

Pasting properties of teff, maize, and potato starches with added microcrystalline cellulose and cellulose nanofiber

By

Reagan Kawuma

Submitted in partial fulfilment of the requirements for the degree

Master of Science (MSc): Food Science

In the

Department of Consumer and Food Science

Faculty of Natural and Agricultural Sciences

University of Pretoria

South Africa

April 2022

DECLARATION

I Reagan Kawuma declare that this dissertation, which I hereby submit for the degree MSc Food Science at the University of Pretoria, has not previously been submitted by me for a degree at this or any other university or institution of higher education.

SIGNATURE: Kawuma

DATE: 20TH/April/2022

DEDICATION

Firstly, I dedicate this MSc research to myself.

Secondly, I dedicate this Master's degree to everyone who supported me through this endeavor.

ACKNOWLEDGMENT

I would genuinely like to appreciate the following people for their support:

My supervisor, Prof Naushad Emmambux for the patient role he played in building and mentoring me into the researcher that I am today. He always kept me on my academic “toes” and pushed me to do. Am forever grateful to him.

The MasterCard Foundation Scholarship Program for facilitating my entire study period. All this would not have been possible if they had not believed in me.

John Lubaale for being my wholesome support structure. You made settling in very effortless and a breeze.

Emmanuel Nekhudzhiga for his reliable laboratory support. He always offered clarity during those tough times when the results were not making sense.

My fellow Masters of Food science colleagues (Sarah, Daddy, Lilian, Nomfundo, Nstepaste) for the light & dark times that we shared to keep each other going.

My family and friends in Uganda for their relentless support and supplications.

Lastly, I would like to thank myself for never giving up even when it was immensely frustrating.

ABSTRACT

Pasting properties of teff, maize, and potato starches with added microcrystalline cellulose and cellulose nanofiber

Reagan Kawuma

Supervisor: Prof. Naushad M. Emmambux

Starch is a plant polysaccharide that is normally utilized in the food industry as a thickening, stabilizing, and gelling agent. Commercially, some of the most used native starches include; maize, cassava, wheat, tapioca, potato, and rice. However, commercial utilization of native starches is adversely affected by the limited functionality of these starches. The functional properties of native starches are adversely affected by prolonged processing time, acidic processing conditions, and extreme heat treatment. To overcome these limitations, native starches are normally modified using chemical and physical methods. Unfortunately, chemical methods involve the use of chemicals such as sulphuric and hydrochloric acids which can raise health concerns amongst consumers and also generate unnecessary industrial waste which can adversely affect the environment. This makes chemical starch modification an unsustainable option. Also, physical modification techniques such as heat-moisture treatment can have extreme energy requirements which can be costly. Therefore, consumers are increasingly pushing for safer food options produced using “clean” energy and/or processing techniques. Hydrocolloids (other than starch) can be utilized to modify native starch functional properties with little or no energy requirement and industrial waste generated. Therefore, this research investigates the effect of plant-sourced cellulose-derivative hydrocolloids on the pasting properties of teff, maize, and potato starches.

Suspensions of starch treated with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) at different concentrations (0%, 0.2%, 0.5%, 2% and 5% w/w) were pasted for 30 minutes (short pasting) and 2 hours (extended pasting) to analyze pasting and viscoelastic properties. At the end of the different pasting cycles, the resulting pastes were divided into three portions. One part of the paste from the different treatments was stored overnight to form gels used to analyze gelling properties. The second portion of the fresh pastes was subjected to light microscopy and the last portion was freeze-dried and subjected to scanning electron microscopy (SEM).

Treating maize and teff starch with increasing hydrocolloid concentrations significantly increased ($P < 0.05$) the peak and final viscosity of the starches. When hydrocolloids were added to the water-rich continuous phase, their primarily hydrophilic nature enables them to bind water via hydrogen bonding within the phase thus forming networks. These networks increased the resistance to flow within the

starch-hydrocolloid system. As the concentration of the hydrocolloids increases, the networks formed within the continuous phase increase thus making the starch-hydrocolloid system highly viscous.

Starches treated with CNF had higher peak and final viscosities. The ultrafine structure of CNF polymers at a nanoscale provides it with a higher hydrodynamic volume than MCC and thus more of its hydroxyl groups are exposed and available for extensive hydrogen bonding with other hydrophilic molecules such as water within the continuous phase. This allows CNF to bind more water than MCC within the starch-hydrocolloid system and thus resulting in starches with higher peak and final viscosities.

Extended pasting cycles (2 hours) did not have any effect on the final starch paste viscosity with or without the hydrocolloids added. Extended pasting cycles result in a lot of friction, impact, and shear forces within the starch-hydrocolloid system which causes a massive breakdown of the starch granules. Light microscopy micrographs taken after the extended pasting cycles show more structural breakdown than those from short pasting cycles this can mainly be attributed to the prolonged shearing experienced during the extended pasting cycles.

The addition of CNF and MCC to potato starch did not show any observable effect on the pasting properties of the starch. This can be attributed to the bulky phosphate group attached to the potato starch chains which probably limited any possible interactions between starch and the hydrocolloids.

Gel strength decreased with an increase in hydrocolloid concentration. The viscoelastic properties showed that an increase in hydrocolloid concentration increased the loss modulus (G'') of the starch pastes. Hydrocolloids through intra and inter-molecular hydrogen bonds form extensive networks within the continuous phase of the starch system. These networks entangle the leached amylose molecules within the continuous phase thus making them unavailable for junction zone formation. As a result, fewer junction zones are formed in the presence of CNF and MCC than with the control. This weakens the starch gel structure formed in the presence of CNF and MCC thus forming gels with lower gel strength.

In conclusion, the addition of CNF and MCC to starch increases the starch paste viscosity whilst lowering gel strength. CNF (a nano-polymer) produces teff and maize starches that have more pronounced paste viscosities and non-gelling properties than MCC (a micro-polymer). Therefore, modified starch produced by the addition of MCC and CNF to starch is a possible “clean” and environmentally safe replacement for chemically and physically modified starches in the food industry because of their increased viscosity and non-gelling properties in food products such as sauces and mayonnaise.

TABLE OF CONTENT

DECLARATION.....	i
DEDICATION	ii
ACKNOWLEDGMENT	iii
ABSTRACT	iv
LIST OF FIGURES.....	viii
LIST OF TABLES	xi
1. INTRODUCTION	1
2. LITERATURE REVIEW	3
2.2 Starch	3
2.2.1 Starch granules	3
2.2.2 Starch wet heat processing	7
2.2.3 Factors affecting native starch rheological properties	14
2.3 Cellulose derivative hydrocolloids	19
2.3.1 Production of cellulose derivative hydrocolloids.....	19
2.3.2 Properties of microcrystalline cellulose (MCC), cellulose nanofibers (CNF), and cellulose nanocrystals (CNC).....	22
2.4 Effect of modification of starch with cellulose derivative hydrocolloids on its rheological properties	23
2.4.1 Pasting properties	23
2.4.2 Gelling and visco-elastic properties	30
2.5 Potential food applications of hydrocolloid modified starches.	32
2.6 Concluding remarks.....	32
3. HYPOTHESIS AND OBJECTIVES	33
3.1 Hypothesis	33
3.2 Objectives	34
4. MATERIALS AND METHODS.....	35
4.1 Experimental design	35
4.2 Materials	36
4.3 Methods	36
4.3.1 Addition of hydrocolloids to starch	36
4.3.2 Teff starch extraction	36
4.3.3 Raw material characterization.....	37
4.4 Analyses.....	37

4.4.1 Pasting properties	37
4.4.2 Gelling properties.....	37
4.4.3 Time-Temperature Sweep (Viscoelastic properties).....	37
4.4.4 Hot Stage Microscopy.....	38
4.4.5 Light microscopy	38
4.4.6 Scanning Electron Microscopy	38
4.4.7 Statistical analysis	39
5. RESULTS	40
5.1 Pasting properties.....	40
5.2 Hot stage microscopy	51
5.3 Light microscopy	53
5.4 Scanning electron microscopy	53
5.5 Gelling properties	58
5.6 Viscoelastic properties.....	63
6. GENERAL DISCUSSION	65
6.1 Methodological consideration	65
6.1.1 Teff starch extraction	65
6.1.2 Pasting properties	65
6.1.3 Gelling and Viscoelastic properties	66
6.1.5 Microscopy.....	68
6.2 Results discussion.....	69
6.2.1 Pasting properties	69
6.2.2 Gelling properties.....	75
7. CONCLUSIONS.....	79
8. REFERENCES.....	80

LIST OF FIGURES

Figure 2.1: SEM images of individual starch granules from teff, maize, and potato starch respectively	4
Figure 2.2: A schematic diagram of the blocklet showing the structural organization of the starch granule.	4
Figure 2.3: Schematic diagram showing side-chain clusters forming the blocklet structures seen at the starch granule surface (Pérez, Baldwin & Gallant, 2009).	5
Figure 2.4: Amylose (A) and amylopectin (B) molecular structures respectively (Mua & Jackson, 1997).	5
Figure 2.5: Single helix amylose structure (Immel & Lichtenhaler, 2000).....	6
Figure 2.6: Double helical amylose structure (Zobel, 1988).	6
Figure 2.7: Schematic diagram showing the arrangement of amylopectin into clusters (Hizukuri <i>et al.</i> , 1986)	7
Figure 2.8: Schematic diagram showing the process of starch gelatinization (Knorr <i>et al.</i> , 2006).....	8
Figure 2.9: DSC curve of native teff starch (Nyakabau <i>et al.</i> , 2013), maize starch (Juneja <i>et al.</i> , 2014), potato starch (de Oliveira <i>et al.</i> , 2018) respectively.	9
Figure 2.10: Pasting profile of native teff starch (Nyakabau <i>et al.</i> , 2013), maize starch (de Oliveira Maior <i>et al.</i> , 2020), potato starch (Lawton <i>et al.</i> , 1999) respectively.....	9
Figure 2.11: Reassociation of amylose molecules and linear chains of amylopectin during retrogradation (Wang <i>et al.</i> , 2015).....	11
Figure 2.12: A generic pasting profile of starch (Rincón-Londoño <i>et al.</i> , 2016).	12
Figure 2.13: Effect of shear rate on the shear stress of maize starch (Adopted from Cengiz & Dogan, 2021).	13
Figure 2.14: Schematic diagram illustrating the effect of starch granule size on the mobility within a starch system.	14
Figure 2.15: Gel strength of potato, maize, and high amylose maize starch after 7 hours and 72 hours of storage respectively (Kasemsuwan, 1995)	15
Figure 2.16: Molecular Structure of cellulose (Nsor-Atindana <i>et al.</i> , 2017).	19
Figure 2.17: Main forms of cellulose derivatives	19
Figure 2.18: Microcrystalline cellulose production from wood pulp (Katakajwala & Mohan, 2020).	21
Figure 2.19: Cellulose nanofiber production from woody biomass using a mechanochemical method (HCW = hot-compressed water) (Moon <i>et al.</i> , 2013).	21

Figure 2.20: Cellulose nanocrystals (CNC) production from woody biomass using acid hydrolysis method (Thompson <i>et al.</i> , 2019).....	22
Figure 2.21: SEM of microcrystalline cellulose and cellulose nanocrystals and fibers	23
Figure 2.22: Orientation of the different components in the starch matrix during pasting.	23
Figure 2.23: Chemical structures of potato starch and carboxymethylcellulose (CMC) (Zhao, 2007).	28
Figure 2.24: Effect of cellulose nanocrystals on storage modulus and loss tangent of normal maize (a, b) respectively (Cui <i>et al.</i> , 2018).	31
Figure 4.1: Experimental design of the research project	35
Figure 5.1: Pasting profiles of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) alone.	41
Figure 5.2: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of teff starch after short and extended pasting cycles.	42
Figure 5.3: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the final viscosity of teff starch after short and extended pasting cycles respectively.	44
Figure 5.4: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of native maize starch after short and extended pasting cycles	45
Figure 5.5: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the peak, breakdown, setback, and final viscosities of native maize starch after the short and extended pasting cycles	47
Figure 5.6: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of native potato starch after short and extended pasting cycles.....	48
Figure 5.7: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the peak, breakdown, setback, and final viscosities of native potato starch after short and extended pasting cycles	50
Figure 5.8: Effects of temperature change (50-90 °C) on the microstructure of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during pasting	52
Figure 5.9: Light microscopy images showing the effect of treating teff starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles.	54
Figure 5.10: Micrographs showing the effect of treating maize starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles.....	55

Figure 5.11: Micrographs showing the effect of treating potato starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles..... 56

Figure 5.12: Scanning Electron Microscopy (SEM) micrographs of freeze-dried maize starch pastes 57

Figure 5.13: Appearance of gels formed by teff, maize, and potato starches..... 59

Figure 5.14: Stress-strain curves of teff and maize starch gels treated with Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) after short pasting cycles. 60

Figure 5.15: Stress-strain curves of teff and maize starch gels treated with Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) after extended pasting cycles. 62

Figure 5.16: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of teff starch during cooling. ... 64

Figure 5.17: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of maize starch during cooling. 65

Figure 5.18: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of potato starch during cooling 66

Figure 6.1: Changes in storage modulus of maize starch paste prepared using a magnetic stirrer hot plate..... 67

Figure 6.2: Changes in storage modulus of maize starch paste prepared using the rheometer. 67

Figure 6.3: Schematic diagram showing the continuous and discontinuous phase components of the starch-hydrocolloid system before and during pasting. 69

Figure 6.4: Critical concentration (C*) of microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) in the starch-hydrocolloid system..... 71

Figure 6.5: Schematic diagram showing the effect of starch granule swelling on the continuous phase 72

Figure 6.6: Schematic diagram illustrating the stabilizing effect of hydrocolloids during pasting. 72

LIST OF TABLES

Table 3.1: Properties of teff, maize, and potato starch granules.....	3
Table 3.2: Effect of chemical and physical modification methods on starch functional properties.....	16
Table 3.3: Effect of food additives on the rheological properties of different starches.....	18
Table 3.4: Common food applications of cellulose derivatives.....	20
Table 3.5: Properties of microcrystalline cellulose, cellulose nanocrystals, and fibers	22
Table 3.6: Summarized studies on the effect of hydrocolloids on the pasting and gelling properties of different starches.....	25
Table 5.1: Pasting properties of teff starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during the short pasting cycles.....	43
Table 5.2: Pasting properties of teff starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during the extended pasting cycle.....	43
Table 5.3: Pasting properties of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during short pasting cycles.....	46
Table 5.4: Pasting properties of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during extended pasting cycles	46
Table 5.5: Pasting properties of potato starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during short pasting cycles.....	49
Table 5.6: Pasting properties of potato starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during extended pasting cycles	49
Table 5.7: Effect of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on granule size of maize starch during pasting.	51
Table 5.8: Effect of Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) addition on the gel hardness of teff, maize potato starches after short pasting cycles.	59
Table 5.9: Effect of Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) addition on the gel hardness of teff, maize, and potato starch gels after extended pasting cycles.	61

1. INTRODUCTION

Starch, a natural biopolymer produced by plants is commonly utilized as a major food component and as a food additive in several foods as a thickener to enhance their texture, flow, and stability (Ma *et al.*, 2019). It is used mostly in sauces, dressings, soups, baking, and confectionery. On a commercial scale, common starch sources include maize, wheat, tapioca, potato, and rice (Huang, *et al.*, 2007). The major shortcoming with the use of normal starch in food products is that it is adversely affected by shear stress, acidic conditions, and heat treatment during processing which affects the stability of the final product (Techawipharat *et al.*, 2008). As a result, these limitations impede the use of normal starch in several food products. To curb these limitations, native starches are usually chemically, physically, genetically, or enzymatically altered to enhance their tolerance to the various processing conditions (BeMiller, 2011).

However, genetic and enzymatic modification of starches is costly, and several physical modification techniques involve the use of high temperatures (above 100 °C) over a prolonged period which makes them energy-intensive and costly (Ma *et al.*, 2019). Also, the production of chemically modified starches involves the use of synthetic chemicals that generate a lot of industrial wastewater which makes them an environmental hazard (Neelam *et al.*, 2012). A new emerging green chemistry trend is increasingly pushing for the use of techniques that use fewer synthetic chemicals and generate little or no hazardous industrial waste (Anastas & Eghbali, 2010).

Hydrocolloids such as non-starch polysaccharides (NSP) from plant sources can be utilized in starch modification with little or no industrial waste generated. Unlike physical starch modification methods, hydrocolloids (other than starch) can modify the starch functional properties without the use of extreme processing conditions of temperature and time. This potentially makes the use of hydrocolloids in starch modification, cost-effective and energy-efficient (von Borries-Medrano *et al.*, 2018). The use of hydrocolloids can shield and/or stabilize starch granules against shear stress forces during processing, enhance food product rheological properties, bind moisture, and avoid syneresis from taking place (Baranowska *et al.*, 2008).

Several NSP have been used to enhance starch pasting and gelling properties in different studies such as gellan, carrageenan, guar gum, xanthan gum, carboxymethyl cellulose, and konjac (Chandanasree *et al.*, 2016; Shi & BeMiller, 2002; Huang *et al.*, 2007; Ma *et al.*, 2019). Starch interactions with other

hydrocolloids are greatly influenced by the type of hydrocolloid used and the source of starch since the different starches vary in the size of granules and microstructure (Techawipharat *et al.*, 2008.).

A lot of research has been done on the use of the aforementioned hydrocolloids which reported that indeed the addition of those hydrocolloids increased the peak and final viscosities of the starch system (Song *et al.*, 2006; Rosell *et al.*, 2011; Linlaud *et al.*, 2010; Shi & BeMiller, 2002). In addition to the above findings, it was observed that hydrocolloids reduced the degree of granule rupturing which consequently stabilized the granules against breakdown (BeMiller, 2011). This was attributed to the hydrocolloid networks which surround the surface of the starch granule surface (Shi & BeMiller, 2002). Even with the above findings, limited literature still exists on the interaction of teff, maize, and potato starch with microcrystalline cellulose (MCC) and cellulose nanofibers (CNF).

MCC and CNF can be used in the starch modification process as an environmentally friendly substitute and cost-effective alternative since they are derived from a readily available source (cellulose) (Ng *et al.*, 2015). MCC and CNF have different diameters: 50-200 μm (Thoorens *et al.*, 2014) and 1-100 nm (Corrêa *et al.*, 2010) respectively. This difference in size enables them to exhibit different effects on the systems they are applied to (Sekhon, 2010). They are readily available, renewable, and sustainable and thus they represent a natural resource of incredible value in today's nanotechnology applications (Techawipharat *et al.*, 2008). CNF exhibits viscoelastic behavior which can enhance starch gelling properties (Moberg *et al.*, 2017). Also, the ability of both MCC and CNF to form highly viscous dispersions even at low concentrations makes them ideal for the modification of starch in low glycemic index foods (Franco & de Muniz, 2015).

The addition of hydrocolloids to teff, maize, and potato starches can improve the structural integrity and overall functional properties of the starch. Therefore, the main aim of this project is to study the interaction of microcrystalline cellulose (MCC) and cellulose nanofibers (CNF) as hydrocolloid sources at different length scales with teff, maize, and potato starches during pasting.

2. LITERATURE REVIEW

In this chapter, literature on the starch structure and composition, with special attention given to teff, maize, and potato starch will be reviewed. The structure and properties of microcrystalline cellulose (MCC) and cellulose nanofibers (CNF) will be discussed. Finally, the effects of starch-hydrocolloid interactions on starch functionality and the research on the chemistry of these interactions are reviewed.

2.2 Starch

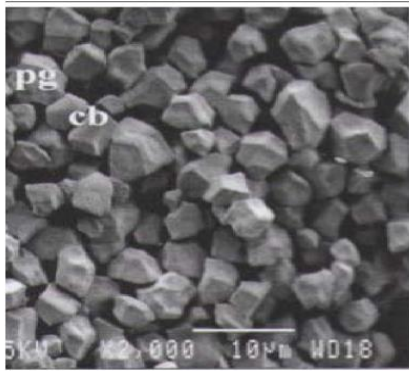
2.2.1 Starch granules

Starch is organized as granular structures. The structure varies from one plant species to another. Typically, the size of starch granules of cereal grains can range from 1 μm to 100 μm in size (Lindeboom *et al.*, 2004). Of the three starches discussed in this review, potato starch granules have the largest granule size (50 – 300 μm) followed by maize (15 - 30 μm) and teff starch (2- 6 μm) respectively (Table 2.1 & Figure 2.1). All three starches have a unimodal granule size distribution.

