The fundamental effect of ingredients on the pasting and retrogradation properties of tapioca and corn starch in excess and limited water solvation medium

Master's thesis in Technology

University of Turku

Department of Biochemistry

Master's Degree Programme in Food Development

November 2018

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First, all glory and honour goes to almighty God for giving me the grace to do this work. I also want to say a special thank you to everyone who has contributed to this thesis work, may God bless you immensely.

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Master's thesis in Technology, 85 p,

Food Development

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Native starches, low cost carbohydrate are employed by the food industry to control the textural and organoleptic properties of several starch based foods, such as baby foods, where starch co-exists and interacts with other food ingredients in the food matrix such as, sugars, acids, salts and lipids. This interaction unpredictably and unavoidably affects the organoleptic properties of the final product. This is why these food applications demand the knowledge of starch pasting and viscosity behaviour, because it is necessary to control the organoleptic properties of the finished products and also to obtain consistent viscosity from batch to batch.

The objective of this study was to investigate the effect of ingredients on the viscoelastic properties of corn and tapioca starch used in the production of selected baby foods. In this study, the sugars and acids profile of the cooking medium where the starch is gelatinized was analyzed with a gas chromatograph coupled with flame ionization detector (GC-FID). The results were utilized to prepare sugars and acids starch model solutions for a process simulation to predict starch rheological behaviour. The viscoelastic properties of experiments were carried out with a Rapid Visco Analyser (RVA).

Experimental results showed that all ingredients tested had a significant dilatant (shear thickening) phenomenon on the starches in excess water medium, while on the other hand, in limited water medium, the ingredients exhibited an inverse effect causing a significant pseudo plastic behaviour (shear thinning) on the starch samples. Lipids caused a significant thixotropic (shear thinning) behaviour and were evidently responsible for the irreproducibility of viscosity profile of starch types when added to the mixture. Acids caused shear thinning behaviour due to glucose hydrolysis and reduction in the degree of polymerization. Furthermore, starch lumps were formed in food matrix when starch dispersions were allowed to sediment and also gelatinized with delayed shearing, causing a clumping together of starch granules.

It can be concluded that corn and tapioca starch gelatinization and pasting required for thickening, textural and organoleptic properties of puree-based baby food matrix gives a better viscoelastic properties in excess water solvation medium, in comparison to limited water medium, since cooking in excess water environment has enough solvent externally available for corn and tapioca starch amorphous growth ring, therefore resulting in total disruption of lamellar and crystalline order resulting in a non-thixotropic characteristics of the finished starch-based puree product.

This study may be used as an applicable model for starch-based food product development.

Keywords: RVA, GC-FID, sugars and acids, tapioca starch, corn starch, amylose and amylopectin, ascorbic acid, lipids, salts, viscosity, pasting and retrogradation.

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1 INTRODUCTION

Starch is a plant polysaccharide, sourced as energy stored in tubers, plant roots or grain kernel endosperm, such as tapioca, potato, rice and corn (Sulaiman, 2011; Vaclavik and Christian, 2014). The smallest unit of starch is glucose, as it serves as a source of energy to humans (4 cal/g), bestowing the brain and nervous system the glucose needed for normal functionality (Vaclavik and Christian, 2014). Starch is made of two major components, which are amylose and amylopectin. Amylose to amylopectin ratio varies according to botanical sources (Huo *et al.*, 2015). Amylose is a linear unbranched polymer, composed of D-glucose units linked together by α 1,4 glycosidic bond and has a degree of polymerization. On the other hand, amylopectin is a much larger high branched glucose polymer linked together by α 1,4 and α 1,6 glycosidic bonds as illustrated in Figure 1 (Huo *et al.*, 2015).

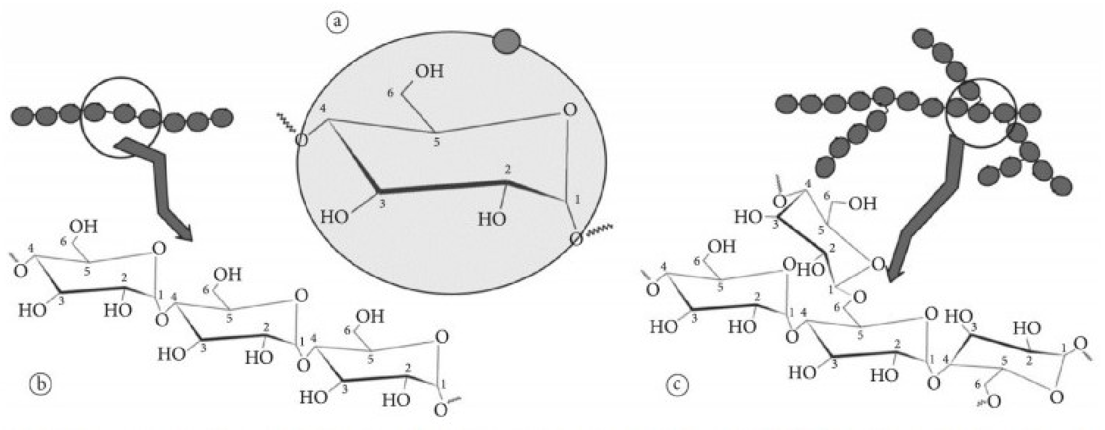


Figure 1: Basic structure design of (a) glucose units (b) amylose and (c) amylopectin, alongside labelling of the atoms and torsion angles.

Source: (Alcázar-Alay and Meireles, 2015)

Native starches, being low-cost carbohydrates, are being employed by the food industry in production of baby food, soups, syrups, desserts, and fruit fillings. Its functionality enables starch to be used for controlling viscosity, mouthfeel, moisture, texture, shelf life, sensory and nutritional properties of foods (Gil and Yoo, 2015). Several of these food applications demand the knowledge and implementation of starch pasting and viscosity behaviour. The understanding of starch gelatinization behavior is necessary, to control the textural and organoleptic properties of finished starch-based products (Xie *et al.*, 2007). In such food applications, starch co-exists and interacts with several ingredients in foods systems like sugars, acids, salts, lipids etc., and this unavoidably and unpredictably may affect the behaviour and functional properties of starch and consequently the physical and textural properties of the finished product (Gil and Yoo, 2015). According to BeMiller and Whistler (2007) and Gil and Yoo (2015), even though starches are easy to handle and process, they can be unstable in processing conditions. The type of starch and its concentration, type and concentration of ingredients in the surrounding medium where starch is cooked play a germane role on the gelatinization, retrogradation (see page 20-22) and rheological properties of native starches. This explains the importance of chronicling the pasting-rheological models of native tapioca and cornstarch solution from experimental data; thereby harnessing and applying knowledge during food formulations and also to promote improved formulations of starch-based food products in further food product development applications (Gil and Yoo, 2015; Huo *et al.*, 2015; Sulaiman, 2011).

Various methodologies have been developed and employed for the rheological, optical and calorimetric study of starch gelatinization phenomena, such as Differential Scanning Calorimetry (DSC), Nuclear Magnetic Resonance (NMR), hot stage microscope, and viscometry (Xie *et al.*, 2007). Furthermore, several studies (Choi and Yoo, 2009; Chun and Yoo, 2006; Gil and Yoo, 2015; Hong *et al.*, 2014; Samutsri and Suphantharika, 2012; Yoo and Yoo, 2005; Zhang *et al.*, 2017) have investigated the effect of different compounds on the pasting properties of several types of starches in mixture with different ionic and non-ionic hydrocolloids, such as, xanthan gum, glucomannan, guar gum, and related texture stabilizers; the knowledge of their study is useful in deciding the textural functional properties of several starch-based foods in mixture with hydrocolloids. However, those approaches are not of direct importance to baby food manufacturing industry, due to infant nutrition safety issues that might arise because of ionic and non-ionic hydrocolloids, like xanthan gum, glucomannan, and guar gum. Furthermore, there are limited or no reports about the fundamental effect of ingredients on pasting and rheological properties of native tapioca, cornstarch and their blend.

1.1 Gelatinization of starch

Gelatinization of starch takes place when starch suspension is heated in water or aqueous medium (Tester and Debon, 2000). It is an irreversible multi-phased process which involves swelling of starch granule, native crystalline melting, birefringence loss, and solubilization of starch (Xie *et al.*, 2007). This process converts starch from a comparatively indigestible, semi crystalline form to a readily digestible, amorphous form (Tester and Debon, 2000).

Naturally starch granules are insoluble in water of cold or ambient temperature; however when heated in aqueous medium, the starch granules begins to swell. At the beginning of gelatinization, water is taken up slowly and irreversibly (Xie *et al*., 2007). At this point water mobility decreases in concurrence with temperature as it increases from 20 to 60 ° C, as starch granules are still stable (Ratnayake and Jackson, 2006; Xie *et al.,* 2007). In the initial swelling of starch granules, the visual properties of granules, such as birefringence are unaltered and swelling could be reversed. When starch granule aqueous suspensions are gradually heated, a certain temperature is attained which weakens forces of hydrogen bonding and then granular materials diffuse inside water, as swelling becomes more pronounced and irreversible, while starch granules begin to lose birefringence, and granular structure is significantly altered (Xie *et al.*, 2007). This temperature is known as the initial gelatinization temperature and it varies for different starch types and sources (Xie *et al.*, 2007; Huang *et al.*, 2014).

The change that occurs after gelatinization is called pasting. During this pasting period further swelling of the granules and disruption of the granules occurs as well as leaching of molecular components from the granules. The changes greatly affect the rheological character of starch solutions and can be evaluated with a viscometer (Huang *et al.*, 2014). Continuous heat application above gelatinization temperature to the aqueous suspension formed continues to disrupt hydrogen bonds, while water molecules are attached to the hydroxyl groups which results in greater swelling of the starch granules as well as crystallites melting (Xie *et al.*, 2007). Consequently due to granular swelling, there is a resultant increase in the paste clarity, paste consistency and starch solubility. As starch granules gets disrupted and collapsed, they lose their integrity and then soluble components such as amylose begin to leach out of the starch granules as they form solution during the process.

McGrane *et al.* (2004) explained the role of hydrogen bonding of the hydroxyl groups of starch via water molecules during gelatinization process. In their paper, they stated that hydrogen bonds are being broken down continuously and subsequently reformed all through the heating cycle. The water molecules that are dissociating are forced into the micellar jungle of bristling hydroxyl groups which binds and entraps them; the free water becomes used up (bound) with a concurrent increase in suspension viscosity as it reaches the maximum viscosity. The O–H…O linkages that holds bound water molecules to the hydroxyl group of starch are destroyed by the energy conferred by increasing temperature as well as agitating shear. This leads to rapid decrease of starch viscosity (McGrane *et al.*, 2004).

1.2 Techniques applied in the study of starch gelatinization behaviour

1.2.1 Starch granule transition phase studied with microscope

Gelatinization of starch can be studied by subjecting the starch dispersion to heat and observing the structural behavioural changes that occurs. In this light, birefringence loss is the phenomena that is been measured via an optical microscope coupled with cross polarizers as well as a heating stage, such as that of kofler hot stage microscope (Zobel, 1984). A light microscope coupled with a heating stage and camera is connected to a computer system in order to visually monitor the swelling behaviour of starch granule as a function of heating from ambient to pre-set temperature. Starch dispersion is prepared at high moisture content in order to avoid over clustering and interference of starch granules observed by the microscope when heated between glass and cover slip (Atichokudomchai *et al.*, 2000; Xie *et al.*, 2007). Burt and Russell studied the gelatinization of low water content wheat starch using light microscopy and DSC, where they observed that the temperature at which complete loss of birefringence occurred increased as water content of starch dispersion increased (1983). Srikaeo and Furst (2006) used a light and scanning electron microscope with image analysis to study the starch microstructural changes during cooking as a function of time and temperature. They discovered that increasing cooking times and temperature was directly proportional to increase in melting and swelling of starch granules.

1.2.2 Gelatinization of starch studied with Differential Scanning Calorimetry (DSC)

DSC has been shown to be an important device to study starch gelatinization (Tananuwong and Reid, 2004; Yu *et al.*, 2006). DSC offers a thermo-analytical approach to examine the gelatinization of starch by studying its chemical and physical properties. The thermograms obtained from the DSC aid in the analysis of transition enthalpies and temperatures (Xie *et al.*, 2007).

In simple terms, DSC method is applied to examine the changes in input energy into a substance reference material; thereafter samples are subjected into a heating and cooling temperature program. This technique works so that when energy is absorbed during thermal transition, there is a concurrent increase in energy by the system to maintain a balance in temperature. As long as the input energy is directly proportional to the absorbed energy during transition, the balancing energy is recorded and yields a peak which is recorded as transition energy on the heat flux versus temperature of the direct calorimetric measurement. Karim and Norziah, (2000), stated that the area under the curve of the peak and its direction is indicative of change in enthalpy (ΔH) and the thermal event that occurred, be it exothermic or endothermic. In relation to the gelatinization of starch, the thermogram from the DSC illustrates the transitional enthalpies that occurred during the melting of double-helical structure in the starch. Furthermore, it gives an accurate measurement of onset, T_o; peak, $T_{p;}$ and conclusion, T_c transitional temperatures during gelatinization (Karim and Norziah, 2000).

According to (Ratnayake *et al.*, 2009), the degree of gelatinization is can be calculated by the formula below:-

Percentage degree of gelatinization (%) = $[(\Delta H_s - \Delta Ht)/\Delta H_s] \times 100$ (1)

Where;

ΔH_s denotes the change in enthalpy in untreated samples.

ΔH_t represents the change in enthalpy of treated sample in identical condition with the same equipment.

Yu *et al.* (2006) examined the major factor that may affect the thermal behaviour of starch during DSC measurement. In their study, they were able to identify three major factors, which are methods of preparing samples, DSC pan type and the conditions of measurement. The study developed a practical guide which could be employed to study starch thermal behaviour.

Liu *et al.* (2006) studied systematically the cornstarch gelatinization behaviour with different amylose and amylopectin content ratio as follows:- (waxy: 0/100, maize: 23/77, Gelose 50: 50/50 and Gelose 80:80/20), as function of temperature (0-200 ° C) and water content (9 to 95 %) with the aid of DSC equipped with a high pressure stainless steel pan. They reported that the amount of enthalpy and endotherms generated is dependent on the amylose to amylopectin ratio, moisture and lipid content and Gelose 80 had high amylose content and it generated a unique endotherm. The endotherms of gelatinization of other corn starches also displayed similar behaviour. In summary, the enthalpy of gelatinization of starch rich in amylopectin is higher in contrast to rice starch in amylose. Hence, the total gelatinization enthalpy increases as a function of increasing amylopectin and water content.

Ratnayake *et al.* (2009) studied the transition in the phases of starch during gelatinization, with starch dispersion in excess water, dilute sucrose and sodium chloride solution using DSC. They observed that phase transition progression differed amongst the starch dispersions. All the phase transitions that occurred gave a resultant change in enthalpy which started to occur from a low temperature with a simultaneous structural change concurrently with progressive endothermic paradigm as temperature increased from low to high. The findings support the hypothesis that the gelatinization of starch occurs over a wide range of temperature and not a sudden transition from order to disorder in a short space of time and temperature, which is also a function of starch type and cooking environment composition.

Rao and Tattiyakul (1999) studied the gelatinization temperature range of 10 and 20 % tapioca starch dispersion with 11 percent moisture and 27 percent dry weight amylose content. In the study, well stirred dispersion was heated with a temperature sweep from 40 °C to 100 °C to determine the starch gelatinization range with a DSC. This study reported range of 60 degrees, 67 degrees and 75 degrees as onset, peak and final gelatinization temperatures respectively. The results correlates with studies by Leach (1965) and Roos (1995). It could be said that the gelatinization of tapioca starch dispersion in water occurs over a 15 degree temperature range.

1.3 Starch processing techniques

1.3.1 Extrusion (super-heated cooking)

According to Harper (1981), during extrusion cooking, starch is super-heated at a pressure ranging from 30 to 60 atm and temperatures of 200-250 ° C at moisture content of about 40 %. These conditions make starch granules undergo the process of gelatinization and melting. Donovan (1979) studied order to disorder phase transitions, as well as melting process of starch that occurs at various moisture contents ranging from excess to low. He mentioned that the process of gelatinization occurs best at a high water content of about 61 % (w/w).

Lawton and Henderson (1972) studied variables which included operating parameters and screw geometry, which could have an effect on corn starch gelatinization. They discovered that the variables of importance were barrel temperature, moisture content, screw speed and geometry. Barrel temperature and moisture had a strong correlation. Their studies showed that utmost gelatinization occurred with higher water content and lower temperature of barrel. Similar were made in the studies from Chiang and Johnson (1977), as they studied the effect of extrusion on wheat starch flour and gelatinization. The authors reported that screw speed, moisture content, temperature, and temperature-moisture content interaction affected the gelatinization of starch during extrusion. In a study by Ibanoglu and Ainsworth (1996), it was shown that the temperature of the barrel, had the most prominent effect on starch gelatinization, as it was measured at constant water content, feed rate and screw speed.

Bhattacharya and Hanna (1987), discovered that an increase in the temperature of the barrel from 115-164 °C, resulted in a concurrent increase in the degree of gelatinization from 73.6 to 98.4 % in chemically modified corn starch (1 % amylose) as well as in an increase from 40 to 55.2 % in native corn starch (30 % amylose). It was apparent that the gelatinization of both corn starch samples increased as a function of increasing temperature. Similarly, Govindasamy *et al*. (1996) obtained similar findings as they observed that sago starch degree of gelatinization increased with increasing temperature of barrel (81-149 °C); however, the increase was less drastic at high feed rates. They further explained that when there is an increase in the temperature of the barrel, hydrogen bonds are disrupted to greater degree, which would result in more amylose solubility and as a result greater gelatinization. Nevertheless, a study by Owusu-Ansah and Voort, (1983), reported an anomalous observation as they discovered that as temperature increases, there was a resultant decrease in the viscosity of starch gelatinization. After further investigation, they were able to attribute the happening to be a result of the choice of screw profile chosen and mechanical shear associated with the profile, which resulted in a complete gelatinization at low temperature. Further heating at this condition led to formation of water soluble carbohydrates. During additional investigation, low pressure was used and this resulted in an expected increase in gelatinization as a function of increasing temperature.

Chiang and Johnson (1977) carried out studies related to the interaction between temperature and water content, as well as the effect of the interaction on gelatinization. They reported that as moisture content increased (18-27 %) at low extrusion cooking temperature (65 °C and 80 °C); starch gelatinization was observed to be decreased. However, at similarly increased moisture content, with increased temperature (95-110 °C), starch gelatinization was observed to increase significantly. This may be because of the temperature driven granular swelling caused by the increase in temperature. Furthermore, Miller and Derby, (1973) stated that enough water in the kettle is important for lubrication purpose to reduce friction.

According to the studies carried out by Govindasamy and Campanella (1996) on sago starch gelatinization in twin-screw co-rotating extruder, moisture content of feed kept at circa 40% led to a higher degree of gelatinization as compared to low water solubility index. However cooking/processing carried out at water content of circa 13 %, would result in restriction of material flow in the cooking (extruder) kettles which causes a resultant increase in the viscosity, degree of gelatinization and resident time. Lawton and Henderson (1972) clarifies that ample water (circa 40% and above) acts as lubrication; also, high water content can also reduce starch viscosity. However extensive heating and uniform distribution of heat accounts for enhanced gelatinization.

Lawton and Henderson (1972) further reported on corn starch gelatinization that 27 % water content for gelatinization is theoretically sufficient bound water requirement of corn starch gelatinization. Therefore, additional water added would not be bound tightly and would be used up for lubrication purposes. This study is also in agreement with that of Gomez and Aguilera where peak gelatinization of corn starch occurred at moisture content of circa 28 %.

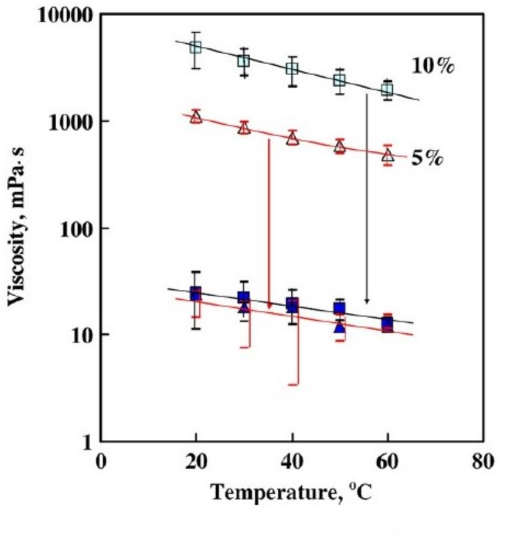
1.3.2 Application of ultrasound for starch viscosity reduction

Power ultrasound has been used in the food industry not only for sterilization, extraction, degassing, and emulsification, but it also has a promising application in controlling the viscosity of starch solutions. Iida *et al.* (2008), in their paper on polysaccharide solution viscosity control, state that ultrasound can be used to effectively reduce the viscosity of starch after gelatinization. They reported that ultrasound can be employed to reduce starch viscosity of starch solutions at high starch concentrations of about 20 to 30 %. Iida *et al.* (2008) evaluated the effectiveness of ultra-sonication by determining the granule disintegration, molecular weight changes, and the process of depolymerization. Iida *et al.* (2008) state the merit of the starch solution viscosity reduction with ultra sound is that, it is a rapid and simple process, which does not require additives or chemicals and most of all does not give rise to high changes in the starch properties, especially in the chemical structure as investigated by NMR spectra. Furthermore, the process can be employed for all kinds of starches (tapioca, corn, potato, and sweet potato etc.).

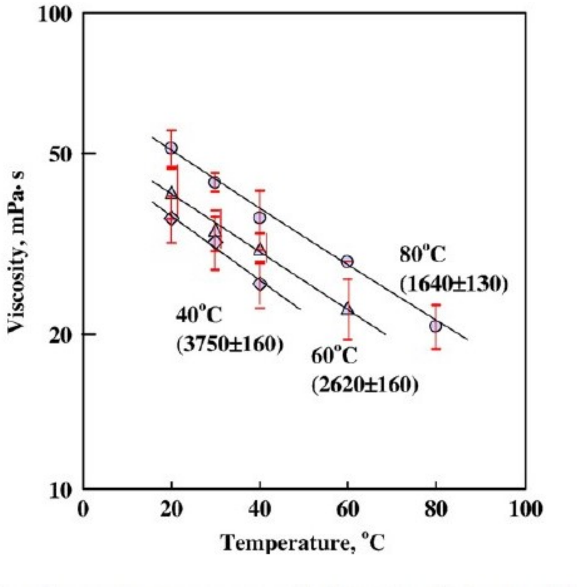
The illustration in figure 2a depicts a characteristic drastic viscosity change of about two orders that occurs during the use of a sonication after gelatinization of 5 and 10 % waxy maize starch solution for 30 minutes. Iida *et al.* (2008) also reported the low viscosity was maintained even after the starch solutions were cooled down to normal room temperature. The same phenomenon was observed for tapioca, cornstarch, potato and sweet potato starches.

The illustration in figure 2b depicts the effect temperature has when simultaneously applied with sonication. It was noticed that viscosity reduction observed with changes in temperature is not very pronounced. As shown in figure 2b, the viscosity reduction observed followed the order of 40 < 60 < 80 °C, that is, more pronounced at 80.

In summary as illustrated in figure 3, the process of heating intiates many physical interaction in the starch granule that results in the gelatinization of starch. However, ultrasound hastens the process of depolymerization of starch granules by separating the amylopectin units as well as amylose units that are leached out from the amorphous gelatinized phase (Jackson *et al.*, 1989). This is because of the weakening of the interaction that occur across polymer molecules, and consequently a reduction in viscosity occurs due to the annihilation of the polymer network (Iida *et al.*, 2008). The annihilation of aggregated and interwined polymer network results in an increase in the amount of free moble polymer molecules. As further reported by Iida *et al.* (2008), after sonication, a reduction in molecular weight of starch was observed with the aid of High Performance Gel Permeation Chromatography (HPGPC).



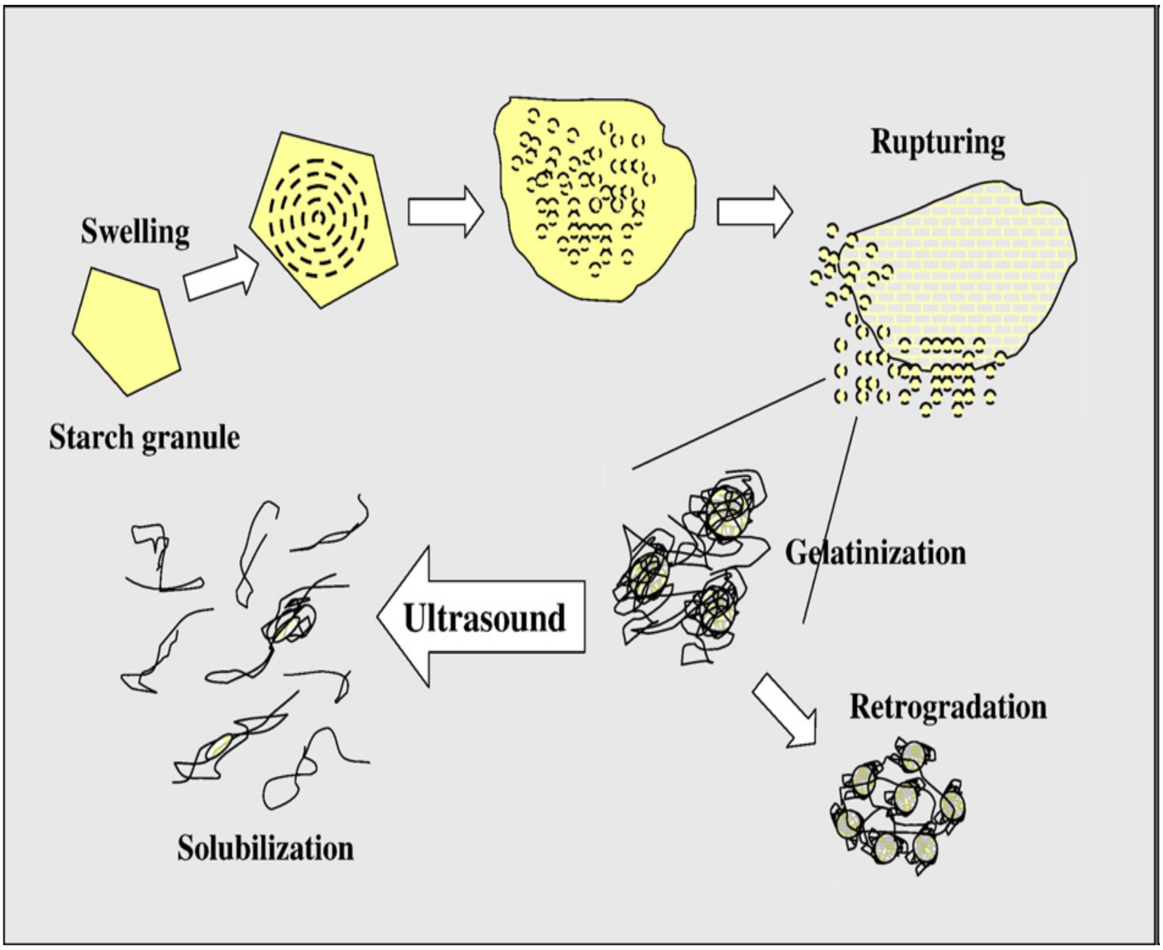
(a)



(b)

Figure 2: (a) Viscosity change of 5 and 10 wt. % waxy maize starch solution by ultrasound treatment (b) Sonication temperature effect on viscosity reduction of 10 wt. %. waxy maize starch solution.

