperature of Peak 2	Extracted from DSC.	^{o}C
Minimum Q Factor	Minimum Q factor from dielectric experiment	n/a
Highest Insertion Loss	Maximum insertion loss from dielectric experiment	n/a
Time when lowest Q Factor Observed	Time at lowest Q Factor (min)	min
Time when maximum Insertion Loss Observed	Time at maximum Insertion Loss (min)	min
End of Test Q Factor	Last Q Factor Data Input	n/a
End of Test Insertion Loss	Last Insertion Loss Data Input	n/a

Table 2-8 Variables Extracted From Data Collected During 2nd 8 Week Study and Inserted Into PCA

Chapter 3
Method Development

A significant portion of time was spent developing methods which would allow representative data to be generated and further analysed. The main research developed an understanding of the base uncoated product leading to an understanding of the materials required for the development of a coated product that could provide crispness. Due to the wide scope of the project method development was required at all points across this research but predominantly in three areas;

1) Dielectric equipment and sample preparation
2) Measuring the physical properties of the uncoated and coated base product
3) Coating development

3.1 Dielectric Equipment and Sample Preparation

3.1.1 Custom built Cavity

A cavity was custom built to enable temperature dependent dielectric measurements to be made of foodstuffs placed within the cavity. However, to achieve this the cavity was placed within a conventional oven and heated to a set temperature and so a series of experiments were necessary to understand how the external temperature would affect the internal temperature of each sample.

3.1.1.1 Calibration of the Oven temperature

An experiment was required to confirm that the temperature within the cavity was identical to the temperature recorded on the digital display of the oven. Initially the plan was to place an infra red camera into the cavity to record the temperature over time. However, on outside communication (Collis, 2016) from Sylatech Ltd. it became apparent that the infra red camera could only provide temperature readings up to 65 ^{o}C and therefore this method had to be discarded. Instead copper constantan thermocouples were placed in the oven cavity to read the temperature over time. It was determined that a period of 30 minutes pre heating was required for the cavity to reach the temperature displayed on the digital oven reader. Figure 3-1 compares the digital oven temperature reading with thermocouples placed inside the oven cavity.

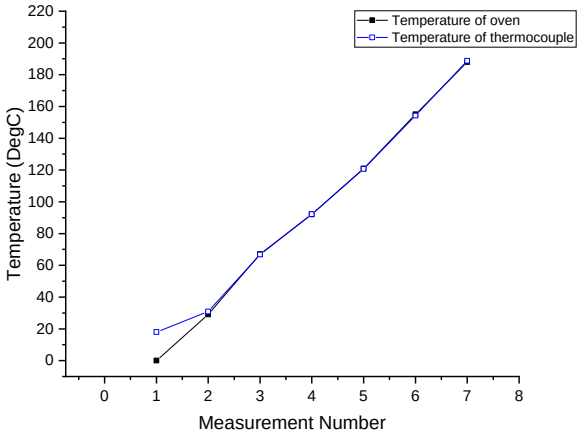


Figure 3-1 Comparison of Oven Temperature Reading (black line) and Thermocouple Temperature Reading (blue line) during same Measurement Period

After this 30 minute pre-heating time, the thermocouples reported the same temperature as the digital cavity and remained stable at the temperatures recorded. The reason measurement 1 in Figure 3-1 is different is that the thermocouple was recording ambient temperature yet the oven was not turned on and therefore a reading of 0 had to be recorded.

3.1.1.2 Determining the position of the samples

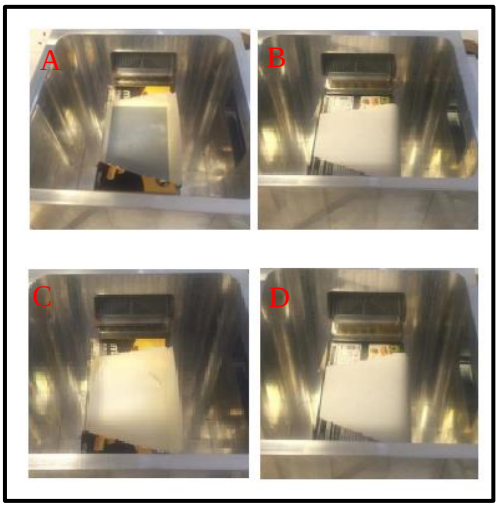


Figure 3-2 Position of Samples in Cavity

A= Susceptor Correct Orientation, B= Susceptor Incorrect Orientation, C= No Susceptor Correct Orientation, D= No Susceptor Incorrect Orientation

As this cavity was novel the importance of geometry and positioning had to be considered prior to beginning experimentation (Figure 3-2). Therefore the outer packaging was placed

into the cavity in different positions with 10 repeat measurements made of each orientation. The dielectric properties of the material were also measured with and without the susceptor element of the packaging. These measurements were all made at 22 +- 1 ºC.

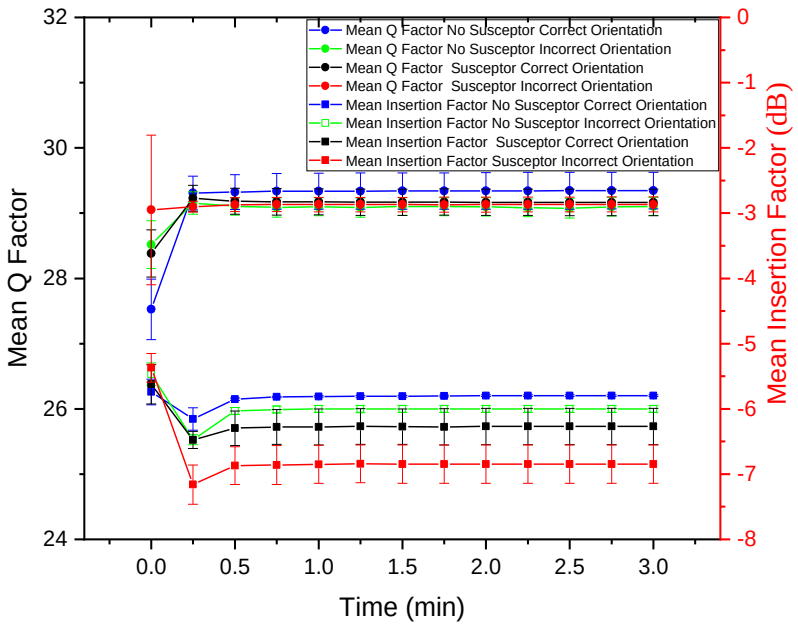


Figure 3-3 Mean Q Factor and Insertion Loss for Different Packaging Orientations at 22+/- 1 ºC using Novel Cavity

The standard error was low with the standard error of samples falling to <0.3 for the Q factor data and <0.3 for the insertion loss. There was an exception in that the Q factor and insertion losses of the empty cavity did vary although once the sample was inserted the standard error reduced to acceptable levels that were precise. As the behaviour for all samples was linear at ambient temperatures this shows that the novel cavity is capable of making repeatable measurements at ambient temperatures. There are differences in dielectric properties between the samples particularly when observing the insertion losses with the samples containing the susceptor providing the highest dielectric activity. Orientation is important with an incorrect orientation and susceptor present providing the highest insertion loss. However, as the insertion loss is affected by reflected losses, dielectric losses and copper losses yet the Q factor which is directly related to dielectric losses did not show as large a difference, this indicates that other losses are occurring dependent on how the sample is positioned. Therefore the susceptor was removed for all future dielectric measurements so that only the effect of the product would be observed. It was also decided to leave the microchip box in its correct orientation during testing as this best represents the current packaging use.

3.1.1.3 Determining the set oven temperature

The temperature at which to set the oven was determined. This is because microwaves could not be used as they would interfere with the dielectric measurement of the material. A temperature had to be determined that would heat the food to find changes in dielectric behaviour as the chips cook, and would not be too time consuming.

3.1.1.3.1 Preheated vs Non-Preheated

The dielectric behaviour of samples in a preheated and non-preheated domestic oven was determined. The oven temperature was set at 100 ºC. Sample A consisted of 100g uncoated frozen product and was placed immediately into the oven. Sample B consisted of 100g of uncoated frozen product and was placed in the oven after 30 minutes of preheating. Both samples were placed in the oven in the current packaging supplied by the manufacturer. The susceptor was not present. Both the Q factor and insertion loss was recorded as observed in figure 3-4.

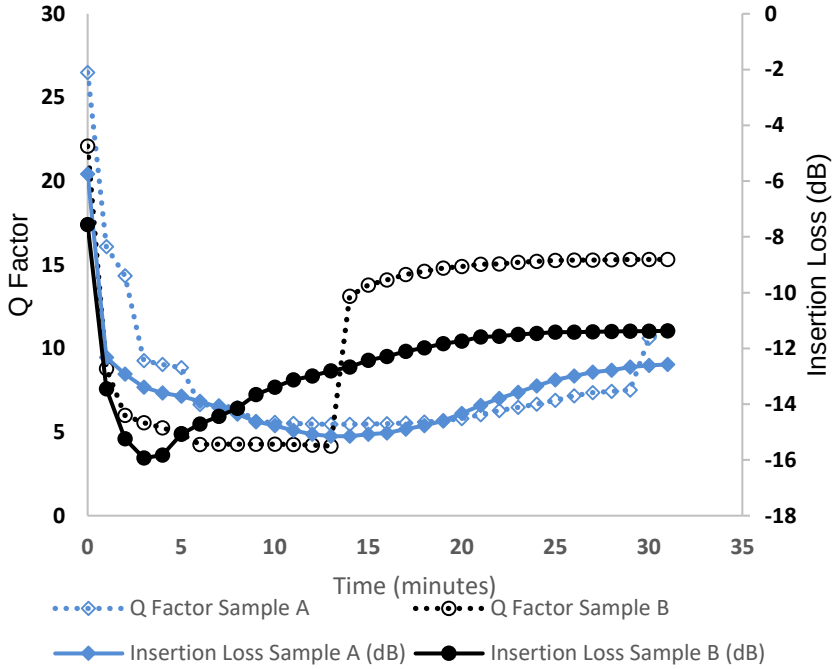


Figure 3-4 Q Factor (dash line) and Insertion Loss (solid line) of Sample A (non-preheated)(blue line) and B (preheated) (black line) at 100 ºC

For sample A (non-preheated) the oven reached 100 ºC on the digital oven temperature reader at 17 minutes. As discussed previously it takes 30 minutes from the temperature reading on the oven to be the actual temperature within the oven cavity.

Q Factor in relation to Dielectric Activity

In general when the Q factor reports a lower value the material within the cavity is said to have increased dielectric activity and when the Q factor increases the material is said to have lower dielectric activity.

Importance of ratio of Free:Bound Water in relation to dielectric activity

As explained previously free water is water that is free to interact with the frequency 2.45GHz. Bound water is water that is not free to interact with the microwave field. (Chaplin 2014) discusses the impact of free and bound water in terms of the frequency. He states that if water is free the water is able to rotate in the GHz frequency, if bound will rotate in the MHz frequency and if in the form of ice will rotate within the kHz frequency. This has implications for the product as it is placed in the microwave in a frozen state and so microwaves at the frequency 2.45 GHz may not be as effective at causing ice to rotate and heat the foodstuff.

Impact of Free:Bound water on the Q Factor in a preheated and non-preheated oven

In sample A (non-preheated oven sample) the temperature is increasing throughout the test compared to sample B which is heating the samples at a constant rate of 100ºC. The Q factor in the non-preheated sample is higher than the pre-heated sample, as in sample B the higher starting oven temperature is causing the bound ice to melt leaving it free to interact with the electromagnetic field, thus resulting in a material with higher dielectric activity and lower overall Q factor. The changes are also more drastic in sample B because the temperature is at 100 ºC. The Q factor decreases on addition of the chips; at minute 14 the Q factor sharply rises by 9 and begins to stabilise till the end of the test. The higher starting temperature causes the free water to evaporate which results in the Q factor rising as the material becomes less dielectrically active. In sample B the Q factor is observed to reach an equilibrium. On looking at the end product for sample B the sample had completely thawed but was still cold. In sample A the changes in Q Factor were less drastic and dropped in stages; by 10 on addition of the chips; by 5 two minutes later and then began increasing very gradually at minute 18. It is only towards the end of the test that the Q factor increases rapidly from 7 to 10. This is due to the temperature in the cavity rising over a period of 30 minutes and causing the gradual melting of ice crystals over a more prolonged period of time than Sample B. The increase in Q factor at the end of the test for Sample A indicates free water was still evaporating and this was confirmed when observing the sample at the end of the cook time. The sample was only partially thawed and ice crystals still present. Therefore by looking at the two samples it was hypothesised that the temperature was not

high enough to promote cooking of the food in a reasonable time frame. One would expect that at higher temperatures, these changes would occur more quickly due to the differences observed in the non-preheated and preheated samples. It would not be expected that the samples reach equilibrium in terms of the Q factor. The fact that sample B does so indicates a flaw with the novel cavity measurement technique. This is because the cavity has a metal lid which prevents moisture from leaving the system as it would be expected that the Q factor would continue to rise as moisture evaporates from the system.

Insertion Loss in relation to Dielectric Activity

The higher the insertion loss the better the material will perform in the microwave. However, as the insertion loss can be altered by reflected losses, dielectric losses and copper losses and does not explain the dielectric properties alone, only the Q factor will be discussed in relation to dielectric properties in this thesis. This is because the Q factor can be directly related to dielectric losses. However, it was decided that the insertion loss would still be measured and incorporated into the PCA observed in the final 8 week study.

3.1.1.3.2 Alternative oven temperatures considered

A pre-heated oven was determined as the least time consuming method to make dielectric measurements. It was also chosen because a microwave heats food rapidly and so a higher starting temperature is a way to best represent this. Therefore a starting temperature needed to be determined which would provide fast and representative results. From the previous experiment it was determined that 100ºC was not high enough to produce the desired end product. Therefore oven temperatures of 150ºC and 180ºC were considered (Figure 3-5). Six repeats for each temperature condition were conducted with the standard error of the mean applied to the resultant data.

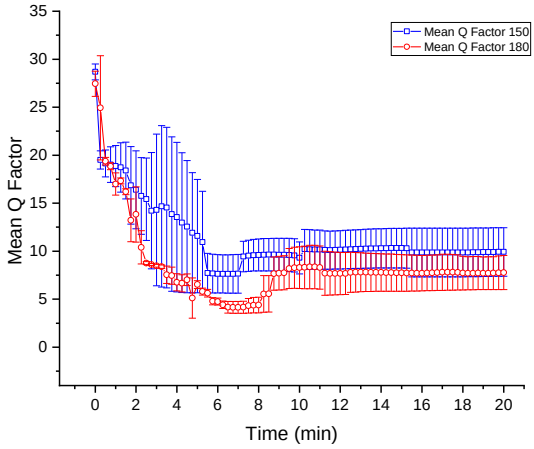


Figure 3-5 Mean Q Factor of 100g Uncoated Microchip Product at 150ºC (blue line) and 180ºC (red line) as a Function of Time

Q Factor in relation to Dielectric Activity

At the higher temperature the Q factor drops more rapidly than the lower temperature samples. This could again be an issue of free and bound water. Whilst free water will evaporate at 100ºC, bound water will need higher temperatures to cause a breakdown in the product structure which subsequently releases the water to interact with the microwave environment. This would result in a lower Q factor as overall more water is free to interact with the electromagnetic field. It would be expected that eventually the Q factor would begin to rise as moisture is removed from the sample via evaporation but this does not occur in the testing period. This is probably due to there being a lid on top of the cavity preventing moisture from completely leaving the system and so instead an equilibrium is reached. The 150 ºC temperature sample reached equilibrium more quickly than the higher temperature sample. If more water is made available at a higher temperature, the Q factor will remain lower for longer before the moisture is evaporated and the Q factor starts to rise.

Oven Temperature selected

The oven temperature selected was 180 ºC. At 150 ºC the dielectric results were variable which could be because the chips are not fully thawed. At 180 ºC the chips were fully cooked and so the higher temperature was chosen due to the theory of free and bound water in relation to the lower Q factor at the higher temperatures.

Effect of 180ºC temperature on empty box dielectrics

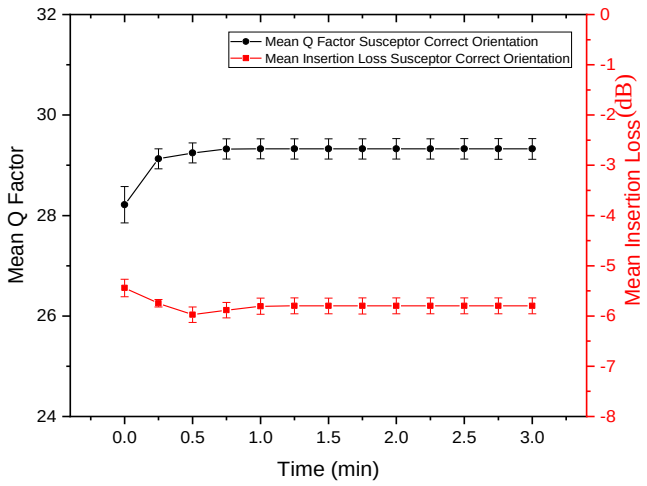


Figure 3-6 Mean Q Factor (n=3) (black line) and Insertion Loss (n=3) (red line) of Empty Microchip Boxes with No Susceptor Present in Correct Orientation

Figure 3-6 observes the effect of 180 ºC on the dielectric properties of microchip boxes in the correct orientation with no susceptor present. Three empty microchip boxes were placed separately in the novel cavity which was contained in a preheated 180 ºC Genlab OV

general purpose oven. The Q factor and insertion loss was recorded every 15 seconds for 3 minutes. The insertion loss was included in this test to determine if the presence of the susceptor had caused the increased insertion losses. The susceptor was removed from the microchip boxes prior to testing. As the insertion loss was similar to the Q factor it was theorised that the susceptor may contain elements that cause signals to be reflected. Therefore the susceptor was not used in the tests going forward. The errors produced were small indicating that repeatable measurements can be made at 180 ºC as well as at ambient. Any differences observed in the results are therefore believed to be due to factors other than means of measurement.

Effect of Coatings in relation to Control Sample

All the samples were tested when they were the same age (5 weeks) with each sample being tested on 3 occasions. As each sample test is destructive and a new 100g batch of sample needed to be tested to get the replicates, it would be expected that natural variation would occur. For these tests the susceptor was not present. The samples tested were;

1) Pre fry application 2% CMC 0% sodium chloride
2) Pre fry application 2% CMC 4% sodium chloride
3) Uncoated control sample

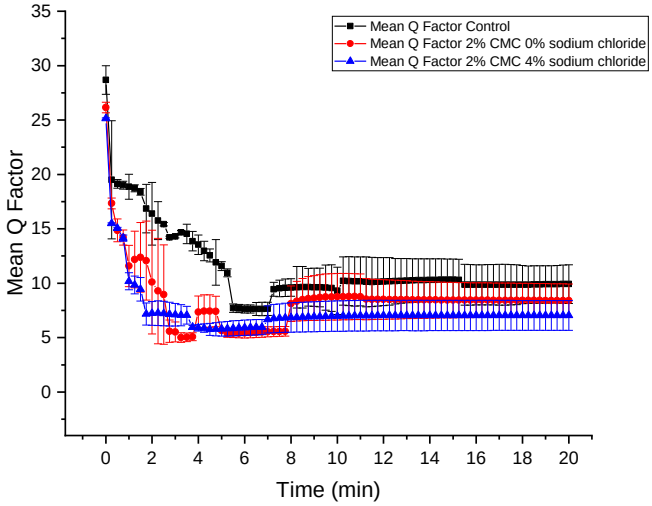


Figure 3-7 Mean Q Factor of 100 g of Control (n=3) (black line), 2% CMC 0% Sodium Chloride (n=3) (red line) and 2% CMC 4% Sodium Chloride (n=3) (blue line) Samples as a Function of Time at 180 ºC

Figure 3-7 shows the effects of the coatings in relation to their dielectric properties. There was variability of all samples, particularly the coated samples. Three sources of variance have been determined;

1) Natural variation due to which sections of the potato are present within the 100 g sample as e.g. the pith has a higher moisture content than the outer medulla
2) Potential issues with uniform coating application
3) Ratio of free:bound water at any one time

3.1.1.4 Determining internal temperature of the chips

Previous experiments regarding temperature had focussed on the external temperature of the oven as opposed to the temperature of the chip. Therefore a final experiment was conducted to determine the temperature of individual chips being heated (Figure 3-8).

Figure 3-8 Method for Determining the Internal Temperature of Chips

3.1.1.4.1 Materials and Methods

100 g of product was measured and placed into the manufacturer's packaging. In a freezer at temperature -18 ^{o}C +/- 1 ^{o}C each chip present in the 100 g sample set was measured for their length and width. A needle was inserted 0.5 cm into the centre of 5 chips present in the 100 g of product. The needle was removed and a copper constantan thermocouple was inserted into each 0.5cm hole. Once all thermocouples had been inserted correctly the sample was transported via a cooler bag to the experimental area. The temperature of each of the 5 chips was logged for 300 seconds (5 minutes) prior to being placed in a preheated 180 ^{o}C oven within the cavity used for making dielectric measurements. The network analyser was not connected at this time so that dielectric measurements were not made so as not to interfere with the measurement. Instead only the internal temperature of each chip over a 45 minute period was recorded.

3.1.1.4.2 Calibration of Thermocouples

Prior to conducting the actual experiment each thermocouple was calibrated in two ways. Firstly the thermocouples were heated in the oven at the same time with no sample present.

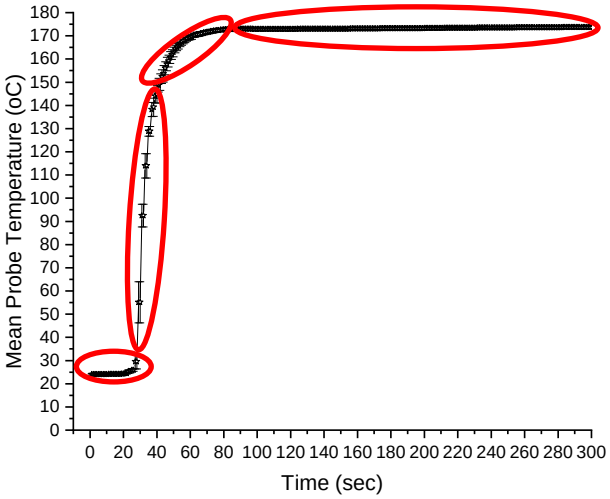


Figure 3-9 Mean Probe Temperature of Thermocouples (n=5) in 180oC Oven with No Sample Present – Red Circles Highlight 4 Areas of Interest

There are four areas of interest in Figure 3-9; the mean temperature and standard error from 0 to 25 seconds, the temperature and error from 26 to 50 seconds; from 51 seconds to 150 seconds and finally from 151 seconds to 300 seconds.

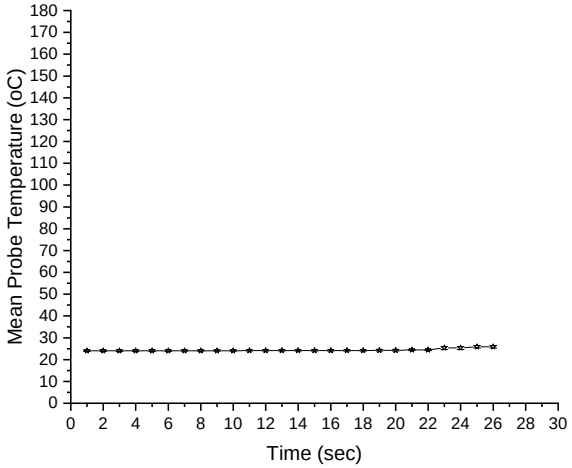


Figure 3-10 Mean Probe Temperature of Thermocouples (n=5) prior to Insertion into Oven (Area 1)

The first area regards time 0 seconds to 25 seconds (Figure 3-10). At this point the thermocouples had not yet been placed in the oven cavity hence the thermocouples gave a constant reading of ambient temperatures. The standard error between the samples here is low suggesting that at ambient temperatures the thermocouples are precise. The temperature differed at most during this stage by 1.64 ºC and at least by 0.92 ºC. Towards the end of the 25 seconds the thermocouples were placed in the cavity. Therefore the temperature of the

last four values began to rise with the highest temperature difference between each probe recorded as 3.99 ºC and lowest of 3.39 ºC.

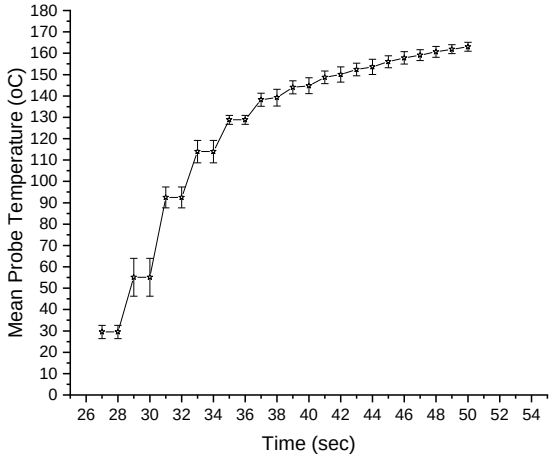


Figure 3-11 Mean Probe Temperature of Thermocouples (n=5) over a 28 Second Period After Being Placed in Oven (Area 2)

A larger error between the thermocouple values was again recorded during area two (Figure 3-11). The largest temperature difference during this window was recorded as 51.14 ºC with the smallest temperature difference recorded as 9.66 ºC. This was in stark contrast to the thermocouple behaviour at ambient temperatures where low errors were reported. Although the oven was preheated to 180 ºC, the oven door had to be opened to place the thermocouples in the cavity. Therefore even though the oven door was sealed it is probable that cooler air entered the oven cavity and caused temperature fluctuations. This theory is further supported by area 3 (Figure 3-12).

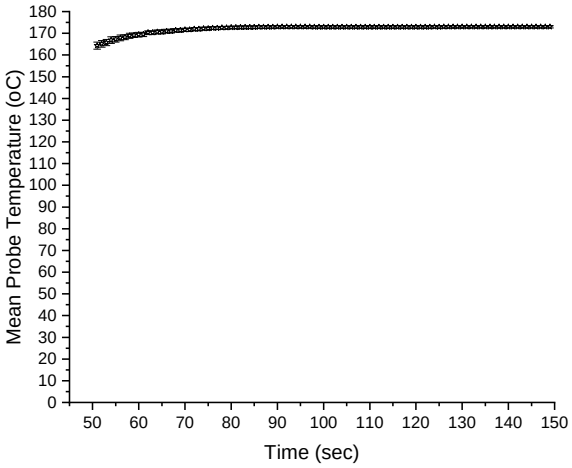


Figure 3-12 Mean Probe Temperature of Thermocouples (n=5) 50 – 150 Seconds After Being Placed in Oven (Area 3)

Area 3 shows that temperature fluctuations within the oven are to blame for large temperature differences of the thermocouples observed. At 50 seconds the temperature difference recorded was 7.11 ºC. This reduced to 2.95 ºC by 150 seconds. This indicates that on opening the oven door cool air was let in and that as the oven begins to reach the set oven temperature the temperature fluctuation between thermocouples does decrease

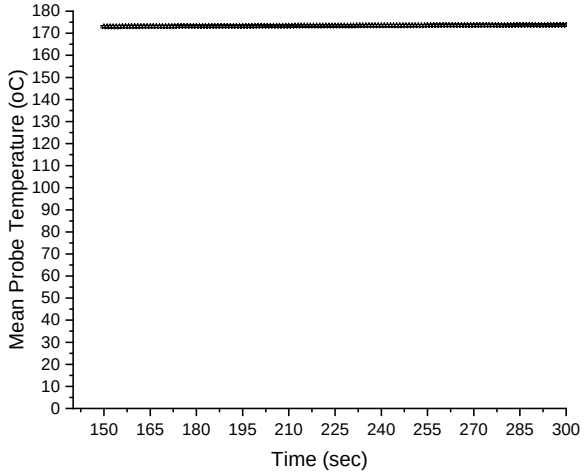


Figure 3-13 Mean Probe Temperature of Thermocouples (n=5) 150 – 300 Seconds After Being Placed in Oven (Area 4)

The final area is between 150 seconds and 300 seconds (Figure 3-13). The error bars are smaller than those seen in Figure 3-12 . The temperature difference between all 5 probes is 2.8 ºC and the fluctuation from this temperature difference over the 150 to 300 second window is 0.24 ºC. Therefore once the oven reaches temperature it can be said that the temperatures of the probe should only differ by 2.8 ºC +/- 0.24 ºC.

Second Calibration of the Thermocouples

Name of Probe	Temperature recorded (ºC)
Platinum Resistance Thermometer	21.80
1A	21.83
1B	22.34
1C	22.94
2A	23.63
2C	23.69

Table 3-1 Calibration of Thermocouples Against a Platinum Resistance Thermometer

The results (Table 3-1) show a range in temperature by +/- 1.834 ºC. However, as each probe is added to the volume of water the temperature slightly increases. These temperature increases could be due to thermal conductivity of the probe in the presence of a medium. To test this theory a computer model was built to confirm temperature differences associated with heating of a chip within the oven at 180 ºC.

3.1.1.4.3 Main Findings

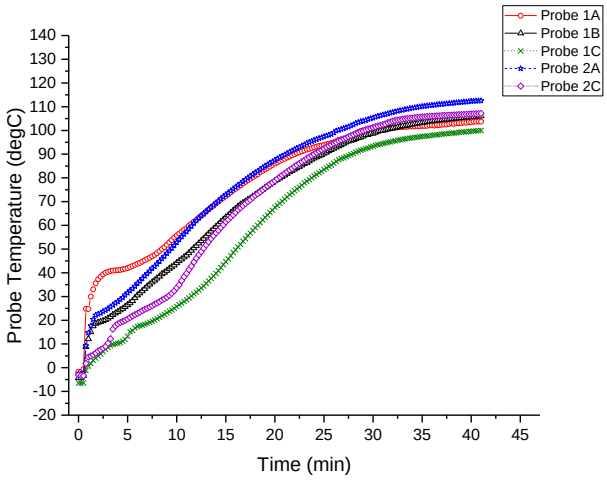


Figure 3-14 Probe Temperature of 5 Thermocouples Inserted Into One Frozen Chip Each Prior to Being Heated in a Pre-Heated 180 oC Oven

The starting temperature of each of the 5 chips before being placed into the preheated oven varied by 4.8 ºC. By taking into account the 1.64 ºC temperature difference recorded between probes during calibration at ambient, there is still a starting temperature difference of 3.16 ºC which can only be explained by natural variation of the product being tested. Probe 1C recorded the lowest starting temperature of -6.51 ºC whilst probe 1A recorded the highest at -1.71 ºC. Figure 3-14 shows that the temperature recorded by probe 1A is increasing much more rapidly than any of the probes. During calibration there was a worry of thermal conduction increasing the temperature more rapidly. As such it was decided that further statistical analysis would also look at the data with and without probe 1A present.

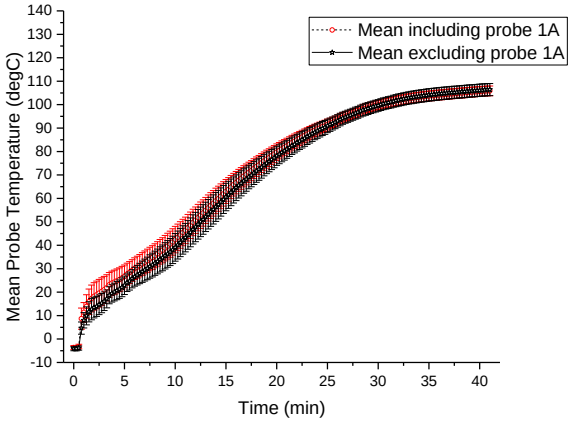


Figure 3-15 Mean Probe Temperature Excluding Probe 1A (n=5) (red line) and Including Probe 1A (n=6) (black line)

As can be observed in Figure 3-15 initially with probe 1A present the average temperature recorded by the probe is higher although after minute 15 probe 1A no longer appears to have a large effect on the average temperature recorded. The product tested has a large degree of natural variation ascertained by the starting temperature difference of each product. Temperature fluctuations exist due to the presence of cool air in the oven due to the door being opened to place the sample inside. The longer the products remain within the oven, the lower the standard error associated with the probe temperatures recorded. Thermal conduction may be an issue as shown during the calibration stage and through the initial behaviour of probe 1A. A computer model was produced to observe the effect of the thermocouple presence on the temperatures recorded.

3.1.1.4.4 Computer Model

A computer model was created using COMSOL Multiphysics Version 5.2a to observe;

a) the heating of a product within an oven set to 180^{o}C
b) the effect of thermocouples in terms of thermal conductivity causing heating of the product in an oven set to 180^{o}C

Time dependent studies were preferred with the heat transfer module being used to model the heating of food. The thermal conductivity, heat capacity, density and latent heat of water were considered. The model was created with assistance from Megan Povey. Data collected from the computer model was analysed alongside real experiments to determine the success of the computer model.

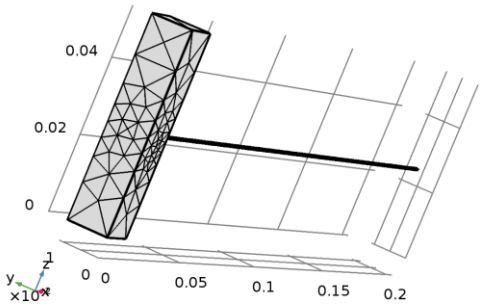


Figure 3-16 Output of Computer Model Created Using COMSOL Multiphysics Version 5.2 a – Observes a Thermocouple Inserted Into a Frozen Chip 0.5mm into the Sample

Figure 3-16 shows the creation of a computer model in which a thermocouple is inserted 0.5 mm into the product. The computer models were produced so that the dimensions of the product could be altered. This allowed for all 5 of the products tested during the thermocouple experiments to be modelled in the computer model. Whilst the computer model is fully functional the model gave the correct internal temperatures of each chip at the beginning of the test but there was a lag observed in the real time experiments in terms of temperature compared to the computer model (Figure 3-17). It was theorised that this was because of cool air entering the oven on addition of the chips to the oven thus affecting the heating rate. Unfortunately due to time constraints a complete solution for this still needs to be determined. As such further work is required to enable real time experiments to be completed which can be directly compared with the computer model.

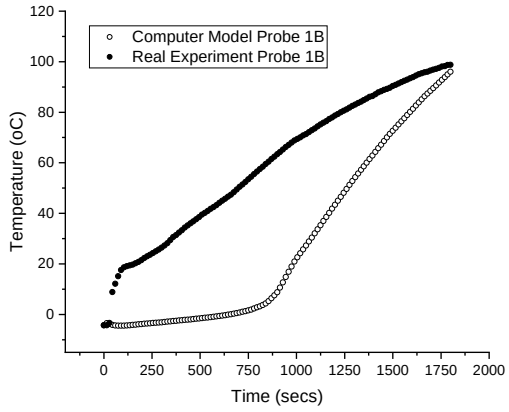


Figure 3-17 Temperature Recorded by Probe 1B in Chip Placed in Pre-Heated Oven at 180ºC (Solid Black Line) and Temperature of Probe 1B Predicted by Computer Model (Perforated Black Line)

3.1.1.5 Limitations with Dielectric Measurements of Novel Cavity

The dielectric activity is measured using conventional heating as opposed to microwave heating. This is problematic due to the different way in which the sample is heated. Microwave heating heats food volumetrically whereas oven heating is achieved by surface heat transfer. Microwave heating causes moisture to leave the centre of the product and move to the surface of the product whilst oven heating heats from the outer surface inwards. Therefore whilst this method does tell us what happens dielectrically to the water in the product as it melts, it does not help to characterise the location of the moisture at every point during the microwave heating process. Another issue was the presence of the cavity lid. The way the machinery was designed meant that a lid had to be placed on top of the cavity during measurement. This affected the dielectric measurement in the latter stages. Namely the Q factor did not continue increasing and instead reached equilibrium. This indicates that the metal lid prevented the moisture from leaving the cavity and some moisture may have condensed onto the metal underside of the lid contributing to dielectric measurements.

The final issue regarded the equipment used to make the measurement. Unfortunately making measurements using this piece of equipment is currently extremely time consuming as automatic data capture was not available. Instead measurements had to be recorded manually. Initially dielectric readings were recorded every minute. However, throughout testing there was a worry that important events were being missed particularly during the first few minutes of heating as the ice melts. Therefore measurements were manually recorded every 15 seconds. This meant that repeat testing was not always possible and so not all experiments could produce enough repeats for statistical analysis.

3.1.2 Method development required for the SPDR

The Split Post Dielectric Resonator (SPDR) presented a unique problem as for samples to be measured accurately only samples with a maximum thickness of 3.5 mm and minimum size of 70 x 70 mm in length could be inserted. Therefore samples had to be developed that fit within these parameters (AgilentTechnologies, 2015). The second issue is that the design of the SPDR does not allow the interior to be adequately cleaned after each experiment. One experiment was concerned with measuring the dielectric properties of 10 different starch powders. As such an experiment had to be designed which would protect the machinery from substances such as powders and still provide reliable results.

3.1.2.2 Sourcing a base material

The first stage involved finding an inert base material that would not interfere with the dielectric measurement and also allow enough of the sample to be attached. Four options were considered;

1) Sellotape
2) Kapton Tape
3) Quartz microscope slides
4) Vacuum bags

3.1.2.2.1 Sellotape

Sellotape was chosen due to its adhesive properties. Corn starch samples were inserted onto the sellotape and then smoothed to give a uniform layer. This was achieved in three ways; high pressure air, painting brush and a metal slider as shown in figure 3-18.

Figure 3-18 Methods Considered as for Adhering Starch Powders to Sellotape Base Material – (l-r): High Pressure Air, Painting Brush, Metal Slider

Sellotape was weighed prior to the corn starch being added and weighed after addition.

Name of Sample	Weight of sellotape (g)	Weight of sellotape and starch after application (g)	Weight of starch on base material (g)
Brush 1	0.220	0.335	0.115
Brush 2	0.221	0.325	0.104
High Pressure Air 1	0.188	0.265	0.077
High Pressure Air 2	0.186	0.265	0.079
Metal Slider 1	0.190	0.290	0.100
Metal Slider 2	0.216	0.334	0.118

Table 3-2 Amounts of Starch Successfully Adhered to Sellotape Using Three Methods

The sample size produced was not large enough and the dimensions of the sellotape did not reach the required 70 mm x 70 mm in size. This method was discarded as the base material.

3.1.2.2.2 Kapton Tape

Kapton tape was considered due to its adhesive properties. It was custom made by Antistat to dimensions of 90 x 90 mm x 0.01 mm. Finally Kapton tape is heat resistant up to 220°C which was useful as the aim was to eventually make temperature dependent dielectric measurements in the custom built cavity.

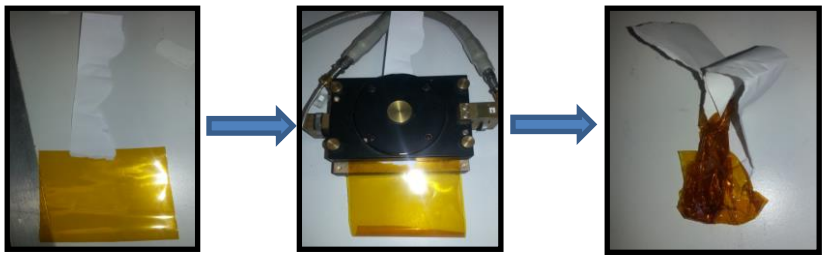


Figure 3-19 Issues Observed when Inserting Kapton Tape Into SPDR

Two Kapton tape pieces applied to each other were required as the exposed adhesive had sticking issues when inserted (Figure 3-19). Three Kapton tape samples were measured in the SPDR 10 times each to ensure that the SPDR was functioning correctly.

3.1.2.2.3 Quartz slides

Quartz slides were custom made to a diameter of 90 x 90 x 0.5 mm. Four blank slides were measured in the SPDR 10 times each to determine the Q factor.

3.1.2.2.4 Vacuum Bags

Four different vacuum bags were cut to size 90 x 90 x 0.2 mm and measured 5 times each in the SPDR to determine the Q factor.

3.1.2.2.5 Dielectric Values for the base materials tested

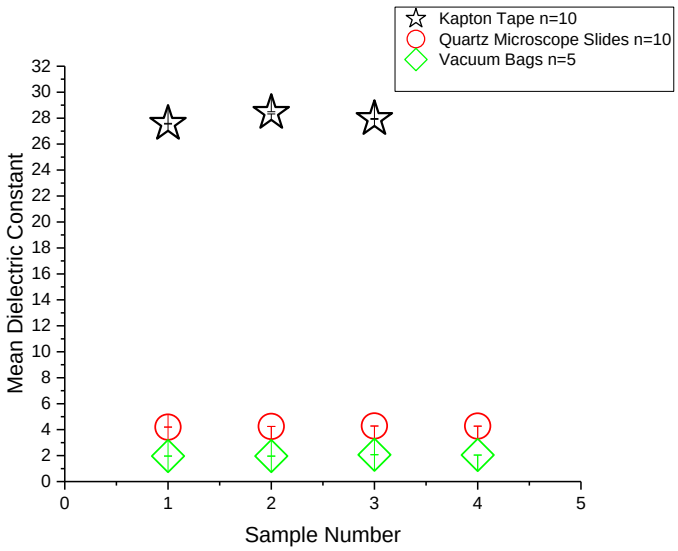


Figure 3-20 Mean Dielectric Constant and Standard Error of Base Materials Kapton Tape (n=10) (black star), Quartz Microscope Slides (n=10) (red circle) and Vacuum Bags (n=5) (green diamond) Inserted into SPDR

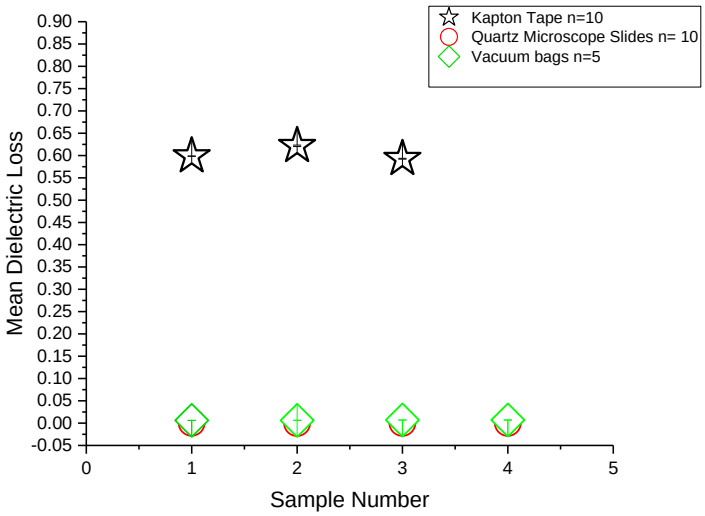


Figure 3-21 Mean Dielectric Loss Factor and Standard Error of Base Materials Kapton Tape (n=10) (black star), Quartz Microscope Slides (n=10) (red circle) and Vacuum Bags (n=5) (green diamond) Inserted into SPDR

The SPDR measured the Q factor at 2.69 GHz which was then translated into the real (*er'*) and imaginary (*er"*) part of the dielectric factor; the constant and the loss. This was achieved via a computer program provided by the manufacturer Agilent Technologies. As discussed the base material needed to be fairly inert in the SPDR so it would not interfere with the dielectric measurement of the samples. A single factor analysis of variance (ANOVA) was conducted to determine if the different base materials were the same in terms of their dielectric properties;

H_o = *All base materials have the same dielectric properties*

H_1 = *At least two of the base materials have different dielectric properties*

The ANOVA (Table 3-3) showed a p value of <0.01 for the dielectric loss and a p value of <0.01 for the dielectric constant of the three base materials tested. As the p values fell below the critical p value limit of 0.05 the null hypothesis can be rejected and it stated that the dielectric factor of at least two of the base materials are different and were therefore not interchangeable. Figures 3-20 and 3-21 show this graphically with Kapton tape giving the highest dielectric readings for both constant and loss. There was a concern that by attaching two Kapton tapes together there was the potential for air bubbles forming which would have affected the dielectric results.

Investigating how similar the base materials are to each other via single factor Analysis of Variance (ANOVA)				
Sample	**Dielectric Constant p value**	**Dielectric Loss Factor p value**	**Reject or Accept Null Hypothesis?**	**Are Samples the Same or Different?**
Kapton Tape	<0.01	<0.01	Reject	Base materials do not have the same dielectric properties
Quartz Microscope Slides				
Vacuum Bags				

Table 3-3 Single Factor ANOVA Investigating How Similar the Base Materials Are to One Another

Investigating how different the dielectric factors are for the same base material via single factor Analysis of Variance				
Sample	**Dielectric Constant p value**	**Dielectric Loss Factor p value**	**Reject or Accept Null Hypothesis?**	**Are Samples the Same or Different?**
Kapton Tape	<0.01	<0.01	Reject	Repeat Kapton Tape samples are not different to each other
Quartz Microscope Slides	<0.01	<0.01	Reject	Repeat Quartz Microscope Slides are not different to each other
Vacuum Bags	<0.01	<0.01	Reject	Vac bags are not different to each other

Table 3-4 Single Factor ANOVA Investigating How Different the Dielectric Properties of the Base Materials are Within Each Base Material Group

Therefore a second single factor ANOVA (Table 3-4) was conducted to observe if a difference existed in the dielectric properties of the same base material and to ascertain that the SPDR was functioning correctly. The hypotheses were as follows;

H_o = *The base material repeats have different dielectric values*

H_1 = *The base material repeats do not have different dielectric values*

Kapton tape had a dielectric constant p value of <0.01 and a loss factor p value of <0.01. Therefore the null hypothesis could be rejected and it stated that the Kapton tape sample repeats were not significantly different indicating that either bubble formation was affecting the results to the same degree or that bubble formation was negligible. Kapton tape was discounted as a base material due to its higher dielectric properties and difficulties with adhering starch powders.

Repeatable dielectric data using the SPDR was possible for the quartz microscope slides and vacuum bags. The quartz microscope slides were discarded as the base material due to issues of attaching the starch powders to the surface as it was feared that starch could enter the internal mechanism of the SPDR and cause damage. Therefore it was decided that vacuum bags would be used and the sample sealed within it to prevent damage to the SPDR.

3.1.2.3 Method development concerning insertion of starch powders into base material vacuum bags

Once the dielectric properties of the base material had been ascertained, a method had to be developed to ensure dielectric measurements of the starch powders could be made. As the SPDR makes geometry dependent measurement, it was important that the starch remained completely flat and uniform in thickness. Three different methods were trialled.

3.1.2.3.1 Method one – Vacuum Sealing

3 g of corn starch was added to each vacuum bag and was vacuum sealed using a Model No J-V002 vacuum sealing machine provided by the food machinery company. This resulted in non-uniform distribution of the starch within the vacuum bag (Figure 3-22).

Figure 3-22 3g of Corn Starch Added to Vacuum Bag (90 x90 mm) and Sealed Using Model No. J – V002 Vacuum Sealer from the Food Machinery Company

The vacuum sealer was effective at disposing of air which could impact dielectric measurement. However, further work was required to ensure a uniform thickness of sample.

3.1.2.3.2 Method two – Application of vibrations

The aim of this experiment was to enable a uniform thickness to develop via the application of vibrations. Vacuum bags were filled with 3 g of starch and then placed on a variable speed mixer. The sides of the vacuum bag restricted the starch from moving. The vibrations also caused starch in the centre of the bag to leave the vacuum bag. This idea was therefore discarded.

3.1.2.3.3 Method three – Application of paint roller, ruler and vacuum sealing

The chosen method involved inserting 3 g of starch into each vacuum bag and distributing the starch across the whole vacuum bag using the edge of a 15 cm ruler. The paint roller was then rolled across the vacuum bag until a uniform layer was observed. Finally each bag was sealed using a vacuum sealer (Figure 3-23).

Figure 3-23 3g of Corn Starch Added to Vacuum Bag (90 x90 mm) and Sealed Using Model No. J – V002 Vacuum Sealer from the Food Machinery Company After Application of Paint Roller and Ruler

However, during the vacuum sealing process some starch became caught in the seal. This resulted in small air gaps and thus enabled the starch to move within the bag. Therefore 2.5 g starch was filled into a space 70 x 70 mm as opposed to the vacuum bags full capacity of 90 x 90 mm. This ensured the seal remained intact, the starch remained immobilised and that the minimum requirements for measurement in the SPDR could be met (Figure 3-24).

Figure 3-24 2.5g of Corn Starch Added to Vacuum Bag (90 x 90 mm) and Sealed Using Model No. J – V002 Vacuum Sealer from the Food Machinery Company

Occasionally when the vacuum sealer was in use, the vacuum bag was dislodged from the sealer due to its light weight and thus the sample was not sealed. Therefore a 1kg weight was placed on each vacuum bag prior to sealing to ensure the bags remained in place (Figure 3-25).

Figure 3-25 Addition of 1kg Weight to 2.5 g Starch Powder Sample Prior to Vacuum Sealing via Model No. J – V002 Vacuum Sealer from the Food Machinery Company

3.1.2.3.4 Conclusion and Limitations of Final Method

Although the vacuum sealing method was utilised there were still limitations. Potential issues arose if on sealing the powder shifted and left clear spaces in the vacuum bag. These had to be re sealed as otherwise this would have affected the dielectric data. As a result this method was exceedingly time consuming.

3.1.2.4 Creation of Gelatinised Starch Powders

The method for the creation of gelatinised starch films can be found in section 2.2.1.2.4. However, method development was required to reach the final method. The films needed to have a powder consistency. Therefore different methods for achieving this were investigated.

3.1.2.4.1 Blender Method

Figure 3-26 Kenwood Blender Containing Starch Powder

A Kenwood blender was utilised to grind gelatinised starch films into a powder (Figure 3-26). However, this approach failed primarily as the blades dimensions were too large to grind the film to a fine powder. As a result this method was discarded.

3.1.2.4.2 Pestle and Mortar

Figure 3-27 Starch Powder and Pestle and Mortar

This method (Figure 3-27) was also discounted as manual exertion was only able to produce a very coarse crystal structure, unsuitable to be packed into vacuum bags.

3.1.2.4.3 High Shear Mixer (Polytron 1600 E)

Figure 3-28 High Shear Mixer (Polytron 1600 E)

The blades on the blender were very thick so it was decided to look for thinner blades to increase chance of blades making contact with particles. A polytron 1600 E was utilised both for its small blades and its shearing capabilities with an rpm up to 30,000 (Figure 3-28). However, it was found that on application to the starch, the starch heated and clumped together. This method was therefore discarded.

3.1.2.4.4 Ball Mill and Sieve

Figure 3-29 Ball Mill and Starch Powder

The final method chosen was a ball mill (Figure 3-29). Each 1.5 kg of gelatinised starch films were placed in the ball mill and rotated at 30 rpm for 2 hours. This resulted in a fine starch powder being produced.

Figure 3-30 Sieve and Starch Powder

The final stage for gelatinised starch powder sample preparation was sieving (Figure 3-30). This was because a comparison between each gelatinised starch sample was required.

3.1.2.4.5 Conclusion and Limitation of Final Method

The main limitation of this method involved the ball mill stage. As the ball mill ground starches into a fine powder, it was very difficult to generate a range of particle sizes to test dielectrically. Therefore the particle sizes tested for their dielectric properties were instead the most abundant. As the native starches all have varying particle ranges, it is difficult to directly compare native and gelatinised starches as a function of particle size on this occasion.

3.1.2.5 Understanding the Importance of Moisture in Relation to Dielectric Activity

As moisture is a driving factor of dielectric activity within the microwave it was important to investigate methods of adding water to powders. This was so that the dielectric activity of the starch powders could be determined at different moisture contents. This was beneficial as it would aid in the development of a coating recipe in terms of the ratio of water: powders required.