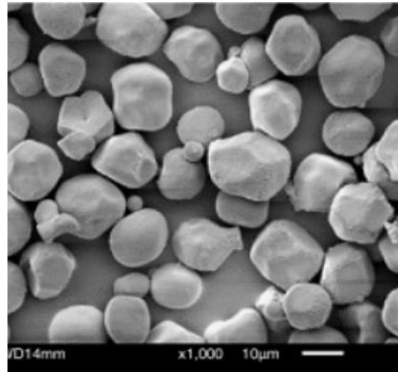
Table 2.1: Properties of teff, maize, and potato starch granules

Property	Teff starch granules	Maize starch granules	Potato starch granules
Granule Size (Diameter)	2- 6 μm (Gebremariam <i>et al.</i> , 2014)	15 - 30 μm (Thomas & Atwell, 1999)	50 – 300 μm (Baldwin <i>et al.</i> , 1998)
Shape	Polygonal (Bultosa <i>et al.</i> , 2002)	Angular and spherical (Whistler & BeMiller, 1997)	Lenticular (Horstmann <i>et al.</i> , 2016)
Size Distribution	Unimodal (Bultosa <i>et al.</i> , 2002)	Unimodal (Peng <i>et al.</i> , 2000)	Unimodal (Helle <i>et al.</i> , 2019)
Amylose content (%)	25–32 Gebremariam <i>et al.</i> , 2014)	25 - 30 (Wang <i>et al.</i> , 1993)	10 - 20 (Qi & Tester, 2016)

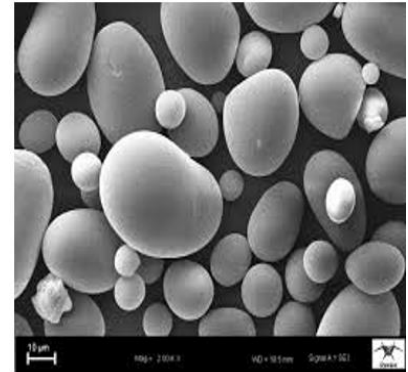
The organization and structure of a starch granule are not completely understood but different models have been suggested to explain it; namely, the blocklet model, fibrillar, and cluster models (Gallant *et al.*, 1997). Amongst the aforementioned models, the blocklet model is most commonly accepted (Pérez *et al.*, 2009).



Teff starch granules
(Bultosa *et al.*, 2002)



Maize starch granules
(Whistler & BeMiller, 1997)



Potato starch granules
(Jiang *et al.*, 2010)

Figure 2.1: SEM images of individual starch granules from teff, maize, and potato starch respectively. According to the blocklet model, the structure of the granules is very hierarchical with several concentric crystalline and semi-crystalline layers (Figure 2.2) that increase in diameter as they extend further away from the center of the granule (hilum) towards the exterior.

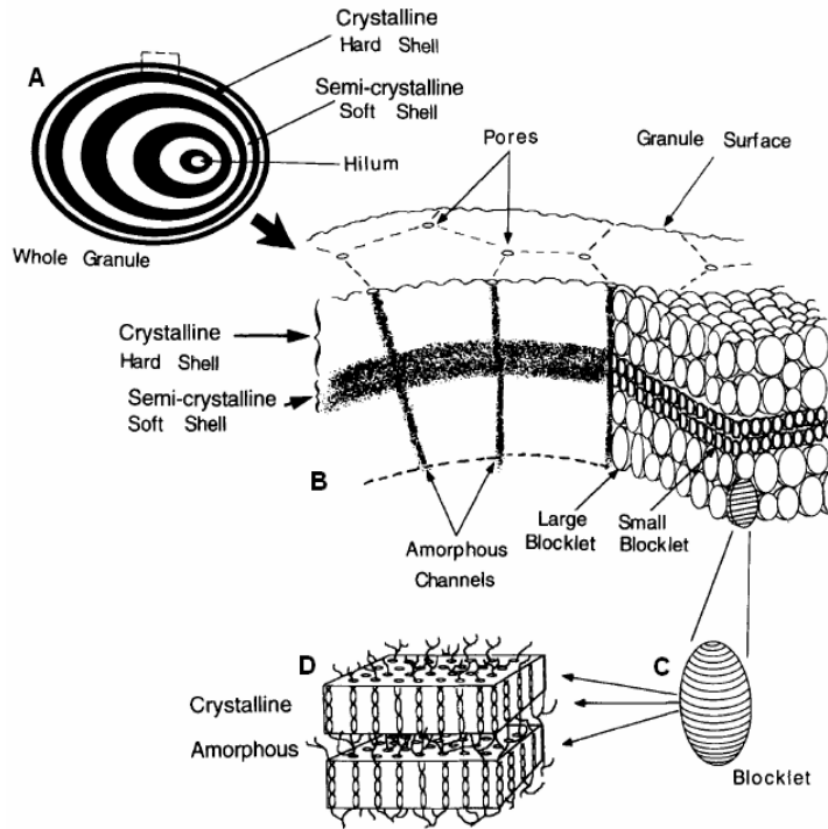


Figure 2.2: A schematic diagram of the blocklet showing the structural organization of the starch granule (Zobel, 1988).

The second level of organization is made up of a blend of soft and hard layers. These layers each have blocklets that vary in size based on the layer of the starch granule they are located in. The crystalline hard layer has large blocklets while the semi-crystalline layer has small sizes (Zobel, 1988).

At the molecular level, these blocklets are composed of alternating crystalline and amorphous lamellae (Figures 2.2 and 2.3). The crystalline lamellae predominantly comprise amylopectin clusters while amylose chains are mostly found in the amorphous part (Zobel 1988 b).

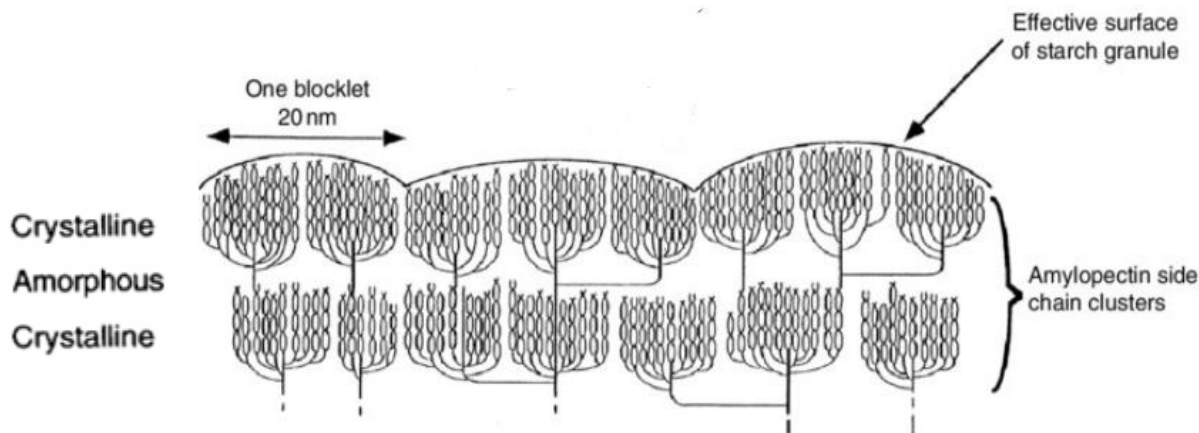


Figure 2.3: Schematic diagram showing side-chain clusters forming the blocklet structures seen at the starch granule surface (Pérez *et al.*, 2009).

Starch is a plant polysaccharide comprising two polymers namely, amylose and amylopectin (Figure 2.4). Starch is isolated in structures known as granules (Pérez & Bertoft, 2010). These polymers are mainly made up of glucose monomers linked together by α (1 \rightarrow 4) glycosidic bonds and different degrees of branching with α (1 \rightarrow 6) glycosidic bonds (Singh, 2011). Although starch is majorly composed of amylopectin and amylose, it also has some minor constituents such as lipids, minerals, proteins, and phosphoester groups (Jane, 2009).

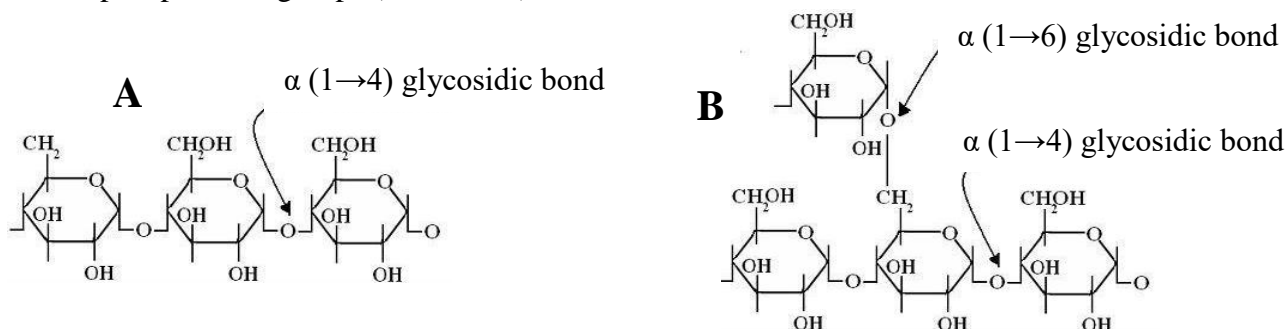


Figure 2.4: Amylose (A) and amylopectin (B) molecular structures respectively (Mua & Jackson, 1997).

Amylose is essentially a linear polymer of glucose monomers containing mainly 99% α (1 \rightarrow 4) glycosidic bonds and less than 1% α (1 \rightarrow 6) glycosidic bonds depending on the starch cultivars and structure (Singh, 2011). Amylose tends to form both single and double helical structures (Figures 2.5 & 2.6) stabilized by intramolecular hydrogen bonds and Van der Waals forces (Oates, 1997).

The helices have a hydrophobic core due to the orientation of the CH groups on the inside of the helix and a hydrophilic exterior due to the orientation of the hydroxyl groups on the outside of the structure (Zobel, 1988). This helical structure facilitates amylose interaction with other molecules which can influence the functionality of starch (Eliasson, 1994). The formation of amylose double helices via junction zones has been reported to cause starch retrogradation and gelling (Chung *et al.*, 2003).

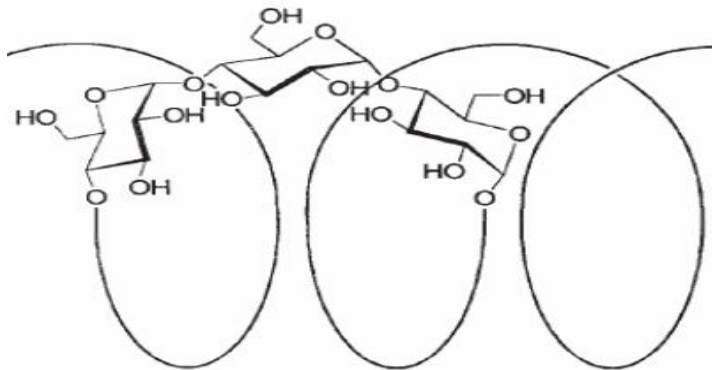


Figure 2.5: Single helix amylose structure (Immel & Lichtenhaler, 2000)



Figure 2.6: Double helical amylose structure (Zobel, 1988).

Amylopectin is a majorly branched polymer comprising about 95% α (1 \rightarrow 4) glycosidic bonds and nearly 5 % α (1 \rightarrow 6) glycosidic bonds also depending on the starch source (Tang *et al.*, 2006). As a result of the amylopectin branching, it forms clusters with three types of chains, namely, A, B, and C, and alternating amorphous and crystalline regions as shown in Figure 2.7. Contrary to B chains, A chains are typically shorter, located at the exterior of the clusters (Parker & Ring, 2001). At the reducing end, amylopectin has C chains which have both long and short chains attached to it.

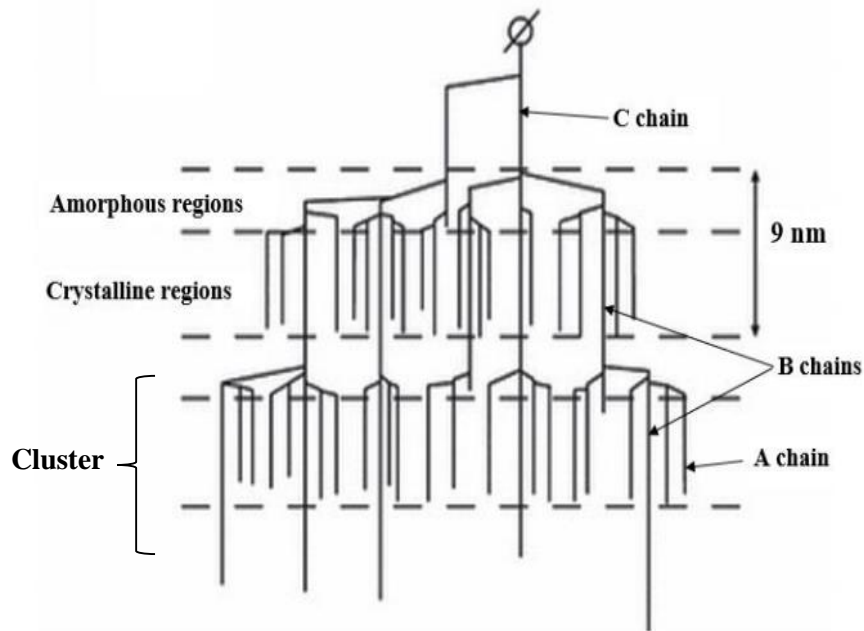


Figure 2.7: Schematic diagram showing the arrangement of amylopectin into clusters (Hizukuri *et al.*, 1986)

2.2.2 Starch wet heat processing

When starch is heated in the presence of adequate water, it undergoes several physical changes which influence its functional properties (Sandhu & Singh, 2007). With the help of specialized equipment and instruments, these processes can be measured and analyzed. For example, DSC (Differential Scanning Calorimetry) can generally measure the thermal properties of starch to measure the gelatinization temperature whereas a rheometer can be used to measure the pasting and retrogradation properties.

2.2.2.1 Gelatinisation

The process of heating quickens the process by which water molecules enter the starch granule through the surface pores into the amorphous channels which permeate the entire granule (Figure 2.8). With adequate hydration and heating, the van der Waals forces and hydrogen bonds in the crystalline regions are weakened causing the molecular collapse of the structure (Oh *et al.*, 2008). The entry of water, and breaking down of intermolecular hydrogen bonds leads to the loss of granule molecular order, birefringence, and crystallinity.

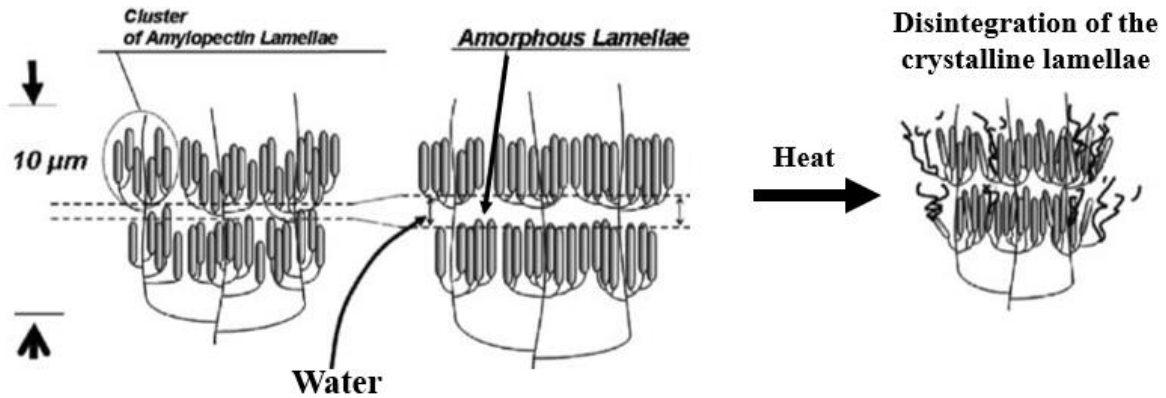


Figure 2.8: Schematic diagram showing the process of starch gelatinization (Knorr *et al.*, 2006)

Generally, due to variations in starch granule attributes, the whole process of gelatinization occurs over a range of temperatures (Parker & Ring, 2001). To monitor and/or determine the process of gelatinization of the different starches, different methods can be used. Spectrophotometric techniques such as Fourier transform infrared (FTIR), X-ray diffraction (XRD), and Nuclear magnetic resonance (NMR) can be used to monitor molecular changes that occur during gelatinization (Karoui *et al.*, 2010). Microscopic examination of granules allows for the observation of the extent of swelling and gelatinization, as well as the integrity and size of the swollen granules (Liu *et al.*, 2009). Thermal techniques such as Differential scanning calorimetry (DSC) have been used to monitor and measure changes in heat flow due to crystallite melting as starches undergo gelatinization.

DSC is a popular method that has been widely utilized to determine gelatinization temperatures of the different starches rapidly and conveniently (Kraugerud & Svihus, 2011). While using DSC, heating temperatures are steadily increased which causes the starch granule crystalline regions to melt (Ratnayake & Jackson, 2006). As a result, an endothermic peak is generated which represents the amount of heat energy required to gelatinize that particular starch. By analyzing the endothermic peak of the DSC thermogram, the onset, peak, and final or completion temperature of gelatinization can be determined.

The gelatinization temperature ranges of teff, maize, and potato starch are 68–80 °C (Bultosa *et al.*, 2002), 60–79 °C (Narziss & Back, 2009), and 60–95 °C (Liu *et al.*, 2009) respectively (Figure 2.9). Higher gelatinization temperatures require higher energy to attain and thus an increased industrial or processing energy cost (Sandhu & Singh, 2007).

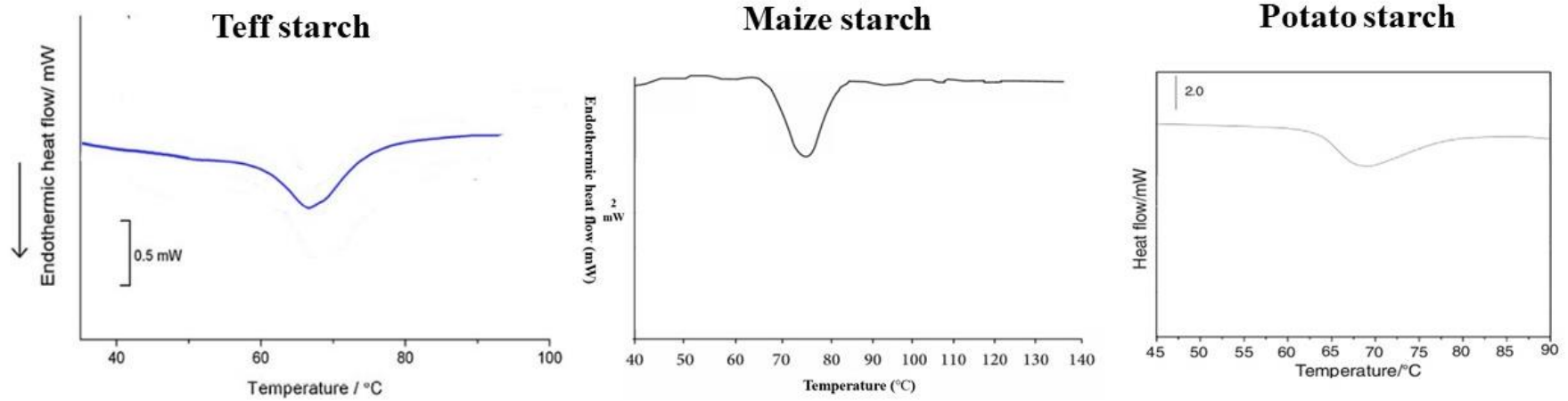


Figure 2.9: DSC curve of native teff starch (Nyakabau *et al.*, 2013), maize starch (Juneja *et al.*, 2014), potato starch (de Oliveira *et al.*, 2018) respectively.

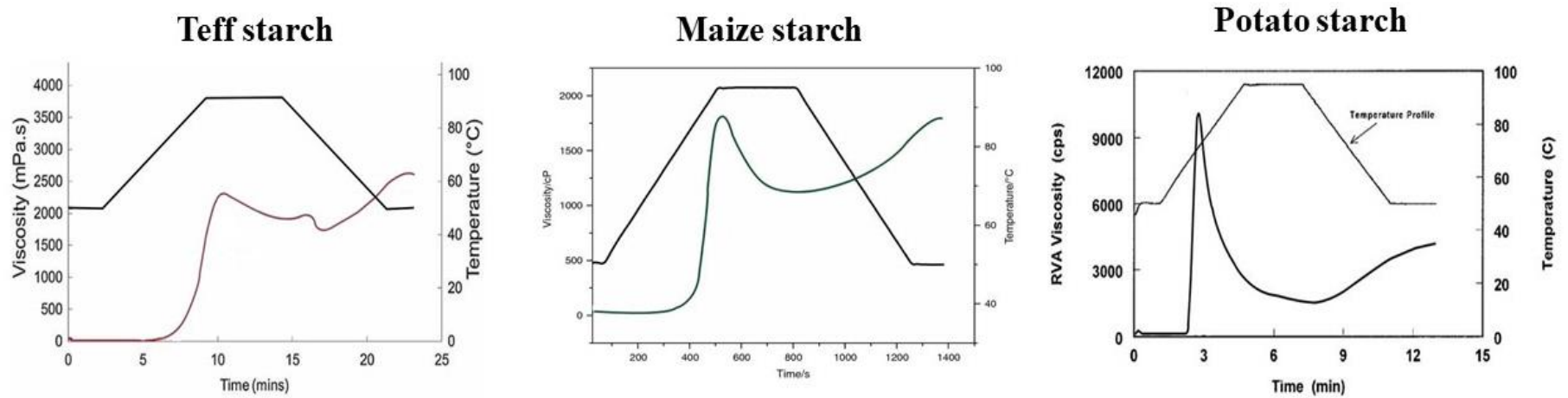


Figure 2.10: Pasting profile of native teff starch (Nyakabau *et al.*, 2013), maize starch (de Oliveira Maior *et al.*, 2020), potato starch (Lawton *et al.*, 1999) respectively.