Source: (Iida *et al.*, 2008)



(b)

Figure 3: (a) Schematic Illustration of a macromolecular event that occurs as starch granules swells and gelatinizes as well as ultrasound effect.

Source: (Iida *et al.*, 2008)

1.3.3 Flash gelatinization of Starch

Karapantsios *et al.* (2000) studied the electrical conductance, heat transport and fluid motion during the gelatinization of starch. It is established that thermal energy is germane to starch viscoelastic behaviour. The researchers studied flash gelatinization and compared different temperatures of starch suspension in cold water and its instant mix with hot water. They wanted to examine if there would be differences in the conductances in both experiments. As shown in Figure 4, there was a difference in conductance K_{app}/K_{max} which they obtained at 80 ˚C target temperature of mixture, where one of the experiments involved instantaneous mixing 40 ˚C starch dispersion with water at 97 ˚C and the other mixing at starch dispersion 54 ˚C with water at 92 ˚C. As a result, they observed a steep increase in conductance signals for both curves at the moment of mixing, followed by a declination in both peaks which both had different conductance values, as shown in Figure 4. The results obtained depict a huge influence of initial mixing conditions (temperature) on pasting behaviour of native starches. The 40 and 97 ° C starch solutions had a reduced K_{app}/K_{max} compared with that of 54 and 92 ° C meaning that the final viscosity of the 54 and 92 ° C starch solution would be higher as compared to the former. This emphasizes the importance of consistent gelatinization temperature profile on starch paste viscosity.

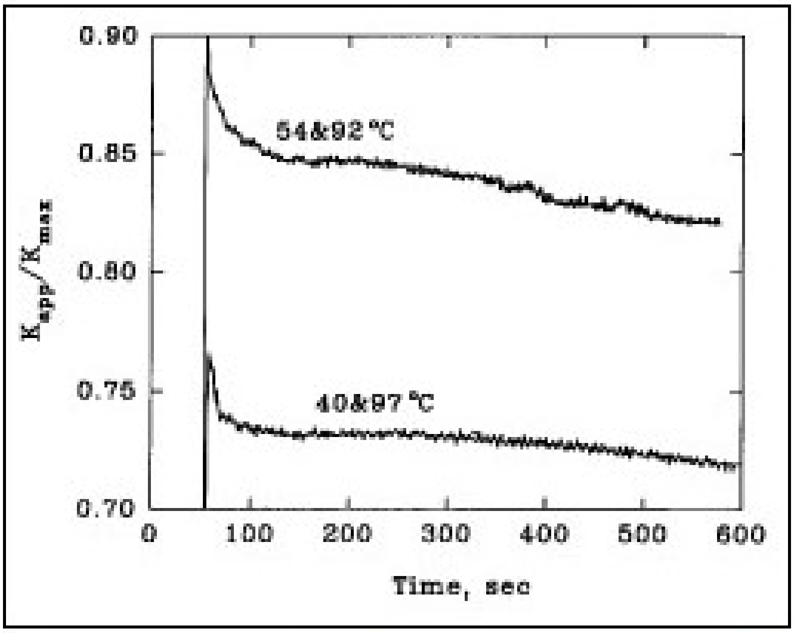


Figure 4: Result indicating conductance signals K_{app}/K_{max} during flash gelatinization (at 92 and 97 °C) procedure leading to differences in starch viscosity at same starch concentration where both experiments had different temperatures of starch dispersions(54 and 40 °C) and 80˚C final mixture temperature.

Source: (Karapantsios *et al.*, 2000).

1.4 Gelatinization of native starch solution and characteristic rheological behaviour

1.4.1 Pasting spectra and rapid visco-analysis

Several empirical methods have been developed for cereal research in order to explore starch gelatinization phenomenon and pasting behaviours, owning to their good correlation to the finished product quality, as well as their ease of use (Cozzolino, 2016). The limitation of these rheological methods is that they are not easily scaled up for actual manufacturing process, their parameters are poorly defined, their results are not easily interpreted and their usage can be time consuming (Cozzolino, 2016). This limitation has been succeeded by the application of rheological parameters that are well understood and defined, such as strain, stress, temperature and time (Cozzolino, 2016).

Walker *et al.* (1988) developed the technology for determining the pasting profiles of starches with a rapid visco analyzer (RVA). The RVA is a peculiar equipment for food product development, process control and quality assurance. This rapid instrument comes with an inbuilt cooking system with temperature sweep, ramped shearing, to test the viscoelastic properties of cereals. Furthermore, the RVA has the ability to suspend starch samples throughout the testing process, as well as applying appropriate shearing and temperature parameters that are similar to that of actual production conditions, hence making it germane for research, process and product development purposes.

The rapid method to determine the quality, characteristic and performance of pasting is of increasing need in research and development and also in the quality control of starch based food. During starch gelatinization in aqueous medium, the starch granules imbibe hot water and begin to swell as they lose their crystalline structure. The viscosity begins to change due to the heating, shearing and cooling and this information of the starch gelatinization profile can be readily assessed by a RVA. Truong *et al.*(2017) reported that rapid visco analysis as its name implies is rapid and indicates accurately the quality and pasting characteristic of starches.

Figure 5 below shows a typical RVA graph. The graph shows the peak viscosity which indicates the highest viscosity attained during gelatinization. The breakdown viscosity shown in the graph indicates the difference between the peak and the minimum viscosity during gelatinization. The setback viscosity shows the difference between highest viscosities during cooling in contrast to lowest viscosity during pasting. The final viscosity indicates the

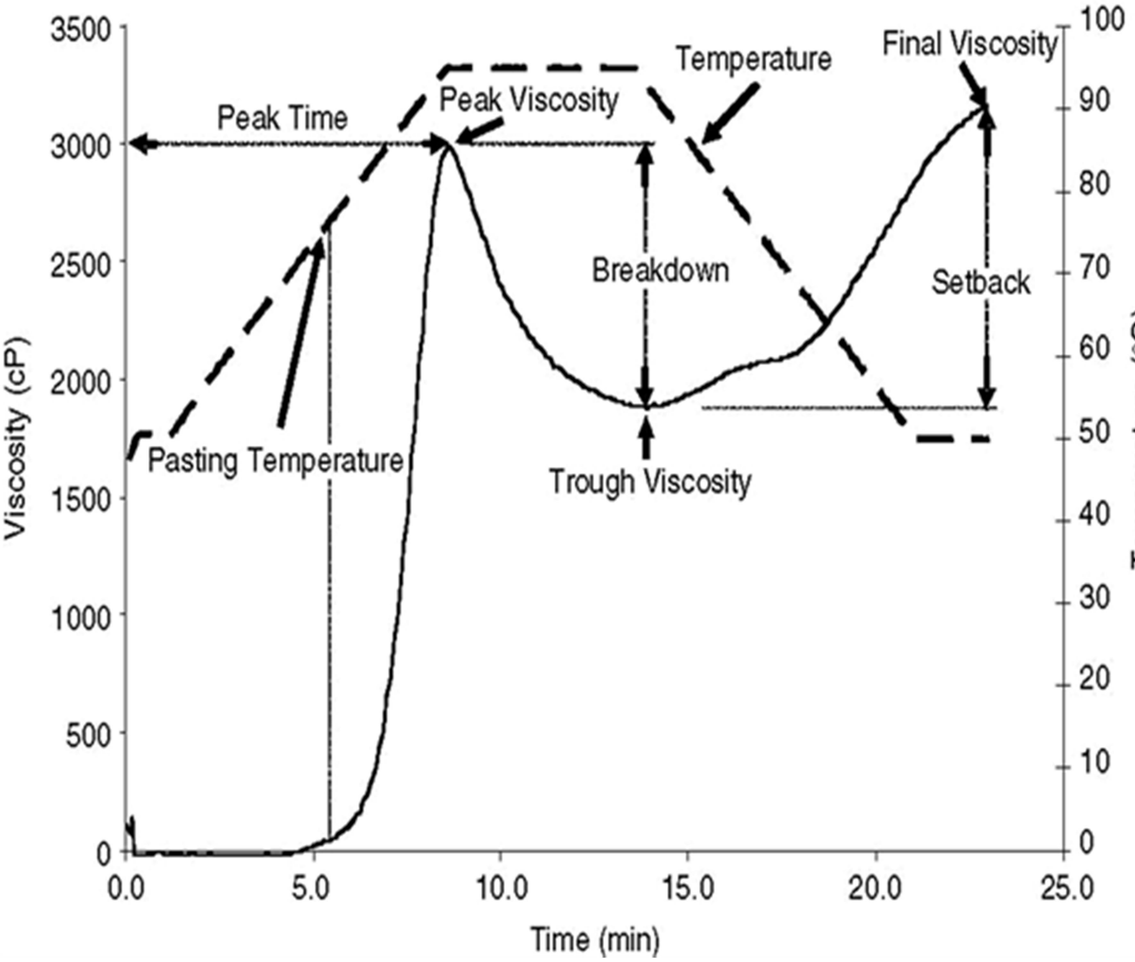


Figure 5: Illustration image indicating a typical RVA pasting graph of native starch granule

Source: Perten (2007)

viscosity attained at the end of the run and at the end of the cooling process after gelatinization (Gil and Yoo, 2015; Perten, 2017).

1.4.2 Pasting and retrogradation characteristics of cornstarch and tapioca starch

Pasting is the phenomenon that where starch granule molecular component exudation and total starch granule disruption which occurs after gelatinization During the pasting process, the molecular order of starches has been broken down which results in an irreversible change associated with starch granule swelling, loss of birefringence and finally viscosity development (Graham and Andrew, 2007). Consequently, these changes have a direct and long-term impact on physical, nutritional, organoleptic and storage quality of the starch based food product. As illustrated in figure 5, the RVA pasting curve yields characteristic pasting parameters, such as pasting temperature, peak viscosity, trough or breakdown viscosity, setback and final viscosity.

Pasting temperature is indicative of the temperature that is required to be attained in order to cook a given starch type, and would also give information about the stability of other constituting components in a food formula, as well as indicating the cost of energy (Cozzolino, 2016; Booth and Bason, 2007; Perten, 2017). The peak viscosity is indicative of the water holding capacity of starch or the matrix at which starch is gelatinized, as it is also indicative of the viscosity load that would be encountered in the cooking kettles. Parameters such as the breakdown viscosity, holding strength, and trough or hot paste viscosity are dependent on shear stress, rate of mixing, water content and starch botanical sources, all of which are important to food and process development, because they the ability of samples to withstand shear stress and heating (Cozzolino, 2016). Set back is the difference between the final and breakdown viscosity and it gives information about realignment or retrogradation of starch molecules, which has direct implication on the textural properties of the finished starch-based products, as the higher the values of the setback, the higher the propensity is for the starch or starch-based product to undergo retrogradation .The final viscosity defines the sample quality and depicts the ability of starch to form a viscous paste or gel after gelatinization and cooling. More importantly, it is well correlated with the final texture of the finished starch based product (Cozzolino, 2016; Perten, 2017).

Retrogradation of starch occurs after gelatinization and pasting of starch if conditions favour it, amorphous alpha glucan chains reforms double helices and probably realign themselves to reform ordered crystallites (Jacobs and Delcour, 1998; Tester and Debon, 2000; Wang *et al*., 2015). During this process two processes occur which are gelation and amylose crystallization, as well as amylopectin recrystallization. In many cases retrogradation of starch may have a detrimental effect on the organoleptic and storage quality of several starchy foods (Jacobs and Delcour, 1998; Tester and Debon, 2000; Copeland and others 2009; Wang and Copeland 2013). By and large, the retrogradation of starch is often considered undesirable by food processors because of its major contribution to the staling of bread and other foods rich in starch, leading to a significant reduction in the to the shelf life of finished food products and consumer acceptance, hence posing a huge challenge to the food processors (Collar and Rosell, 2013). Karim and Norziah stated that starch retrogradation has been found to be desirable in the production of breakfast cereals, Chinese rice vermicelli, parboiled rice, dried mash potatoes, etc., owing to modification of mechanical, structural and sensory properties (2000). Nutritionally, starch retrogradation has been found to be favourable, because enzymatic digestion of retrograded starch is slower, while the release of glucose into the blood stream is moderate, which may be important in the prevention of obesity and diet-related diseases (Copeland *et al.*, 2009; Wang *et al.*, 2015).

1.5 Starch chemical structure and its effect on pasting and retrogradation

Naturally, starch granule is made up of amylopectin and amylose units, which are the main components of starch (98 % percent of total dry weight). In addition, starch is composed of minor inherent components such as, protein, lipids, and phosphorus, which may also give significant characteristic to native starch (Table 1) (Copeland *et al.*, 2009).

Different starches have distinct pasting profiles at concentration of starch dispersion in water. Generally, the distinct characteristics of different native starches during gelatinization, retrogradation, viscosity, appearance and clarity, taste and texture after cooking and cooling is a function of its amylose and amylopectin ratio (AM/AP) ratio, the molecular structure (shape, size, crystallinity, molecular weight, chain length of amylopectin branching) as well as the minor components (protein, lipids, and phosphate) (Sulaiman, 2011). It has been concluded by several investigators that starch viscosity profile and gelatinization temperature is dependent on the native starch physico-chemical properties and the matrix to which starch is gelatinized (Chang and Lin, 2007; Liu *et al.*, 2006; Tester and Debon, 2000). In addition, starch pastes have their characteristic properties such as viscosity, stability, texture, clarity, taste and texture.

Several studies have shown that different starch types gelatinize at different temperature. However in a particular starch type, the increase in amylose content would have a slight concurring reduction to the gelatinization temperature. Chen *et al.* (1998) reported that amylopectin distribution and branch chain length has a major determining effect on the gelatinization of starches. They mentioned further, that provided starches do not have structural differences such as that of the phosphate monoester contents, it is expected that starches with branch chain lengths that are longer would display higher gelatinization temperatures and higher viscosity note. For instance, corn starch with high amylose content and waxy maize starch both contain long branch chains possesses higher gelatinization temperature in contrast to waxy and native rice starch with short branch chains, as they are known to exhibits low gelatinization temperatures. Chen *et al.* (1998) further reported that the rate of retrogradation of starch is influenced by the amylopectin branch chain length, meaning that starches with shorter chain length have lower tendencies of retrogradation in contrast with those with longer branch chain length and high amylose content, which have high retrogradation rates.

It is established that amylose is radially present in starch granules and entwined with amylopectin. Copeland *et al.* (2009), reported that native starch inherent lipid content is somewhat proportional to its amylose content, the more the amylose content, the higher lipid contents and vice versa. Tester and Morrison (1998) stated that in a single helical formation, about 50 percent of high amylose starch samples are known to form complexes with lipids. Similarly, starch phosphate monoesters increase the clarity and peak viscosity resultant from their charge repelling, as they also improve starch paste stability and decline retrogradation.

Furthermore, the high amylose content in starch granules has a positive correlation with hot paste viscosity of starch granules and it increases shear thickening. Increasing amylose content also increases setback viscosity, a phenomenon responsible for starch solutions to form a matrix of gel network (Chen *et al.,* 1998). On the other hand, waxy starches possess lower peak viscosity than native starches. This is because the amylose in native starch is intertwined with the amylopectin and holds the swollen starch granule integrity, resulting in a high peak viscosity. However, the final viscosity may not be necessarily significantly different (Chen *et al.*, 1998).

Table 1: (a) Physicochemical properties of native starch (b) Amylose contents of various starch types

(a)

	Corn	Waxy corn	Wheat	Potato	Tapioca
Amylose Content (%)	28	0	28	21	17
Lipid content (%)	0.7-0.8	0.15-0.2	0.8-0.9	0.05-0.1	0.1
Protein content (%)	0.35	0.25	0.4	0.06	0.1
Phosphorus content (%)	0.02	0.01	0.06	0.08	0.01
Pasting Temperature (°C)	75-80	65-70	80-85	60-65	65-70

Source: Yuryev (2002)

(b)

Source	Apparent amylose (%)	Absolute amylose (%)
A-type starch		
Normal maize	29.4	22.5
Rice	25.0	20.5
Wheat	28.8	25.6
Barley	25.5	23.6
Cattail millet	19.8	15.3
Mung bean	37.9	30.7
Chinese Taro	13.8	13.8
Tapioca	23.5	17.8
B-Type starch		
Amylomaize V	52.0	27.3
Amylomaize VII	68.0	40.2
Potato	36.0	16.9
Green leaf canna	43.2	22.7
C-type starch		
Water chestnut	29.0	16.0

Source: (Jane *et al.,* 1998)

Note: 'Apparent and absolute amylose contents of starches are based on the measurement of iodine affinity of defatted whole starch and of fractioned and purified amylopectin respectively' (Jane *et al.,* 1998).

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1.6 Current work

1.6.1 Statement of problem

Starch has a wide range of application in the food industry, such as been used as a thickening agent, gellating agent, calorie optimization purposes. As a thickening agent, the properties of native starches do not precisely meet the needs of the food industry; hence there could be significant and perceived variation in product viscosity and texture from every production batch (Jacobs and Delcour, 1998).

The viscosity of a food product has a direct relationship with the magnitude of perceived flavor and taste of food, because it contributes to the signal processing in the brain (Anastasiades *et al.,* 2002; Ferry *et al.,* 2004). Some consumers believe more thickened food products are richer, some perceive a low viscosity product that has deviated from the norm has been deteriorated in quality. This creates a need to produce food products with consistent viscosity at every batch of production of a product brand.

To obtain product with consistent viscosity profile, several studies have shown that native starch granules could be modified to the desired functional properties of use. For example, native starch granules could be modified chemically via acetylation and or cross linking (Jacobs and Delcour, 1998). However, the growing need of interest, especially for baby food application is from the approach of physical optimization modification method, such as substitution of processing steps, process flow method, ingredients used, starch type and source, as well as formulation methods, all of which are considered to be natural and of high safety (Jacobs and Delcour, 1998). This premise was further buttressed by Rezler and Poliszko (2010) as they stated that the structure and eating quality of any starch based food product could be influenced by either optimizing the composition or processing conditions. This explains why the knowledge from the influence of ingredients on the pasting and retrogradation properties of corn and tapioca starch would be useful for facilitating the optimization in product development and process design, as well as evaluating the organoleptic properties and also extending the application to the starch based infant food product in improving the food formulation methods.

1.6.2 Aims of study

- To study the process parameters that could cause puree-starch based product rheological inconsistency and proffer solution suggestions.

- To study the influence of ingredients on the pasting and retrogradation properties of corn and tapioca starch in excess and limited water solvation medium.

1.6.3 Study approach

- To investigate the production of PM and NBC to understand the causative factors that may be responsible for viscosity variations and lump formation in the named products.
- To carry out quantitative and qualitative analysis of sugars and acids profile of PM and NBC with a gas chromatography.
- To investigate the effect of ingredients on the pasting rheology of starch used in production of starch-based baby food with the aid of a RVA.

1.6.4 Economic importance of thesis work

PM and NBC are known to plays an important role in infant nutrition in the Nordic countries, especially Finland. Inconsistencies in their textural organoleptic properties, will lead to consumers (infant) product rejection, high product complains, with inevitable reduction in product demand. This explains why proper understanding of the pasting rheological properties of models of gelatinization matrix could help to serve as a guideline or blueprint for optimizing, improving and further advancing the product formulation with consistent textural properties from batch to batch. This study proffers applicable suggestions that do not require chemical modification or additional food additive. Furthermore, the pasting-rheological models will be proficient as a predictive model for starch based food developers in food formulations by predicting apparent and dynamic viscosity of starch based finished product. More importantly, it would also save money from trial and error in food formulations as regards textural organoleptic properties of developed starch based food products. The rheological models that would be elicited from experimental work upon implementation would help minimize to the barest minimum the inline rejection of finished product, customer companies and may also ameliorate food process design.

2 Experimental details

2.1 Problem investigation

2.1.1 Consumer complaints analysis

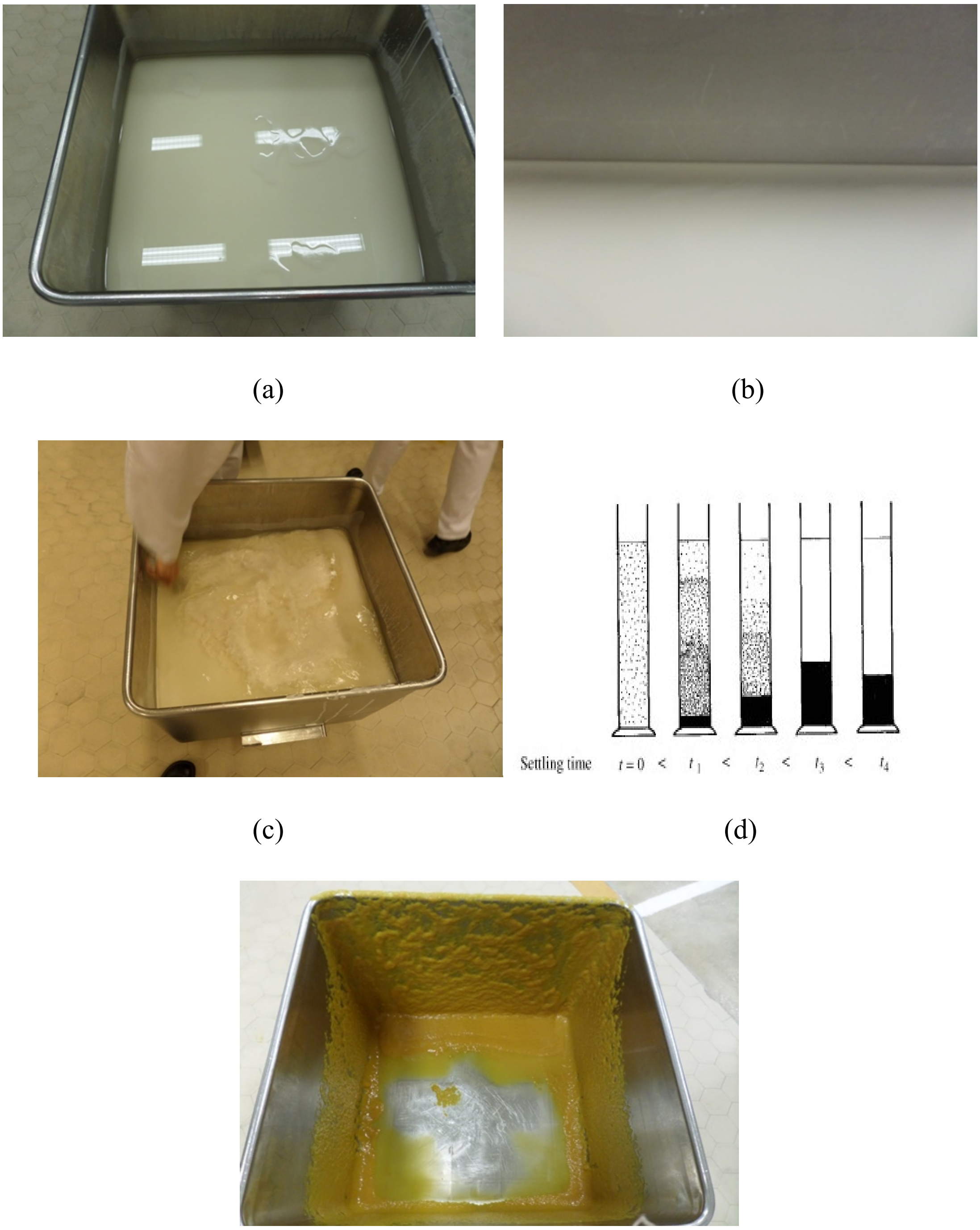
The consumer complaints data from all the months of year 2017 updated till March, 2018 was accessed and analyzed in other to properly understand the nature and frequency of baby food quality complaints. The consumer complains where categorized into categorizes made easy to understand by prospective customers such as, allergic reaction, appearance in jar, bad smell, damaged cover, dent in cap, dirty packaging, dry texture, hair, insects, leaking lid, liquid, liquid after feeding, liquid after heating, liquid during feeding, liquid during heating, liquid during storage, lumpy, metal in jar, mold, plastic, spoilt, stomach ache, taste, texture, thick, underweight, vacuum, water separated, vegetable, vomiting, wrong information, wrong product, yarn. Focus was given to the rheological and product textural categories, such as dry texture, watery (low viscosity), liquid during storage (weeping), too thick (too viscous), and water separated (syneresis), as well as lump development. The data was analyzed in the bid to validate problem, as well as to determine the products to focus on for this thesis work.

Furthermore, data from inline control on the production line was analyzed in order to check if there is a correlation in contrast to the data analyzed from the consumer complaint data.

2.1.2 Production line investigation

Time was spent in the production hall to observe the processing parameters, as well as the production behaviour of the cookers that may be responsible for the development of lumps and low viscosity textural organoleptic properties of baby food. Enumerated below are the following hypotheses created from inline observation that may be causative factors for lump development and low final product viscosity.

- During the different production batches of PM, it was observed that tapioca starch, used as a thickener in the baby food, as shown in figure 6 (a-c), was left standing for about one hour thirty minutes after mixing in water without continuous agitation. This aroused a hypothesis that the sediment starch in water might be responsible for lump development in the gelatinized medium.



(a) (b)

(c) (d)

(e)

Figure 6: (a, b, c) Digital image showing sediment starch during PM production. (d) Schematic diagram illustrating the hypothesis of settling of starch dispersion as a function of time (Sajeev *et al*., 2002). (e) Digital image of puree remnant in bins.

- After puree has been cascaded into the cooking kettle, appreciable amount of puree is left in the cascading bins which might cause a difference in moisture content in product in different batches.
- Water priming was dosed manually into the cooking kettles.

2.2 Study design

This study was carried out at Suomen Nestlé Turku factory, University of Turku, and at Ravintoraisio laboratory.

The sugar and acid analysis of mango puree (MP) samples before starch addition (starch gelatinizing and pasting environment) and the finished product NBC was carried out at the University of Turku, department of Biochemistry, Food Chemistry and Food development unit. The experiments on the pasting-rheological properties of corn and tapioca starch were carried out at the Ravintoraisio laboratory, Raisio.