3.1.2.5.1 Sample Preparation

Silica provided by Whitehouse Scientific and at three different particle ranges – 38-45 µm, 90-106 µm and 355-425 µm – and corn flour bought from Morrisons in February 2015 were selected to investigate water binding ability of powders.

Figure 3-31 Preparation Method For Silica and Corn Flour

Figure 3-31 shows the sample preparation method. The starting moisture of each of the samples were measured using the method in section 2.2.1.2.2. The silica had a starting moisture content of 0% on a dry weight basis and the corn flour had a starting moisture content of 19%. Samples were produced via the addition of deionised water at 19%, 25%, 50%, and 75% as a function of the total weight of the sample with 100% of deionised water addition reflecting a sample containing 1.5g of product and 1.5g of deionised water for silica based samples and 1.5g of product and 1.215g of deionised water for corn flour based samples. When referring to % this is expressed on a dry basis and not a wet basis. No additional moisture was added to the 19% corn flour sample due to the inherent moisture content being 19%. Although 19% added moisture was added to the silica samples due to their starting moisture of 0%. Each of the samples were vacuum sealed using the method in section 2.2.1.2. At this point silica samples of particle size 355-425 µm were discarded due to issues with vacuum sealing larger particle sizes. For each experimental condition 4 samples were tested by placing in vacuum bags, placing in the SPDR with the Q factor and frequency measured. These were translated into the dielectric constant and loss factor by means of Agilent Technologies computer software.

3.1.2.5.1 Results

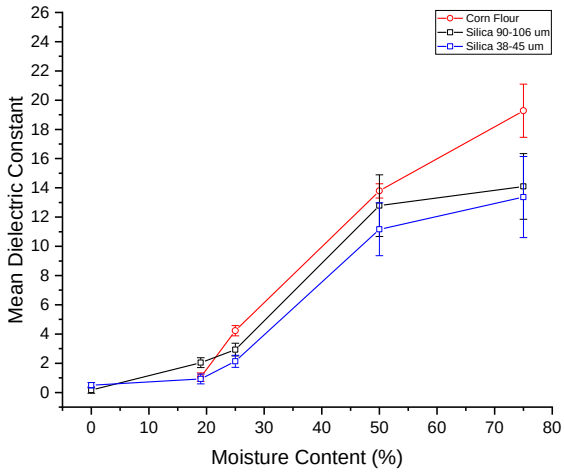


Figure 3-32 Mean Dielectric Constant (n=4) of Corn Flour (red line), Silica 90-106 µm (black line) and Silica 38-45 µm (blue line) inserted into SPDR

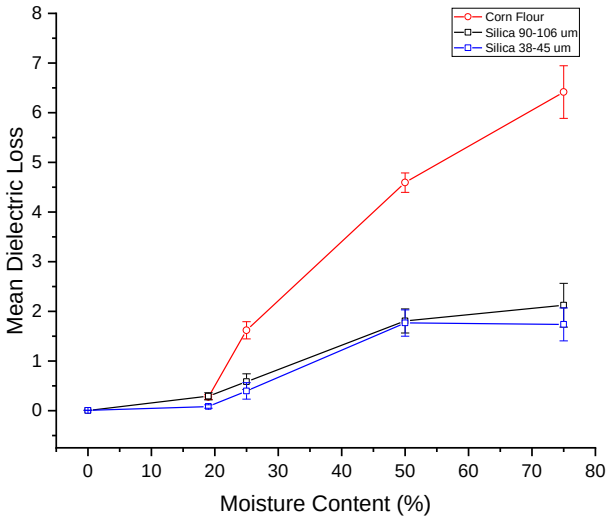


Figure 3-33 Mean Dielectric Loss (n=4) of Corn Flour (red line), Silica 90-106 µm (black line) and Silica 38-45 µm (blue line) inserted into SPDR

Figures 3-32 and 3-33 observe the mean dielectric constant and loss of each of the samples. As the moisture content increased the dielectric constant and loss factor increased. For silica samples, particle size had an effect on dielectric properties with the larger particle sized samples having larger dielectric activity. According to (Verma, 2017) moisture adsorbs to the surface of silica as opposed to being absorbed and so it would be expected that more water would adsorb to the surface of the lower particle size silica and be unavailable to rotate on application of the electromagnetic field due to its increased surface area.

For corn flour samples, the dielectric constant and loss was higher than that of the silica samples with the exception of 19% moisture (the natural moisture) present within the native starch structure. Whilst water was bound to both silica samples, added water is not bound within the starch matrix within one hour of sample preparation. A reason why corn flour may perform better than silica can be observed by looking at the values for 19% moisture. Corn flour naturally has a moisture level of 19% so no additional water was added to these samples. At this % the dielectric constant and loss is similar to the two silica samples indicating that the moisture is bound and it is only on additional moisture being added that the dielectric values begin to differ. This suggests that corn flour interacts with the moisture naturally present differently to moisture that is added and that there may be a saturation level. This would leave the added water free to rotate on application of the electromagnetic field.

However, there are limitations with method preparation due to mixing issues. At 19% moisture content where no additional moisture is added the standard error is low. However, as the added moisture level increases the standard error also increases suggesting mixing issues.

3.1.2.5.2 Summary

1) As moisture content increases dielectric activity increases
2) Silica interacts with water via adsorption
3) Certain materials may have saturation levels with natural moisture levels vs added moisture levels being considered
4) Current methodology is prone to error due to mixing issues

3.1.2.5.3 Next Steps

The method depicted in section 2.2.1.2.3 was used to alter the moisture contents of different powders. The method of direct addition of water to starch samples was discounted as the method was deemed more prone to error and more time consuming.

3.1.2.6 Extrusion

Vacuum sealing used in 2.2.1.2 was utilised for both native starches and gelatinised starch powders. Production of gelatinised starch samples was more challenging than their native starch counterparts. Therefore extrusion was investigated as a potential preparation method. As dissociated NaCl can influence dielectric properties varying NaCl levels were included to look at the effect of NaCl addition on dielectric properties of two commercial batters and two gelatinised starches (YE60 and BA75). Samples were made with 40% added water. The samples produced are found in Table 3-5. This water was not deionised as water from the Nottingham University pilot plant was used due to the large sample sets.

Sample Code	**Condition 1**	**Condition 2**	**Condition 3**	**Condition 4**	**Condition 5**	**Condition 6**
BA75	No added salt	2.5% Saline	5% Saline	10% Saline	20% Saline	30% Saline
YE60	No added salt	2.5% Saline	5% Saline	10% Saline	20% Saline	30% Saline
Home fries batter	As received	-	-	-	-	-
Micro Chips Batter	As received	-	-	-	-	-

Table 3-5 Extruded Samples Produced

A pre-requisite for the extruded sample was that they had to be a minimum size of 70 x 70 mm in length and width. However, the extruder used only had a nozzle size of 30 mm. Therefore three strips of the sample had to be produced which were then placed together whilst hot and left to set. This resulted in a non-uniform extrudate being produced (Figure 3-34).

Figure 3-34 Extrudates of YE60 Produced with No Added Salt

Therefore to enable the samples to be used in the SPDR a uniform layer had to be produced.

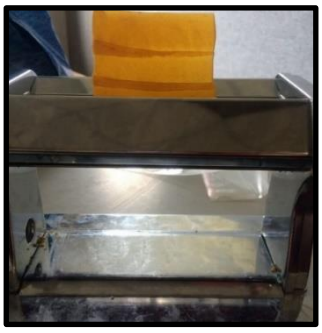


Figure 3-35 Pasta Roller Used to Make Extrudates Uniform Geometry

A pasta roller was used to achieve a uniform layer (Figure 3-35). However, it was noted that whilst the roller did produce a uniform sample shape, moisture was removed from the product during this process. For this reason and thawing and re-freezing issues, the extruded samples were no longer investigated for their dielectric properties.

3.2 Method Development for measuring the physical properties of the product

The physical properties of the samples produced were investigated to determine if factors such as storage time, coatings and heating time had a significant effect on the end product. In some cases methods needed to be developed from product concept and in other cases adapted from standard procedures in order to determine each factors importance.

3.2.1 Acoustic and Mechanical Measurement

From previous research (Chen et al., 2005, Varela et al., 2006) it became apparent that an acoustic envelope detector (AED) attached to a Stable Microsystems Texture Analyser TA-XT.plus was a

suitable method to measure the sound produced on application of force to the sample. However, in order to make representative measurements the correct probe fixture and test settings had to be determined. In this way both acoustic and mechanical data could be collected.

3.2.1.1 Probe Selection

The probe selected needed to be representative of the texture of the product felt on human consumption. From private consultation (Povey, 2014) the probe most useful for this project was the Volodkevich jaw attachment. The Volodkevich jaw is built to 'simulate a human incisor tooth biting through food.' (StableMicroSystemsApplicationStudies, 2016) This was because mechanical results needed to be compared to sensory tests performed on the product at the same time point. Before the Volodkevich jaw could be used, the test settings had to be determined.

3.2.1.2 Test Speed

For some experiments using the texture analyser, the AED was broken and therefore could not be used. Experiments were performed on the product with the AED present and not present to ascertain suitable test speeds. According to (Flavel et al., 2002) .the maximum speed of a human jaw is 50 mm/s. According to (Szczesniak and Hall, 1975) humans subconsciously adapt their biting behaviour and pressure dependent on the foodstuff and different people apply different biting forces. Therefore there is no simple measure to determine the mouthfeel of a product using mechanical measurement alone. Further complicating this field of study is the Weber-Fechner Law as discussed in section 1.2.3. With all these factors in mind the test setting decisions were also made in relation to the product being tested. The total width of the product is 10mm and the aim was to observe differences in mechanical measurement and sound between the crispier exterior and softer interior. Test speeds of 50 mm/s had to be discounted as data looking at the difference between the two layers could not be generated at these speeds. According to (Exponent 2017) the Volodkevich jaw measured the firmness of hydrated sweetcorn and they used test speeds of 2 mm/s to look at differences in sweetcorn due to factors such as harvest time, blanching time and sweetcorn variety. The test speed was initially chosen as 1mm/s for 10 seconds so that 10 parts of the chips would be considered as the probe pierced the chip.

3.2.1.2.1 Test Speed Experiments (without Acoustic Envelope detector)

For the frozen storage tests the AED was broken and so method development was performed just using the Volodkevich jaw.

The product was measured for its dimensions and then placed in the Volodkevich jaw lower rung. The top probe was placed 1 cm above the product with Table 3-6 providing the test settings.

Test Mode	Return to Start
Type of Test	Compression
Pre-Test Speed	1 mm/s
Test Speed	1 mm/s
Post-Test Speed	10 mm/s
Distance	10 mm
Trigger Force	0.49N
Load Cell	30Kg

Table 3-6 Test Speed Parameters for Volodkevich Jaw when AED Not Present

At the start of the test the probe moved downwards until a force of 0.049 N was detected. Once this trigger point was reached, data was collected for 10mm as the probe moved downwards at a speed of 1mm/s before returning to its original position. After 7.5 mm the probe would usually cleave through the whole product meaning that further forces detected were due to the probe hitting the bottom plate. In most cases the test would abort as the forces became too high.

For the frozen storage work presented in section 4.1 a distance of 5 mm was chosen as the total product thickness was 0.5 mm. For the remaining products adopting this test method a distance of 7.5 mm was used. This was because these test products were a minimum of 1 cm in thickness and so 7.5 mm was chosen to reduce the likelihood of the probe cutting through the product and causing a large force increase.

3.2.1.2.2 Test Speed Experiments with Acoustic Envelope Detector

Over the course of the frozen experiments which did not use the AED, the test speed of 1 mm/s was too fast for the mechanical data generated to be useful. There was a worry that important events were being missed. Therefore it was decided for the first set of mechanical data alongside the AED would use a test speed of 0.1 mm/s. (Chen et al., 2005) utilised the AED when investigating the crispiness of biscuits. As part of their research they investigated the positioning of the microphone of the AED and looked at nine different positions. They determined that the acoustic signal was strongest when the microphone was 1 cm from the sample and at a 45 degree angle. Less variation was observed when placing the microphone 1 cm away from the sample.

As such the microphone was always placed at a 45 degree angle 1 cm from the sample to maximise the audio signal. It was decided that a filter would be applied before collecting data. The filter enables background noise to be filtered out if it is below 1kHz. In practice this worked very effectively particularly because it gives a much higher signal:noise ratio as most

environmental noises are below 1kHz. An example of raw acoustic data with a filter applied is given in figure 3-36.

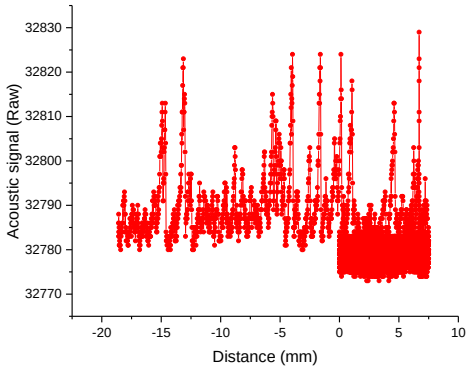


Figure 3-36 Typical Raw Data Acoustic Signal at 0.1 mm/s Produced by AED with Filter Present on Application of Volodkevich Jaw to Individual Chip

Raw acoustic signals were produced at a 0.1 mm/s test speed. For samples sizes reflecting 100 g once these raw data was translated to a sound pressure level in dB no acoustic signal was recorded. This was not the case during the initial coating development work when a smaller sample set was used as acoustic events were still recorded in db/SPL. This is because the smaller sample size products tested were much crispier than those produced on a larger scale.

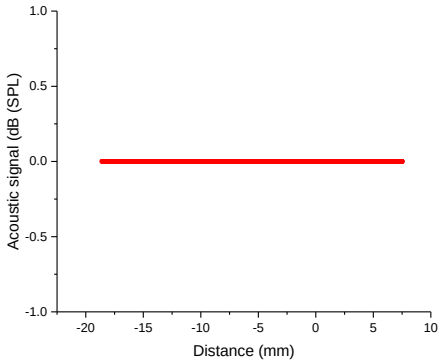


Figure 3-37 Acoustic Signal Recorded (dB(SPL)) by AED on Application of Volodkevich Jaw to Individual Chip at a 0.1 mm/s Test Speed

When 100 g of sample was tested acoustic events were not recorded at a 0.1 mm/s test speed even when audible cracks were heard by the investigator (Figure 3-37). It was theorised that the probe was moving too slowly. It was decided that the AED was a more relevant predictor of crispy and crunchy textures than the force profile alone. In some cases the probe compressed but did not pierce the product resulting in different force profiles being generated for the same product. As a result the test speed was increased to 1 mm/s. The gain of the AED was also investigated.

Originally the gain was set at 0 but unfortunately this also prevented a clear signal from the sample being read due to the increased bandwidth. Therefore repeat testing was performed until the gain was high enough to separate the signal from the surrounding ‘noise’. The gain was therefore set at 2. This was the case for all samples where acoustic events were recorded regardless of the probe speed.

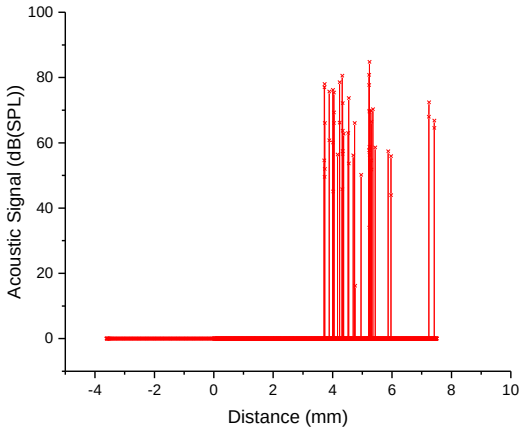


Figure 3-38 Acoustic Signal Recorded (dB(SPL)) by AED with Filter on and a Gain of 2 on Application of the Volodkevich Jaw to Individual Chip at a Test Speed of 1 mm/s

With the filter on and a gain of two, signals could be easily distinguished. According to the user guide for the AED even at the highest gain the bandwidth still only falls to 40 kHz which would still capture acoustic signals from the sample. Therefore, increasing the gain is not believed to impact negatively on the collection of data. The acoustic signal begins monitoring the acoustic signal before the probe has started moving and reaches the chip and also monitors the sound for a few seconds after the test completing. As Figure 3-38 finished at 7.5mm into the product all data after this point should be discarded as it is not representative of the sample. By increasing the test speed from 0.1 mm/s to 1 mm/s this allowed for acoustic signals to be identified when larger sample sizes were microwaved and individual chips later tested. Unfortunately for some of the research the test speed was set at the lower speed as in earlier experiments the relationship between the lower and higher test speed had not been determined. Where this is the case in future chapters it will be made clear at what test speed the research was conducted.

3.2.1.3 Sensory Panel

Sensory panels were conducted by (Beasley, 2015) whilst mechanical tests were performed by the primary investigator on the product at the same time point. Mechanical tests were conducted at 1 mm/s but an AED was not present. The sensory questionnaire is shown in Figure 2-2. During the

sensory panel assessors were asked to describe the colour, texture and flavour in their own words. The sensory panel occurred once every 8 weeks and then at month 7.

Method development in this case did not occur as sensory panels were completed by (Beasley, 2015). However, there are limitations with the above approach. The main issue is that these sensory panels focus on acceptability and liking. This does not lend itself to a comparison between two products as it does not allow for preference to be looked at. Ideally another question could be asked to determine preference between samples so as to ascertain which products perform better than others. During the final sensory panel of the product at 7 months old, they were asked if the two products were the same or different and 100% of respondents confirmed the products were different. The 7 month old product was described as hollow and darker in colour compared to the fresh sample which was labelled as soft and paler by 80% of respondents.

3.2.2 Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

Figure 3-39 DSC and TGA Used to Conduct Experiments

As discussed in section 2.2.4.4 and 2.2.4.5, DSC and TGA standard methods were used during the coating development phase of the research. DSC was used to understand if phase changes were occurring in the product e.g. starch retrogradation over a period of 8 weeks. TGA was used alongside moisture measurements to determine drying behaviour of the samples. However, before the final method could be determined method development had to occur to ensure a representative sample could be produced. Several factors had to be considered.

3.2.2.1 Sample Size

Whilst DSC and TGA (Figure 3-39) are both widely used they do have one main limitation and it regards their sample size. Only samples weighing in mg can be used. As the object being tested is 100 g per full product this provided a challenge regarding representative samples. Therefore different parts of the product were considered separately with the sample being separated into the dry crispy exterior and the soft fluffy interior. Work was conducted with the assistance of Algy Kazlauciunas from the department of Colour Science, University of Leeds.

3.2.2.1.1 Separation of Outer and Inner Product

A method had to be devised to separate the outer skin from the interior product. A Weck-Prep blade from Quorom Technologies was used on both thawed and frozen product to remove the top outer layer. This method worked well and the outer layer was removed. Removing the outer layer was the best method. When thawed the product became very wet resulting in moisture transferring to the investigators hands and so there was a worry that this would affect the results of the TGA and DSC analysis. The product remaining was the inner product but determining which part of the product to select needed further consideration. A limitation of this method is its manual nature as it is easy to not just take the top layer but also some of the inner as well.

3.2.2.1.2 Selection of Inner Product Sample

As discussed in section 1.3, the potato is not homogenous. Therefore it was important to determine which section should be selected for use in the TGA and DSC. To do this a small experiment was conducted. Two potatoes weighing 116.5 g and 114.2 g respectively were peeled and placed in a reactive red dye at two different concentrations; 0.5% and 1%. Every 5 minutes the potatoes were removed from the dye and a potato peeler used to remove a thin layer of the dyed tissue (Figure 3-40). This was then observed under a microscope. It was found that the red dye was too pale to give a clear image on the microscope and therefore a different dye and higher concentration was chosen for repeat tests. The next dye considered was reactive blue dye and two potatoes weighing 105.9 and 106.1g were placed in solutions of concentration 1% and 2% respectively. On this occasion the potatoes remained in the solution for 40 minutes yet at 5 minute intervals the potatoes were removed and a potato peeler extracted a thin layer of the material before being placed in the dye. Every 5 minutes a thin layer was taken from the same part of the potato to observe how the moisture entered the potato. Samples taken during a later time point were closer to the inner part of the potato. Each potato slice was taken lengthways across the potato. By the end of the 40 minute period the centre of the potato had been reached. It was determined that a dye of 2% reactive dye was required for contrast.

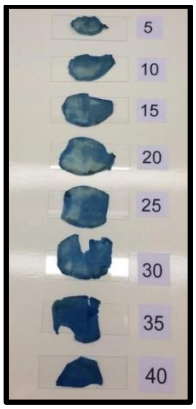


Figure 3-40 Potato Slices taken from Raw Maris Piper Potatoes Every 5 Minutes

A Vickers M41 Photoplan microscope was used to take photomicrographs of each 5 minute stage using a Nikon D90 DSLR attached to the microscope using a Hama T2 microscope adapter. A nominal magnification of 6.25x was used with a eyepiece and objective lens of 2.5x. One potential limitation of this method is that the whole section could not be photographed and instead interesting areas had to be searched for and photographed separately. The photomicrograph taken of the potato slice taken at minute 15 showed channels (Figure 3-41).

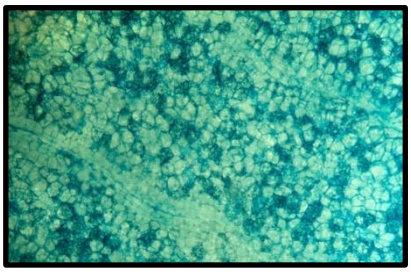


Figure 3-41 Potato Slice At Minute 15

The potato slice taken at minute 35 showed no evidence of channels as did the potato slice at minute 40 (Figure 3-42). Also from looking at minute 40 the potato is completely blue as opposed to having large patches of white. The centre of the potato is known as the pith and is where the potato structure has the lowest solids content and highest moisture content. Therefore to try and make the samples more representative the inner sample would only be taken from the centre of the longest chips in the sample set. Due to the way the potato is sliced the longest chips are more likely to consist of potato that originally formed part of the pith as opposed to the vacuole ring. It was decided to take sample from the pith of the potato as from looking at the micrographs this area of the potato looked more homogenous.

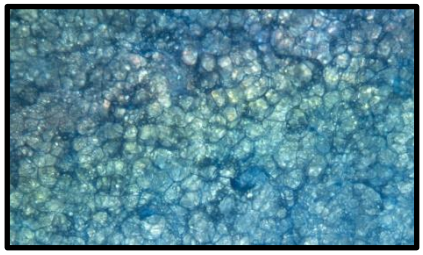


Figure 3-42 Potato Slice at Minute 40

3.2.2.1.3 Weighing the Sample

Each sample produced was weighed to 10 mg and the DSC and TGA were repeated to gain a measurement of the precision of the test method. Due to time limits only 2 repeats of the inner and outer were produced for the DSC and 3 repeats were produced for the outer in TGA.

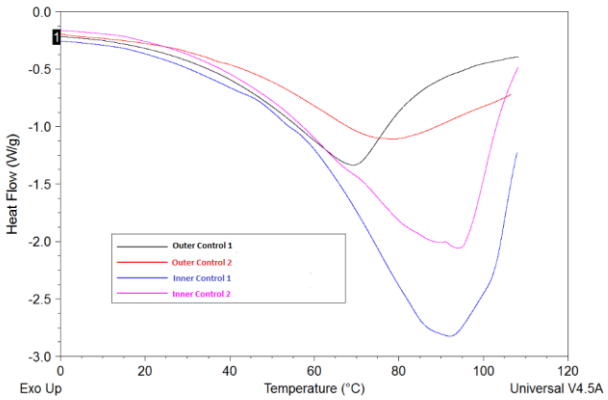


Figure 3-43 Repeat DSC Plots of Outer Layer and Inner Layer for Uncoated Control Sample During Week One of Investigation

For the DSC (Figure 3-43), despite careful selection of the sample there was still variability between the samples. However, the repeats did show that there was a difference in the DSC between the outer and the inner which was to be expected. Therefore it indicates that the DSC is able to distinguish between the outer and the inner and that fine-tuning was required to reduce the variability. The TGA data also showed variability for the samples. The mean residue was 76.99% , the standard error was recorded as 3.55 and the standard deviation was recorded as 6.14. This indicates that the samples are not close to each other and not close to the population mean either. Alterations needed to be made to the sample preparation to reduce the errors observed. During the initial sample preparation stage samples were cut using a Weck-Prep blade and then transported to the testing area. The sample was weighed on scales and then inserted into the machine. It was during this phase that it was observed that the sample was losing weight rapidly during the weighing process. As the sample size was so small, excess moisture was evaporating rapidly into the 18 ^{o}C testing environment. Therefore it was decided to stop the weighing practice and instead estimate the weight of sample going directly into the machine. By weighing, the sample entering the DSC and TGA was no longer representative of the starting sample due to the moisture evaporation. Once prepared, sample was placed in a desiccator and immediately used. When a sample was required it was made as needed as opposed to keeping the sample chopped in the freezer. Six repeats of the inner were tested in the DSC and TGA to observe the effects of these modifications to the end results. The results of this set of data can be found in section 5.5.3.3 and 5.5.3.4.

3.3 Method Development for the development of the coating

3.3.1 Coating Development

One of the main aims of this research was to produce a crispier product within the domestic microwave. As such coatings were looked at in terms of their dielectric properties. Once the dielectrically active coating ingredients of CMC and NaCl had been determined it was important to develop the production method.

3.3.1.1 Coating Concentration and Production Process

The coating preparation had to be considered carefully. The first aspect was to determine the viscosity of the CMC. The second area was the concentration of sodium chloride to add to the coating. This had to be considered for two reasons;

1) Sodium chloride reduces the viscosity of CMC
2) Too high a sodium chloride concentration would result in rejection on a sensory basis.

The final area to consider was where in the production process the coating would be applied. Unfortunately due to project confidentiality an overview of the production process itself cannot be provided. However, there was a discussion in terms of where in the process a coating could and should be applied. It was therefore decided that coatings would be applied to the base product before frying, after frying and after freezing.

3.3.1.1.1 Determination of CMC product and application method

Three different CMC powders were provided by Dow; Clear +Stable CRT 30, Walocel C 1000 (09) and Walocel C 1000 (07). Clear + Stable CRT 30 provided the lowest viscosity of 30 mPas in a 2% solution. Walocel C 1000 (09) and Walocel C 1000 (07) provided the same higher viscosity of 1000 mPas in a 2% solution but differ according to sodium concentration on its backbone. Two different amounts of sodium on the backbone were provided with 1000 (07) having a low degree of substitution and 1000 (09) having a high degree of substitution. Two different levels of sodium substitution were provided due to activity of sodium in the microwave. It is not known if the sodium would be able to interact with the microwave field when CMC is dissolved in solution. Initially there were two options for applying a coating; via a dry powder or via liquid application. According to the manufacturer (McCain, 2013, Bellecom-Allen, 2015) liquid applications are preferred due to issues with powder clumping and non-uniform dispersal. During the starch powder investigation one of the main issues was powder dispersal due to differing particle sizes.

A method had to be determined to create a liquid CMC product. As CMC is hygroscopic it quickly became apparent that mixing CMC powder with water resulted in clumping and was

therefore unsuitable as a coating. On private consultation with (Bellecom-Allen, 2015) CMC was mixed with oil first to form a paste and then water was added quickly before being shear mixed for 10 minutes using a Silverson shear mixer at speed 1200 rpm (Figure 3-44).

Figure 3-44 Preparation of CMC Coating in Pilot Plant

NaCl is added after the CMC water mixture has been shear mixed. The mixture is then mixed for a further 5 minutes. This is because (Dow, 2016) have determined that dissolved CMC is more stable against NaCl addition than CMC which is added to NaCl and water. Therefore the viscosity development of CMC is less likely to be impacted.

Name of hydrocolloid	**Concentration of CMC in solution (%)**	**Concentration of sodium chloride (%)**	**Concentration of sunflower oil (%)**
Clear + Stable CRT 30	2	0	10
		2	10
		5	10
	5	0	10
		2	10
		5	10
Walocel 1000 (07)	2	0	10
		2	10
		5	10
	5	0	10
		2	10
		5	10

Walocel 1000 (09)	2	0	10
		2	10
		5	10
	5	0	10
		2	10
		5	10
Control	0	2	10
	0	5	10

Table 3-7 Recipe of Coatings Produced During Initial Coating Preparation

The concentration of CMC was set at a high and low level and these levels were confirmed from observing the literature with the final coating recipes outlined in Table 3-7 (Xue and Ngadi, 2007, Karrout et al., 2015, Jia et al., 2014, Bellecom-Allen, 2015). There were issues with determining the correct concentration of NaCl for a coating. According to (Dinicolantonio et al., 1984) preferences for NaCl are related to dietary consumption of NaCl and therefore regardless of the level chosen this will not suit the entire population. Consideration must also be given with regards to safe levels of NaCl in the diet. According to the (NHS, 2018) this safe limit is 6g of salt per day for adults although currently adults in the UK eat an average of 8.1 g. The (NHS, 2018) state that a low limit of salt in a food is 0.3 g per 100 g whilst a high amount is more than 1.5 g of salt per 100g. Another factor to consider is that the concentration within a coating will not translate to the same concentration in the whole product as only a thin layer is placed onto the product. A final consideration was in terms of dielectric properties. (Peyman et al., 2007) investigated the dielectric properties of NaCl solutions between 0.001 and 5 mol/L at 20 ^{o}C and over the frequency range 0.13- 20 GHz. They observed that at the microwave frequency as the NaCl concentration increased so did the dielectric properties. (Buchner et al., 1999) observed that for concentrations <1mol/L the permittivity remained constant regardless of temperature but increased as a function of concentration. On considering all of these factors and on discussion with (Bellecom-Allen, 2015) it was decided sodium chloride levels of 0%/0 mol/L, 2%/0.34 mol/L and 4%/0.68 mol/L would be used. This translated to 2 g per 100 g for the 2% solution and 4 g per 100 g for the 4% sodium chloride. According to the (NHS, 2018) these levels would be considered high but because they are present in only a coating higher levels were chosen to try and increase the NaCl concentration so their dielectric effects could be observed.

The viscosity of the end solution was considered. As the solution needed to be cost effective, current McCain Food systems for their batters were used. On private correspondence with

(Haldenby, 2016) it was determined that for optimum batter conditions, the temperature of the batter be between 14-18 ^{o}C with a target of 16 ^{o}C. This is because a colder batter produced a superior in line performance as blow off is less and the batter is less likely to contaminate the oil as rapidly. It was also confirmed that batter viscosities were measured using a B6 flow cup.

Figure 3-45 Testing Viscosity of Coatings Using B6 Cup

The batter is inserted into the B6 flow cup and then timed (Figure 3-45). The time is stopped when a bead drop is observed (break in the flow of the coating). A typical batter used by the manufacturer takes 6/7 seconds to exit the B6 flow cup.

Results.

CMC Type	CMC (%)	Sodium Chloride (%)	Temperature (^{o}C)	B6 Flow Cup (sec)
1000 (07)	2	0	15.8	40.41
1000 (07)	2	4	15.2	38.62
1000 (09)	2	0	15.8	38.44
1000 (09)	2	4	15.3	37.12
1000 (09)	5	0	15.5	Gel too viscous to run as fluid
30	2	0	16.3	5.83
30	2	2	16.3	5.45
30	2	4	16.5	5.43
30	5	0	15.8	33.56
30	5	2	15.4	36.75
30	5	4	15.6	35.23

Control (no CMC)	-	2 (+10% oil)	16.3	3.73
Control (no CMC)	-	4 (+ 10% oil)	16.5	3.66

Table 3-8 Temperature and Viscosity of Each of the Coatings Produced

Table 3-8 shows the results of the B6 flow cup on each of the coatings tested. Not all solutions were produced. The higher viscosity CMC samples (1000 (07) and (09)) produced too high a viscosity for the current manufacturing process regardless of whether NaCl was added. The CMC sample suitable was CRT 30 as this gave values similar to that of the B6 flow cup optimum for the manufacturers factory. The CRT 30 at 5% CMC concentration was too high for the flow cup and so the concentration was revised down to 3.5% as the upper limit.

3.3.1.1.2 Development of Post Freezer Coating Application

This was performed on a domestic scale using chips created in the Scarborough pilot plant. Deionised water was used when preparing the coating. Deionised water was not used during chip creation and as such there may be variations in the result due to differing ion concentrations in the water used. A B6 flow cup was also not available as there was a delay in delivery. As such the batters were kept between 15- 16 ^{o}C to ensure the batter was as similar as possible to the batter used during the pre and post fryer application. As a post freezer liquid application was required an OXO Good Grips silicone draining board was cut into the shape of the turntable of a microwave. The rivets in the draining mat were present to capture surplus liquid coating so the product would not be sat in the liquid (Figure 3-46). The chip product used for this proof of concept experiment were remaining microchips produced in the pilot plant by McCain Foods for the frozen project experiments conducted by (Beasley, 2015).

Figure 3-46 Silicone Draining Mat Containing CMC and Sodium Chloride Coated Chips

The coatings produced were;

1) 2% CMC 0% sodium chloride

2) 2% CMC 2% sodium chloride
3) 2% CMC 4% sodium chloride
4) 3.5% CMC 0% sodium chloride
5) 3.5% CMC 2% sodium chloride
6) 3.5% CMC 4% sodium chloride

Two different coatings were tested at the same time to reduce the effect of differing microwave fields. The microwave was allowed to cool for 5 minutes between each experimental run. Coatings were applied in a walk in freezer at -18^{o}C so that the chip product did not begin to thaw during coating application. Each coating was tested 3 times and results were recorded visually and verbally (Figure 3-47).

Figure 3-47 Post Freezer Application of 2% CMC 0% Sodium Chloride Products

The products were heated in the microwave immediately after application and 1 week later after being left in a freezer at -18^{o}C. A 'fizzing' noise was observed for the products microwaved immediately after application. This was not the case for the product microwaved one week later. It was determined that in the product heated immediately after application there was an improvement in product crispness. This was stated verbally by the investigator and 5 others working in the laboratory at the time. However, the product tested a week later had reverted to its original 'soggy' state. This indicated that storage was having an impact on the product.

The fizzing noise observed during the heating of the crispier product was of interest as it was not present for the control samples or the sample heated a week later. This occurred across all CMC and CMC and NaCl coatings. 50 ml of each of the six coatings were weighed and heated in the microwave. Immediately on application of microwaves the fizzing noise appeared and increased in amplitude. After 40 seconds the amplitude of the fizzing sound reduced until there was silence. Coatings that contained more NaCl produced a higher amplitude than samples without. The CMC NaCl and CMC coatings only produced the fizzing noise when the solution was still liquid. On opening the microwave once the fizzing noise had disappeared each of the six coatings resembled a dry powder. As deionised water was used the fizzing can be attributed to the presence of the CMC and NaCl alone and not due to ions present within the water. This therefore

indicates that the theory of a self limiting coating is realistic as the ionic material is only able to interact with the microwave field when in the presence of water. The role of CMC as a polyelectrolyte was also proven. The fizzing noise did not occur in samples that had been stored for a week. There was a concern that the domestic freezer at -18ºC was not cold enough to freeze the coating and that the coating may be detaching from the product and remain in the packaging as opposed to interacting with the microwave field.

Figure 3-48 Coating Applied Post Freezer Being Inserted Into Blast Freezer

A second quick freezing process was incorporated to freeze the coating onto the chip. Chips were placed in a blast freezer at -30 ºC for 20 minutes prior to being transferred to a domestic freezer at -18ºC (Figure 3-48). On microwaving after storage the fizzing reappeared and so this method was kept as it successfully adhered the coating to the chips. To look at the fizzing further chips were coated in dry Clear+Stable CRT 30 CMC until they were fully coated (Figure 3-49).

Figure 3-49 Chips Coated with Dry Clear+Stable CRT 30 CMC After Heated in 700W Microwave Oven for 2 minutes 40 Seconds

On heating, the product became burnt towards the centre of the chip. It was also found that eating the product resulted in extreme drying of the mouth, attributed to the hygroscopic nature of CMC. On heating this product in the microwave no fizzing occurred and therefore it was theorised that in its dry form the CMC is not behaving dielectrically. This shows that for the CMC to behave as a polyelectrolyte water is required. Instead, the CMC is so hygroscopic it is pulling moisture from the centre of the chip causing the chip to become dehydrated and resulting in the texture observed in Figure 3-49 on opening the chip after heating.

3.3.1.1.3 Product Variation Issues

During post freezer coating method development, the presence of the silicone draining mat had an effect on the product.

Figure 3-50 Post Freezer Coated Samples Heated in 700 W Microwave for 2 Minutes 40 Seconds

On testing the uncoated microchips left over from the (Beasley, 2015) frozen project, the chips darkened in colour and started to burn long before the recommended cooking period of 2 minutes 40 seconds was reached (Figure 3-50).

Figure 3-51 Silicone Mat Placed Into Bottom of Microchip Boxes

As such attention was focused on the silicone draining mat. The rivets in the draining mat were theorised to promote heating, possibly due to excess moisture collecting below the product, superheating and causing the temperature within the microwave to increase thus driving off moisture from the surface. Therefore the silicone was placed into the bottom of a microchip box 100g of the product was heated in the microwave (Figure 3-51). The chips produced were crispy. As the silicone appeared to be promoting product crispness a larger scale experiment was performed. Microchips were bought from 4 different shops in Leeds to try and reduce errors due to poor product handling by suppliers and tested against the factory produced product.

Figure 3-52 Comparison Between Chips Used During (Beasley, 2015) Study and Shop Bought Microchips

As can be observed in Figure 3-52 it became apparent that the factory produced products were a different product compared to the microchip product currently on sale; particularly in terms of product cut size. For the shop bought microchips the silicone draining mat had limited effect on promoting crispness possibly due to the larger cut size and therefore more moisture. On consulting McCain Foods, it became apparent that the microchip product sent for testing during the frozen storage experiments were different as they were a product which not only had a different cut size but also had undergone a further drying stage.

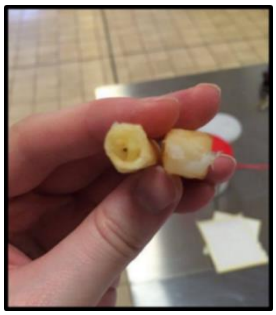


Figure 3-53 Hollow Centre of (Beasley, 2015) Chips

The product used in the frozen storage experiments was 8 weeks old when it was used for the coating application proof of concept. On opening this product as compared to product bought from a commercial retailer, the factory produced product was hollow in the centre, indicating it contained less moisture (Figure 3-53). As such the silicone draining mat was discarded as a potential solution and so was not used during the result generation stage.

3.3.1.1.4 Cooking Time of Product Developed

As the coated product was different to the original uncoated products the cooking time was observed. A series of experiments were conducted where cooking times of 2 minutes 40 seconds, 3 minutes, 3 minutes 30 seconds, 4 minutes and 4 minutes 30 seconds were used with a one minute rest at the end of heating. The mechanical data was observed using a Volodkevich jaw attached to a Stable Microsystems Analyser with a test speed of 1 mm/s and the number of force

drops calculated across 3 chips as depicted in table 3-9. A force drop was deemed valid if the force applied dropped by 0.049 N. This level was chosen as it was the default test setting provided by Stable Microsystems for the Volodkevich jaw probe attachment.

Time	Number of force drops across 3 chips	Standard Error
2 minutes 40 seconds	25	1.45
3 minutes	25	1.76
3 minutes 30 seconds	21	1.73
4 minutes	100	1.65
4 minutes 30 seconds	794	2.23

Table 3-9 Number of Force Drops and Standard Error Calculated For Each Heating Time Considered

From observing the data and physical examination of the testing product it was determined that a 4 minute cook time would also be observed alongside the manufacturer guidelines of 2 minutes 40 seconds as it was at this point that the product was affected.

3.4 Final Note Regarding Method Development

As method development occurred throughout the whole project there are instances in the results chapters where different parameters were used. This was unavoidable due to the novel nature of this project. Where results differ from the final method listed in chapter 2 this will be clarified in each results section.

Chapter 4
Understanding the dielectric, physical and chemical properties of the base product

As microwave heating is an extremely complex issue it was important to characterise the base product; in this case uncoated microchips produced by McCain Foods. Factors including storage, dielectric properties and chemical properties; in particular ionic content were considered. Over the course of chapter 4 these factors shall be considered separately. From the learnings observed in this chapter it was possible to create coated potato products, the results of which are in chapter 5.

4.1 Frozen Storage of Base Product

During the method development phase discussed in section 3.1.1.5 free and bound water are present. The free/bound water findings extend to frozen storage due to the interaction of ice and liquid water within the microwave environment. As discussed by (Chaplin, 2014) in section 1.6.1.2 liquid water will rotate on application of an electromagnetic field in the microwave frequency, and ice will rotate in the kHz long radiowave frequency. The interaction of ice and water in relation to the electromagnetic field is discussed further in section 1.6. As a logical next step it would be expected that bound ice will not interact as well as free liquid water. On cooking in the microwave the ice does melt to become free water. The storage of the product in a domestic freezer at -18±2 ^{o}C has an impact on the end product week by week. If ice crystals are able to propagate week by week this may increase the total moisture in the system. On private correspondence with the manufacturer (McCain, 2013) they stated that they believe the product changes mostly over the first two weeks. Therefore storage time was considered as a factor for why the product alters so drastically.

4.1.1 Product Preparation

As discussed in section 2.1.1 uncoated microchips were produced by the manufacturer and sent to the principal investigator (Beasley, 2015). Control samples produced at the beginning of the eight week storage test and fresh samples, produced every week as a comparison were tested. The investigators were informed that the samples produced had undergone the same production process as uncoated microchips that were currently on sale in the UK market. However, on later experiments performed it was determined that this was not the case and that an additional drying phase had been incorporated to these products. The product was also a different cut size; 3/8 inch cut as opposed to ½ inch cut size usually created for the UK market.

4.1.2 Materials and Methods

Every week for 8 weeks the products were measured using two different measurement techniques; acoustic and mechanical measurement and a sensory panel. The test settings and parameters are noted in sections 2.1.1. The cooked product was heated for 2 minutes 40 seconds and left to stand for 1 minute and underwent acoustic and mechanical measurement and a sensory panel every week. Frozen product was also tested every week but was tested using the acoustic and mechanical method only.

4.1.3 Frozen Product Results

As discussed in section 2.1.1 only the mechanical measurements could be taken of the frozen products as the AED was broken at the time of experimentation.

4.1.3.1 Frozen Force Profile Theory

It was expected that the force profile produced would appear similar to Figure 4-1.

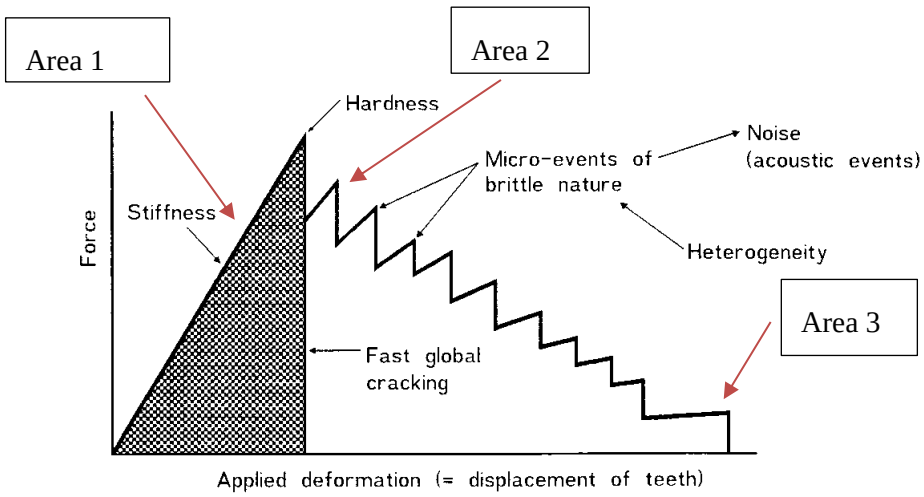


Figure 4-1 Typical Force Displacement Plot

Area 1 observes the outer skin of the potato resisting the force applied to it and as such the force increases until the probe punctures the outer layer. The force is expected to drop slightly but as the soft inner part is still frozen the force applied to the product remains high and this is signified by Area 2. Area 3 represents the end of the product where the probe reaches the outer skin on the bottom of the chip and pierces through the product meaning that no more force is needed.

4.1.3.2 Actual Force Profile

Every week, with the exception of weeks 1 and 2, 6 different chips were tested in the Volodkevich jaw for both the control and fresh product. During week 1, 18 chips were tested for the control sample only with six chips being measured at three different time points across the

week. During week 2, 36 chips were tested with 6 chips measured at three time points during the week for both fresh and control samples. Figure 4-2 shows the mean force produced by the frozen samples during week 1 as a function of displacement. To understand chip microstructure as the probe travelled through it, the mean force was plotted against the % the probe travelled through the chip.

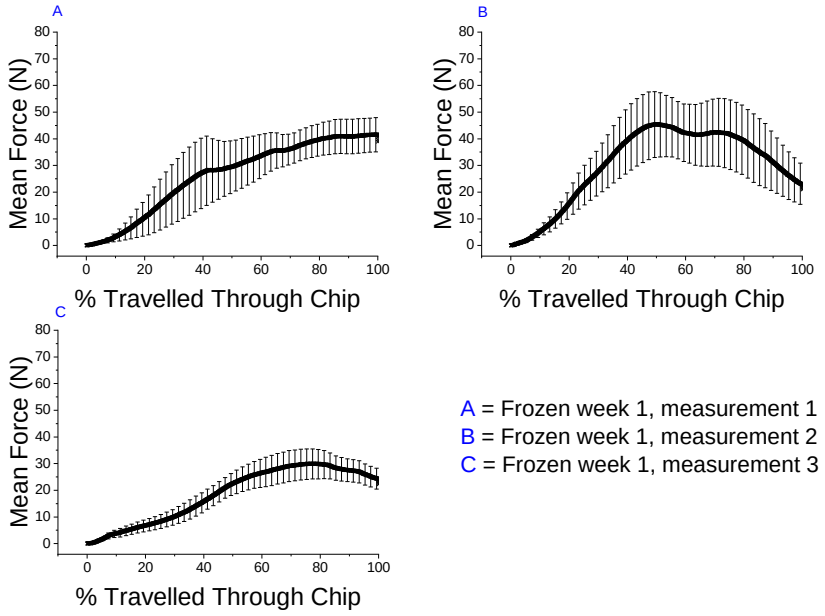


Figure 4-2 Mean Force (n=6) Recorded During Week One of Frozen Uncoated Chips

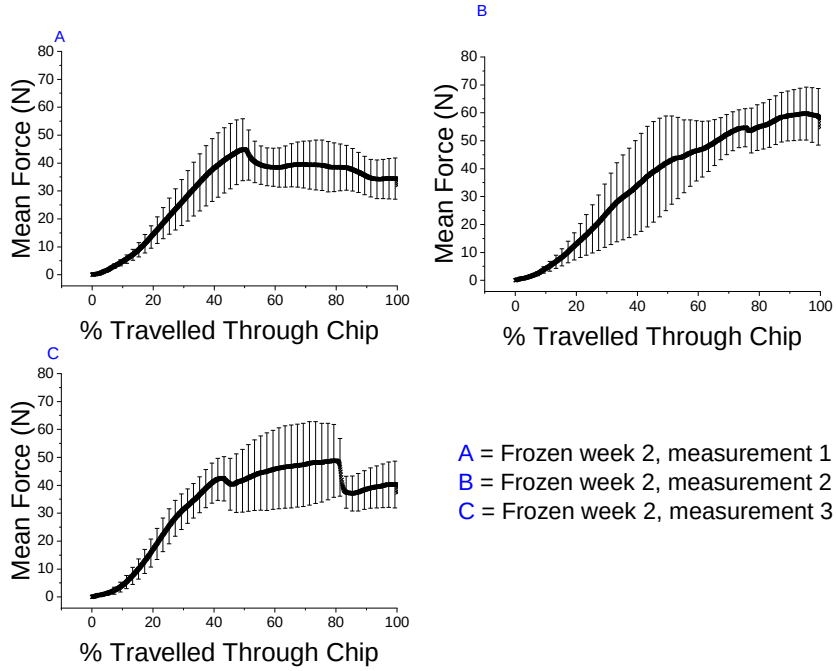


Figure 4-3 Mean Force Recorded (n=6) During Week 2 for Frozen Uncoated Chips

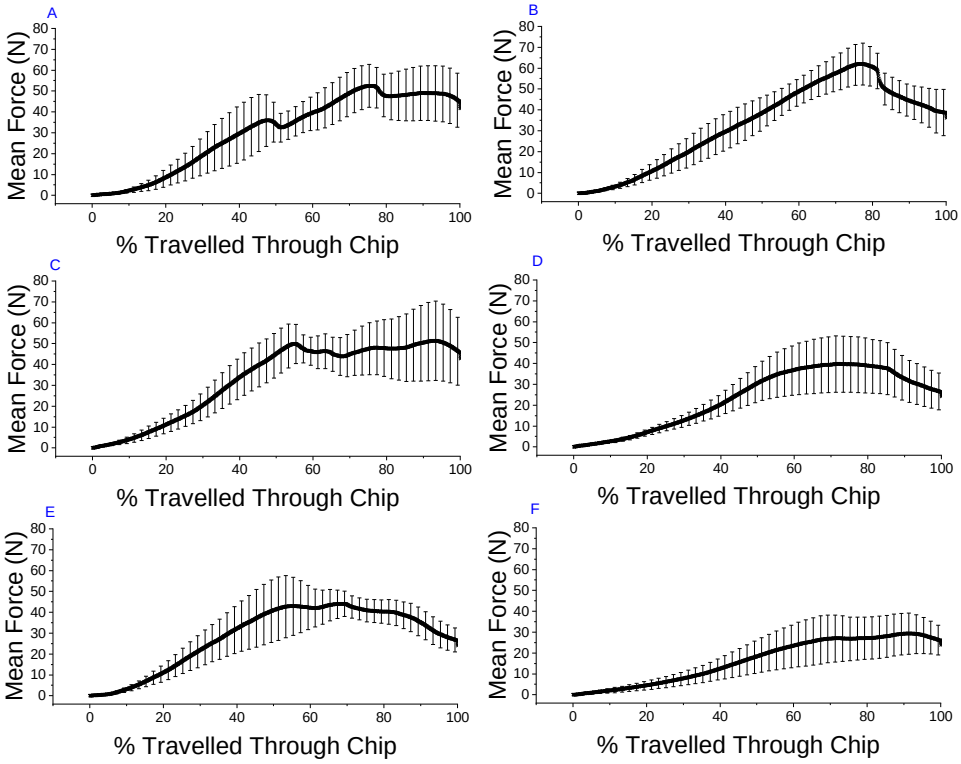


Figure 4-4 Mean Force Recorded (n=6) For Frozen Uncoated Chips

A = Week 3, B= Week 4, C= Week 5, D= Week 6, E= Week 7, F= Week 8

Figures 4-3 and 4-4 present the mechanical data for weeks 2 and weeks 3, 4, 5, 6, 7 and 8 respectively. To determine if a significant difference in the frozen structure was detected, the area under the curve of each force displacement curve was extracted before undergoing statistical testing. For all statistical tests the confidence level was set at 0.95 and the null hypothesis was set as all the areas under the curve are the same. A paired two sample for means two tailed t-test was conducted for the week 1 measurement 1 (w1m1) mean against the week 8 mean. A p value of <0.01 was recorded. As such the null hypothesis can be rejected and it stated that the product does change over the 8 week period when in a frozen state. According to the manufacturer they observed that they saw more changes in the product during weeks 1 and 2. Therefore a one way ANOVA of the mean was conducted for week 1 and then week 2 to determine if the product changed over this time. The null hypothesis in these cases was that the frozen structure of the product does not alter over a week with the alternate hypothesis being that the sample does alter over a week. For the week 1 ANOVA a p value of <0.01 was recorded. Therefore the null hypothesis could be rejected and it stated that the frozen structure of the product altered over the first week. The ANOVA conducted for week 2 recorded a p value of <0. 01 and so the null hypothesis could be rejected. An ANOVA was also conducted observing the changes in the force

mean between weeks 3 to 8. A p value of <0.01 was recorded indicating that the product differed over this period. Finally an ANOVA was conducted observing all the measurements taken week to week. The p value generated was <0.01 so it can be stated that the frozen product is not the same over the entire 8 week period. From observing Figure 4-4, there appears to be a large degree of error between each of the 6 chips measured which may impact the statistical data as all statistics were performed as a function of the mean. Section 4.1.5 attempts to understand this variation further.