2.2.2.2 Starch rheology

The pasting process involves the change in viscosity as a result of heat and water-induced starch granule swelling (Kumar & Khatkar, 2017). During pasting, several soluble molecular components of the starch granule such as amylose are exuded into the continuous phase. When starch granules are heated within or above their gelatinization temperature range, they rapidly imbibe water causing them to swell (Ratnayake & Jackson, 2006). Swollen granules reduce the inter-granular distance thus reducing mobility within the system and this is reflected in the increased viscosity. This process is referred to as pasting and it is a very essential step in the application of starches as thickening agents (Berski *et al.*, 2011).

During the pasting process, a phenomenon called gelatinization also occurs which involves the irreversible loss of starch granule morphological order (Figure 2.8). Gelatinization occurs when starch granules in presence of excess water are heated causing them to swell and the crystalline layers within to melt (Chen *et al.*, 2015).

After pasting, when the viscous starch solution is left to cool, its viscosity starts to increase again forming a gel (Hoover *et al.*, 1994). This is because of the re-interaction and rearrangement of amylose molecules and linear chains of amylopectin via junction zones forming more crystalline and ordered three-dimensional helical structures (Figure 2.11: c & d) (Wang *et al.*, 2015). The interaction is mostly by hydrogen bonding.

During short and long-term retrogradation, the amylose molecules and linear chains of amylopectin molecules re-associate and entangle themselves forming junction zones (Ye *et al.*, 2016). The linear nature of these chains enables them to rearrange easily via multiple inter and intra hydrogen bonds. This form of molecular entanglement leads to the formation of the gel structure (Tsai *et al.*, 1997) As more of these bonds are formed, the gel structure becomes more compact causing the exudation of the water that was entrapped within the starch system in a process called syneresis.

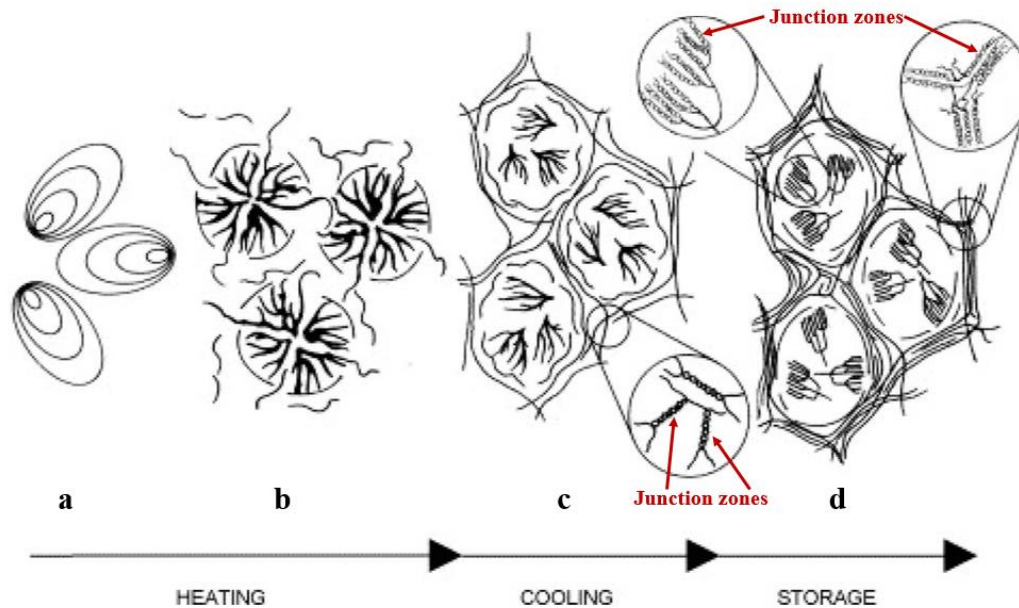


Figure 2.11: Reassociation of amylose molecules and linear chains of amylopectin during retrogradation (Wang *et al.*, 2015)

Retrogradation time can range from several minutes to several days (Wang *et al.*, 2015). Starches with higher amylose content tend to form firmer gels because more molecular entanglements can take place forming more crystalline structures (Li *et al.*, 2019). Also, due to the high amylose content, more junction zones can be formed giving the gel a firmer texture (Schrieber & Gareis, 2007). Retrogradation is a key process in starchy food production that is monitored because it affects the textural attributes and digestibility of the final food product. (Copeland *et al.*, 2009).

A rheometer is one of those instruments that can be used to measure changes in the rheological properties of starch pastes with regulated stirring and temperature conditions over time (Lagarrigue & Alvarez, 2001). Using the pasting curves plotted by the rheometer, we can understand the changes that occur during pasting and retrogradation (Figure 2.12).

With the help of a starch pasting curve, the pasting properties of that specific starch such as peak, breakdown, final viscosities, pasting time, and temperature are determined. The pasting profile as a function of temperature typically involves the heating phase followed by the holding phase and finally the cooling phase. The starch pasting properties also change as the pasting profile transitions from one phase to another (Karwasra *et al.*, 2017).

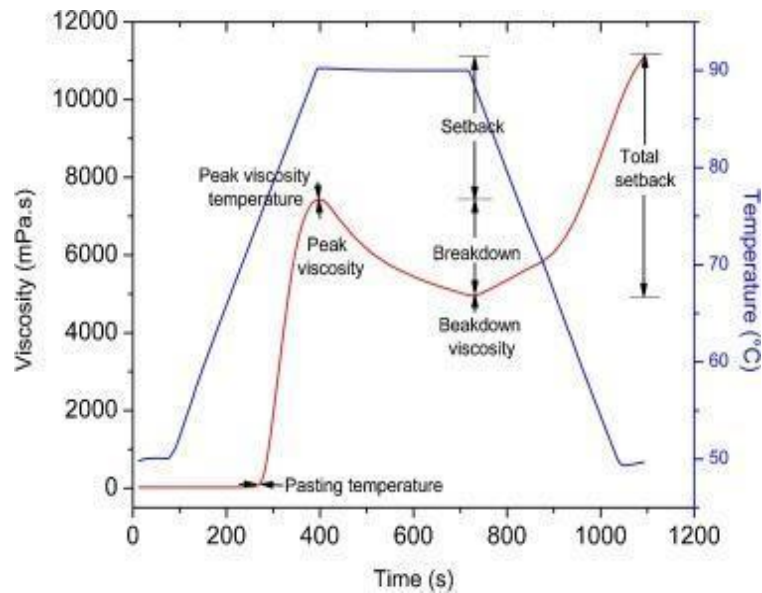


Figure 2.12: A generic pasting profile of starch (Rincón-Londoño *et al.*, 2016).

As explained earlier, the pasting process starts during the heating phase in the presence of excess water and is depicted by the sharp increase in viscosity. Starch gelatinization continues throughout the temperature holding phase and is depicted by the increase in the breakdown viscosity as several starch granules are rupturing at this stage. Finally, in the cooling phase, retrogradation starts to take place as the amylose molecules rearrange to form junction zones. For most starches, this is depicted by the increase in the setback viscosity.

Because of the uniqueness of the different starches and their chemical compositions, each starch has a unique pasting profile (Figure 2.10). Potato starch normally has higher peak and breakdown viscosities followed by maize and teff starch respectively (Horstmann *et al.*, 2016). Potato starch has a significantly higher concentration of bulky phosphate monoester groups covalently bonded with glucose molecules than maize and teff starches (Schirmer *et al.*, 2013). These bulky phosphate groups create intermolecular spaces that can bind more water during pasting which increases the degree of granule swelling. As a result, this increases the starch paste's peak viscosity.

Furthermore, potato starch has the largest starch granules in comparison to maize and teff starch (Table 2.1). Large starch granules tend to have higher swelling power than smaller granules because the large granules can absorb more water through their pores during the pasting process (Horstmann *et al.*, 2016). The presence of large starch granules in potato starch implies that it is very susceptible to significant breakdown when exposed to continuous shear forces (Arendt & Bello, 2008).

Using the rheometer, we can also determine the starch flow properties as they change with variations in shear rate. After pasting, starch molecules tend to reassociate and entangle forming a thick mass or paste. At zero or low shear rates, these entanglements remain intact which gives the starch paste a high viscosity. The starch paste exhibits the upper Newtonian plateau because the viscosity remains relatively constant (Aho *et al.*, 2015).

As the shear rate increases, the formed molecular entanglements disentangle leading to a rapid decrease in the paste viscosity (von Borries-Medrano *et al.*, 2017). With a steady increase in shear rate, most of the significant molecular associations amongst starch molecules are broken. Any further shearing beyond this critical point starts to realign the breakdown starch components in the direction of the shear. This whole process is referred to as shear thinning.

Eventually, as the shear rate increases further, the viscosity becomes constant again exhibiting a lower Newtonian plateau (Figure 2.13). At this point, very limited molecular entanglements exist which generally have no significant effect of the viscosity of the whole system.

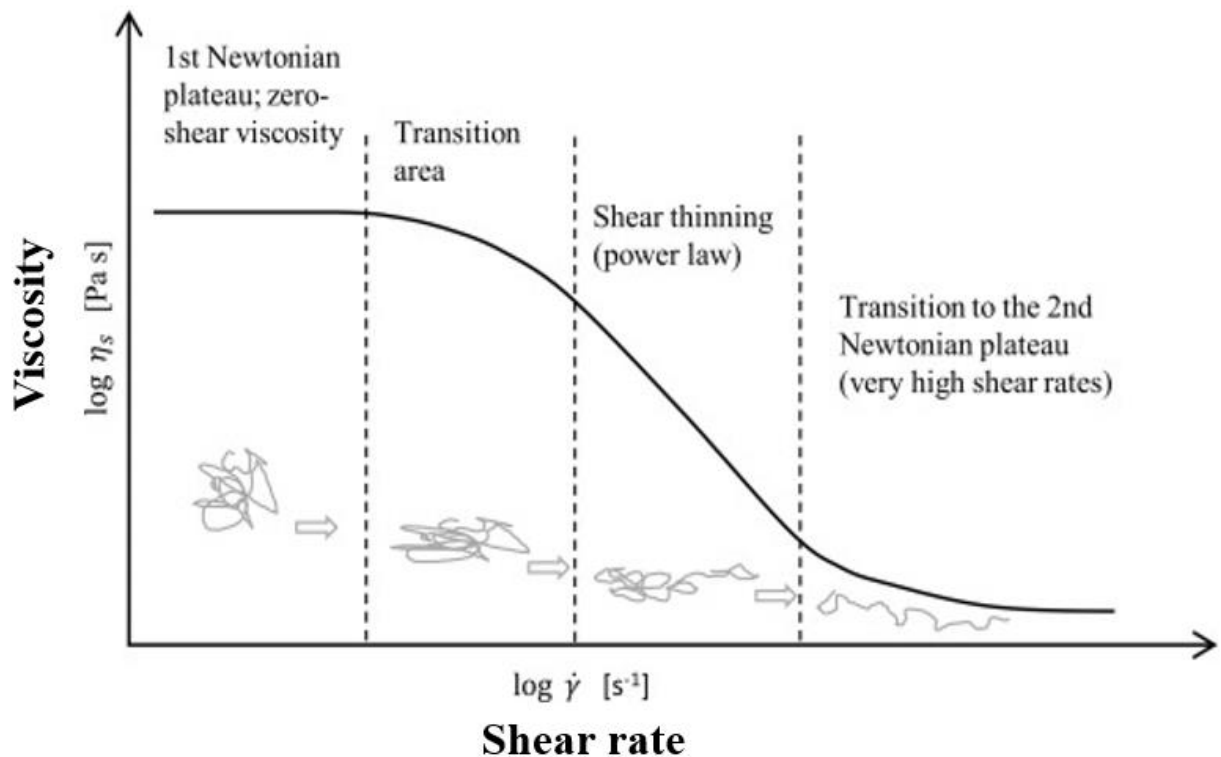


Figure 2.13: Schematic diagram showing the effect of shear rate on the viscosity (Aho *et al.*, 2015).

2.2.3 Factors affecting native starch rheological properties

2.2.3.1 Starch granule size

Differences in starch granule size can affect the pasting properties of native starch. Starches with larger starch granules tend to form more viscous systems than those with smaller ones (Horstmann *et al.*, 2016).

Potato starch possesses large starch granules which ultimately increase the resistance to flow within the continuous phase (Noda *et al.*, 2006). The larger granules reduce the available inter-granular spaces for mobility within the starch system which increases the molecular friction as they move against each other (Figure 2.14).

This is reflected in the exponentially high viscosity of potato starch (Figure 2.10). Such properties are very desirable for use as thickening agents in food products such as fillings, sauces, and soups (Zhang *et al.*, 2011).

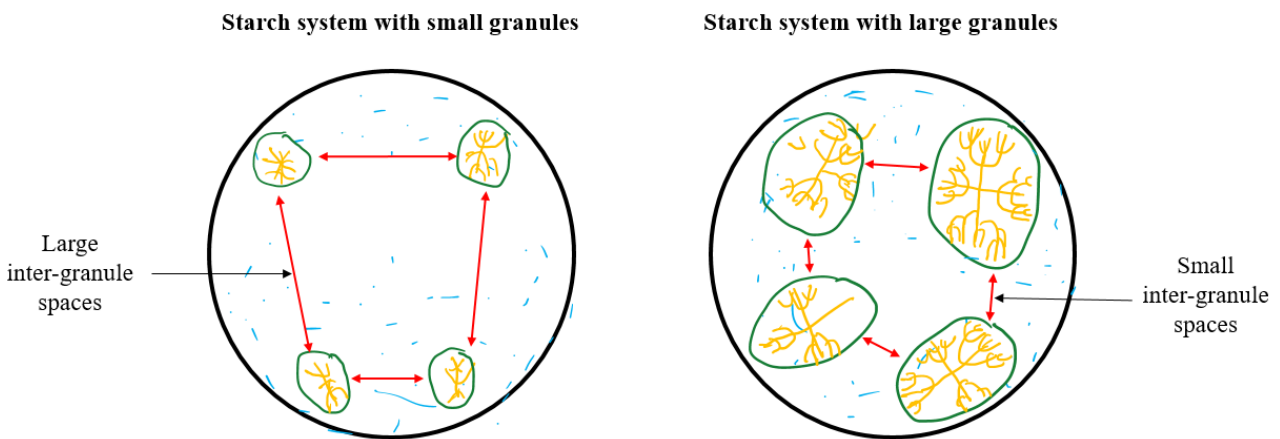


Figure 2.14: Schematic diagram illustrating the effect of starch granule size on the mobility within a starch system (Own work).

2.2.3.2 Amylose content size

Generally, for short-term starch gelation to occur, leached amylose molecules have to rearrange to form junction zones that form three-dimensional gel structures (Bultosa *et al.*, 2002). The essentially linear structure of amylose enables it to easily rearrange forming junction zones and molecular entanglements during gelling. Therefore, the higher the amylose content, the more inter and intramolecular entanglements that can occur and thus resulting in more rigid gel structures (Schrieber & Gareis, 2007).

As gels become firmer, gel strength increases, and consequently their storage modulus (G') also increases (Panaras *et al.*, 2011). Starches such as high amylose maize starch with higher amylose

content tend to have high gel strength (Liu *et al.*, 2019) (Figure 2.15). Also as discussed earlier, gel formation is typical of retrogradation which may be undesirable in certain foods such as bread, sauces, and cake because it leads to syneresis.

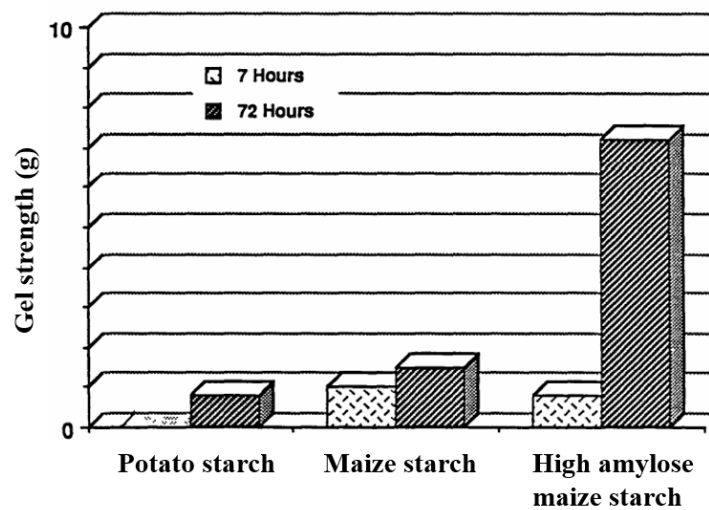


Figure 2.15: Gel strength of potato, maize, and high amylose maize starch after 7 hours and 72 hours of storage respectively (Kasemsuwan, 1995)

2.2.3.3 Starch modification

When subjected to typical processing conditions, native starch has limited functionality. In processes that require the use of high processing temperatures, native starch has limited stability and can thus easily break down (Eliasson, 2017). Also, native starch easily retrogrades upon cooling (Bao & Bergman, 2004). As a result, native starch is modified to improve its versatility in food for industrial food applications.

Physical and chemical methods of starch modification are commonly utilized to address the limitations of native starch (Table 2.2). Physical methods such as radiation, hydrothermal treatment, and pre-gelatinization have been used to improve starch solubility in cold water and consistency (Ashogbon & Akindayo, 2014). Although physical starch modification methods are generally regarded as safe and simple, those that involve heat treatment and mechanical modification can be energy-intensive making them costly. Chemical starch modification methods such as oxidation, etherification, or esterification can also be used to retard retrogradation and syneresis in starches (Satrapai & Suphantharika, 2007).

Table 2.2: Effect of chemical and physical modification methods on starch functional properties

	Method	Effect on functional properties
Chemical	Esterification and etherification	Improved shear and thermal stability. Retard retrogradation (BeMiller & Whistler, 2009)
	Oxidation	Retard retrogradation. Increased solubility (Han <i>et al.</i> , 2005)
Physical	Hydrothermal treatment	Improved shear and thermal stability and paste viscosity (Lim <i>et al.</i> , 2003).
	Pre-gelatinization	Improved cold water solubility and granule swelling (Lawal, 2019)
	Annealing	Increased starch granule size. Improve thermal stability (Krithika & Ratnamala, 2019)

Although chemical modification methods can enhance starch functional properties, the use of chemicals in starch modification can be quite expensive and raises a lot of health concerns from consumers (Ziaud-Din *et al.*, 2017; Gill *et al.*, 2018). As a result, less costly and hazardous starch modification methods such as the use of organically sourced food additives are being investigated and utilized to create safer food options.

2.2.3.4 Additives

Common food additives used in starchy foods usually include such as proteins, salt, lipids, hydrocolloids, etc, which can influence its behavior (Furia, 1973). These additives tend to interact with starch components such as amylose chains and/or can also coat the starch granules thus affecting the degree of granule swelling and amylose leaching (BeMiller, 2011).

From Table 2.3, the addition of proteins, salts, and hydrocolloids has generally been reported to increase the peak and final viscosity of starches (Alloncle *et al.*, 1989; Bahnassey & Breene, 1994; Sudhakar *et al.*, 1995; Biliaderis *et al.*, 1997; Baranowska *et al.*, 2008; Zhang *et al.*, 2018). This is partly attributed to the hydrophilic nature of these additives which improves the water-binding capacity of the starch system (Mahmood *et al.*, 2017). This increases the swelling power of the starch granules which also makes the starch system more viscous. These hydrophilic additives have also been reported to reduce

the rate of starch short-term retrogradation by interacting with amylose molecules making it unavailable for gel formation (Baranowska *et al.*, 2008).

Hydrophobic additives such as fatty acids have also been reported to increase the peak viscosity (Wokadala *et al.*, 2012; D'Silva *et al.*, 2011). In a study by Maphalla and Emmambux (2016), the addition of stearic acid to maize and teff starch increased the final viscosity of the starches and this was attributed to the formation of amylose-lipid complexes.

Given that most previous studies have focused on the effect of singular additives on the rheological properties of individual starches, there is more work to be done to understand the synergistic effect of combining multiple additives in a single starch system. This synergism could amplify the effects of the individual additives when used simultaneously within a starch system.

There is also extensive literature on hydrocolloid and starch interactions because they can be organically sourced to create a food-safe starch-modification alternative. However, several of the hydrocolloids studied are not readily and commercially available and thus an unsustainable alternative. On the other hand, cellulose is a readily available biopolymer from plant sources and can thus be utilized to produce cellulose derivative hydrocolloids as a sustainable and environmentally friendly alternative. Some cellulose derivative hydrocolloids such as carboxymethylcellulose and methylcellulose have already been used in other studies to modify starch rheological properties (Table 2.6).

There is more room to further explore and understand the effects of other cellulose derivative hydrocolloids on the different starches and their functional properties.

Table 2.3: Effect of food additives on the rheological properties of different starches.