The sugars and acids analysis of the MP and NBC was carried out to understand the performance and behaviour of corn and tapioca starch in their respective sugars and acids cooking media. Results obtained were used to prepare model gelatinization environment for studying the pasting and retrogradation properties of the corn and tapioca starch.

Furthermore, the effect of the major ingredients of the food products as described on the food package and recipe on the pasting behaviour of corn and tapioca starch samples were tested individually. Ingredients added directly to the starches before cooking as observed on the production line were also considered.

2.3 Materials and methods

Native and non-waxy corn and tapioca starch were used in this study. The corn and tapioca starch samples were obtained from Nestlé *Oy*, Turku-Finland. All compounds and reagents used in this work were of analytical grade and obtained from Suomen Nestle and University of Turku Finland.

2.3.1 Sugar and acid analysis

Trial experiment was carried out to (data not shown) determine the optimum concentration of MP that was best for gas chromatography analysis result. The test results showed that 1g per 40 ml of milli Q water was optimum and was used for the sugar and acid analysis protocol.

Two internal standards were used for this analysis, which were xylitol and tartaric acid. For sugar and acid internal standards, 0.5 g of xylitol and tartaric acid respectively was weighed and dissolved with milli Q water into respective volumetric flasks.

The external standard mixtures were prepared for the purpose of identifying and calculating the correction factors. For this, 0.5 g/ 100 ml of D-fructose, D-glucose, sucrose, xylitol, malic acid, citric acid, quinic acid, ascorbic acid, galacturonic acid and tartaric acid were respectively weighed with weighing machine (Mettler Toledo XSE205 dual range) and dissolved into milli Q water.

The conditions of the GC-FID used for this experiment can be found in Table 2.

One gram of each replicate samples were weighed and diluted into 40 ml of milli Q water in a beaker. The samples in beakers were placed upon a magnetic mixer (thermo scientific Cimarec I poly) for homogenization with the aid of magnetic stirrers for 30 minutes. Subsequently, 9 ml of each of the samples was transferred with a pipette into a falcon tube. Thereafter, 0.5 ml of xylitol and tartaric acid internal standards were pipetted into each of the replicate samples. The samples were then centrifuged at 3000 rpm for 3 minutes to obtain two distinct phases. The upper phase was collected and transferred into another set of clean falcon tubes. The upper phase (300 µL) was filtered using a syringe and 0.45 µm RC filters into auto-sampling bottles. The samples were evaporated to dryness under nitrogen flow at 50 °C with the aid of heating block for 30 minutes. The dried samples were kept in the desiccator over P_2O_5 overnight. The next day trimethyl silyl derivatives were prepared by adding 500 µL of Tri-Sil reagent (Pierce, Rockford, IL, USA) into each of the samples and agitating or 5 minutes. Subsequently 100 µl of the samples were transferred into new vials. Finally, the samples were cooled down to room temperature for 30 minutes before the gas chromatographic analyses.

All experiments were performed in triplicate.

Table 2: Gas chromatograph conditions

Instrument	
GC-FID	Shimadzu GC – 2010 Plus with auto-injector AOC – 20i/ Auto-sampler AOC – 20s, flame ionization detector and Lab-solutions software (Shimadzu corp., Kyoto, japan)
Column	SPB$^{\text{TM}}$-1 (30 m x 0.25 mm ID, liquid film 0.25 µm, supelo, Bellefonte, PA, USA)
Analytical conditions	
Carrier gas	Helium, flow rate 1.9 ml/min
Injection temp.	210˚ C
Injection mode	Split/
Injection volume	1µl
Column temp. (initial)	150 ˚C
Temp. 100 ◦C	Hold 2 min; Rate 4.0 ˚C/min
210 ◦C	0 min; 40.0 ˚C/min
275 ◦C	5 min;
Total analysis time	28.625 min
Detector temp.	290 ˚C

2.3.2 Sugars and acids content calculations

The sugars and acids content of samples are calculated with reference to Linderborg *et al.*, (2011) and Zheng *et al.,* (2009).

It should be noted that the citric acid used for external standard preparation is a monohydrate and was taken into account during calculations.

$M (H_2O) = 18.015 \text{ g mol}^{-1}$ (1)

M (Citric acid monohydrate) = 210.14 g / mol (2)

Corrected mass of citric acid, $m_{\text{citric acid}}$ = weighted mass (M x (citric acid monohydrate) – (H_2O)) / M (citric acid monohydrate) (3)

Inputting equation 1 and 2 into equation 3;

The sugars and acids are calculated according to equation 5 and 6 below, where (A = area of the GC peak, C = concentration of the compounds, K = Correction factor for each analyte).

$$\frac{Aanalyte}{Canalyte} = \mathrm{K}\,\frac{Astandard}{Cstandard} \qquad (4)$$

Changing of subject of formula from equation 4, therefore;

$$\mathrm{K} = \frac{Aanalyt \ \text{x Cinternal standard}}{Canalyte \text{ x Ainteranl standard}} \qquad (5)$$

$$\text{C analyte} = \frac{Aanalyte \text{ x Cstandard}}{K \text{ x Astandard}} \qquad (6)$$

Example calculation for one replicate measurement for citric acids.

From equation 4;

Calculating correction factor for citric acid;

$$\text{K of citric acid} = \frac{\text{519419 x 5.07 mg/ml}}{\text{4.6079 mg/ml x 639986}} = 0.8930 \qquad (7)$$

The correction factors of sugars and acid can be found in Table 3.

Calculating the concentration of citric acid in diluted puree sample from equation 6;

$$= \frac{\text{44733 x (5.07/20)}}{\text{0.8930 x 253321}} = 0.0677 \text{ mg/ml.} \qquad (8)$$

However, from the protocol experiments, 1 gram of puree sample was weighed and diluted into 40 ml beaker for homogenization. Thereafter, 9 ml of diluted sample was transferred into test tubes with addition of 0.5 ml each of sugars and acids internal standard respectively (Detailed protocol enumerated in chapter three).

The average actual weight of 1 gram samples diluted in 40 ml of water in beaker was 39.3063 g. That of samples transferred into test tube was 9.1068 g, while that of sugars and acids internal standard was 1.0743 g. Hence, to quantify the sugars and acids content in semi solid puree samples in 100 ml bases, the formula below was derived.

Let;

(y) = the concentration of diluted sample calculated above.

(z) = the concentration of analyte (i.e. sugars or acids) in semi solid puree sample.

Hence;

$$\mathrm{z} = \frac{\frac{(y*39.3063)}{9.1068}}{1.0743} \qquad (9)$$

Input equation 8 into 9.

Therefore, the concentration of citric acid (z) in mango puree = 0.2766 g /100 ml.

Table 3: Data showing correction factors (K)

Compound list	GC peak areas collected	Correction value	Concentration (g/ 100ml)
Xylitol	790988	1	5.0500
Fructose	524162	0.6620	5.0550
Glucose	795582	0.9881	5.1400
Sucrose	530668	0.6643	5.1000
Myo-inositol	10049	0.9958	5.0350
Tartaric acid	639986	1	5.0700
Malic acid	524807	0.8298	5.0100
Citric acid	519419	0.8930	4.6070
Quinic acid	672651	1.0625	5.0150
Ascorbic acid	576198	0.8906	5.1250
Galacturonic acid	235567	0.3669	5.0850

2.5.2 Pasting test

Tests were carried out to determine the optimum concentrations for testing. The pasting tests were performed with a Perken Elmer RVA, while adopting a standard method 1 measurement profile, approved by the international association for Cereal Science (ICC) No. 162, and American Association of Cereal Chemists (AACC) Method 76-21 and The Peoples Republic of China Food Profession Standard LS/T 6101-2002. Also, the calibration can be traced to Quality System requirement and ISO9000 standards. Viscosity measurements were taken in centipoise (cP) (1 cP =1 mPa.s (Milli-Pascals)). This method has been designed for quality control (QC), comparing samples, to investigate the effect of formulations, to assess the degree of the activity of amylases in flours, as well as to ascertain the degree of modification during the manufacturing process, hence well suited for the purpose of this study (Perten, 2018).

The temperature profile of the heating and cooling were programmed as follows; The starch dispersions were held at 50 °C for one minute, followed by gradual heating at an incremental rate of 4.5 °C/ min from 50 to 95 °C and subsequently held at 95 °C for 5 minutes. Thereafter, the temperatures were set to cool back to 50 °C at a decreasing rate of 4.5 °C/ min, and immediately held at 50 °C for 5 minutes. The rotational speed of the gelatinization was set to an initial of 960 rpm for 10 seconds and 160 rpm for the rest of the test. Afterwards the peak viscosity, breakdown viscosity, setback viscosity, and final viscosity as well as the gelatinization temperatures of the starch dispersions were determined.

Each of the RVA test was performed in triplicate.

For excess water and limited water medium experiments, 1.5 ± 0.1 g and 3.5 ± 0.1 g of starch samples, respectively, were dispersed into 25 ml aqueous medium as bases, either in simulation model solutions or distilled water.

First, the corn and tapioca starch samples were dissolved in distilled water for both excess water and limited water conditions in order to compare with results from other model solutions. Distilled water in dispensette bottle top dispenser discharged 25 ml distilled water into the RVA aluminum canister and primed with a plastic Pasteur pipette to the accuracy of ± 0.01. Thereafter, 1.5 or 3.5 g (excess or limited water condition) samples were transferred into RVA aluminum canister and homogenized manually to enable even dispersion of starch granules with a the RVA paddle stirrer for about 30 seconds prior to insertion into the RVA machine. Afterwards, the RVA tower was pushed down in to run the sample experiments.

PM Model solutions (PMMS) were prepared by adding sugars and acids according to the sugar and acid profile of the cooking samples before star

ch was added to mango puree in the cooking kettle one on the production line of PM (see Table 4a). Similarly, NBC Model solutions (NBCMS) were prepared by adding sugars and acids present in the NBC product itself (see Table 4b). It wasn't possible to obtain the cooking puree samples of NBC, because it is no longer in frequent product resulting from too many customer complains about the product textural organoleptic properties. Furthermore, PMMS with oil and NBCMS with oil moieties where prepared with the same respective sugar and acid profile; however with further addition of 4 % v/v of rapeseed oil added to the aluminum canister prior to every RVA test per replicate for both excess water and limited water conditions.

To study the effect of lipids on the viscoelastic properties of cornstarch and tapioca starch, rapeseed oil in water moiety was prepared at different concentrations, which were, 2, 3, 4, 5 % v/v per 25 ml of water . Afterwards, corn and tapioca starch respectively were dispersed into the corresponding solvation mediums for excess and limited water solvation bases.

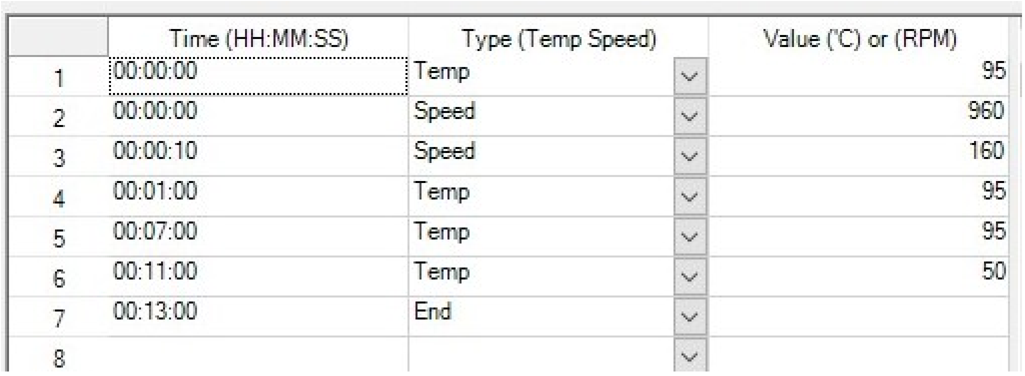
Ascorbic acid model solutions at different concentrations were prepared to determine the effect of ascorbic acid on the pasting of corn and tapioca starch. For that, 25 ml of 0.25, 0.5, 1 or 2 % (w/v) ascorbic acid solution were weighed into the aluminum canister of the RVA machine and subsequently 1.5 and 3.5 g (excess and limited water solvation bases) of starches were dispersed into the respective ascorbic acid solution. Subsequently, the dispersions were manually homogenized for 20 seconds in the aluminum canister with the aid of the paddle stirrer. Finally, the RVA tower was pushed down in other to run the experiment.

The test of pH on the pasting property was carried out by using citric acid as the pH reducing compound. In this experiment, 100 ml of distilled water in a reagent bottled was placed on a magnetic stirrer simultaneously with rotating magnetic stirrer and pH electrode inserted. Intermittently, citric acid was added slowly into the reagent bottle containing the distilled water until the desired pH of 2.5 was attained. Afterwards, 25 ml of the adjusted solution was transferred into the RVA canister and either 1.5 or 3.5 g (excess or limited water solvation mediums, respectively) of starches was dispersed for corresponding tests.

To study the effect of salinity on the pasting properties of corn and tapioca starch, 0.25, 0.5, 1, and 2 % w/v NaCl solution were prepared. Thereafter, 25 ml of the NaCl solution was transferred into the RVA canister and 1.5 and 3.5 g (excess and limited water solvation medium, respectively) of starches were dispersed for corresponding tests.

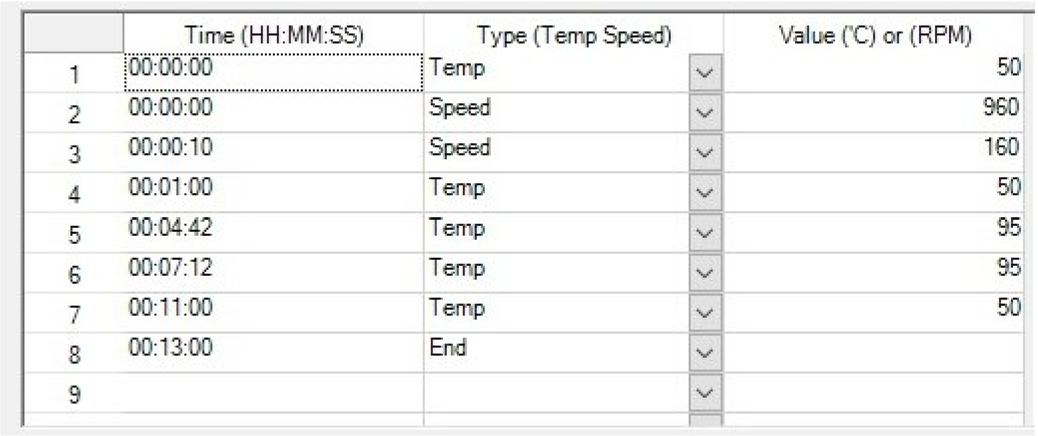
2.5.3 Lump simulation experiment

A hypothesis was generated during the inline observation of PM that starch sedimentation may be the causative factor for lump development during the cooking of starch paste. Thus, as shown in Figures 7 and 8, simulated flash gelatinization profile was designed to cook corn and tapioca starch at one minute delayed shearing, as well as instant shearing respectively, while comparing sedimented starch dispersion to homogenous starch dispersion. This test was carried out for both excess water and limited water conditions.



	Time (HH:MM:SS)	Type (Temp Speed)	Value (°C) or (RPM)
1	00:00:00	Temp	95
2	00:00:00	Speed	960
3	00:00:10	Speed	160
4	00:01:00	Temp	95
5	00:07:00	Temp	95
6	00:11:00	Temp	50
7	00:13:00	End	
8			

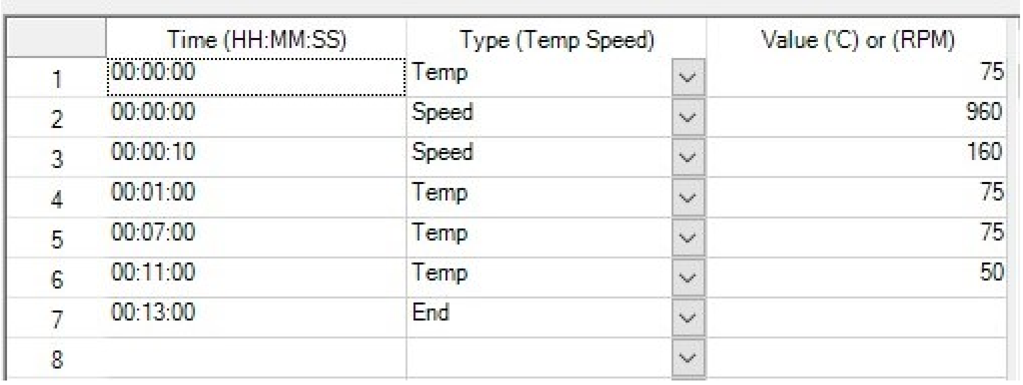
(a)



	Time (HH:MM:SS)	Type (Temp Speed)	Value (°C) or (RPM)
1	00:00:00	Temp	50
2	00:00:00	Speed	960
3	00:00:10	Speed	160
4	00:01:00	Temp	50
5	00:04:42	Temp	95
6	00:07:12	Temp	95
7	00:11:00	Temp	50
8	00:13:00	End	
9			

(b)

Figure 7: (a) Instant shearing for cornstarch gelatinization. (b) Delayed shearing for cornstarch gelatinization.



	Time (HH:MM:SS)	Type (Temp Speed)	Value ('C) or (RPM)
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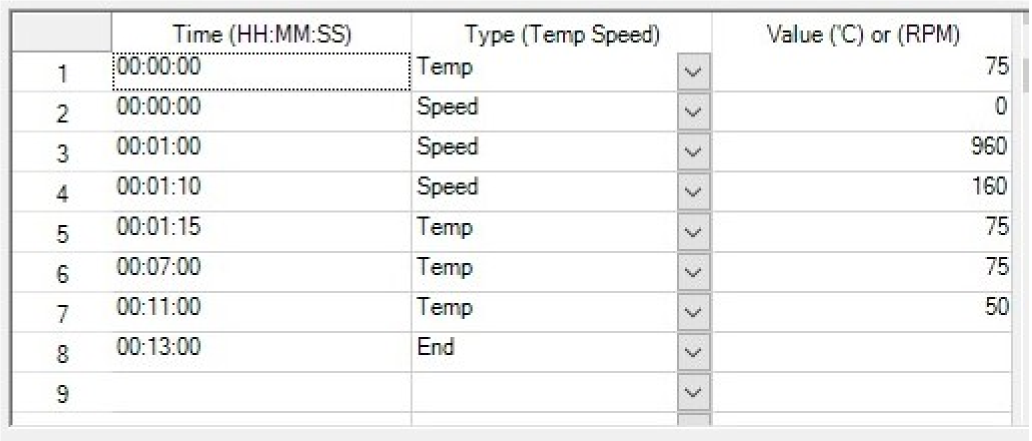
2	00:00:00	Speed	960
3	00:00:10	Speed	160
4	00:01:00	Temp	75
5	00:07:00	Temp	75
6	00:11:00	Temp	50
7	00:13:00	End	
8			

(a)



	Time (HH:MM:SS)	Type (Temp Speed)	Value ('C) or (RPM)
1	00:00:00	Temp	75
2	00:00:00	Speed	0
3	00:01:00	Speed	960
4	00:01:10	Speed	160
5	00:01:15	Temp	75
6	00:07:00	Temp	75
7	00:11:00	Temp	50
8	00:13:00	End	
9			

(b)

Figure 8: (a) Instant shearing for Tapioca starch gelatinization (b) Delayed shearing for Tapioca starch gelatinization

2.5.4 Statistical analysis

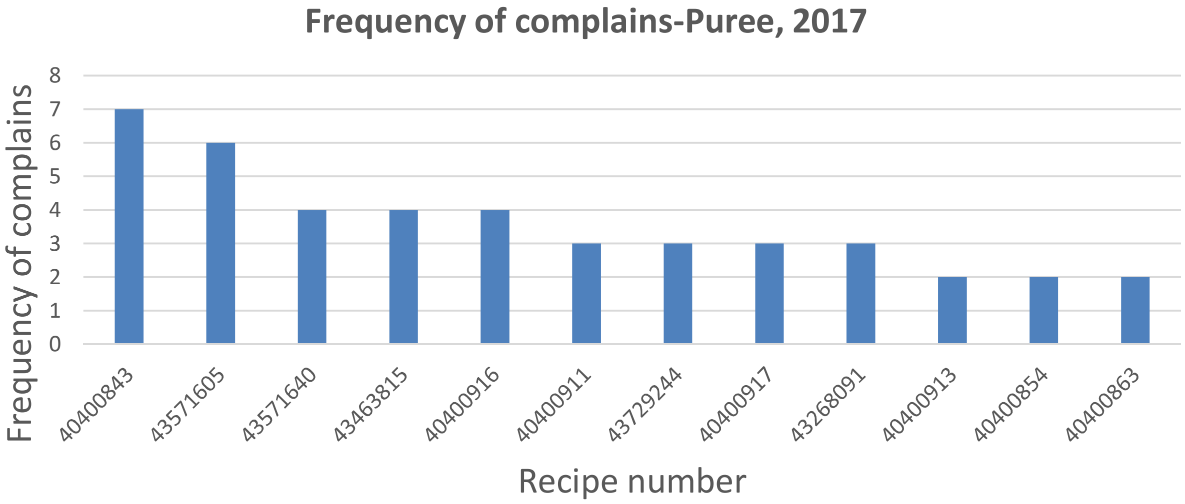
All data obtained from the RVA experiments were reported as means of triplicate assays. One way analysis of variance (ANOVA) and Tukey’s test at a significant level of $p < 0.05$ was used to determine the level of significance amongst mean values of triplicate assay using graph pad prims 7.05 for Windows (GraphPad Software, CA USA).

3 RESULTS AND DISCUSSION

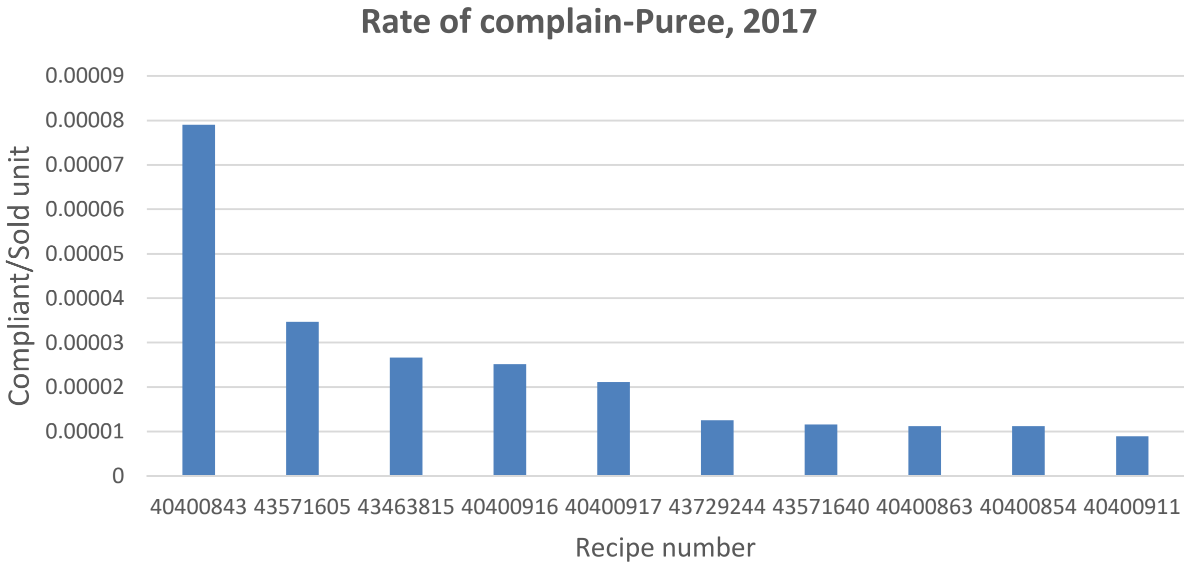
3.1 Problem investigation

Customer complains data base was assessed and analyzed (not all data shown). From all the consumer complaint categories of the textural organoleptic properties, the common complaint was about the product being either too watery (low viscosity), or had lumps developed in them. Hence, this thesis was designed to study these inconsistences.

The figure 9 in this section shows the results obtained from the consumer complaint data of the puree-matrix baby food products. From these results, it is observed that products with recipe number 40400843 and 43571605 had the highest correlating frequency and rate of complains for the year 2017. The products are named NBC and PM for this purpose of this work. Hence this study was designed and fashioned to solve the problem of rheological inconsistencies, as it relates to the textural organoleptic inconsistences of NBC and PM.



(a)

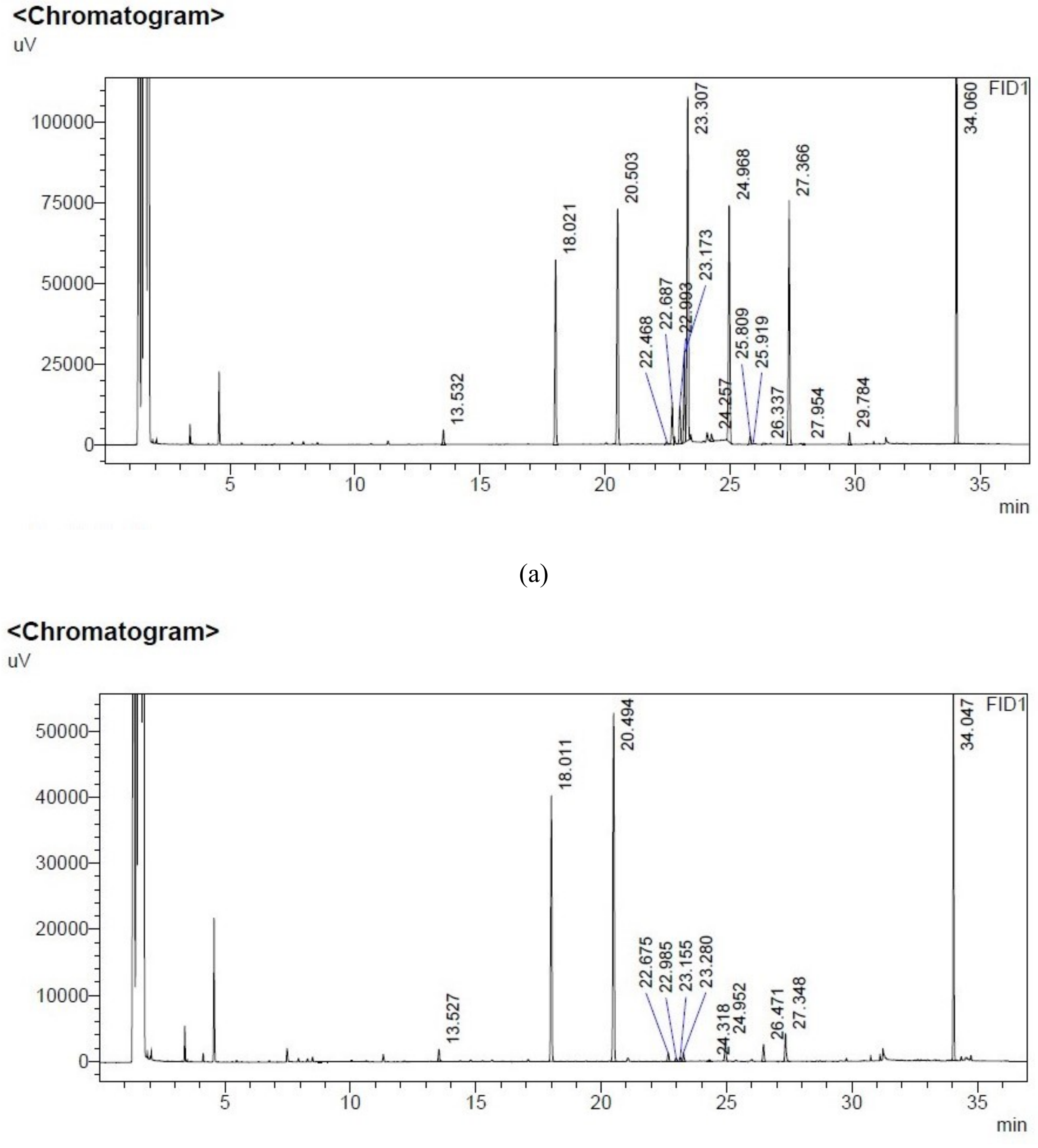


(b)

Figure 9: Consumer complaints of baby food product s with puree matrix (a) Frequency of complains (b) Rate of complaints.