The shape of the force curves does follow the force profile expected. In most of the Figures there is a period of force increase as the product resists the probe, followed by a small force decrease as the probe fractures the product. However, the chips are different in that they do not all complete the force plot theorised in Figure 4-1 in the testing time. In some cases the force is still increasing indicating the product is still resisting the probe or that the probe has reached the end of the chip and is beginning to hit the metal base. In some cases the product is plateauing and would be considered to have reached Area 2 of Figure 4-1. Finally in some cases the force plot is actively decreasing indicating that these products have reached Area 3.

4.1.3.3 Second Derivatives

The second derivative of the raw data was taken using Origin Pro Software. This was performed to give a ratio of the change in pressure. When the pressure applied to a sample is constant (in this case at 1 mm/s) the graph produced is also constant. However, if the product resists the force being applied and/or allows the force probe to move through the foodstuff there is a change in the amount of energy stored or lost by the material. This can be depicted via the peaks and troughs of the second derivative. The second derivative measures the rate of energy change in the sample. Therefore, it was decided to isolate the lowest force peak produced as this is where the highest degree of microstructural breakdown in the product can be observed, as the material is no longer resisting the force applied as before. Figure 4-5 shows an example of the second derivative recorded for a frozen chip during w1m2c6 (week 1 measurement 2 chip 6).

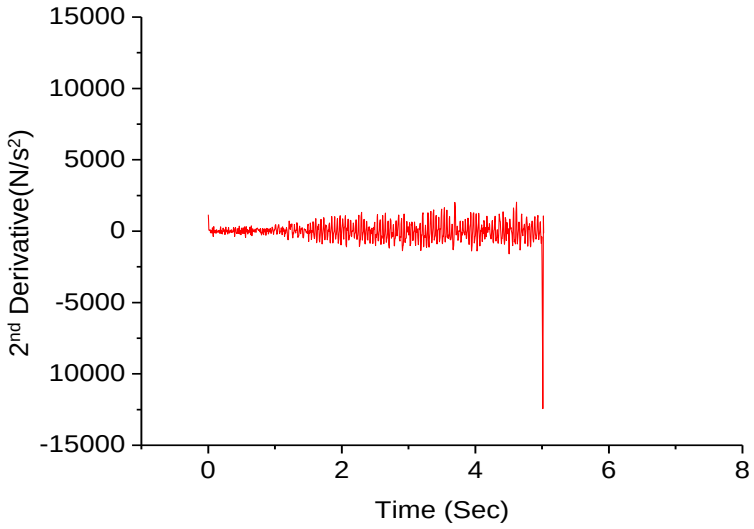


Figure 4-5 Second Derivative for Week 1 Measurement 2 Chip 6

From looking at the second derivative it is possible to see areas where there is more energy storage and loss due to the size of the peaks. Once this area was determined, it was plotted separately in Origin Pro. The data was also smoothed via 11 point Sovitzky-Golay smoothing and this is shown in Figure 4-6. Whilst slight differences did occur on smoothing, the decision was taken not to smooth the remaining data due to the concern that important data was being missed.

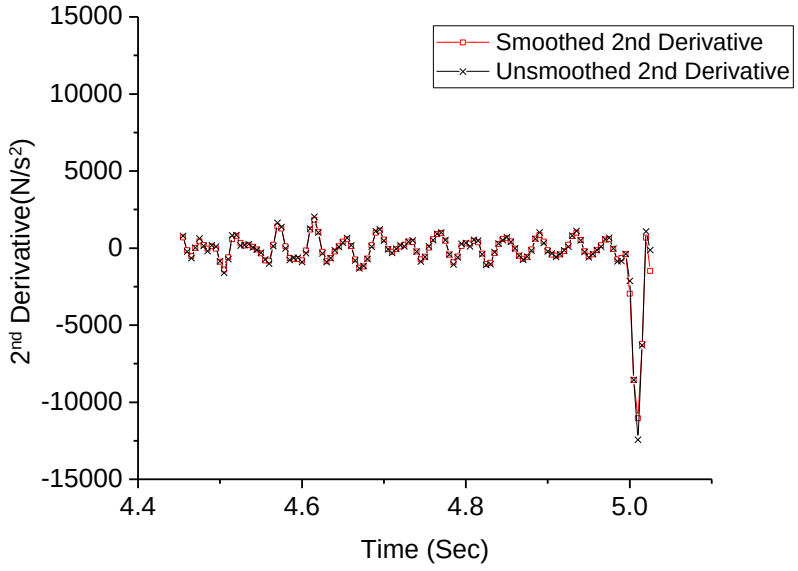


Figure 4-6 Unsmoothed Second Derivative (black line) of Week 1 Measurement 2 Chip 6 and Smoothed (red line) using 11 point Sovitzky-Golay Smoothing at 4.4 to 5 Seconds Through Test

The final analysis performed on this data was the log function. This is due to the Weber-Fechner law as discussed in section 1.2.3. As the test speed was set at 1 mm/s, both time and distance can

be used interchangeably in this instance. The second derivative was plotted against the % the probe travelled through the chip as a function of width of the sample.

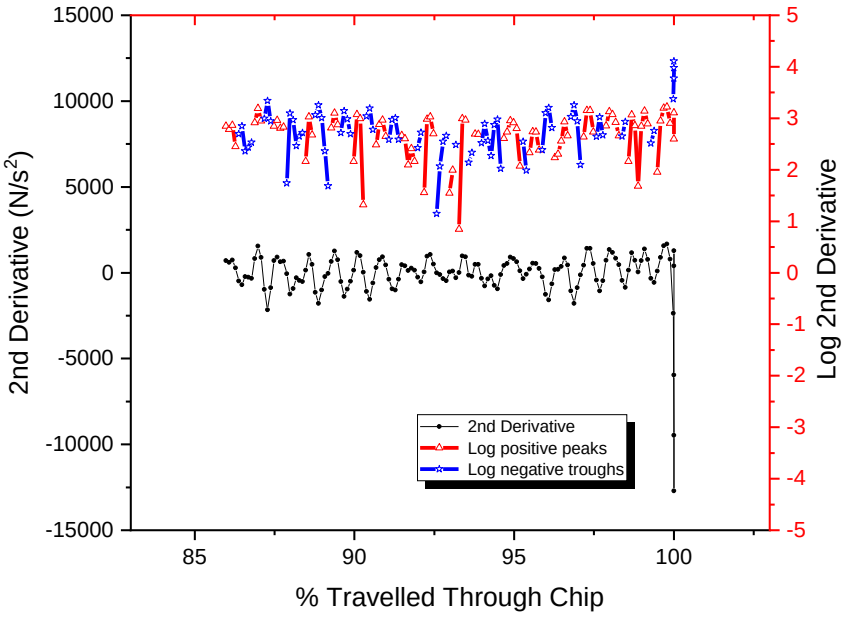


Figure 4-7 Unsmoothed 2nd Derivative of w1m2c6 (black line) plotted as a Function of % Travelled Through Chip Against the Log of the 2nd Derivative in the Form of Positive Peaks (red line) and Negative Troughs (blue line)

Whilst logs cannot themselves be negative, a change in the log is what is of interest. By converting the negative peaks to positive numbers the change in log can still be determined. In the above example, the greatest variation is observed in the 2nd derivative when the probe has travelled 85% to 100% through the samples and is -13000 N/s^{-2}. This negative value is depicted in the negative log peak as a mirror image. For positive logs it is not a mirror image and instead represents the shape of the positive 2nd derivative points.

4.1.3.3.1 Variation of 2nd Derivative

Figure 4-8 shows 2nd derivatives produced by 6 frozen chips measured during week one during measurement period one. Differences do exist between the product even when measured during the same time period. This is likely due to the non-homogenous nature of the potato product.

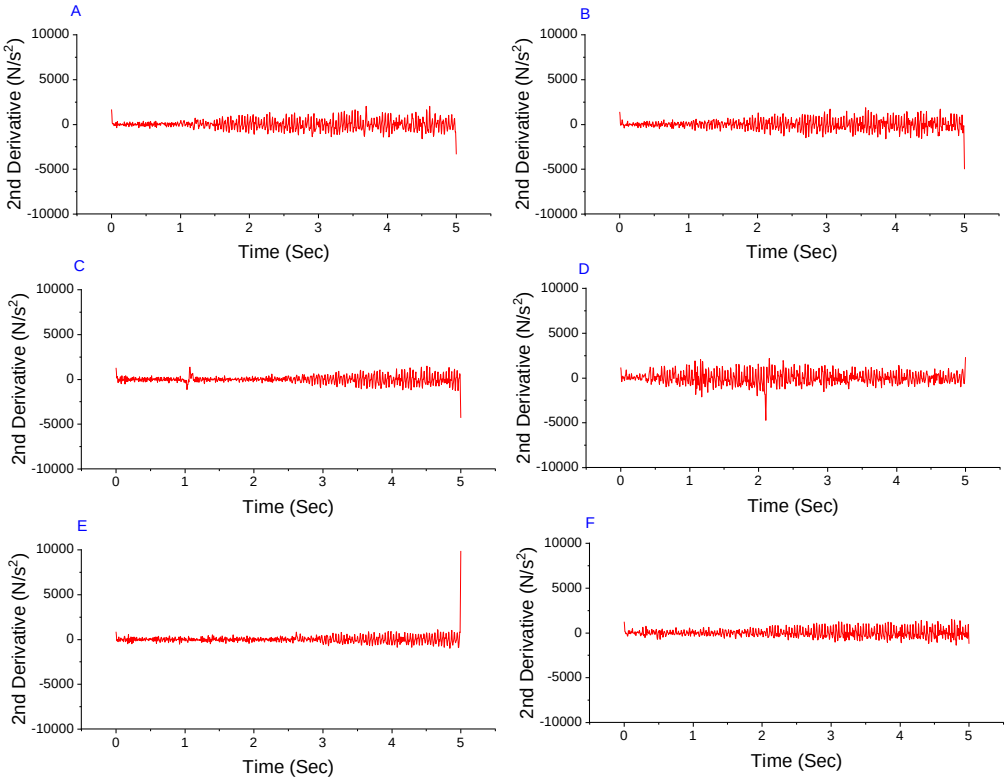


Figure 4-8 2nd Derivatives of Frozen Uncoated Chips

A= w1m1c1 (week1 measurement 1 chip 1), B= w1m1c2, C=w1m1c3, D= w1m1c4, E= w1m1c5, F= w1m1c6

Due to the large amount of data collected not all data shall be presented in this thesis with just one example given. However, all data shall be discussed.

4.1.3.3.2 Log and 2nd Derivatives for Frozen Uncoated Product

Figure 4-9 shows example log 2nd derivatives for measurements taken during week one for the frozen product.

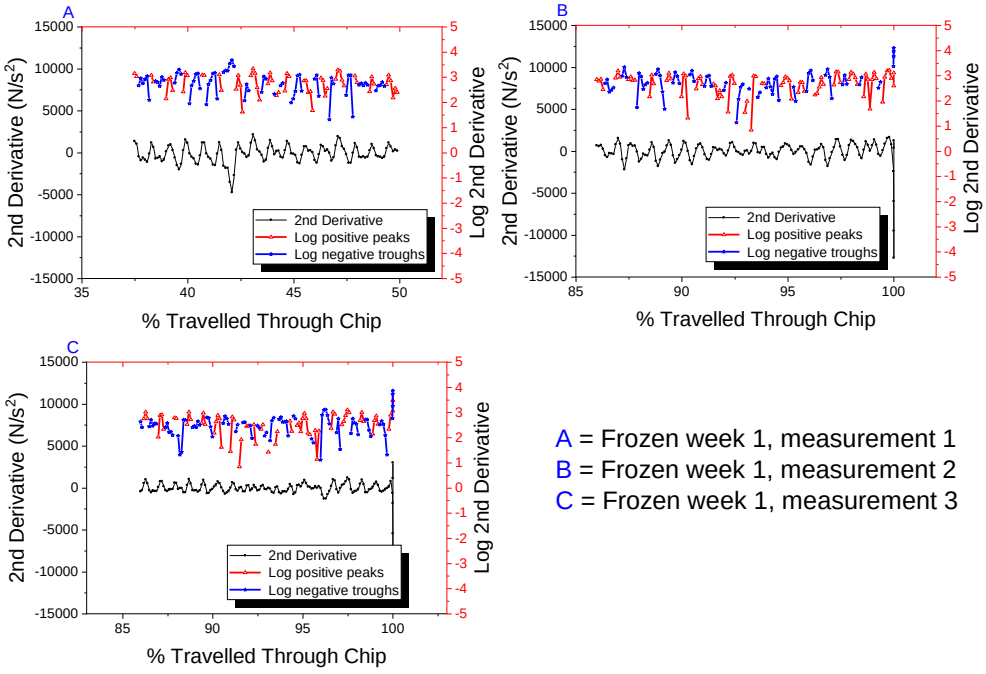


Figure 4-9 2nd Derivative (black line) and Log Measurements (red and blue lines) of Uncoated Frozen Chips During Week One

During week 1 the maximum change in log is from 1 to 4 indicating that there is a 30x perceptible difference in product hardness. A general pattern which is found in Figure 4-10 can be observed across all frozen samples.

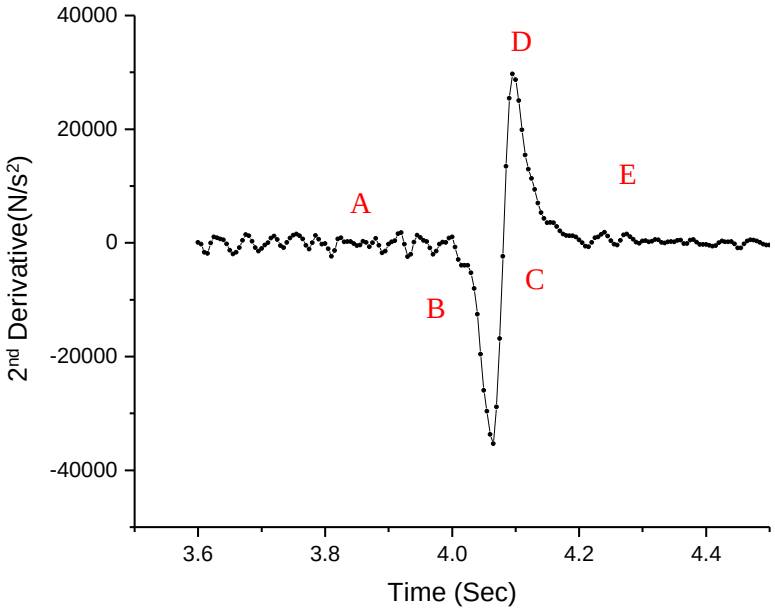


Figure 4-10 General 2nd Derivative Pattern Observed in Chip Product

‘A’ depicts a period of small energy storage and loss. ‘B’ depicts a sudden large energy release by the product as it pierces the outer skin of the product. ‘C’ depicts a large increase in energy storage as the probe moves to new material in the microstructure. ‘D’ indicates a further microstructural breakdown as the energy that is stored is immediately released. ‘E’ shows how the material returns to a fixed state of small energy storage and losses as the probe moves through the product. In most cases a deviation from the fixed state only occurred once in the testing window before returning to a fixed state. In general most samples recorded their highest energy storage and loss either at the end or the beginning of the testing window. This is not unexpected as at these points the probe would be interacting with the outer skin on the top or bottom of the chip.

The same pattern of behaviour can be observed across the remaining 8 weeks whereby there is a state of small energy storage and losses followed by a large energy loss, storage and loss before the sample returns to a fixed state. It suggests that the microstructure when frozen is alike with 96% of the 72 samples reporting the largest microstructural breakdown 10% into the product. The log difference is again recorded as 3 and despite the force recorded by the Volodkevich jaw differing across the samples measured every week, the perceptible difference remained identical across all frozen samples tested with the exception of week 5 where a log difference of 4.5 was recorded for some samples. The highest energy release was recorded as -40000 N/s^{-2} and was observed after 5 weeks of storage.

4.1.4 Cooked Product Results

4.1.4.1 Expected Cooked Force Profile

The mechanical method is highlighted in section 2.2.1 and utilised a Volodkevich jaw probe attached to a Texture Analyser. On application of a force it is expected that a force curve similar to Figure 4-1 would be observed. Area 1 observes the outer skin of the potato resisting the force applied to it and as such the force increases. At a certain point area 2 should be reached whereby the total force applied is too great and the outer skin is punctured. Area 3 represents the soft inner centre. It would not be expected that the soft mash core would resist the probe and as such a decrease in the amount of force required to deform the product would be expected. However, it would be expected that area 3 would show a non-linear line and that small peaks and troughs would be observed due to the non-homogenous nature of the product.

4.1.4.2 Actual Force Profile

As with the frozen products, 6 different chips were tested each week for each test condition meaning 12 chips were tested each week; 6 for the control sample and 6 for the fresh product. Initially the aim was to test at three time points during weeks 1 and 2 before being measured once a week from week 3 onwards. However, due to equipment issues, data could not be generated for

week 1. In terms of presentation the mean force profile and standard error was calculated. To best represent the data the time and distance series were converted to % travelled through the chip.

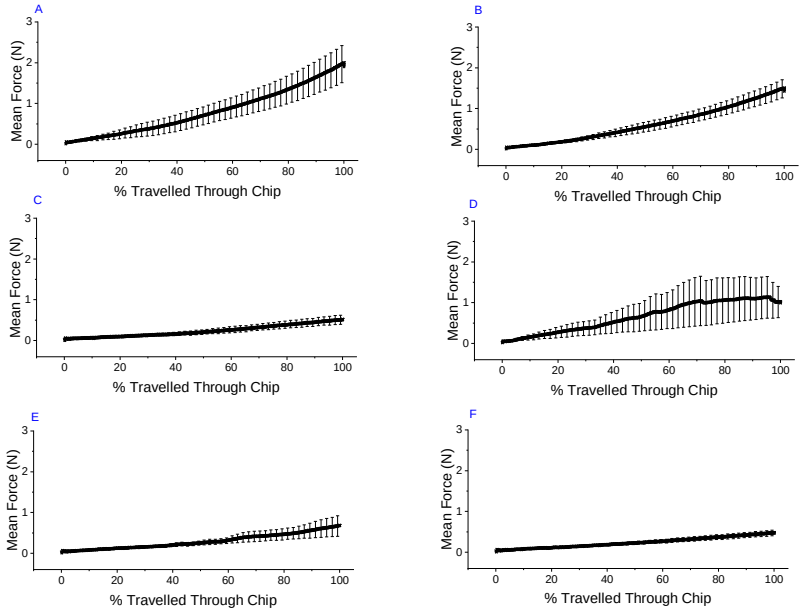


Figure 4-11 Mean Force (n=6) of Uncoated Cooked Chips as a Function of % Travelled Through Chip

A= w2m1 control, B= w2m1 fresh, C= w2m2 control, D= w2m2 fresh E= w2m3 control F= w2m3 fresh

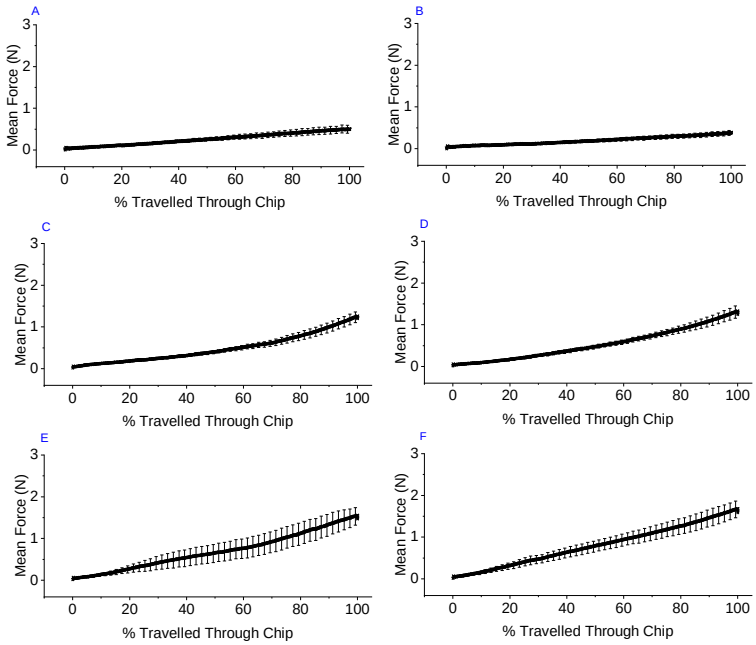


Figure 4-12 Mean Force (n=6) of Uncoated Cooked Chips as a Function of % Travelled Through Chip

A= w3 control, B= w3 fresh, C= w4 control, D= w4 fresh, E= w5 control F= w5 fresh

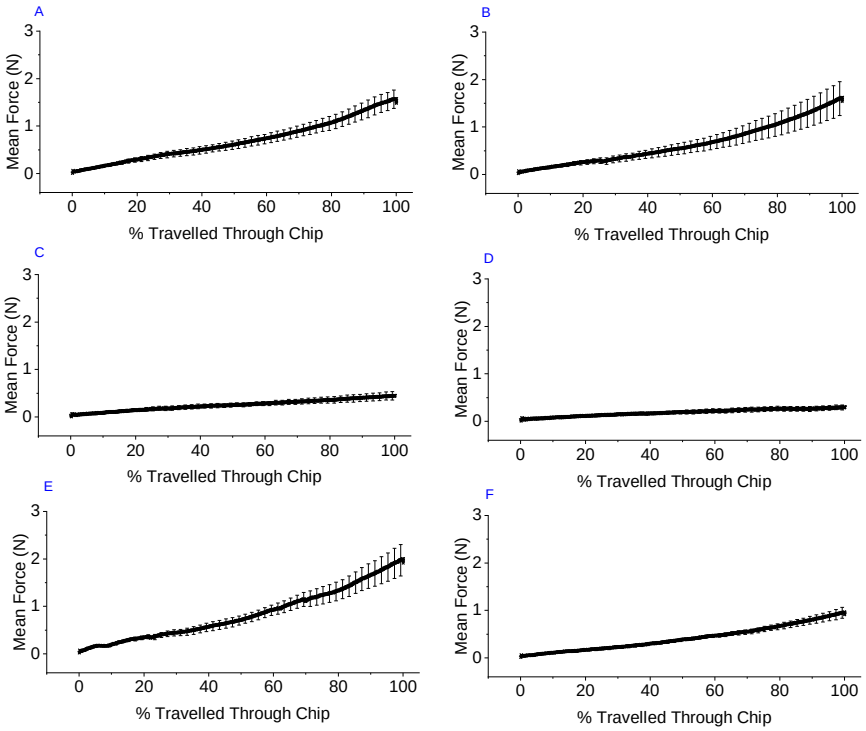


Figure 4-13 Mean Force (n=6) of Uncoated Cooked Chips as a Function of % Travelled Through Chip

A= w6 control, B= w6 fresh, C= w7 control, D= w7 fresh, E= w8 control F= w8 fresh

Figures 4-11, 4-12 and 4-13 observe the displacement curve plots for weeks 1-2, 3-5 and 6-8 respectively. In comparison to the frozen samples, the cooked samples' error bars are visibly smaller regardless of whether the samples were control or fresh. The fresh samples measured during week 2 measurement 2 showed the largest variability. As the samples are batch cooked this could contribute to the errors shown. However, as the error bars are generally small this instils confidence in the pilot plant method McCain Foods adopt for production of microchips.

The cooked product recorded lower force levels with the maximum mean force recorded as 3N compared to the 40000N recorded by frozen samples. The force curves did not follow the predicted force profile suggested in Figure 4-10. This could be because the product was soft. In most cases a small increase can be observed before the force levels out. This could indicate the difference in product hardness between the outer skin and inner is very small. Therefore this product would be considered soft and fairly homogenous as there is no difference between the two layers. The control samples in general do show a larger increase in the force required to deform the product particularly in Figure 4-13.Statistical analysis was performed by taking the max force for each of the 6 chips measured during each measurement point. The following statistical tests were performed;

1) A paired two sample for means, two tailed t-test

2) Two Way Analysis of Variance with replication

The null hypothesis for the t-tests was the area under the force displacement curve is the same. For the ANOVA the null hypothesis was the area under the force displacement curve is different for the fresh samples and the area under the force displacement curve is the same for the control samples. T-tests were conducted every week to determine if the fresh samples measured were different to the control samples. Two ANOVAs were conducted to determine if the fresh product differed over the 8 week testing period and if the control product differed over the same period as a function of the max force. On application of the t-test, during week 2 the p value for m1 was <0.01, for m2 it was <0.01 and for m3 it was <0.01. The null hypothesis can be rejected and it stated that the control and fresh samples are not the same. For the t-test for week 4 the p value was <0.01. For weeks 5 and 6 the p values were <0.01 and <0.01 respectively. Finally the p values for weeks 7 and 8 were <0.01 and <0.01 respectively. Across every week the null hypothesis could be rejected. As such the control and fresh samples can be labelled as not the same. The second statistical test performed was the ANOVA. In both cases the p value was <0.01 meaning that the null hypothesis could be rejected. The fresh samples week to week can be considered as not different and the control samples can be considered not the same. In terms of the force profile the cooked control samples differ week to week whilst the fresh remain statistically similar. This agrees with the manufacturers observation that frozen storage has a large impact on the end texture of the product.

4.1.4.2 Second Derivatives

Due to the large amount of data generated visual depiction of the second derivative will only be given for an example sample from weeks 2 and 4 as shown in Figure 4-14.

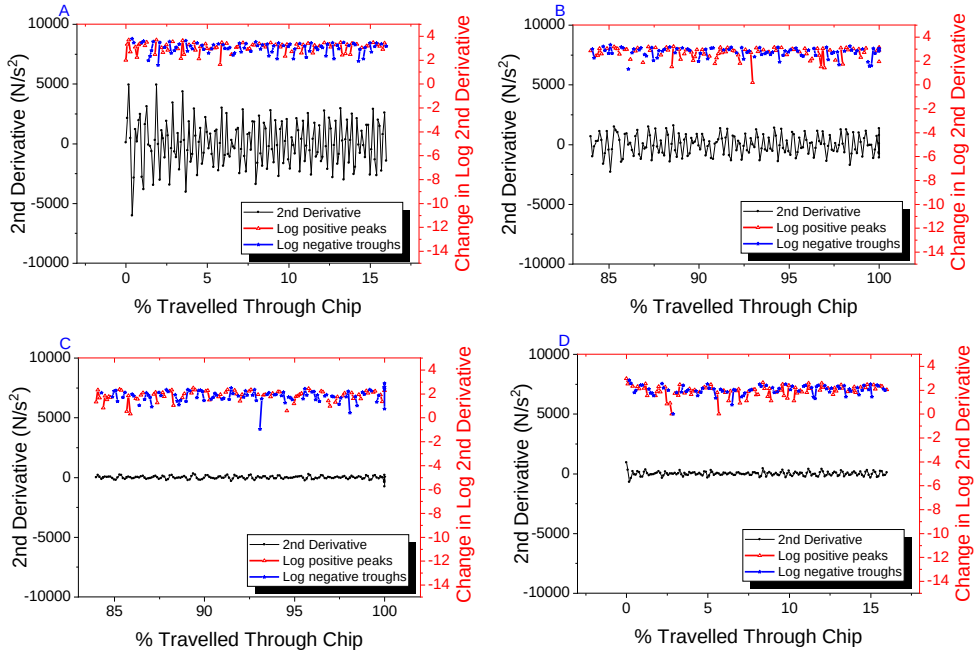


Figure 4-14 2nd Derivative (black line) and Logs (red and blue lines) of Uncoated Cooked Control (A+C) and Fresh (B+D) Microchips

A= w2m3 control, B= w2m3 fresh, C= w2m3 control, D= w2m3 fresh

The second derivatives for the cooked products were not as consistent as the frozen data. During week 2 and 3 the lowest energy release was recorded as -6000 N/s^2 with energy storage of 9000 N/s^2. In general control chips had larger negative losses than the fresh chips although these events occurred infrequently. For the most part the control and fresh chips showed similar energy storage and release patterns every week. In weeks 4,5 and 6 the largest energy release was 2500 N/s^2. The energy storage and release values fluctuated by the same range every week regardless of if they were fresh or frozen. On observing the logs the biggest change in the log is 3.5 which is similar to that observed in the frozen samples.

4.1.5 Natural Variation

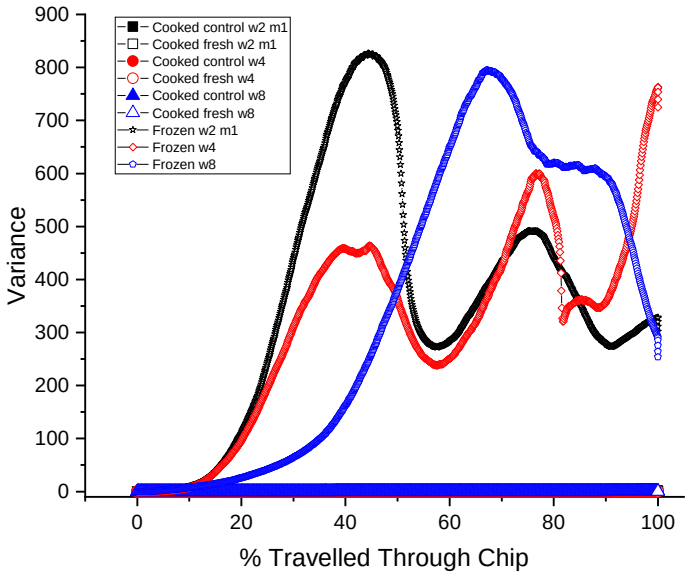


Figure 4-15 Natural Variation of Cooked and Frozen Chips Over an 8 Week Period

Figure 4-15 observes the variance between 6 chips taken at 2 weeks, 4 weeks and 8 weeks for frozen samples and cooked control and fresh samples. For the cooked samples there is little variance between the samples between each week with each of the 6 chips recording a low variance. The frozen samples record much higher variances with the highest variance of 847 recorded during w2 m1. Due to the variation in the force for frozen samples, natural variation of the product was considered. To investigate this, one box of frozen product and one box of cooked product were measured using the Volodkevich jaw at a test speed of 1 mm/s. Each chip present in the box had its top length, bottom length and width measured.

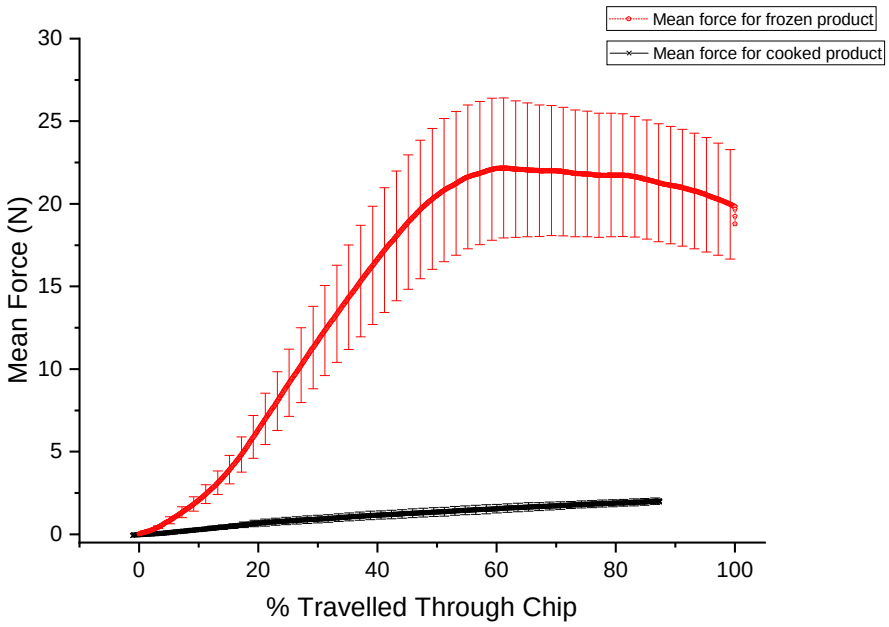


Figure 4-16 Mean Force (n=30) of Cooked (black line) and Frozen (red line) of all chips present within a Microchips Box as a Function of % Travelled Through Chip

Figure 4-16 shows the mean force produced by all 30 chips present within a McCain microchip box before cooking and after cooking. Unfortunately as the test method is destructive different boxes from the same batch were used to investigate variation. From the error bars the main variation in texture occurs when the product is frozen and when the probe has moved for 60%. Once the sample is cooked the variation reduces with no visible error bars produced. The mean force is greater for frozen samples than cooked samples. However, when observing samples individually some frozen samples recorded much larger forces with the highest force for chips 1, 3 and 6 recording forces of 69.49 N, 76.02 N and 77.35 N respectively. In some cases the highest force recorded by some products was more similar to the cooked product with chips 28 and 30 reporting a highest force of 4.31 N and 3.73 N respectively. Samples towards the end of the test may have begun to thaw, therefore resulting in lower forces being generated. In the case of cooked products the mean force was much lower with the highest force produced by chip 25 being 6.37 N. 73% of cooked samples had a highest force of either 1 or 2 N.

In conclusion it appears that variation in the product is present in terms of product length, where a maximum difference of 4.9 cm was observed, and in terms of natural variation due to the physiology of the potato discussed in section 1.3. The greatest factor affecting product variation is the microwave. Before being microwaved the product is highly variable yet on application of the microwave this variability is greatly reduced.

4.1.6 Sensory Results

	Week	Overall	Crispness	Texture	Colour	Flavour
Significant Difference	2	N	N	N	N	N
	3	N	N	N	Yes	N
	4	N	N	N	N	N
	5	N	N	N	N	N
	6	N	N	N	N	N
	7	Yes	N	Yes	Yes	Yes
	8	Yes	N	N	Yes	Yes
	7 months	N	N	N	Yes	Yes

Table 4-1 Observing if Significant Differences in Attributes Investigated During Sensory Testing were Observed (N= Not Significant, Y= Significant)

Table 4-1 shows the results of the sensory panels. To determine if a significant difference was found, an ANOVA with a 95% confidence limit was applied as well as a Tukey Test which measures the difference between sample means with a 5% confidence limit. Table 4-2 shows the average scores given by panellists for the five attributes considered. Significant differences were seen during week 7 and 8 of storage for several attributes. During week 3 there was a noticeable difference in colour between the fresh sample and the cooked sample with a comment that the fresh sample during week 3 was visibly more cooked. This difference is due to variation caused during processing of the product. For some participants fresh samples were preferred for their colour than control samples but this did not translate into a significant difference. In terms of overall acceptability fresh products were always preferred for weeks 2 to 8. During weeks 7 and 8 the average score for the control product fell below 5 meaning that the control product was disliked by the majority of participants. In terms of crispness the control sample always fell below 5 meaning it was disliked by the majority of participants. The fresh samples also scored less than 5 every week with the exception of week 3 where it scored an average of 5.07. Panellists stated that they disliked the control product as it was ‘ too soggy’ during weeks 1 to 2. From week 8 onwards the panellists stated that the control samples were becoming hollow in the centre.

Week		Overall	Crispness	Texture	Colour	Flavour
1	Control	5.35	4.59	4.18	5.71	4.29
2	Control	5.73	3.27	4.87	5.13	5.87
	Fresh	6.07	4.47	5.33	5.67	6.20
3	Control	5.36	4.36	5.07	4.86	5.43
	Fresh	6.00	4.57	5.20	6.50	5.93
4	Control	5.95	4.11	5.05	4.79	5.68
	Fresh	5.89	3.95	5.11	5.89	5.84
5	Control	5.70	4.40	4.95	5.65	5.45
	Fresh	5.75	4.25	5.40	5.85	5.95
6	Control	5.76	4.94	5.00	4.94	5.88
	Fresh	6.56	4.65	4.94	5.41	5.41
7	Control	4.93	4.20	4.40	5.13	4.73
	Fresh	6.00	5.07	5.67	6.33	6.07
8	Control	4.67	4.80	4.40	5.27	4.67
	Fresh	5.73	4.27	5.13	6.33	5.80
7 months	Control	4.89	4.72	5.00	7.11	5.22
	Fresh	5.78	3.89	5.33	4.67	6.33

Table 4-2 Average Scores For Each Attribute and Sample Type on Sensory Testing Reported as a Function of Time (1= dislike extremely, 9=like extremely)

In terms of the texture a significant difference was observed at week 7 with panellists preferring fresh samples over control samples. The highest texture score for the control sample was 5.07 in week 3 meaning that the sample was neither liked nor disliked. In terms of the flavour of the product both the fresh and the control sample reported values over 5 for the first 5 weeks. During week 7 and 8 the control samples fell below 5. Panellists commented throughout testing that the product was bland and under-salted. The samples were tested 7 months later with the control being tested against a fresh product. It was noted by 100% of panellists that the control product was crispier than the fresh product. However, there was no significant difference recorded. Based

on the results it appears that for some of the panellists tested, they preferred a softer product whereas other panellists preferred a crispier product. It was noted by 95% of panellists that the control product was hollow in the centre. It was also stated by 100% of panellists that both the control and fresh samples were dry. The only significant differences were recorded for the flavour and colour of the samples. The control sample recorded an average score of 7.11 in terms of the colour of the product meaning that the control colour was 'liked moderately' whilst the fresh sample average score was 4.67. The fresh sample was preferred in terms of flavour as it produced an average score of 6.33 whilst the control samples scored an average of 5.22.

4.1.7 Limitations of Experiment

The main limitation is that the product tested underwent an extra drying step which has affected the end result. During investigations looking at different coatings the development of ice crystals was observed. However, ice crystals were never observed for this experiment and this is possibly due to less total moisture being present. As such this affects the total moisture in the system and as water is able to interact with the microwave environment may impact how the product performs compared to the uncoated product that has not undergone an extra drying step. The other major limitation of this project regards the sensory questionnaire. Whilst it did observe participant liking of a product it did not allow for participants to directly choose a product. Therefore if this experiment were to be repeated, a question regarding preference for one sample over the other would be incorporated. The final limitation regards variation within the frozen product. There is higher variation depicted in the frozen products compared to the cooked products. Coupled with the error bars and the natural variation of the frozen products compared to the cooked products, there is more confidence in the statistical analysis performed on the cooked samples than the frozen samples. Despite the larger errors the force perception was identical for all samples in the frozen product except week 5 indicating the product is similar. The highest structural breakdown occurred either at the beginning or end of the test in the majority of the frozen samples.

4.1.8 Learnings and Outcomes

The main outcome from this set of experiments regards the importance of the microwave. Whilst frozen products varied greatly chip to chip in terms of force measurement, this variance was greatly reduced once the product was cooked regardless of whether it was a fresh product (stored for only 4 days prior to experimentation) or a control product which was stored for as many as 8 weeks prior to testing. Based on the force results, storage does not impact the variability of the cooked product as the interaction of the microwave overrides its importance. The second derivatives of the frozen products suggested a period of smaller energy storage and releases prior to a larger energy release and storage consistent with the point at which the probe would come into contact with the outer skin on either side of the potato. From observing the force curves the

frozen product is affected by storage as the product alters week to week. Every week the force profile indicated that the control and fresh samples were statistically different. On observing the 2nd derivatives the same pattern of energy storage and loss is observed. However, the energy stored and released was lower indicating a softer product. Despite the control and fresh samples being different in terms of the actual force applied, on creation of the second derivative, the fresh and control samples differed by the same fluctuating range every week regardless of if they were control or fresh. This could again be due to the interaction of the microwave. Each control and fresh sample were placed in the same microwave at the same time prior to being measured. As such the microwave field may be driving the microstructural response of the product. The sensory panel only showed a difference in preference from week 7 onwards. As discussed the colour difference observed in week 3 could have occurred as the process involves batch cooking. On observing the force profiles, the mean force for the fresh samples during week 7 and 8 fell and were closer to 0 N whilst the mean force for the control was closer to 0 N in week 7 and 2.5 N in week 8. This indicates the product became harder in week 8 which concurs with comments made by the panellists. Despite the control product hardening, the fresh sample was still preferred in weeks 7 and 8 indicating that consumers prefer a softer product compared to a crispier product that is more hollow. During analysis it was noted that the probe was moving too quickly and as a result important events were being missed. Despite frozen products being hard, microstructural breakdown was only being observed towards the end of the test even when the product was pierced on application of the probe. Therefore the test speed was reduced to 0.1 mm/s to attempt to capture smaller changes. Unfortunately this research was conducted using a product that had undergone an extra drying step. This may have prevented the remaining moisture from interacting with the product on storage as it ordinarily would have. It is difficult to draw conclusions regarding the interaction of bound and unbound water on storage using this study alone.

A storage investigation was also conducted on coated product and this is presented in section 5.4 and 5.5. Whilst the storage investigation for coated products was different to this investigation learnings could still be taken from this experiment in terms of storage of the base product. This was because uncoated base product was subjected to the same storage conditions as the coated product. However, due to time constraints data was only collected from the product once it had been cooked within the microwave.

4.2 Dielectric Properties of the Base Product

As microwave heating is a form of dielectric heating it was important to understand the dielectric properties of the base material prior to the addition of coatings.

To perform the dielectric measurement two measurement techniques were used; the Split-Post Dielectric Resonator (SPDR) and a novel method using a cavity built to the dimensions of a 2.45 GHz microwave oven. The stainless steel cavity was produced by Sylatech Ltd. under the instruction of the manufacturer McCain Foods. Both methods were connected to an Agilent Technologies Network Analyser and are considered as resonant cavity measurement techniques.

4.2.1 Dielectric Activity of Microchip Centre using SPDR technique

Due to the experiments on the silica and corn flour found in section 3.1.1.5, the next step was to investigate the centre of a microchip product. It is known that water is a driving factor of dielectric activity. The silica and corn flour work had shown in the form of the corn flour that added water was not immobilised whilst on addition of water to the silica this was immobilised. The ratio of bound and free water could impact how the uncoated product heats within the microwave environment. On microwave heating water is driven to the surface from the centre of the product. Initially due to storage conditions the moisture is present in the frozen state and as such the water is considered bound. It is of interest to characterise the dielectric properties of the centre of the product as it thaws. Also of interest is that the uncoated microchips undergo processing involving water and become soggy due to moisture being driven out from the centre of the chip. As such this experiment was conducted to determine if, when frozen and thawed, the dielectric properties of the centre of the microchip differed and whether the matrix of the chip was able to bind the water to prevent it interacting within the microwave.

4.2.1.1 Sample Preparation of Microchip Inner

The sample preparation of the product can be found in section 2.1.2.1. The sample was left in the SPDR to thaw over a period of 30 minutes as it was not possible to perform temperature dependent measurements. The presence of the vacuum bag was to ensure the moisture was contained and could not damage the SPDR machinery.

4.2.1.2 SPDR Results

As found during section 3.1.2.2.5 vacuum bags have minimal impact on the dielectric properties. Despite the microchip products producing an average moisture content of 78.77% from five moisture measurements taken, on addition of the product the sample was too conductive for a reading to be observed. During the coating work presented in 5.1 ambient native starch samples were able to record Q factors at higher moisture contents. It would be expected that the frozen samples would be less conductive than the ambient samples as frozen water is less able to interact with the electromagnetic water than water at ambient temperatures. It may be that the native starch samples are able to ‘hold on’ to the water making it less free to interact with the microwave field. It may also be that the potato sheet samples contain ions whilst the starch samples do not. As ions are able to interact with the electromagnetic field when dissociated, it could be that the

presence of ions are also a driving factor for dielectric measurement. After 5 minutes of thawing, Q factor values were recorded for the potato sheet sample with a Q factor of 408.9. This value only lasted for 10 seconds before the sample became too conductive and no further results could be collected over the 30 minute testing period. This could be due to the interaction between ions and water as ions only become active on dissociation in the presence of liquid water.

The raw potato used was an Innovator Potato provided by McCain Foods. In each of the 10 measurements the potato sample was too conductive indicating that the sample may be more dielectric due to other components present within the potato matrix.

4.2.3 Proof of Concept: Effects of Ions and Water vs Water alone

Figure 4-17 (L-R) Washed Potatoes and Unwashed Potato Samples

To investigate if the presence of ions were causing the failure to gain any measurements in the SPDR, an experiment was conducted observing if the dielectric effect of washed potatoes (ions washed away) in distilled water was smaller than the effect of unwashed potatoes placed back into the ion-distilled water mix used to wash the first sample. This aimed to show that the potatoes were too conductive due to the presence of ions and water instead of just water alone.

To prepare the sample 1.2 kg of Innovator potatoes were peeled and sliced into 1 cm^3 pieces. 600 g of the potatoes were added to a beaker containing muslin and washed with 800 ml of distilled water. The potatoes were placed in the water for 30 minutes before the muslin was wrapped around the potatoes and excess moisture expelled into the beaker. The 600 g of potatoes were then placed in another beaker and 800 ml of distilled water was added. This sample was labelled as the washed sample. Another 600 g of chopped potatoes was placed in the 800 ml of discarded liquid used to wash the first sample (Figure 4-17).

Figure 4-18 Preparation of Potato Samples

Both samples were placed in a water bath at 100ºC and heated until a mashed potato was formed. The starting moisture of the two samples were taken. 20 g of each potato mash at a time was spread onto aluminium foil measuring 20 x 20 cm and placed in an oven at 105 ºC. Samples were dried down to 20%, 30%, 40%, 50%, 60% and 75% as a % of the original moisture content on a dry weight basis for both mash potatoes. In total five 2.5 g samples of both of the mashes for each moisture conditions was packaged into a vacuum bag using the method discussed in section 2.2.1.2. Figure 4-18 shows the preparation of the potato samples.

4.2.3.1 SPDR Results

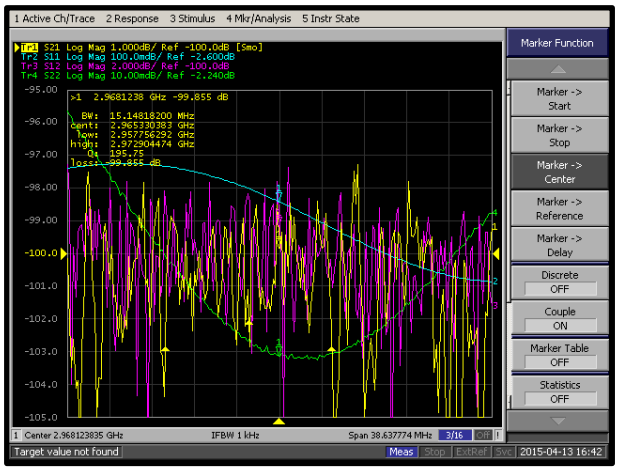


Figure 4-19 SPDR Results for 20% Moisture Washed Potatoes

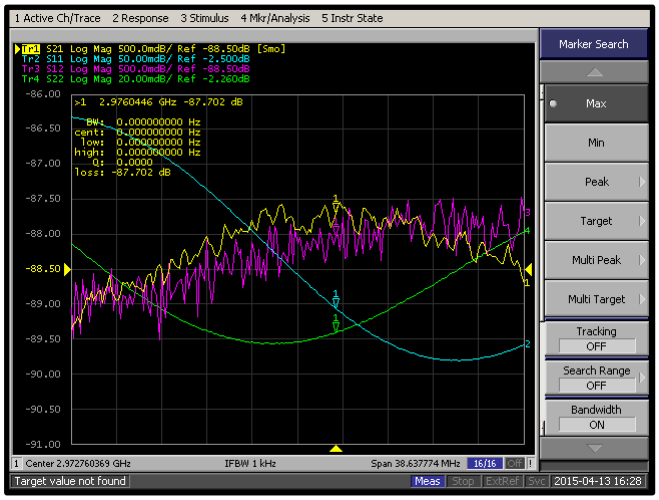


Figure 4-20 SPDR Results for 20% Moisture Unwashed Potatoes

For all mash samples tested at 30%, 40%, 50%, 60% and 75% regardless of whether washed or present in ion rich liquid the sample was still too conductive to get a reading. However, at 20% moisture content, the washed sample was less conductive than the ion rich sample (Figures 4-19 and 4-20). This indicates that ions do contribute to dielectric activity although water still appears to be the largest driving factor.

4.2.4 Ionic Component Determination in Raw Potato and Microchip Product Centre

As the proof of concept work suggested that ions do contribute to the dielectric heating the ion content of the microchip product and raw Innovator potato was observed. Atomic absorption spectroscopy (AAS) was applied to determine the presence of certain ionic materials within the processed product and a raw potato. The raw potato sample was sent by the manufacturer and consisted of Innovator potatoes. The processed product is currently made using either Maris Piper or Innovator samples. Unfortunately for the processed product it was unknown whether they consisted of Maris Piper or Innovator potatoes making a direct comparison difficult. From observing (McCance and Widdowson, 2002) ionic materials such as sodium, potassium and calcium among others were found within potato products undergoing different processing. Therefore it was decided that the constituents named by (McCance and Widdowson, 2002) would also be tested for in the research sample set. This was achieved with the exception of selenium and chlorine as the equipment was unavailable.

4.2.4.1 Results

All measurements were converted to mg/100g dependent on original dilution factors.

Ionic Material	Processed Product (mg/100g)	Innovator Potato (mg/100g)	McCance and Widdowson, raw, flesh only
Sodium	9.3	23.4	2
Sodium Chloride	23.3	58.6	n/a
Magnesium	0.8	0.5	21
Manganese	0.8	0.7	0.1
Zinc	1.2	0.6	0.3
Potassium	414.6	647.6	443
Calcium	9.3	23.4	7
Copper	0.3	0.7	0.06
Iron	6.3	7.8	0.3
Phosphate	46.7	47.4	34

Table 4-3 Ion Content Determined in Processed Microchip and Raw Innovator Potato Alongside a Reference Raw Potato

Table 4-3 observes the ion contents determined via the investigator and a reference ion content reading by (McCance and Widdowson, 2002). In general the raw Innovator potato had a higher mineral content than both the processed sample and the reference (McCance and Widdowson, 2002) which also observed skinless raw potato. It would be expected that the processed product would have a higher mineral content due to its lower water content although this was not the case. This could be because the processed products are made with a different botanical source of potato. This suggests that the botanical source of potato chosen has an impact on mineral levels. All components measured with the exception of magnesium and potassium levels in the processed product were higher than the reference sample. This could be because the reference sample used old potatoes and so mineral content may have deteriorated over time. It could also indicate that the manufacturer have succeeded in producing a potato species with higher ionic material contents. The results indicate that there are many ions present within the end product which, although reduce on processing are still present to interact with the microwave field. It also indicates there is an option to replace lost ionic components or increase certain ionic compounds to achieve a desired effect in the microwave environment.

4.2.5 Dielectric Properties of 100g of uncoated base product as a function of temperature

The dielectric properties of 100g uncoated product may be found in section 5.5.3.7. This is so direct comparisons can be made with the coated products.

Chapter 5
Understanding the underlying principles required for the creation of a coating which promotes product crispiness

Based on learnings generated from investigating the base uncoated microchip product, coatings were investigated to determine if the product could be improved in terms of its crispness. A coating with high dielectric activity was desired so as to promote heating in the microwave and drive moisture from the product surface. As microwave heating is a form of dielectric heating, it was important to measure the dielectric properties of coatings as well as to select ingredients with known dielectric properties. Therefore initial experiments were undertaken to look at the dielectric properties in more detail. This chapter will also observe the effect of storage on these coated products whilst also investigating how storage affects the coated products ability to promote product crispness.