Type of Additive (s)	Reference	Starch used	Additive (s)	Important findings
Proteins	Lu <i>et al.</i> , 2012	Maize	Lysine Glycine	The addition of lysine decreased the pasting temperature and setback viscosity while peak viscosity, breakdown, and swelling power increased. Glycine has no significant effect on the pasting properties of maize starch. Loss modulus and tan delta of maize starch increased in the presence of lysine and glycine.
Salts	Samutsri & Suphantharika, 2012	Rice	Sodium chloride Calcium chloride	The addition of sodium and calcium chloride significantly increased the peak, breakdown, and final viscosities of rice starch. The pasting temperature was also increased in the presence of salts.
Lipids	Singh <i>et al.</i> , 2002	Maize Potato	Myristic acid Stearic acid	Stearic acid addition decreased the peak elastic modulus of maize starch but increased that of potato starch. Myristic acid addition to both maize and potato starch decreased the peak elastic modulus. Syneresis decreased with the addition of both fatty acids.
Hydrocolloids	Ma <i>et al.</i> , 2019	Maize	konjac glucomannan (KG)	The addition of KG increased the peak, breakdown, and final viscosity. Maize starch treatment with KG also increased storage and loss modulus.
	Funami <i>et al.</i> , 2005	Wheat	Guar gum, tara gum, locust bean gum & konjac glucomannan	Each polysaccharide increased the peak & setback viscosity of wheat starch while the pasting temperature was lowered. After storage at 4 °C for 24 hours, the tan delta of the starch pastes increased significantly.

2.3 Cellulose derivative hydrocolloids

Cellulose is one of the most available biopolymers primarily consisting of β -d-glucopyranose units bonded together by β -1,4-glycosidic bonds (Shen *et al.*, 2010) (Figure 2.16). It is formed mainly in plant cell walls, some bacteria, and algae through photosynthesis. Cellulose has found use in the food industry because of its abundance, availability, renewability, biodegradability, and ease of recycling (Pennells *et al.*, 2020)

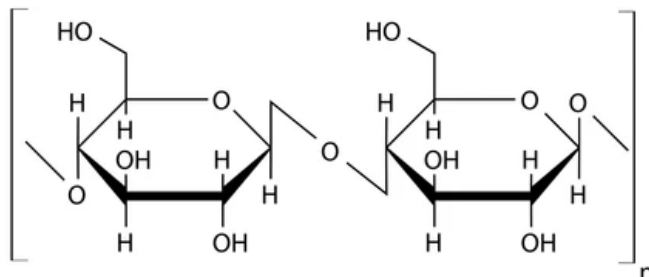


Figure 2.16: Molecular Structure of cellulose (Nsor-Atindana *et al.*, 2017).

2.3.1 Production of cellulose derivative hydrocolloids.

Cellulose derivative materials are often produced from wood pulp as the main raw material. Wood constitutes approximately 40–50 wt % cellulose, of which half of it exists in nanocrystal form and the other half in the amorphous form (Dufresne, 2013). As a result of the strong cellulose Intra and intermolecular hydrogen bonding, it is very resistant to several processing conditions (Vilarinho *et al.*, 2018). To utilize cellulose more in food applications (Table 2.4), it is often physically and/or chemically modified with mineral acids and bases to produce cellulose derivative hydrocolloids. Cellulose derivatives are mainly categorized into two groups namely; cellulose ethers and esters (Figure 2.17) (Osorio *et al.*, 2020).

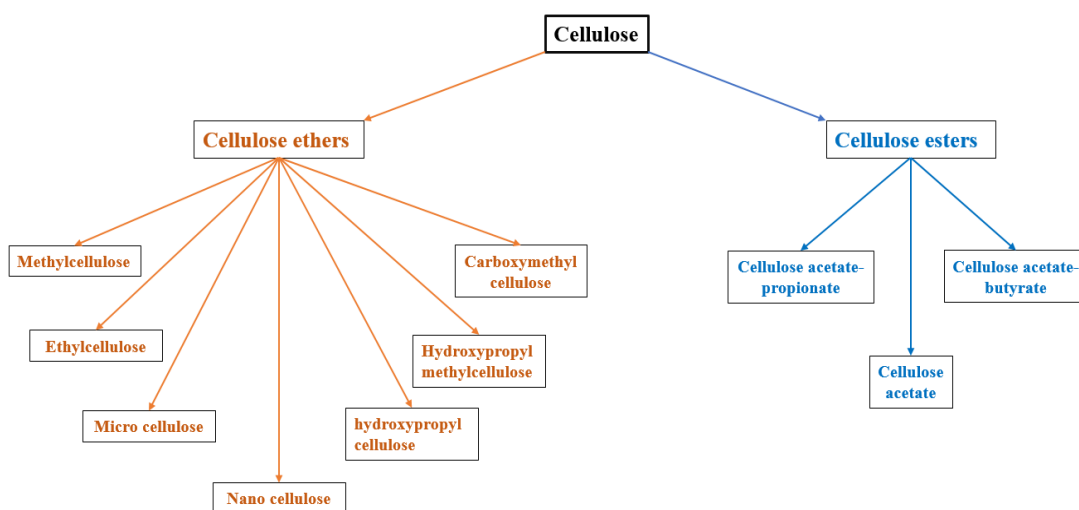


Figure 2.17: Main forms of cellulose derivatives (Own work)

Table 2.4: Common food applications of cellulose derivatives.

	Food applications	Cellulose derivative
Cellulose ethers	<ul style="list-style-type: none"> Thickening agent in pie fillings and seasonings 	Methylcellulose (Osorio <i>et al.</i> , 2020)
	<ul style="list-style-type: none"> Anti-crystallization agent in ice-cream 	Carboxymethyl cellulose
	<ul style="list-style-type: none"> Emulsion stabilizing agent 	(Teixé-Roig <i>et al.</i> , 2018)
	<ul style="list-style-type: none"> Water binding agent in bread 	Hydroxypropyl cellulose
		(Onyango <i>et al.</i> , 2009)
	<ul style="list-style-type: none"> Film-forming agent in flavor encapsulation 	Ethylcellulose (Yang <i>et al.</i> , 2014)
	<ul style="list-style-type: none"> Anti-caking agent in flours and spices Texturizers in soft candies and sour cream 	Micro cellulose (Ventura-Cruz & Tecante, A., 2021)
<ul style="list-style-type: none"> Stabilizing agent and a functional food ingredient as dietary fiber and to reduce the caloric value of food 	Nanocellulose (Serpa <i>et al.</i> , 2016)	

Generally, cellulose ethers are the main group of cellulose derivatives utilized in the food industry (Tosh, 2014).

Cellulose esters are formed when cellulose-rich material (such as cotton linters) is treated with acetic acid and acetic anhydride in the presence of sulfuric acid acting as a catalyst (Wang *et al.*, 2018).

Generally, most cellulose ethers are produced by treating cellulose (from wood pulp or cotton linters) with sodium hydroxide followed by alkyl halide or an epoxide (Hon, 2001). During these chemical reactions, hydroxyl groups attached to the cellulose chains are substituted by ether groups (Gelardi *et al.*, 2016).

For purposes of this review, the individual processes involved in the production of the following cellulose ethers (microcrystalline cellulose, cellulose nanocrystals, and fibers) are illustrated in the flow diagrams below (Figures 2.18-20).

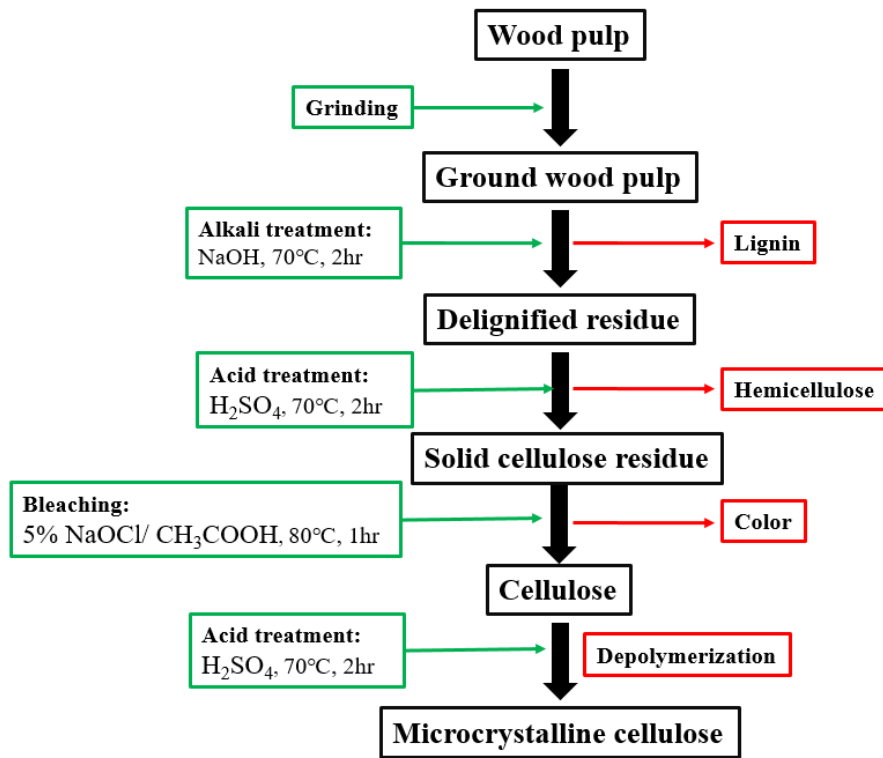


Figure 2.18: Microcrystalline cellulose production from wood pulp (Katakajwala & Mohan, 2020).

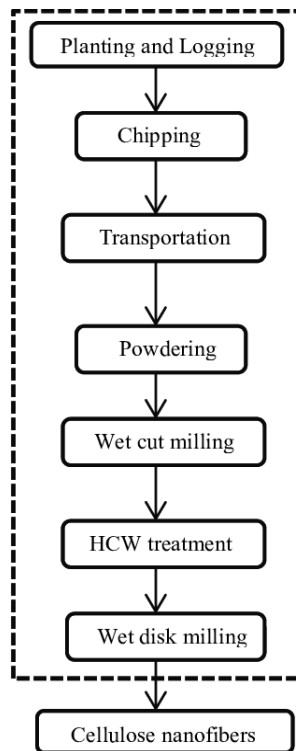


Figure 2.19: Cellulose nanofiber production from woody biomass using a mechanochemical method (HCW = hot-compressed water) (Moon *et al.*, 2013).

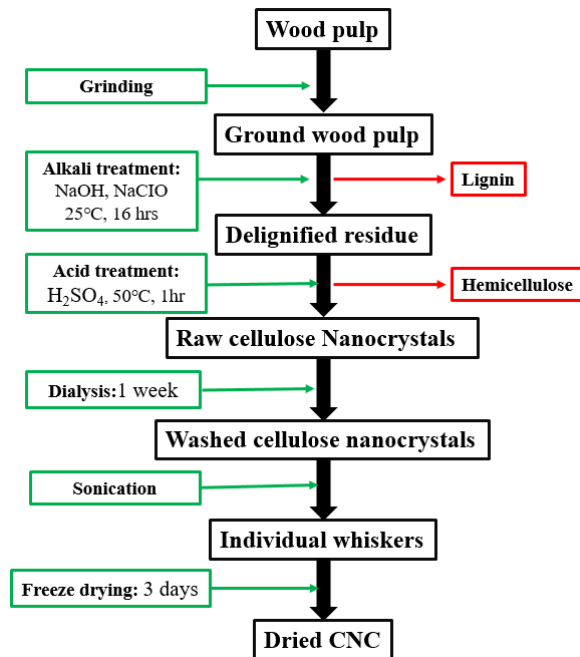


Figure 2.20: Cellulose nanocrystals (CNC) production from woody biomass using acid hydrolysis method (Thompson *et al.*, 2019).

2.3.2 Properties of microcrystalline cellulose (MCC), cellulose nanofibers (CNF), and cellulose nanocrystals (CNC)

All these cellulose derivatives possess similar cellulose properties such as odorless, low density, high surface-area-to-volume ratio, and biodegradability (Du *et al.*, 2016; Chaerunisaa *et al.*, 2019). Both MCC and CNC are crystalline while CNF is fibrous in structure (Figure 2.21). Other properties of MCC, CNC, and CNF are summarized in the table below.

Table 2.5: Properties of microcrystalline cellulose, cellulose nanocrystals, and fibers

Property	Microcrystalline cellulose	Cellulose nanocrystals	Cellulose nanofibers
Structure	Crystalline (37-93%) (Rasheed <i>et al.</i> , 2020; Terinte <i>et al.</i> , 2011)	Crystalline (70-85%) (Ciolacu, 2018; Xu <i>et al.</i> , 2013).	Fibrous (Ansari & Berglund, 2016)
Morphology	Particulate (Thoorens <i>et al.</i> , 2014)	Needle-like structures (Xu <i>et al.</i> , 2013)	Highly entangled, web-like structures (Xu <i>et al.</i> , 2013)
Particle size (Diameter)	50 – 200 µm (Thoorens <i>et al.</i> , 2014)	50-200 nm (Xu <i>et al.</i> , 2013)	1-100 nm (Corrêa <i>et al.</i> , 2010)
Particle Size (Length)	250–500 µm (Kian <i>et al.</i> , 2020)	100-600 nm (Islam & Rahman, 2019)	0.5–2 µm (Ansari & Berglund, 2016).

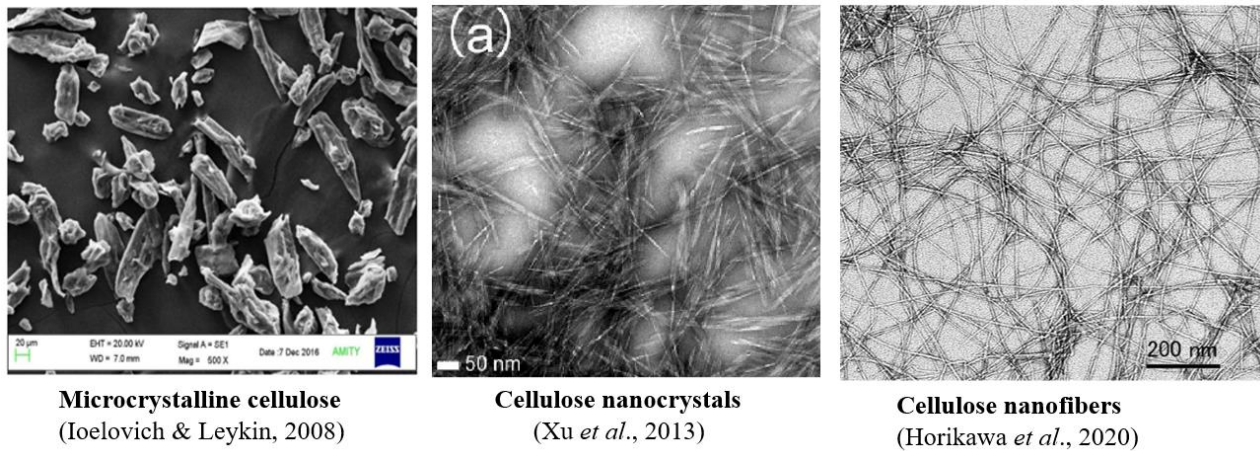


Figure 2.21: SEM of microcrystalline cellulose and cellulose nanocrystals and fibers

2.4 Effect of modification of starch with cellulose derivative hydrocolloids on its rheological properties

For purposes of this literature review, starch modification with cellulose-based hydrocolloids will be discussed with emphasis on their effect on pasting, gelling and visco-elastic properties.

2.4.1 Pasting properties

Table 2.6 indicates that the modification of starches with cellulose derivative hydrocolloids generally increases the peak and final viscosities of the starches. The pasting time and temperature of starches are however reported to decrease generally in the presence of cellulose derivative hydrocolloids.

The pasting properties of starch are influenced by both the components of the continuous and dispersed phase and how they interact with each other (Rao & Tattiyakul, 1999). The continuous phase contains the water solubilized hydrocolloid and leached amylose molecules while the dispersed phase comprises suspended starch granules and “ghosts” (Figure 2.22).

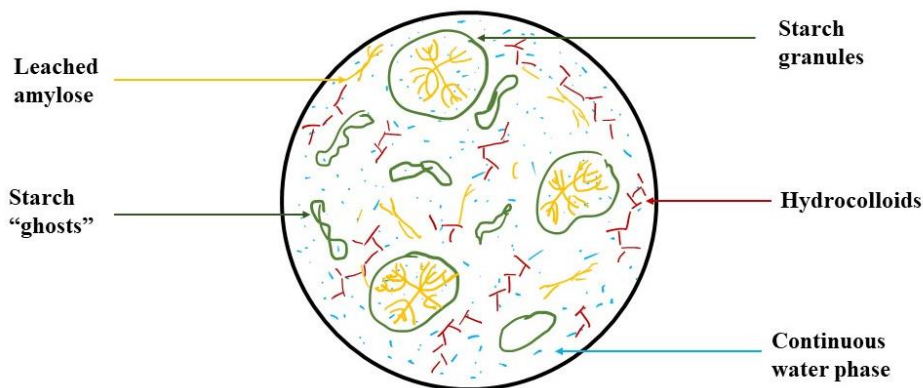


Figure 2.22: Orientation of the different components in the starch system during pasting (Own work).

According to Díaz-Calderón *et al.* (2018), pasting maize starch with cellulose nanofibrils increased the peak, breakdown, and final viscosity of the starch while the pasting temperature of the starch decreased with the addition of the hydrocolloid. Hydrocolloids in the presence of water form inter and intramolecular hydrogen bonds within the continuous phase of the starch system (Chaisawang & Suphantharika, 2005). These bonds form a network of intertwined and entangled hydrocolloid polymers that trap starch granules within the continuous phase thus increasing the overall starch system viscosity (Song *et al.*, 2008). These same networks have been reported to surround the surface of the starch granules thus reducing the rate at which granules rupture (Funami *et al.*, 2005). Swollen and unruptured starch granules reduce the effective space within the continuous phase to reduce molecular mobility. This eventually leads to an increase in paste viscosity and a drop in pasting temperature.

Similar behavior was observed in other studies (Table 2.6) such as Rojas *et al.* (1999) when HMPC was added to wheat starch leading to an increase in peak viscosity. Also, Mukprasirt *et al.* (2002) reported an increase in peak and final viscosity of rice starch when methylcellulose was added. This was again attributed to the highly viscous nature of methylcellulose which lead to the formation of interlinked hydrocolloid networks within the continuous phase. As a result, there is an increase in the overall viscosity of the rice starch.

Several researchers have proposed an interaction between leached amylose and hydrocolloids as another contributing factor to the increase in peak and final viscosities when hydrocolloids are added to starches (Bahnassey & Breene, 1994; Satrapai & Suphantharika, 2007; Funami et al. 2005). However, Yoshimura et al. (1988) and Tran *et al.* (2008) were opposed to the occurrence of such interactions. In Yoshimura's study, the treatment of maize starch with konjac-glucomannan significantly inhibited syneresis which meant that the hydrocolloid interacted with the free water within the continuous phase rather than the starch components.

Table 2.6: Summarized studies on the effect of hydrocolloids on the pasting and gelling properties of different starches.

Starch Properties	Reference	Starch(es) used	Cellulose Derivative Hydrocolloids Used	Important findings
Pasting properties	Rojas <i>et al.</i> , 1999	<ul style="list-style-type: none"> ● Wheat 	<ul style="list-style-type: none"> ● Hydroxypropyl methylcellulose (HPMC) 	Pasting time and temperature decreased while the peak viscosity increased.
	Shi & BeMiller, 2002.	<ul style="list-style-type: none"> ● Maize ● Rice ● Waxy maize ● Tapioca ● Potato ● Wheat 	<ul style="list-style-type: none"> ● Carboxymethylcellulose (CMC) ● HPMC 	Peak viscosity of all the starches increased in the presence of hydrocolloids except for potato starch which decreased when CMC was added to it.
	Mukprasirt <i>et al.</i> , 2002	<ul style="list-style-type: none"> ● Rice 	<ul style="list-style-type: none"> ● MC 	There was a significant increase in peak, breakdown, and final viscosities.
	Cui <i>et al.</i> , 2018	<ul style="list-style-type: none"> ● Maize ● Sweet potato 	<ul style="list-style-type: none"> ● Cellulose nanocrystals (CNC) 	CNC slightly increased the peak viscosity of both starches.
	Díaz-Calderón <i>et al.</i> , 2018	<ul style="list-style-type: none"> ● Wheat ● Maize 	<ul style="list-style-type: none"> ● Bacterial cellulose nanofibrils 	The addition of cellulose nanofibrils increased the peak, breakdown, and final viscosity of wheat and maize starch.

				However, the pasting temperature decreased.
Gelling Properties	Kohyama & Nishinari, 1992	<ul style="list-style-type: none"> ● Sweet potato 	<ul style="list-style-type: none"> ● MC 	MC slowed retrogradation forming soft gels.
	Eidam <i>et al.</i> , 1995	<ul style="list-style-type: none"> ● Maize 	<ul style="list-style-type: none"> ● CMC 	CMC accelerated gelation. Increased gel strength.
	Cui <i>et al.</i> , 2018	<ul style="list-style-type: none"> ● Maize ● Sweet potato 	<ul style="list-style-type: none"> ● CNC 	CNC inhibited short-term retrogradation of both maize and potato starch.
	Xu <i>et al.</i> , 2019	<ul style="list-style-type: none"> ● High amylose maize starch 	<ul style="list-style-type: none"> ● MCC 	The addition of MCC to high amylose maize starch increased gel hardness.
Visco-elastic properties	Eidam <i>et al.</i> , 1995	<ul style="list-style-type: none"> ● Maize 	<ul style="list-style-type: none"> ● CMC 	CMC increased loss modulus (G'') and lowered storage modulus (G')
	Techawipharat <i>et al.</i> , 2008	<ul style="list-style-type: none"> ● Rice ● Waxy rice 	<ul style="list-style-type: none"> ● MC ● CMC ● HPMC 	<p>The addition of these hydrocolloids increased the tan delta values of rice starch.</p> <p>Tan delta values of waxy rice starch were unchanged with the addition of hydrocolloids.</p>
	Xiong <i>et al.</i> , 2017	<ul style="list-style-type: none"> ● Wheat 	<ul style="list-style-type: none"> ● MCC ● CMC 	Tan delta values increased with the addition of MCC and CMC.