3.2 Sugars and Acids content calculations

Figure 10 shows the peaks of the chromatogram of mango puree and NB, from where the peak areas used to calculate the correction factor (k) and quantification of sugars and acids of mango puree and NBC. Table's 4a & b shows the sugars and acids profile of the puree gelatinization medium of mango puree and NBC, results of which was utilized during the preparation of PMMS and NBMS respectively.



(a)

(b)

Figure 10: GC-FID chromatograms showing sugar and acid profiles of (a) MP (b) NBC

Table 4: (a) Sugar and acid content of samples of MP before starch was added to kettle. (b) Sugars and acid profile of NBC.

(a)

Analyte	**Compound**	**g/ 100 ml**
Sugars	Fructose	3.1766
	Glucose	2.2323
	Sucrose	3.2742
	Myo-inositol	0.0395
Acids	Malic acid	0.0887
	Citric acid	0.2766
	Quinic acid	0.0386
	Ascorbic acid	0.0556
	Galacturonic acid	0.0417

(b)

Analyte	**Compound**	**g/ 100 ml**
Sugars	Fructose	0.0780
	Glucose	0.1496
	Sucrose	1.1399
Acids	Malic acid	0.0546
	Citric acid	0.0283
	Quinic acid	0.0061

The pasting characteristics elucidated during this thesis work reflects and contemplates the shear thickening or dilatant, shear thinning or pseudoplasticity, non-Newtonian behavior of starch samples in excess and limited water conditions, which could give insight about the suitability of starch samples for food production application, as regards what medium they are optimally gelatinized.

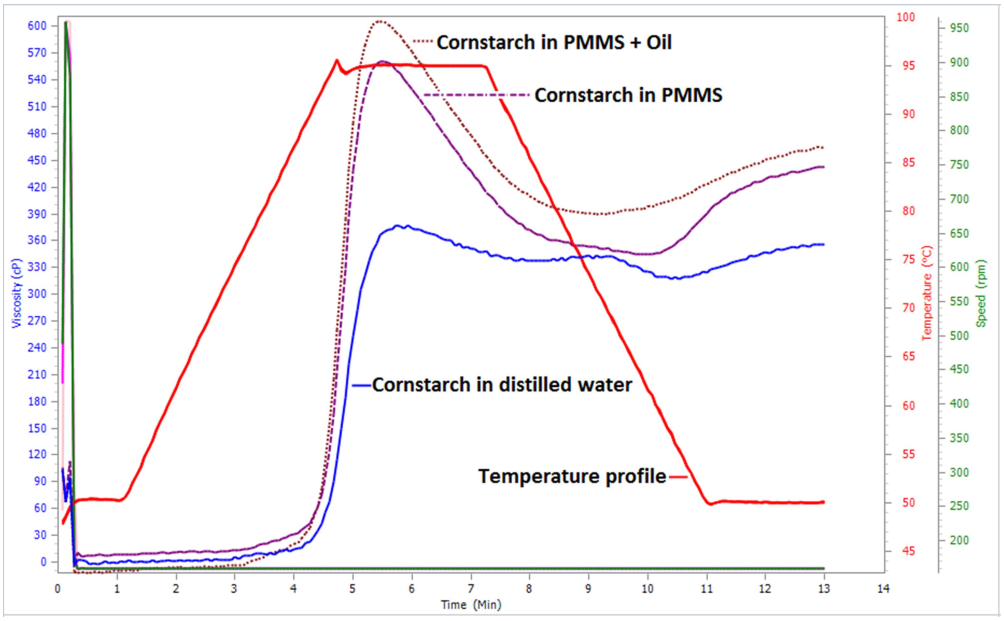
3.3 Effect of model solutions on the gelatinization of corn starch and tapioca starch

3.3.1 Effect of PMMS on corn and tapioca starch gelatinization

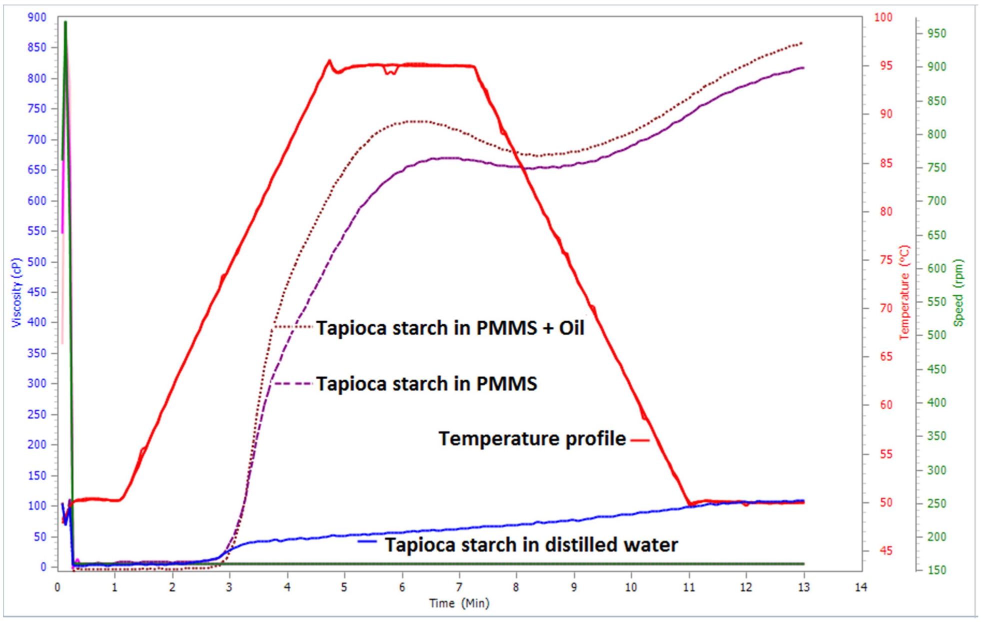
Excess water PMMS with and without oil solvation medium had a significant dilatant effect ($p < 0.0001$) on corn starch viscoelastic properties as compared to the control as shown in Figure 11a. The peak viscosity was observed to rise more significantly ($p < 0.0001$) in the PMMS with oil medium in contrast to PMMS without oil. The final pasting viscosity was also significantly increased ($p = 0.0009$ and $p = 0.0006$) for PMMS and PMMS-oil interphase, respectively in contrast to the control (Table 5a). Corn starch in PMMS had a significant increase ($p = 0.0008$) in the retrogradation propensity in contrast to the control, while corn starch in PMMS with rapeseed oil interphase impacted a significant reduction ($p = 0.0469$) in the retrogradation properties offset by the PMMS solution as shown in Table 5a.

Similarly as that of corn starch, tapioca starch showed a shear thickening behaviour in excess water PMMS with and without oil moiety observable in Figure 11b. As shown in Table 5b, PMMS and PMMS with oil had a significant and progressive increase ($p < 0.0001$ and $p < 0.0001$) on the peak viscosity of tapioca starch as compared to the control. Further, similar significant progressive ($p < 0.0001$ and $p < 0.0001$) shear thickening effect was observed for the final pasting viscosity of tapioca starch in these solvation environments in comparison to the control (Table 5b), as also visible on the RVA pasting spectra, Figure 11b. Table 5b, shows that PMMS had a significant increase ($p < 0.0001$) on the retrogradation tendencies of control tapioca starch; however when rapeseed oil was added, there was a significant reduction ($p < 0.0001$) in the retrogradation tendencies of tapioca starch offset by PMMS, similarly with corn starch.

This viscoelastic characteristics show that both corn and tapioca starch are suitable and may be applied for the production of PM, provided the cooking medium is in excess water. This also implies that addition of oil to this medium prior to gelatinization may retard the retrogradation tendencies of the starch type used as offset by the gelatinizing medium.



(a)



(b)

Figure 11: (a) RVA spectra showing the effect PMMS with and without oil on corn starch viscoelastic properties in excess water medium. (b) RVA spectra showing the effect PMMS with and without oil on tapioca starch viscoelastic properties in excess water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 5: (a) Eigenvalues of the effect of PMMS on the pasting and retrogradation properties of cornstarch (excess water medium) (b) Eigenvalues of the effect of PMMS on the pasting and retrogradation properties of Tapioca starch (excess water medium).

(a)

Samples	**Peak Viscosity (cP)**	**Final Viscosity (cP)**	**Setback Viscosity (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Cornstarch in distilled water	377.6 ± 2.1^{a}	364.6 ± 7.7^{a}	47.0 ± 7.0^{a}	5.64 ± 0.1	93.2 ± 0.9
Cornstarch in PMMS	562.6 ± 6.4^{b}	444.6 ± 2.5^{b}	102.3 ± 13.8^{b}	5.42 ± 0.1	92.1 ± 0.5
Cornstarch in PMMS + Oil	604.3 ± 1.1^{c}	451.3 ± 21.9^{b}	70.3 ± 3.5^{c}	5.47 ± 0.1	91.5 ± 0.0

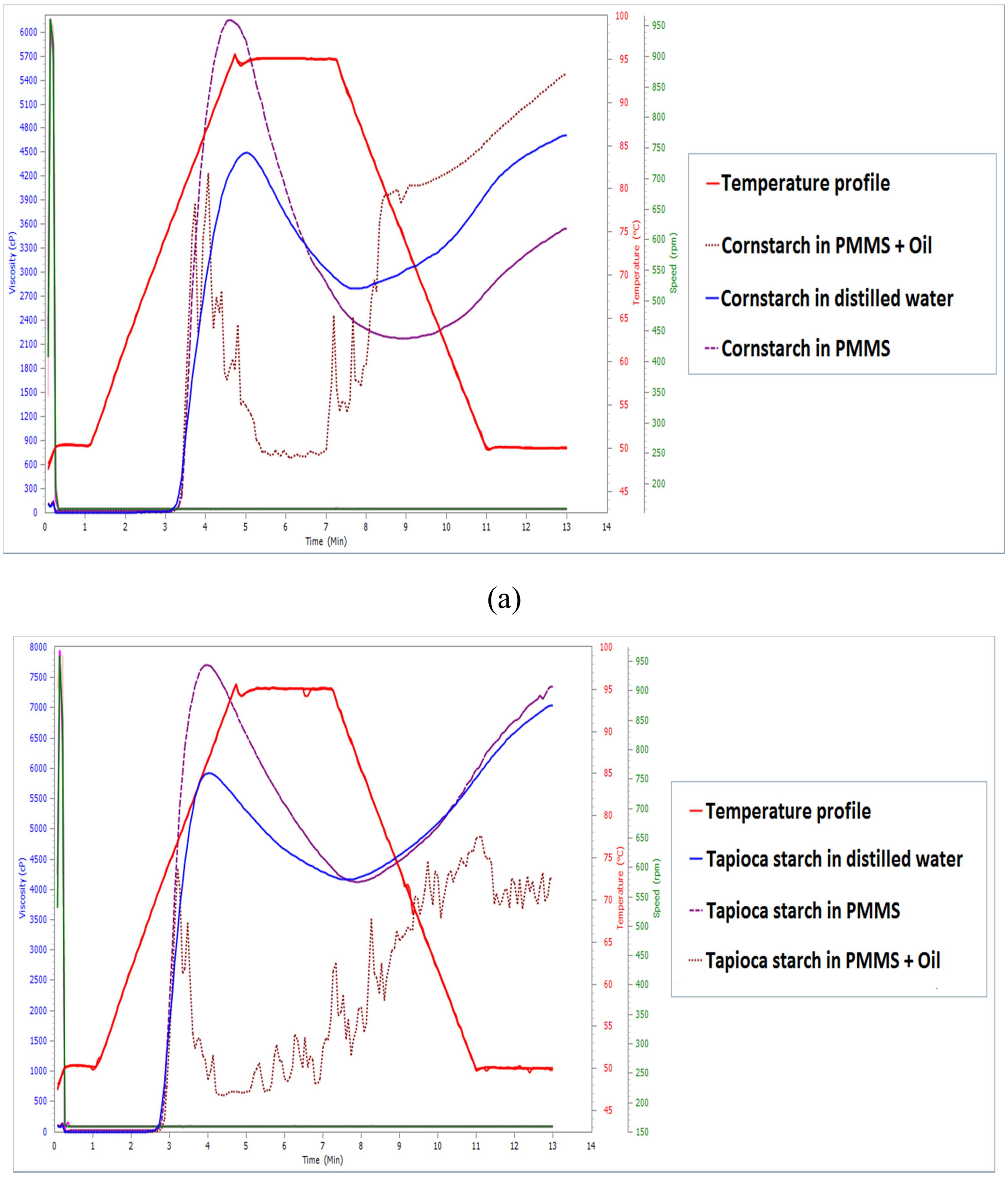
(b)

Sample in PMMS	**Peak Viscosity (cP)**	**Final Viscosity (cP)**	**Setback Viscosity (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Tapioca starch in distilled water	63.3 ± 0.6^{a}	108.3 ± 0.6^{a}	50.0 ± 1.0^{a}	7.0 ± 0.0	-
Tapioca starch in PMMS	675.6 ± 5.5^{b}	820.6 ± 4.7^{b}	162.6 ± 1.5^{b}	6.7 ± 0.1	75.8 ± 0.5
Tapioca starch in PMMS + Oil	730.0 ± 1.2^{c}	853.0 ± 21.9^{c}	180.3 ± 3.5^{c}	6.2 ± 0.1	75.0 ± 0.0

Results expressed as viscosity of starch sample (means ± SD; *n* = 3). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

In limited water medium, PMMS had a significant increase ($p = 0.0025$) on the peak viscosity of corn starch as compared to the control; however the peak viscosity of the PMMS in oil interphase had no significant influence ($p = 0.8615$) as compared to the control as shown in Table 6a. Although with an increased peak viscosity, PMMS had a significant ($p = 0.0490$) thixotropic behaviour on the final viscosity of cornstarch as compared to that cooked in distilled water as depicted in Figure 12a. The lipid interphase PMMS had an unprecedented and unstable influence on the viscoelastic properties of cornstarch in limited water medium, as shown in Figure 12a, as there was no reproducibility in replicate experiment in this gelatinizing medium. However, PMMS and PMMS in oil interphase had no significant influence ($p = 0.8472$ and $p = 0.1824$) on the retrogradation tendency of cornstarch gelatinized in this limited water cooking medium as compared to cornstarch cooked in distilled water as shown in Table 6a.

Limited water PMMS had a significant dilatant effect ($p < 0.0001$) on the peak viscosity of tapioca starch as shown in Table 6b and the viscoelastic RVA spectra in Figure 12b. The addition of 4 % (v/v) rapeseed oil to this system resulted in a significant shear thinning behaviour ($p = 0.0003$) on the peak viscosity of tapioca starch as compared to the control cooked in distilled water as shown in Figure 12b. Table 6b shows that PMMS had no significant effect ($p = 0.9477$) on the final viscosity of tapioca in limited water medium as compared to the control. Lipid addition to the PMMS medium caused a huge significant ($p = 0.0019$) shear thinning behaviour on the final pasting viscosity of tapioca starch as compared to both the control and PMMS without oil as illustrated in Table 6b and Figure 12b. On the other hand, PMMS with oil interphase had a reducing effect on the tendency of retrogradation of tapioca starch in limited water condition. Furthermore, as shown in Figure 12b, tapioca starch cooked in PMMS with oil interphase had a huge collapse on gelatinization of tapioca starch and also showed no chances of reproducibility similarly as in corn starch application. Nonetheless, cornstarch's gelatinization potential was not truncated as compared to tapioca starch which had a huge lag in its swelling capacity as shown in the pasting spectra in Figure 12 a & b respectively.



(a)

(b)

Figure 12: (a) RVA spectra showing the effect PMMS with and without oil on corn starch viscoelastic properties in limited water medium. (b) RVA spectra showing the effect PMMS with and without oil on tapioca starch viscoelastic properties in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 6: (a) Eigenvalues of the effect of PMMS on the pasting and retrogradation properties of cornstarch (Limited water medium). (b) Eigenvalues of the effect of PMMS on the pasting and retrogradation properties of Tapioca starch (Limited water medium).

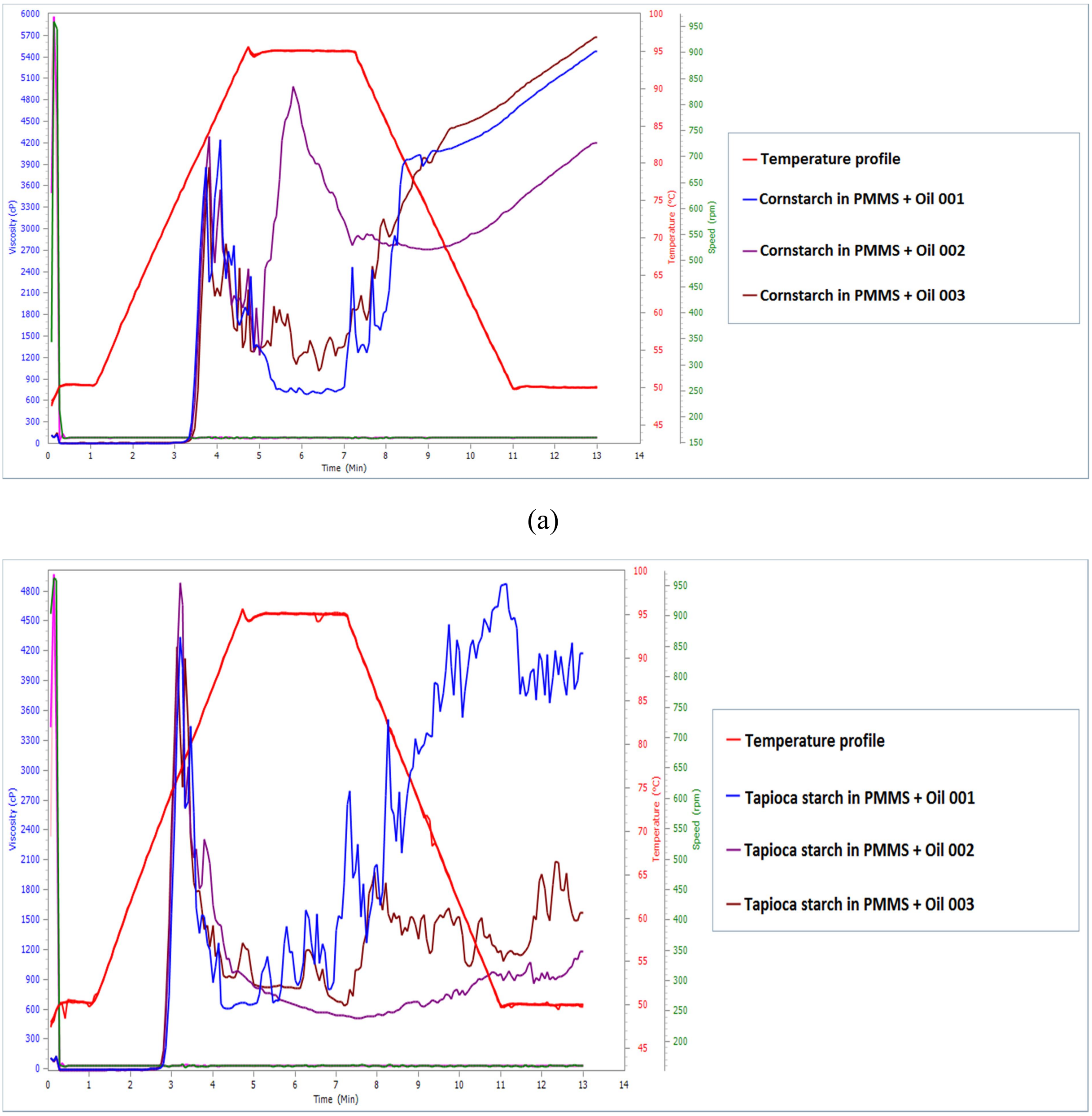
(a)

Sample in PMMS	Peak Viscosity (cP)	Final Viscosity (cP)	Setback Viscosity (cP)	Peak Time (min)	Pasting Temp (^{o}C)
Cornstarch in distilled water	4511.0 ± 34.7^{a}	4709.6 ± 30.0^{a}	1846.0 ± 60.0^{a}	5.0 ± 0.0	76.4 ± 0.4
Cornstarch in PM-MS	6121.0 ± 5.5^{b}	3549.0 ± 4.7^{b}	1356.6 ± 1.6^{a}	4.6 ± 0.1	77.6 ± 0.5
Cornstarch in PMMS + Oil	4367.6 ± 10.0 ^{bc}	5114.0 ± 5.3^{a}	3644.3 ± 4.7^{a}	4.5 ± 0.1	77.6 ± 0.5

(b)

Sample in PMMS	Peak (cP)	Final Viscosity (cP)	Setback (cP)	Peak Time (min)	Pasting Temp (^{o}C)
Tapioca starch	5968.0 ± 41.3^{a}	7093.6 ± 49.8^{a}	2907.0 ± 34.1^{a}	4.02 ± 0.0	69.2 ± 0.4
Tapioca starch in PMMS	7737.0 ±22.1^{b}	7334.6 ± 8.08^{a}	3201.3 ± 23.1^{a}	3.93 ± 0.0	70.1 ± 0.4
Tapioca starch in PMMS + Oil	4490.6 ± 345.6^{c}	2308.0 ± 1629.8^{b}	1660.3 ± 1494.8^{a}	3.18 ± 0.0	70.6 ± 0.5

Results expressed as viscosity of starch sample (means ± SD; *n* = 3). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).



(a)

(b)

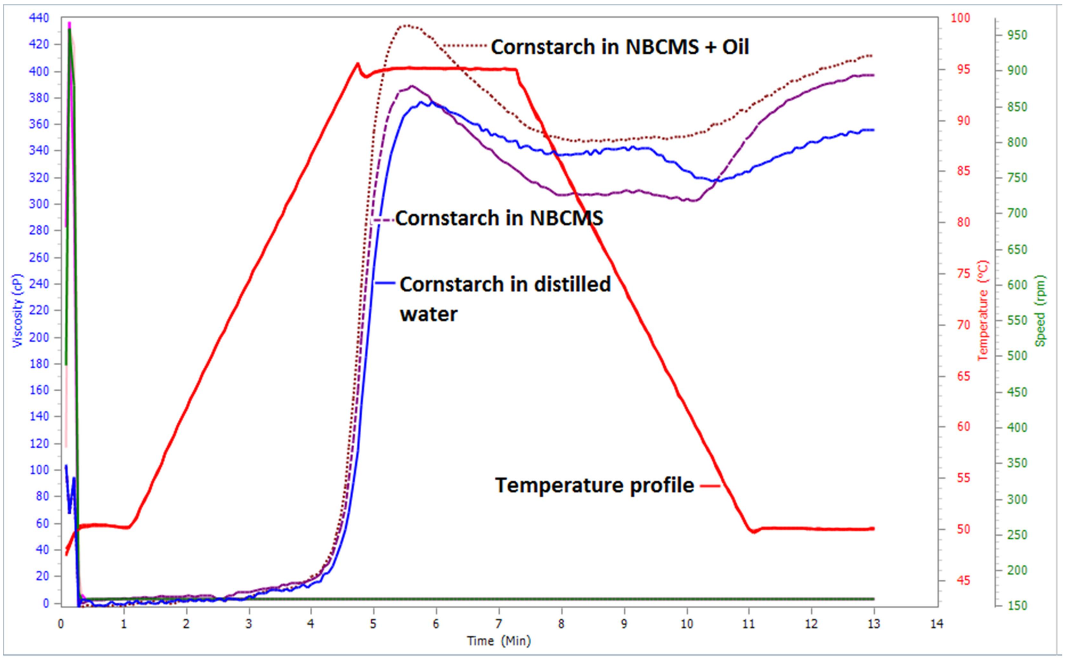
Figure 13: (a) RVA spectra showing the effect of PMMS with rapeseed oil on reproducibility of corn starch viscoelastic properties in limited water medium in three replicates. (b) RVA spectra showing the effect of PMMS with rapeseed oil on reproducibility of tapioca starch viscoelastic properties in limited water medium in three replicates.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

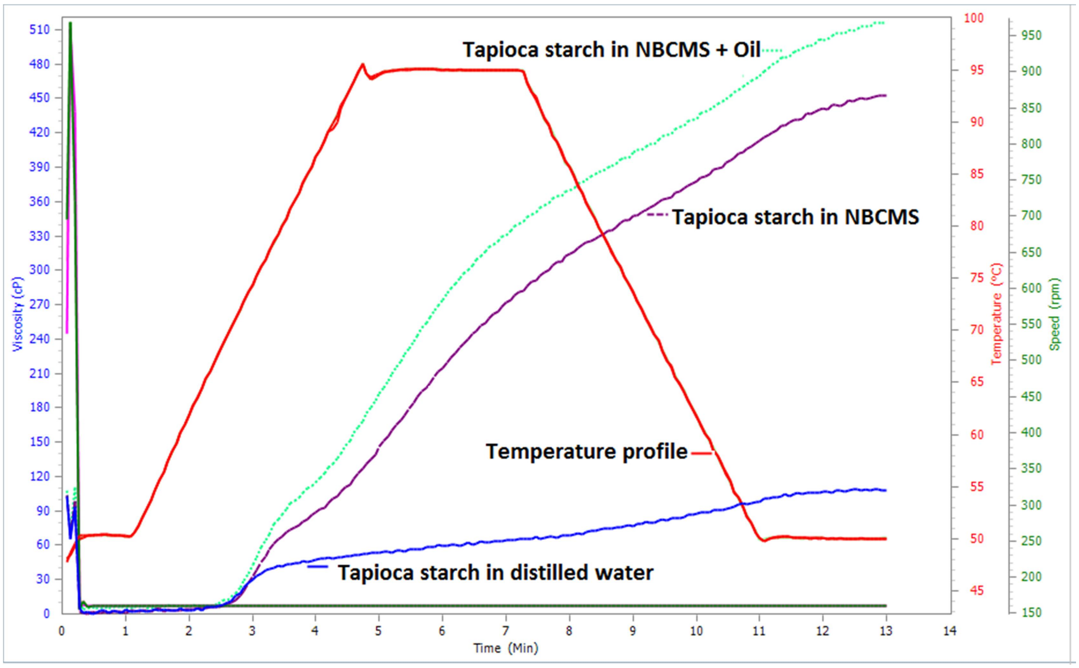
3.3.2 Effect of NBCMS on corn and tapioca starch gelatinization

As shown in Table 7a, the peak viscosity of cornstarch in excess water NBCMS was significantly increased ($p = 0.0041$) as compared to the control. Also the addition of oil to NBCMS resulted in further significant shear thickening behaviour which was similar to the results form PMMS experiments. NBCMS resulted in a significant dilatant behaviour ($p = 0.0036$) of the final viscosity of cornstarch in contrast to the cornstarch cooked in distilled water; however, further oil addition had no significant impact ($p = 0.8613$) on the final viscosity note of the cornstarch in NBCMS as shown in Table 7a and RVA spectra in figure 14a. The retrogradation susceptibility was increased significantly ($p = 0.0045$) in NBCMS, notwithstanding the addition of oil to NBMS significantly reduced ($p = 0.0269$) the amylose realignment tendency set off by NBCMS from Table 7a.