5.1 Dielectric activity of Starch powders using SPDR

McCain Foods currently uses starches as part of the base recipe for their coatings. Initially the aim was to use a starch powder as a base for the coating and so starch powders were investigated in terms of their dielectric properties. Botanical sources of starch vary greatly in terms of amylose:amylopectin ratio, granule size and other factors. Therefore it was decided to investigate if differences occurred based on the following factors;

1) Botanical source of the starch (10 different types)
2) Starch processing method (native starch, gelatinised starch at 63-90 μm and 90-125 μm)
3) Relative Humidity environment (0%, 33%, 75%, 95%, 100%)

The samples were measured using the SPDR at ambient temperature as at this time the novel cavity was in production and not available for use.

5.1.1 Sample Preparation of Native starches

Sample preparation of the native starches was performed as stated in section 2.2.1. All samples were coded on delivery and so will be referred to by their respective codes in this thesis. The relative humidities were altered so the dielectric properties of the powders could be measured as a function of the moisture content. The codes can be found in table 5-1.

Name of Coded Starch based powder	
MU56	NU06
YG10	YE60
DW69	KF57
OV12	PJ46
YF61	BA75

Table 5-1 Coded Starch Based Powders

5.1.2 Sample Preparation of Gelatinised starches

Sample preparation of the gelatinised starches was performed using the 10 native starches and used the method observed in section 2.2.1.2.4. All samples produced shall be named as gelatinised followed by the code of the native starch used to produce the sample.

5.1.3 Measurement Procedure

The measurement procedure is highlighted in section 2.2.1.2. Five samples of each condition were measured but only one measurement of each sample tested was taken. This was because method development in section 3.1.1 has shown that repeatable measurements could be taken using the SPDR without fear of measurement errors.

5.1.4 Natural Variation

As starch is a raw material it was important to test the effect of natural variation on the dielectric properties. Five different samples were tested for each of the 10 starches in both their native form and their two gelatinised starch conditions. The differences observed within each sample set were then investigated to determine the natural variation range in the dielectric results gathered. Table 5-2 observes the natural variation in the 10 native starches. Table 5-3 observes the natural variation of the 10 starches when gelatinised and at two different particle sizes.

Sample	Natural Variation Dielectric Constant Native Starch	Natural Variation Dielectric Loss Factor Native Starch	Standard Deviation for Dielectric Constant Native Starch	Standard Deviation for Dielectric Loss Native Starch
K457	0.441	0.128	0.222	0.064
MU56	0.217	0.157	0.205	0.067

PJ46	1.00	0.218	0.393	0.088
BA75	1.295	0.259	0.507	0.104
YG10	0.871	0.138	0.322	0.059
YE60	0.148	0.059	0.052	0.021
OV12	1.00	0.297	0.615	0.122
YF61	0.712	0.126	0.341	0.064
NU06	0.826	0.161	0.341	0.064
DW69	0.384	0.104	0.149	0.039

Table 5-2 Comparison of Standard Deviation and Natural Variation in Dielectric Properties for Each of the 10 Coded Native Starches

Sample	Natural Variation Dielectric Constant Gelatinised Starch (63-90 µm)	Natural Variation Dielectric Loss Factor Gelatinised Starch (63-90 µm)	Standard Deviation for Dielectric Constant Gelatinised Starch (63-90 µm)	Standard Deviation for Dielectric Loss Gelatinised Starch (63-90 µm)
K457	0.250	0.063	0.106	0.023
MU56	0.340	0.036	0.122	0.015
PJ46	0.600	0.090	0.217	0.038
BA75	1.680	0.218	0.712	0.089
YG10	0.780	0.073	0.323	0.029
YE60	0.880	0.075	0.373	0.030
OV12	0.710	0.151	0.318	0.056
YF61	0.290	0.081	0.108	0.035
NU06	0.450	0.058	0.176	0.023
DW69	0.260	0.024	0.097	0.010

Table 5-3 Comparison of Standard Deviation and Natural Variation of Dielectric Properties for Gelatinised Versions of Each Coded Starch with Two Different Particle Sizes

The standard deviation results showed that every starch for every relative humidity and processing condition fell within one standard deviation of the mean for both the dielectric constant and the loss. This shows that the method used is robust. However, on observing the data measurement by measurement it was observed that there was a difference in terms of range. This

is not unexpected due to issues such as particle size distribution. From observing the ranges presented in Table 5-3, the natural variability differed in the 75% RH condition between the starches considered. The biggest range produced resulted from the BA75 sample which differed by 1.295. However, five samples may not give a full representation of the true natural variation but they do provide an indication. Some starches had a larger natural variation than others possibly due to their particle size distribution. During investigations by (McCain, 2015) it was determined that the particle size range of the starches were as depicted in Table 5-4.

Starch Code	Particle Size Range (µm)
K457	2.2 - 38
MU56	6 - 30
PJ46	14 - 54
BA75	6 - 150
YG10	1.8 - 50
YE60	2.2 - 160
OV12	15 - 60
YF61	5 - 32
NU06	1.5 - 80
DW69	2 - 22

Table 5-4 Particle Size Ranges of Each Coded Starch

Despite YE60 starch samples producing a particle size range of 2.2 – 160 µm this was not reflected in the natural variation in the dielectric data gathered as a range of 0.148 was found for the dielectric constant and a 0.059 range was found for the dielectric loss. The loss factor range produced the lowest value of the 10 native starches thus indicating that particle size may not impact the starches dielectric behaviour as BA75 with a particle size range of 6 – 150 µm produced the 2nd largest range in dielectric loss of 0.259. On further investigation into the origins of BA75 it was determined that high levels of phosphorous and potassium are present leading to ionic conduction and this may explain why there is a larger degree of natural variation in BA75 than YE60. Dependent on how they are bound into the starch structure and which part of the starch is measured dielectrically this could result in some BA75 samples having a large degree of variation compared to other BA75 samples. In terms of the gelatinised samples, the range in particle size is at a set value due to the sieving process. A larger range could suggest an inconsistency with sample preparation and it may be that whilst efforts were taken to prevent air being present in the sealed vacuum bag, sample may not have been completely uniform across the measurement area due to being displaced on application of the vacuum sealer. According to

(Pace et al., 1968) the dielectric constant (ε') of air is 1 and as a result air gaps could affect the measurement. However, because the standard deviation is <1 in all cases it suggests that natural variation is less likely to be an issue when sample is taken from the same batch. The effect of air gaps cannot be discounted though because it could be that whilst the results are similar to each other, there could be air gaps present in all samples thus affecting the results. Instead the standard deviation provides an indication of the test methods success. Finally the standard error reduced as the relative humidity reduced which suggests that moisture is not spread evenly throughout the samples as moisture is a driving factor of dielectric activity and there is less moisture present at the 0% relative humidity condition.

5.1.5 Results and Discussion

Initially five different relative humidity conditions were considered; 100% RH, 95% RH, 75% RH, 33% RH and 0% RH. However, with the exception of BA75 and YE60, 100% RH samples had to be discarded from the investigation because of mould growth when the starches were placed in this environment. As such only the effect of the four remaining relative humidities shall be observed. To analyse the data it was decided that a Three Factor ANOVA would be performed using SPSS Version 2 on both the dielectric constant and the loss separately. A Three Factor ANOVA with replication was chosen as this would enable interactions to be observed between starch type (botanical source), relative humidity and the starch processing method as well as enabling statistical analysis of each factor individually (Single Factor ANOVA) and against another factor (Two Factor ANOVA). An overview of the interactions, null hypotheses and alternate hypotheses investigated are given in Table 5-5. Where there is a tick ✓ present indicates which of the hypotheses was shown to be accepted.

Dependent Factor	**Independent Factor 1**	**Independent Factor 2**	**Null Hypotheses Main Effects**	**Alternate Hypotheses Main Effects**	**P Value observed Main Effects**	**Interactions Null Hypothesis**	**Interactions Alternate Hypothesis**	**P Value observed Interactions**
Dielectric Constant	Starch Type	Relative Humidity	Dielectric constant is the same for each starch type	Dielectric constant is not the same for each starch type ✓	***<0.01***	There is no interaction between relative humidity and starch type	There is an interaction between relative humidity and starch type ✓	***<0.01***
			Dielectric constant is the same for each relative humidity	Dielectric constant is not the same for each relative humidity ✓	***<0.01***			
Dielectric Loss Factor	Starch Type	Relative Humidity	Dielectric loss is the same for each starch type	Dielectric loss is not the same for each starch type ✓	***<0.01***	There is no interaction between relative humidity and starch type	There is an interaction between relative humidity and starch type ✓	***<0.01***
			Dielectric loss is the same for each relative humidity	Dielectric loss is not the same for each	***<0.01***			

				relative humidity ✓				
Dielectric Constant	Starch Type	Starch Processing Method	Previously Observed	Previously Observed	***n/a***	There is no interaction between starch type and starch processing method ✓	There is an interaction between starch type and starch processing method	***0.02***
			Dielectric constant is the same for each starch processing method ✓	Dielectric constant is not the same for each starch processing method	***0.312***			
Dielectric Loss Factor	Starch Type	Starch Processing Method	Previously Observed	Previously Observed	***n/a***	There is no interaction between starch type and starch processing method ✓	There is an interaction between starch type and starch processing method	0.034
			Dielectric loss is the same for each starch	Dielectric loss is not the same for each starch processing method	***0.327***			

			processing method ✓					
Dielectric Constant	Starch Processing Method	Relative Humidity	Previously observed	Previously observed	***n/a***	There is no interaction between the relative humidity and the starch processing method ✓	There is an interaction between the relative humidity and the starch processing method	0.118
Dielectric Loss Factor	Starch Processing Method	Relative Humidity	Previously observed	Previously observed	***n/a***	There is no interaction between the relative humidity and the starch processing method ✓	There is an interaction between the relative humidity and the starch processing method	0.349

Dependent Factor	**Independent Factor 1**	**Independent Factor 2**	**Independent Factor 3**	**Interactions Null Hypothesis**		**Interactions Alternate Hypotheses**	**P Value Observed for Interaction**	
Dielectric Constant	Starch Type	Relative Humidity	Starch Processing Method	There is no interaction between starch type, relative humidity and starch processing method✓		There is an interaction between starch type, relative humidity and starch processing method	***0.06***	
Dielectric Loss Factor	Starch Type	Relative Humidity	Starch Processing Method	There is no interaction between starch type, relative humidity and starch processing method ✓		There is an interaction between starch type, relative humidity and starch processing method	***0.485***	

Table 5-5 Three Factor ANOVA Observing the Effect of Starch Processing Method, Relative Humidity and Starch Type on the Dielectric Properties

The main findings for this experiment based on the ANOVAs at a 95% confidence limit were as follows;

1) The dielectric properties (constant and loss) are different dependent on the botanical source of starch in both native and gelatinised samples
2) The dielectric properties differ in terms of the relative humidity
3) No difference was observed in dielectric properties between native and gelatinised starch samples of the same botanical source
4) There is an interaction between the relative humidity and the botanical source of the starch in terms of dielectric properties
5) There is an interaction between the botanical source of the starch and whether the starch was in its native or gelatinised forms (starch processing method)
6) There is no interaction between the relative humidity and the starch processing method
7) There is no interaction between the botanical source of starch, relative humidity and the starch processing method.

5.1.5.1 Dielectric Properties as a function of Botanical Source of Starch, Relative Humidity and Starch Processing Method

According to the ANOVA the dielectric properties differed dependent on the source of starch. Across all relative humidity conditions and starch processing methods the dielectric properties of the sample did differ. Figures 5-1 and 5-2 show this behaviour at the 75% RH condition.

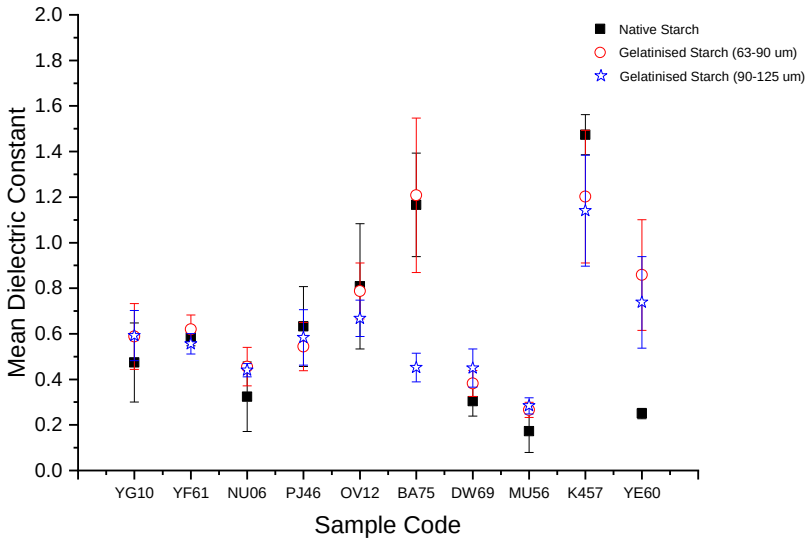


Figure 5-1 Mean Dielectric Constant (n=5) for 10 native starches (black square), 63-90 µm Gelatinised Starch (red circle) and 90-125 µm Gelatinised Starch (blue star)

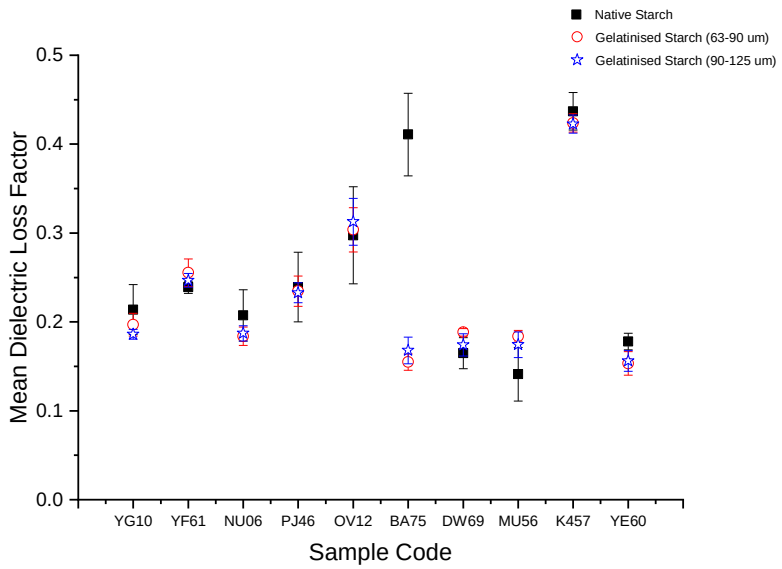


Figure 5-2 Mean Dielectric Loss (n=5) for 10 Native Starches (black square), 63-90 µm Gelatinised Starch (red circle) and 90-125 µm Gelatinised Starch (blue star)

Sample BA75 and K457 showed the highest dielectric properties compared to the other starches. In the case of BA75 this is not surprising due to the presence of phosphorous groups in this starches structure which may contribute to dielectric heating. However, this difference could also be attributed to starch polymorphs. Interestingly all of the starches tested were type A polymorphs with the exception of starch PJ46 (type C) and BA75 (type B). As B type polymorphs typically contain more pockets of water than A type polymorphs this could also explain why BA75 tended to result in higher dielectric activity at higher relative humidities. At lower relative humidities BA75 had dielectric properties more similar to the other 9 starches which could occur due to less moisture being present in 'pockets' to drive the dielectric properties. The fact K457 is showing higher dielectric properties is also interesting as this starch has a higher amylose content. The starches containing a higher ratio of amylopectin (NU06 and YE60) are noted to have much lower dielectric properties. When in their native form the mean differences in terms of dielectric constant and loss are 1.224 and 0.260 between K457 and YE60 and 1.150 and 0.230 between K457 and NU06. MU56 and YE60 are the same form of starch with YE60 containing higher amylopectin ratio. As can be observed the dielectric properties for these two starches was very similar at the 75% RH condition in the native starch and this was reflected regardless of relative humidity condition with the exception of 0% RH. At the lower relative humidity condition, the differences between samples were much smaller with the difference between samples MU56 and YE60 recorded as 0.818 and 0.117. On observing the MU56 samples there were small air gaps present which may have affected the end result causing higher dielectric properties to be reported.

The ANOVA also determined that the dielectric properties of the sample alter as a function of the relative humidity. From observing the data it was found that as the relative humidity of the

sample increases the dielectric properties of the sample also increases. Figure 5-3 observes this behaviour for starch BA75 although this behaviour was also followed for all starches and starch processing conditions. Finally it was observed that there was no statistical difference in terms of dielectric properties between native starch dielectric measurement and whether the starch was gelatinised. This is of particular interest as during the chip production process, the product is fried. By determining that there is no difference dielectrically between a native starch and a gelatinised starch of the same botanical source this shows the manufacturer they have a more robust coating system allowing them to apply coatings at different points in the production process without concern that the starch element of their coatings will be affected dielectrically.

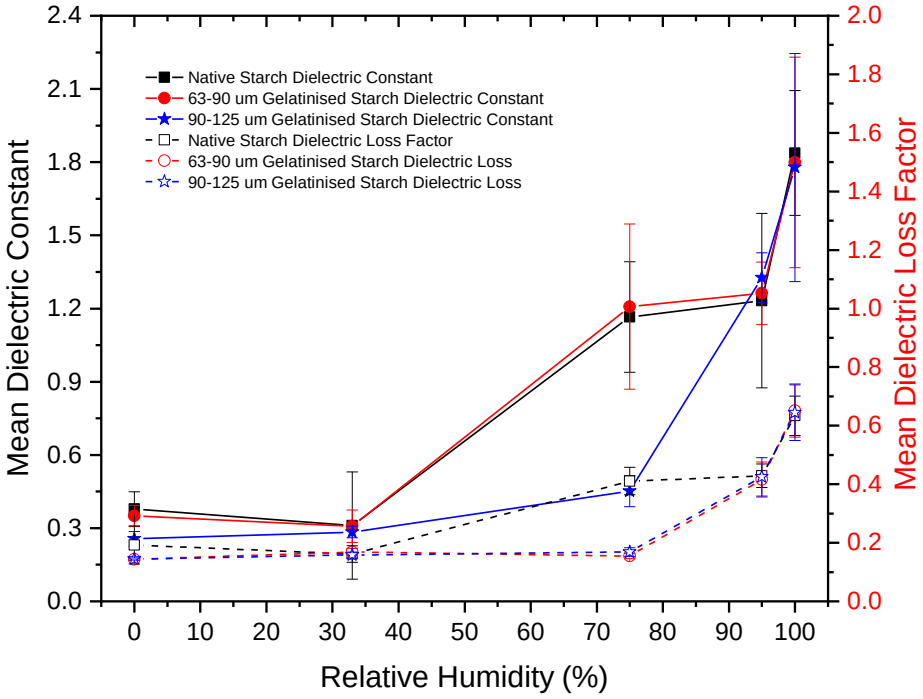


Figure 5-3 Mean Dielectric Constant (n=5) and Mean Dielectric Loss (n=5) as a Function of Relative Humidity and Form of Starch

5.1.5.1 Interactions between the Botanical Source of Starch, Relative Humidity and Starch Processing Method

The ANOVA observed an interaction between the relative humidity and the botanical source of the starch. From observing the data this interaction was that as the relative humidity increases the dielectric properties will also increase. An interaction exists between the botanical source of the starch and the starch processing method. As the dielectric properties are the same regardless of starch processing method, the interaction is believed to be that each of the 10 sources of starch are different to each other at each type of starch processing method but are the same for each individual starch in terms of the starch processing method.

5.1.6 Overall Conclusions

This investigation has observed differences in terms of dielectric properties, but it is not known if these will have the same perceived effect on leaving the microwave. This experiment does show that gelatinisation does not negatively impact the end dielectric properties as they remain the same as their respective native starch. One limitation that the gelatinised sample produces ranges of particle sizes which are different to the native starch. Whilst this was considered by observing two different types of gelatinised starch, the particle size distributions were still close to each other and so it may be that at other particle range distributions dielectric differences will be observed. The most important finding was that water is a driving factor of dielectric properties which agrees with all the literature in this field. However, it is not water content that drives dielectric activity but the ratio of bound:unbound moisture which must be considered when formulating a coating.

5.1.7 Popcorn Experiment

Following the work conducted on bound water and free water in relation to starches an experiment was performed observing the temperature at which water leaves the starch backbone and becomes 'free.' To achieve this sunflower oil was heated in a deep fat fryer to a range of different temperatures. 50g of corn kernels at a time were added to the fryer and it was observed if the corn 'popped.' When the corn kernels popped this was the temperature at which the water within becomes superheated, thus increasing the pressure and causing the kernel to explode. Table 5-6 observes the experimental findings.

Experiment Number	Temperature (^{0}C)	Corn Popped?	Comments
1	180	Yes	All corn popped after 4 minutes
2	140	No	Corn did not pop at all within 20 minutes
3	170	Yes	All corn popped after 6 minutes
4	150	Started	Corn popped but all had not popped within 20 minutes
5	160	Yes	All corn popped after 9 minutes

Table 5-6 Observations Made During Popcorn Experiment

Water is released from the starch backbone via frying at 160-170ºC but may begin this process as early as 150ºC. This is of interest as whilst the frying process does free water previously bound the product is stored in the freezer. At this point it is highly likely the starch will have attempted to reorder itself and so may have bound water within its matrix once again. As microwave temperatures do not exceed 160-170ºC within the microwave, bound water could still be an issue in relation to starch based coatings.

5.2 Determination of Coating Ingredients

According to the literature (Gabriel et al., 1998, Metaxas, 1996) materials are able to heat in the microwave via ionic conduction and/or dipolar polarisation. Components which could allow both mechanisms to occur is desirable. The main issue regarding the development of a crispy product within the microwave is due to the movement of moisture from the centre of the product to the surface. This moisture is then not removed from the system during the microwaving process thus leading to the development of a soggy product. There was also the desire to produce a coating that could also provide a physical barrier helping to prevent or reduce moisture moving from the centre of the product to the outer surface and thus reduce the likelihood of a soggy product being created. To achieve this journals were consulted to determine potential ingredients which could contribute to the final coating. The ingredients considered are found in section 5.2.1.

5.2.1 Hydrocolloids

Hydrocolloids were of interest due to their water binding ability and the fact that some hydrocolloids are polyelectrolytes; i.e. they have a charge in the presence of water. Three different hydrocolloids were considered; hydroxypropylmethlycellulose/methyl cellulose, carboxymethylcellulose and dextrin.

5.2.1.1 Hydrocolloids of Interest

5.2.1.1.1 Dextrin

Dextrin was selected for further consideration as it provides a clean label. According to (Salvador et al., 2005) it produced the crispiest product. However, this study was associated with frozen squid that was deep fried and domestic microwave heating was not a part of the process. Literature searches have also failed to suggest dextrin can provide the dual benefit of providing a physical and a chemical interaction within the microwave.

5.2.1.1.2 Hydroxypropylmethylcellulose (HPMC)/ methylcellulose (MC)

HPMC/MC is beneficial in terms of application as at lower concentrations it does not appear to have a shear thinning effect. (Xue and Ngadi, 2007) also suggested that it reduces oil uptake in

fried products which could be beneficial for the manufacturer. Finally (Phillips and Williams, 2009) state that both MC and HPMC gels have been found to form on heating and that this is caused due to hydrophobic interaction of methyl groups.

5.2.1.1.3 Carboxymethylcellulose (CMC)

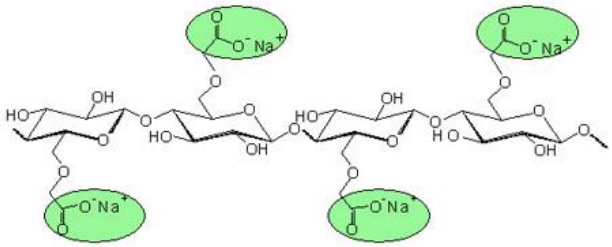


Figure 5-4 Structure of Carboxymethylcellulose (Dow, 1995-2018)

The final hydrocolloid of interest was CMC. (Jia et al., 2014) showed that CMC was able to prevent ice recrystallization in frozen batter. This is of interest as during the manufacturing process of the potato based product it is frozen and is vulnerable to abuse in the freezer on transport and once in the possession of the end consumer. Larger ice crystals which may increase the total moisture at the surface of the product on microwave heating can be formed due to freeze thaw cycles. Therefore CMC may alleviate the negative effect of ice crystal formation on the end product. (Torres et al., 2012) also suggested it was the most hygroscopic of the hydrocolloids they tested. Finally (Chaplin, 2015) identified this structure as a polyelectrolyte, as when in the presence of water, it can dissociate and potentially contribute to surface heating of the chip. (Chaplin, 2015) observed CMC is a cellulose derivative which is created via a 'reaction with alkali and chloroacetic acid.' Differences between cellulose and this structure are that CMC molecules are shorter and rod like in shape. One potential impact for this project is that with increased ionic strength the viscosity of CMC is reduced which could have implications for sample preparation. The integrity of the physical barrier between moisture and surface may also become compromised. However, as it is hygroscopic and is able to hold water this may not be an issue. CMC has also been found to dissolve in cold water and so its functionality would become apparent regardless of the temperature of the moisture leaving the core of the chip.

5.2.1.2 Sample Sourcing and Determination of the Hydrocolloid base

To acquire hydrocolloids Linda Bellecom-Allen (Bellecom-Allen, 2015) a hydrocolloid expert from Dow was consulted. CMC was chosen due to the following characteristics: ice crystal retardation, polyelectrolyte, swells in presence of water and hygroscopic. During this meeting the importance of sodium was also considered as CMC contains sodium within its backbone. Currently it is unknown if this sodium becomes free to interact when CMC dissociates. Method development in this area included sample preparation, determining CMC concentration and

determining CMC viscosity. Dow were able to provide three different CMCs at three different viscosities; CRT 30, CRT 1000 (07) and CRT 1000 (09).

5.2.1.3 Ionic material contribution to coating

Ions are present within the raw and end processed product. It is currently unknown if the ions present in the raw potato are free to interact with the microwave field or whether they remain trapped within the matrix. As the product remains soggy, it is indicative that the ions are either not being dissociated or are dissociated but not present in high enough quantities to have an impact on the end product crispness. Therefore it was decided to incorporate ions within the coating to replace what is lost during the processing and determine whether this has an impact on the end product. It was decided NaCl would be used due to the previous work conducted by (Glover et al., 2013). NaCl was also chosen as it may also improve sensory perception of the product. However, one issue was to determine the NaCl concentration that would produce the required textural benefit without compromising sensory enjoyment. The concentrations of both the hydrocolloid and sodium chloride was considered in section 3.3.1.

5.2.1.4 Self Limiting System

A combination of CMC and NaCl were the components placed in the coating to support the self-limiting system. This theory is presented in section 1.7.

5.3 Initial Coating Experiments

The CMC/NaCl coatings needed to be applied to the product at different points during the production process to ascertain product suitability. Therefore initial tests on a small scale were required to look at pre-fryer, post fryer and post freeze coating applications.

5.3.1 Materials and Methods

The coatings were created for pre and post fryer and post freeze applications as described in section 3.3.1. Once the coating had been developed it was taken to the pilot plant in Scarborough to be applied to the product at different points during the production process; pre-fryer, post fryer and post freezer. Due to time constraints post freezer application was performed in Leeds. As a result whilst the post freezer application results cannot be directly compared to the pre and post fry applications they can provide an indication of product efficacy and suitability.

Name of Solution	CMC Type	CMC (%)	Sodium Chloride (%)	Pre and Post Fryer B6 Flow Cup (sec)	Post-Fryer Pick Up (%)
A	CRT30	2	0	5.86	5.76
B	CRT30	2	2	5.15	5.62
C	CRT30	2	4	5.59	6.52
D	CRT30	3.5	0	10.70	7.60
E	CRT30	3.5	2	11.31	8.61
F	CRT30	3.5	4	13.61	9.09
G (control)	-	0	2 (+10% oil)	3.73	-
H (control)	-	0	4 (+ 10% oil)	3.66	-

Table 5-7 Pre and Post Fryer Coating Recipes Including Viscosity and Post Fryer Pick Up of Each Coating

As is shown in Table 5-7 the pick-up was also recorded. This is a measure of the amount of coating taken up by the product. To achieve this 10 uncoated chips were weighed, coated and then weighed again. The difference in weight was determined and expressed as a % to give the total pick up of coating across the sample set. Due to time constraints, during the proof of principle experiments the pick-up was only measured for post fryer coating application. The viscosity of the coating was measured using a B6 flow cup provided by McCain Foods and is discussed in detail in section 3.3.1. At the lower CMC concentration, the batter produced was within the current McCain Foods guidelines in terms of viscosity with the higher CMC concentration of 3.5 % taking slightly longer with flows times between 10 and 13 seconds for pre and post fry coating applications. During creation of the post freezer coating, a B6 flow cup was not available and so coatings were produced between 15 and 16 ^{o}C to ensure similar viscosities were produced. The coatings were coated onto the original microchip product only for pre and post fryer coating applications. However, for the post freezer application method performed at Leeds University manually, the coating was also applied onto other McCain Foods products. This was to determine

if the CMC coating could act as its own individual coating or whether it could aid an already existing coating to produce desirable results. As such a home fry product was chosen to test as this already contains a coating of its own. Due to an additional blast freezing step being added during domestic post freezing, the pick-up of the frozen product could also be measured.

Coating Components	Pick up (%)
2% CMC 0% sodium chloride	5.21
2% CMC 2% sodium chloride	5.43
2% CMC 4% sodium chloride	6.31
3.5% CMC 0% sodium chloride	7.27
3.5% CMC 2% sodium chloride	8.15
3.5% CMC 4% sodium chloride	8.97
2% sodium chloride +10% sunflower oil	-
4% sodium chloride + 10% sunflower oil	-

Table 5-8 Post Freezer Pick up of Each Coating Recipe

For post freeze coating application (Table 5-8) deionised water was used. This was not possible for products prepared at the pilot plant for pre and post fryer applications. Therefore the initial results are a proof of principle and care must be taken when comparing the post freeze application results to the other results. Once the coatings were applied to all products (uncoated microchips for pre and post fryer application and home fry and uncoated microchips for post freeze) they were stored in a domestic freezer at 18 ^{o}C for 4 weeks prior to testing. A Volodkevich jaw and AED attached to a Stable Microsystems Textural Analyser was used to characterise the products being tested. The test settings and parameters may be found in section 2.2.2.2. Based on the nature of the product it would be expected that a force profile as depicted in Figure 4-1 would be observed.

Figure 5-5 Location of the Three Samples Within the Microwave for Every Product and Sample Type

Due to time constraints and pilot plant time available only small batches of each of the coatings were provided. Instead of 100 g of sample being measured, 3 chips were tested separately (Figure 5-5). Fresh uncoated control microchips were also measured to ensure that any differences were due to the coating as opposed to the volume of product in a microwave. A silicone draining board was also cut to the diameter of the microwave turntable to collect waste as the coated product heated. All chips were tested when they were 4 weeks old. Some data was deleted due to the nature of the texture test conducted.

5.3.2 Results and Discussion

Before discussing the effect of the coatings on the end product it was important to understand the effect of microwaving 3 chips on the uncoated microchip product as opposed to 100g of the end product. Due to space limitation only one force and acoustic plot of each coating and application method is given. Two other graphs for each coating have also been produced which shall be referenced but will not be depicted visually. All three control samples have been depicted as a measure of precision of the test method.

From observing Figure 5-6 no acoustic data was generated for the uncoated microchip product thus indicating the product being tested was soft in nature.

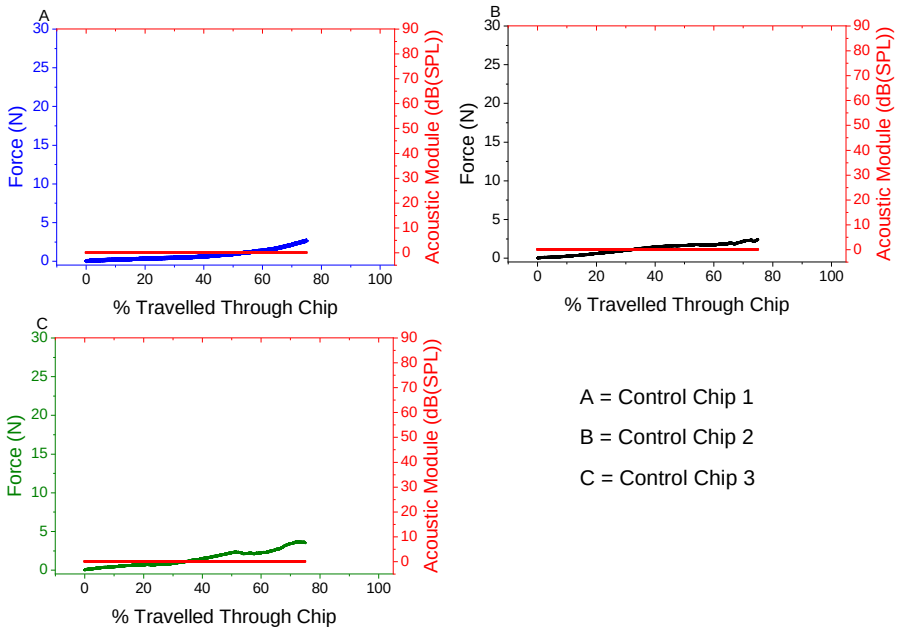


Figure 5-6 Force and Acoustic Signal Recorded by Volodkevich Jaw and AED at 0.1mm/s as a Function of % Travelled Through Chip for Uncoated Control Microchips

The highest force produced by the probe was 4N. On physical examination of the product, the products were fairly homogenous and no noticeable difference existed between the outer and

inner layer which could explain why no acoustic signals were detected in this case. There was little resistance to the probe and so the typical force curve depicted in Figure 4-1 did not occur.

5.3.2.1 Pre Fryer Coating Results

5.3.2.1.1 2% CMC Coating Results

All 2% CMC and NaCl coatings promoted product crispness as a function of acoustic events.

Figure 5-7 2% CMC 0% Sodium Chloride Pre Fryer Coated Microchips After Heating for 2 Minutes 40 Seconds in a 700W Oven

2% CMC and 0% NaCl produced the product observed in Figure 5-7. The coating caused the product to burn slightly and on breaking apart the chip a honeycomb structure was found inside. As CMC is hygroscopic it is probable that moisture is attempting to leave the internal structure to move towards the surface of the chip on storage. The honeycomb structure is due to pockets of empty space where the water originally resided.

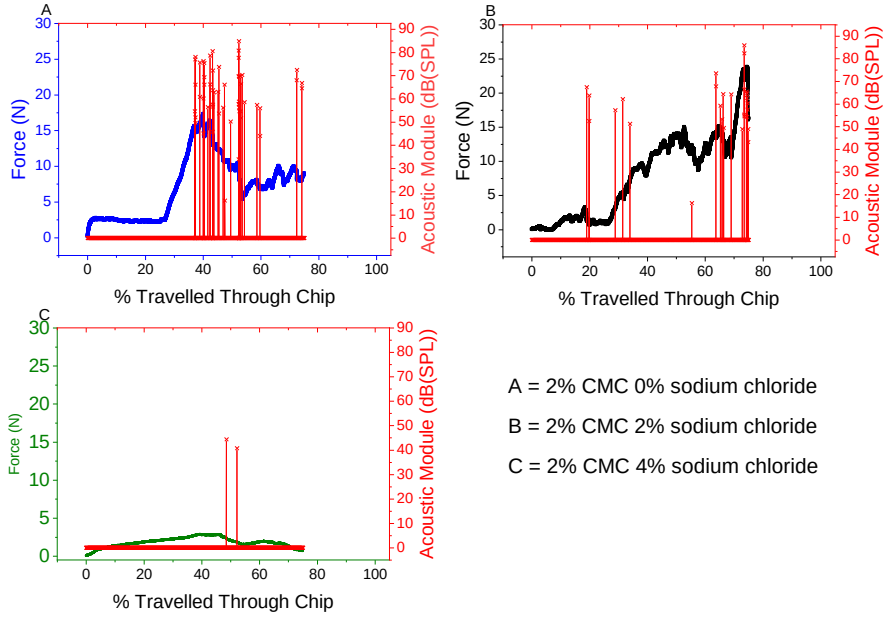


Figure 5-8 Force and Acoustic Signals Recorded for Pre Fry 2% CMC Coating Applications as a Function of % Travelled Through Chip

Figure 5-8 observes the force and acoustic signals produced for pre fry 2% CMC coatings with varying levels of NaCl. The 2% CMC 0% NaCl coating produced the best results in terms of product crispness. It could be that the CMC is binding the water leaving it unable to interact and dissociate the NaCl. It was also determined that 2% CMC and 4% NaCl produced a product which was not as crispy as the other coated products. It has been theorised that at 4% NaCl not all of the NaCl is dissociated and is in fact competing for available moisture with the CMC, resulting in a product in which the CMC and NaCl is not dissociated enough to produce a crispier response than the lower concentration samples. However, NaCl may still be beneficial as CMC on its own resulted in a product that was inedible whilst the addition of NaCl resulted in a crisp and edible product.

5.3.2.1.2 3.5% CMC Coating Results

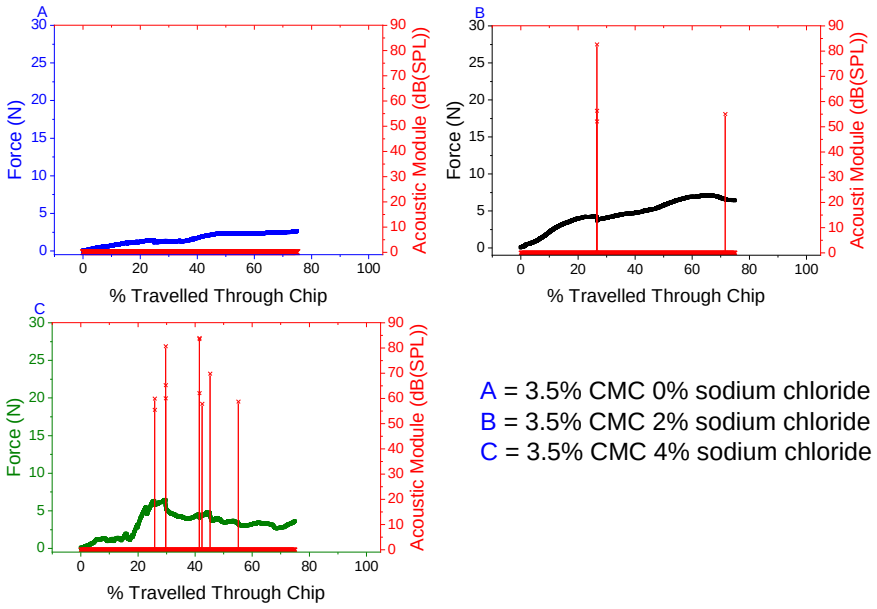


Figure 5-9 Force and Acoustic Signals Recorded for Pre Fry 3.5% CMC Coating Applications as a Function of % Travelled Through Chip

Figure 5-9 observes the pre fry 3.5% CMC coating applications with varying levels of NaCl. On increasing the concentration of CMC the 3.5% CMC 0% NaCl coating resulted in products that were softer than the uncoated control microchips as only 2 N or lower was required to deform the product. The uncoated control force level was 4 N. On inspecting the internal structure, holes had started forming. The addition of 2% NaCl improved product crispness as can be observed by the two acoustic peaks recorded. The formation of an internal honeycomb structure was more noticeable than the CMC coating with no NaCl. The addition of 4% NaCl created a product similar to the product observed undergoing a 2% CMC 2% NaCl coating. Multiple sound peaks were observed across the whole test and on observation the outer skin was crisp. However, at the

highest NaCl and CMC level issues arose due to dehydration from the inner core as the moisture was pulled to the surface by the hygroscopic CMC.

5.3.2.1.3 Conclusions

Coating	Number of acoustic peaks recorded (per 3 chips)	% of total acoustic events heard for all pre fryer coatings
Uncoated microchips	0	0
2% CMC 0% sodium chloride	91	66.9
2% CMC 2% sodium chloride	20	14.7
2% CMC 4% sodium chloride	4	2.9
3.5% CMC 0% sodium chloride	0	0
3.5% CMC 2% sodium chloride	4	2.9
3.5% CMC 4% sodium chloride	17	12.5
0% CMC 2% sodium chloride	0	0
0% CMC 4% sodium chloride	0	0

Table 5-9 Number of Acoustic Peaks Observed for Each Coating per 3 Pre Fryer Application Chips

The total number of acoustic peaks across all pre fry products tested is provided in Table 5-9. 2% CMC 0% NaCl provided the highest number of acoustic peaks. However, the product produced was inedible. In 2% CMC applications, NaCl hindered crispness development as the concentration increased. The number of acoustic peaks recorded was 20. In terms of pre-fryer coating application 2% CMC 2% NaCl performed the best as it produced a crispy product which was edible and lacked the honeycomb structure observed in other products. Coatings containing 3.5% CMC performed differently. CMC on its own resulted in a product softer than the control and also recorded no acoustic peaks. However, on addition of NaCl the product improved in terms of crispness. The two coatings which performed the best across the three samples tested were 2% CMC 2% NaCl and 3.5% CMC and 4% NaCl. They also recorded a similar incidence of acoustic events across testing. It was noted that the pre fryer coatings resulted in a much louder noise on application to the fryer than products that were coated post fryer.

5.3.2.2 Post Fryer Coating Results

5.3.2.2.1 2% CMC Coating Results

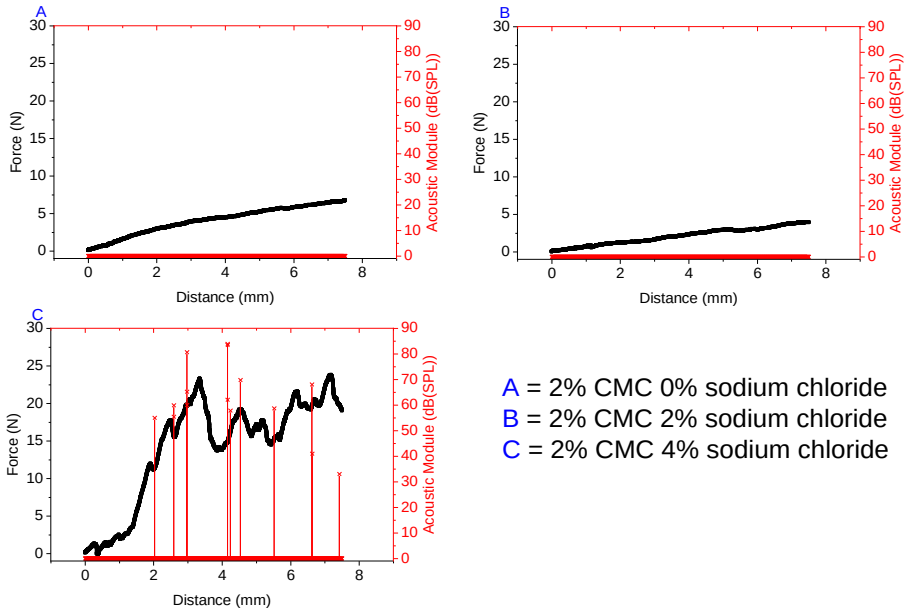


Figure 5-10 Force and Acoustic Signals Recorded for Post Fry 2% CMC Coating Applications as a Function of % Travelled Through Chip

Figure 5-10 observes the force and acoustic plots for post fryer coatings with 2% CMC and varying NaCl concentration. 2% CMC has very little impact on product crispness when applied post fryer with the exception of 2% CMC 4% NaCl. This was surprising as one theory before testing was that if applied pre fryer some of the coating would be lost within the fryer. However, this was performed on a small product size and so further tests must be undertaken to understand the effect of the coatings during the application process. Acoustic peaks were only recorded for 2% CMC 4% NaCl. At a higher NaCl concentration the product is able to crispen and in both pre and post fry coating applications, the frying stage appears vital for coating success or failure.

5.3.2.2.2 3.5% CMC Coating Results

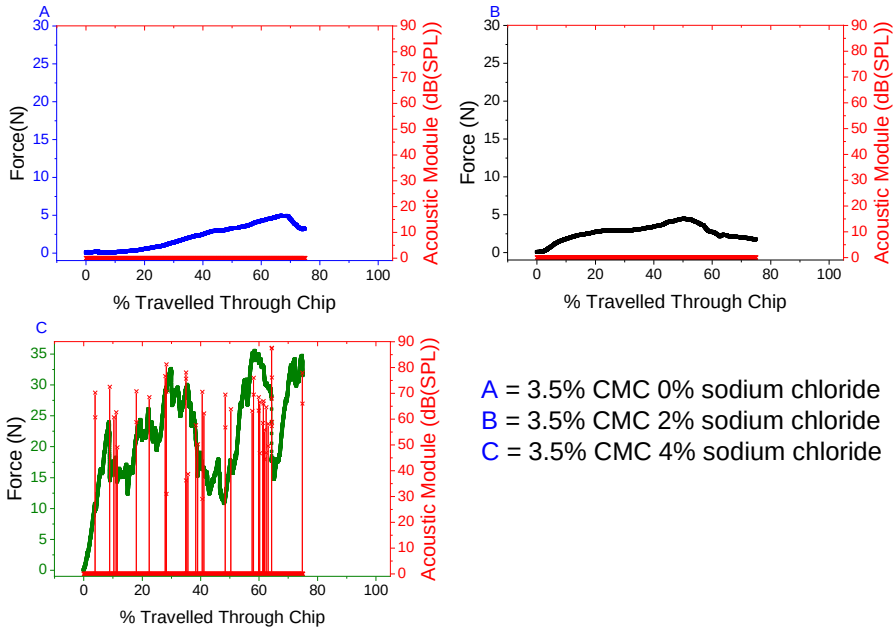


Figure 5-11 Force and Acoustic Signals Recorded for Post Fry 3.5% CMC Coating Applications as a Function of % Travelled Through Chip

A similar theme occurs on increasing the CMC to 3.5% (Figure 5-11). No acoustic peaks were recorded until 3.5% CMC 4% NaCl. However, the acoustic peaks recorded were for the most part due to one chip as was the case with the 2% CMC 2% NaCl application. It would be of interest to perform a large scale study as there appear to be two different products produced post fryer at the higher 4% NaCl level; a crispy product and a soft product more akin to the uncoated control product.

5.3.2.2.3 Conclusions

Coating	Number of acoustic peaks recorded (per 3 chips)	% of total acoustic events heard for all post fryer coatings
Uncoated microchips	0	0
2% CMC 0% sodium chloride	0	0
2% CMC 2% sodium chloride	0	0
2% CMC 4% sodium chloride	30	34.9
3.5% CMC 0% sodium chloride	0	0

3.5% CMC 2% sodium chloride	0	0
3.5% CMC 4% sodium chloride	56	65.1
0% CMC 2% sodium chloride	0	0
0% CMC 4% sodium chloride	0	0

Table 5-10 Number of Acoustic Events Observed for Each Coating per 3 Post Fryer Application Chips

The coatings that caused improved crispness resulted from coatings containing 4% NaCl based on the acoustic results (Table 5-10). All other coatings applied post fryer resulted in a product with no acoustic peaks like the uncoated control products. NaCl appears to contribute to lessen the effect of 2% CMC but promote crispiness when CMC is at 3.5%.

5.3.2.3 2% and 4% sodium chloride control samples for pre and post fryer application

As NaCl appeared to have an impact when in conjunction with CMC, products were also coated pre and post fryer with two different coatings made to volume with water;

1) 0% CMC 2% NaCl + 10% sunflower oil
2) 0% CMC 4% NaCl + 10% sunflower oil

In both the pre and post fryer application, the coatings were brought up to volume with water in the pilot plant and so can be directly compared.

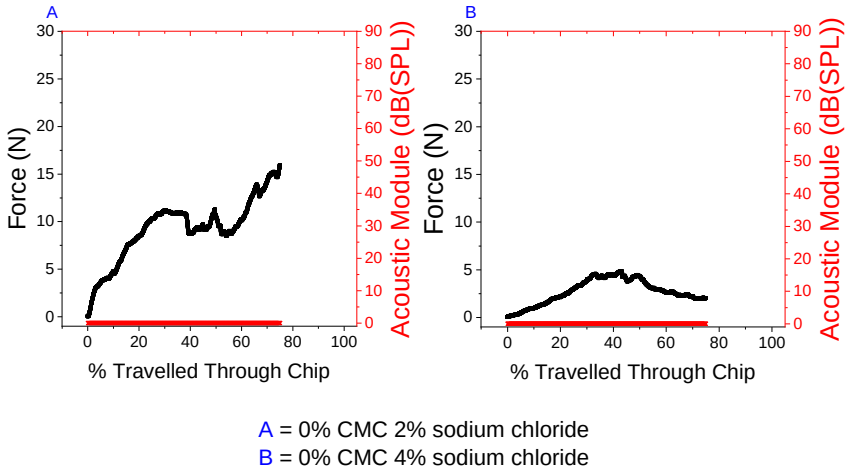


Figure 5-12 Force and Acoustic Signals Recorded for 2% and 4% Sodium Chloride Coating Applications as a Function of % Travelled Through Chip

2% and 4% NaCl produced no acoustic events when applied pre fryer across all three samples tested indicating that NaCl only has its effect when applied in conjunction with CMC. As with the pre fryer samples, post fryer samples produced no acoustic events. This suggests that NaCl only promotes crispness when added in conjunction with CMC.

Figure 5-13 Example of a Laminar Structure

There was the development of a laminar structure on the interior of the potato products observed (Figure 5-13). This is caused by moisture attempting to leave the product via the path of least resistance and so the moisture attempts to leave the chip along the potato cells or channels of the product. This laminar structure was not observed in the 2% NaCl control samples.

5.3.2.4 Post Freezer Coating Results

Coatings were applied to both an uncoated microchip product and a Home fry product to observe the effect of the CMC/ NaCl mixture on a product already containing a coating and one without. Whilst products were tested after 4 weeks of storage on application of the coating, the home fry product was bought from the shop and therefore the age of the product could not be ascertained.

5.3.2.5 Microchip Product Results

5.3.2.5.1 2% CMC Coating Results

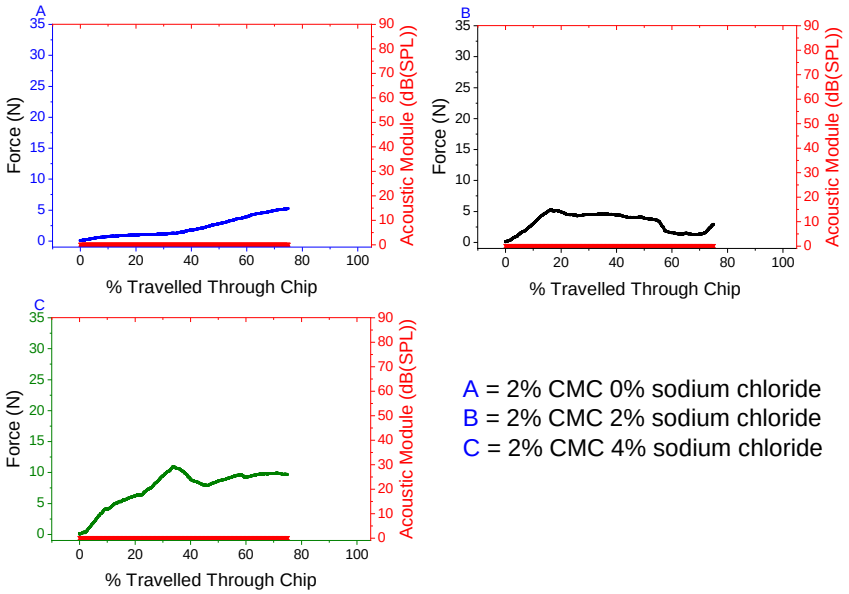


Figure 5-14 Force and Acoustic Signals Recorded for Post Freezer Microchip 2% CMC Coating Applications as a Function of % Travelled Through Chip

On addition of 2% CMC and varying NaCl levels post freezer no acoustic events were produced indicating the product was not crisp (Figure 5-14). On addition of 4% NaCl in conjunction with 2% CMC the presence of peaks and troughs was observed indicating that the product is not homogenous as it indicates periods of energy storage and release within the product. However, unlike in other applications this did not result in an acoustic event being recorded. A higher max force >10N was required to deform the product. These products were slightly hollow inside when present in the 2% CMC 0% NaCl coating. At 2% CMC and 2% NaCl the product was not hollow, was crisper on the outside and softer in the centre as depicted by the force plot. Acoustic events were not recorded. At 2% CMC and 4% NaCl the product produced showed differentiation between a crisp outer skin and a soft mash potato core as depicted by the peaks and troughs. Acoustic events were not detected.