However, both the G' and G'' decrease with the addition of MCC and CMC. A slight insignificant increase in G' and G'' was observed as hydrocolloid concentrations increased from 5% to 10%.

Cui *et al.*, 2018

- Maize
- Sweet potato
- CNC

An increase in the concentration of CNC from 0% to 10% increased the tan delta and decreased the G' of maize and potato starch.

In a study by Tran *et al.* (2008) on the effect of xanthan and carboxymethyl cellulose (CMC) –cassava starch modifications on the amount of freezable water in starch gels, a linear decrease in the amount of freezable water as the hydrocolloid concentration was observed. He thus concluded that there existed no probable interactions between the CMC, xanthan gum, and cassava starch components. This suggests that indeed not all hydrocolloids will probably interact with starch molecules.

Although generally, some studies (Díaz-Calderón *et al.*, 2018; Mukprasirt *et al.*, 2002) report an increase in starch breakdown viscosity in the presence of cellulose derivative hydrocolloids, a study by Gularte and Rosell (2011) reported a decrease in breakdown viscosity of maize starch when modified with CMC and HPMC. This was attributed to the probable surrounding of the maize starch granules with CMC or HMPC hydrocolloid fibrils during pasting which stabilized the starch granule structure. There is limited microscopy-based research that has been done to understand and confirm the effect of hydrocolloids on the microstructure of starch granules and the interactions thereof during the pasting.

Every hydrocolloid influences starch pasting properties uniquely based on the chemical structure, ionic charge, concentration of the hydrocolloid used, and nature of starch (Ptaszek & Grzesik, 2007).

Shi and BeMiller, (2002) reported a decrease in peak and final viscosities when carboxymethylcellulose (CMC) was added to potato starch. It was suggested that there is highly probable that molecular repulsive forces are in play thus inhibiting the interaction between potato starch and CMC (Yuris, 2018). Potato starch and CMC have negatively charged side chains because of the presence of phosphate and carboxyl groups respectively (Figure 2.23). This further proves that the properties of the hydrocolloid used can influence the pasting properties of native starch, but also depend on the source of starch.

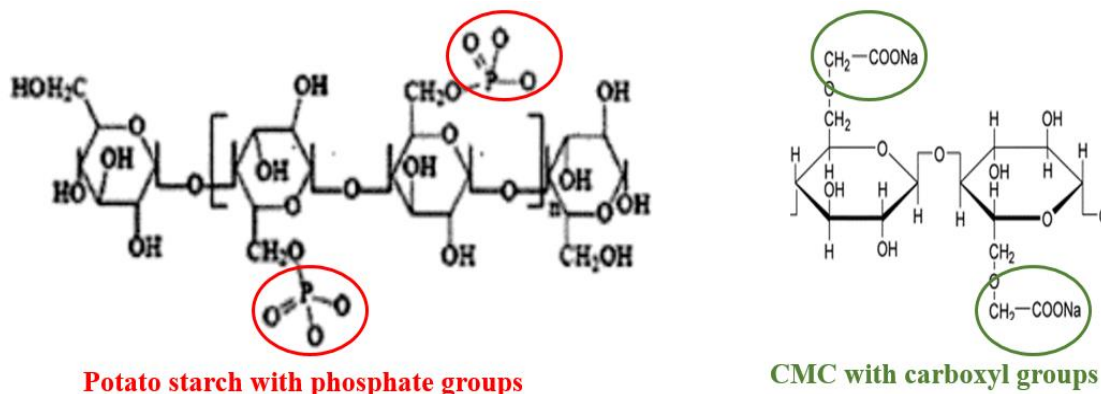


Figure 2.23: Chemical structures of potato starch and carboxymethylcellulose (CMC) (Zhao, 2007)

Several studies have reported before that hydrocolloids are hydrodynamically and/or thermodynamically incompatible with other hydrocolloids thus leading to phase separation (Alloncle & Doublier, 1991; Ahmed & Williams, 2001; Lui *et al.*, 2003; Ravindran & Matia-Merino, 2009). Phase separation tends to favor interaction between or amongst molecules that are similar and like polymers (Kim *et al.*, 2006). As a result, addition of a less solvent polymer to a starch polymer solution can lead phase separation (van Langenhove, 2015). This is caused by the mutual exclusion of each polymer from the local domain of the other causing their effective concentrations to increase within their respective domains (Dickinson, 1998).

The conditions that facilitate phase separation vary amongst polymers. The structural conformation, molecular size and chemical composition of a biopolymer influence their thermo/hydrodynamic compatibility with starch macromolecules (Grinberg & Tolstoguzov, 1997). Branched polymers and those with large side groups tend to experience steric hindrance which limits their interactions with starch polymers within the system thus leading to phase separation (Cirillo *et al.*, 2015). Also, the presence of charged groups on the polymer chain can adversely affect its association with starch polymers that have similar charges leading to electrostatic repulsion (Shalviri *et al.*, 2010). This phenomenon has been reported in several studies where xanthan gum (anionic) has been added potato starch which has negatively charged phosphate groups covalently bonded to its polymer chains (Cai *et al.*, 2011; Petri, 2015). These factors can influence the thermodynamic compatibility of the different hydrocolloids with starch biopolymers and can thus potentially lead to phase separation (Ptaszek *et al.*, 2015).

Generally, polymer-polymer thermodynamic compatibility means that two or more polymers exist within the same phase and the more miscible the polymers are within a system, the more thermodynamically compatible they are (David, 1996). In a thermodynamically compatible polymer-polymer system, favorable interactions take place which can facilitate miscibility and phase stability amongst the polymers and vice versa if the polymers are thermodynamically incompatible (Olabis, 2012). Such interactions that can take place amongst thermodynamically compatible polymers can include but are not limited to: hydrogen bonding, dipole-dipole, ionic or covalent bonding, etc.

Similarity in chemical structures facilitates thermodynamic compatibility amongst polymers which enables polymers to associate with each other within the system (Eidam *et al.*, 1995). For example, the presence of “free” hydroxyl groups on the amylose polymer chains enables it form hydrogen bonds with several hydrocolloids and exhibit miscibility and increased starch paste viscosity (Lui *et al.*, 2003).

Depending on the nature of biopolymers in the system, phase separation normally occurs in two different forms namely: associative and segregative phase separation (Fang *et al.*, 2006) (Figure 2.24).

In associative phase separation, polymers interact with each other via attractive interactions concentrating the polymers in one phase and the other phase containing mainly the solvent which creates a clear two-phase system (Pathak *et al.*, 2017). The attractive interactions between polymers in associative phase separation can include; hydrogen bonding, Van der Waals forces, electrostatic and hydrophobic interactions, etc. (David, 1996). As a result of these interactions, polymers tend to form complexes which may either be soluble or insoluble (Pathak *et al.*, 2017). Christianson (1982) reported the formation of complexes between guar gum and amylose polymers due to hydrogen bonding when the gum was added to wheat starch which led to associative phase separation.

On the other hand, segregative phase separation occurs when polymers as a result of repulsive forces are separated into two different phases (Pathak *et al.*, 2017). The repulsive forces can exist between polymers with similar charges or nonionic polymers (Gupta *et al.*, 1999). According to Cai *et al.* (2011), as a result of the existence of similar (negative) charges between xanthan gum and potato starch, electrostatic repulsions occurred within the potato starch-xanthan gum system which led to segregative phase separation in the microstructure.

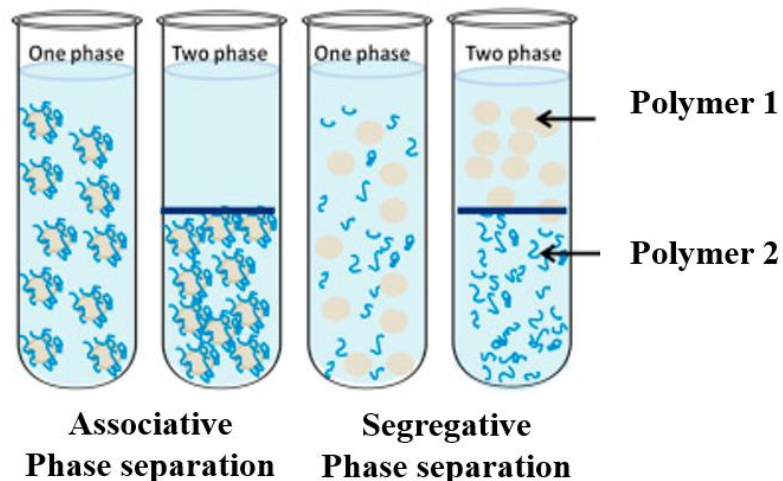


Figure 2.24: Schematic diagram showing the difference between associative and segregative phase separation (Chun *et al.*, 2014)

Generally, the term thermodynamic incompatibility between polymers is used to indicate the separation of polymers into two different aqueous phases with one phase being rich in one of the polymers and the other phase rich in the other polymer (Pathak *et al.*, 2017).

2.4.2 Gelling and viscoelastic properties

According to Cui *et al.* (2018), the addition of cellulose nanocrystals to maize and potato starch inhibited gelation and short-term retrogradation thus forming gels with lower G' and increased $\tan \delta$ values (Figure 2.25). Also, Xiong *et al.* (2017) a significant increase in $\tan \delta$ values of wheat starch when treated with MCC and CMC. The process of short-term retrogradation is greatly dependent on the availability of amylose molecules and their ability to form junction zones without which the gelation process is inhibited or retarded.

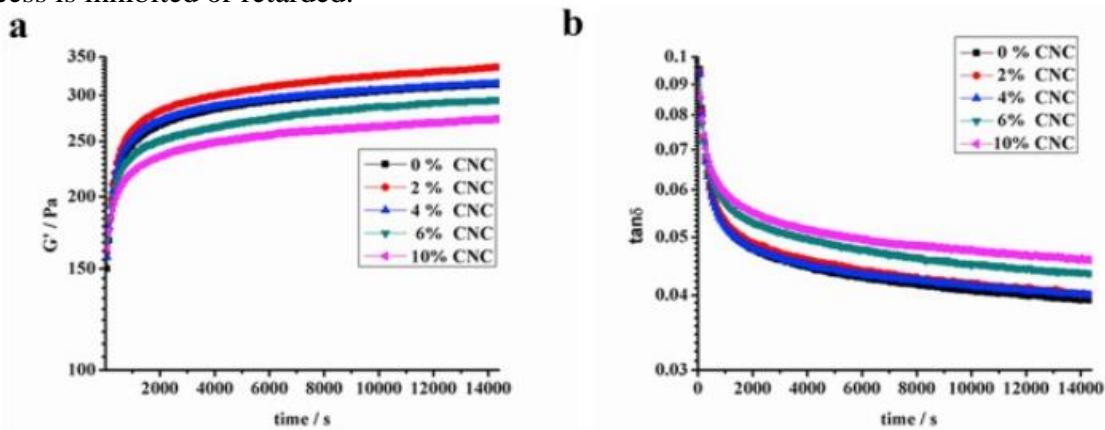


Figure 2.25: Effect of cellulose nanocrystals on storage modulus and loss tangent of normal maize (a, b) respectively (Cui *et al.*, 2018).

In a study by Smitha *et al.* (2008), it was reported that when wheat starch was pasted with HPMC and CMC, the surface of the granules was surrounded by the hydrocolloid networks thus reducing the rate at which starch granules ruptured and consequent amylose leaching. As a result, the amylose content within the continuous phase is reduced which retards the process of short-term retrogradation. Also, earlier suggestions of hydrocolloid-leached amylose interactions imply a limited availability of amylose molecules for gelation. The formation of a hydrocolloid network within the continuous phase has been proposed to entangle leached amylose preventing them from effectively forming junction zones. Therefore, in the presence of certain hydrocolloids, starch gel strength is weakened. When non-starch polysaccharides were added to wheat starch, Sasaki *et al.* (2000) concluded that hydrocolloids can bind moisture within the food system. This can be beneficial in starch food products that are susceptible to syneresis.

However, when MCC was added to high amylose maize starch, the gel strength was significantly increased (Xu *et al.*, 2019). High amylose maize starch possesses an amylose content of at least 50-90% which increases the amount of leached amylose molecules available for gel formation (Sasaki *et al.*, 2000; BeMiller, 2011). Liu *et al.*, 2003 also observed an increase in gel strength and hardness when yellow mustard mucilage (YMM) was added at (0.2, 0.5, and 0.8%, w/w) to rice and wheat starches.

This was attributed to the probable crosslinking between YMM and leached amylose molecules forming junction zones which made the gel structure more elastic. Panaras *et al.* (2011) proposed that the increase in the storage modulus (G') may not necessarily reflect retrogradation but maintenance of the viscous profile initiated by the addition of the hydrocolloid within the continuous phase.

2.5 Potential food applications of hydrocolloid modified starches.

The ability of hydrocolloid modified starches to form highly viscous systems can be employed in the production of thickening agents to be used in foods such as sauces, fillings, and soups (Winuprasith & Suphantharika, 2015). Hydrocolloid modified foods can form intermolecular networks which can be used to encapsulate key ingredients and flavors. Also, their ability to inhibit retrogradation can be utilized to prevent staling in baked food products and gravies (Franco, 2015). Due to their soft gels, hydrocolloid-modified foods can be utilized as fat replacers in low glycemic index foods (Corrêa *et al.*, 2010). Finally, their ability to influence texture through viscosity enhancement can be employed in the dairy and meat industries to improve the succulence of the final products (Abdel-Aal & Gallagher, 2009).

2.6 Concluding remarks

The literature on the interaction of potato and maize starch with hydrocolloids exists. However, no extensive research has been done on the interaction of teff with cellulose-based hydrocolloids and most especially microcrystalline cellulose and cellulose nanofiber.

- The modification of native starch with hydrocolloids increases paste viscosity which has been attributed to the hydration of the hydrocolloids thus forming an initial viscous network and the interaction of the leached amylose and hydrocolloids.
- Also, several hydrocolloids reduce gel strength which signifies a reduction in retrogradation. This has been attributed to the surrounding of the starch granules by the hydrocolloid polymers which reduces the rate of granule rupture. Thus, fewer amylose molecules are available for gel formation. The entanglement of the leached amylose molecules within hydrocolloid networks has been suggested to retard retrogradation.
- Although several studies have been undertaken to understand the effect of several hydrocolloids on the functional properties of the different starches, there is very limited literature on the cellulose nanofiber and its effect on starch rheological properties.
- Therefore, this research investigated the effect of microcrystalline cellulose and cellulose nanofiber on the rheological properties of teff starch in comparison to that of potato and maize starch.

3. HYPOTHESIS AND OBJECTIVES

3.1 Hypothesis

The addition of microcrystalline cellulose (MCC) and cellulose nanofibers (CNF) to teff, maize, and potato starch will increase the peak and final viscosity and decrease the gel strength of the starches. When added to the starches, hydrocolloids form a network within the continuous water phase via inter and intramolecular hydrogen bonding around the starch granules leading to the initial increase in paste viscosity (Pongsawatmanit & Srijunthongsiri, 2008). Due to the large starch granule size of potato starch, it will have the highest peak and final viscosity when modified with MCC and CNF (Horstmann *et al.*, 2016). As shearing continues, some of the starch granules are ruptured causing more amylose to be leached into the continuous water phase. Some of the leached amylose molecules interact with the hydrocolloids via hydrogen bonding forming a network that contributes to the overall increased final viscosity (Funami *et al.*, 2005). When the leached amylose molecules interact with the hydrocolloids, there is a reduced number of available amylose molecules and as a result, fewer junction zones are formed which are necessary for gel formation (Bahnassey & Breene, 1994). Junction zones are formed when amylose molecules rearrange themselves to form a three-dimensional structure leading to a gel-like structure (Williams, 2007). As a result, the presence of hydrocolloids in the starch system will reduce the overall gel strength.

CNF will form more viscous starch systems than MCC. As discussed earlier, the interaction between the leached amylose and hydrocolloids in the continuous phase contributes greatly to the formation of a viscous starch system. Both amylose and CNF exist in nano-dimensions and will most probably form more hydrogen bonds leading to a more viscous starch system than that with MCC (Bertoft, 2017). Also, CNF exists in a fibrous nature which enables it to trap more disintegrated starch granule debris and leached amylose molecules thus forming a more viscous system (Corrêa *et al.*, 2010). The fibrous nature of CNF forms extensive networks within the continuous phase thus increasing the resistance to flow within the starch-hydrocolloid system.

By the same aforementioned principle, starches pasted with CNF will form weaker gels than those with MCC. The highly fibrous nature created by the cellulose nanofibers inhibits the amylose rearrangement process necessary for gel formation. Generally, for short-term retrogradation to occur, amylose molecules have to rearrange forming a three-dimensional structure that leads to a gel (Huang *et al.*, 2007). Cellulose nanofibers can not only trap amylose molecules but also interact with them more

effectively via hydrogen bonding than microcrystalline cellulose thus rendering the amylose unavailable for the gel formation process (Dufresne, 2013). This characterizes steric hindrance.

Teff starch treated with MCC and CNF will also show more resistance to shear in terms of less granular breakdown during pasting in comparison to maize and potato starch. Linlaud *et al* (2010) reported that during starch pasting, hydrocolloids form networks around starch granules via hydrogen bonding causing them to swell without immediately rupturing. Possibly due to the small surface area of the teff starch granules, hydrocolloids can easily form networks around the teff starch granules via hydrogen bonding thus stabilizing its structure better. Unlike teff starch, maize and potato starch granules due to their large surface area will require more hydrocolloid polymers to form networks around them and stabilize their granules and they will thus undergo the largest breakdown.

Starches that undergo long pasting will show a more pronounced increase in final viscosity than those that are short pasted. During long pasting, more starch granules undergo structural breakdown, and thus more amylose is leached into the continuous water phase (Chandanasree *et al.*, 2016). The more leached amylose molecules present in the continuous phase; the more interactions that are likely to occur with the hydrocolloids. Molecular entanglement between the hydrocolloid and amylose occurs as a result of intermolecular hydrogen bonding which leads to the formation of the network within the system (BeMiller, 2011). This network increases the resistance to flow within the continuous phase which can be reflected in the more pronounced increase in final viscosity.

3.2 Objectives

To determine the effects of MCC and CNF on the pasting, gelling, and microstructure properties of commercial teff, maize, and potato starch with the aim of producing various ‘clean label’ starches for different applications.

4. MATERIALS AND METHODS

4.1 Experimental design

Figure 4.1 shows the experimental design of the research. Teff, maize, and potato starches with and without hydrocolloids treatment (microcrystalline cellulose (MCC), cellulose nanofibers (CNF)) were be pasted to determine the pasting properties. The gelling properties were then be determined. The pastes were also be analyzed for their microstructure and nanostructure.