Figure 14b and Table 7b shows that excess water NBCMS had a fivefold significant ($p < 0.0001$) shear thickening effect on the pasting and final viscosity note of tapioca starch as compared to the control. Furthermore, NBCMS with lipid interphase further impacted inherent oil viscosity which had a significant increase ($p < 0.0001$) on the viscoelastic properties of tapioca starch in excess water NBCMS as shown in figure 14b. The retrogradation tendency of tapioca starch was increase significantly ($p = 0.0021$) by cooking in NBCMS, however cornstarch gelatinized in NBCMS with oil interphase significantly reduced (0.0296) the retrogradation tendency off set by NBCMS as shown in Table 7b.



(a)



(b)

Figure 14: (a) RVA spectra showing the effect NBMS with and without oil on corn starch viscoelastic properties in excess water medium. (b) RVA spectra showing the effect NBMS with and without oil on tapioca starch viscoelastic properties in excess water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 7: (a) Eigenvalues of the effect of NBMS on the pasting and retrogradation properties of cornstarch (excess water medium) (b) Eigenvalues of the effect of NBMS on the pasting and retrogradation properties of tapioca starch (excess water medium).

(a)

Samples	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Cornstarch in distilled water	377.6 ± 2.1^{a}	364.6 ± 7.7^{a}	47.0 ± 7.0^{a}	5.64 ± 0.1	93.2 ± 0.9
Cornstarch in NB model solution	395.6 ± 5.9^{b}	403.0 ± 6.0^{b}	96.0 ± 3.5^{b}	5.60 ± 0.1	93.2 ± 0.1
Cornstarch in NB model solution + Oil	433.0 ± 3.5^{c}	406.6 ± 11.0^{b}	69.6 ± 15.6^{ac}	5.51 ± 0.0	92.4 ± 0.1

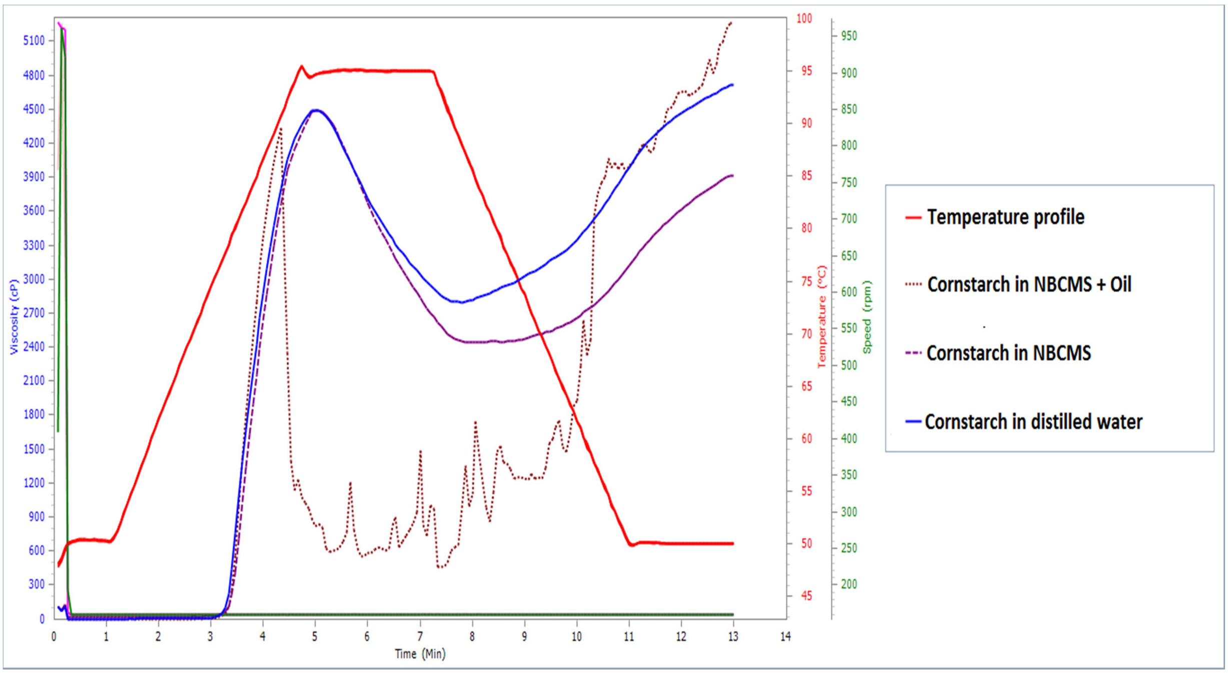
(b)

Sample	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Tapioca starch in distilled water	63.3 ± 0.6	108.3 ± 0.6^{a}	50.0 ± 1.0^{a}	7.0 ± 0.0	-
Tapioca starch in NB model solution	278.7 ± 5.9	458.0 ± 6.0^{b}	230.3 ± 2.9^{b}	7.00 ± 0.0	-
Tapioca starch in NB model solution + Oil	323.7 ± 6.4	509.33 ± 7.0^{c}	238.00 ± 2.7^{ac}	7.00 ± 0.0	-

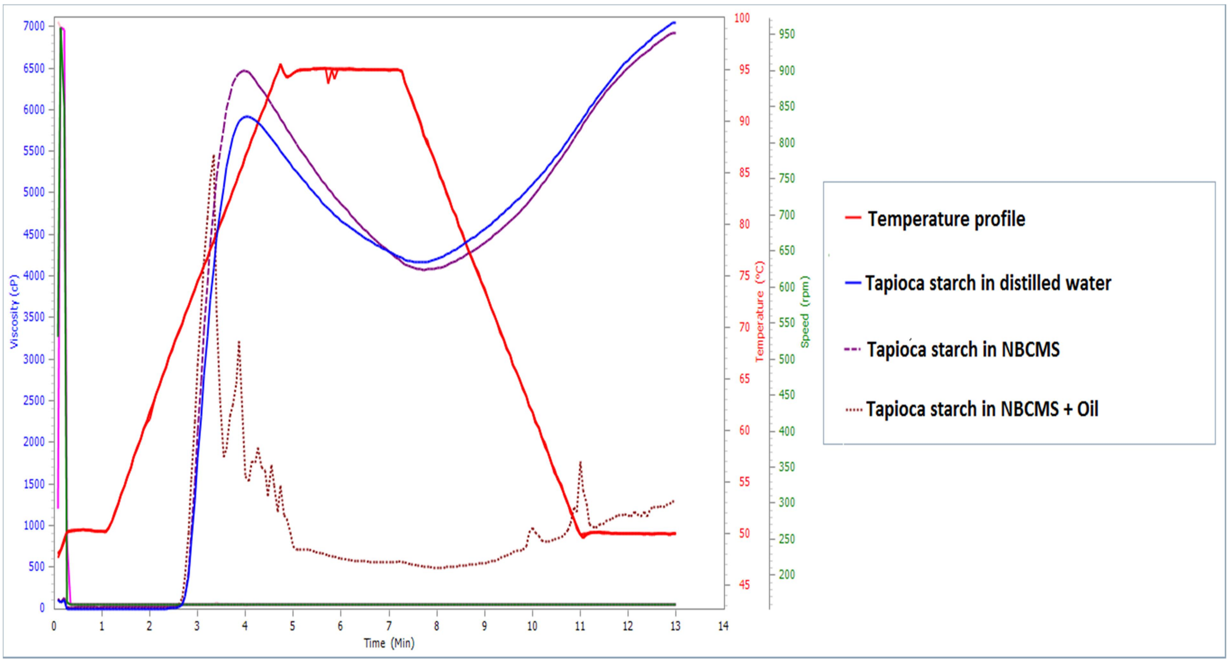
Results expressed as viscosity of starch sample (means ± SD; $n = 3$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

In limited water solvation environment, NBCMS and NBCMS with oil interphase had no significant effect on the peak viscosity of cornstarch in contrast to the control sample gelatinized in distilled water as shown in figure 15a. However, NBCMS had a significant ($p = 0.0224$) shear thinning influence on the final pasting viscosity of cornstarch in contrast to control cooked in distilled water as shown in Table 8a and viscoelastic spectra in Figure 15a. NBCMS with oil interphase had neither significant increase nor decrease ($p = 0.4244$) on the viscoelastic features of the final viscosity of cornstarch when compared to the cornstarch cooked in distilled water as statistically depicted in Table 8a. Nonetheless from in three replicate experiments, Figure 16a shows observable deviations in the viscoelasticity for cornstarch cooked in NBCMS with oil interphase as compared to the control. This indicates the inconsistent viscosity profile corn starch would impact when utilized for the production of the finished product NBC. The propensity for retrogradation of cornstarch was not significantly influenced ($p = 0.8622$ and $p = 0.0645$) by the NBCMS and NBCMS with oil interphase respectively as shown in Table 8a.

From Table 8b, it can be seen that NBCMS had no significant reduction ($p = 0.9590$) on the final viscosity of tapioca starch as compared to the control; however, a significant pseudo-plastic effect ($p = 0.0002$) was observed for tapioca starch cooked in NBCMS with oil interphase to the extent that the tapioca gelatinization was observed to collapse, as shown in Figure 15b. Further, there was a huge significant deviation in replicate pasting spectra of tapioca starch in NBCMS with oil environment, indicating that there is no chance of reproducibility of final product viscosity with this cooking environment, as depicted in Figure 16b. This result indicates the unsuitable of tapioca starch for use in NBCMS with oil interphase, as it has no functional desirability to the viscoelastic properties of NBC product or in retardation of retrogradation of tapioca starch if used for this application. The retrogradation tendencies of tapioca starch cooked in NBCMS had no significant effect ($p = 0.9992$) on the viscoelastic properties as compared to the control; however, the cooking in NBCMS with oil had a huge and significant decrease ($p = 0.0143$) in the retrogradation tendencies of tapioca starch as compared to NBMS and the tapioca starch cooked in distilled water.



(a)



(b)

Figure 15: (a) RVA spectra showing the effect NBMS with and without oil on corn starch viscoelastic properties in limited water medium. (b) RVA spectra showing the effect NBMS with and without oil on tapioca starch viscoelastic properties in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 8: (a) Eigenvalues of the effect of NBMS on the pasting and retrogradation properties of cornstarch (limited water medium). (b) Eigenvalues of the effect of NBMS on the pasting and retrogradation properties of tapioca starch (limited water medium).

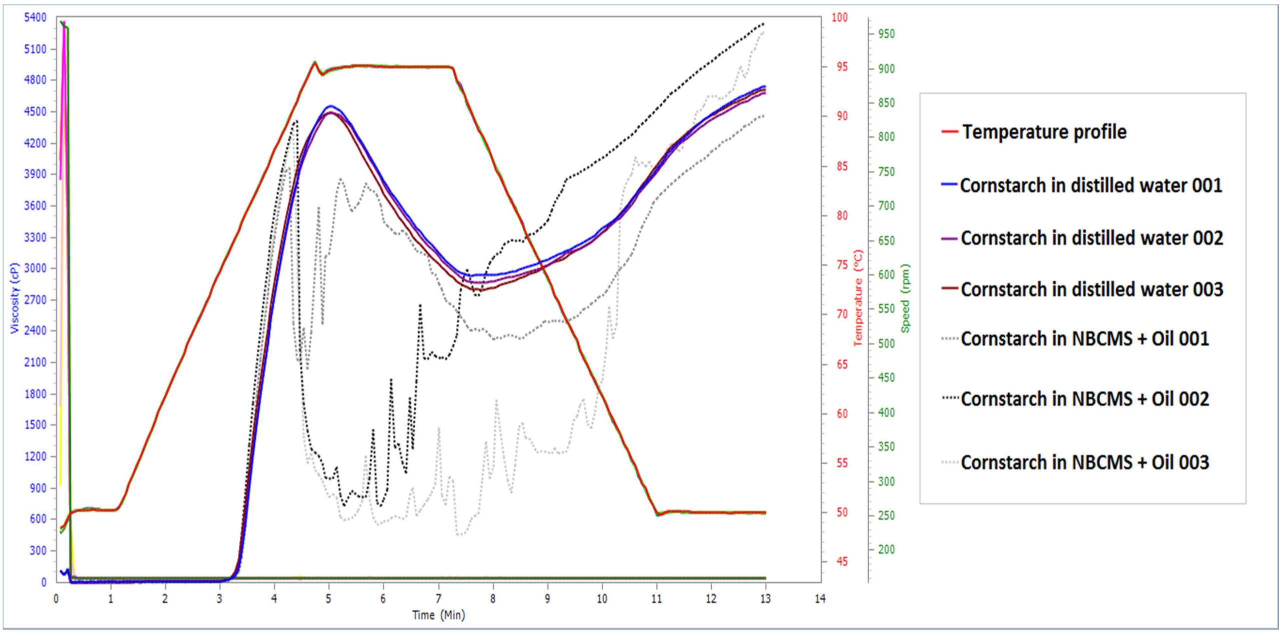
(a)

Sample in NBMS	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Cornstarch in distilled water	4511.0 ± 34.7^a	4709.6 ± 30.0^a	1846.0 ± 60.0^a	5.0 ± 0.0	76.4 ± 0.4
Cornstarch in NB model solution	4465.6 ± 40.6^a	3846.7 ± 59.2^b	1488.0 ± 28.2^a	5.0 ± 0.0	76.4 ± 0.4
Cornstarch in NB model solution + Oil	4239.3 ± 237.6^a	5019.7 ± 484.8^{ac}	3797.7 ± 1444.6^{ab}	4.3 ± 0.1	76.6 ± 0.5

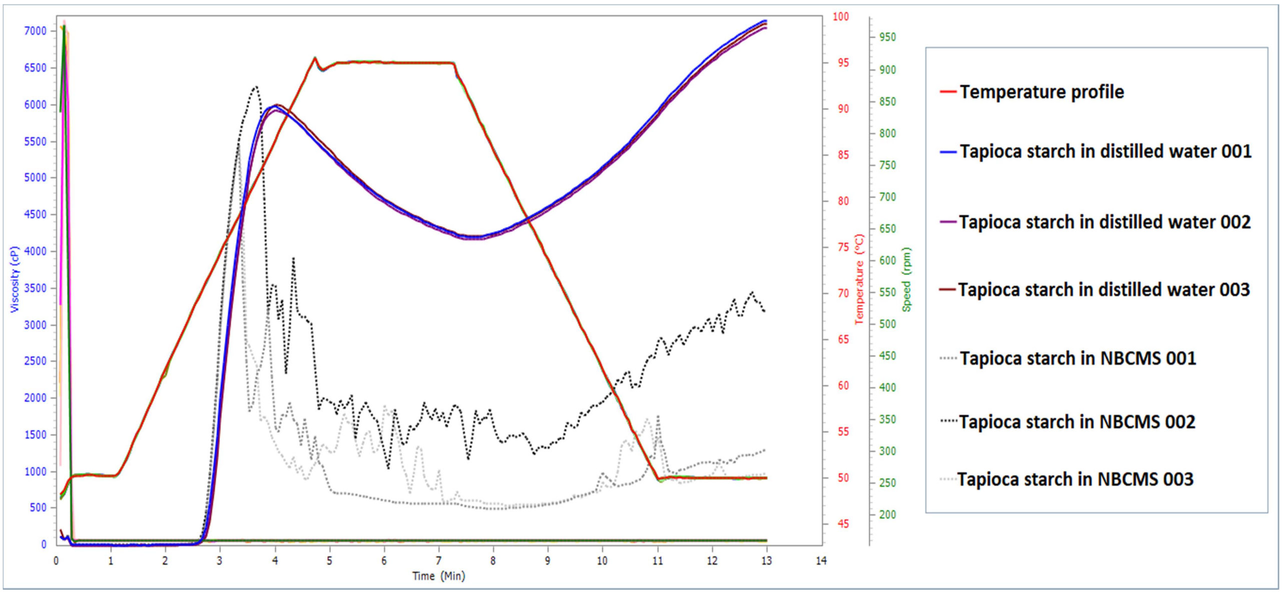
(b)

Sample in NBMS	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
Tapioca starch	5968.0 ± 41.3	7093.6 ± 49.8^a	2907.0 ± 34.1^a	4.0 ± 0.0	69.3 ± 0.4
Tapioca starch in NBMS	6451.7 ± 15.8	6937.0 ± 26.1^a	2923.7 ± 110.7^a	3.9 ± 0.0	69.4 ± 0.5
Tapioca starch in NBMS + oil	5732.0 ± 451.4	1814.6 ± 1200.2^b	1123.7 ± 906.1^b	3.4 ± 0.2	68.8 ± 0.0

Results expressed as viscosity of starch sample (means ± SD; $n = 3$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).



(a)



(b

Figure 16: (a) RVA spectra showing the effect of NBMS with rapeseed oil on reproducibility of corn starch viscoelastic properties in limited water medium in three replicates (b) RVA spectra showing the effect of NBMS with rapeseed oil on reproducibility of tapioca starch viscoelastic properties in limited water medium in three replicates.

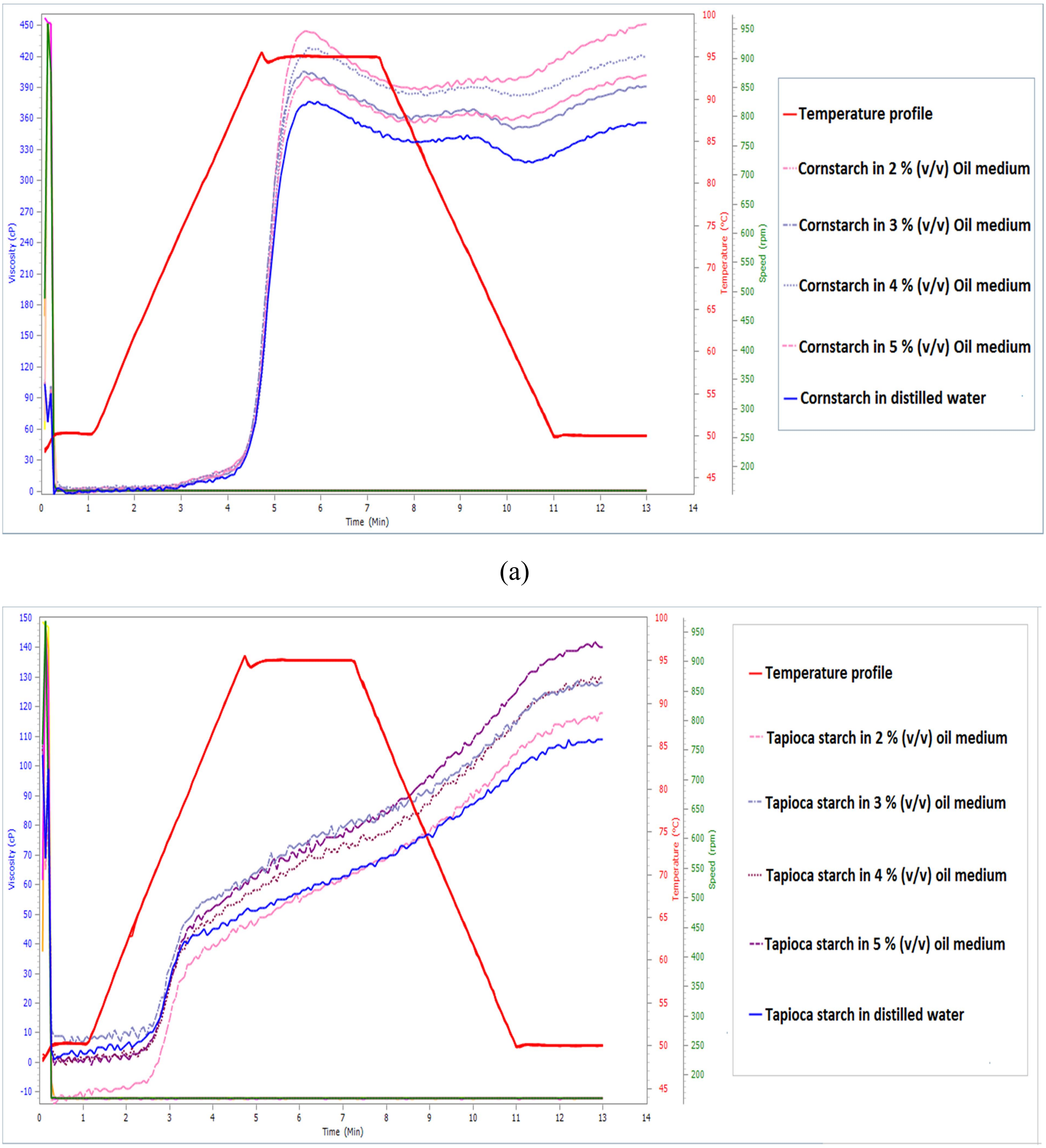
Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

The corn starch and tapioca starch samples cooked in PMMS and NBCMS excess water solvation environment may have had a dilatant behaviour due the sugar content of MP and NBC from the sugars and acids profile obtained from GC analysis. As shown in Table 4 a & b the total sugar profile of MP was 8.7 g/ 100 ml as compared to 0.5 g/ 100 ml of acids. It is important to note that the sucrose, glycerol and glucose have large density of hydroxyl groups per carbon. Also, hydrogen bonding occurs between starch to starch, as well as starch to solvent and this has importance in the determination of granule structure and plasticization (Perry and Donald, 2002). This means that change in hydroxyl group of starch molecule will inevitably have a significant impact on the gelatinization behaviour of the starches. The result from PMMS and NBCMS supports the studies by Perry and Donald (2002), which demonstrates that sugars enters into the starch granules and participate actively in the plasticization and gelatinization process. Plasticization is the process that changes the structure of a polymer making it easier to bend or more flexible. Sugars have been shown to facilitate the gelatinization of starch as effectively as water; hence their synergistic effect on swelling and solvent imbibition results in facilitation of total crystalline order and lamellar disruption (Donovan et al., 1979; Kirby *et al*., 1993; Forssel *et al*., 1997; Sala and Tomka, 1993). Therefore the plasticization action of sugars and excess water availability may be the reason for the shear thickening of tapioca and corn starch in PMMS and NBCMS excess solvation medium. This result indicates that what matters most is the ease at which the plasticizing solution enters into the starch granules, particularly into the growth ring of the starch granules. However, this phenomenon is not analogous to the limited water solvation medium, where there is an induced hindrance in the ingress of the plasticizing sugars; hence the plasticizing ability of the solvating medium becomes rendered dormant. This is because the external available solvent to the starch granule is readily depleted; hence corporative plasticization action is halted, leading to a significant thixotropic or non-significant dilatant behaviour of starches cooked in limited water PMMS and NBCMS medium. Further swelling will be largely dependent on the gelatinization driven by additional thermal endothermal energy than in excess water medium, which will elevate the granular swelling and molecular mobility leading to a biphasic gelatinization in limited water medium (Perry and Donald, 2002).

3.3.3 Effect of Lipids on the pasting and retrogradation properties of cornstarch and tapioca starch

As shown in Table 9a, the increasing concentration of rapeseed oil in water interphase is shown to have a significant dilatant effect (p = 0.0290, 0.0024, 0.0003) on the pasting and final viscosity of cornstarch as also illustrated by the RVA viscosity spectra in Figure 17a. The increase in viscosity observed in the pasting spectra in Figure 17a may be due to the progressive increase of the addition of rapeseed oil with inherent viscosity to the cooked corn starch solution, thus the starch-water system did not hinder water penetration into the starch granule, since sufficient water was available, which was required for corn starch swelling. Table 9a indicates that the retrogradation propensity of cornstarch in this medium was not significantly influenced by the increasing concentration of lipid in the cooking medium.

Similarly with cornstarch, Figure 17b; it was illustrate that rapeseed oil had a progressive increase on the viscoelastic properties of tapioca starch cooked in water-rapeseed oil interphase with increasing concentration of lipids in excess water medium. However on the contrary to cornstarch, 2 and 3 % (v/v) lipids had no significant increase or decrease (p = 0.1343, 0.9759) to the retrogradation tendencies. Notwithstanding, the increasing and higher concentrations from 4 to 5 % (v/v) lipids had a significant increase (p = 0.0161 and 0.0007) on the retrogradation propensity of tapioca starch in this medium as shown in Table 9b.



(a)

(b)

Figure 17: (a) RVA spectra showing the effect lipids on corn starch viscoelastic properties in excess water medium. (b) Graph of final viscosity of tapioca starch viscoelastic properties in water-oil interphase (excess water condition).

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 9: (a) Eigenvalues of the effect of lipids on the pasting and retrogradation properties of cornstarch (excess water medium). (b) Eigenvalues of the effect of lipids on the pasting and retrogradation properties of tapioca starch (excess water medium).