5.3.2.5.2 3.5% CMC Coating Results

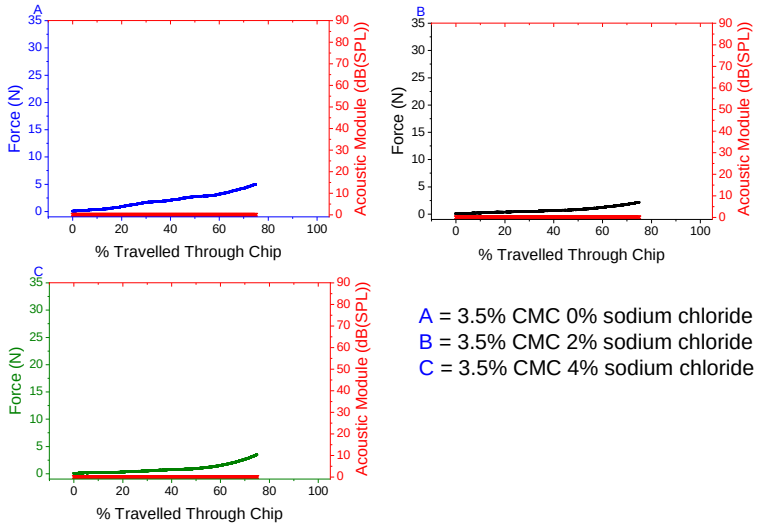


Figure 5-15 Force and Acoustic Signals Recorded for Post Freezer Microchip 3.5% CMC Coating Applications as a Function of % Travelled Through Chip

On increasing the CMC concentration to 3.5% this negatively affected microchips for a post freezer application (Figure 5-15). The presence of peaks and troughs was not observed in any of the 3.5% coated products. No acoustic events were recorded. It is possible that CMC applied post freezer is less effective than CMC applied pre and post fryer. As CMC applied post freezer appears to perform less well, indicates that where in the process a coating is applied is important in terms of improving end product satisfaction. The investigator observed that on biting into products coated with 2% CMC and 0% NaCl 'pockets of crispness' could be observed and so it is possible that the probe may have missed these areas where the product did provide crispness. On

application of NaCl these pockets of crispness could no longer be observed and the product became soft.

5.3.2.6 Home Fry Product Results

Prior to the tests being conducted the cooking time had to be determined as this product is usually prepared in a conventional oven as opposed to a microwave oven. As such one coated chip was placed within the microwave environment.

Figure 5-16 Post Freezer Coated Home Fry Product After Cooking in 700W Microwave

The usual cooking time for microwave chips is 2 minutes 40 seconds at 700W with a pause at 1 minute to 'shake' the contents prior to being returned to the microwave. Figure 5-16 shows the chip after 1 minute of heating. The darker areas on the surface of the chip are where the coating was present indicating it does have an effect. Only one chip was present in the microwave and so is not representative. On addition of 3 chips to the microwave the full 2 minute 40 seconds heating time could be observed and a cooked product produced. As with all other experiments the following results provide an example force plot of the different coating applications. This is primarily due to space in the thesis. The only exception is the control sample where all three force plots and acoustic data is presented.

5.3.2.6.1 Control Home Fry Sample

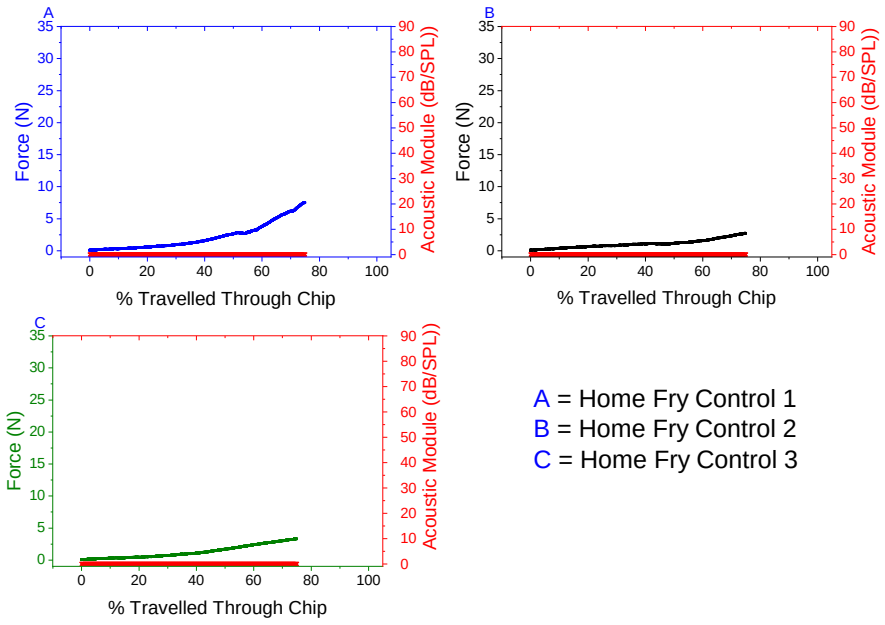


Figure 5-17 Force and Acoustic Signals Recorded for Post Freezer Uncoated Home Fry Samples as a Function of % Travelled Through Chip

The control sample is considered as a Home fry with no additional CMC/sodium chloride coating. It was determined that no acoustic events were recorded by the uncoated Home Fry (Figure 5-17). The force profile produced suggest a softer product as in all three cases a force <5 N was sufficient to cause deformation of the product. There is very little increase in the force required indicating that the product is homogenous in nature.

5.3.2.6.2 2% CMC Coating Results

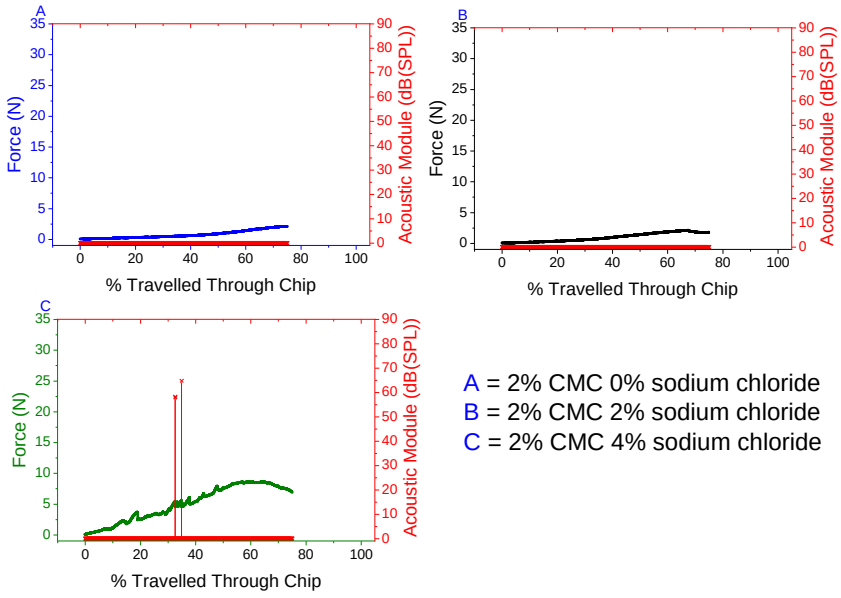


Figure 5-18 Force and Acoustic Signals Recorded for Post Freezer Home Fry 2% CMC Coating Applications as a Function of % Travelled Through Chip

Figure 5-18 observes a 2% coating application on a Home Fry Product. The addition of 2% CMC and varying levels of NaCl had an effect on the product only when 2% CMC was applied in conjunction with 4% sodium chloride. For 2% CMC 0% NaCl and 2% CMC 2% NaCl no acoustic events were recorded and the force required to deform the product remained <5 N as with the control samples. 2% NaCl addition resulted in a poorer performance as the max force lowered to 2.6 N. There was little increase across both coatings in the force required to deform the product indicating a product that is homogenous. On application of 4% NaCl, acoustic events are recorded with a gradual increase in the force required to deform the product. The shape of the force curve differs with the appearance of peaks and troughs indicating a product which is not homogenous in nature. The max force produced was 9 N. A post freezer application of the same coating on microchips produced no acoustic peak. The NaCl and CMC could be interacting with the Home Fry batter thus producing a different result.

5.3.2.6.3 3.5% CMC Coating Results

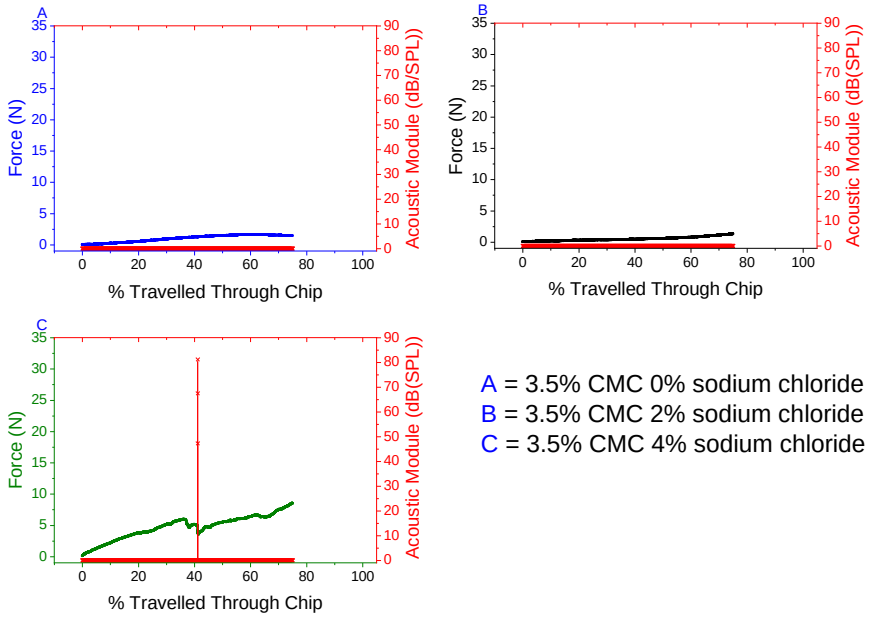


Figure 5-19 Force and Acoustic Signals Recorded for Post Freezer Home Fry 3.5% CMC Coating Applications as a Function of % Travelled Through Chip

Acoustic events were only recorded for the CMC coating when in the presence of 4% NaCl (Figure 5-19). Acoustic events were observed when the force plot produced peaks and troughs as opposed to smooth lines. At 4% NaCl the product produced is not homogenous whilst for coatings containing 0% NaCl and 2% NaCl increasing the CMC concentration to 3.5% had no effect on the end product. On observing 3.5% CMC and 4% NaCl the acoustic events occur later than the 2% CMC and 4% NaCl product although the number of acoustic events remains similar with acoustic events being recorded around one major acoustic event. An observation made by the investigator was that the Home Fry products were not as desirable in terms of crispness as other coating applications which had recorded acoustic events.

5.3.2.7 2% and 4% sodium chloride 0% CMC samples for Home Fry and Microchip Coating Applications

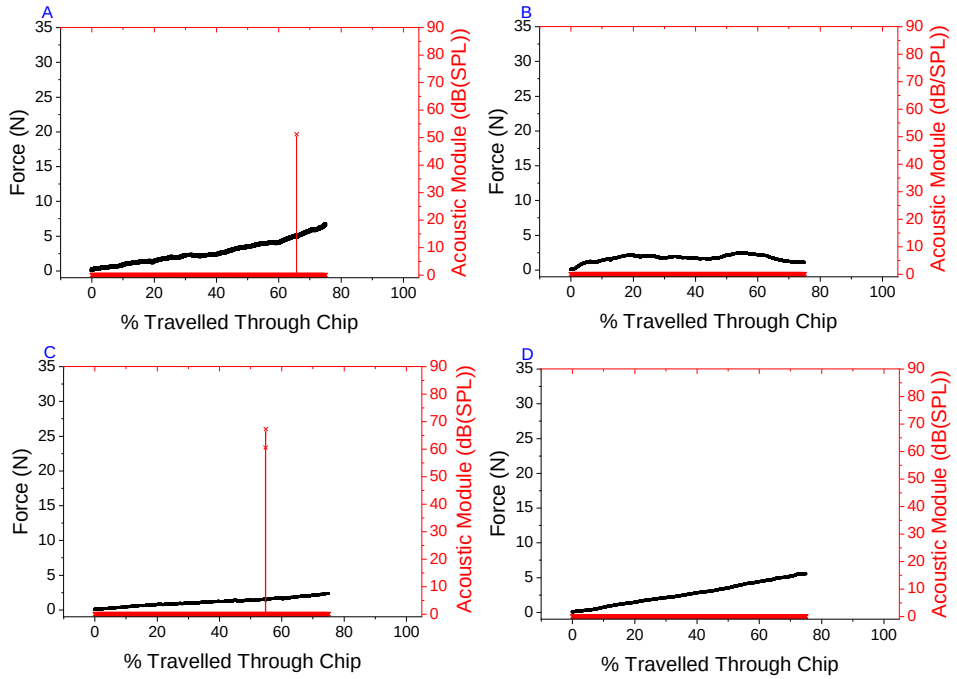


Figure 5-20 Force and Acoustic Signals Recorded for 2% and 4% Sodium Chloride Applications for Homefry (A 2%, C 4%) and Microchip (B 2%, D 4%) as a Function of % Travelled Through Chip

To observe the effect of CMC and NaCl separately coatings were applied containing 0% CMC and 2% NaCl and 0% CMC and 4% NaCl to the Home Fry product (Figure 5-20). The microchip product produced no acoustic events which is not surprising as no acoustic events were recorded under any testing condition during post freezer coating application. For Home Fry post freezer applications acoustic events were recorded in the case of both 2% NaCl and 4% NaCl coatings. At lower NaCl concentrations, CMC inhibited the ability of the product to promote crispness. At higher NaCl concentrations no additional benefit was observed. However, CMC may show its benefit after weeks of storage due to its ability to retard ice crystal growth.

5.3.2.8 Conclusions

Coating	Sample Type	Number of acoustic peaks recorded (per 3 chips)	% of total acoustic events heard for all after frozen coatings
Uncoated microchips	Microchip	0	0
	Home Fry	0	0

2% CMC 0% sodium chloride	Microchip	0	0
	Home Fry	0	0
2% CMC 2% sodium chloride	Microchip	0	0
	Home Fry	0	0
2% CMC 4% sodium chloride	Microchip	0	0
	Home Fry	5	45.45
3.5% CMC 0% sodium chloride	Microchip	0	0
	Home Fry	0	0
3.5% CMC 2% sodium chloride	Microchip	0	0
	Home Fry	0	0
3.5% CMC 4% sodium chloride	Microchip	0	0
	Home Fry	3	27.27
0% CMC 2% sodium chloride	Microchip	0	0
	Home Fry	2	18.18
0% CMC 4% sodium chloride	Microchip	0	0
	Home Fry	1	9.09

Table 5-11 Number of Acoustic Events for Each Coating Applied Post Freezer per 3 Chips

Application of coatings post freezer resulted in no acoustic peaks for any microchip sample (Table 5-11). On addition of coatings to the Home Fry product acoustic peaks could only be observed for coatings containing 4% NaCl. However, it was also found that on applications containing 0% CMC and both 2% NaCl and 4% NaCl, acoustic events were recorded indicating that CMC may be negatively impacting the development of crisp textures.

5.3.3 Overall Conclusions

Due to CMC being hygroscopic, moisture is driven to the surface of the product after storage of 4 weeks within a domestic freezer at -18 ^{o}C. This series of experiments only used 3 chips within the microwave instead of a normal 100 g product size. Due to the excess moisture associated with a larger product size, it is theorised that the effects of hygroscopic CMC will be less detrimental to the end product. NaCl concentration was considered due to issues such as microwave screening

and end product acceptance. Where in the process the coating was applied had an impact on the acoustic and mechanical data produced by the coated microchips. For post freezer applications, the addition of CMC was detrimental to the development of crisp coatings whilst for pre and post fryer applications CMC needed to be present in the coating in conjunction with NaCl to provide the benefit. This is because in both pre and post fry applications containing 2%/3.5% CMC and 4% acoustic events were produced. On observing coatings containing 4% NaCl and 0% CMC, for pre and post fry applications no acoustic events were produced and the products were soft. For post freezer coatings acoustic events were not recorded for any sample. However on application to Home Fry products in which a coating is already present, CMC appeared to have a negative impact on crispness formation. As a result the application process needs to be understood further as where in the process the coating is applied directly impacts the relationship between CMC and NaCl.

5.3.4 Next stage of experiments required

The coating was functioning using certain applications. However, as this was a small sample set the aim was to reproduce all of the coatings on microchips and microwave using 100g of product for each microwaving period. As CMC is hygroscopic there were concerns regarding the migration of moisture over time. As such an 8 week shelf life test to determine if storage impacted the ability of the coating to promote crispiness was also required.

5.4 First 8 week study

Initially the plan was to reproduce all the coated products on a larger scale to observe the effect of the coatings on a 100 g pack size. Due to lack of available time in the McCain Foods Pilot Plant, this was not possible. Instead only one coating from the original six coating conditions could be selected to mass produce. As 2% CMC showed improvement in two out of the three application methods during initial testing this was selected to form part of the coating. The NaCl level of 4% was selected as this was the highest level and so differences would be more evident when tested against the uncoated control sample. NaCl gave different effects on the product dependent on the concentration of NaCl, concentration of CMC and where in the process it was applied. It was hoped that the higher NaCl concentrations would show any differences more readily. Ideally all coating conditions needed to be tested. This is because the coating condition was selected based on preliminary results observing 3 chips at a time instead of the 100 g sample. As such it is unknown if this concentration of CMC and NaCl is the best concentration for a full 100 g sample. Whilst the following results are true for 2% CMC and 4% NaCl, this may not occur at other concentrations and so concentration levels do need to be considered in the future.

5.4.1 Materials and Methods

As discussed in section 2.2.3.2 a Stable Microsystems Texture Analyser was used in conjunction with a Volodkevich jaw attachment and AED to collect the data. A recon loss method (2.2.3.1) was also employed to understand the effect microwaving has on the end weight of the product in terms of moisture loss. The speed of the Volodkevich jaw probe was set at 0.1 mm/s.

Sample Type	Dry Loss (%)	Fry Loss (%)	Pick Up (%)	Temperature of Coating (ºC)	B6 Flow Cup (seconds)
Control (uncoated base product)	6.27	24.32	n/a	n/a	n/a
Pre Fry	5.1	15.67	9.8	15.7/18.6	6.06/5.37
Post Fry	4.84	20.29	11.11	15.7/18.6	6.06/5.37
Post Freeze	5.47	24.32	11.76	15.7/18.6	6.06/5.37

Table 5-12 Dry Loss, Fry Loss, Pick up, B6 Flow Cup Viscosity and Temperature of Coating Recorded as a Function of Sample Type

The samples were prepared using the method highlighted in section 2.2.3 with Table 5-12 providing information regarding the dry loss, fry loss, pick up, temperature of the batter and viscosity. The same 2% CMC and 4% NaCl coating was used for all three coating applications. The coatings were prepared at 15.7ºC in keeping with McCain Foods operating procedures. The coating was placed in an enrober at its starting temperature of 15.7ºC. To avoid contamination of the sunflower oil used during the frying stage, the post frying coating application occurred first. As a result this caused the temperature of the coating in the enrober to increase to 18.6ºC. Therefore all post fryer, pre fryer and post freezer coating applications were placed in a coating >18ºC. The dry loss, fry loss and pick up was also calculated for each of the coating application methods. Whilst for most samples the dry loss and fry loss were similar, products applied pre fryer resulted in a fry loss of 15.67%, 5% lower than any other application. It suggests that the application of CMC and NaCl pre fryer allows the product to retain a further 5% of moisture than if the coating is applied at other points during the process. It agrees with the previous results suggesting that dependent on the application process, the product is physically altered. The pick-up of the product is also less than post fry and post freeze applications, although this is not surprising as the pre fryer coating has to undergo the frying process and so loss of product is more likely. Pre fry application of the CMC NaCl coating resulted in a ‘popping’ noise being heard during the frying process which increased in frequency and then fell silent. This could have been

due to debris as the sample moved through the fryer or it could be related to the behaviour of CMC. This is because when in liquid format CMC was noted to ‘fizz’ and ‘pop’ and go silent when dry and so the popping may be caused by the same mechanism as observed in the microwave but with a different heating source. The samples were heated for 2 minutes 40 seconds and for 4 minutes and the reasons for this can be found in Table 3-9. Measurements were taken on the same day every week for 8 weeks.

5.4.2 Results and Discussion

5.4.2.1 Recon Loss

The recon loss is a measure of the starting weight of the sample prior to insertion into the microwave, against the end weight of the sample on leaving the microwave environment. It is calculated in the form of a %. Whilst only products heated for 4 minutes were produced via mechanical and acoustic testing the recon loss was also taken for products heated for 2 minutes 40 seconds as per manufacturer guidelines. After this initial weighing the product was left to stand for 1 minute prior to being weighed again and this is shown in Figure 5-21. All samples cooked for 4 minutes irrespective of application method resulted in higher recon losses than product heated for 2 minutes 40 seconds. This is because more moisture has been able to leave the product during the prolonged cooking time. On standing, the moisture loss increased slightly for every sample tested compared to the product 1 minute earlier.

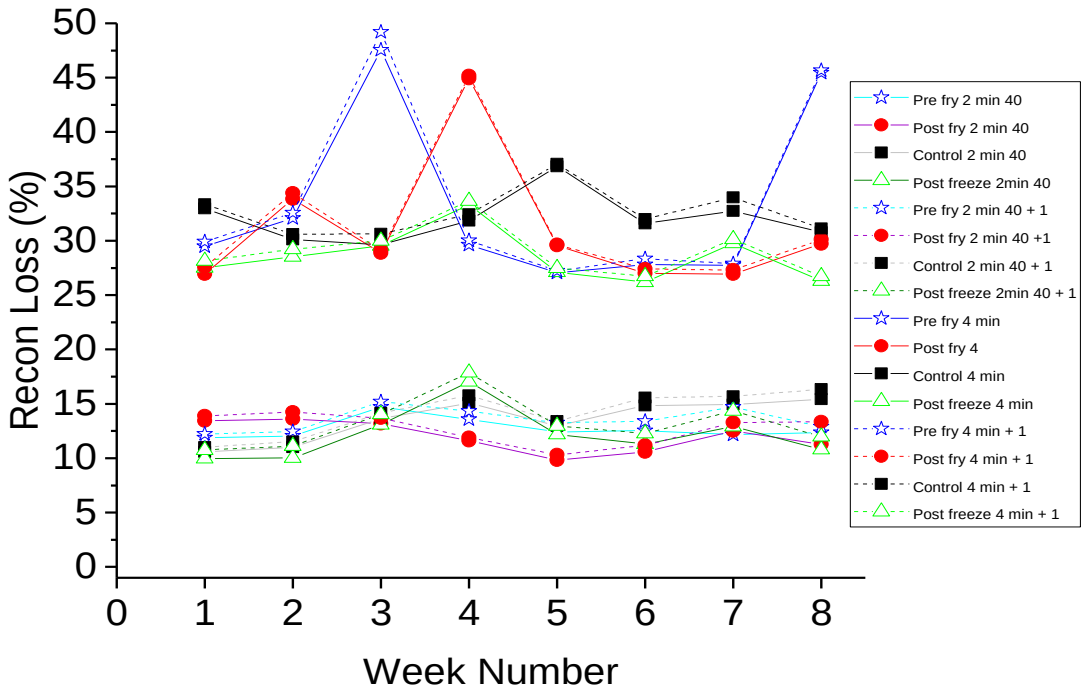


Figure 5-21 Recon Loss for First 8 Week Study For a Variety of Coating Applications at Heating Times of 2 Minutes 40 Seconds and 4 Minutes + 1 minute resting time

There are two main determinations to be made from this data set. The first relates to the CMC application method and the second relates to the control uncoated sample. From observing the recon data for 2 minutes 40 seconds heating time, the differences between samples are less pronounced than at 4 minutes. However, for a 4 minute cooking time, during week 3, the pre fry application results in a 47.54% and a 49.20% recon loss after standing for 1 minute. The nearest recon loss to this is provided by a post freeze application with recon losses of 29.55% and 29.99% respectively. By week 4 the pre fry levels return to the recon losses observed for pre fry in week one with levels of 29.62% and 30.02% being recorded. During week 4, post fry coating applications increase their recon losses to 44.91% and 45.19% before returning to levels more consistent with the other samples in week 5. The differences between pre fry and post fry applications may be due to the fry losses with pre fryer samples retaining 5% more moisture than post fryer applications. Several theories for these observations have been considered and are as follows;

1) The CMC and sodium chloride coating are having an effect on moisture migration in the starch structure
2) Water is leaving the starch structure and then because it is in an enclosed space is being reabsorbed one week later
3) The results are anomalous – fragile ice crystals at the surface of the product fall off during heating causing a larger degree of moisture loss during this one week. Pre fryer samples were shown to retain more moisture during the frying process which may be why they were more likely to have this issue. However, one of the properties of CMC is its ability to inhibit ice crystal formation although moisture migration could result in fragile ice crystals forming.

With the exception of the pre fry application at 4 minutes heating, by the end of week 8 the control chips have a higher recon loss than CMC applied coatings during all points of the process. The same can also be found for chips heated for 2 minutes 40 seconds. The recon loss agrees with the investigators observation at week 8 that the CMC coated products are not as crispy as the control product. This correlation is more noticeable at the 4 minute cooking time although this is because a higher cooking time allows for a higher % of moisture to leave the product. Moisture or lack thereof is what is giving the chips their crispness.

5.4.2.1.1 Recon Loss Considerations

Whilst the recon loss provides an indication that the product is changing in terms of its end moisture content, it is difficult to determine with absolute certainty the changes occurring every week. This is because no repeats of the recon loss data could be made as the recon loss measurement is destructive and only one batch of product could be produced due to time

constraints in the manufacturer pilot plant. Therefore a further 8 week study planned to include recon loss data to determine if a similar pattern of events occurred on the product in the microwave. Storage is making a difference to the product, confirmed by the acoustic and mechanical data, although replication of the data is required to understand why.

5.4.2.2 Acoustic Data

On testing a larger sample size a detrimental impact occurred in terms of acoustic events. For all 96 samples tested only 25 produced an acoustic event and of those 25 only 8 produced more than 2 acoustic events across the testing window. This is of interest as the cook time was 1 minute 20 seconds more than the 3 chips heated during the initial coating experiments phase. During method development in section 3.3.1.1.4 when a 4 minute cook time was chosen, it was also found that the 2 minutes 40 seconds cook time resulted in similar acoustic outputs being recorded. In this study development of crispier exteriors and softer interiors occurred which towards the end of the 8 week testing period saw some samples developing a honeycomb or laminar structure in the product centre. In the coatings with CMC, ice crystals were not observed. Within the control sample the development of ice crystals could be clearly observed. It would be expected that the number of acoustic peaks would have increased as the product dehydrated and altered although this was not the case. Therefore, a consideration was made in terms of the probe speed and an experiment conducted as discussed in section 3.2.1.2 of the method development section. During the frozen storage work conducted with (Beasley, 2015) a test speed of 0.1 mm/s was most beneficial to measure microstructural breakdown due to the concern that important events were being missed and so this test speed was adopted for both the initial coating development and first 8 week study. However, this consideration was made without the presence of the AED. The AED was first utilised during the initial coating tests where only 3 chips were being tested and as a result the products were crispier and therefore more acoustic events could be recorded at a lower test speed. Due to the results exhibited during this stage of the work, it was discovered that a faster probe speed resulted in more acoustic events being recorded. Therefore a second 8 week study incorporated the mechanical test at a test speed of 1 mm/s.

5.4.2.3 Force Curves

Due to the large amounts of data generated only data collected during weeks 1, 3, 5 and 8 shall be depicted in the form of force curves although data from the other weeks shall also be discussed. Figures 5-22, 5-23, 5-24 and 5-25 show the mean force curves produced during a 4 minute cook time for each process application.

5.4.2.3.1 Week One

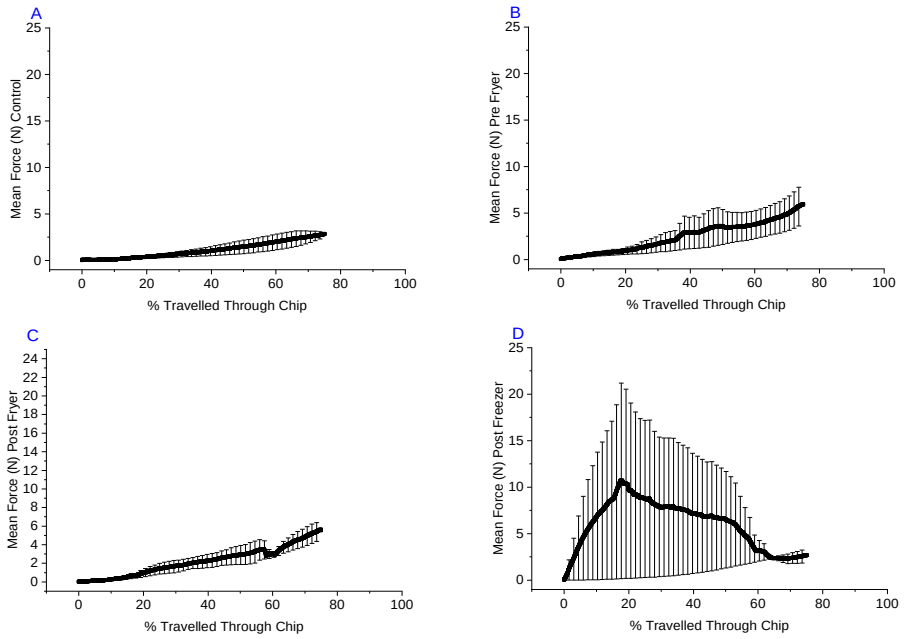


Figure 5-22 Mean Force Curves (n=3) For 2% CMC 4% Sodium Chloride Applications During Week One

A = Control, B= Pre Fry, C = Post Fry, D = Post Freeze

5.4.2.3.3 Week Three

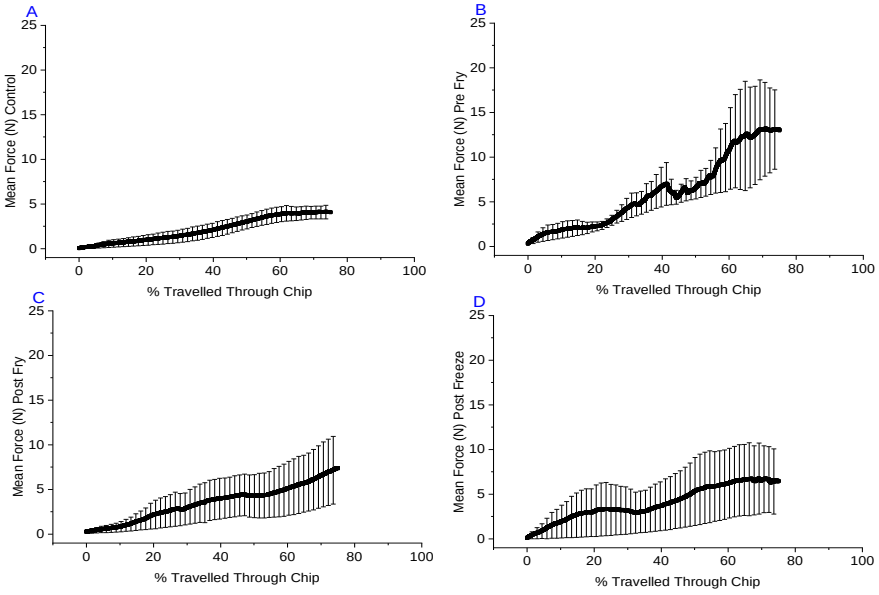


Figure 5-23 Mean Force Curves (n=3) For 2% CMC 4% Sodium Chloride Applications During Week Three

A = Control, B= Pre Fry, C = Post Fry, D = Post Freeze

5.4.2.3.4 Week Five

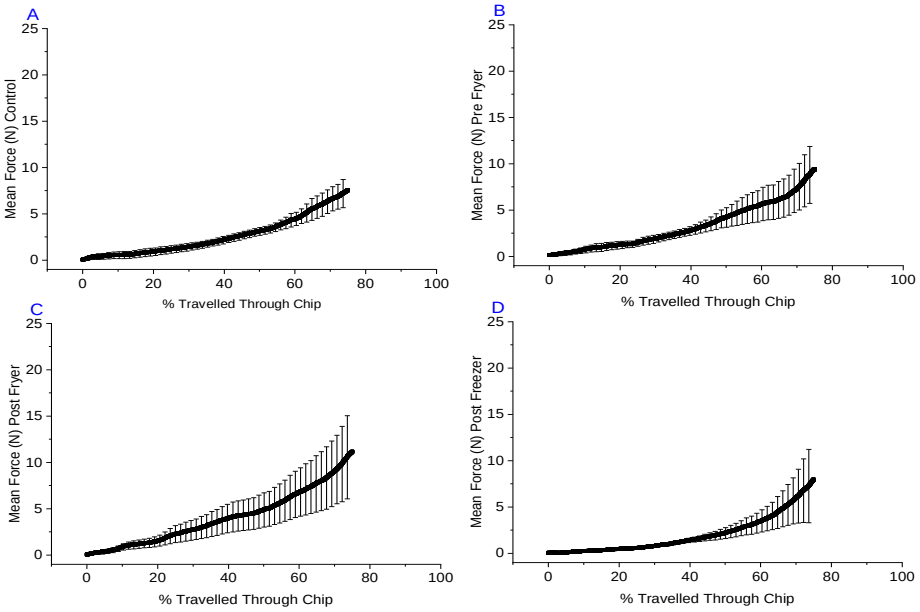


Figure 5-24 Mean Force Curves (n=3) For 2% CMC 4% Sodium Chloride Applications During Week Five

A = Control, B= Pre Fry, C = Post Fry, D = Post Freeze

5.4.2.1.5 Week Eight

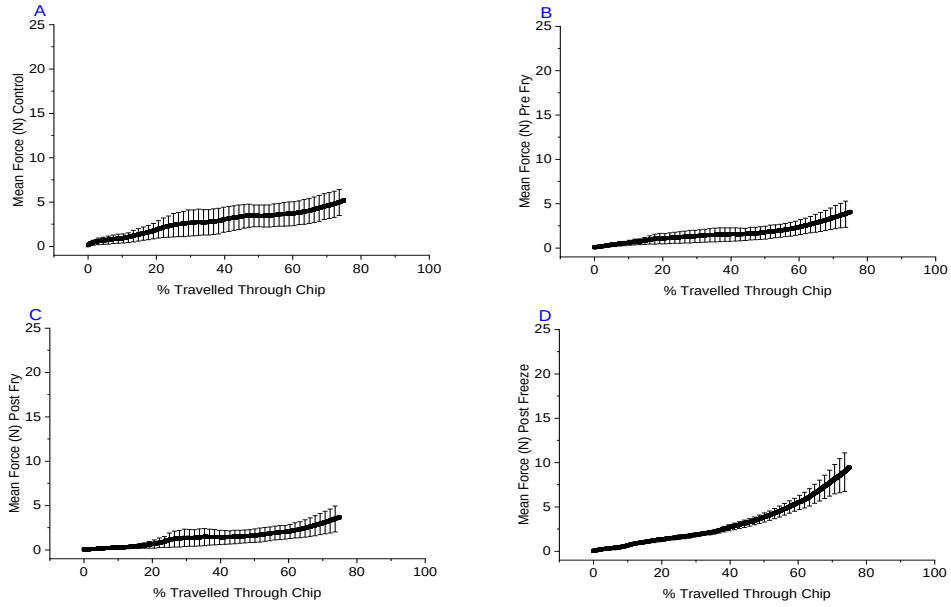


Figure 5-25 Mean Force Curves (n=3) For 2% CMC 4% Sodium Chloride Applications During Week Eight

A = Control, B= Pre Fry, C = Post Fry, D = Post Freeze

5.4.2.3.6 Discussion of Force Curves

On observing the manufacturer cooking guidelines of 2 minutes 40 seconds, addition of coating had little impact on the product crispness. However, the CMC based coatings did have an effect when heated for 4 minutes in a 700W microwave oven. One theory is that the 2 minute 40 seconds does not provide adequate time for the CMC and NaCl to 'activate'. However, the increased crispness could be due to evaporation as indicated by the higher recon loss levels. By the end of the 8 week shelf life a 4 minutes cook time resulted in the control uncoated product being 'severely dehydrated'. For CMC coated products the samples were deemed to be drier than the products heated for 2 minutes 40 seconds but without the inedible nature of the control products. This is supported by the recon loss where the control samples resulted in the highest recon loss after week 8, with the exception of pre fry applications at 4 minute. It was determined that pre fry applications resulted in a superior product.

From observing the force profiles the natural variation between the samples must be considered. At the start of the storage test, the control samples had very little variation between the samples tested with a standard error of 0.86 being recorded. However, by week 8 the control samples were showing a larger standard error (1.48) indicating that the product ages differently even when within the same storage conditions. Whilst the variation of the control samples did increase over the 8 week period, the standard error was still smaller than the products coated with CMC based coatings. The highest variation in week 1 was on post freeze applications with a standard error of 10.57 being recorded indicating uniformity of coating may be an issue. Due to coating being applied post freezer and post fryer, product became attached to the susceptor resulting in targeted heating of certain samples on heating in the microwave. Post fryer applications recorded highest standard error of 1.18 in week 1 whilst pre fry applications observed a highest standard error of 2.21. It would be expected that the post fryer coating application would have a higher standard error than pre fry coatings and indicates that factors other than samples 'sticking' to the susceptor may be causing the product to behave differently across the 3 samples tested. The standard error decreased for post freezer samples and from week 5 onwards the standard error remained low during the beginning of the texture tests with higher standard errors starting to appear 4.5mm into the chips microstructure. In some cases the chips were compressed before being pierced and vice versa which could indicate why the standard error began to increase in the later part of the tests. The highest standard errors recorded for weeks 5 and 8 were 4.63 and 2.44. For pre fryer applications, the standard error increased to 6.22 during week 3 but then decreased to 3.31 and 1.60 by week 8. This correlates with the recon loss where the most noticeable change in the pre fry products was during week 3. For post fryer applications the highest standard error increased in week 3 (3.87) and week 5 (4.84) but decreased to 1.52 by week 8. From observing the variability between the product, week 3 of storage had the biggest impact on the coated products in terms of

product efficacy whilst prolonged storage had an effect on the control uncoated product. The investigator observed differences between the samples when testing week to week. During week 1 control chips were soft with a fluffy centre and the smooth force curves reflect this behaviour. A recon loss of 33.36% was recorded. For pre fry applications the chips were crisper with the appearance of laminar internal structures. The jagged force curves reflect this change compared to the control product. A recon loss of 29.92% was recorded. Post fryer chips were 'sweatier' in the box than the pre fry and control products and the chips stuck together with the coating acting as an adhesive. The chips were described as fluffy but starting to develop an internal honeycomb structure. The recon loss was recorded as 27.56%. Post freezer chips felt slimy with the coating acting as an adhesive. The recon loss was 28.14%. By week 3 the control chips were drier than previous weeks, with the development of honeycomb structures with holes present in the microstructure where the moisture had migrated out of the product. This product was not desirable. A recon loss of 30.64% was recorded, Pre fryer products during week 3 were drier than previous weeks and the ends of the product had begun to crispen. During week 3 the pre fry products were noticeably different to all other products tested. A recon loss of 49.20% was recorded. Post fryer products at week 3 were different to each other with some chips retaining a soft inner core and other chips starting to become hollow. Overall the products had crispened compared to previous weeks. The recon loss was 29.11% During week 3 post freeze applications resulted in a product that clumped together with great difficulty of being separated. The recon loss was 29.99%. During week 4 the post fry product altered the most drastically with the highest recon loss of 45.19%. Surprisingly the chips were limp compared to the previous week with only slight crispening at the edges of the product. By week 5 the post fryer chips were less dehydrated than the control samples with a chewy texture developing. The product adhered to each other and was difficult to separate. The recon loss was 29.64%. By week 5 the control chips were hollow on the inside with holes where moisture used to be present. This could explain why the standard error increased for the control samples. Ice crystals had begun to develop on the control product but not for the coated products. The recon loss was 37.08%. For pre and post freeze the recon losses were 27.22% and 27.48%. Pre fryer products were described as easy to separate with a mash present in the product centre and crisp outer corners. Post freezer products resulted in chips that stuck together and the development of a chewy texture despite a softer interior. By week 8 the control product was crisp with the development of burnt flavours and a hollow centre. The recon loss was 36.84%. All coated products resulted in a chip that was softer than the control products. Ice crystal formation was not observed for coated products. The recon losses were between 27% and 29% and were therefore lower than the recon loss recorded for the control product. Overall it was determined that whilst the control product produced the most dehydrated product, it was the pre fry coating application that resulted in the most desirable chip. However, larger standard errors across the coated products indicate coating application issues.

5.4.2.4 PCA

Due to the large number of data produced, a Principal Component Analysis (PCA) was performed which incorporated the 2nd derivative. For each sample 14 different variables were extracted from the mechanical and acoustic data and are described in section 2.2.3.3. All 14 variables were inserted into the PCA. This was to determine which variables were responsible for the variances observed, if any, and if this altered week by week. PCA was conducted on all four products (coated, pre fry, post fry, post freeze) separately and as a function of time to allow an understanding of the variance within the same product group and between the different products on a bi weekly basis. The main aims of the PCA was to determine where variation occurred in relation to the following questions

1) Is there a difference on storage of the samples?
2) Is there a difference dependent on where in the process a coating is applied?

The relationship between the variables was considered. This was part of the pre screening process where redundant variables were removed from the PCA prior to final analysis. Pre screening was performed on all samples on a bi-weekly basis and also in terms of different coating applications.

5.4.2.4.1 Complete 8 week data set PCA pre-screening

Pre-screening occurred to determine which variables were redundant and could be discarded. In this case redundant variables are defined as variables which explain the same variability.

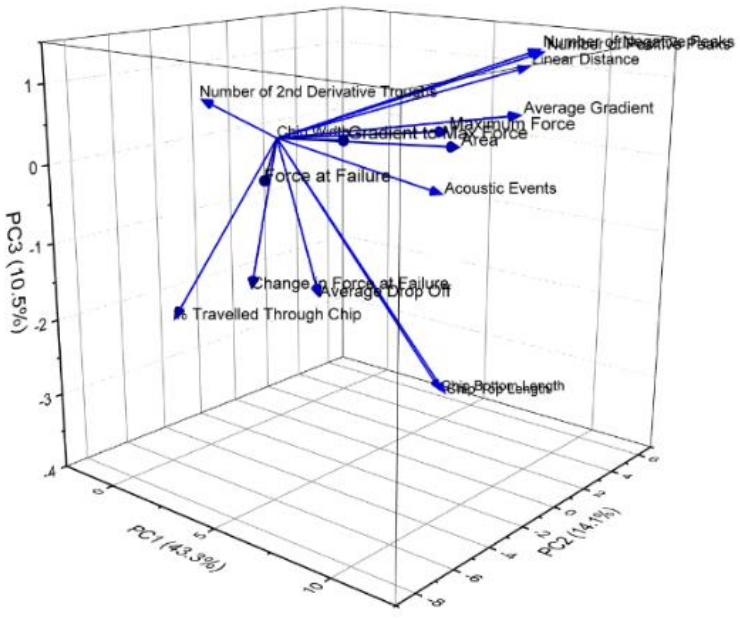


Figure 5-26 Pre-Screen Loading Plot of 1st 8 Week Study

Figure 5-26 depicts the covariance of the extracted variables across the whole 8 week period for all 96 samples tested. In this case all covariances have been standardised by one as the variables

consist of different measurements and scales. The loading plot produced accounts for 67.9% of the variability observed. Factors which account for the same variation in results are the chip top and bottom length and the number of negative troughs and positive peaks. The top length of the microchip and bottom length of the microchip were dependent on each other. This is not surprising as this is entirely due to the manufacturing process as opposed to any influence on storage. It was also determined that the number of positive and negative peaks and troughs were dependent on each other. These two factors represent the peaks and troughs observed in the force plots produced on application of the Volodkevich probe and relate to energy stored and released from the chips' microstructure. The chip top and bottom length were combined to form the variable mean chip length. The number of positive peaks were not incorporated into the PCA. The number of negative troughs was chosen as negative troughs refers to the drop in force on application of a mechanical probe and according to the literature, this correlates with product crispness and energy released on application of force. All remaining variables were kept.

CV and Correlation Coefficient

The pre-screening was continued by calculating the coefficient of variation (Figure 5-27) and the correlation coefficient (Table 5-13) of the remaining variables. By understanding the interaction between the variables this will aid understanding of the loading plots in the PCA.

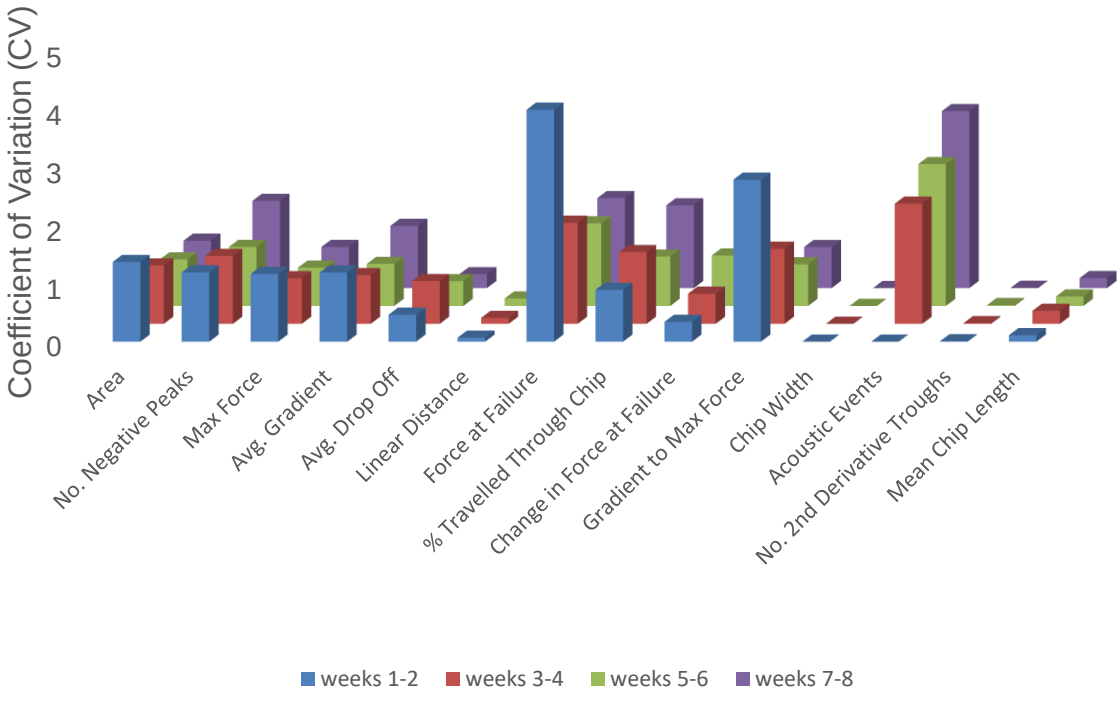


Figure 5-27 Coefficient of Variation for Variables Inserted into PCA

During weeks 1-2 the variation in the data was highest for the force at failure. This indicates that the samples are different structurally and agrees with McCain's view of rapid transformations in the product within the first two weeks. Interestingly the % travelled through the chips shows a much lower CV than the force at failure indicating that whilst there are differences in where in the product microstructure the sample fails, other factors such as product hardness could be contributing to the variation observed in the force at failure variable. As the linear distance CV is low, it indicates that the microstructure is behaving fairly similarly in terms of deformation. The fact that the CV of the 2nd derivative troughs is also low agrees with this theory. Slight variation in chip length is expected due to the geometry of a potato.

During weeks 3-4 the largest variation occurs due to the number of acoustic events. As acoustic events are directly associated with product crispness this indicates that the samples being tested are different during this time period. This is different to the previous two weeks where variation in acoustic data was non-existent as no acoustic events were observed. During this period it was observed that from weeks 1 and 2 all the CVs (with the exception of acoustic events and mean chip length) reduced, indicating that during this time period, the products tested were more homogenous. Many of the mechanical variables had similar variances. Variation is similar for most variables which is not unsurprising as all are mechanical parameters with the exception of acoustic events. The number of 2nd derivative troughs have little to no variation in their data set during weeks one and two. It suggests that regardless of coating type during weeks 3 and 4 the rate of energy release is the same. In terms of acoustic events the variation observed increases as a function of time with the largest variations in the data observed during weeks 7-8. This indicates that the crispness of the product is different amongst samples and could be due to;

1) Natural variation in the product
2) Product is different as a result of a coating/no coating

At this stage it is not known which of the factors above could be explaining the change. However, what is clear is that the rate of variation in terms of acoustic events increases in variance as a function of time, indicating that storage has an effect on the end product. The number of negative peaks also shows the highest variation during weeks 7-8 agreeing that during this period the samples are different. As chip width is constant, a CV cannot be calculated as the data is the same and this is the same across the testing window. The correlation coefficient was also calculated for each variable across the testing window. This was achieved using Pearson's coefficient of correlation (Table 5-13). A score of 1 is equal to a highly correlated set of variables with values closer to 0 indicating no correlation. If a * is present this indicates that the correlation determined is significant to a 95% confidence interval. Strong correlations (>0.9) have been highlighted in red to show which variables are dependent on one another.