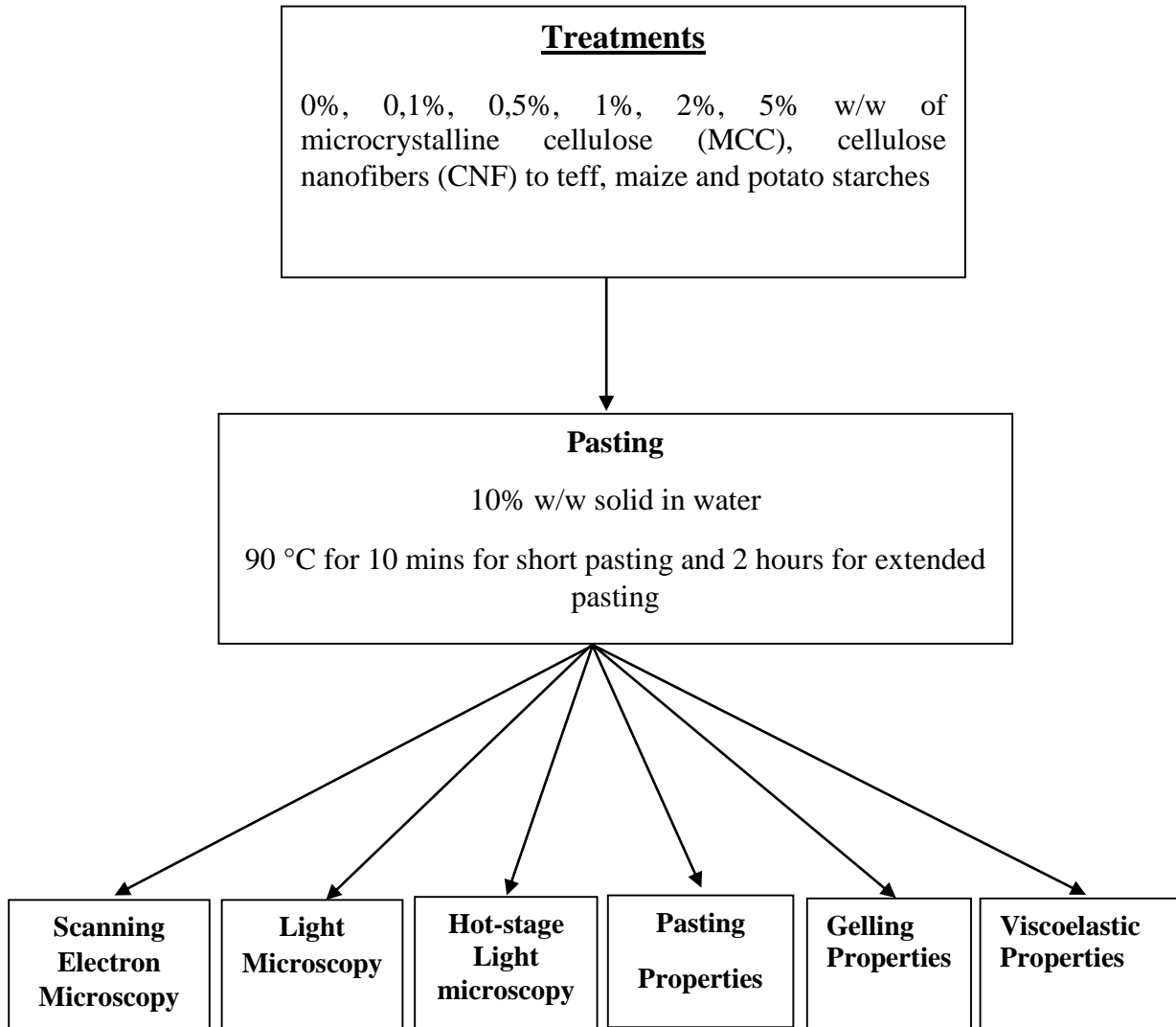


Figure 4.1: Experimental design of the research project

4.2 Materials

Microcrystalline cellulose Avicel® (MCC) was purchased from Food Machinery and Chemical Corporation (FMC) (Shanghai, China). Cellulose nanofiber (CNF) was donated by the Sappi Group (Johannesburg, South Africa).

Commercial maize starch (Amyral©) and potato starch were procured from Tongaat hullet® (Edenvale, South Africa). Teff starch was extracted from Witkop, a white teff variety purchased from Pannar (Kroonstad, South Africa).

4.3 Methods

4.3.1 Addition of hydrocolloids to starch

The different hydrocolloids (MCC and CNC) at different concentrations (0% as control, 0,2%, 0,5%, 2%, 5% w/w) were first be solubilized separately in warm distilled water at 50 °C and then added to a starch suspension to form a homogenous dispersion.

4.3.2 Teff starch extraction

The method described D'Silva (2009) was used to extract the teff starch with some modifications from Bultosa *et al.* (2002). Teff grains were sieved first to remove foreign particles and then milled using a hammer mill to pass through a 500 µm screen. The resultant flour was then defatted thrice with hexane using a ratio of 1-part flour to 3 parts hexane and stirred at 25 °C for 1 hour. At the end of every defatting stage, the flour and hexane were filtered and the defatting process was repeated with fresh hexane. In the final stage, the residual hexane in the flour was then evaporated off under the fume hood. The defatted flour was then suspended in distilled water in a ratio of 1-part flour to 5-parts distilled water and wet-milled using a Retsch Mill ZM 200 (Haan, Germany) with a 250 mm opening screen, followed by sieving (to remove the fibrous components in the flour) with 75 µm and 38 µm hand sieves sequentially and centrifuged (to remove the insoluble protein) at 8000 rpm for 10 min at 25 °C. The supernatant was decanted off after centrifuging and the brown protein layer was scraped off using a spatula. The remaining starch pellet was resuspended in distilled water and centrifuged, the supernatant was decanted off and the brown layer was scraped off. This process was repeated until a white starch pellet remained. The white starch pellets were thereafter freeze-dried.

4.3.3 Raw material characterization

The moisture, protein, and ash contents of teff, maize, and potato starch were determined using the American Association of Cereal Chemists (AACC) methods 44-15A, 46-30, and 08-01 respectively. Teff starch moisture, protein, and ash contents were 3.36%, 1.37%, 0.18% (dry basis) respectively. Maize starch moisture, protein, and ash contents were 14%, 0.14%, and 0.93% (dry basis) respectively. Potato starch moisture, protein, and ash contents were 16%, 0.10%, and 1.1% (dry basis) respectively.

4.4 Analyses

4.4.1 Pasting properties

Physica MCR 101 Rheometer, (Anton Paar, Graz, Austria) with Rheoplus software® was used to determine the pasting properties with the Toolmaster™ measuring system (ST24-2D/2V/2V-30). The 10% (w/w) starch and hydrocolloid mixtures were suspended in distilled water to make a total volume of 16g according to Maphalla and Emmambux (2015). The pasting cycle began with an initial stirring of 960 rpm at 50 °C for 30 seconds and then 160 rpm for the entire period thereafter. The temperature was increased to 90 °C at a rate of 5.5 °C/min and held at this temperature for 30 minutes for short pasting and 2 hours for extended pasting. The pastes were cooled from 90 °C to 50 °C at a rate of 5.5 °C/min and maintained at 50 °C for at least 10 minutes.

4.4.2 Gelling properties

Gelling properties were determined according to Bultosa and Taylor (2004) with modifications. Starch pastes were hot-filled into plastic syringes (50mm height x 18mm diameter) whose tips had been cut open. The starch pastes were stored overnight in the syringes at about 23 ± 1 °C. Gel hardness was analyzed using the EZ-test texture analyzer EZ-L, Shimadzu (Tokyo, Japan) with a P/20p cylinder probe (20 mm diameter). With the help of a thin thread, cylindrical blocks were cut (17mm height x 18mm diameter) from gelled starch samples after being extruded from the syringes. The probe compressed each cylindrical gel block by 5 mm and retracted from the sample. The maximum force was noted.

4.4.3 Time-Temperature Sweep (Viscoelastic properties)

The time-temperature sweep of the paste starch was done using a Physica MCR 101 Rheometer (Anton Paar, Graz, Austria). The measurements were done using the bob and cup geometry with a diameter of 2.7 mm at a gap distance of 1 mm. To determine the linear viscoelastic range (LVE),

an amplitude sweep was done. A strain of 0.5% was used which was within the LVE. The temperature sweep test was performed from 85°C to 23°C at a cooling rate of 5°C/min and kept at 23°C for 2 hours. From this analysis, results of storage modulus (G'), complex viscosity (η^*), loss modulus (G''), and tan delta ($\tan \delta$) were obtained.

4.4.4 Hot Stage Microscopy

Changes in starch granule morphology in the presence of microcrystalline cellulose and cellulose nanofiber at different concentrations were observed using hot stage microscopy (Hari *et al.*, 1989). The starch suspensions were observed using a VS3 Series Biological Trinocular Light Microscope from Micromet Scientific with a Biowizard Image Analysis software (Delhi, India) with a polarising filter lens. The sample was heated from 50°C to 90°C at about 5°C/min on a hot plate using a Linkam CO 102 thermostat. Micrographs of the sample were taken at intervals of 10 °C as observed under the microscope. Images were taken at 200X magnification.

4.4.5 Light microscopy

Samples of the starch paste (about 5mg dry basis) were dispersed in about 1 ml of 30% glycerol and gently mixed with a drop of iodine stain solution. A drop of the stained starch suspension was placed on a glass slide, covered with a glass coverslip, and observed using a VS3 Series Biological Trinocular Light Microscope from Micromet Scientific with a Biowizard Image Analysis software (Delhi, India). Images were taken at 400X magnification. This test was carried out on freshly pasted samples.

4.4.6 Scanning Electron Microscopy

The shape, size, and surface features of the treated and untreated starch pastes were observed using scanning electron microscopy. The method described by Liu *et al.*, 2012 was used with some modifications. Freeze-dried starch paste samples were mildly size-reduced to form coarse powders. Particles of the individual starch paste powders were mounted on an aluminum stub covered with double-sided adhesive tape and sputter-coated with a thin gold film (about 20nm in thickness). Scanning Electron Microscopy (SEM) micrographs were obtained using a JEOL JSM-5800 LV SEM (Tokyo, Japan) at an accelerating potential of 5kV. Observations were done at 2500 x magnifications. This analysis was carried out on freeze-dried starch paste samples.

4.4.7 Statistical analysis

Multivariate analysis of variance (MANOVA) was used to determine significant differences due to the addition of MCC, and CNF and the different concentrations as independent variables. Means were compared using Fischer's least significant test (LSD) at a 5% level of significance using Statistica version 8 software (Weiß, 2007). Experiments were repeated at least thrice unless stated otherwise.

5. RESULTS

5.1 Pasting properties

Figures 5.2, 5.4, and 5.6 show the pasting properties of teff, maize, and potato starch when treated with microcrystalline (MCC) or cellulose nanofiber (CNF). The addition of MCC or CNF at increasing concentrations (0%, 0.2%, 0.5%, 2%, and 5%) to maize starch significantly increased ($P \leq 0.05$) the peak, breakdown, and final viscosities. Treatments with 0.5% (w/w) hydrocolloid concentration or less generally did not have any significant effect ($P > 0.05$) on the pasting properties of all the starches used in this research.

Potato starch had the highest peak viscosity followed by maize and teff starch respectively. Unlike potato and maize starches, teff starch treatments showed a plateau viscosity with no peak and breakdown viscosity. Figure 5.1 shows the pasting profiles of CNF and MCC alone both pasted at 5% (w/w) hydrocolloid concentrations. Although the CNF final viscosity (47.06 mPa.s) was three times higher than that of MCC (13.59 mPa.s), both were far lower compared to the potato (3944 mPa.s), maize (3066 mPa.s) and teff starches (4008 mPa.s) (Tables 5.2, 5.3 & 5.5).

Maize starch treatments with CNF showed significantly higher ($P \leq 0.05$) peak, breakdown, setback, and final viscosities than those with MCC (Table 5.3 & 5.4). Overall, these properties increased linearly with an increase in CNF concentration (Figure 5.5). Changes in maize and teff starch pasting properties in the presence of MCC were rather generally slow and gradual (Figure 5.3).

Treating potato starch with MCC or CNF generally did not show any significant effect ($P > 0.05$) on the peak, breakdown, and final viscosities for both short and extended pasting cycles below hydrocolloid concentrations of 5% (w/w) (Table 5.5). A linear increase in peak, breakdown, and setback viscosities of potato starch with CNF was observed as hydrocolloid concentration increased from 2-5% (w/w) (Figure 5.7).

During the extended pasting cycle, all CNF or MCC treatments of teff, maize, and potato starches did not affect ($P > 0.05$) the final and setback viscosities of the different starches after extended pasting (Tables Table 5.2, 5.4 & 5.6). Also, during the extended pasting cycles, unlike potato starch, maize and teff starches both showed a second peak followed by a higher breakdown in viscosity. That second peak was higher with the increase in hydrocolloid concentration.

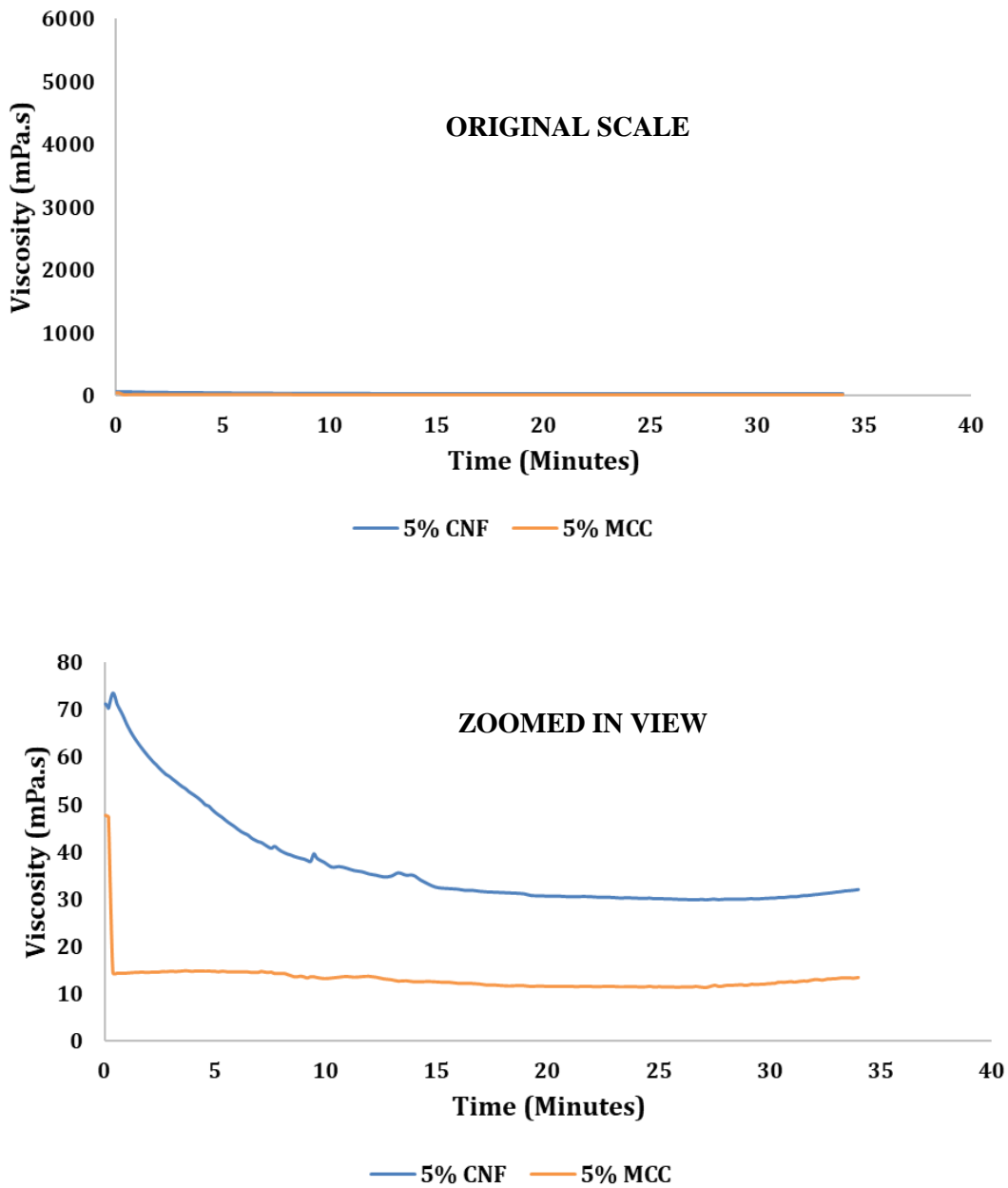


Figure 5.1: Pasting profiles of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) alone.

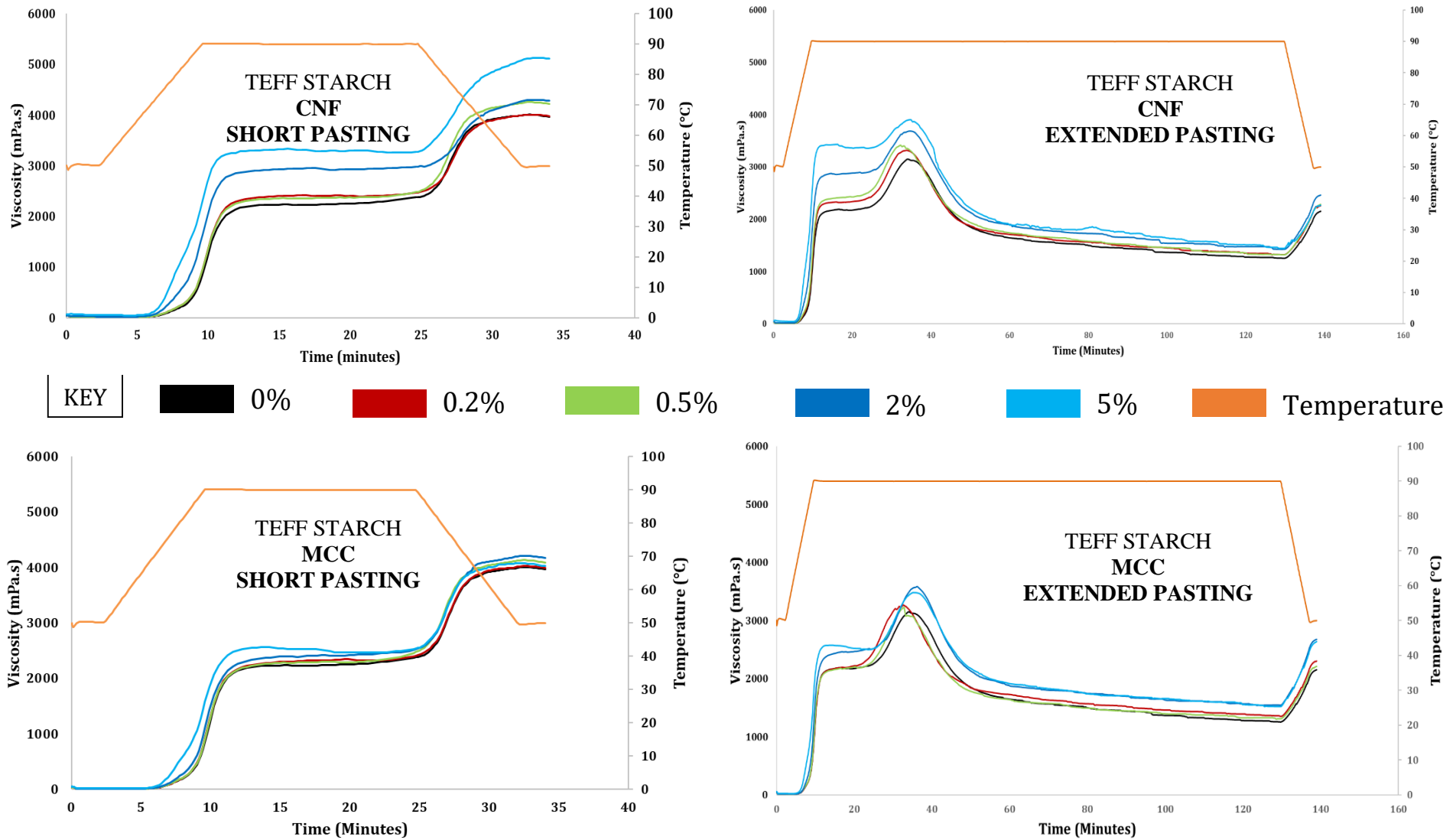


Figure 5.2: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of teff starch after short and extended pasting cycles.

Table 5.1: Pasting properties of teff starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during the short pasting cycles.

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	*ND	ND	ND	ND	ND	ND	4008a ± 37	4008a ± 37
0.2%	ND	ND	ND	ND	ND	ND	4021a ± 26	3972a ± 48
0.5%	ND	ND	ND	ND	ND	ND	4080b ± 84	4250b ± 33
2%	ND	ND	ND	ND	ND	ND	4186c ± 12	4391b ± 103
5%	ND	ND	ND	ND	ND	ND	4201c ± 66	4936c ± 119

*ND - During the short pasting cycles, teff starch treatments did not have peak viscosity but a plateau. Therefore, other than the final viscosity, other (peak, breakdown, and setback) viscosities could not be determined.

Means within the same column with different letters are significantly different ($P \leq 0.05$)

Table 5.2: Pasting properties of teff starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during the extended pasting cycle.

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	ND	ND	ND	ND	ND	ND	2245a ± 85	2245a ± 85
0.2%	ND	ND	ND	ND	ND	ND	2247a ± 23	2273a ± 25
0.5%	ND	ND	ND	ND	ND	ND	2325a ± 46	2236a ± 27
2%	ND	ND	ND	ND	ND	ND	2563b ± 87	2785b ± 106
5%	ND	ND	ND	ND	ND	ND	2621b ± 93	2802b ± 144

*ND - During the extended pasting cycle, teff starch treatments did not have peak viscosity but a plateau. Therefore, other than the final viscosity, other (peak, breakdown, and setback) viscosities could not be determined.