Sample in % (v/v) Lipids	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
CS in 0	377.6 ± 2.1	364.6 ± 7.7^{a}	47.0 ± 7.0^{a}	5.64 ± 0.1	93.2 ± 0.9
CS in 2	399.3 ± 4.7	403.0 ± 19.5^{a}	53.0 ± 15.7^{a}	5.7 ± 0.0	93.5 ± 0.5
CS in 3	406.3 ± 4.2	408.7 ± 24.0^{b}	57.0 ± 23.5^{a}	5.7 ± 0.1	93.5 ± 0.5
CS in 4	426.7 ± 2.1	429.0 ± 8.2^{c}	50.7 ± 11.0^{a}	5.9 ± 0.1	93.5 ± 0.5
CS in 5	440.0 ± 5.0	447.7 ± 3.1^{d}	70.7 ± 8.0^{a}	5.7 ± 0.0	92.7 ± 0.6

(b)

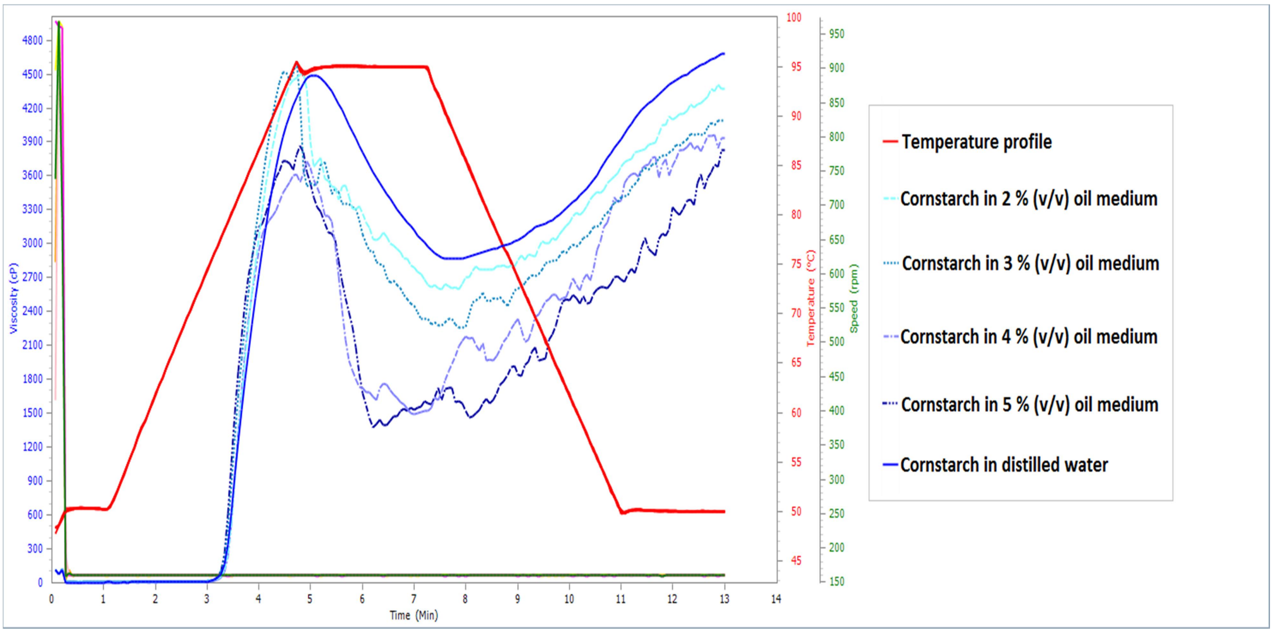
Sample in % (v/v) Lipids	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
TS in 0	63.3 ± 0.6	108.3 ± 0.6^{a}	50.0 ± 1.0^{a}	7.0 ± 0.0	-
TS in 2	63.3 ± 1.5	113.7 ± 3.8^{a}	57.7 ± 3.8^{a}	6.9 ± 0.1	-
TS in 3	75.3 ± 8.1	122.3 ± 13.4^{a}	51.7 ± 6.7^{a}	6.8 ± 0.1	-
TS in 4	75.7 ± 1.5	130.0 ± 1.0^{b}	61.7 ± 0.6^{b}	6.9 ± 0.0	-
TS in 5	77.7 ± 0.6	139.0 ± 1.7^{c}	68.0 ± 1.7^{c}	6.9 ± 0.1	-

Results expressed as viscosity of starch sample (means ± SD; $n = 3$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

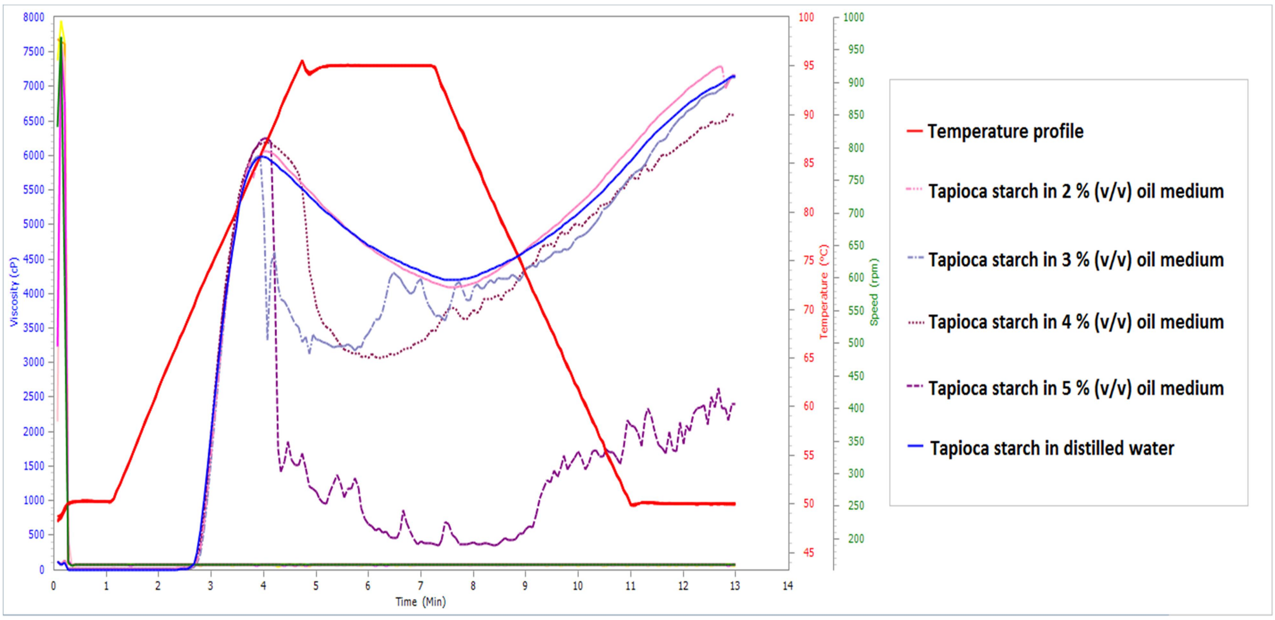
As shown in Figure 18a, the increasing content of lipid in the water-oil gelatinization matrix of cornstarch in limited water solvation condition caused a shear thinning effect on the peak and final viscosity of cornstarch paste which was more pronounced significantly at 5 % concentration of rapeseed oil. Table 10a shows that the setback viscosity had neither significant increase nor decrease ($p > 0.005$), indicating that lipids do not have an undesirable impact on the amylose realignment of cornstarch in limited water medium. The viscoelastic pasting spectra shown in Figure 19a indicate there was an observable inconsistency in viscoelastic profile of cornstarch cooked in water-oil moiety in contrast to distilled limited water gelatinization medium, indicating impossibility in reproducibility of viscosity profile of food products gelatinized in lipid-water moiety.

The final pasting viscosity of tapioca starch in water-oil interphase resulted in an inconsistent viscosity profile especially at higher concentrations of 5% (v/v) of rapeseed oil, where the gelatinization potential of tapioca starch was truncated as compared to the control, as depicted in pasting spectra in Figure 18b, where average final viscosity of control tapioca starch solution and tapioca starch in 5% rapeseed oil was 7093.67 and 3156.67 cP respectively. This indicates that at higher concentrations of rapeseed oil, tapioca starch gelatinization would experience a truncation and collapse, which is caused by lipids competing with water absorption by the starch granules, thereby hindering the water imbibition tapioca starch requires for the desired pasting kinetics. It is also worthy of mention that at 5 % (v/v) rapeseed oil in limited water medium, there were more inconsistent pasting profiles for tapioca starch as compared to the control, as shown in Figure 19b. Similarly with cornstarch, rapeseed oil had no significant influence on the retrogradation tendencies of tapioca starch as shown in Table 10b.

Notwithstanding the pasting temperature of cornstarch in distilled water and that of varying concentrations of lipid had no significant different as shown in Table 10a & b. The reason for the irreproducibility in the pasting spectra's of limited oil-water moiety where the starch samples have been cooked may be due to the immiscibility and thermal-instability of oil and water interphase of oil and water, as well as an uneven distribution of heat during cooking of starch samples, because when oil is poured into a medium containing water, the oil is immiscibly and unevenly distributed in the gelatinizing medium. It is important to note that oil and water have different boiling points and surface tensions; hence even heat transfer to the starch granule during gelatinization is unlikely.



(a)



(c)

Figure 18: (a) RVA spectra showing the effect lipids on corn starch viscoelastic properties in limited water medium (b) RVA spectra showing the effect lipids on tapioca starch viscoelastic properties in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra’s are illustrations from one experiment test run.

Table 10: (a) Eigenvalues of the effect of lipids on the pasting and retrogradation properties of cornstarch (limited water medium). (b) Eigenvalues of the effect of lipids on the pasting and retrogradation properties of tapioca starch (limited water medium).

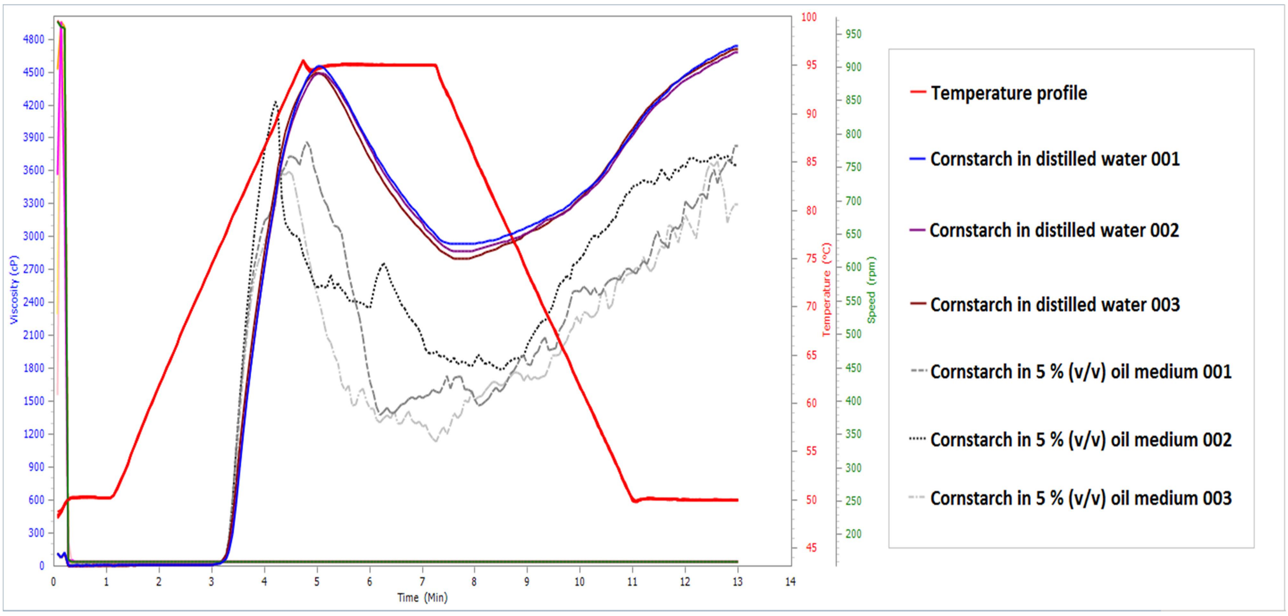
(a)

Sample in % (v/v) Lipids	**Peak Viscosity (cP)**	**Final Viscosity (cP)**	**Setback Viscosity (cP)**	**Peak Time (min)**	**Pasting Temp (°C)**
CS in 0	4511.0 ± 34.7	4709.6 ± 30.0^{a}	1846.0 ± 60.0^{a}	5.0 ± 0.0	76.4 ± 0.4
CS in 2	4508.3 ± 44.6	4270.7 ± 124.1^{a}	1869.3 ± 348.2^{a}	4.8 ± 0.1	76.9 ± 0.0
CS in 3	4358.7 ± 597.7	4134.0 ± 105.5^{a}	2171.7 ± 411.8^{a}	4.5 ± 0.3	76.4 ± 0.4
CS in 4	3921.3 ± 167.1	4266.0 ± 377.1^{a}	2557.3 ± 683.5^{a}	4.5 ± 0.4	76.6 ± 0.4
CS in 5	3897.7 ± 323.1	3592.3 ± 269.8^{b}	2160.7 ± 293.5^{a}	4.5 ± 0.3	76.1 ±0.0

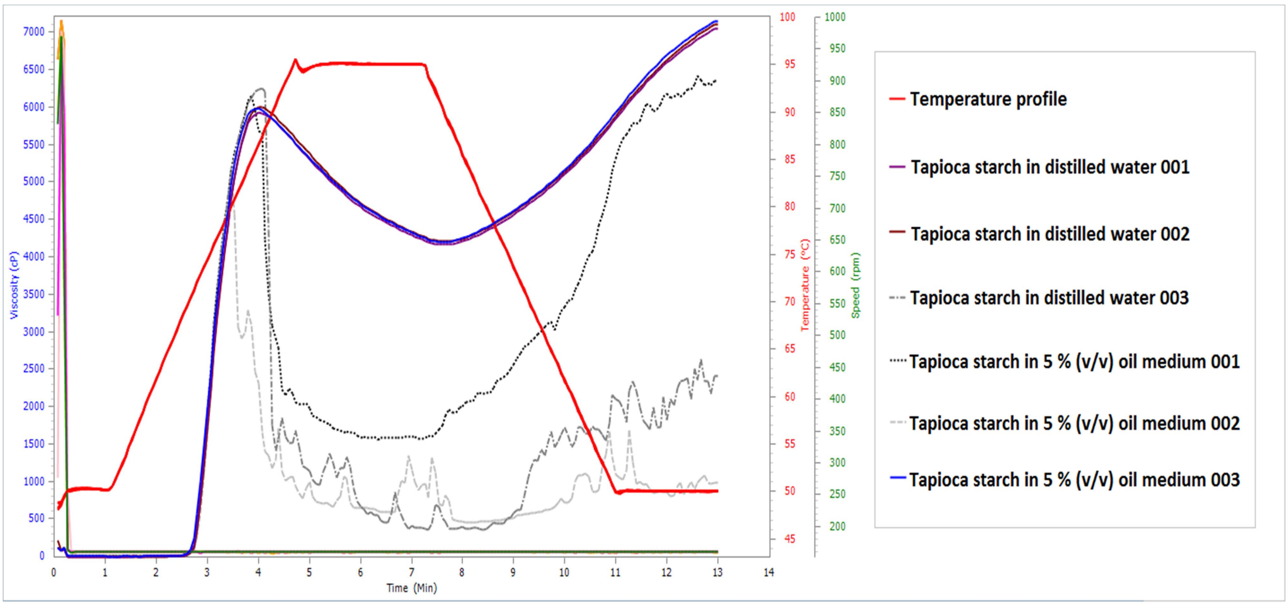
(b)

Sample in % (v/v) Lipids	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (°C)**
TS in 0	5968.0 ± 41.3	7093.7 ±49.8^{a}	2907.0 ±34.1^{a}	4.0 ± 0.0	69.3 ± 0.4
TS in 2	6078.3 ± 78.6	7362.0 ±175.9^{a}	3660.7 ± 980.2^{a}	4.1 ± 0.0	69.57 ± 0.1
TS in 3	5980.3 ± 141.3	7528.3 ±349.9^{a}	3798.7 ±251.9^{a}	4.0 ± 0.0	69.9 ± 0.5
TS in 4	6145.7 ± 196.0	7498.0 ±816.8^{a}	3557.7 ±41. 9^{a}	3.9 ± 0.2	69.6 ± 0.0
TS in 5	5518.7 ± 545.9	3156.7 ±2827.2^{b}	2334.0 ± 2206.3^{a}	3.6 ± 0.2	69.6 ± 0.1

Results expressed as viscosity of starch sample (means ± SD; $n = 3$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).



(a)



(b)

Figure 19: (a) RVA spectra showing the effect of 5 % (v/v) lipid on cornstarch starch apparent viscosity reproducibility in limited water medium. (b) RVA spectra showing the effect of 5 % (v/v) lipid on cornstarch starch apparent viscosity reproducibility in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

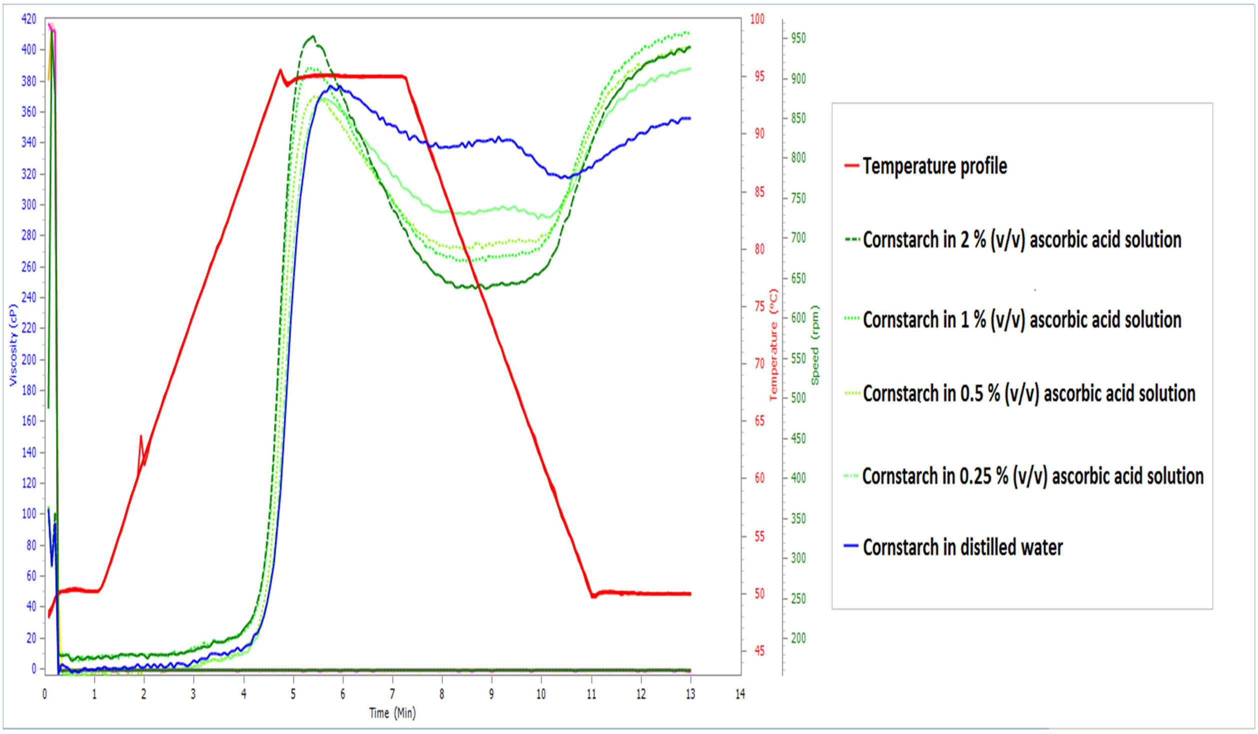
Further according to Putseys *et al*. (2010) lipids cooked with starch in limited water medium have a pseudo plastic viscoelastic properties on starch samples, because they are capable of having interactions with starches and forming inclusion complexes resulting in amylose helical cavity entrapment called amylose-lipid complexes. According to Blazek (2008), the driving force for the formation of this complexes is the hydrophobic nature of lipids which involves the water-oil moiety to transfer hydrophobic guest molecules from moiety to the less polar region of the amylose helix, and then minimizes the dipole-dipole interactions, as well as enthalpic and entropic parameters required for solvation, which causes a resultant shear thinning or truncation in gelatinization as shown in Figures (13, 14, 16, 17). On the other hand, this phenomenon was not so in excess water medium, where starch granules have enough external water for starch imbibition required for starch to swell to its maximal gelatinization capacity, while the oil impacts its inherent viscosity to the cooked starch samples giving it a dilatant behaviour, as shown in results of all excess oil-water moieties.

The starch-water environment where the starch is cooked would hinder the penetration of water into starch granules, which would obstruct starch granule swelling especially in limited water medium, which in turn would inhibit amylose leaching during cooking. This would cause a constraint and result in more sluggish amylose retrogradation. According to (Copland *et al.*, 2009), the presence of free lipids in starches or the addition of lipids to starch or starch-based food retards the retrogradation of starch based food even during storage. The shorter the fatty acid chain of the lipids, that is, added monoglycerides (polar lipids), the more it had the ability to effectively retard retrogradation, improve freeze-thaw stability and reduce stickiness (Germani *et al.*, 1983). This explains why long chain polyunsaturated rapeseed oil used in this experiment was unable to significantly reduce the retrogradation tendencies of corn and tapioca starch gelatinized in oil-distilled water medium; however, it had a huge significant reduction on the corn and tapioca starch cooked in PMMS and NBMS. According to Putseys *et al.*, (2010), Lipids have also been reported to form complexes with amylopectin, which will hinder retrogradation in a more direct way.

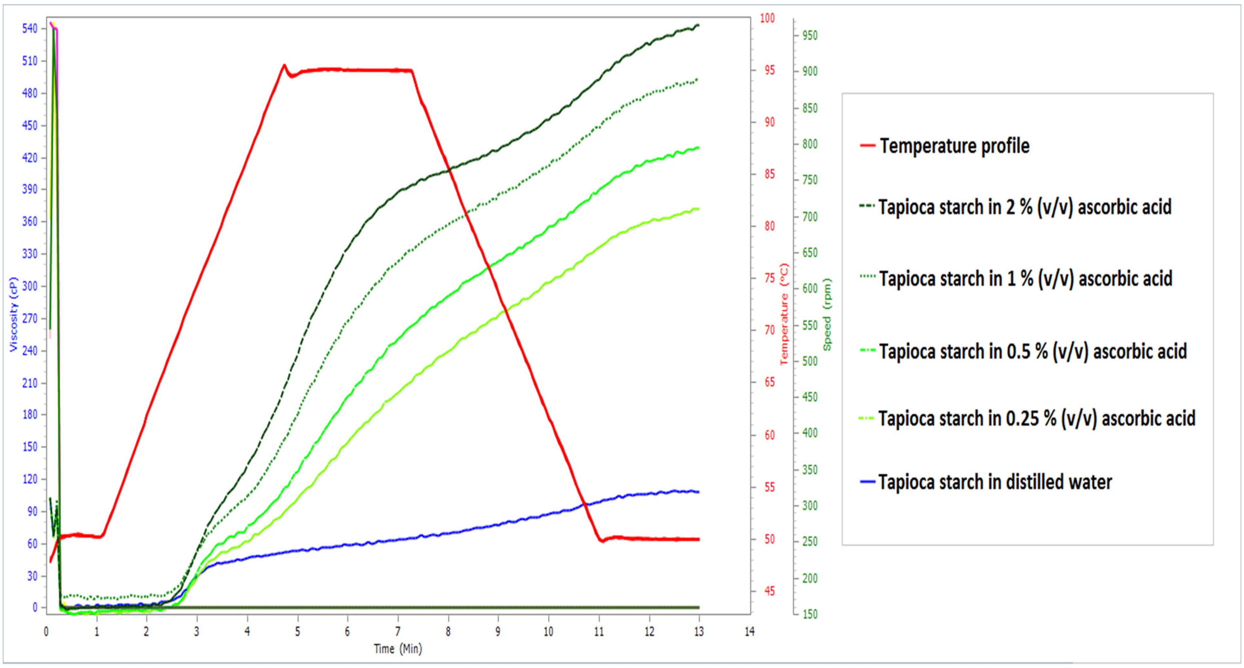
3.3.4 Effect of Ascorbic acid on pasting and retrogradation

From the results obtained, it was observed that ascorbic acid had a significant shear thinning effect ($p = 0.0015, 0.0117, 0.0005, 0.0076$) on the viscoelastic properties of cornstarch in excess water system at all concentrations tested as shown in Figure 20a. The maximum shear thickening behaviour was observed at 0.25 % (w/v) concentration. As shown in Table 11a, ascorbic acid had a continuous significant increase in the retrogradation tendency ($p < 0.0001$) of cornstarch in excess water ascorbic acid solution, with corresponding increase in ascorbic acid concentration.

In excess water condition, as shown in Table 11b, a significant increase ($p < 0.001$) in the final viscosity was observed for tapioca starch cooked with increasing concentration of ascorbic solution as compared to tapioca starch cooked in distilled water. Furthermore, as observed by Figure 20b and Table 11b, there was a fivefold increase in the viscosity of the final paste at 2 % (w/v) ascorbic acid solution. This indicates a more significant impact on the viscoelasticity of tapioca starch than cornstarch in excess water ascorbic acid solvation medium. Ascorbic acid had a significant increase ($p < 0.0001$) in the retrogradation tendency of tapioca starch from 0.25 to 2 % (w/v) ascorbic acid solution. However, with increased retrogradation tendency, at 2 % (w/v) ascorbic acid solution, a significant decrease ($p = 0.0001$) in setback viscosity was observed as compared to 0.25 % (w/v) ascorbic acid solution. This indicates that 2 % (w/v) ascorbic acid gave the most significant increase in pseudo-plasticity and the least tendency for retrogradation of tapioca starch in excess water medium.



(a)



(b)

Figure 20: (a) RVA spectra showing the effect ascorbic acid on corn starch viscoelastic properties in excess water solvation conditions (b) RVA spectra showing the effect ascorbic acid on tapioca starch viscoelastic properties in excess water solvation conditions.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 11: (a) Eigenvalues of the effect of Ascorbic acid (AA) on the pasting and retrogradation properties of cornstarch (CS) (excess water medium) (b) Eigenvalues of the effect of Ascorbic acid (AA) on the pasting and retrogradation properties of tapioca starch (TS) (excess water medium).