Weeks		Area	Number of Negative Peaks	Max Force	Average Gradient	Average Drop Off	Linear Distance	Force at Failure	% Travelled Through Chip	Change in Force at Failure	Gradient to Max Force	Chip Width	Acoustic Events	Number of 2nd Derivative Troughs	Mean Chip Length
1-2	**Area**	1.00	0.87*	0.99*	0.91*	0.79*	0.35	0.96*	0.41*	0.61*	0.97*	-	-	0.19	0.23
3-4		1.00	0.88*	0.93*	0.90*	0.47*	0.75*	0.47*	-0.02	0.75*	0.91*	-	0.69*	0.12	0.20
5-6		1.00	0.53*	0.87*	0.63*	0.51*	0.69*	0.63*	0.15	0.12	0.91*	-	0.72*	-0.07	0.37
7-8		1.00	0.74*	0.94*	0.83*	0.63*	0.41*	0.65*	-0.02	0.51*	0.93*	-	0.54*	-0.40	0.11
1-2	**Number of Negative Peaks**	0.87*	1.00	0.87*	0.95*	0.61*	0.44*	0.80*	0.46*	0.64*	0.83*	-	-	0.02	0.28
3-4		0.88*	1.00	0.84*	0.85*	0.24	0.76*	0.30	-0.07	0.54*	0.72*	-	0.50*	0.11	0.05
5-6		0.53*	1.00	0.37	0.88*	0.17	0.77*	0.20	-0.19	-0.16	0.36	-	0.63*	-0.01	0.50*
7-8		0.74*	1.00	0.73*	0.93*	0.39	0.81*	0.61*	-0.08	0.22	0.71*	-	0.35	-0.27	0.16
1-2	**Max Force**	0.99*	0.87*	1.00	0.91*	0.75*	0.37	0.95*	0.44*	0.59*	0.97*	-	-	0.18	0.24
3-4		0.93*	0.84*	1.00	0.92*	0.56*	0.72*	0.37	-0.02	0.58*	0.79*	-	0.53*	0.13	0.22
5-6		0.87*	0.37	1.00	0.53*	0.35	0.56*	0.45*	0.13	0.10	0.99*	-	0.53*	0.00	0.21
7-8		0.94*	0.73*	1.00	0.82*	0.47*	0.52*	0.50*	-0.06	0.47*	1.00*	-	0.50*	-0.31	0.05

1-2	**Average Gradient**	0.91*	0.95*	0.91*	1.00	0.75*	0.43*	0.87*	0.47*	0.64*	0.88*	-	-	0.04	0.36
3-4		0.90*	0.85*	0.92*	1.00	0.65*	0.76*	0.46*	0.15	0.58*	0.77*	-	0.53*	0.16	0.16
5-6		0.63*	0.88*	0.53*	1.00	0.33	0.76*	0.25	-0.11	-0.14	0.53*	-	0.57*	0.05	0.53*
7-8		0.83*	0.93*	0.82*	1.00	0.40	0.73*	0.50*	-0.08	0.43*	0.81*	-	0.43*	-0.33	0.1
1-2	**Average Drop Off**	0.79*	0.61*	0.75*	0.75*	1.00	0.06	0.74*	0.33	0.67*	0.74*	-	-	0.22	0.33
3-4		0.47*	0.24	0.56*	0.65*	1.00	0.31	0.50*	0.40	0.23	0.38	-	0.21	0.07	0.25
5-6		0.51*	0.17	0.35	0.33	1.00	0.22	0.55*	0.41*	0.15	0.42*	-	0.22	0.05	0.29
7-8		0.63*	0.39	0.47*	0.40	1.00	0.06	0.79*	0.52*	0.59*	0.45*	-	0.39	-0.52*	0.31
1-2	**Linear Distance**	0.35	0.44*	0.37	0.43*	0.06	1.00	0.41*	-0.09	0.25	0.42*	-	-	0.12	0.08
3-4		0.75*	0.76*	0.72*	0.76*	0.31	1.00	0.36	-0.16	0.62*	0.60*	-	0.56*	0.23	0.30
5-6		0.69*	0.77*	0.56*	0.76*	0.22	1.00	0.11	-0.38	-0.29	0.57*	-	0.52*	-0.21	0.65*
7-8		0.41*	0.81*	0.52*	0.73*	0.06	1.00	0.27	-0.09	0.07	0.51*	-	0.30	-0.14	0.11
1-2	**Force at Failure**	0.96*	0.81*	0.95*	0.87*	0.74*	0.41*	1.00	0.25	0.63*	1.00*	-	-	0.24	0.20
3-4		0.47*	0.30	0.37	0.46*	0.50*	0.36	1.00	0.56*	0.68*	0.24	-	0.73*	0.05	0.09
5-6		0.63*	0.20	0.45*	0.25	0.55*	0.11	1.00	0.70*	0.57*	0.49*	-	0.40	0.02	-0.01
7-8		0.65*	0.61*	0.50*	0.50*	0.79*	0.27	1.00	0.46*	0.28	0.47*	-	0.31	-0.22	0.22

1-2	**% Travel Through Chip**	0.41*	0.46*	0.44*	0.47*	0.33	-0.09	0.25	1.00	0.08	0.27	-	-	-0.07	0.14
3-4		-0.02	-0.07	-0.02	0.15	0.40	-0.16	0.56*	1.00	0.22	-0.79	-	0.05	-0.05	-0.16
5-6		0.15	-0.19	0.13	-0.11	0.41*	-0.38	0.70*	1.00	0.79*	0.13	-	0.04	0.06	-0.32
7-8		-0.02	-0.08	-0.06	-0.08	0.52*	-0.09	0.46*	1.00	0.41*	-0.70	-	0.06	-0.20	0.28
1-2	**Change in Force at Failure**	0.61*	0.64*	0.59*	0.64*	0.67*	0.25	0.63*	0.08	1.00	0.64*	-	-	0.23	0.32
3-4		0.75*	0.54*	0.58*	0.58*	0.23	0.62*	0.68*	0.22	1.00	0.64*	-	0.95*	0.08	0.25
5-6		0.12	-0.16	0.10	-0.14	0.15	-0.29	0.57*	0.79*	1.00	0.08	-	0.04	0.12	-0.14
7-8		0.51*	0.22	0.47*	0.43*	0.59*	0.07	0.28	0.41*	1.00	0.49*	-	0.55*	-0.45*	0.20
1-2	**Gradient to Max Force**	0.97*	0.83*	0.97*	0.88*	0.74*	0.42*	1.0*	0.27	0.64*	1.00	-	-	0.23	0.20
3-4		0.91*	0.72*	0.79*	0.77*	0.38	0.60*	0.24	-0.79	0.64*	1.00	-	0.56*	0.10	0.28
5-6		0.91*	0.36	0.99*	0.53*	0.42*	0.57*	0.49*	0.13	0.08	1.00	-	0.55*	-0.05	0.24
7-8		0.93*	0.71*	1.00*	0.81*	0.45*	0.51*	0.47*	-0.70	0.49*	1.00	-	0.51*	-0.32	0.06
1-2	**Chip Width**	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-4		-	-	-	-	-	-	-	-	-	-	-	-	-	-
5-6		-	-	-	-	-	-	-	-	-	-	-	-	-	-
7-8		-	-	-	-	-	-	-	-	-	-	-	-	-	-

1-2	**Acoustic Events**	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3-4		0.69*	0.50*	0.53*	0.53*	0.21	0.56*	0.73*	0.05	0.95*	0.56*	-	1.00	0.12	0.26
5-6		0.72*	0.63*	0.53*	0.57*	0.22	0.52*	0.40	0.04	0.04	0.55*	-	1.00	0.05	0.39
7-8		0.54*	0.35	0.50*	0.43*	0.39	0.30	0.31	0.06	0.55*	0.51*	-	1.00	-0.39	0.20
1-2	**Number of 2nd Derivative Troughs**	0.19	0.02	0.18	0.04	0.22	0.12	0.24	-0.07	0.23	0.23	-	-	1.00	-0.09
3-4		0.12	0.11	0.13	0.16	0.07	0.23	0.05	-0.05	0.08	0.10	-	0.12	1.00	0.14
5-6		-0.07	-0.01	0.00	0.05	0.05	-0.21	0.02	0.06	0.12	-0.05	-	0.05	1.00	-0.1
7-8		-0.40	-0.27	-0.31	-0.33	-0.52*	-0.14	-0.22	-0.20	-0.45*	-0.32	-	-0.39	1.00	-0.16
1-2	**Mean Chip Length**	0.23	0.28	0.24	0.36	0.33	0.08	0.20	0.14	0.32	0.20	-	-	-0.09	1.00
3-4		0.20	0.05	0.22	0.16	0.25	0.30	0.09	-0.16	0.25	0.28	-	0.26	0.14	1.00
5-6		0.37	0.50*	0.21	0.53*	0.29	0.65*	-0.01	-0.32	-0.14	0.24	-	0.39	-0.1	1.00
7-8		0.11	0.16	0.05	0.1	0.31	0.11	0.22	0.28	0.20	0.06	-	0.20	-0.16	1.00

Table 5-13 Pearson Correlation Coefficient Table For Each Variable (Close to +1 indicates positive correlation, close to -1 indicates negative correlation, close to 0 indicates no correlation)

Variables which strongly correlated were the area and max force as with the exception of weeks 5-6 the correlation was >0.9. The max force and gradient to max force also strongly correlated as the correlation was >0.9 for all weeks except weeks 3-4. The force at failure and max force strongly correlated (0.95) during weeks 1-2 but after this point the correlation was not as strong and by weeks 7-8 was 0.5. The number of acoustic events and the change in force at failure strongly correlated (0.95) during weeks 3-4. This could be because acoustic events are associated with release of energy on failure of the microstructure. However, this relationship was not observed for the remaining period of testing. The number of 2nd derivative troughs showed no correlation with any variable. This was surprising as the 2nd derivative is associated with energy release and so it would be expected to correlate with the number of acoustic events. As this was not observed, it suggests that the test speed was too slow to capture the acoustic events needed to observe this relationship. The linear distance observed no strong correlations with any other variables although for weeks 3 onwards a correlation of 0.7-0.8 was observed between the linear distance and the number of negative peaks in the mechanical data. This is not surprising as the less smooth the data, the longer the linear distance should be.

Pre-Screening of Loading Plots

By determining the relationships between the variables and their CVs this aids understanding of the loading plots. The loading plots describe the weightings of the variance with longer arrows indicating the variables responsible for a larger degree of the variance. Figure 5-28 shows the loading plot for weeks 1-2. The matrix used was a correlation matrix which is a covariance matrix standardised to 1. This matrix was chosen as all of the variables have differing scales and by standardising this makes comparison between variables possible. With highly correlated variables the loadings would be similar making it possible to reduce the number of variables considered. Similarly, variables with low weightings <0.3 are deemed not to contribute significantly to the variation observed within the data and so these variables can also be removed. At first appearances the loading plot suggests that the number of 2nd derivative troughs is an important variable. However, by observing the correlation coefficient and CV this variable is shown to have very little variability week to week and shows no correlation with the other variables. By observing on the loading plot where the 2nd derivative variable lies (close to 0) this also shows that this variable does not contribute to the variability observed in the data set. As such it was removed. The linear distance was kept as whilst strong correlations (>0.9) were not observed and the CV was low there was still a correlation observed with other variables in the data set. The chip width and number of acoustic events were also removed from weeks 1-2 as they showed no variation in terms of the CV, correlation matrix and loading plot. The loading plot coefficients were then observed in more detail. Variables which have the same values are depicted on top of each other in a loading plot and are said to be redundant meaning that only one of the variables is

required to define the variability. This can be confirmed by observing the coefficient number of each variable contributing to a PC plane. Values close to 0 account for very little variability in the data set. This is because as part of the PCA test, the data is centered on the mean of each variable meaning that a value close to 0 indicates no variance from the data set. From observing the coefficient, the area, max force, force at failure, average gradient and gradient to max force explained similar coefficients explaining the same variances (0.36). As the CV was high for both the gradient to max force and the force at failure these variables were retained. The remaining variables were discarded. In PC1 the variables with the least explaining power were the mean chip length, linear distance and % travelled through the chip as they had coefficients of 0.126, 0.155 and 0.156 respectively. These variables would have been removed from analysis had they not had explaining power in PC2 and PC3. The loading plot with the second derivative present is found in Figure 5-28 whilst the final loading plot is found in Figure 5-29.

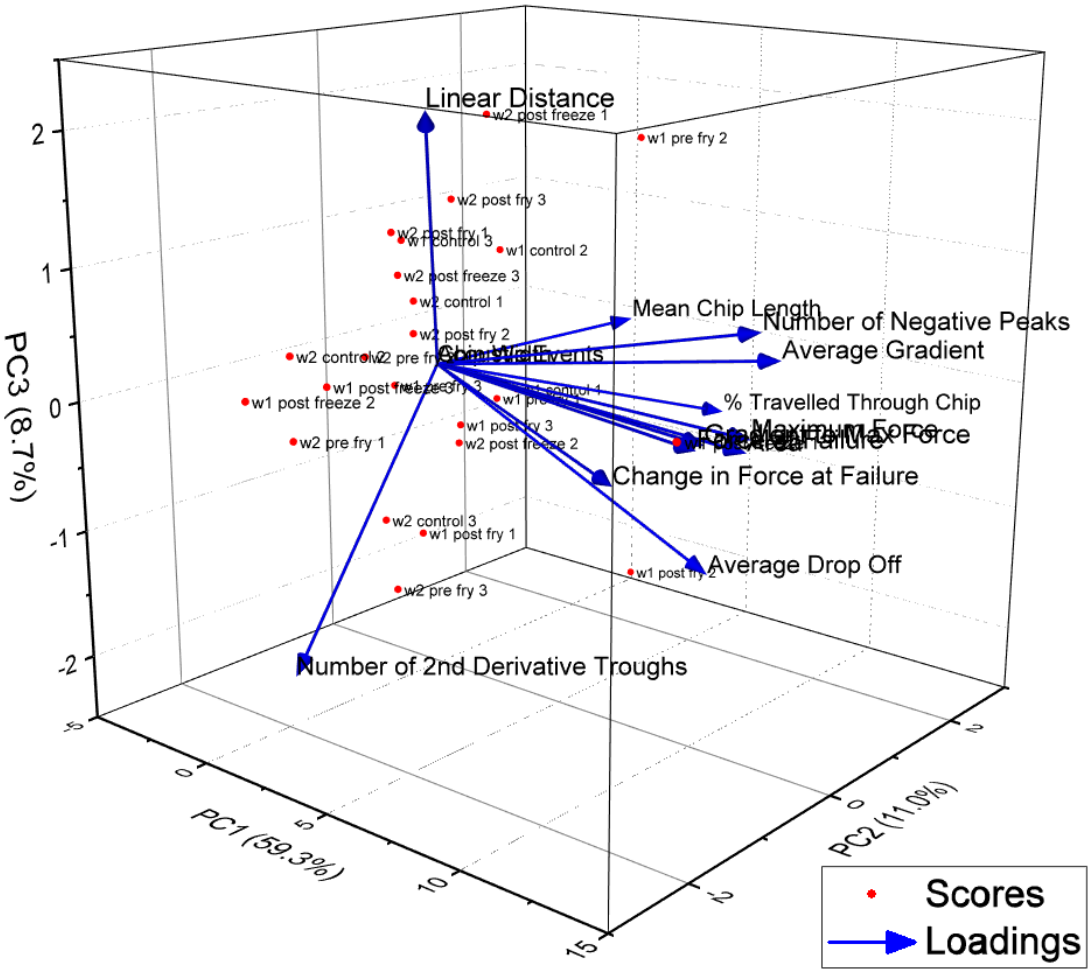


Figure 5-28 Loading and Score Plot Containing 2nd Derivative for Weeks 1-2

Pre-screening was also applied to weeks 3-4, 5-6 and 7-8 which is not visually depicted in this thesis. This was achieved by observing the CV, correlation coefficient and PCA loading plots in order to determine which variables could be discarded.

5.4.2.4.2 PCA Discussion

By observing the coefficients for PC1, PC2 and PC3 for weeks 1-2 (Figure 5-28) the area, max force, gradient to max force and force at failure accounted for the highest variance in 59.3% of the data set (PC1) with a coefficient observed >0.35. In 11 % of the data (PC2) the biggest contributors were the linear distance and the % travelled through the chip. All other variables fell below the 0.3 threshold so are said to not contribute significantly to the variability shown in 11% of the data. In PC3 (8.7 % of the data) the mean chip length accounted for the largest variance in the data. The change in force at failure provided the second largest explaining power. As PC1 accounted for 59.3% of the data the variables showing the highest variation in the data within this principal component are the most important overall in terms of accounting for variation in the data set.

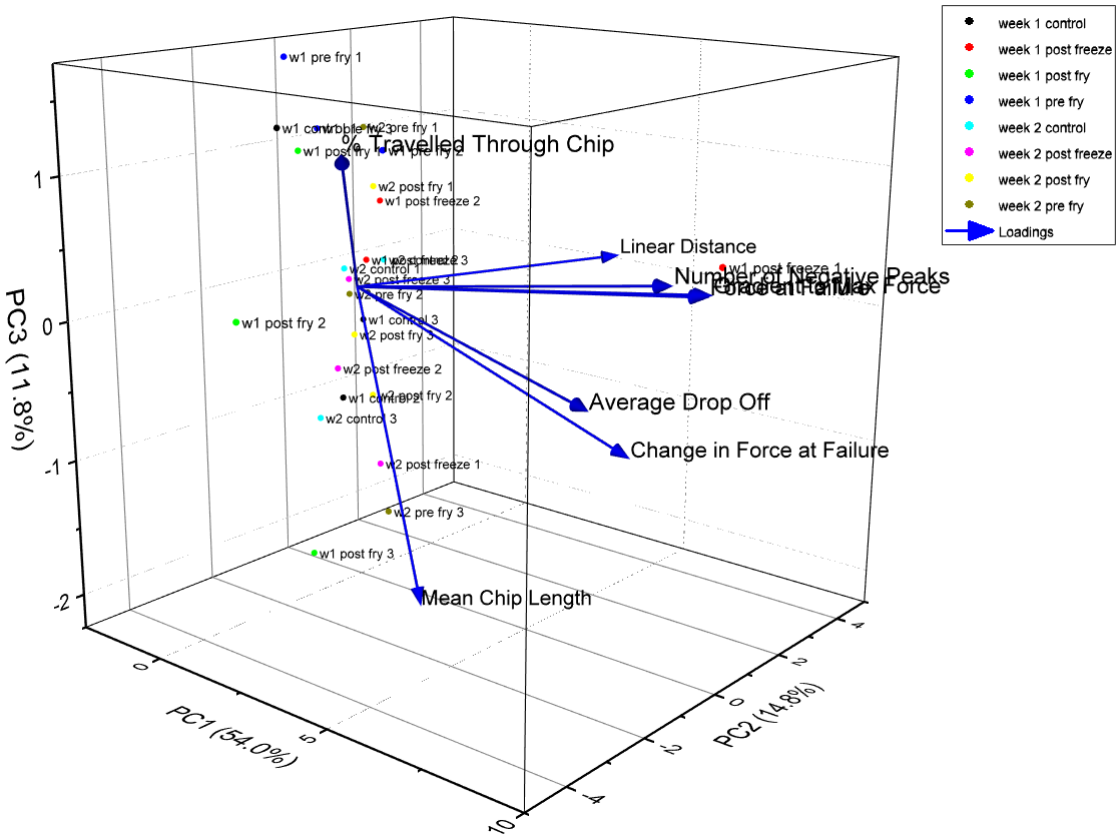


Figure 5-29 Final Loading Plot for Weeks 1-2

When the loading plot is in the form shown in Figure 5-29 it is difficult to show which variable is accounting for the variance in each principal component. Therefore the model was rotated to show planes xy, zx and yz. Figure 5-30 shows a projection of the planes.

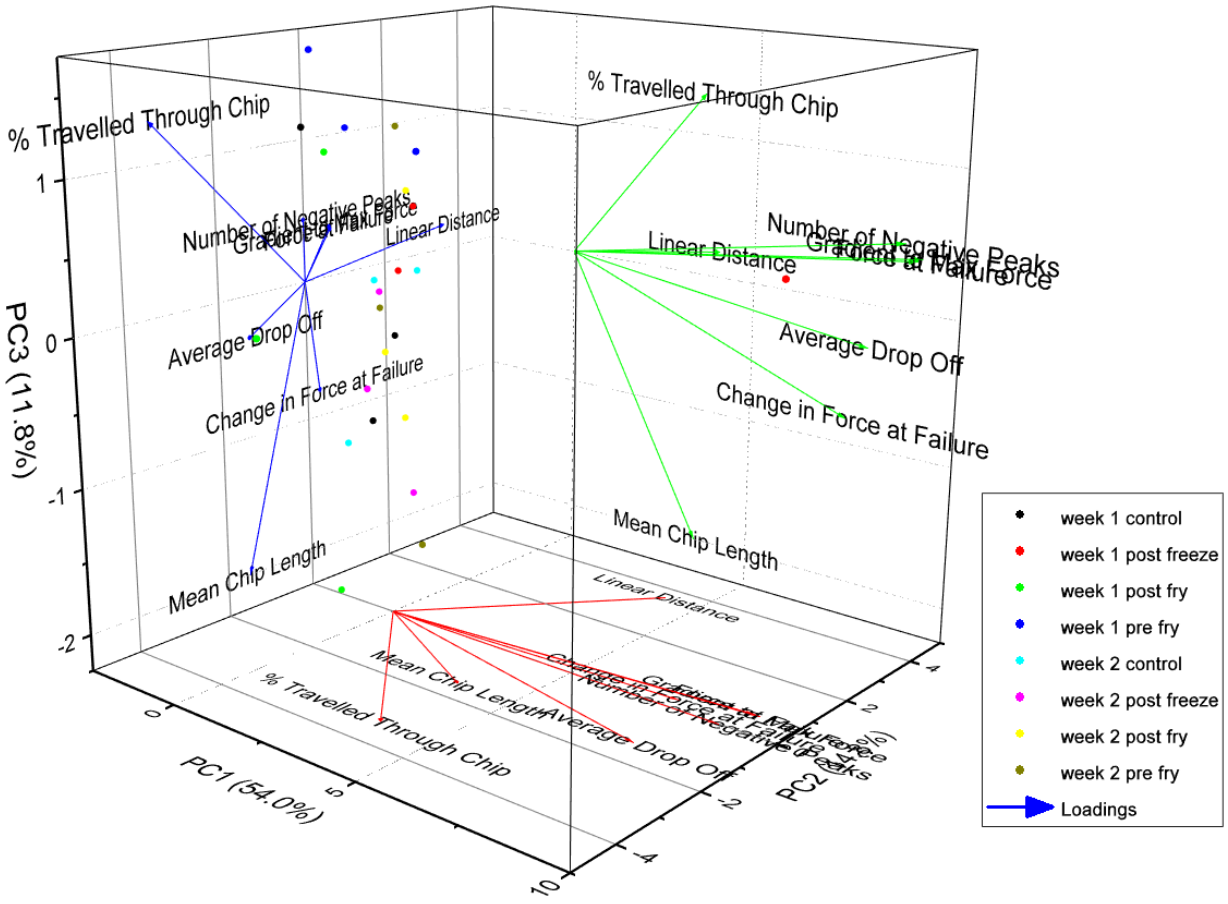


Figure 5-30 Loading and Score Plot For Weeks 1-2 PCA with Planes Projected

To determine which values should be considered for each principal component the coefficient produced for each loading plot was observed. Only variables >±0.3 were considered as having explaining power. From observing the space they occupy in PC1 only the average drop off showed a separate direction of variance with the force at failure, change in force at failure, number of negative peaks and gradient to max force. By observing the CV the force at failure had the greatest variance. The correlation coefficients in table 5-13 showed there was a correlation between the four variables from 0.63 to 1. Therefore, all variables except the force at failure can be discarded. For PC1 at week 1, the force at failure and the average drop off explain the variability observed in PC1 during weeks 1-2. The same method was applied to determine the variation in PC2. In terms of PC2 the linear distance and % travelled through the chip explain the variance. They are also negatively correlated denoted by their position opposite one another in the loading plot. All other variables were not considered as they fall below <±0.3. The variables explaining PC3 were the mean chip length and % travelled through the chip which are negatively correlated and the change in force at failure. A summary of the variables explaining each principal component for each of the testing weeks is found in table 5-14.

In terms of whether the samples are different dependent on coating type can also be observed in Figure 5-30. Whilst the majority of the variance is in PC1 only 3 samples were present in the PC1 field; week1 post freeze, week 1 post fry and week 2 pre fry. All remaining samples were present in the PC2 and PC3 planes. As PC2 and PC3 account for 26.6%, the three samples in PC1 are the samples causing the highest variance in the data set. Interestingly none of the samples are the same. The remaining samples are in the PC2 and PC3 plane with variation caused by the linear distance, % travelled through the chip, mean chip length and change in force at failure. Therefore whilst the CV shows that that force at failure caused the biggest change this is not actually the case as only 3 of the 24 samples were present in PC1. It was observed that week 1 pre fry data was clustered together with the variance being impacted by the linear distance and the % travelled through the chip. Week 2 post freeze samples were also clustered together with their variance explained by linear distance and mean chip length. During weeks 1-2 the samples are not differentiated by sample type or week number with the exception of pre fry samples which are clustered together during week 1 but then dispersed during week 2 and post freeze samples which are dispersed during week one and clustered during week 2. This indicates that storage has affected the product as it is no longer being explained by the same variables.

Week Number	PC1 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC1	PC2 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC2	PC3 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC3	Variables not explaining Variability	Number of Variables explaining variability
1-2	Force at Failure	0.44984	Linear Distance	0.66813	Mean Chip Length	-0.76103	Number of 2nd Derivative Troughs, Chip Width, Number of Acoustic Events, Max Force, Gradient to Max Force, Number of Negative Peaks, Average Gradient, Area	6
	Average Drop Off	0.39560	% Travelled Through Chip	-0.61735	% Travelled Through Chip	-0.31416		
					Change in Force at Failure	0.48820		
3-4	Area	0.43732	% Travelled Through Chip	0.70842	Average Drop Off	-0.56634	Number of 2nd Derivative Troughs, Mean Chip Length, Chip Width, Number of Negative Peaks, Linear Distance, Average Gradient	8
	Change in Force at Failure	0.40799						
	Number of Acoustic Events	0.39428	Average Drop Off	-0.56634	Number of Acoustic Events	0.47818		

	Gradient to Max Force	0.38155						
	Force at Failure	0.32906	Force at Failure	0.47667	Max Force	0.34619		
5-6	Area	0.43502	% Travelled Through the Chip	0.56357	Average Drop Off	0.57373	Number of 2nd Derivative Troughs, Mean Chip Length, Chip Width, Max Force, Linear Distance, Average Gradient	8
	Number of Acoustic Events	0.36005	Change in Force at Failure	0.50448	Change in Force at Failure	-0.42610		
	Number of Negative Peaks	0.35193	Force at Failure	0.42423	Number of Negative Peaks	-0.42820		
					Gradient to Max Force	0.34361		
7-8	Area	0.37155	% Travelled Through Chip	0.53959	Change in Force at Failure	-0.38061	Chip Width, Average Gradient, Gradient to Max Force, Max Force, Force at Failure	9
			Average Drop Off	0.40881	Number of Acoustic Events	-0.35977		

	Number of Negative Peaks	0.33254	Linear Distance	-0.32561	Mean Chip Length	0.32519		
			Change in Force at Failure	0.31461	Number of 2nd Derivative Troughs	0.31105		
					Number of Negative Peaks	0.30762		

Table 5-14 Variables Explaining the Variance Observed in the Data During Weeks 1-2, 3-4, 5-6 and 7-8

Weeks	% of the data explained PC1	% of the data explained PC2	% of the data explained PC3	Total Variability Explained (%)
1-2	54	14.8	11.8	80.6
3-4	57.3	20.1	14.0	91.4
5-6	46.5	27.5	8.3	82.3
7-8	48.9	16.9	9.1	74.9

Table 5-15 Variability of the Data Set Explained by Each Principal Component as a Function of Time

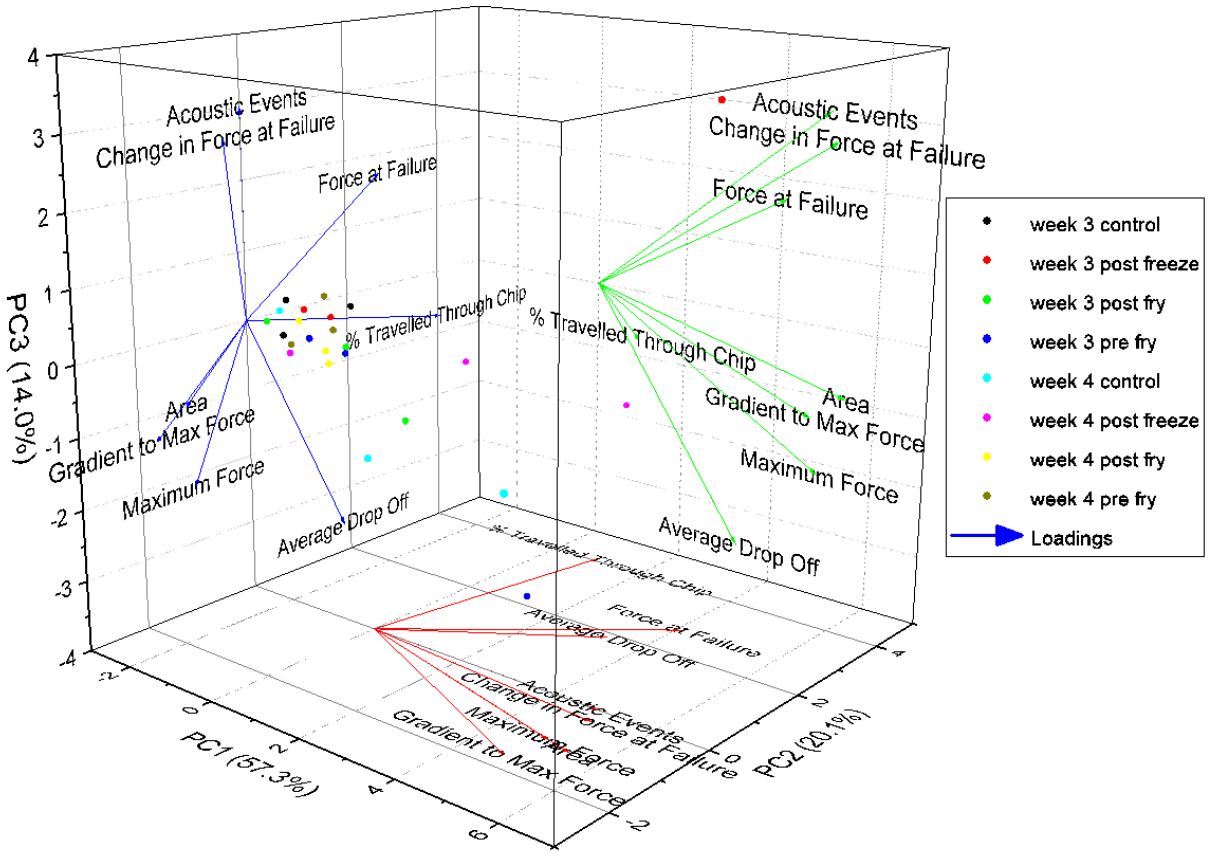


Figure 5-31 Loading and Score Plot for Weeks 3-4

Table 5-15 gives an overview of the variability of the data explained by each principal component as a function of week number. The sample becomes more homogenous during weeks 3-4 (Figure

(5-31). There are more extreme samples explained by all three PCs and these are week 3 post freeze 2, week 3 pre fry 2 and week 4 control 3. The remaining data is explained by PC2 and PC3 meaning the variation in most of the data set is due to % travelled through the chip as the variable most explaining the variance, followed by the average drop off, force at failure, number of acoustic events, change in force at failure and max force. By observing the correlation coefficients in table 5-13 the variables could be reduced in PC3 with change in force at failure removed due to its high correlation with the number of acoustic events. During week 3 two out of the three pre fry samples remain in this cluster with all pre fry samples present by week 4 indicating a sample that becomes homogenous as a function of time during this period. All week 3 controls, week 4 post frys and week 4 pre frys are present in the cluster. Whilst at week 3 the control samples are homogenous, by week 4 the control samples are scattered. As the coated samples bar post freeze are present in the cluster at week 4, this indicates that the coating is having an effect on the sample by keeping them more homogenous in nature as the variances explaining them are the same. Storage is having an effect on the samples as during week 1-2 the samples were not clustered together indicating they are different (with the exception of week 1 pre fry and week 2 post freeze samples) whilst during weeks 3-4 the majority of samples are explained by the same variances indicating samples which are more similar.

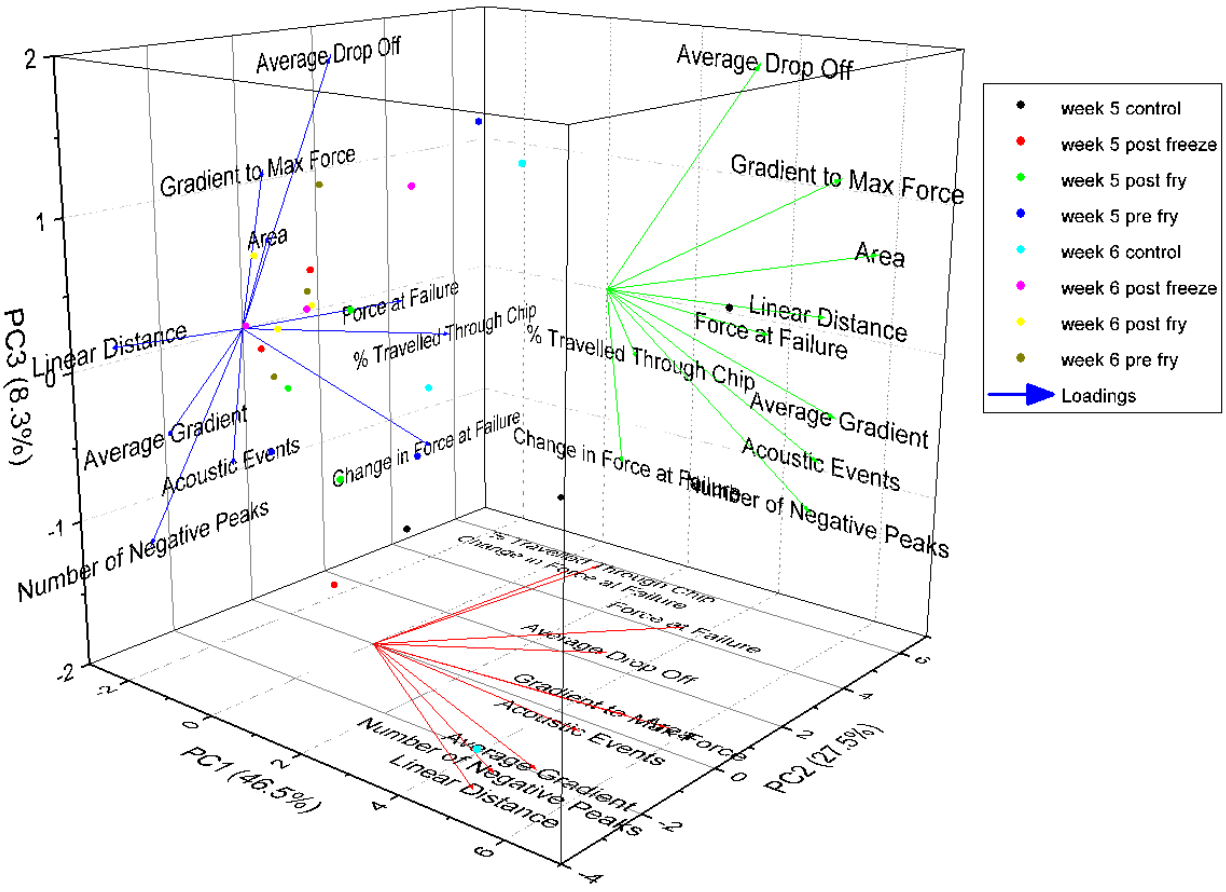


Figure 5-32 Loading and Score Plot for Weeks 5-6

By weeks 5-6 (Figure 5-32) the samples are once again dispersed unlike in weeks 3-4 although week 6 pre fry and post fry are clustered together in a similar region. Week 5 post fry samples are also clustered together with week 5 pre fry samples being dispersed further apart. In the case of post freeze applications, across both weeks, 2 of 3 samples are close together. This could be due to the sample sticking to the susceptor and causing uneven heating to occur in the last remaining sample. The control samples vary across this period over both weeks indicating that the coating in a pre-fry or post fry form may help to keep the samples more homogenous. The sample variances are mainly explained by PC2 and PC3 with the variables giving explaining power in order of importance being; % travelled through chip, change in force at failure, force at failure for PC2 and average drop off, change in force at failure, number of negative peaks and gradient to max force. By observing the correlation coefficients in table 5-13 this set of variables can be reduced further to % travelled through the chip for PC2 with all other variables remaining for PC3. The graph for weeks 7-8 is not depicted. However, the results are found in tables 5-14, 5-15 and 5-16.

Week Number	Are control samples clustered?	Variables that explain cluster-control	Are pre-fry samples clustered?	Variables that explain cluster – pre fry	Are post fry samples clustered?	Variables that explain cluster -post fry	Are post freeze samples clustered?	Variables that explain cluster – post freeze
1	N	-	Y	% travelled through chip, Linear Distance	N	-	N	-
2	N	-	N	-	N	-	Y	Linear distance, change in force at failure, mean chip length
3	Y	% travelled through chip, force at failure, average drop off	N	-	N	-	N	-

4	N		Y	% travelled through chip, force at failure, average drop off	Y	% travelled through chip, force at failure, average drop off	N	-
5	N	-	N	-	Y	Force at failure, % travelled through chip, gradient to max force, acoustic events	N	-
6	N	-	Y	Avg drop off, gradient to max force, force at failure, % travelled, change in	Y	% travelled through chip, force at failure, average drop off	N	-

				force, acoustic events				
7	N	-	Y	Avg drop off, Acoustic events, Change in force at failure	N	-	N	-
8	N	-	Y	Avg drop off, Acoustic events, Change in force at failure	Y	Avg drop off, Acoustic events, Change in force at failure	N	-

Table 5-16 Determining Whether Samples of the Same Type have the Same Variance as a Function of Time and which Variables Explain the Variability Observed

5.4.2.5 Overall Conclusion

During testing it became apparent that the test speed of 0.1 mm/s was too slow for the chip microstructure to break down and produce sound levels that could be collected by the AED. Therefore it was decided that the acoustic data was more important for determining crispness than the mechanical data and so the test speed was increased to 1 mm/s to better reflect this. The test speed chosen was still slower than human biting speed. Through method development it was ascertained that acoustic data could still be generated at these lower speeds. The acoustic data also does not take into account the effect of vibration through the bone which also contributes to human sensory perception of product crispness. However, it is hoped that the data will, in conjunction with the other six test methods utilised during the second 8 week study provide a realistic theory of the mechanisms occurring within the product.

In terms of the PCA the following conclusions were made;

1) The variability of the data is lower than predicted by the CV as the majority of the samples across the 8 week period were represented by PC2 and PC3 as opposed to PC1.
2) Coated samples (in particular pre fry and post fry) had a higher incidence of being clustered together over the 8 week period meaning that similar variances were explaining the variability of the data in those weeks.
3) Storage has an effect on the products produced where in some weeks samples were clustered together and in other weeks samples were spread apart and could not be explained by the same variances.
4) Pre fry samples were clustered together in 5 of the 8 weeks and the top variables observing the variance within the sample set were the number of acoustic events, change in force at failure, force at failure, average drop off, linear distance and % travelled through the chip. All of these variables are related to the microstructure of the product indicating that even within the same week the microstructure of the pre fry product differs. However, as discussed it could also be that the test settings were not suitable for measuring the product causing variability in the data set. As such it would be interesting to observe when the probe speed is altered if the number of acoustic events and mechanical measurements show less variability within coating groups and larger variability over an 8 week storage period.
5) Post fry samples were clustered together in 4 out of the 8 weeks. The same conclusions were drawn for this set of data as for pre fry.
6) Both control and post freeze samples rarely clustered together indicating that the samples are different across the 8 weeks and within each week with the exception of one occasion. This indicates that the samples produced are much more variable than pre and post fry samples as the variances cannot be ascertained.

The recon loss data and observations from the investigator did notice a difference in the end product dependent on coating. It was found that week 3 to 4 may provide a change in the products microstructure for pre and post fry applications in terms of moisture loss. As moisture is associated with less crisp products it is of interest to repeat this 8 week shelf life again whilst incorporating other techniques to gain a better idea of how storage is affecting the end product.

The investigator noted that pre fryer application resulted in the most desirable product as by week 8 the uncoated product became dehydrated and inedible. For post freeze and post fryer coating applications the product stuck to the susceptor at the bottom of the McCain box. In their current form post fryer and post freezer applications are not a viable product as in some cases the chips would scorch the bottom of the box thus presenting a fire risk. This predominantly occurred when the coating was applied post freezer.

5.4.2.6 Next stage of experiments required

Pre fry coating applications resulted in the most desirable product as both post fry and post freeze applications resulted in a product that stuck together and was therefore inedible. It was decided that a second 8 week study would be conducted to observe the effect of a pre fry coating application in more detail. The first aim was to incorporate more investigative techniques to provide a further understanding of how a pre fry application method promotes the different textures observed in the end product. The second aim was to produce a replicate of the recon loss data to determine if the first recon loss at 4 minutes was an anomaly. The third aim was to incorporate another coating to look at the effects of NaCl in the presence of CMC and so the two coatings chosen were;

1) 2% CMC and 4% NaCl
2) 2% CMC and 0% NaCl

Due to the potential risks of ice crystal formation it was also important to ascertain if handling of the product every week was causing moisture to evaporate from the sample every time product was required to perform a test. If so this would affect the end product. Therefore it was decided to weigh the sample every time. The details of this may be found in section 2.2.4.1

Finally, storage was observed to have a large effect on the product on a week by week basis so it was decided to perform another 8 week study utilising more investigative techniques to further understand the mechanisms occurring on storage.

5.5 Final 8 week study

As discussed in section 5.4.2.6 this investigation was conducted with multiple aims;

1) Incorporate more investigative techniques

2) Incorporate another coating to observe pre fryer application in more detail
3) Investigate the effect of storage on moisture loss
4) Determine if changing the probe speed affects the conclusions from a Principal Component Analysis.
5) Investigate the mechanisms altering within the product on storage

5.5.2 Materials and Methods

The materials and methods used can be found in section 2.2.4. Due to the large number of investigative techniques applied it was decided after analysing aspects of the data to condense the data from the different techniques into different factors which could be inputted into a PCA. The factors chosen are listed in section 2.2.4.8. Data for week 4 could not be generated and so is omitted from this 8 week study.

Sample	Dry Loss (%)	Fry Loss (%)	Pick-Up (%)	Temperature of Coating (°C)	B6 Flow Cup Time (secs)
Control	6.75	25.79	n/a	n/a	n/a
2% CMC 0% NaCl	6.75	31.2	6.05	16.5	6.18
2% CMC 4% NaCl	6.75	29	6.73	17.2	5.63

Table 5-17 Dry Loss, Fry Loss, Pick up, B6 Flow Cup Viscosity and Temperature of Coating Recorded as a Function of Sample Type

Table 5-7 observes the fry losses, pick up, temperature of the batter, dry losses and viscosity of the samples tested. Whilst in the previous 8 week study the fry loss was 15.67% during this study the pre fry fry loss was 31.2% which was higher than those recorded for the post fry and post freeze values of 20.29% and 24.32% during the first 8 week study. This could be because the pick up in the first 8 week study was 9.8% whilst for this study was only 6.05%. As such a thicker coating could promote a lower fry loss. This is not unreasonable due to CMC being hygroscopic.

5.5.3 Results and Discussion

5.5.3.1 Effect of Storage on Moisture Loss

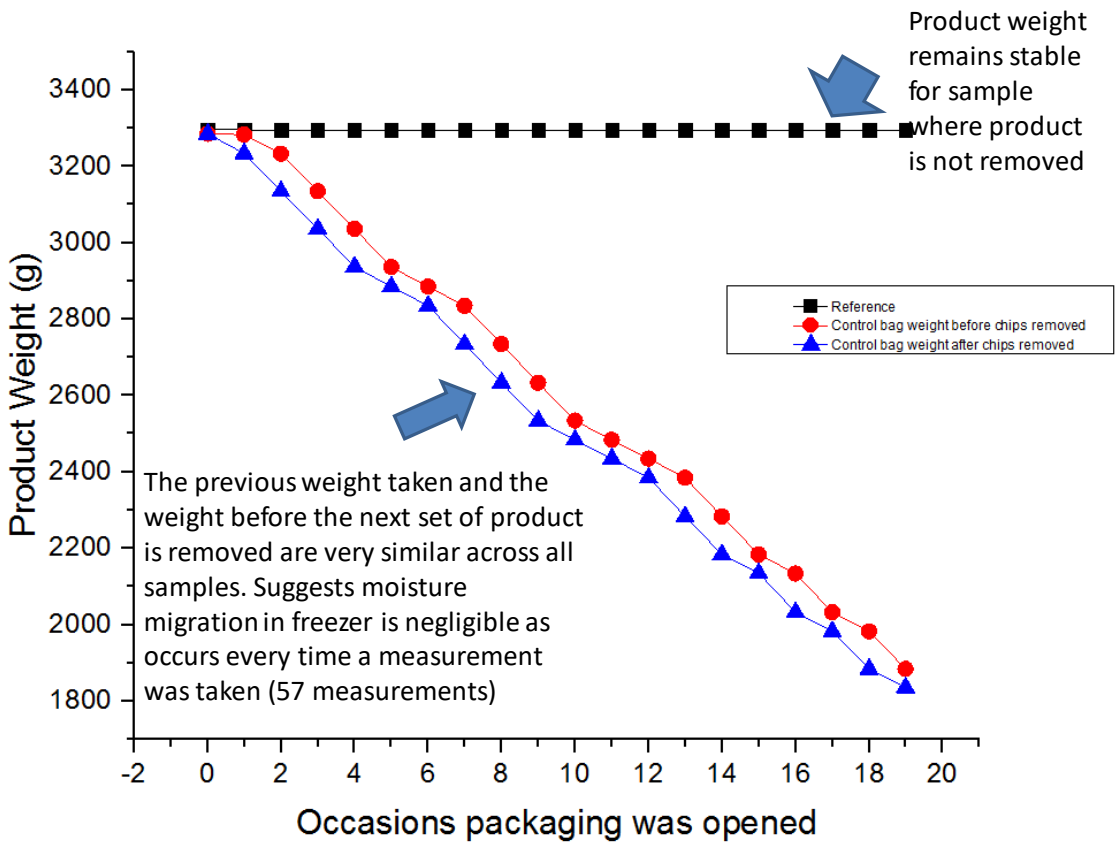


Figure 5-33 Effect of Storage on Control Weight as a Function of Occasions Packaging Opened & Change in Weight When Sample Removed

The effect of storage in the freezer on moisture loss was considered. From observing Figure 5-33 storage does not cause moisture loss within the current packaging as the weight remained the same before sample was removed. The same result was observed for the two coated samples and so for all samples tested moisture loss on storage did not occur on the whole sample. However, moisture loss and migration may still occur within products as ice formation was observed in the control sample as early as week 3. Ice crystals were not observed in the coated samples until week 7/8. This means that whilst the total weight remains the same, moisture migration within the package is occurring.

5.5.3.2 Recon Loss and Moisture Findings

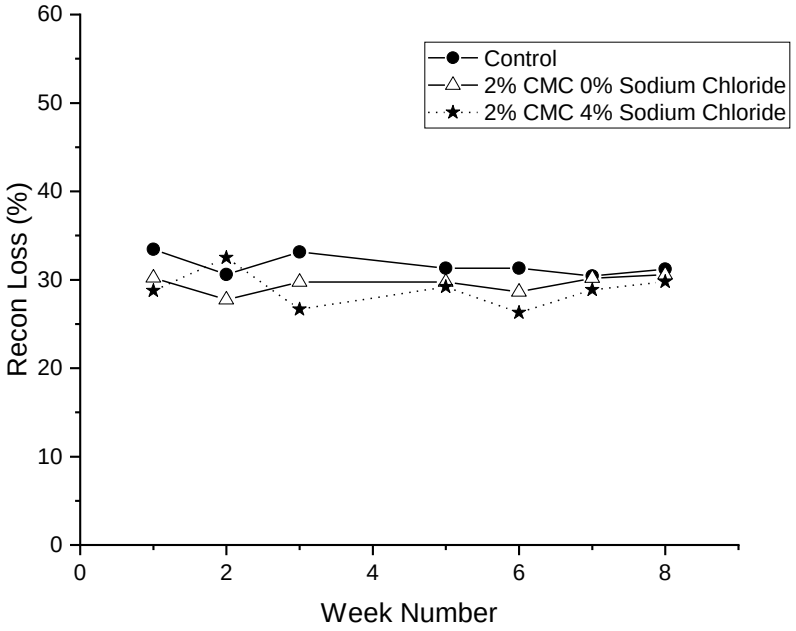


Figure 5-34 Recon Loss for Control (black square), 2% CMC 0% NaCl (black triangle) and 2% CMC 4% NaCl (black star) Heated for 4 Minutes

The recon loss data was repeated to observe if the peaks observed previously were anomalous. Figure 5-34 shows that no peaks were present and it is therefore theorised that peaks observed during the 1st 8 week study are likely due to the presence of fragile ice crystals. However, the remaining recon loss data does follow the trend seen previously where overall the control values had the highest recon loss at the end of the 8 week period. The recon loss does differ over the 8 week period indicating that the moisture content is altering either due to where in the potato the chips are taken from, the ratio of free water:bound ice and water migration processes. The recon loss of samples containing NaCl was less stable than the control and samples containing only CMC with the a range of 6% recorded. The control and CMC 0% NaCl samples only differed amongst themselves by 2% across the whole testing window.

Week Number	Moisture Content Control Inner (%)	Moisture Content 2% CMC 0% Sodium Chloride Inner (%)	Moisture Content 2% CMC 4% Sodium Chloride Inner (%)
1	76.72	78.63	77.88
2	78.19	78.63	78.73

3	79.50	73.61	81.74
5	76.69	73.61	79.17
6	82.74	80.41	83.28
7	80.17	84.76	81.80
8	81.03	81.20	83.70

Table 5-18 Moisture Content of Inner Layer of Control Uncoated Samples, 2% CMC 0% Sodium Chloride Samples and 2% CMC 4% Sodium Chloride Samples

Week Number	Moisture Content Control Outer(%)	Moisture Content 2% CMC 0% Sodium Chloride Outer (%)	Moisture Content 2% CMC 4% Sodium Chloride Outer (%)
1	29.54	34.57	37.60
2	30.56	35.64	30.94
3	29.69	29.11	34.16
5	27.76	29.13	31.71
6	30.60	31.06	33.31
7	29.69	27.65	29.15
8	29.13	30.21	33.61

Table 5-19 Moisture Content of Outer Layer of Control Uncoated Samples, 2% CMC 0% Sodium Chloride Samples and 2% CMC 4% Sodium Chloride Samples

Tables 5-18 and 5-19 show the moisture content of the outer and the inner part of the potato over an 8 week period. As expected the inner samples had a much higher moisture content than the dehydrated outer. The moisture content of the control inner sample tended to increase towards the end of the test. This is not surprising as ice crystals were observed on the control sample and not on the coated samples thus suggesting that moisture is migrating within the sample. It is also expected that the inner moisture contents would fluctuate more readily due to their high moisture contents as during measurement it is possible that moisture may have been transferred to the Weck-Prep blade when cutting as it was noted that the inner sample felt very wet. The moisture content of the outer control layer remains fairly stable although it does fluctuate week by week which also suggests that moisture could be migrating within the sample. Natural variability is a

possibility although during sampling only the longest chips were selected so that a similar part of the potato was measured each week (pith). However, in the case of the coated samples the moisture content behaves differently. As the outer layer is dehydrated it is surprising that rapid fluctuations in the moisture content are occurring on a weekly basis. The moisture contents vary by 6.99% for the 2% CMC 0% NaCl sample and 8.45% for the 2% CMC 4% NaCl sample. In contrast the control sample outer layer only varies by 2.98% over the testing window. This is of interest as the coating is having an impact on moisture migration within the product. As CMC is hygroscopic it is not surprising that moisture is being drawn to the surface of the product. In the case of the 2% CMC 0% NaCl coating the highest outer moisture contents are during the first 2 weeks and so it is likely that during this stage the CMC is drawing moisture to the surface. By week 3, the CMC coating with no NaCl is more similar to the control sample. However, the 2% CMC 4% NaCl coating behaves differently. The moisture content both increases and decreases by a large degree on a weekly basis. This leads to the theory that the presence of sodium in the coating is enabling a form of 'chemical oscillation'. It is believed that when frozen the CMC promotes the migration of free (unbound) liquid (non-frozen) water from the centre of the product to the surface. The presence of this moisture at the surface causes the dissociation of CMC and NaCl into Na^+ and Cl^- ions into the free water solution. Due to a higher salt concentration at the surface, the free water containing the dissociated NaCl ions diffuse into the centre of the chip. The presence of sodium and chloride ions depresses the melting point of ice resulting in a higher rate of frozen bound ice converting into mobile liquid water. As a result the NaCl concentration in the centre of the product is reduced and so the mobile water migrates to the surface coating. This results in more NaCl ions becoming dissociated and the increased NaCl concentration causes further diffusion into the centre of the product where further ice melting occurs. This process is repeated until an equilibrium is reached and no further migration of water or ions occur. This equilibrium is believed to be causing the fluctuations observed in the coating containing the sodium chloride. A visual model of this behaviour is found in Figure 5-35.