Means within the same column with different letters are significantly different ($P \leq 0.05$)

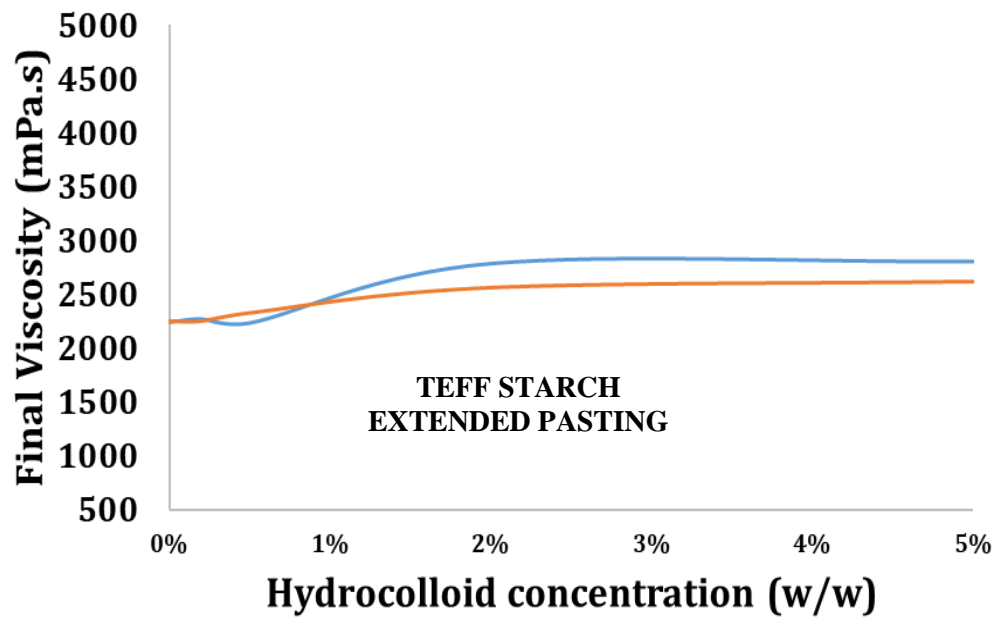
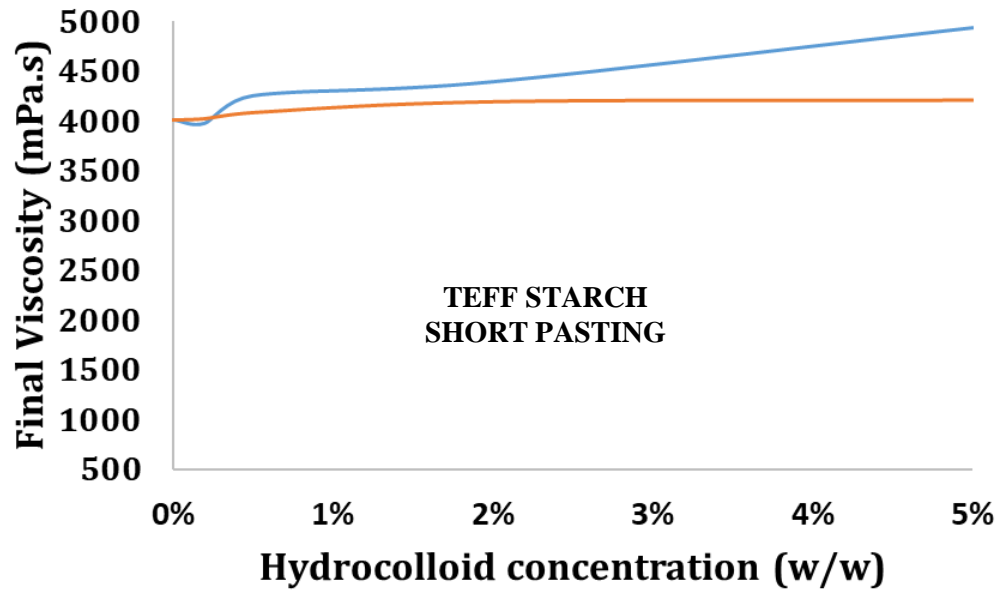


Figure 5.3: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the final viscosity of teff starch after short and extended pasting cycles respectively.

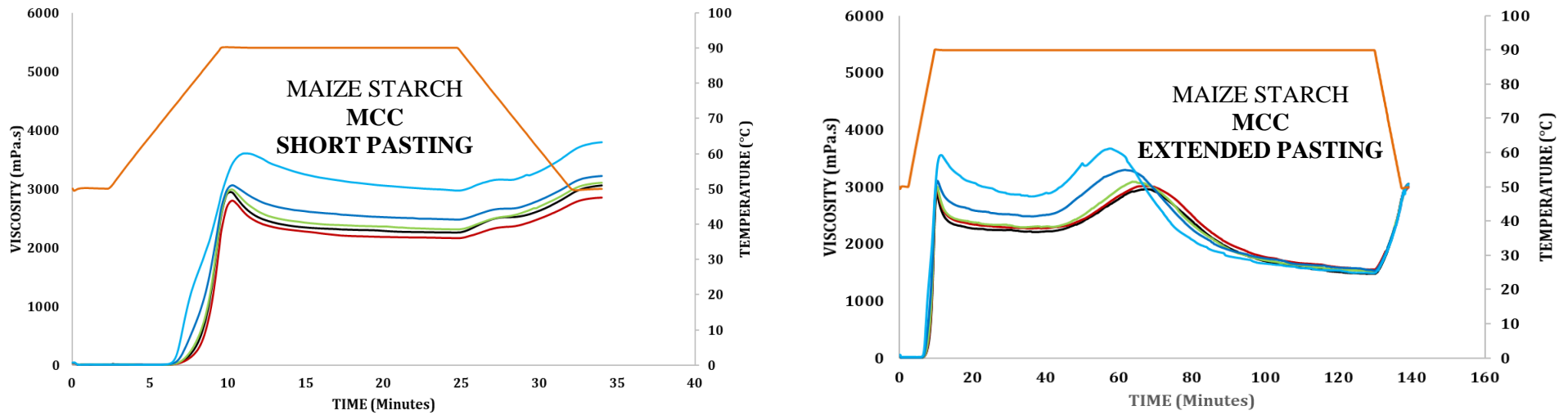
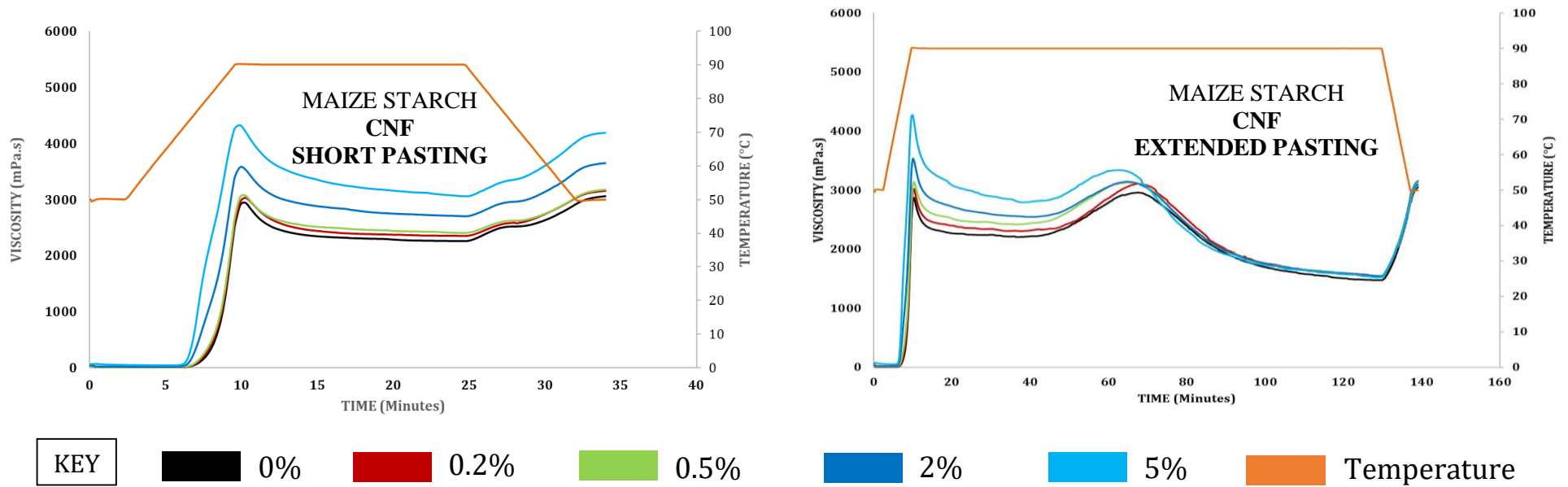


Figure 5.4: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of native maize starch after short and extended pasting cycles

Table 5.3: Pasting properties of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during short pasting cycles

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	2944a ± 66	2944a ± 66	661a ± 38	661a ± 38	836b ± 32	836b ± 32	3066a ± 35	3066a ± 35
0.2%	2946a ± 40	3023b ± 39	663a ± 9	672a ± 27	766a ± 61	778a ± 47	3082a ± 11	3143b ± 12
0.5%	3002b ± 38	3085c ± 51	676a ± 27	698a ± 21	771a ± 13	787a ± 30	3168b ± 62	3168b ± 81
2%	3063c ± 17	3563d ± 15	680a ± 32	860b ± 54	801b ± 57	945c ± 25	3221c ± 19	3623c ± 30
5%	3636d ± 28	4313e ± 22	720b ± 14	1293c ± 42	896c ± 66	1184d ± 59	3780d ± 23	4176d ± 12

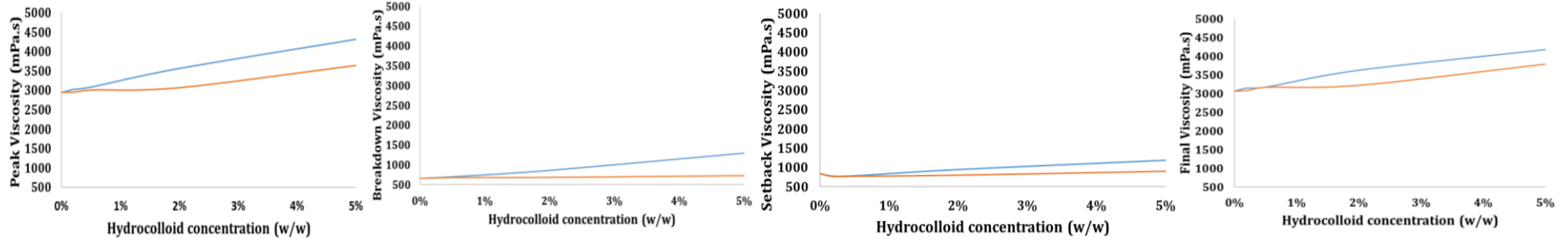
Means within the same column with the different letters are significantly different ($P \leq 0.05$)

Table 5.4: Pasting properties of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during extended pasting cycles

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	2890a ± 27	2890a ± 27	1415a ± 18	1416a ± 17	1582a ± 77	1582a ± 77	3056a ± 57	3056a ± 57
0.2%	3032b ± 51	2999ab ± 18	1520b ± 86	1503b ± 43	1515a ± 77	1556a ± 65	3027a ± 40	3051a ± 103
0.5%	3021b ± 30	3120b ± 17	1532b ± 31	1612c ± 46	1525a ± 35	1566a ± 40	3018a ± 25	3074a ± 17
2%	3077b ± 27	3561c ± 124	1550b ± 22	2059d ± 62	1537a ± 53	1563a ± 29	3064a ± 47	3065a ± 37
5%	3539c ± 61	4483d ± 103	2059c ± 64	3004e ± 118	1574a ± 21	1674b ± 83	3067a ± 17	31533a ± 68

Means within the same column with the different letters are significantly different ($P \leq 0.05$)

MAIZE STARCH SHORT PASTING



KEY



Cellulose nanofiber (CNF)



Microcrystalline cellulose (MCC)

MAIZE STARCH EXTENDED PASTING

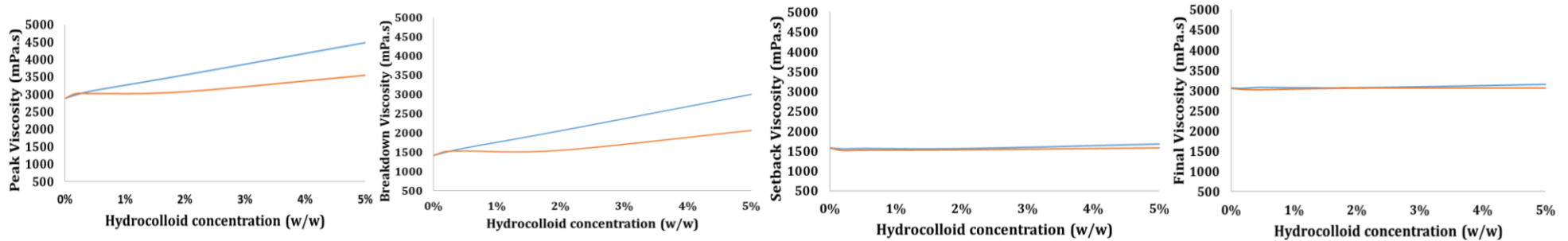


Figure 5.5: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the peak, breakdown, setback, and final viscosities of native maize starch after the short and extended pasting cycles

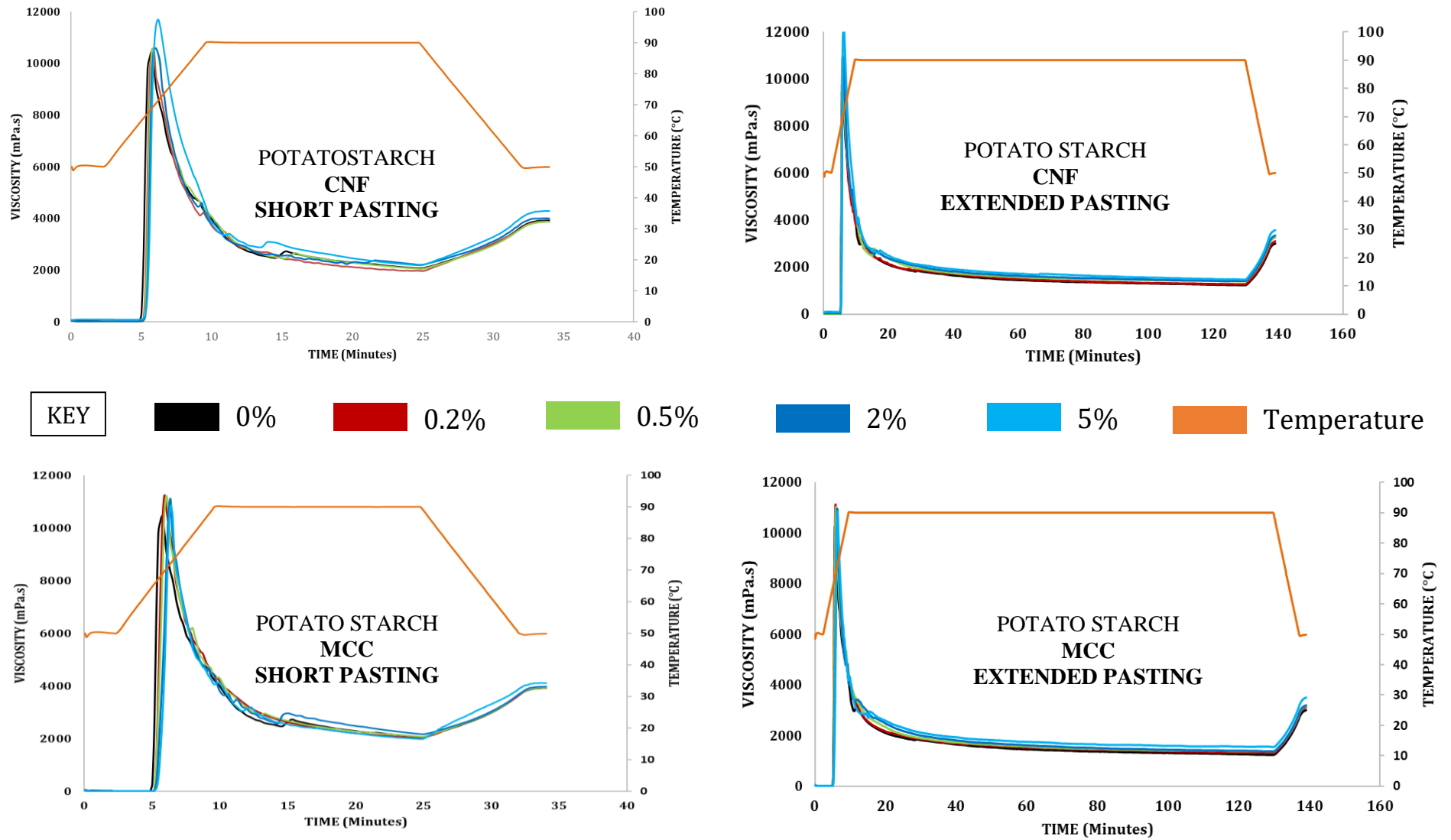


Figure 5.6: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the pasting properties of native potato starch after short and extended pasting cycles

Table 5.5: Pasting properties of potato starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during short pasting cycles.

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	10490a ± 122	10490a ± 122	8407a ± 157	8407a ± 157	1861a ± 12	1861a ± 12	3944a ± 40	3944a ± 40
0.2%	11086c ± 170	10603a ± 78	9035c ± 183	8625a ± 51	1864a ± 52	1904a ± 60	3947a ± 42	3962a ± 35
0.5%	11030c ± 168	10633a ± 166	8951c ± 163	8658a ± 155	1866a ± 65	1932a ± 96	3950a ± 81	3987a ± 72
2%	10843b ± 255	10643a ± 345	8651b ± 291	8661a ± 404	1873a ± 67	1955a ± 147	3952a ± 32	4077a ± 66
5%	10643ab ± 193	11583b ± 193	8667b ± 281	9496b ± 51	2063b ± 177	2135b ± 32	4159b ± 184	4222b ± 112

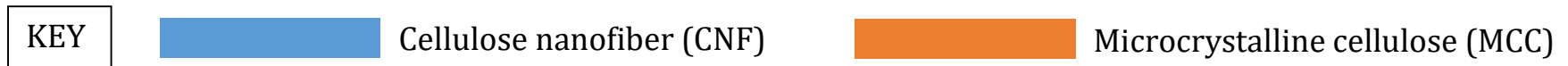
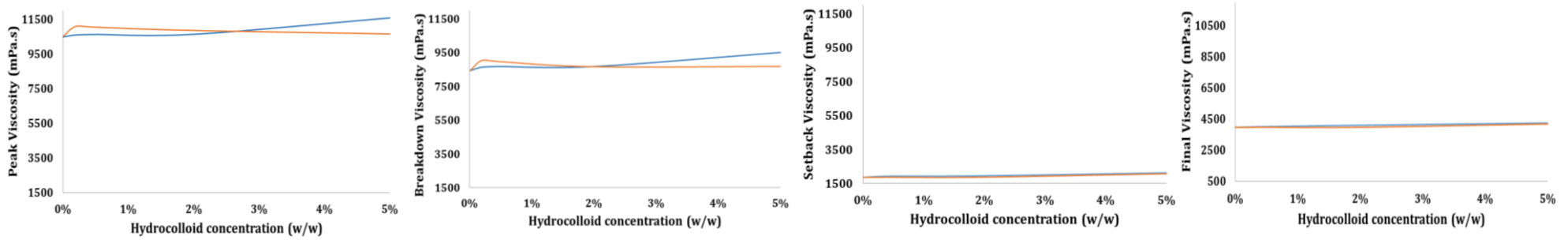
Means within the same column with the different letters are significantly different ($P \leq 0.05$)

Table 5.6: Pasting properties of potato starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during extended pasting cycles

Hydrocolloid concentrations	Peak Viscosity		Breakdown Viscosity		Setback viscosity		Final Viscosity	
	MCC	CNF	MCC	CNF	MCC	CNF	MCC	CNF
0%	10533a ± 324	10533a ± 324	1869a ± 39	9243a ± 292	1869a ± 39	1869a ± 39	3159a ± 75	3159a ± 75
0.2%	10936a ± 172	10777a ± 50	1866a ± 66	9439a ± 105	1832a ± 14	1866a ± 66	3164a ± 69	3203a ± 131
0.5%	10902a ± 20	10643a ± 250	1891a ± 35	9223a ± 313	1811a ± 14	1891a ± 35	3141a ± 39	3312a ± 46
2%	10850a ± 111	11060b ± 151	1868a ± 55	9702a ± 156	1858a ± 55	1868a ± 55	3221a ± 90	3226a ± 104
5%	10660a ± 202	11960c ± 217	1918a ± 76	10580b ± 134	1918a ± 110	1918a ± 76	3169a ± 86	3328a ± 116

Means within the same column with the different letters are significantly different ($P \leq 0.05$)

POTATO STARCH SHORT PASTING



POTATO STARCH EXTENDED PASTING

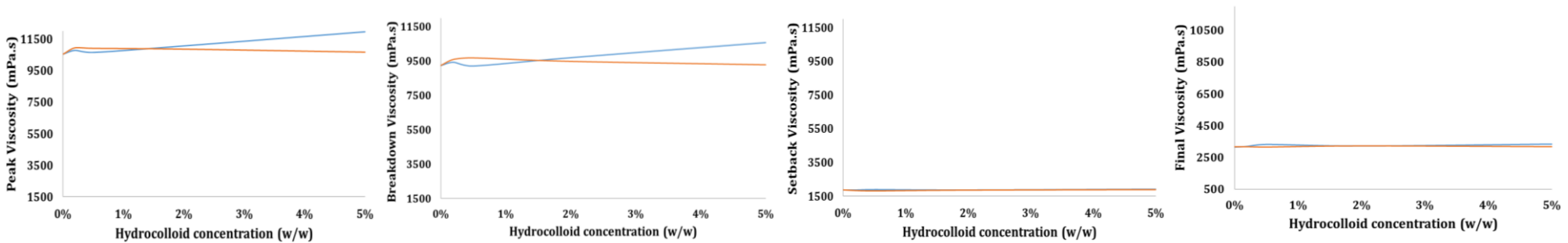


Figure 5.7: Effects of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on the peak, breakdown, setback, and final viscosities of native potato starch after short and extended pasting cycles

5.2 Hot stage microscopy

Figure 5.8 shows the changes in starch granule morphology and extent of granule swelling as temperatures increased from 50 °C to 90 °C during the pasting in the presence of CNF and MCC. At the beginning of the pasting cycle (50 °C), starch granules were essentially small, unswollen, and sparsely dispersed within the system. Starch treatments with CNF and MCC had significantly less swollen ($P \leq 0.05$) starch granules at 50 °C than the control (Table 5.7). As temperatures increased from 50 °C to 70 °C, several starch granules started to swell and rupture.