Sample in % (w/v) AA	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
CS in 0	377.6 ± 2.1	364.6 ± 7.7^{a}	47.0 ± 7.0^{a}	5.64 ± 0.1	93.2 ± 0.9
CS in 0.25	372.3 ± 4.2	402.3 ± 12.7^{b}	110.0 ± 11.3^{b}	5.5 ± 0.1	92.9 ± 0.5
CS in 0.5	369.3 ± 0.6	392.3 ± 7.5b^{c}	119.3 ± 9.2^{bc}	5.45 ± 0.0	92.4 ± 0.5
CS in 1	386.0 ± 2.6	408.0 ± 6.1^{bcd}	147.7 ± 8.0^{d}	5.4 ± 0.0	91.9 ± 0.5
CS in 2	404.3 ± 4.0	394.3 ± 9.3^{bcde}	160.0 ± 4.6^{de}	5.3 ± 0.1	91.1 ± 0.5

(b)

Sample in % (w/v) AA	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
TS in 0	63.3 ± 0.6	108.3 ± 0.6a	50.0 ± 1.0a	7.0 ± 0.0	-
TS in 0.25	207.3 ± 5.7	378.7 ± 6.5b	214.7 ± 2.1b	7.0 ± 0.0	-
TS in 0.5	255.0 ± 5.2	431.3 ± 3.2c	227.0 ± 2.0c	7.0 ± 0.0	-
TS in 1	321.3 ± 2.5	491.0 ± 1.7d	221.7 ± 0.6bcd	7.0 ± 0.0	-
TS in 2	387.0 ± 1.7	537.3 ± 5.5e	195.3 ± 7.0e	7.0 ± 0.0	-

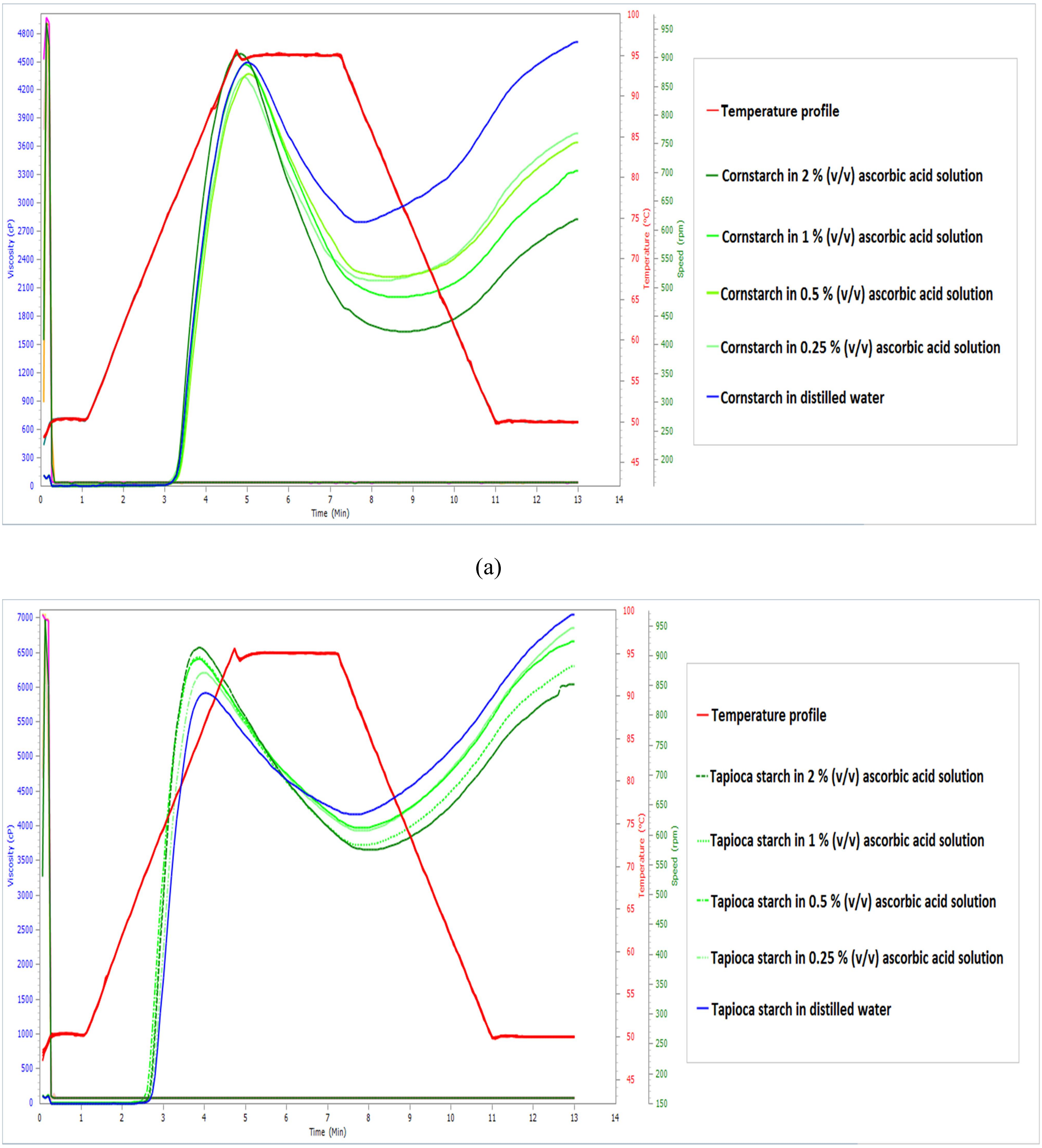
Results expressed as viscosity of starch sample (means ± SD; *n* = 3). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

In limited water medium, there was no significant difference in the water holding capacity as indicated by the peak viscosity of corn starch as observed in the gelatinization spectra in Figure 21a, as a significant progressive shear thinning effect ($p < 0.001$) was observed in the final pasting viscosity of cornstarch, with corresponding increase from 0.25 to 2 % (w/v) ascorbic acid concentration in contrast to the control, as shown in Table 12a. The retrogradation propensity decreased significantly ($p < 0.001$) with increasing concentration of ascorbic acid Table 12a.

In limited water system, ascorbic acid had a significant progressive reduction ($p < 0.001$) on the final pasting viscoelasticity of tapioca starch, as depicted in table 12b. Thus, the more ascorbic acid added in limited water gelatinizing environment, the more resultant shear thixotropic effect was observed Figure 21b. This similar phenomenon was observed for tapioca and corn starch cooked in an environment where the acidity of the solvation environment was adjusted to pH 2.5 with citric acid, shown in Figure 22 a & b and Table 13 a & b. As observed in Table 12b, the more the apparent viscosity of tapioca starch was reduced with increasing concentration of ascorbic acid, the more there was a significant decrease in the setback value indicating a corresponding reduction in amylose realignment, thus a reduced retrogradation tendency. Nonetheless, ascorbic acid at 0.25 % had no significant effect ($p = 0.1596$) on the retrogradation of tapioca starch solution as compared to the control as depicted in Table 12b.

According to Madoka *et al.* (2004), starch gelatinized in acidic medium results in the hydrolysis of amylose and amylopectin which causes a concurrent thioxtrophy in the viscoelastic properties of the starch paste. This occurs because acids enter into the starch granules and causes the hydrolysis of glucose chains in the starch granules and consequently the glucose chains leaches out and causes more glucose chains entanglement in contrast to the control. Furthermore, the acids cause the precipitation of starches which results in the reduction in the degree of polymerization of glucose molecules and cause a lag in the apparent viscosity of the resultant starch paste.

It is however important to note that no study has shown the shear thinning effect of acids on starch granules, when the acids where added after the gelatinization and pasting of starch had occurred. Hence if acids are added to starch cooking medium after pasting, glucose chain hydrolysis may be averted.



(a)

(b)

Figure 21: (a) RVA spectra showing the effect ascorbic acid on corn starch viscoelastic properties in limited water solvation conditions (b) RVA spectra showing the effect ascorbic acid on tapioca starch viscoelastic properties in limited water solvation conditions.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

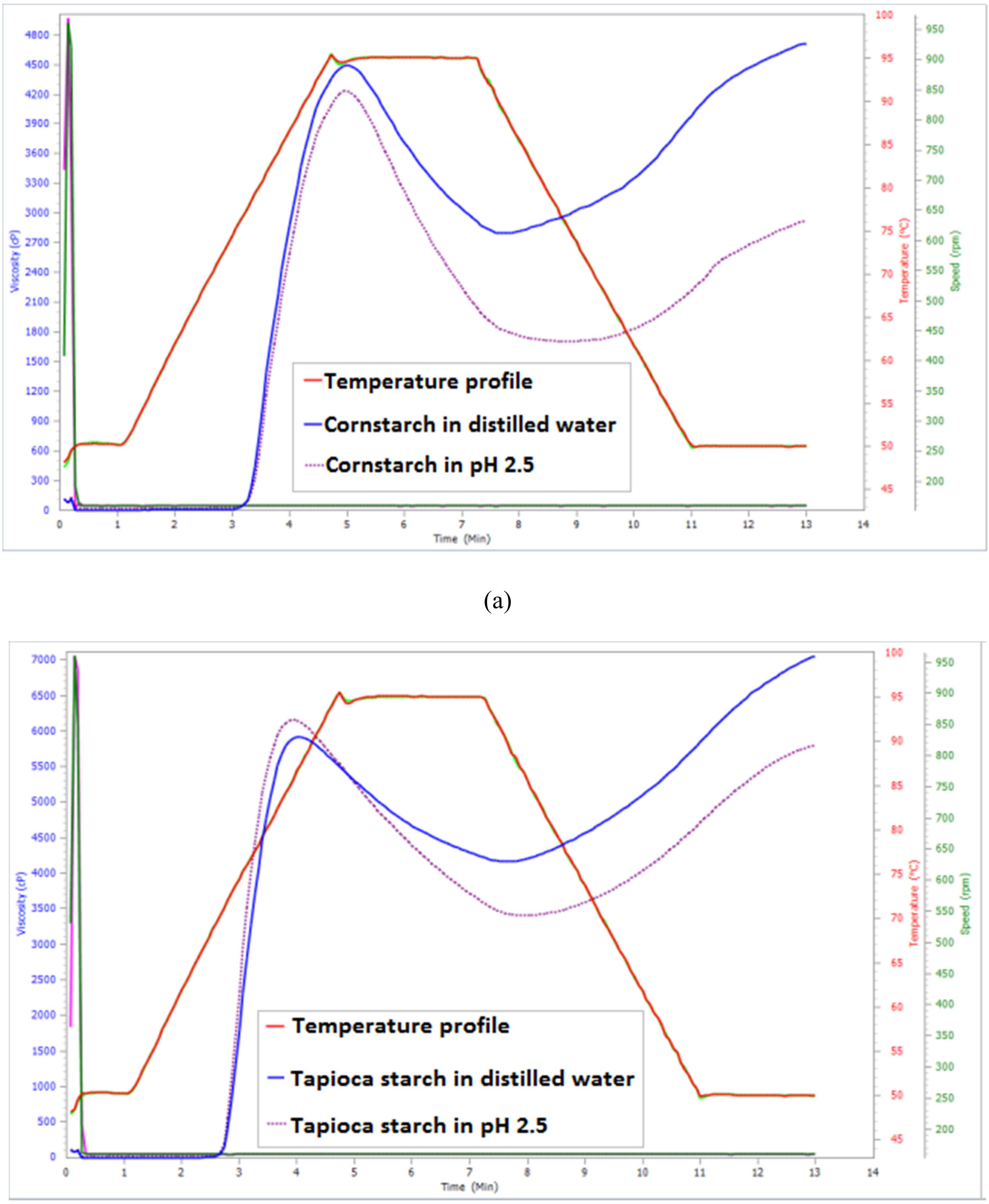
Table 12: (a) Eigenvalues of the effect of Ascorbic acid (AA) on the pasting and retrogradation properties of corn starch (CS) (limited water medium). (b) **:** Eigenvalues of the effect of Ascorbic acid (AA) on the pasting and retrogradation properties of tapioca starch (TS) (limited water medium).

Sample in % (w/v) AA	Peak (cP)	Final Viscosity (cP)	Setback (cP)	Peak Time (min)	Pasting Temp (^{o}C)
CS-0	4511.0 ± 34.7	4709.6 ± 30.0^{a}	1846.0 ± 60.0^{a}	5.0 ± 0.0	76.4 ± 0.4
CS-0.25	4347.3 ± 16.2	3728.3 ± 27.1^{b}	1562.7 ± 12.7^{b}	4.9 ± 0.0	75.2 ± 0.0
CS-0.5	4398.7 ± 29.0	3657.7 ± 18.5^{bc}	1424.7 ± 21.7^{c}	5.0 ± 0.0	76.9 ± 0.1
CS-1	4449.7 ± 31.5	3342.3 ± 17.2^{d}	1336.7 ± 3.2^{cd}	4.9 ± 0.0	76.4 ± 0.4
CS-2	4610.7 ± 1.7	2884.7 ± 5.5^{e}	1193.3 ± 7.0^{e}	4.9 ± 0.0	76.1 ± 0.0

(b)

Sample in % (w/v) AA	Peak (cP)	Final Viscosity (cP)	Setback (cP)	Peak Time (min)	Pasting Temp (^{o}C)
TS in 0	5968.0 ± 41.3	7093.6 ± 49.8^{a}	2907.0 ± 34.1^{a}	4.02 ± 0.0	69.2 ± 0.4
TS in 0.25	6233.3 ± 55.0	6827.7 ± 73.4^{b}	2807.3 ± 108.3^{b}	3.9 ± 0.1	69.0 ± 1.0
TS in 0.5	6370.3 ± 36.4	6641.3 ± 15.6^{c}	2687.7 ± 4.0^{c}	3.8 ± 0.0	68.18 ± 0.5
TS in 1	6415.3 ± 17.9	6285.3 ± 22.8^{d}	2566.0 ± 10.6^{bcd}	3.8 ± 0.0	68.4 ± 0.5
TS in 2	6589.3 ± 15.9	6027.0 ± 13.0^{e}	2435.0 ± 61.4^{e}	3.85 ± 0.0	68.5 ± 0.5

Results expressed as viscosity of starch sample (means ± SD; $n = 3$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).



(a)

(b)

Figure 22: RVA pasting spectra showing the effect of pH 2.5 acidity on corn and tapioca starch (a) RVA spectra showing the effect ascorbic acid on corn starch viscoelastic properties in limited water solvation conditions. (b) RVA spectra showing the effect ascorbic acid on tapioca starch viscoelastic properties in limited water solvation conditions.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 13: (a) Eigenvalues of the effect of acidity on the pasting and retrogradation of corn starch (CS) (limited water medium). (b) Eigenvalues of the effect of acidity on the pasting and retrogradation of tapioca starch (TS) (limited water medium).

(a)

Sample in Citric Acid	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^oC)**
CS in distilled water	4511.0 ± 34.7	4709.6 ± 30.0	1846.0 ± 60.0	5.0 ± 0.0	76.4 ± 0.4
CS in pH 2.5	4271.0 ± 32.1	2926.0 ± 8.7	1202.7 ± 10.4	5.0 ± 0.0	76.3 ± 0.4

(b)

Sample in Citric Acid	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^oC)**
TS in distilled water	5968.0 ± 41.3	7093.6 ± 49.8	2907.0 ± 34.1	4.02 ± 0.0	69.2 ± 0.4
TS in pH 2.5	6144.3 ± 46.3	5759.3 ± 31.4	2444.7 ± 50.0	3.9 ± 0.0	69 ± 0.5

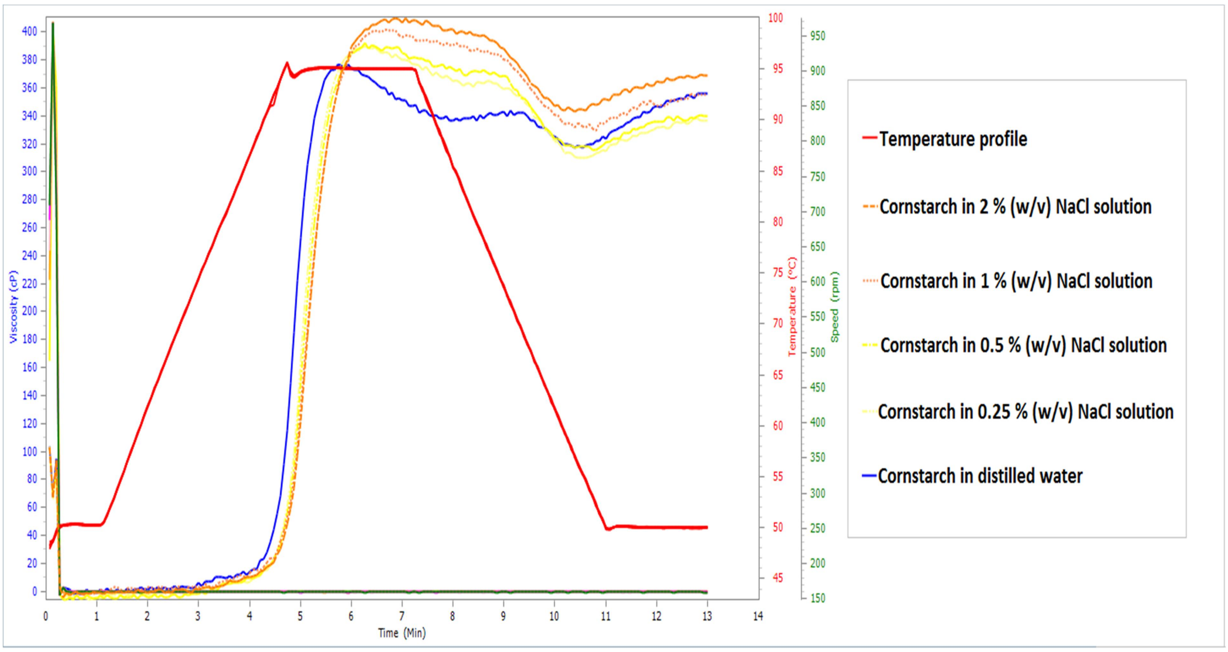
Results expressed as viscosity of starch sample (means ± SD; $n = 2$). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

3.3.5 Effect of salinity on pasting and retrogradation of corn and tapioca starch

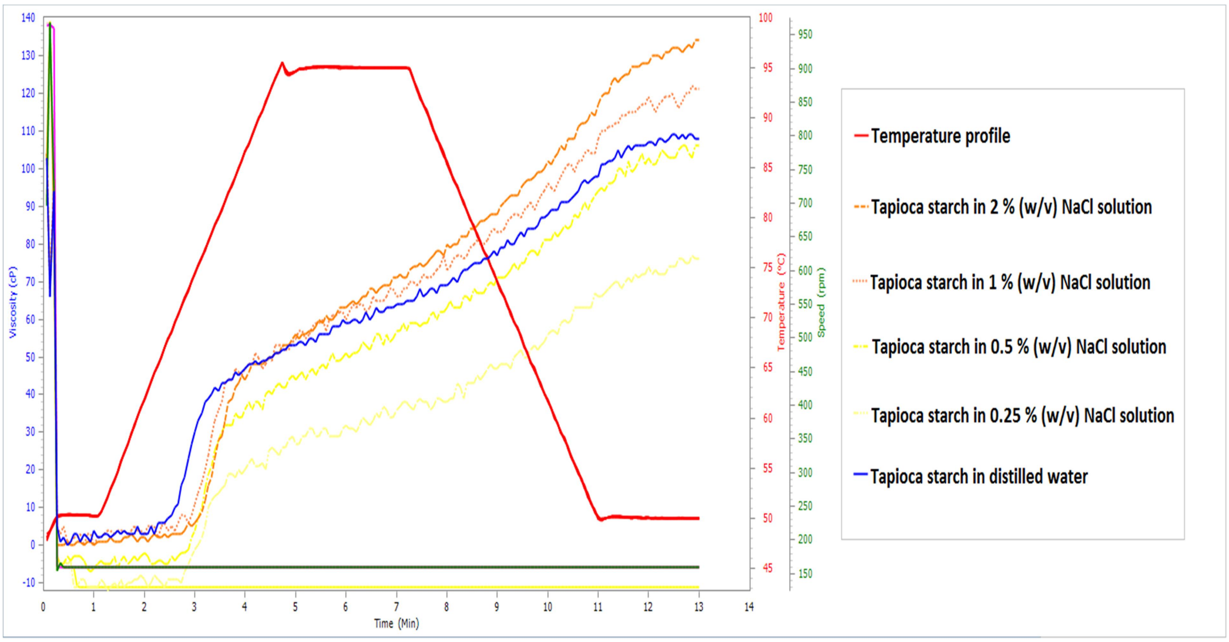
As shown in Table 14a, in excess water solvation medium, sodium chloride (NaCl) had a significant dilatant effect ($p = 0.0008$, $p < 0.0001$, $p < 0.0001$, $p < 0.0001$) on the peak viscosity of corn starch with increasing concentration of NaCl salt from 0.25 to 2 % (w/v). A nonlinear shear thinning behaviour followed by a non-significant effect was observed on corn starches final pasting viscosity with increasing concentration of NaCl, as illustrated in Table 14a and Figure 23a. NaCl had a significant reducing effect ($p = 0.0003$, $p < 0.0001$, $p < 0.0001$, $p < 0.0001$) on starch retrogradation propensity; however, at increasing concentrations (1 and 2 % (w/v)), notwithstanding had similar significant effect of amylose realignment with lower NaCl concentration (0.25 and 0.5) as shown in Table 14a.

NaCl had a similar influence on the viscoelasticity of tapioca starch in comparison to corn starch final pasting viscosity in excess water solvation medium as shown in Figure 23b. Table 14b shows that NaCl at different concentrations had different effects on the apparent final pasting viscosity of tapioca starch as compared to the control. At 2 % (w/v) concentration, NaCl had a significant shear hardening effect ($p = 0.0074$) on final pasting viscosity, while lower concentrations (0.25, 0.5, and 1 % w/ v) had no significant effect ($p = 0.0934$, 0.9918, 0.4649, respectively) on the viscosity of tapioca starch as shown in Table 14b. NaCl had no significant effect on retrogradation of tapioca starch at concentrations below 1% (w/v) as compared to the control; however its effect on increasing retrogradation tendency began to increase from 1-2 % (w/v) concentration of NaCl concentration in the gelatinization matrix, as shown in Table 14b.

NaCl is a strong electrolyte, as the metal anion (Cl^-) and cation (Na^+) in gelatinization medium influences interactions between water molecules and starch, thus resulting in starch-starch and starch-water hydrogen bonds interaction and consequently causing an inhibition in the pasting process which is more pronounced at lower concentrations, as observed from the pasting spectra of tapioca starch in excess water medium in Figure 23a. However, according to Zhang *et al.*, (2017) and Gil and Yoo, (2015), with increasing concentration of salinity, the observed gradual increase in the apparent viscosity is as a result of the salt-starch interactions reducing the mobility of the molecular starch chain segments, resulting in a slight increase in peak and final viscosity as compared to the control spectra as shown in Figure 23a.



(a)



(b)

Figure 23: (a) RVA spectra showing the effect of salinity on tapioca starch viscoelastic properties in excess water solvation conditions. (b) RVA spectra showing the effect of salinity on tapioca starch viscoelastic properties in excess water solvation conditions.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 14: (a) Eigenvalues of the effect of salinity on the pasting and retrogradation properties of cornstarch (excess water medium). (b) Eigenvalues of the effect of salinity on the pasting and retrogradation properties of tapioca starch (excess water medium).

(a)

Sample in % (w/v) NaCl	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
CS in 0	377.6 ± 2.1^{a}	364.6 ± 7.7^{a}	47.0 ± 7.0^{a}	5.64 ± 0.1	93.2 ± 0.9
CS in 0.25	387.7 ± 2.1^{b}	338.0 ± 1.7^{b}	28.0 ± 1.0^{b}	6.2 ± 0.1	95.4 ± 0.4
CS in 0.5	392.0 ± 2.0^{bc}	340.3 ± 2.5^{bc}	24.0 ± 1.0^{bc}	6.4 ± 0.1	95.0 ± 0.6
CS in 1	402.3 ± 2.5^{d}	352.0 ± 3.0^{d}	24.3 ± 2.1^{bdc}	6.5 ± 0.1	94.6 ± 0.1
CS in 2	409.0 ± 1.0^{e}	368.3 ± 2.1^{a}	25.3 ± 0.6^{bcde}	6.9 ± 0.1	94.5 ± 0.1

(b)

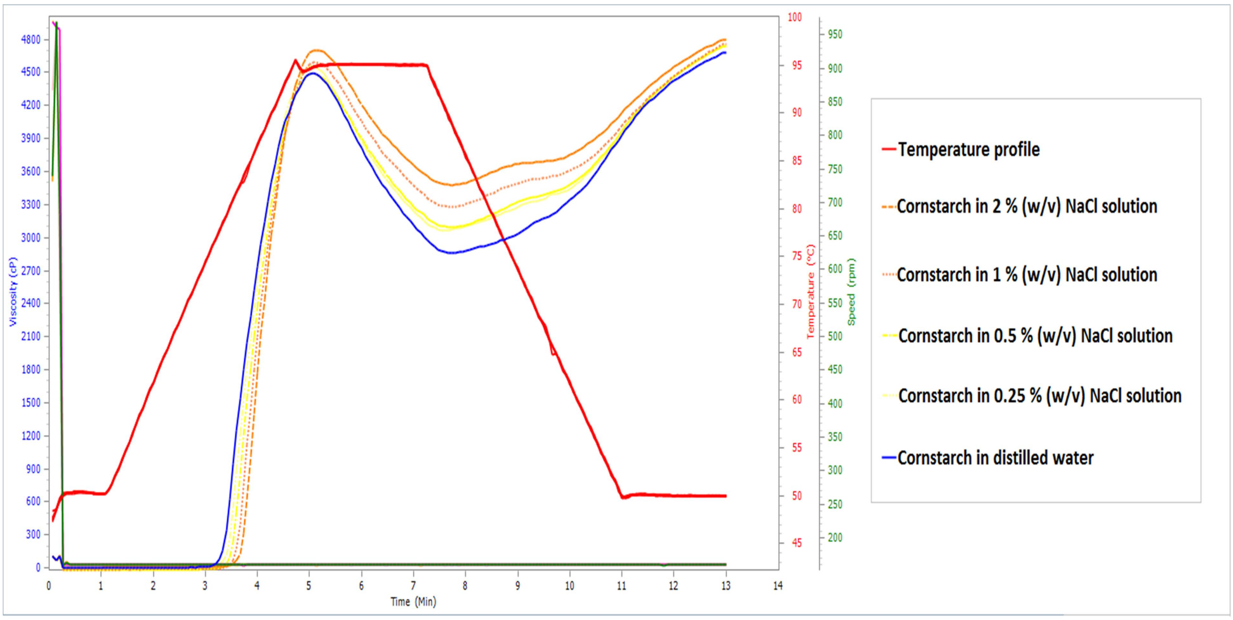
Sample in % (w/v) NaCl	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
TS in 0	63.3 ± 0.6	108.3 ± 0.6^{a}	50.0 ± 1.0^{a}	7.0 ± 0.0	-
TS in 0.25	50.0 ± 11.5	92.7 ± 14.5^{ab}	49.7 ± 3.2^{ab}	6.8 ± 0.2	-
TS in 0.5	61.3 ± 4.0	106.0 ± 1.0^{abc}	51.7 ± 3.8^{abc}	6.93 ± 0.1	-
TS in 1	66.3 ± 1.5	117.7 ± 3.1^{acd}	58.0 ± 1.0^{cd}	7.0 ± 0.1	-
TS in 2	70.7 ± 0.6	133.0 ± 1.0^{de}	69.7 ± 1.5^{e}	6.9 ± 0.0	-

Results expressed as viscosity of starch sample (means ± SD; n =3). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

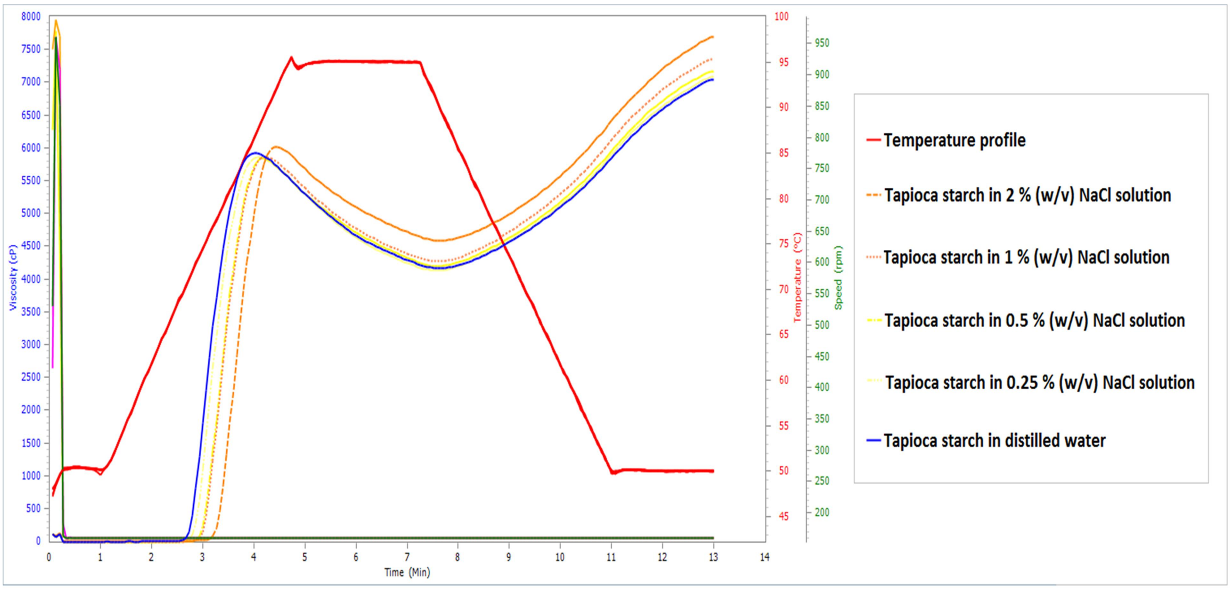
In limited water solvation conditions, NaCl had a significant increase ($p = 0.0049$) in apparent peak viscosity at 2 % (w/v) NaCl solution; however lesser concentration (0.25, 0.5, and 1 % w/v) had no significant effect ($p = 0.9984$, $p > 0.9999$, $p = 0.7541$, respectively) as compared to the control as shown in Table 15a. NaCl had no significant effect ($p = 0.8776$, $p > 0.9999$, $p = 0.8337$, 0.1393) on the final cooked viscosity of corn starch, even at increasing pasting temperatures as shown in Table 15a and Figure 24a. Furthermore, it was observed that with increasing concentration of NaCl, corn starch had a corresponding increase in the retrogradation tendencies in limited water environment.