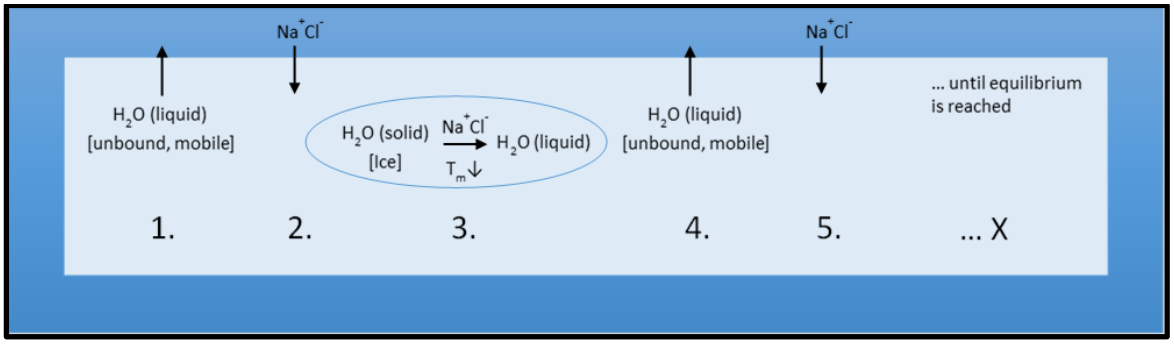


Figure 5-35 Visual Representation of the Chemical Oscillator Theory (dark blue = coating, light blue = chip) (Koehler, 2017)

5.5.3.3. DSC Main Findings

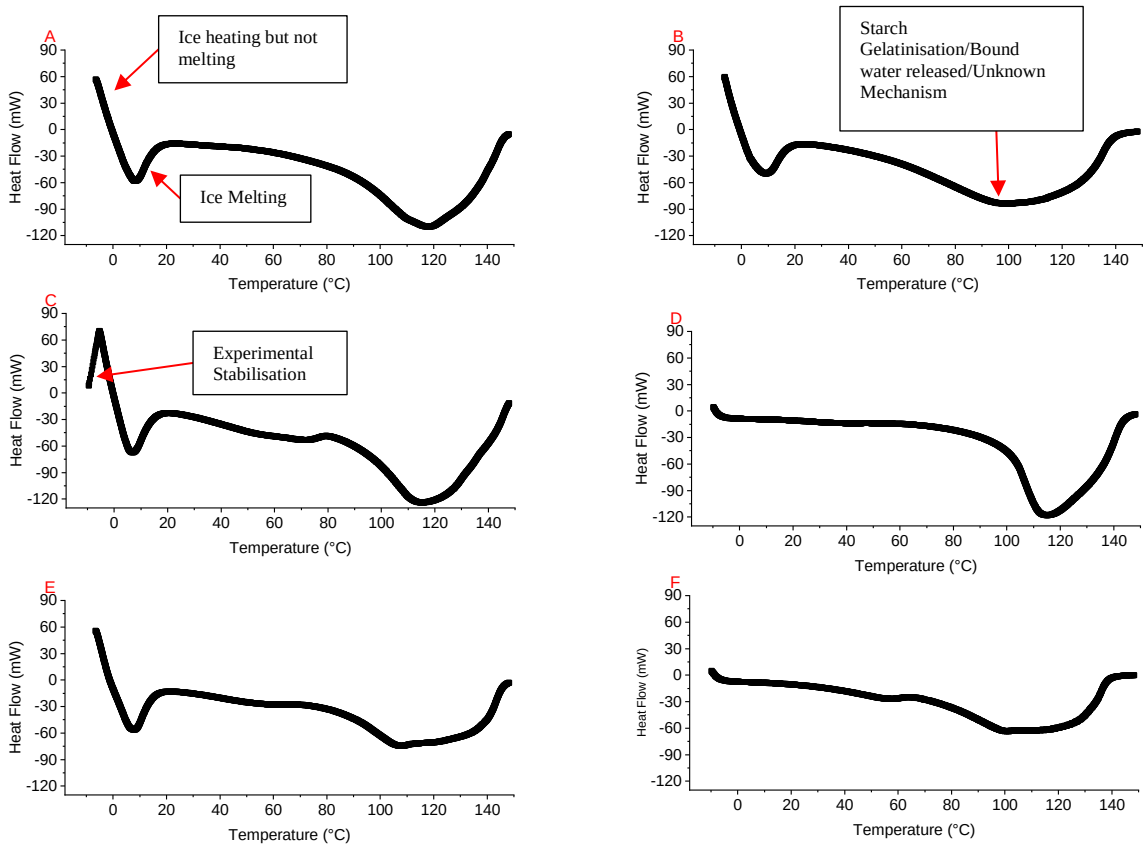


Figure 5-36 DSC Repeat Control Inner Uncoated Microchips with Important Behaviours Identified

A= C1, B=C2, C=C3, D=C4, E=C5, F=C6

The DSC test parameters are located in section 2.2.4.4. On observing the DSC controls (Figure 5-36 there are four areas of interest;

1) Experimental Stabilisation – This data shall be removed from investigation as does not reflect the sample i.e. ice will not melt until 0°C so peak could be due to disparity between temperature of pans as run first starts and before equilibrium is maintained
2) Ice heating but not melting
3) Ice melting
4) Starch Gelatinisation/Bound water released/Unknown Mechanism

In 4 out of the 6 control samples tested this behaviour is observed. However, in controls 4 and 6 the melting of ice was not observed. This indicates that the sample was not transferred to the DSC and the experiment started before the ice had begun to melt. It is important to note that the gelatinisation temperature of potato is within the region 58-72 °C with final fragmentation of the starch granule occurring >100 °C (Blanshard and Lillford, 1993). During this process it is not

unreasonable to suggest that water bound to the swelling granules could be released and impact dielectric heating. This is shown in Figure 1-11 in work conducted by (Sipahioglu and Barringer, 2003) whereby the dielectric constant was found to increase when gelatinisation occurred. However, this was found to occur at a lower temperature (≈ 70 °C) than the peaks observed in the Figure 5-36. This could have occurred because starch gelatinisation would have occurred to a degree in the fryer when creating the potato fries where smaller granules would have gelatinised. As the potatoes were dehydrated from entering the fryer, it is not unfeasible that higher temperatures and a longer time period in the DSC would be required to allow the larger starch granules to firstly swell and then rupture. This is because for gelatinisation to occur an excess of water is required as well as heat. However, it could be due to another mechanism as discussed in Figure 5-37.

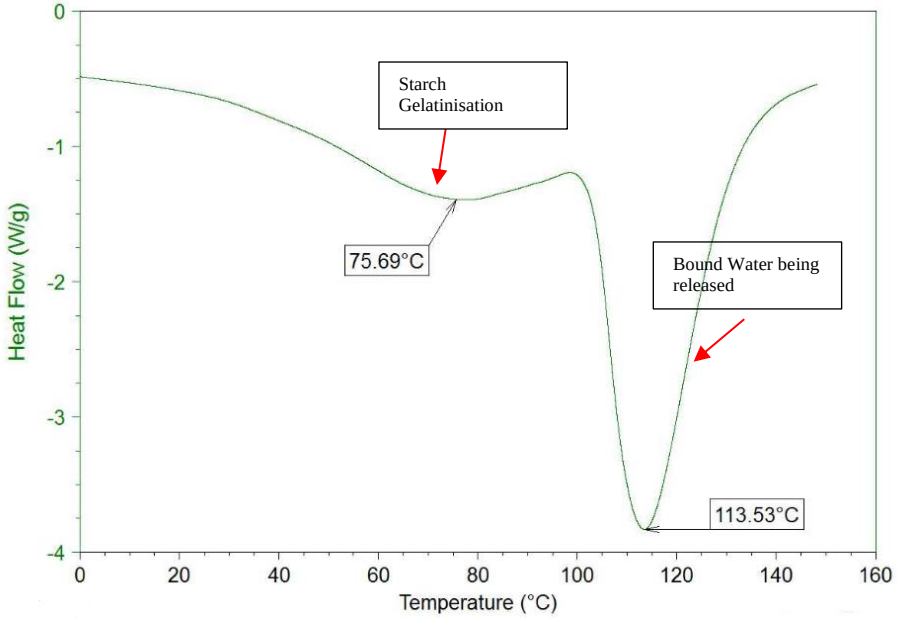


Figure 5-37 DSC Produced for week 5 Control Outer Layer Sample

It was found that whilst most of the samples tested had one large peak across the 70 °C to 140 °C region, for some samples regardless of outer/inner layer a slight peak within the potato starch gelatinisation temperature range was observed. This was followed by a second larger peak > 100 °C. This suggests that the solitary elongated peak observed in the other samples could be observing starch gelatinisation and then the release of bound water resulting in an elongated higher temperature peak. As this product is complex, this larger peak at higher temperatures could also be due to mechanisms currently unknown.

On analysing the coated and uncoated samples on a weekly basis the same areas of interest were observed with the exception of the occasional starch gelatinisation separate peak. These two distinct peaks for starch gelatinisation and another unidentified peak occurred every week for the

control samples regardless of inner/outer layer from week 3 onwards till the end of the test. The lowest gelatinisation temperature peak was 54.63 °C with the highest being 77.23 °C. For the coated samples this was not the case, as whilst separate gelatinisation peaks were observed for the two coated samples for the inner samples in week 3, separate gelatinisation peaks were not observed in the outer layer samples. This could be because the CMC is holding onto the moisture and therefore preventing it from entering the starch granules and allowing gelatinisation to occur. It could be that gelatinisation is occurring within the elongated peak occurring > 100 °C although further work would be required to ascertain this. By week 5 only the control samples are observing a distinct gelatinisation peak with the coated samples presenting the elongated peak over a larger temperature range. This is with the exception of 2% CMC 4% NaCl inner layer where a separate gelatinisation peak of 63.78 °C is recorded. During week 6 both the control samples had a separate gelatinisation peak with peak temperatures of 75.69 °C recorded for the outer layer and 67.61 °C recorded for the outer layer. Only the sample containing CMC and NaCl in its outer layer measurement recorded a separate gelatinisation peak of 77.23 °C, the highest peak gelatinisation temperature recorded. During week 7 whilst the control samples show distinctive gelatinisation peaks, only the coated sample containing CMC and NaCl in its outer layer observes a separate starch gelatinisation peak of 75.69 °C. This supports the chemical oscillator theory as the NaCl is affecting the location of the moisture within the sample week to week. In week 7 it appears that enough moisture is present within the outer layer of the sample to enable gelatinisation to take place. During week 8 only the control samples and CMC 4% NaCl outer layer contained a separate gelatinisation peak with gelatinisation temperatures of 65.77 °C for the coated sample and 63.78 °C and 62.15 °C for the control outer layer and inner layer respectively.

In terms of the PCA it was decided to just input the larger solitary peak as this will better show the variance in the data set as these peaks have a larger temperature range when the gelatinisation peak is not observed. As the sample weight was different for each sample the data produced could not be quantitatively compared. Therefore it was decided to parameterise the four areas of interest. This data would then be inputted into the PCA to observe the relationship between variables as well as to observe the variance within the data set to determine if storage has an impact on the products produced.

Behaviour	**Parameters Extracted**
Experimental Stabilisation	None- Ignored as not representative to sample
Ice Heating but not Melting	Slope and Intercept
Ice Melting	Area Under Peak

	Onset Temperature End Temperature Temperature at which heat flow is maximum when ice is melting
Starch Gelatinisation/Bound Water Release/Unknown Mechanism Peak	Area Under Peak Onset Temperature End Temperature Temperature at which heat flow is maximum when ice is melting

Table 5-20 Parameters Extracted From DSC Data and Inserted into PCA

Table 5-20 shows the parameters extracted from each of the four areas of interest highlighted from the DSC. For each of the variables extracted, they were entered into the PCA separately as inner and outer samples. As the sample size differed between samples, the temperature at which max heat flow occurred has been observed as opposed to the heat flow itself as this will differ as a function of sample size.

5.5.3.3.1 Ice Melting Vs Ice Sublimation

During the investigation a period of ice melting was observed. However, it was uncertain if due to the small sample size, the ice was simply transforming to a liquid state or subliming (changing from a solid to a gas and bypassing the liquid state). As free liquid water is required to promote dielectric heating in the microwave, it was important to investigate whether the ice was subliming or melting.

To investigate this, a deionised water sample and a Maris Piper potato sample were placed in the DSC under the following conditions;

1) Sample held at -10°C for 20 minutes
2) Sample held at -5°C for 20 minutes
3) Sample held at 0°C for 20 minutes
4) Sample heated from -20°C to 5°C at a rate of 1°C/ minute

Each test was repeated 5 times. No peak was detected for either the deionised water or Maris Piper potato samples held at -10°C, -5°C or 0°C. Figure 5-38 observes the mean heat flow for the Maris Piper potato and the standard error of the mean.

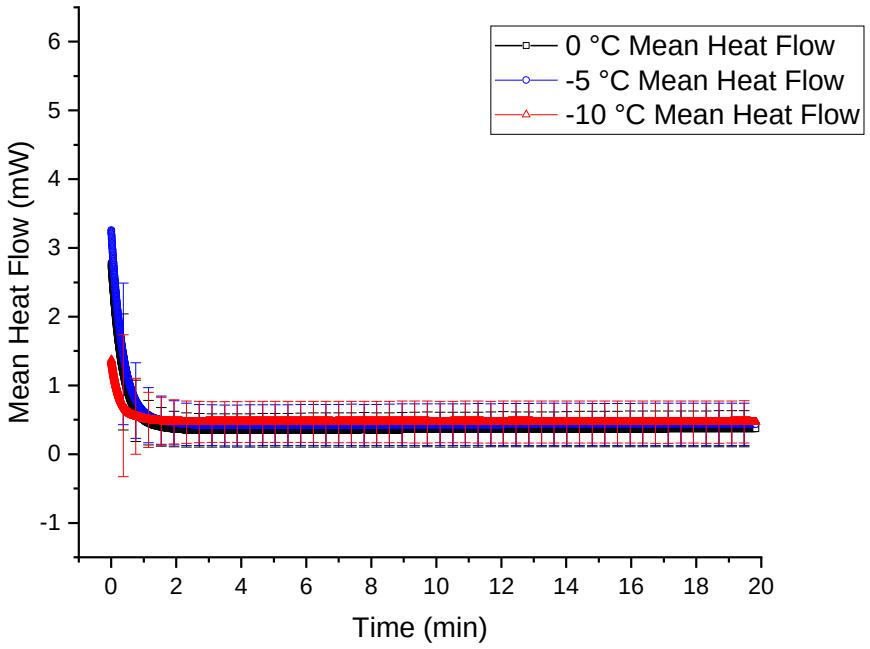


Figure 5-38 Mean Heat Flow of Maris Piper Potato Samples held at 0 °C, -5 °C and -10 °C (n=5)

On observing the samples heated from -20°C to 5°C a peak was observed for both the deionised water and Maris Piper sample after 0°C where the maximum peak temperature observed in the ice melting peak was 1.32°C for the Maris Piper potato sample and 3.42°C for the deionised water sample. This is not surprising as the impurities present in the potato would be expected to cause ice to melt more quickly than a pure water sample. As no endothermic peaks activity was observed in either sample set, it was determined that the ice is melting on application of heat rather than subliming. Therefore as the ice melts, the resultant liquid water would be expected to contribute to dielectric heating.

5.5.3.3.2 DSC Overall Conclusions

In most cases the melting of ice was missed by the DSC but that is due to the sample not being inserted into the machinery in time to always observe this behaviour. Despite method development, the melting of ice endotherm was only observed 3 times across the testing window which is not surprising due to the size of the samples tested being in mg. Therefore this data was not incorporated into the PCA.

A large peak near/over 100 °C was observed in every sample regardless of coating type and inner/outer layer. Initially this was believed to be starch gelatinisation. However, during the experiment from week 3 onwards another peak was observed mainly in the control samples within the temperature range usually associated with potato starch gelatinisation. As such it suggests that

the sample is undergoing a physical transformation that is not fully understood. One theory is that this is bound water becoming released from the product and as such may be important in terms of dielectric heating within the microwave. The presence of a starch gelatinisation peak is not surprising as whilst the samples do undergo a frying process, the process occurs too rapidly to allow gelatinisation of larger starch granules.

It is important to note that the role of water within this system is very complex and has many interactions such as;

1) Bound Ice
2) Free Water
3) Water and Ions
4) Water Bound to Starch
5) Water Bound to Carboxymethylcellulose
6) Mobility of water due to hygroscopic nature of carboxymethylcellulose
7) Mobility of water due to concentration gradient of sodium chloride
8) Drying of saturated outer layer
9) Formation of ice crystals (in control samples more commonly)

Therefore further work is required to determine with certainty which physical changes are occurring within the product.

5.5.3.4 TGA Main Findings

The TGA method was developed as observed in section 3.2.2 with the final method outlined in section 2.2.4.5. Prior to the main experiment being conducted 6 repeat samples were measured. These were uncoated control samples. The 6 TGA controls all showed a similar behaviour, indicating the TGA measurement is repeatable as a function of shape of the drying curve produced but not intensity of drying due to the different amount of samples used. To quantify this behaviour the coefficient of determination function was applied to determine specific areas of drying relating to traditional drying theory as discussed in section 1.6.1.5. Using this method is suitable as it measures mass loss on heating and is therefore directly concerned with measuring the moisture content of a sample and how it evaporates.

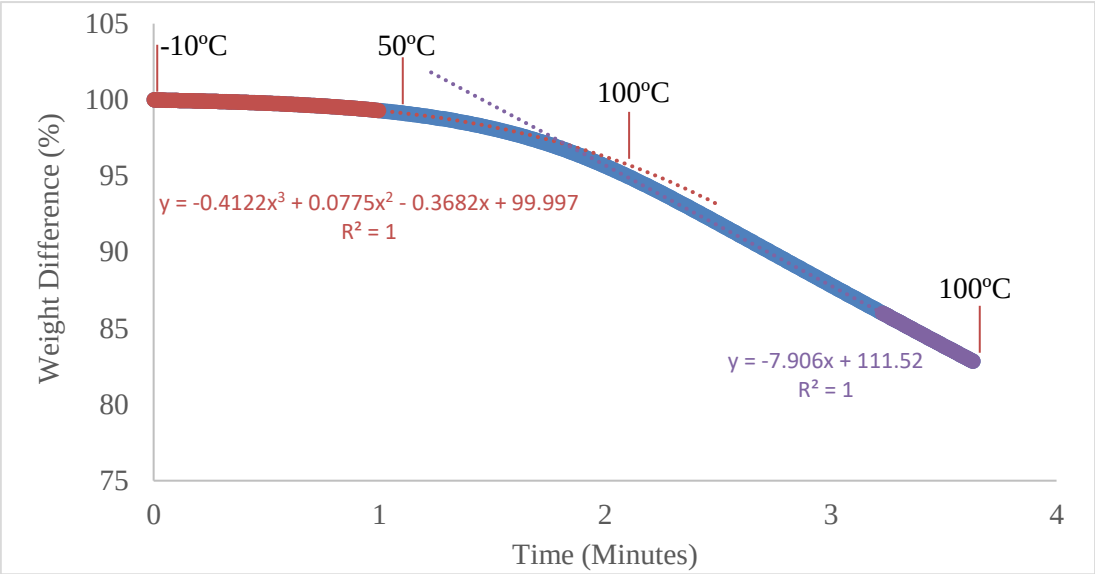


Figure 5-39 Example TGA Behaviour From Repeated Uncoated Control Inner Samples

To determine the physics of the samples the coefficient of determination function was applied as discussed in section 1.6.1.5. For the majority of the inner samples, two different fits occurred (Figure 5-39). Initially there was a period of non-linear behaviour which is not associated with drying. Instead it was hypothesised that ice melting is occurring at the beginning of the test meaning ice is being converted to liquid water. This period is defined as an increasing rate period. The second distinctive behaviour is a linear drying period and so this can be associated with a constant rate period where the surface is fully saturated and drying occurs by surface transfer. By the end of the test the sample was still within the constant rate as the drying behaviour remained linear. Therefore the surface of the sample is still considered to be saturated as if the sample entered the fallng rate this would mean that the saturated region had retreated towards the centre of the product where moisture loss would then be governed by heat mass transfer. This is of interest as the TGA was heated for a period of time similar to the temperature and time that the product would have been subjected to within the microwave. It indicates that the centre of the sample is moisture rich and that moisture is not able to evaporate sufficiently for the second drying phenomenon to occur. This means that the current microwave methodology will struggle to cause sufficient evaporation of moisture that will promote product crispness. However, by week 8 the coating containing 2% CMC and 0% NaCl exhibited a different behaviour whereby the melting of ice and constant rate were observed as well as a further polynomial behaviour of order 2 was observed thus indicating that the product had entered the falling rate as it is a non-linear behaviour. This has implications as it suggests that the presence of CMC is affecting the way in which the moisture is migrating and causing moisture to evaporate more quickly. It was

noted by the investigator that the samples containing CMC and no NaCl were drier by week 8 than the other two samples.

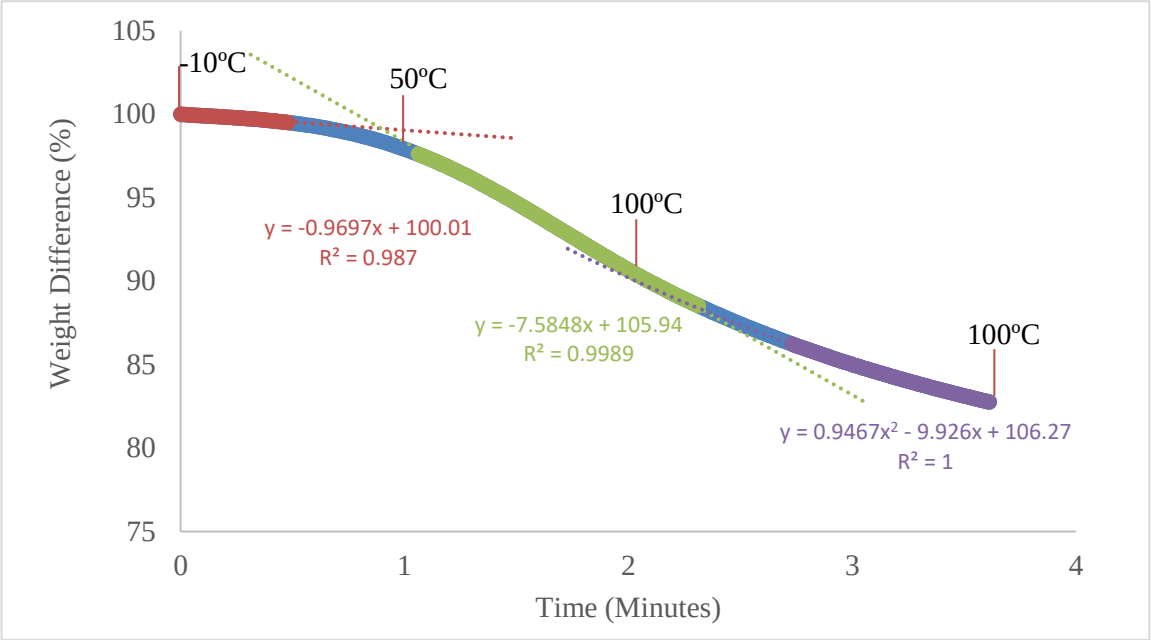


Figure 5-40 Example TGA Behaviour From Repeated Uncoated Control Outer Samples

The outer layer of the sample provided a different behaviour for every sample regardless of coating and week (Figure 5-40). This was apart from 2% CMC 0% NaCl and 2% CMC and 4% NaCl samples during week 8. The majority of samples exhibited two linear drying periods followed by a polynomial period. Therefore, the outer sample has two constant rate periods followed by a falling rate period. It is not unexpected that a falling rate period is observed as the outer layer is dehydrated and so there is less moisture present to evaporate in the testing window compared to the inner sample. It was theorised that during the first constant rate period, the bound ice melts and supersaturates the surface of the product and starts to evaporate. During the second constant rate period the temperature has increased and water bound into the chip matrix becomes free and results in a second constant rate period and further evaporation that is not limited by mass transfer. In the case of the coated samples during week 8 a polynomial behaviour is observed followed by a linear behaviour and a further polynomial behaviour. This indicates that the product is undergoing ice meting followed by a constant rate behaviour and a falling rate behaviour. However, the coating containing no NaCl takes longer to exit the ice melting (1 minute 11 seconds) than the coating with NaCl (1 minute 5 seconds). This is not surprising as the presence of NaCl depresses the melting point of ice causing the process to occur more quickly.

As the coated samples for week 8 both differed from previous behaviour in both the inner and outer samples this suggests that the coated samples are influencing the end product. To understand the TGA data further important behaviours were identified and extracted for insertion into the PCA (Table 5-21).

Sample Name	Trend line fit for 1st physical behaviour	R^2 Value for 1st physical behaviour	Trend line fit for 2nd physical behaviour	R^2 Value for 2nd physical behaviour
Control Inner 1	Polynomial (order 3)	1	Linear	1
Control Inner 2	Polynomial (order 3)	1	Linear	1
Control Inner 3	Polynomial (order 3)	1	Linear	1
Control Inner 4	Polynomial (order 3)	0.9996	Linear	1
Control Inner 5	Polynomial (order 3)	0.9998	Linear	1
Control Inner 6	Polynomial (order 3)	0.9987	Linear	1

Table 5-21 R^2 Trendline Analysis of 6 TGA Controls and Behaviours Observed

On analysing the TGAs produced during the main experiment, the drying profile of the inner sample was the same for each inner sample tested regardless of coating type. This was the case with the exception of week 8 whereby the 2% CMC 0% NaCl coating had a different drying behaviour. During week 1 the control inner also had a different drying profile although this was the first sample tested in the TGA and so may be more of a methods issue. The drying behaviour observed reflected the rest of the inner samples but was set at a lower temperature and so may not have reached the next drying behaviour.

In terms of the outer samples, the majority of samples exhibited the same drying behaviour as their fellow outer samples with the exception that in week 8 different behaviours were observed for CMC no NaCl outer and CMC and NaCl outer.

Behaviour	Parameters Extracted
Time at which Constant Rate Starts	Subtracted from TGA data by R^2 function
Time at which Constant Rate ends	Subtracted from TGA data by R^2 function
Time at which Falling Rate Begins	Subtracted from TGA data by R^2 function

Table 5-22 Important Behaviours and Parameters Extracted From TGA Data For Insertion Into PCA

Table 5-22 observes the variables extracted from the TGA data for insertion into the PCA analysis. For each variable extracted, they were entered into the PCA separately as inner and outer samples.

5.5.3.5 Acoustic Data

The acoustic data test parameters are found in section 2.2.4.2. The chemical oscillator theory is once again supported by the acoustic data. During weeks 6-8 the samples containing 2% CMC and 0% NaCl produced the most acoustic events. Initially this was surprising as the NaCl was expected to interact with the microwave field and promote electromagnetic heating. However, as NaCl is believed to migrate to the centre of the product before returning to the surface and migrating to the centre again until equilibrium is reached, by week 6-8 NaCl is having an impact on the end product. NaCl is clearly present within the inner sample as opposed to just the surface layer. It is hypothesised that the presence of NaCl is depressing the melting point of ice. As ice is not free to interact with the microwave field, by depressing the melting point this allows for a higher ratio of water to become free as NaCl enters the centre of the product. From observing the TGA data which heated samples to a maximum temperature of 100^{o}C (a temperature which the microwave itself will struggle to surpass) samples never reached a horizontal plateau and between weeks 3-8 the inner part of the sample never reached the falling rate period regardless of coating type. The one exception was the 2% CMC 0% NaCl coating during week 8. The outer layer did reach a falling rate for all samples which is not surprising due to the much lower moisture content at the dehydrated fried surface. This indicates that at the microwave heating time and temperature the inner samples are saturated with moisture thus allowing soggy textures to remain instead of crisp outer textures. As moisture will be driven to the surface during microwave heating this will also have an impact on the outer layer and so will prevent the falling rate from being observed. As the sample containing 2% CMC and 0% NaCl did reach a falling rate during week 8 for the inner part this suggests that the presence of CMC may be able to promote a faster drying rate by week 8 which is of interest for the development of crisp textures. This agrees with the popcorn experiment discussed in section 5.1.7 whereby bound water was observed to become free at 160-170 ^{o}C. Due to the ability of the NaCl to migrate with the water and depress the melting point of

ice this causes the system to be ‘flooded’ with water that is not effectively evaporated within the parameters of the microwaving process. Water becoming free gradually to interact with the microwave field is preferable compared to mass release of liquid water.

Table 5-23 provides the acoustic data. In terms of desirable acoustic profiles, the investigator observed that lower intensity acoustic signals with multiple acoustic events produced the most desirable products . However, further work is required in this area to understand if the relationship between the intensity of the acoustic events and the number of acoustic events could predict products with desirable crisp textures. During the first three weeks, control products produced the most acoustically noisy products with the highest consistency with the exception of the 2% CMC 0% NaCl product during week 1. However, from week 5 onwards, the coated samples also started contributing to the acoustic events observed. This again could be due to time being required to allow moisture migration processes to occur such as transportation of dissolved NaCl ions, transportation of water due to presence of CMC and formation of ice crystals in control samples amongst other factors.

Week Number	Sample Name	Number of Acoustic Events	% Contribution to Total	Max Acoustic Signal (dB(SPL))
1	Control 1	5	71.4	67
	Control 2	0	0	0
	Control 3	2	28.6	34
	2% CMC 0% NaCl 1	51	53.7	80
	2% CMC 0% NaCl 2	12	12.6	70
	2% CMC 0% NaCl 3	32	33.7	70
	2% CMC 4% NaCl 1	0	0	0
	2% CMC 4% NaCl 2	0	0	0
	2% CMC 4% NaCl 3	0	0	0
2	Control 1	17	46	67
	Control 2	10	27	74
	Control 3	10	27	81
	2% CMC 0% NaCl 1	0	0	48
	2% CMC 0% NaCl 2	3	100	66
	2% CMC 0% NaCl 3	0	0	0
	2% CMC 4% NaCl 1	0	0	0
	2% CMC 4% NaCl 2	0	0	0
	2% CMC 4% NaCl 3	12	100	58
3	Control 1	30	36.6	72
	Control 2	0	0	0
	Control 3	52	63.4	83

	2% CMC 0% NaCl 1	0	0	0
	2% CMC 0% NaCl 2	8	42.1	59
	2% CMC 0% NaCl 3	11	57.9	56
	2% CMC 4% NaCl 1	9	25.7	64
	2% CMC 4% NaCl 2	15	42.9	58
	2% CMC 4% NaCl 3	11	31.4	54
5	Control 1	8	42.1	61
	Control 2	7	36.8	59
	Control 3	4	21.1	53
	2% CMC 0% NaCl 1	10	62.5	56
	2% CMC 0% NaCl 2	4	25	53
	2% CMC 0% NaCl 3	2	12.5	53
	2% CMC 4% NaCl 1	5	29.4	55
	2% CMC 4% NaCl 2	6	35.3	57
	2% CMC 4% NaCl 3	6	35.3	58
6	Control 1	16	50	62
	Control 2	5	15.6	59
	Control 3	11	34.4	58
	2% CMC 0% NaCl 1	36	69.2	68
	2% CMC 0% NaCl 2	12	23.1	67
	2% CMC 0% NaCl 3	4	7.7	53
	2% CMC 4% NaCl 1	0	0	0

	2% CMC 4% NaCl 2	0	0	0
	2% CMC 4% NaCl 3	0	0	0
7	Control 1	12	57.1	62
	Control 2	6	28.6	57
	Control 3	3	14.3	53
	2% CMC 0% NaCl 1	11	34.4	64
	2% CMC 0% NaCl 2	6	18.8	55
	2% CMC 0% NaCl 3	15	46.8	62
	2% CMC 4% NaCl 1	8	72.7	54
	2% CMC 4% NaCl 2	3	27.3	53
	2% CMC 4% NaCl 3	0	0	0
8	Control 1	8	57.1	56
	Control 2	2	14.3	53
	Control 3	4	28.6	54
	2% CMC 0% NaCl 1	7	77.8	61
	2% CMC 0% NaCl 2	2	22.2	54
	2% CMC 0% NaCl 3	0	0	0
	2% CMC 4% NaCl 1	11	52.4	57
	2% CMC 4% NaCl 2	4	19	53
	2% CMC 4% NaCl 3	6	28.6	54

Table 5-23 Number of Acoustic Events Observed Per 3 Chips as a Function of Coating Type and Week Number

5.5.3.6 Mechanical Data

5.5.3.6.1 Week 1

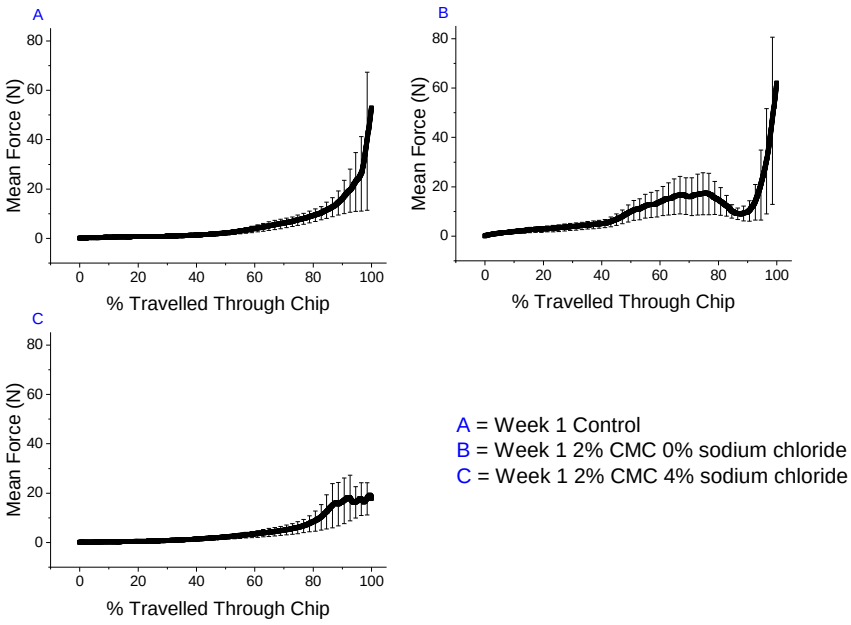


Figure 5-41 Force Curves For Week 1

The mechanical data test parameters are found in section 2.2.4.2. During week one the investigator noted differences between the microstructure of the same sample (Figure 5-41). For some control chips the centre was moist and 'fluffy' whilst other control chips had developed a honeycomb structure. 2% CMC and 0% NaCl samples had a crisp outer and soft inner whilst the 2% CMC 4% NaCl samples presented with some samples where the inner had started to separate from the outer sample or were soft. Soft chips with NaCl present produced a hissing noise on application of the probe which was not recorded by the acoustic envelope detector (AED). Samples containing 2% CMC and 0% NaCl produced the most acoustic events.

By week 2, some control chips were soft in nature whilst other control chips presented with a dehydrated core which was turning hollow. For the soft control chips the probe compressed as opposed to piercing the product. For 2% CMC 0% NaCl samples softer chips were recorded than those observed in the controls. These chips also felt wetter than the control chips which was also noted by the moisture measurements in section 5.5.3.2. On analysis of the potato core the mash was intact and moist. For 2% CMC 4% NaCl, most of the products were soft and again produced a hissing sound which was not picked up by the AED. However, a large variation was found for one sample with multiple acoustic events observed. On analysis of the potato microstructure, in two distinct behaviour were observed with a crispy outer region giving way to a moist interior. As

the number of acoustic events was high (12) but the max acoustic signal was low compared to other samples (58 (dBSPL)), this promotes the argument that a series of acoustic events with smaller max acoustic signals are more desirable than one large acoustic signal in terms of product crispness.

5.5.3.6.2 Week 3

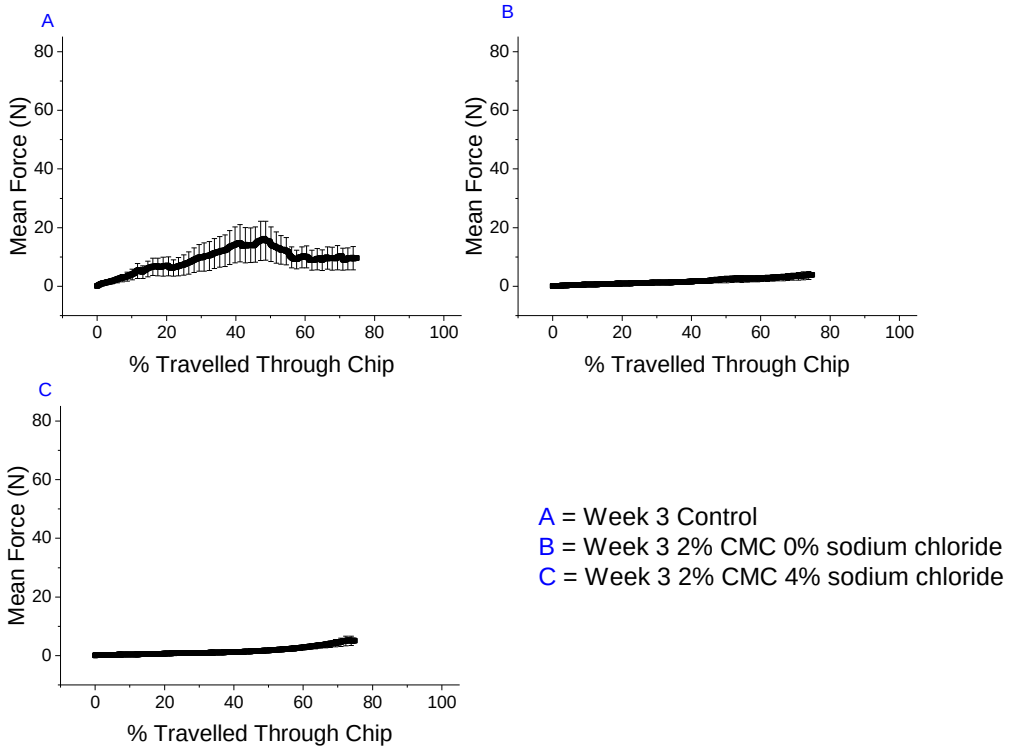


Figure 5-42 Force Curves For Week 3

By week 3 the two coatings containing CMC resulted in more homogenous samples with the control samples observing more extreme behaviours (Figure 5-42). Some control samples had developed a burnt taste and were browner in colour. Some control chips were soft and in these cases the probe compressed as opposed to pierced the product. This suggests that the outer layer is not crisp and behaves like the inner core as it is unable to withstand any deformation. During this time the development of ice crystals was observed on storage for control samples although ice crystals were not present on samples containing CMC. For 2% CMC 0% NaCl the products were softer than the previous week with only the corners beginning to crispen. In some cases the outer was crisper than the inner and in some cases the outer felt dry as opposed to crisp The 2% CMC 4% NaCl samples were more uniform in texture with similar numbers of acoustic events being recorded. On analysing the inner core, the mash was wetter and the probe mostly compressed as opposed to pierced the product. This indicates a homogenous product with little resistance. These

observations were supported by the recon loss and moisture measurements presented in section 5.5.3.2.

5.5.3.6.3 Week 5

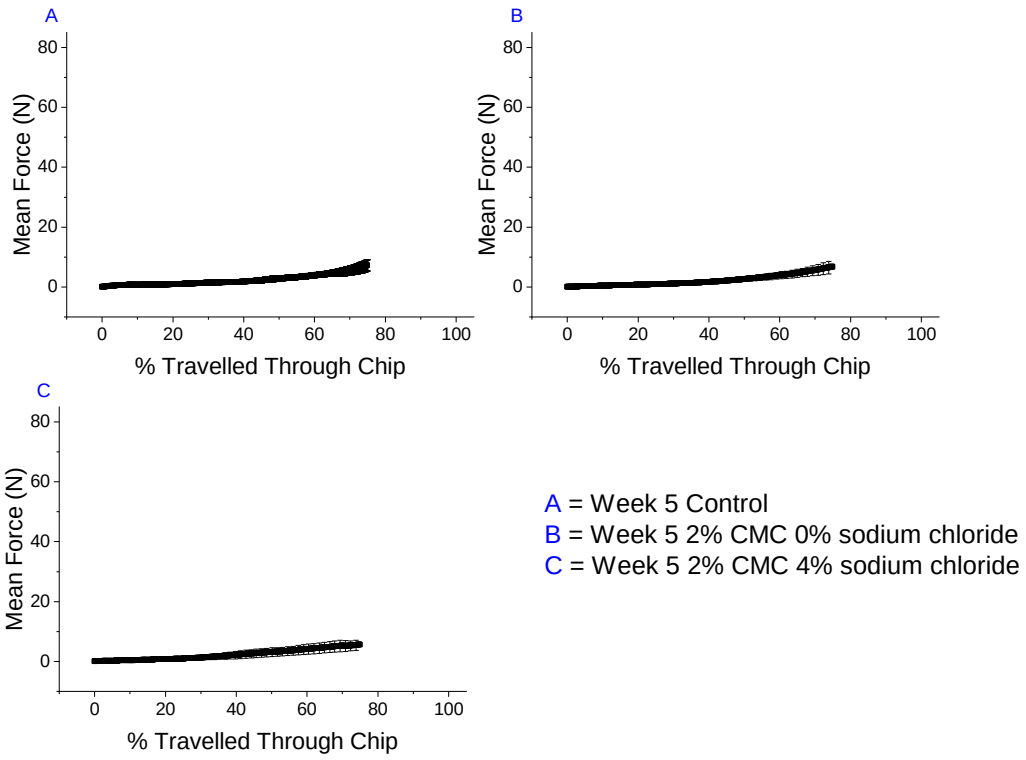


Figure 5-43 Force Curves For Week 5

By week 5 all samples were more homogenous (Figure 5-43). The control chips had developed a darker colour on storage and ice crystals were present. On analysing the internal structure, a crumbling texture was observed with acoustic events being observed mainly towards the end of the testing window. The recon loss and moisture content were lower this week than during week 3 (2-3%) which could help explain the textures observed. The 2% CMC 0% NaCl samples and 2% CMC 4% NaCl samples during week 5 produced the most desirable textures of those observed. In both cases a series of small acoustic events occurred with a lower max acoustic signal of 53-58 dB (SPL) observed once again supporting the argument for multiple smaller intensity acoustic events rather than large singular acoustic events in the development of crisp textures. Interestingly, during week 5 the samples containing NaCl swelled with the outer being crisp and the inner feeling wetter. This supports the theory highlighted in section 5.5.3.2 of the chemical oscillator as water is clearly migrating within the product to cause this phenomena to be observed.

5.5.3.6.4 Week 6

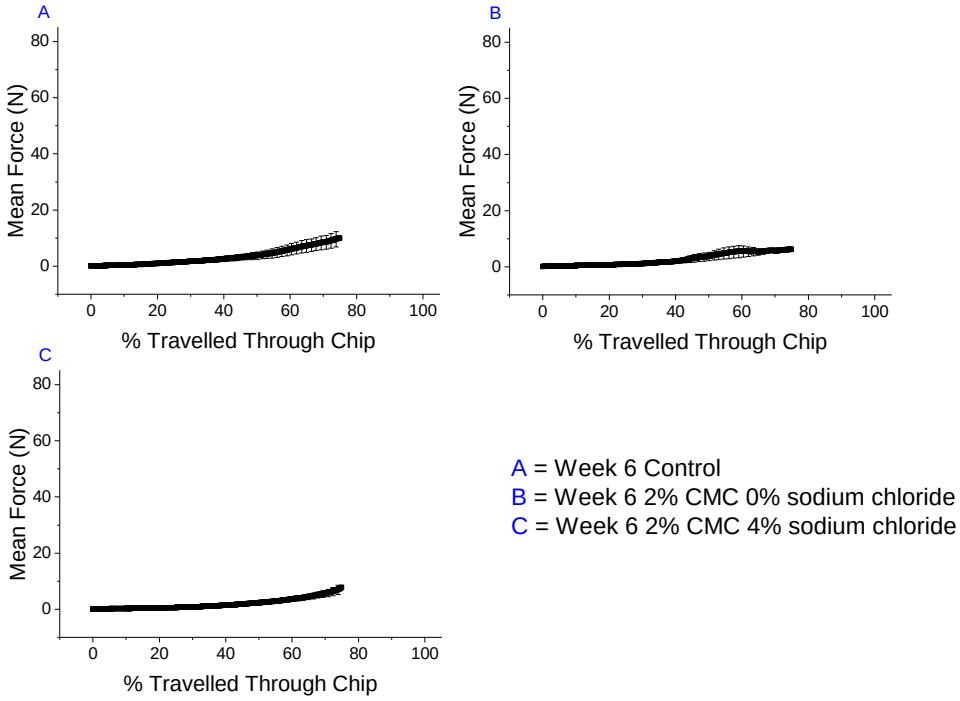


Figure 5-44 Force Curves for Week 6

During week 6 the control samples were less homogenous than week 5 (Figure 5-44). Some chips presented with crisp outers whilst others were dry as opposed to crisp. The development of ice crystals was once again observed. The samples containing 2% CMC and 0% NaCl had a differentiated coating with a texture akin to a light tempura batter. There was a slight difference observed between chips with some chips softer than others. However, the chips produced were dry on the outside and moist in the centre. The 2% CMC 4% NaCl samples were no longer swollen and produced chips where the inner core was completely intact with a wet mash present. The chips produced this week were wetter than the other coated samples this week and the chips were not crisp.

By week 7 the control samples depicted three different behaviours where some chips had a crisp outer and intact mash inner. However, the majority of control samples were dry with the inner mash presenting with a crumbling texture indicating that the product has become dehydrated. The control sample continued to present with ice crystals indicating moisture migration out of the product. The 2% CMC 0% NaCl samples once again presented with a tempura like batter outer structure. However, the samples in week 7 were less crisp than those observed in week 6. For the majority of samples tested the probe pierced as opposed to compressed although on one occasion slight compression was observed before the sample was pierced. The 2% CMC 4% NaCl samples were soft with crisp corners. They also felt a lot wetter than the other samples once again agreeing

with the chemical oscillator theory whereby the sodium chloride has travelled to the centre of the product and depressed the melting point of ice thus causing more water to be free. Small ice crystals were also observed on the 2% CMC 4% NaCl samples possibly due to the excess of free water. However, the ice crystals observed in these samples were smaller in size and less numerous than those observed on the control samples.

5.5.3.6.5 Week 8

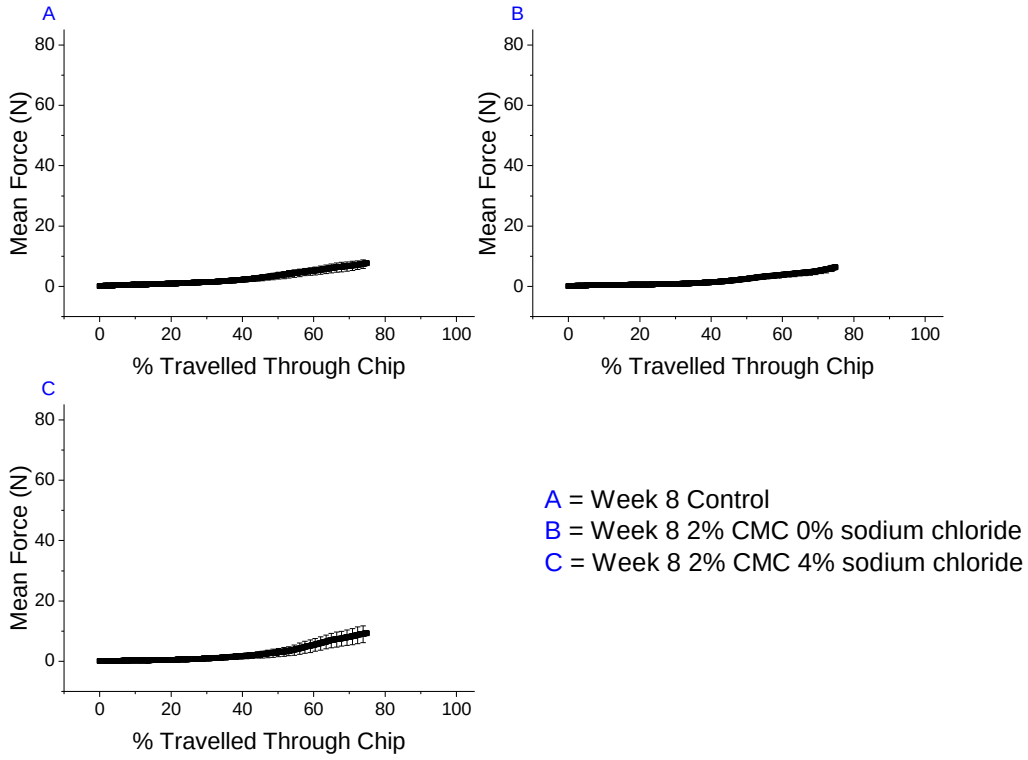


Figure 5-45 Force Curves for Week 8

By week 8 the control samples had developed a chewy texture via further dehydration on storage (Figure 5-45). Large ice crystals were also observed on the control samples. In most cases the mash was coming away from the outer layer of the chips. On application of the probe the samples were compressed as opposed to pierced indicating that the outer layer and inner layer are similar and therefore both share a chewy texture. The 2% CMC 0% NaCl coatings resulted in products that were either soft, greasy or were not pierced by the probe on application of force. The product constantly changes over the 8 week period as previously these samples produced the most desirable results. The 2% CMC and 4% NaCl samples provided structures that were either soft or had developed a laminar structure in the centre. In all cases the product was dry but the mash had begun to separate from the outer layer. Ice crystals were also observed for the two CMC based coatings.

The control product had water bound into its matrix and ice crystals present on the surface resulted in the product feeling wetter. over the course of 8 weeks. The 2% CMC 4% NaCl sample resulted in a product that over time depressed the melting point of ice resulting in a higher ratio of free:bound water. This resulted in a product that over time became softer in nature before beginning to dehydrate during week 8. The 2% CMC 0% NaCl sample produced the most desirable product with optimum crispness observed in weeks 4-6 with weeks 2-3 resulting in softer chips as water migrated towards the CMC and weeks 7-8 resulting in products that were once again softer. This could be due to the formation of ice crystals during these weeks that were not present during previous weeks. On heating in the microwave these samples would melt at the surface and so may not have evaporated sufficiently to allow a crisp texture to develop.

5.5.3.6.6 Statistical Difference of Mechanical Data and Acoustic Data

Three areas were observed;

1) Are the mechanical properties of each coating type different to each other?
2) Do the mechanical properties of each coating type differ within each coating type group as a function of time?
3) Do the coatings differ to each other as a function of time?

To answer these questions the area under the force displacement curve of each sample was observed. This is because the behaviour of the whole microstructure on application of the probe is important and taking the area gives one value as opposed to thousands of data points which can then be easily compared as a function of coating type and week number. A two way ANOVA with replication was performed to answer question 2. The null hypotheses were as follows;

1) The mean area under the force displacement curve of each coating type are the same
2) The mean area under the force displacement curve are the same each week
3) There is no interaction between the coating type and week number

The p values for coating type and week number were 0.113 and 0.348 respectively. As such the null hypothesis could not be rejected indicating that the samples were the same mechanically every week not considering coating type and that the area under the force displacement curve was the same for each coating type not considering time. The p value for the interaction between coating type and week number was <0.05 indicating that there is an interaction between coating type and week number. This indicates that the coating type and week number are statistically significant only when in combination. This shows that there is no significant difference between each coating within a single week and one coating over a period of 8 weeks. If all coatings are considered over an 8 week period a statistically significant difference is observed. Therefore this suggests that coated samples do differ as a function of week number and vice versa.

The mechanical data suggests that there is no statistically significant difference between control and coated samples within the same week. However, this analysis was only performed on one factor extracted from the mechanical data set and so may not explain exactly what is occurring within the whole mechanical data set. Due to probe speed increases that important mechanical data has been lost thus affecting the results observed. This is of interest as during the first 8 week study a significant difference (<0.05) was reported between the control and pre 2% CMC 4% NaCl sample at the slower probe speed. An interaction was also observed at the slower probe speed of <0.05. Whilst mechanical data will be inputted into the PCA to explain the variance, it is unknown how representative this data is of the samples tested. To determine if altering the test speed is the correct course of action a two way ANOVA with replication was also performed on the number of acoustic events. The test speed was increased due to concerns that the test speed was too slow to cause acoustic events to occur. The null hypotheses for this set of tests were;

1) The mean number of acoustic events for each coating type is the same
2) The mean number of acoustic events is the same for each week
3) There is no interaction between the coating type and the week number

On performing the ANOVA the p values for hypotheses 1,2, and 3 were <0.01, <0.01 and <0.01 respectively. This means the null hypothesis can be rejected and it stated that each coating type is different to each other both within the same week and that the number of acoustic events also differs dependent on the week number. There is also an interaction between the coating type and week number. This is important as it highlights that the test speed is too slow for meaningful data from the mechanical data to be generated and that important measurements are being missed. At these test speeds the mechanical data is not telling us anything about the crispness of the data but the acoustic data is.

5.5.3.7 Dielectric Data Observations

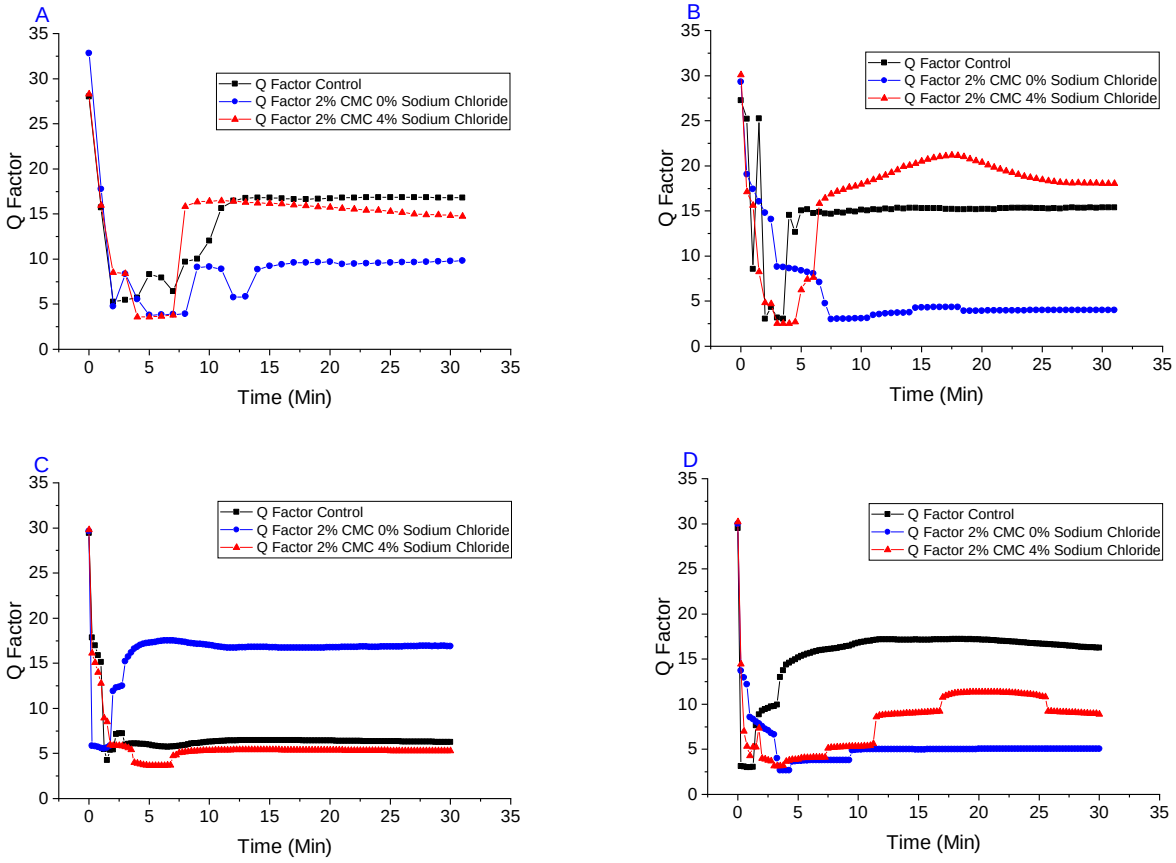


Figure 5-46 Q Factor for A= Week 1, B= Week 3, C= Week 5, D= Week 8 Measured Using Novel Cavity

The materials and methods for investigating the dielectric properties are outlined in section 2.2.4.6. Whilst the dielectric data produced can give a qualitative understanding of how effective a material is able to heat itself within the microwave environment, further work is required to convert the Q factor into the dielectric constant and loss. Further work would also be required to understand if the resultant differences in constant and loss would translate to a real world difference. Care must be taken when interpreting the dielectric results as they were gained using a conventional oven. As discussed in section 1.4.5.1, conventional heating occurs via surface heating and subsequent mass transfer compared to volumetric heating within the microwave and interaction with polar and ionic compound interspersed throughout the sample. It is also expected that because the samples were placed within a pre-heated oven, the rate at which the alterations in the Q factor occurred would be quicker than when microwaving initially. However, as microwaving is associated with higher heating rates than conventional heating it may be that the rate at which these differences occur is similar although further testing is required to determine the difference in rate between the two methods.

Figure 5-46 shows the Q factor for all sample conditions from week 1 to week 8. During week 1 the 2% CMC 0% NaCl sample showed the largest initial Q factor drop on addition of the oven with a drop of 28 recorded whilst for the control and 2% CMC 4% NaCl samples the reduction was 23 and 20 respectively. This agrees with the acoustic data where during week 1 the highest number of acoustic events was recorded by the 2% CMC 0% NaCl followed by the control samples. The samples containing NaCl resulted in no sound peaks being recorded. The dielectric data also agrees with the mechanical data generated. This could be because CMC is a polyelectrolyte. Polyelectrolytes only become active in the presence of water and it may be that not enough moisture is available to cause CMC and NaCl to become dissociated in the same coating hence the higher dielectric activity of the 2% CMC 0% NaCl. During week 2 the sample containing NaCl maintained the lowest Q factor of 5 by the end of the test compared to the control sample and 2% CMC 0% NaCl. This is important as it indicates that it takes 2 weeks before the moisture migrates to the surface of the chip (when CMC is present) in adequate amounts to cause dissociation of the NaCl as well as the CMC and their resultant interaction with the electromagnetic field. This somewhat agrees with the mechanical and acoustic data in that some of the samples containing NaCl are producing acoustic events and are crisp whilst some remain softer in nature. This could be due to uneven coating distribution or could be that in some chips with lower starting moistures it takes longer for a high enough quantity of moisture to cause dissociation. Further work would be required to determine if this is the case although it suggests that chips from the pith section of the potato contain higher moisture to solid ratios. By week 3 the samples containing NaCl have the least dielectric activity. This is interesting as it suggests that the NaCl has concentrated heating of the sample surface causing evaporation and thus deactivation of the NaCl ions. The samples with the highest dielectric activity were the 2% CMC 0% NaCl samples. The 2% CMC 0% NaCl coating also performed better than the control sample. However, this was not reflected in the acoustic and mechanical data with the control samples producing ‘crisper’ products. This could be due to dehydration of the control sample on storage which would result in drier products and subsequently cause the sample to become less dielectrically active through the loss of moisture. The reason the 2% CMC 0% NaCl coating may not have performed as well acoustically, could be due to CMC holding onto the moisture or not enough moisture being present to cause dissociation of CMC and resultant surface heating. By week 5 the dielectric activity of the samples has altered again with the sample containing NaCl performing best dielectrically. This agrees with the chemical oscillator theory highlighted in section 5.5.3.2. It appears as though water has diffused to the surface of the sample, caused ions to dissociate and due to the high NaCl concentration at the surface has caused water to migrate into the centre of the product carrying NaCl ions. These ions have depressed the melting point of ice, resulting in more free water being available to interact with the microwave field and enabling the NaCl to remain active for longer. However, in terms of mechanical and acoustic measurements all

three samples performed in a similar way with acoustic events being observed for all samples. The control sample performed similarly this week to the 2% CMC 4% NaCl samples, although this coincided with the development of more numerous ice crystals on the outer layer of the control samples which could have improved the dielectric activity of the control samples as they melted. For the remainder of the dielectric tests the 2% CMC 4% NaCl continued to alter from having the highest dielectric activity to the lowest dielectric activity. This was associated with the ions becoming inactive and dissociating dependent on the migration of water. Whilst for the control and 2% CMC 0% NaCl samples the Q factor remained fairly smooth, the samples containing NaCl typically had many peaks and troughs across the testing window. Currently it is unknown exactly what mechanisms these peaks and trough depict. However, it is believed to be associated with water migration and subsequent interaction with NaCl. It could be that the CMC and NaCl are competing for the moisture resulting in frequent dissociation and inactivation of each material. By the end of the study, the samples containing 2% CMC 0% NaCl had the highest dielectric activity possibly due to the hygroscopic nature of CMC which retards the production of ice crystals and holds onto moisture and the fact that CMC is a polyelectrolyte. In the case of the control samples they became increasingly more dehydrated on storage resulting in lower dielectric activity interspersed with higher periods of activity possibly due to the presence of fragile ice crystals. Further work is required to understand the mechanisms occurring within these three distinct systems. However, what is clear is that rapid reversals in the sample physiology are occurring in terms of days and weeks within at least the first 8 weeks of storage.

One important note is that it would have been expected that the Q factor would slowly rise as the moisture evaporated as opposed to reaching a horizontal plateau. This occurred due to the presence of a lid on the cavity which caused water vapour to be created allowing it to contribute to the dielectric activity observed and thus prevent a gradual rise in Q factor. The dielectric data needed to be parameterised for insertion into the PCA. Table 5-24 shows the variables extracted.

Behaviour	**Parameters Extracted**
Lowest Q Factor Observed	Minimum Q Factor
Highest Insertion Loss Observed	Maximum Insertion Loss
Time when lowest Q Factor Observed	Time at lowest Q Factor (min)
Time when max Insertion Loss Observed	Time at max Insertion Loss (min)
End of Test Q Factor	Last Q Factor Data Input
End of Test Insertion Loss	Last Insertion Loss Data Input

Table 5-24 Dielectric Behaviours and Parameters Extracted For Insertion Into PCA

5.5.3.8 Principle Component Analysis

All of the variables were inserted into the PCA. However, it was necessary to abbreviate the variables due to their length. Table 5-25 provides the original variable as well as its coded name. As discussed previously parameters extracted from the ice melting peaks from the DSC were discarded as only 3 incidences were observed across the whole experiment and more data is required for the result to be meaningful. In total 41 variables were inserted into the second 8 week study.

Variable Number	Variable	Coded Name
1	Area Under Force Displacement Curve	AFD
2	Number of Positive Peaks	NPP
3	Number of Negative Troughs	NNT
4	Max Force	MF
5	Average Gradient	AG
6	Average Drop Off	ADO
7	Linear Distance	LD
8	Force at Failure	FF
9	% Travelled Through the Chip at First Failure	%TC
10	Change in Force at Failure	CFF
11	Gradient to Force at Failure	GFF
12	Chip Width	CW
13	Chip Top Length	CTL
14	Chip Bottom Length	CBL
15	Number of Second Derivative Troughs	2ndD
16	Number of Acoustic Events	NAE
17	Max Acoustic Signal	MAS
18	Recon Loss	RL
19	Time at which Constant Rate Starts Inner	TGA CRSI

20	Time at which Constant Rate Starts Outer	TGA CRSO
21	Time at which Constant Rate Ends Inner	TGA CREI
22	Time at which Constant Rate Ends Outer	TGA CREO
23	Time at which Falling Rate Starts Inner	TGA FRI
24	Time at which Falling Rate Starts Outer	TGA FRO
25	Internal Moisture Content	IMC
26	Outer Moisture Content	OMC
27	Area Under the Peak During Bound Water Release/Unknown Mechanism Inner	DSC AI
28	Area Under the Peak During Bound Water Release/Unknown Mechanism Outer	DSC AO
29	Onset Temperature During Bound Water Release/Unknown Mechanism Inner (Peak 2)	DSC OP2I
30	Onset Temperature During Bound Water Release/Unknown Mechanism Outer (Peak 2)	DSC OP2O
31	End Temperature During Bound Water Release/Unknown Mechanism Inner (Peak 2)	DSC EP2I
32	End Temperature During Bound Water Release/Unknown Mechanism Outer (Peak 2)	DSC EP2O
33	Temperature at which Heat Flow is Maximum at Bound Water Release/Unknown Mechanism Inner (Peak 2)	DSC MHFI
34	Temperature at which Heat Flow is Maximum at Bound Water Release/Unknown Mechanism Outer (Peak 2)	DSC MHFO
35	Minimum Q Factor	MQ
36	Highest Insertion Loss	HIL
37	Time when lowest Q Factor Observed	TMQ
38	Time when highest Insertion Loss Observed	TLO

39	Q Factor at End of Test	QET
40	Insertion Loss at End of Test	IET
41	Maximum Second Derivative Negative Value	M2ndD

Table 5-25 Variables Considered for PCA and their Code Name

As the number of second derivative troughs did not correlate with any mechanical parameter there was a concern that this was due to the probe speed. Therefore because acoustic events were also not recorded the probe speed in this case was increased. For this PCA it was also decided to include the variable M2ndD. This is defined as the maximum value of the second derivative trough recorded. In the previous PCA weeks 1-2, 3-4, 5-6 and 7-8 were observed separately. Due to the large number of variables this is not possible as the number of variables exceeds the total number of observations. Therefore the whole 8 weeks shall be observed first alongside the CV table and Pearson's correlation coefficient. By doing so, the number of variables can be reduced by determining which variables are redundant and explain one another. After this reduction a PCA shall be performed observing weeks 1-2, 3-6 and 7-8.

5.3.3.8.1 CV and Pearson's Correlation Coefficient

Due to space restrictions within this thesis, the Pearson Correlation Coefficient table shall not be depicted. A Pearson's correlation table was produced to a 95% confidence limit for weeks 1-2, 3-6 and 7-8. An example of this table is found in Table 5-13 which was used during the first 8 week study PCA. The Pearson's correlation tables for this study shall be used alongside the CV and preliminary loading plot of the PCA to determine redundant variables as a method of pre-screening prior to the main PCA being conducted. One of the main reasons for a pre-screening is to reduce the number of variables. This is because currently there are 41 variables but only 24 observations for the PCA's looking at weeks 1-2, 3-6 and 7-8. In order for a PCA to function the number of observations must be equal or more than the number of variables inserted into the PCA. Therefore pre-screening is being conducted to reduce the number of the variables to <24.

On performing the CV analysis some variables returned negative values due to negative means being recorded. The CV provides an understanding of the dispersion of a variable in relation to other variables. A CV is appropriate to measure dispersions across different variables with different measurement methods as the measurement is made observing the ratio of the standard deviation to the mean. Usually the coefficient of variance falls between 0 and 1. However, it can exceed 1 in cases where the standard deviation is larger than the mean. In cases where the CV is negative, this could be because the mean is negative and/or the standard deviation is close to 0.

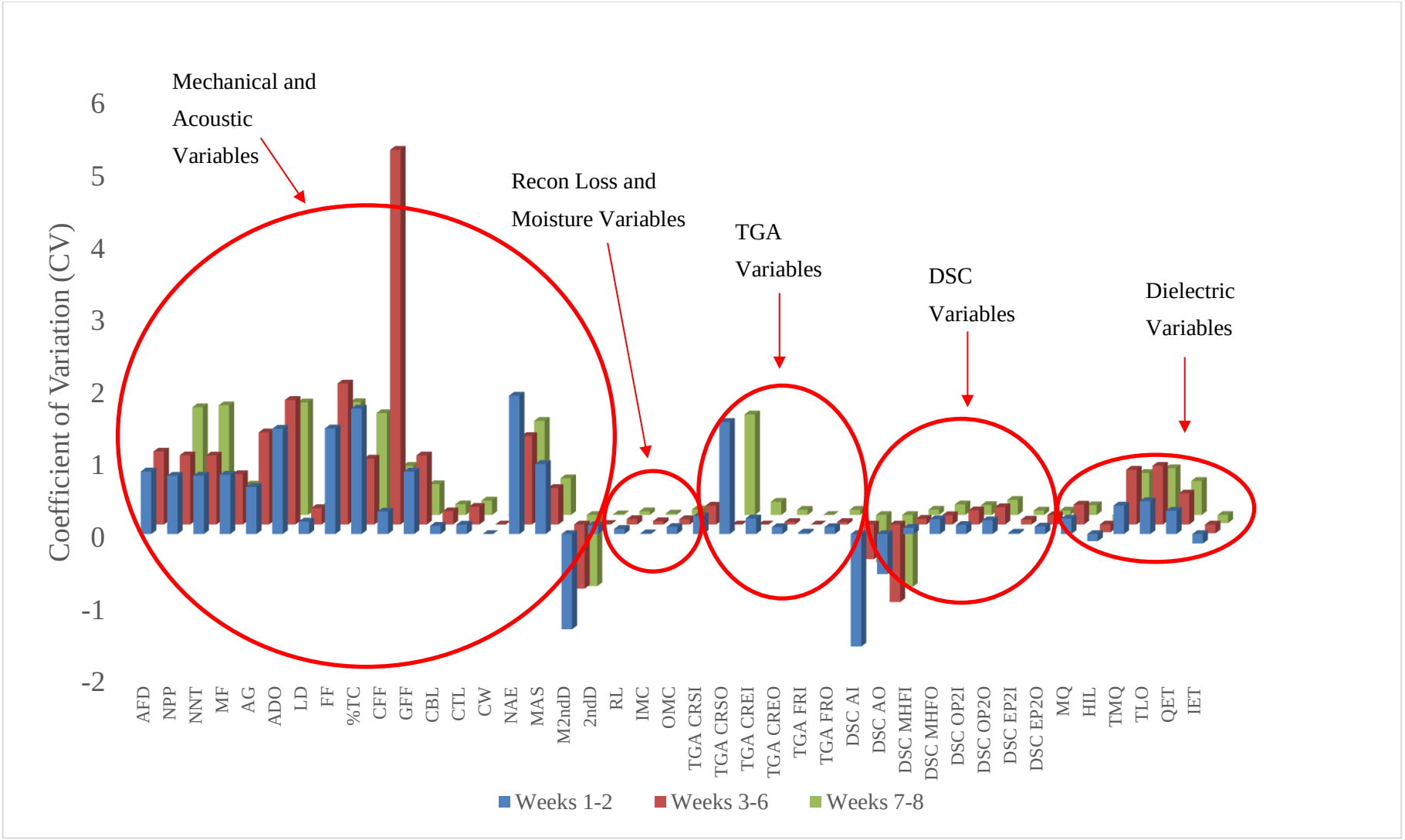


Figure 5-47 CV for Variables Inserted into 2nd 8 Week Study PCA

Figure 5-47 shows the coefficient of variation observed for the variables. The variables extracted via each measurement roughly show similar variances with a few notable exceptions e.g. the change in force at failure which is expected due to changes in the sample on storage. As discussed previously where the mean is negative the CV also appears as negative and so whilst the variance can be observed for these samples a negative value does not denote a negative variance.

On observing the Pearson's correlation coefficient a strong correlation (>±0.7) between the number of second derivatives/highest second derivative and the number of acoustic events and max acoustic signals was not observed. Usually a correlation would be expected as the second derivative of a force displacement curve is directly related to the rate of energy release as the microstructure fails and as sound is produced on the release of energy from the product a correlation would normally be expected. However, as previously discussed, the probe speed was increased and the ANOVAs performed in section 5.5.3.6.6 highlighted that whilst the mechanical area parameter failed to show significance, the number of acoustic events did. This indicates that the faster probe speed caused significant events to be lost during measurement highlighting that the mechanical data is not representative of the sample as any acoustic events that occurred are directly related to the product microstructure behaviour. The max second derivative should also directly correlate to the max acoustic signal as this is where the largest energy release occurs and so because this correlation was not observed across any week, the mechanical data shall be removed from the PCA analysis as it is not representative of the sample set.

Unfortunately during the pre-screening phase the number of variables causing variance exceeded the number of observations within each PCA e.g. weeks 1-2, 3-6 and 7-8 even with the removal of the mechanical data. Therefore two PCAs were produced instead observing weeks 1-3 and weeks 5-8. This does make it more difficult to separate out the variables explaining the largest variances each week and so this PCA is more limited than the first 8 week study. However, it will still provide an insight into the factors responsible for the variability observed at the beginning of storage compared with towards the end of storage. To reflect this change the CV graphs were replotted and although not depicted in this thesis they were considered alongside the revised Pearson's coefficient tables.

5.3.3.8.2 Main PCA

Variables were excluded using the revised CV and Pearson's correlation coefficient table alongside a PCA plot containing data from all 8 weeks (Figure 5-48). As can be observed many variables are superimposed therefore indicating that they account for a similar variance in the data set.

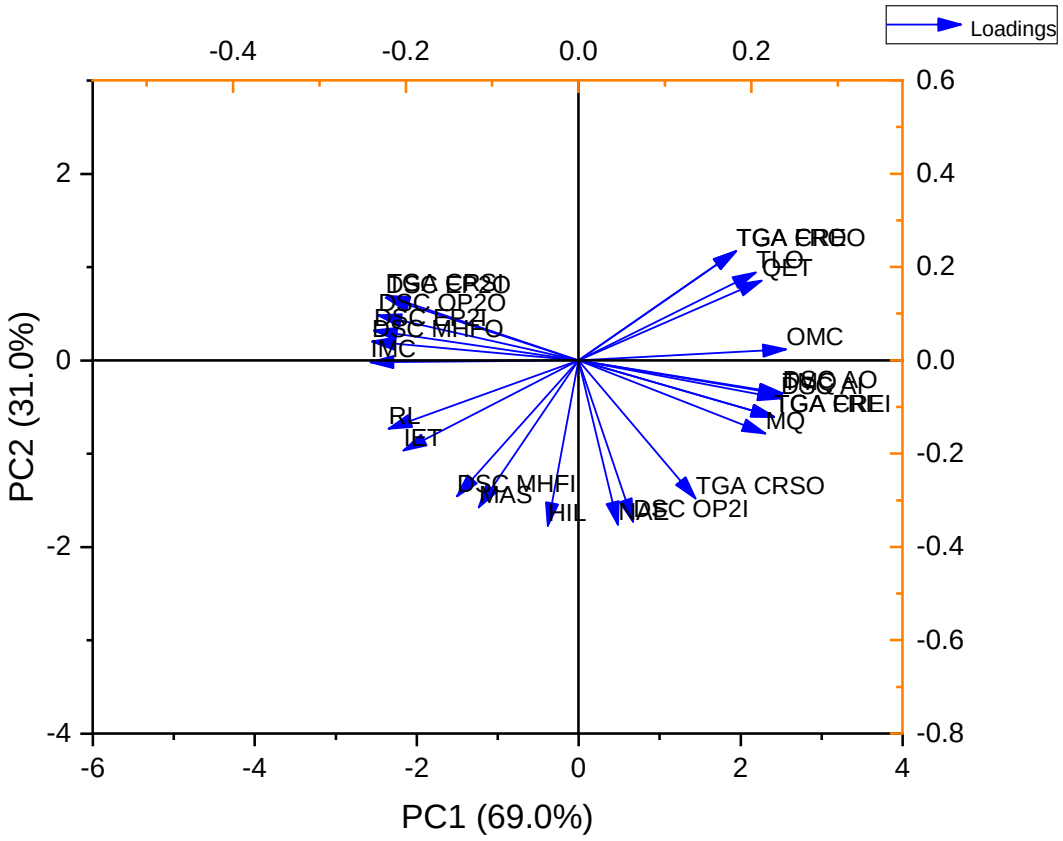


Figure 5-48 PCA for 8 week Study with Mechanical Variables Removed

Table 5-26 observes the variables selected for weeks 1-3 which explain the highest degree of variability in the data set alongside their principal components. On observing the Pearson's correlation the variables with the highest correlation was the IMC and OMC as they correlated with RL, the TGA extracted variables, the DSC extracted variables and the dielectric variables with correlations >±0.8 or higher. All TGA variables had a correlation to one another >±0.9 and therefore only one TGA variable was selected to be inserted into the PCA. This also occurred with the DSC data resulting in only one DSC variable being selected for the final PCA. Whilst the recon loss had a high correlation with the IMC and OMC (>±0.9) the recon loss was retained as it was a separate measurement. Dielectric data was also correlated but less so than the TGA and DSC data and as such three dielectric data variables have been incorporated into the final PCA. In terms of acoustic event data NAE and MAS, these variables did not correlate with any other variable and were therefore inserted into the final PCA as they explain variance in the data which cannot be explained by any other variable.

Variables inserted into weeks 1-3 PCA	
NAE	MAS
IMC	TGA CRSO
DSC AI	QET
MQ	HIL
RL	

Table 5-26 Variables Inserted Into Weeks 1-3 PCA

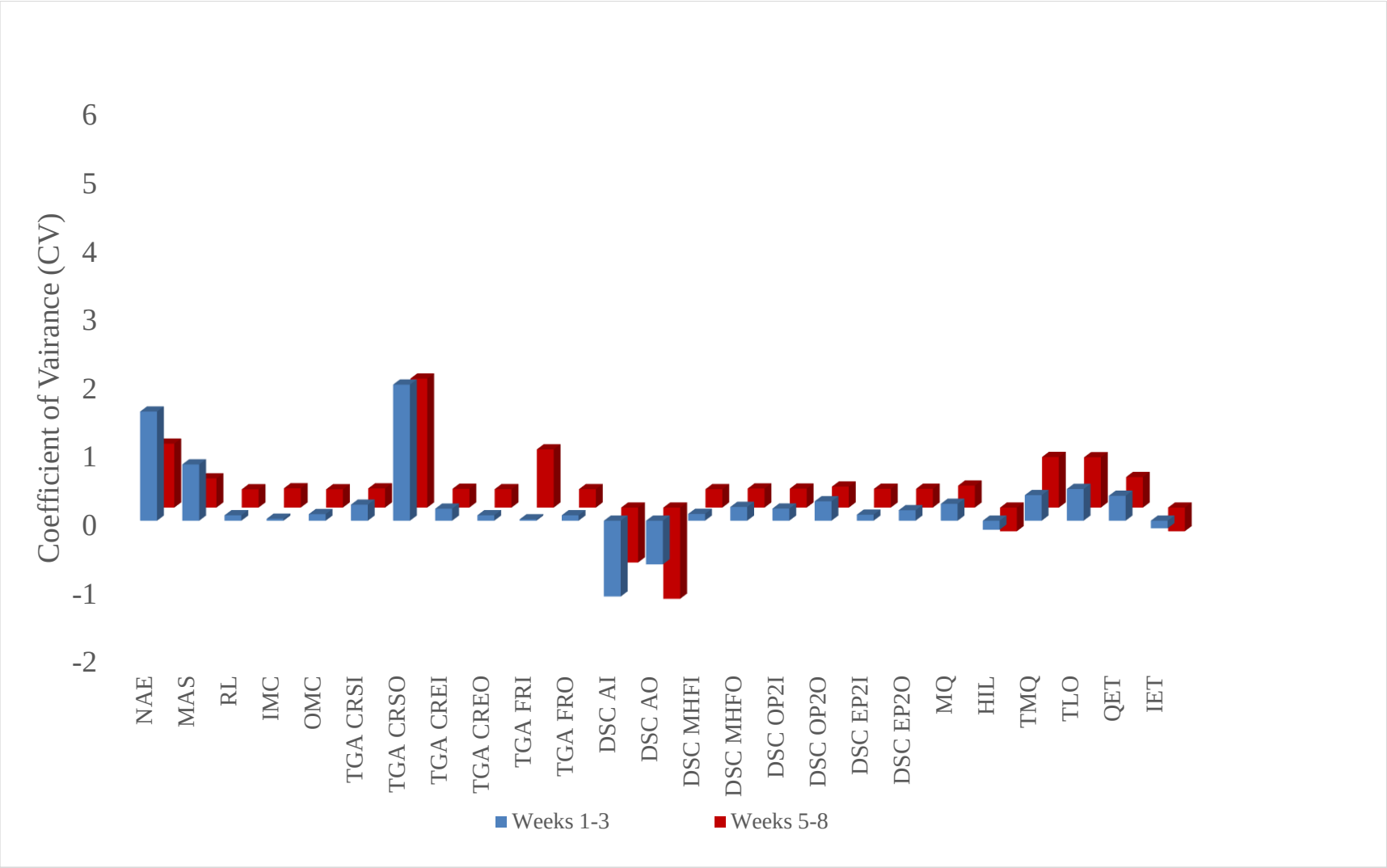


Figure 5-49 Updated Coefficient of Variation for Variables Inserted Into 2nd 8 Week Study

Week Number	PC1 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC1	PC2 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC2	PC3 Variables with explaining power (>0.3 or <-0.3)	Coefficient Value PC3	Number of Variables explaining variability
1-3	HIL	-0.46605	NAE	-0.46658	DSC AI	0.55215	9
	IMC	0.42056	MAS	-0.44716			
	QET	0.41801	HIL	-0.35022	RL	-0.52808	
	MQ	-0.41044	MQ	-0.35022			
	RL	0.34300	DSC AI	-0.33346	TGA CRSO	0.50817	
	MAS	0.33014	TGA CRSO	-0.31377			
5-8	TMQ	-0.57696	RL	-0.53731	IMC	-0.61631	8
	TLO	-0.56796			DSC AO	-0.48615	
			MAS	-0.51796	MAS	0.40149	
	QET	0.47840	TGA CRSO	-0.41133			
			DSC AO	-0.31286			

Table 5-27 Variables Explaining the Variability in The Data Set During Weeks 1-3 and Weeks 5-8

Weeks	% of the data explained PC1	% of the data explained PC2	% of the data explained PC3	Total Variability Explained (%)
1-3	33.4	24.2	17.2	74.8
5-8	29.9	23.7	22.3	75.9

Table 5-28 Amount of Variability in the Data Set Explained by Each Principal Component

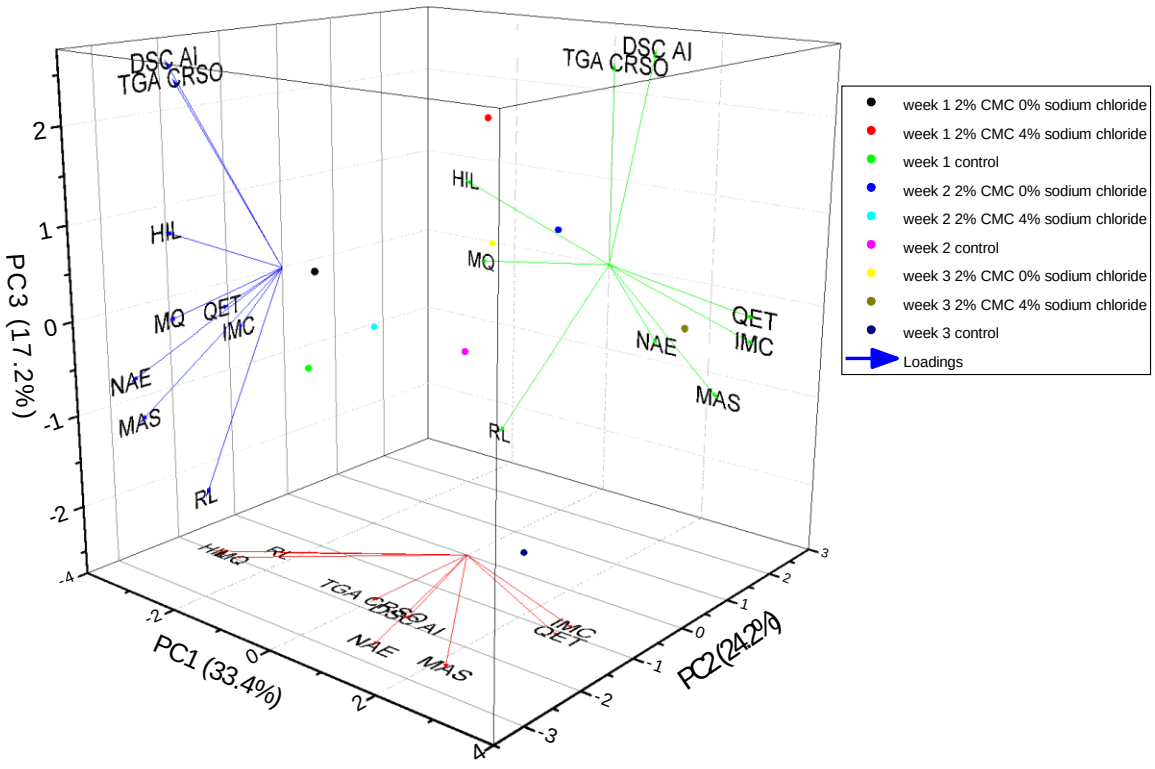


Figure 5-50 Loading and Score Plot for Weeks 1-3

Figure 5-50 shows the combined loading and score plot for weeks 1-3. Unfortunately due to time constraints in most cases only one repeat could be taken for each variable. As a result it means that cluster analysis was not possible for this PCA and so only the variability in the data set as a function of time could be observed. By performing 7 different measurement techniques, an indication of the mechanisms occurring within the 8 week storage period could be observed. However, due to the analysis of the variables individually, it has been shown that the samples also differ as a function of coating type.

Both acoustic variables were included in the PCA as they contributed to a high CV. According to Figure 5-49 the variability in terms of the CV for acoustic variables is higher during weeks 1-3 than weeks 5-8. This agrees with the observations made by (McCain, 2013) that the product alters most dramatically on storage within the first two weeks. In the weeks 1-3 PCA, PC1 accounts for 33.4%, PC2 accounts for 24.2% and PC3 accounts for 17.2%. Table 5-27 observes the coefficient values for PC1, PC2 and PC3 during weeks 1-3. A higher coefficient value indicates a higher contribution to the variation observed within that principal component. As with the previous 8 week study a threshold of >±0.3 was set. In PC1 the largest variable in the data set was the HIL (highest insertion loss) followed by the IMC (inner moisture content), QET (Q factor at end of test) and the MQ (Max Q factor). The variables accounting for the greatest variance in the data during the first three weeks are associated with the moisture content and resultant dielectric properties. This suggests that the product changes on storage due to either week number or coating type which is supported when the dielectric data and moisture readings were investigated in section 5.5.3.2 and 5.5.3.7. On observing the dielectric properties it was concluded that the different coating types had a large impact on the dielectric properties as a function of time. However, the variation could also in part be associated with the time in which the oven is able to recover its set temperature after the oven door is opened and the samples placed within it. This is because as discussed previously cooler air enters the oven on opening door thus affecting the temperature.

However, the variations are being observed within a short space of time and so is indicative of an extremely volatile sample on storage within the first 3 weeks. As weeks 1-3 had to be tested together the fact that there are no repeats (with the exception of acoustic events) is an advantage as it shows that any differences occurring are due to either the week number or coating type. The other variables contributing to PC1 were the RL (recon loss) and the MAS (max acoustic signal). As the recon loss is associated with moisture and the max acoustic signal is associated with product crispness this suggests that during the first three weeks the product crispness is altering. However, caution must be taken when analysing the acoustic data as in this instance repeats were possible. As a result any variance observed could also be due to equipment error as opposed to just differences based on week number or coating type.

In PC2 the variables explaining the variation were in order of importance NAE (number of acoustic events), MAS (max acoustic signal), HIL (Highest insertion loss) MQ (Max Q factor), DSC AI (area under peak 2 inner) and TGA CRSO (time at which constant rate starts outer). PC2 explains 24.2% of the variance in the data set with the acoustic data explaining most of the variance. Again this could either be due to measurement errors or that there are differences based on week number and/or coating type. On analysis of the acoustic data in 5.5.3.5. it is likely that the differences are due to week number and the coating type. As the acoustic data is directly

related to the microstructure of the samples and as such it can be stated that the samples are altering as a function of time and coating type within the first 3 weeks.

PC3 accounts for 17.2% of the variance in the data set. The variables with the highest explaining power were the DSC AI, RL and the TGA CRSO. As the DSC AI is associated with the area under peak 2 which is associated with an unknown mechanism and/or a combination of starch gelatinisation and bound water being released this suggests that the sample is different either as a function of week number or coating type. Differences in the recon loss are related to the amount of moisture that is evaporated on heating and as there are changes in the recon loss this also indicates that the samples are changing as a function of week number and/or coating type. Again this agrees with the chemical oscillator theory which all of the other 7 methods of measurement agree with as well.

On observing the scores within the PCA they are evenly spread across the 3 principal components. The variances observed in weeks 1 control are mainly due to the RL, for week 2 are HIL, DSC AI and TGA CRSO and for week 3 are IMC and QET. The week 3 control variation is found in the PC1/PC2 plane as opposed to the PC2/PC3 plane indicating the variation is greater for the control sample in week 3. For 2% CMC 0% sodium chloride samples, the variation is explained in week 1 by RL, for week 2 by TGA CRSO, DSC AI and HIL and for week 3 by MQ and HIL. All these samples are present in the PC1/PC3 plane with the exception of week 1 which is present in the PC2/PC3 plane therefore indicating that the sample becomes more variable after week 1. For 2% CMC 4% sodium chloride the variance is explained in week 1 by HIL, TGA CRSO and DSC AI, during week 2 by RL and during week 3 by NAE, MAS, IMC and QET.

The next PCA created observed weeks 5-8. Variables were removed in the same way as for the PCA performed on data in weeks 1-3. The variables selected for insertion into the PCA can be found in table 5-29. Whilst TGA FRI did result in a large CV this was because only two data points could be collected and as a result this variable was not included in the PCA.

Variables inserted into weeks 5-8 PCA	
NAE	MAS
IMC	TGA CRSO
RL	DSC AO
TMQ	TLO
QET	

Table 5-29 Variables Inserted Into Weeks 5-8 PCA

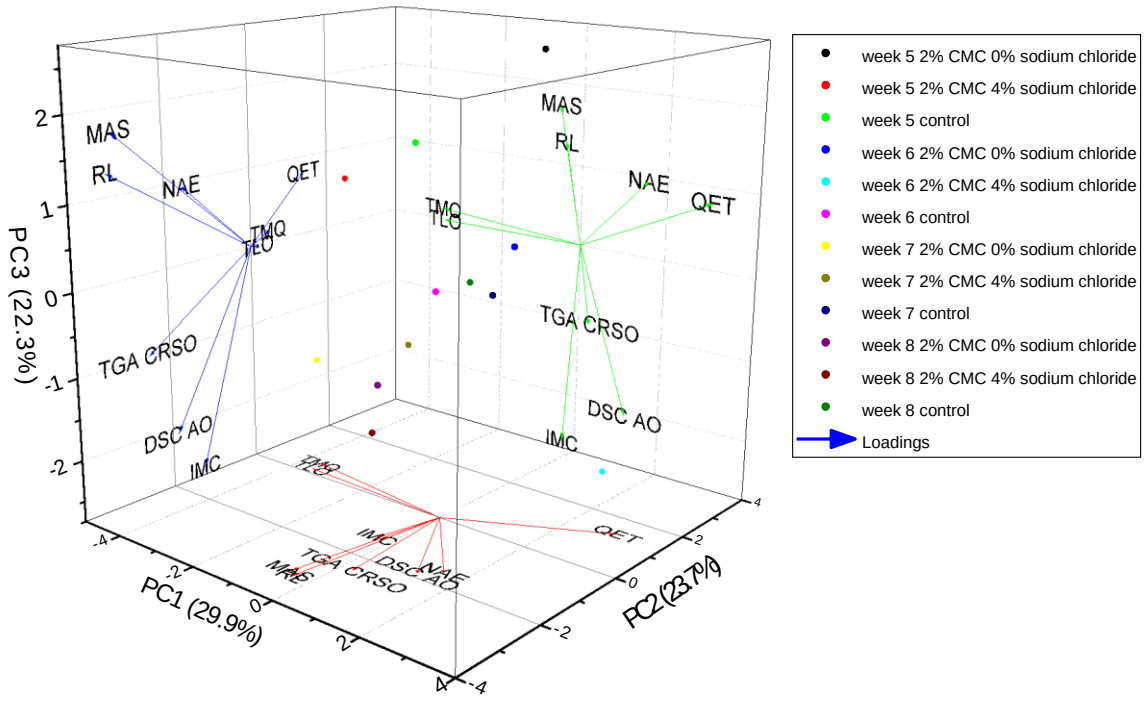


Figure 5-51 Loading and Score Plots For Weeks 5-8

Figure 5-51 shows the combined score and loading plot for weeks 5-8. From observing the CV the variation in the data caused by the acoustic data is reduced in weeks 5-8 compared to weeks 1-3. This is confirmed as the MAS is only important in PC2 and PC3 which account for 23.7% and 22.3% of the variation whilst in weeks 1-3 the acoustic data accounted for variation in PC1 and PC2. As the acoustic data is related to the microstructure of the product it confirms the observations made by (McCain, 2013) that storage has the largest impact on the product microstructure within the first two/three weeks of storage.

The variables which account for the greatest variance in PC1 were QET, TLO and TMQ. These variables are related to the dielectric properties and on analysing the dielectric samples it is not surprising that the greatest dielectric variance occurs during weeks 5-8. This is because not only do the dielectric properties of each samples change drastically each week but there are more weeks within this PCA to consider. This supports the idea that moisture is migrating and changing as there are such large variations in the data set which cannot be accounted for by the means of measurement alone. In PC2 the variables causing the variance were RL, MAS, TGA CRSO and DSC AO. The variation in PC2 is caused by a combination of the moisture, DSC, TGA and acoustic data. Again the variation in dielectric data is not surprising for the reasons highlighted above. However, the fact that the TGA data is resulting in variation is of interest as it once again

supports the chemical oscillation and water migration hypothesis as dependent on where the moisture has migrated this will impact when the sample enters and leaves the constant rate and falling rate. In the case of the DSC it suggests that the product microstructure is altering as a function of week number/ coating type. Finally PC3 is associated with the IMC, DSC AO and the MAS. PC3 is more similar to PC2 during weeks 5-8 indicating that the moisture content, acoustic data and DSC data is more variable during weeks 5-8 than weeks 1-3. This is not surprising as there are two extra weeks present within the data set and storage has already been observed to show changes in the product (section 5.5)

In terms of scores, they were found in all planes of the PCA. For control samples all scores were found in the PC1/PC3 plane. Week 5 was defined by TMQ, TLO, RL and MAS. Week 6 was defined by TLO, TMQ, IMC and TGA CRSO. Week 7 was defined by TLO, TMQ, IMC and TGA CRSO. Week 8 was defined by TLO, TMQ, IMC and TGA CRSO. For 2% CMC 0% NaCl week 5 was in the PC1/PC3 plane, week 6 was in the PC1/PC3 plane and weeks 7 and 8 were in the PC2/PC3 plane. The variables explaining the variances for week 5 were MAS and RL. For week 6 the variables were TMQ, TLO, IMC and TGA CRSO. For week 7 the variables were IMC, DSC AO, TMQ and TLO and for week 8 were IMC and QET. For 2% CMC 4% NaCl scores were present in weeks 5 in the PC2/PC3 plane, for weeks 6 and 8 in the PC1/PC2 plane and in week 7 were in the PC1/PC3 plane. The variables causing variance in week 5 and 6 were QET, TMQ and TLO. For week 7 the variables were IMC, TMQ and TLO and for week 8 were QET, TMQ and TLO. For nearly every week and coating condition the dielectric properties observed the highest degree of variance thus indicating that the coatings produced were behaving differently in terms of dielectric properties. It also suggests that storage has an impact on the end product in terms of its dielectric properties.

5.5.4 Conclusion

The main finding was that over an 8-week shelf life all 3 products produced were consistently inconsistent. Several processes were observed as being influential in the results generated;

1) Presence of bound and unbound water
2) Presence of sodium chloride
3) Presence of CMC
4) Effect of there being a lid on the dielectric cavity (Q factor stabilised instead of increasing and as water vapour has dielectric activity this means moisture could not leave the testing space)
5) Migration of moisture and the presence of a chemical oscillator
6) Development of ice crystals
7) Processing condition and coating type

8) Age of product stored

By using all 7 of the investigative techniques, it was determined how all the products tested were changing as a function of time and processing condition. These changes related to the;

1) Internal moisture of the product over time
2) External moisture of the product over time
3) Recon loss of the product over time
4) Ratio of bound: unbound water
5) Ice crystal formation
6) Q factor as a function of time
7) Insertion Loss as a function of time
8) Temperature at which constant rate started in both the inner and outer layers
9) Time at which constant rate started in both the inner and the outer layer
10) Presence or lack of presence of a falling rate
11) Location of moisture within the product
12) Number of acoustic events
13) Max acoustic signal

Chapter 6
Summary and Next Steps

6.1 Summary

At the start of this investigation the following questions were posed;

1) Can accurate data be acquired on the dielectric activity of food which will allow for it to be modelled in a microwave oven?
2) Can the storage, dielectric and physical properties of the base uncoated product be understood in order to determine requirements for a coating to promote crispness?
3) Can a coating be developed which improves the product in terms of crispness?

Whilst understanding the dielectric properties of foods is important in developing crisp textures, arguably the most important factor is moisture; the moisture content, the form it is in – free (liquid water) or bound (ice, water bound to starch, water bound to CMC), the location of moisture within the product and the impact of storage on the moisture content. This is because with decreasing free water and total water, the dielectric properties will also decrease and this was observed in the uncoated sample. However, whilst the dielectric properties did decrease on storage the uncoated sample was still crisp at week 8. This crispness was ascertained by the number of acoustic events and drying behaviour observed in the TGA. This highlights that measuring the dielectric properties of a food material alone will not predict how that food will heat within the microwave and instead it is the state of the water that is the driving factor of a materials ability to produce crisp textures on application of an electromagnetic wave.

Initially when formulating the aims for this thesis the complex role of moisture had not been fully considered. Therefore at this stage the creation of a computer model incorporating the dielectric properties of the food material would be fruitless. Further work is required to understand the impact of moisture migration and form as a function of storage before a representative computer model can be produced.

The storage investigations concluded that uncoated and coated products vary widely in terms of physical properties as a function of time. However, the incorporation of ionic material and materials that could interact directly with water did have an impact with a 2% CMC 0% NaCl coating producing the most desirable product by the end of the 8 week testing period. This supports the self-limiting theory although further work is required to understand the moisture mechanisms and transformations within the product causing this change. The end products produced were not crisp enough to promote a change in the end product recipe by the manufacturer. However, it does provide an indication of how products can be developed to promote crisp textures from the domestic microwave in the future.

The main findings of this project can be separated in terms of dielectric understanding, measurement techniques understanding, processing understanding and moisture understanding. Dielectrically it was observed that different botanical sources of starch have statistically differing dielectric properties. This was also observed when the starches were gelatinised although no significant difference in dielectric properties was observed between native and gelatinised starches of the same type. This is an important finding as the manufacturer can apply starches dependent on the dielectric properties required without fear that the frying process which causes gelatinisation will affect the end dielectric properties of the starches. However, further work is required to understand if the dielectric properties measured will translate into an observable effect in the microwave. A second determination was related to moisture in that the dielectric properties were affected by the ratio of free:bound water with naturally occurring moisture bound into the native starch matrix and added water free to interact with the microwave field. It was also observed that silica is able to immobilise water and reduce its dielectric activity.

As regards measurement techniques the biggest learning regarded the Volodkevich jaw mechanical test speed. Whilst previous researchers had succeeded in generating acoustic and mechanical data at 0.1 mm/s for this product type useable acoustic data was only generated at 1mm/s. This highlights that the probe speed needs to be set dependent on the sample being tested and that as the majority of the chip sample desires a soft texture (inner layer) this can affect measurements of thin crispy layers.

An important learning for the manufacturer was in terms of processing. Where in the process a coating was applied (pre-fryer, post fryer or post freezer) had a large impact on the mechanical, acoustic and physical properties of the product. Post fryer and post freezer coatings observed issues with coatings becoming stuck to the susceptor present in the packaging. This resulted in increased surface heating and burning on the sides of the chips attached to the susceptor. Therefore the manufacturer should apply coatings pre fryer to prevent this from occurring. In the first 8 week study the fry loss was much lower than the other samples indicating that where in the process a coating is applied can impact the moisture retained on application to the fryer. In terms of acoustic data, a series of smaller acoustic events accompanied by a smaller maximum acoustic signal was preferable in terms of crisp textures, as opposed to one or two acoustic events and a larger max acoustic signal.

The most numerous findings in this thesis regarded the moisture. During initial coating tests, the development of laminar and honeycomb structures was observed and this was attributed to the interaction of moisture as it left the inner layer and moved to the surface on application of the microwave field in the case of laminar structures and due to migration of moisture on storage leaving empty air pockets in the case of honeycomb structures. Bound water was released from the starch backbone at temperatures of 160-170 ^{o}C determined during the popcorn experiments.

The gradual release of bound water may be preferable as opposed to mass release of bound water as this will help prevent previously crisp outer textures developing saturated soggy textures which are unable to become dehydrated once more within the short microwaving time frame. Uncoated samples dehydrated as a function of storage whilst the coated samples did not. Ice crystal formation was delayed in the coated samples and the presence of ice crystals on the uncoated sample did result in increased dielectric activity of the sample. This was related to the ratio of free:bound water as once the fragile ice crystals at the surface melted they were not bound by the food matrix and so the dielectric activity was increased.

One of the most important findings regarded the theory of moisture acting as a chemical oscillator, enabling the movement of other charged particles as a function of storage. This has large implications for the end product as impacts how a certain food will perform on application of the microwave. The 1st and 2nd 8 week studies have highlighted that storage of the product results in multiple transformations which often interact. These studies have shown that the problem is more complex than previously thought and that manufacturers should consider understanding the effects of storage further before developing a frozen product which shall be reheated in the microwave. In addition, as the product changes so rapidly on storage, the manufacturer should also consider recipes that 'mature' on storage as opposed to being an end product entering the freezer.

6.2 Future Work

One area in which future work would be insightful relates to NaCl. NaCl is only active when dissociated in water to become sodium and chlorine ions. In doing so they bind to water making water unable to rotate. (Gabriel, 1996) observed that at lower salt concentrations, the NaCl did bind to some water but, the remaining water, had less interaction from hydrogen bonds and so was able to have a lower relaxation time than pure water thus resulting in more rapid rotations within the same space of time and promoting heating. It would be of interest to observe if lower concentrations of NaCl could improve dielectric heating of the samples by allowing a higher ratio of free:bound water.

It would also be of interest to investigate different types of salt such as potassium chloride as a function of dielectric properties as it is unknown if different salts could promote different dielectric properties. Also potassium chloride does not have the negative health connotations that NaCl has and as such the concentration range considered for investigation would be higher.

Throughout the project, moisture, the form it is in and the location of the moisture has been the driving factor in understanding this product. Further work should be directed at understanding the state of moisture within the product. Only then will a method to develop suitably crisp textures be derived.

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