In limited water condition, NaCl had a significant shear hardening effect ($p = 0.0016$ and <0.0001) on tapioca starch at concentration from 1 and 2 % (w/v) respectively, having a similar viscoelastic phenomenon to that of the excess water medium, as shown in Table 15b and illustrated in Figure 24b. Similarly with the phenomenon of tapioca starch in excess water NaCl solution, NaCl had no significant impact ($p = 0.9504$ and $p = 0.9237$, respectively) on the retrogradation properties of tapioca starch at concentration lower than 1% (w/v) as shown in Table 15b. Thus, at higher NaCl concentrations 1 and 2 % (w/v) the amylose realignments increased significantly ($p = 0.0423$ and $p = 0.0003$ respectively). It could be summarized that NaCl below 1 % (w/v) had no effect on the apparent viscosity and retrogradation of corn and tapioca starch in limited water solvation medium.

Generally, the effect of salt on the gelatinization phenomena is dependent on the salt concentration and the starch gelatinizing medium. The increase in the pasting and final viscosities of corn and tapioca starch in the presence of increasing monovalent salt concentration is due to NaCl electro viscous effect (Winter and Loiselle, 1958). Anions have been shown to be gelatinizing agents in a salty medium, hence they have huge tendencies to disrupt the hydrogen bonds between the starch chains, hence resulting in higher viscosity profile of starch gelatinized in a salty matrix; also the cations cause reductions in intermolecular repulsion which promotes granular network formation and impacts on non-thixotropic behaviour of starch, evident from the results of the limited water solvation medium (Sudhakar *et al.*, 1995). NaCl cation and anion has the ability to cause disruption in the hydrogen bonding between starch molecules, there hindering the amylose realignments of corn starch molecules, thus reducing the retrogradation propensities as it can be observed from the setback viscosity values in Tables 15a and 15a of the excess water solvation medium.



(a)



(b)

Figure 24: (a) RVA spectra showing the effect of salinity on corn starch viscoelastic properties in limited water solvation conditions (b) RVA spectra showing the effect of salinity on tapioca starch viscoelastic properties in limited water solvation conditions.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

Table 15: (a) Eigenvalues of the effect of salinity on the pasting and retrogradation properties of cornstarch (CS) (limited water medium). (b) Eigenvalues of the effect of salinity on the pasting and retrogradation properties of tapioca starch (TS) (limited water medium).

(a)

Sample in % (w/v) NaCl	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
CS 0	4511.0 ± 34.7^{a}	4709.6 ± 30.0^{a}	1846.0 ± 60.0^{a}	5.0 ± 0.0	76.4 ± 0.4
CS in 0.25	4520.3 ± 50.1^{a}	4734.0 ± 6.0^{a}	1641.0 ± 59.8^{a}	5.1 ± 0.0	78.0 ± 4
CS in 0.5	4509.7 ± 17.0^{a}	4707.7 ± 32.9^{a}	1562.7 ± 173.1^{b}	5.1 ± 0.1	79.1 ± 0.9
CS in 1	4550.7 ± 35.7^{a}	4736.7 ± 20.2^{a}	1513.0 ± 37.6^{c}	5.1 ± 00	79.4 ± 0.0
CS in 2	4671.0 ± 54.6^{b}	4778.0 ± 51.6^{a}	1249.7 ± 93.6^{d}	5.2 ± 0.1	81.2 ± 0.5

(b)

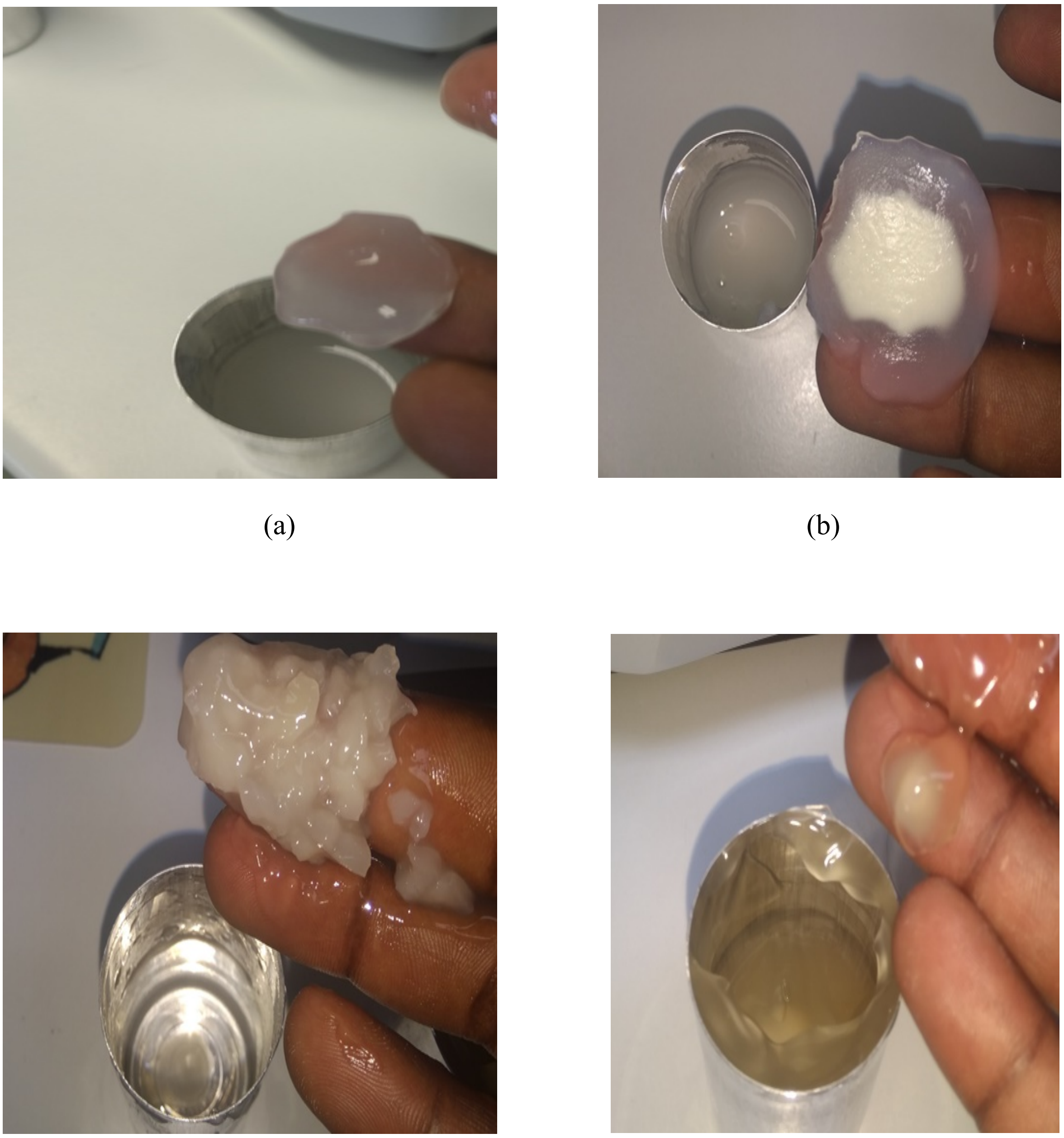
Sample in % (w/v) NaCl	**Peak (cP)**	**Final Viscosity (cP)**	**Setback (cP)**	**Peak Time (min)**	**Pasting Temp (^{o}C)**
TS in 0	5968.0 ± 41.3	7093.6 ± 49.8^{a}	2907.0 ± 34.1^{a}	4.0 ± 0.0	69.2 ± 0.4
TS in 0.25	5834.7 ± 22.2	7076.7 ± 7.5^{a}	2933.7 ± 47.1^{a}	4.1 ± 0.0	70.9 ± 0.5
TS in 0.5	5852.7 ± 30.2	7162.0 ± 31.1^{a}	2937.3 ± 54.0^{a}	4.2 ± 0.0	72.3 ± 0.4
TS in 1	5841.7 ± 19.7	7292.7 ± 52.0^{b}	3035.3 ± 41.48^{b}	4.3 ± 0.0	73.3 ± 1.0
TS in 2	6010.3 ± 31.1	7720.0 ± 56.6^{c}	3165.3 ± 51.7^{c}	4.5 ± 0.0	75.1 ± 0.5

Results expressed as viscosity of starch sample (means ± SD; *n* = 3). Different letters (a, b, c) in a column indicate significant differences amongst the starch samples ($P < 0.05$).

3.4 Lump simulation results

All samples that were evenly dispersed, with or without delayed shearing, resulted in a well gelatinized and smooth starch solution void of any lump formation. Furthermore, no lump formation was found for starch solutions whose starch dispersion was allowed to sediment but had instant shearing with an initial of shear rate of 960 rmp for 10 seconds and continuous shearing for 160 rpm. On the other hand, as shown in Figure 25, significant lump was formed for all samples that was left to settle for 30 minutes and also had a one minute delayed shearing. This occurred because starch granules had been left to settle for about 30 minute causing a significant coagulation of starch at the bottom of the canister and subsequently being placed in a heating medium where flash gelatinization took place for both starch types. In there, an instantaneous flash gelatinization phenomenon took place, allowing the clumped starch granules to swell unequally before the shearing began. This phenomenon concurs with the observation by Vaclavik and Christian (2014) which states that starch lumps are formed during the gelatinization, as a result of clumping together or unequal swelling of individual starch granules. This explains why it is important that starch granules can swell separately and independently, which can be achieved by continuous stirring of starch dispersion in cold water and an initial shearing at 960 rmp circa prior to temperature ramp, as well as continuous shearing as the temperature sweeps.

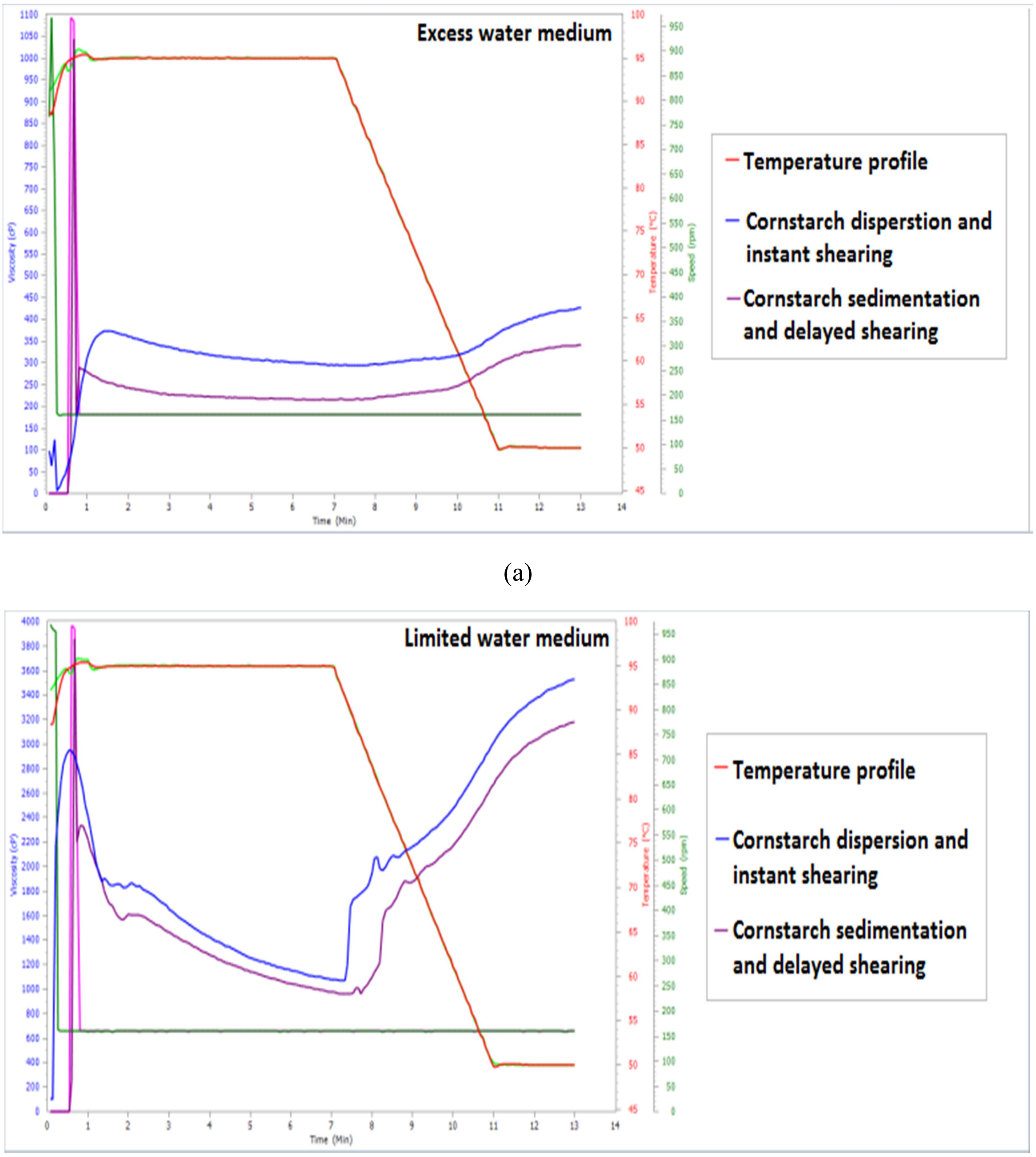
It is important to mention that lump generation and reduction in the viscoelastic gelatinization potential of corn and tapioca starch are mutually inclusive. As shown in the pasting spectra in Figures (26a 26b and 27b), the viscosity and gelatinization potential of corn and tapioca starch paste was observably shown to be reduced for ‘sedimented and delayed shearing’ samples which yielded lumps in contrast to the ‘dispersion and instant shearing’ samples of both starch types. This is because starch lumps are made up of a network of gelatinized starch covering a mass of uncooked starch and invariably reduces the starch available for gelatinization functionality in the gelatinizing matrix. Figure 27a had an error in the test runs because the lump formed during experiments were over the torque limits set for the experiment test profile of the RVA.



(a) (b)

(c) (d)

Figure 25: Digital image showing lump development of starch samples in sedimentation and delay shearing simulation conditions. (a) Cornstarch in excess water medium. (b) Cornstarch in limited water medium. (c) Tapioca starch in excess water medium (d) Tapioca starch in limited water medium.

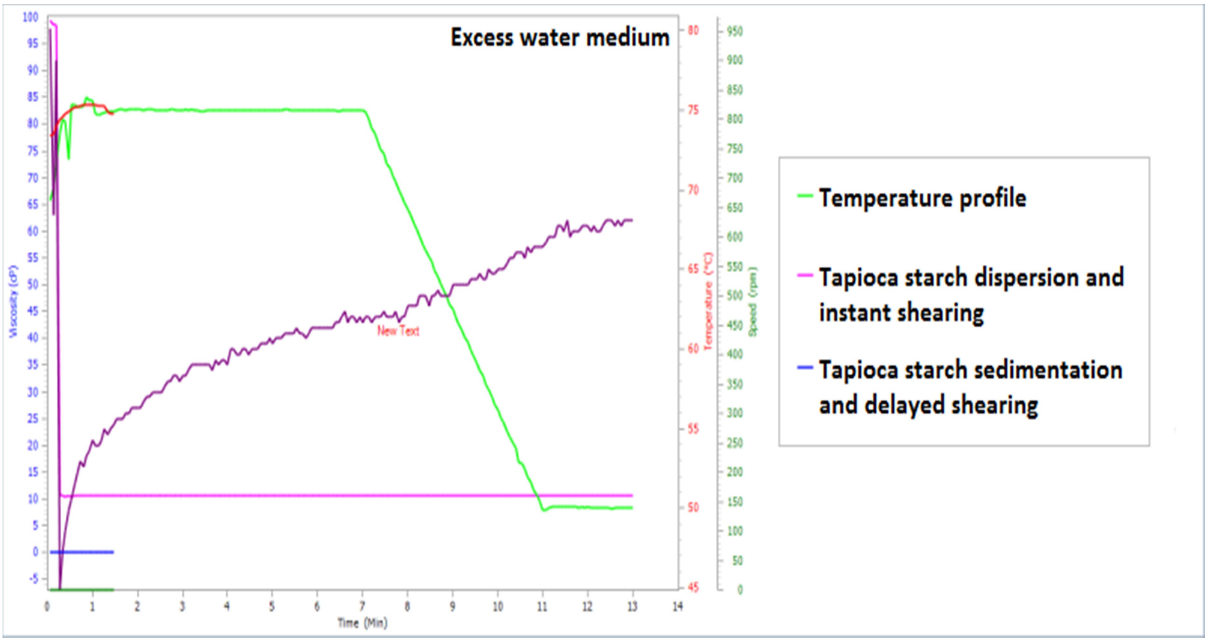


(a)

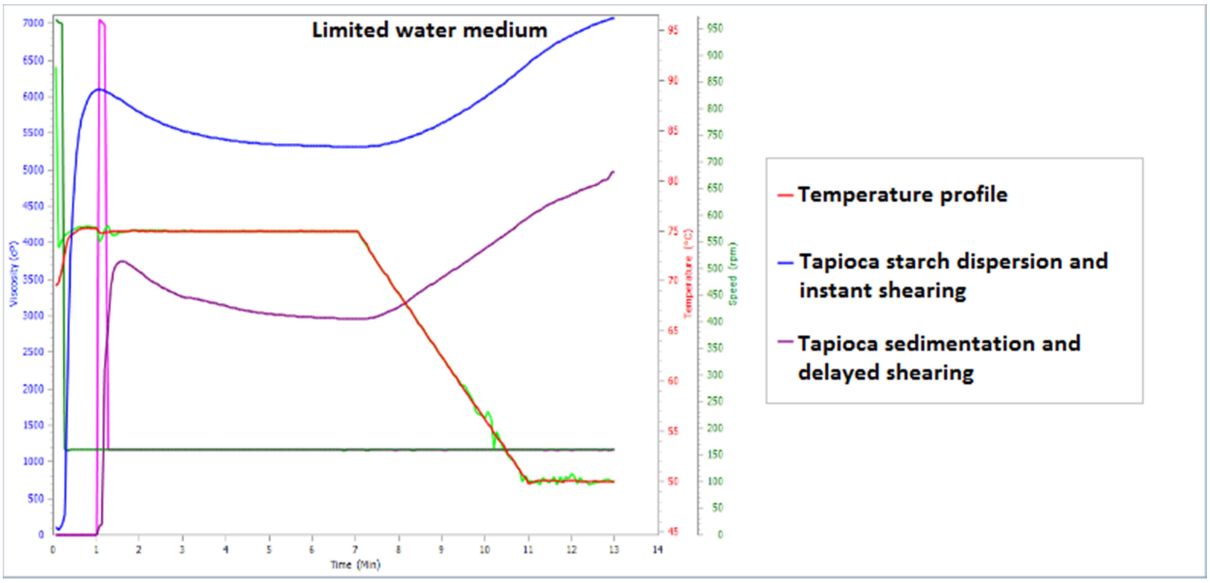
(b)

Figure 26: Lump simulation experiments RVA spectra of corn starch samples with and without lump development (a) Corn starch (dispersion and instant shearing vs. sedimentation and delayed shearing) in excess water medium (b) Corn starch (dispersion and instant shearing vs. sedimentation and delayed shearing) in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.



(a)



(b)

Figure 27: Lump simulation experiments RVA spectra of tapioca starch samples with and without lump development (a) Tapioca starch (dispersion and instant shearing vs. sedimentation and delayed shearing) in excess water medium (b) Tapioca starch (dispersion and instant shearing vs. sedimentation and delayed shearing) in limited water medium.

Note: x axis = Time in minutes, y1 = Viscosity in centipoise y2 = Temperature in degree Celsius (˚C) and y3 = Speed in revolutions per minute (rpm). Pasting spectra's are illustrations from one experiment test run.

CHAPTER FIVE

CONCLUSION

All evidences presented in this study shows that the pasting and rheological properties of corn and tapioca starches are significantly influenced by the interaction of starch samples with ingredients and the water availability of the solvation medium at which they are cooked, as starch samples shear thickening, pseudo plasticity and retrogradation properties were influenced by the varying concentrations of ingredients tested in excess and limited water solvation mediums.

Corn and tapioca starch had a good gelatinization potential in excess water PMMS and NBCMS, as well as in their respective model solutions in oil moiety. In limited water environment an inverse response was exhibited, as tapioca starch had a good swelling potential in PMMS and NBCMS in contrast to their control, while on the other hand, corn starch had a thixotropic behaviour in PMMS and dilatant phenomenon in NBCMS. Furthermore, oil addition to PMMS and NBCMS had undesirable and irreproducible viscoelastic effects on both corn and tapioca starch types, and emphatically caused a huge lag the swelling potential of tapioca starch in limited water cooking environment. From all ends of results obtained, tapioca starch is the suitable starch for cooking of PM food product and corn-starch for NB food product; however, excess water environment is more desired based on these simulation experiments. In order to prevent the undesirable effect of oil on irreproducibility and pseudo plastic effect of starch samples, oil should be added after starch gelatinization has occurred. Oil addition to the PMMS and NBCMS with oil moiety resulted in a reduction in the retrogradation tendencies offset by both PMMS and NBCMS.

Both starch corn and tapioca starch samples cooked in excess water with oil moiety exhibited a shear thickening effect on corn and tapioca starch, owing to the impact of viscosity of the oil in water medium after sufficient water in the excess water medium has been used up for starch maximal swelling potential. In limited water medium, lipids interacted with less polar region of the amylose helix causing an amylose-lipid complex with a resultant non-dilatant behaviour of corn starch and at higher oil interphase a truncation and lag in tapioca starch gelatinization. The lipid addition invariably is responsible for the irreproducibility of corn and tapioca starch cooked in NBCMS and PMMS with oil moiety.

Gelatinization in acidic limited water medium resulted in a decrease in the viscoelastic properties of corn and tapioca starch due to the hydrolysis of glucose chains from starch pastes, leading to reduction in the degree of polymerization. However this can be averted by adding acidic substances to starch solutions after gelatinization phenomena has occurred.

Lump development in starch based food product occurs as a result of inability of starch granules to swell independently when the starch samples are been allowed to clump together either by sedimentation and/or when the starch samples undergoes a significant delay in shearing during gelatinization in the cooking environment, be it in excess or limited water medium creating a network of gelatinized starch over uncooked mass of starch. Hence, starch granules must be made to swell separately by proper dispersion in cold water prior to gelatinization followed by instant and continuous shearing during gelatinization process.

Several experiments was carried out to compare the gelatinization behaviour of corn and tapioca starch in excess and limited water solvation medium, where an observable similar trend was exhibited for corn and tapioca starch samples in different ingredient solutes. In excess solvent medium, the onset of granule swelling and crystallinity rupturing always occurs as a one step process that takes place continuously and simultaneously, since solvents can be easily ingressed into the starch amorphous growth ring and act as plasticizer which facilitates gelatinization; therefore the corporative synergy of compound in excess water results in total disruptions of starch lamellar and crystalline order, hence resulting in a non-thixotropic behaviour of starch solutions. On the other hand, in limited solvation medium the crystalline rupturing is initiated at the same temperature as that of excess water environment; however, the rate of decrease in crystallinity is significantly slower at the point at which an increase in the granular rupturing occurs. This is notably the point at which external available water required for further imbibition and swelling is exhausted, thus the swelling and ingression of water in limited medium reduces the amorphous growth rings electron density of starch granules which makes the amorphous lamellae remains unaffected and therefore results in a pseudo plastic phenomenon. To champion this limited water limitation, additional thermal energy input is required to cause a thermal driven granule molecular mobility and granular swelling. This phenomenon was not studied in this thesis work and may be considered for further research.

The results from this study may be used as an applicable model for corn and tapioca starch based food product development and product optimization.

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