At 70 °C, almost all the granules in the control maize starch sample were generally swollen and ruptured. In CNF and MCC treatments, only a few of the granules were observed to be swollen while others are seen to still maintain their initial size.

As the temperatures increased further from 70 °C to 90 °C, most of the starch granules present in the control sample were all swollen and disfigured while treatments with CNF and MCC still had many intact and less swollen granules even at 90 °C. Generally, starch-treated with CNF and MCC showed a lower degree of swelling, and treatments with CNF had significantly lower starch granule sizes at the end of the pasting cycle as temperatures were increased from 50 – 90 °C (Table 5.7).

Table 5.7: Effect of cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on granule size of maize starch during pasting.

Treatments	Granule size (μm)	
	At 50 °C	At 90 °C
Control	15.89a \pm 0.78	20.11a \pm 0.24
5% MCC	10.55b \pm 0.12	16.89b \pm 0.51
5% CNF	10.47b \pm 0.38	15.67c \pm 0.33

Means within the same column with the different letters are significantly different ($P \leq 0.05$)

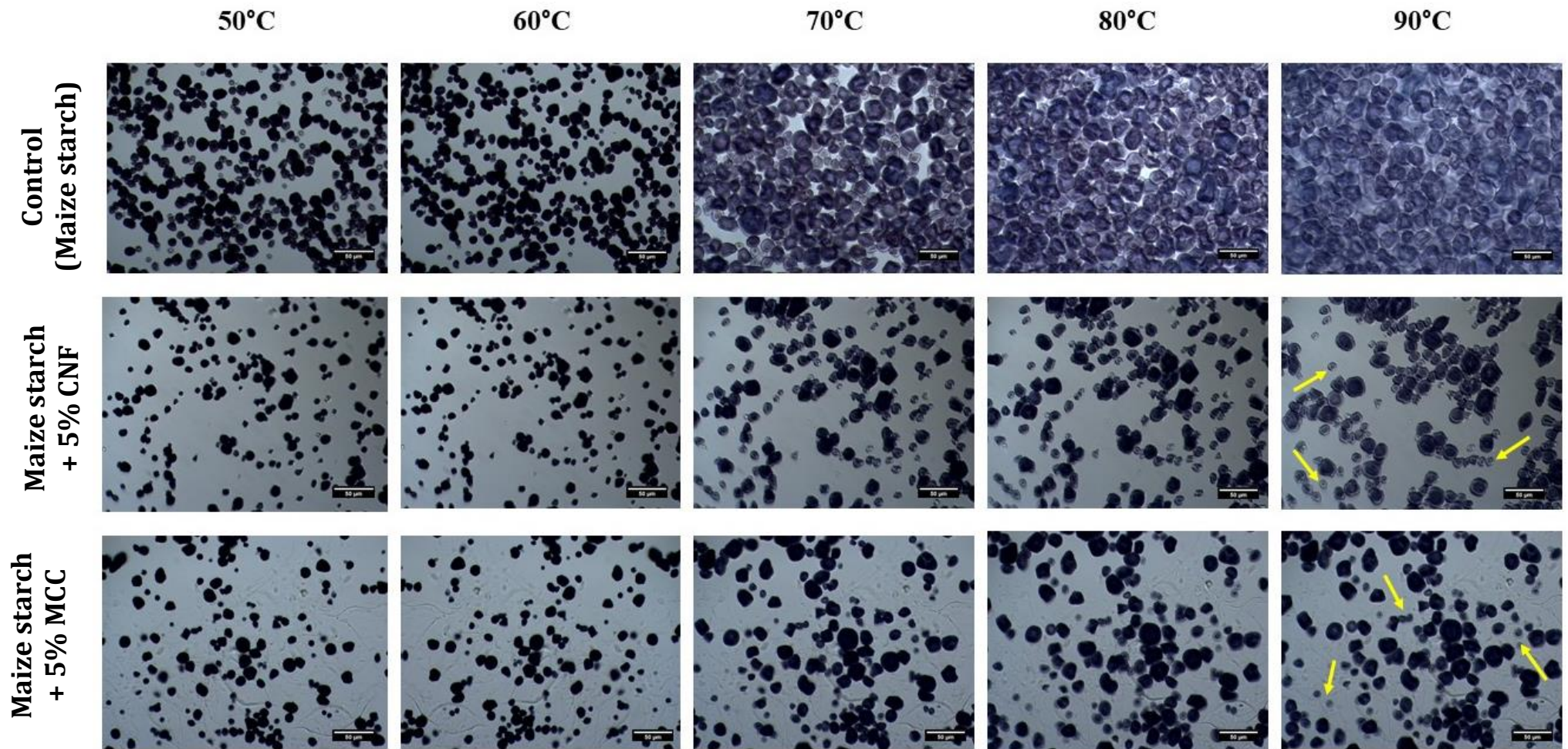


Figure 5.8: Effects of temperature change (50-90 °C) on the microstructure of maize starch with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) during pasting

5.3 Light microscopy

Micrographs from light microscopy show that relatively more starch granules remain swollen and unruptured after short pasting when teff and maize starches are treated with CNF or MCC (Figures 5.9 & 5.10). Treatments with CNF were observed to have exudates within the starch system.

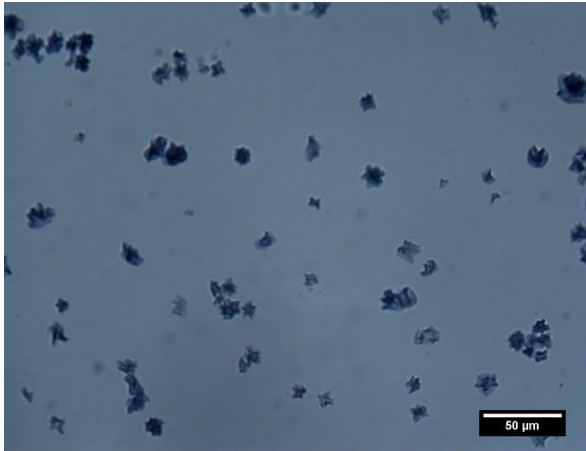
Unlike teff and maize starches, potato starch even in presence of CNF or MCC could not resist the effect of shearing for both short and extended pasting cycles (Figure 5.11) Also, for teff and maize starches, extended pasting cycles disintegrated the starch granule structures even in the presence of CNF or MCC.

5.4 Scanning electron microscopy

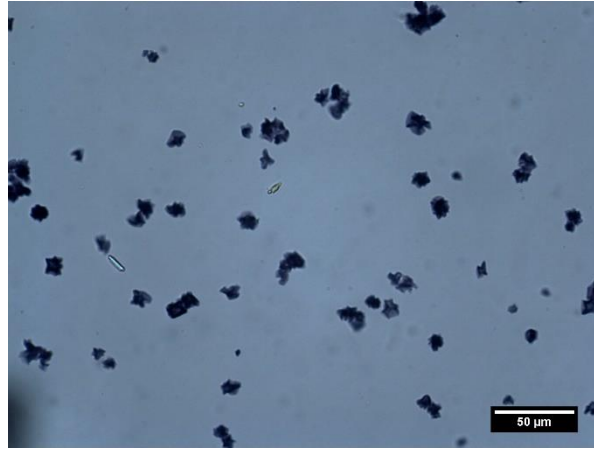
Micrographs of the structure of freeze-dried starch pastes treated with CNF or MCC are shown in Figure 5.12. It was observed that control starch pastes (without CNF or MCC) had a less compact structure well as those treated with CNF or MCC showed a more compact structure. CNF treated starch systems were observed to be more compact than the control and MCC in the structure.

With regards to extended pasting cycles, micrographs show a disintegrated and less orderly structure of the starch system.

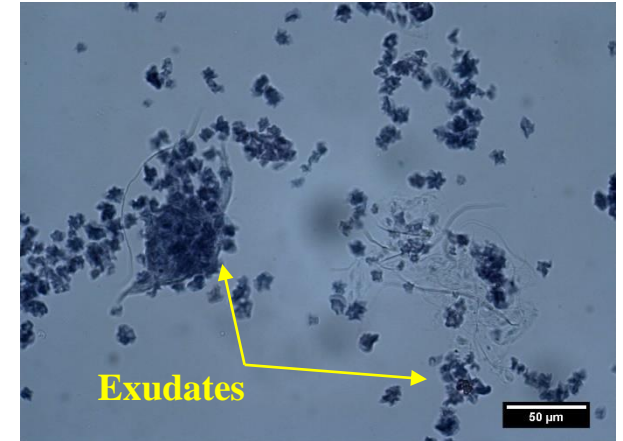
**TEFF STARCH
CONTROL**



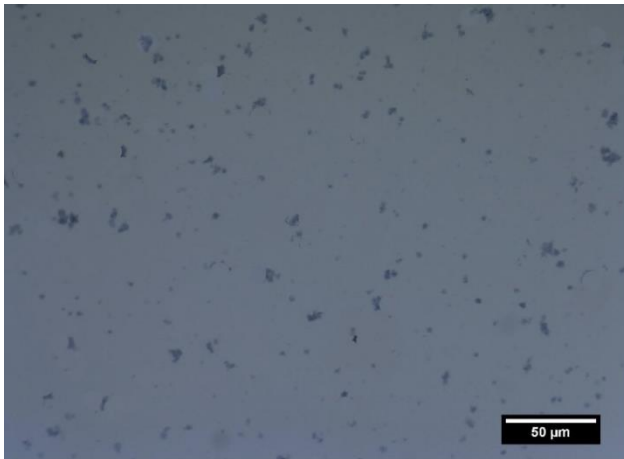
**TEFF STARCH
5% MCC
SHORT PASTING**



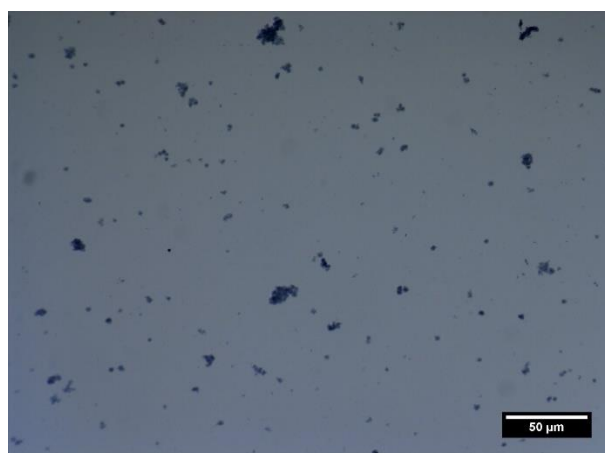
**TEFF STARCH
5% CNF
SHORT PASTING**



**TEFF STARCH
CONTROL
EXTENDED PASTING**



**TEFF STARCH
5% MCC
EXTENDED PASTING**



**TEFF STARCH
5% CNF
EXTENDED PASTING**

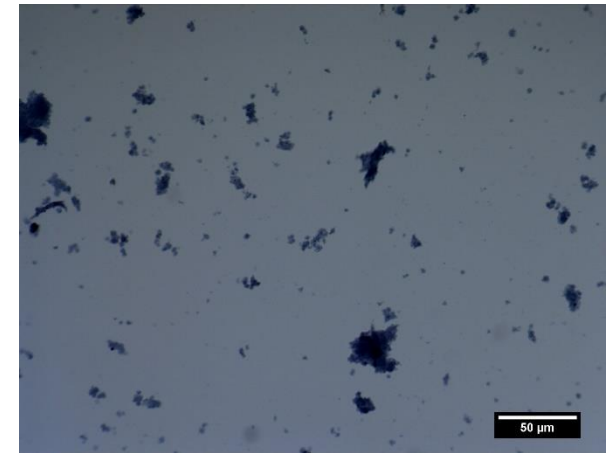
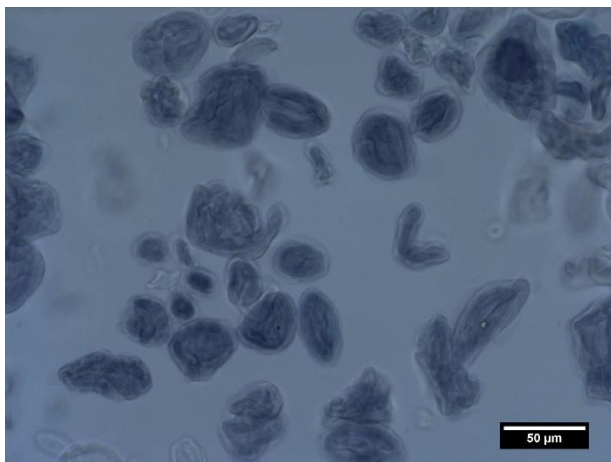
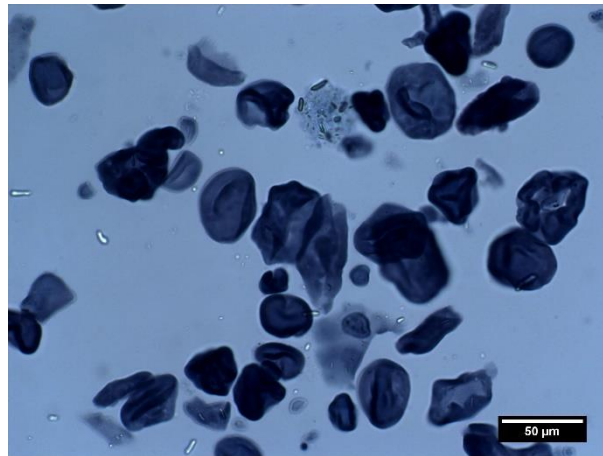


Figure 5.9: Light microscopy images showing the effect of treating teff starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles.

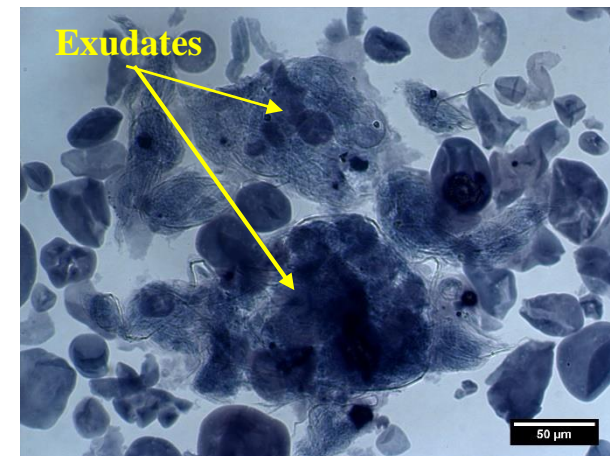
**MAIZE STARCH
CONTROL
SHORT PASTING**



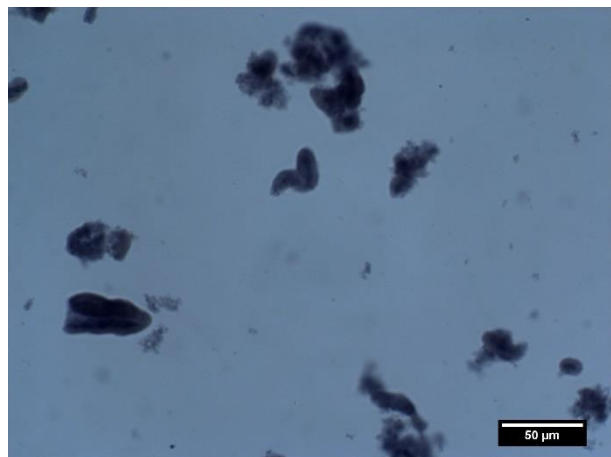
**MAIZE STARCH
5% MCC
SHORT PASTING**



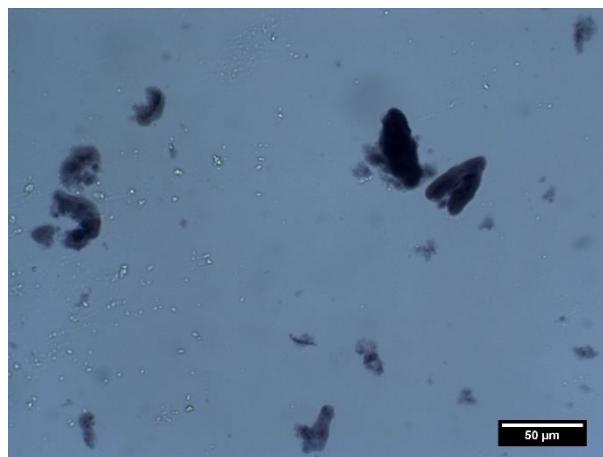
**MAIZE STARCH
5% CNF
SHORT PASTING**



**MAIZE STARCH
CONTROL
EXTENDED PASTING**



**MAIZE STARCH
5% MCC
EXTENDED PASTING**



**MAIZE STARCH
5% CNF
EXTENDED PASTING**

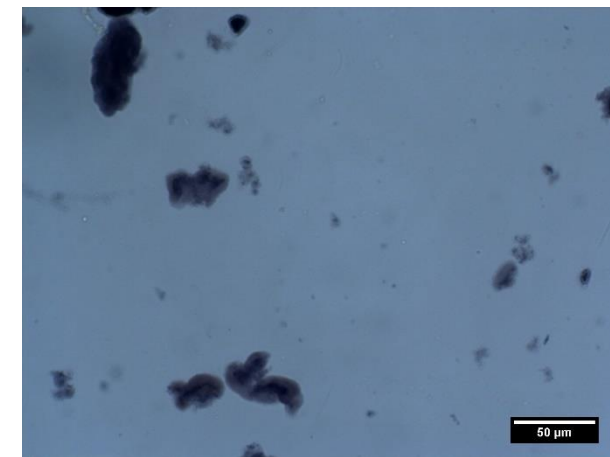
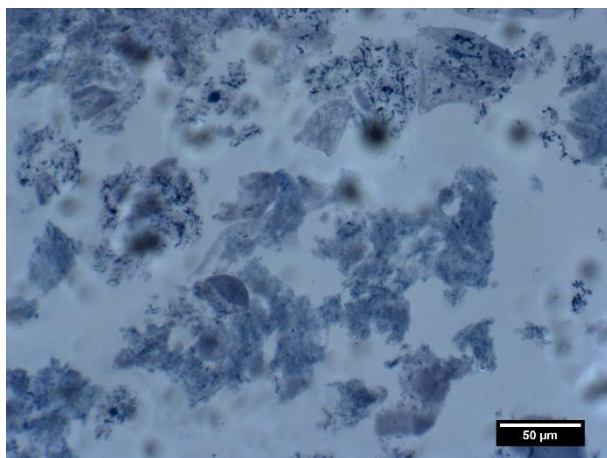
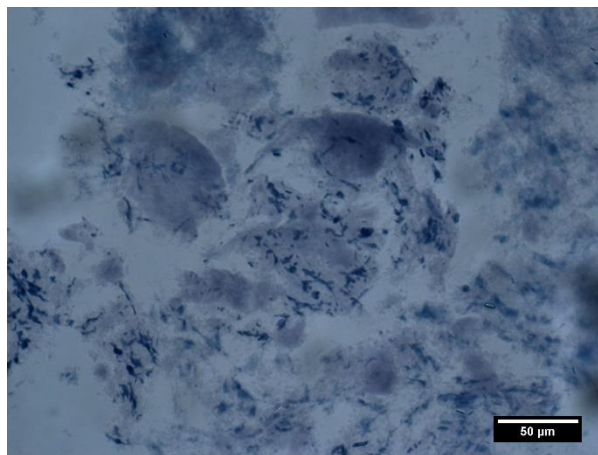


Figure 5.10: Micrographs showing the effect of treating maize starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles.

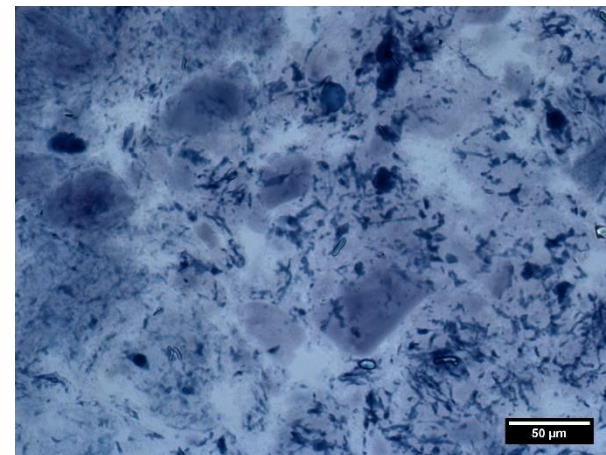
**POTATO STARCH
CONTROL
SHORT PASTING**



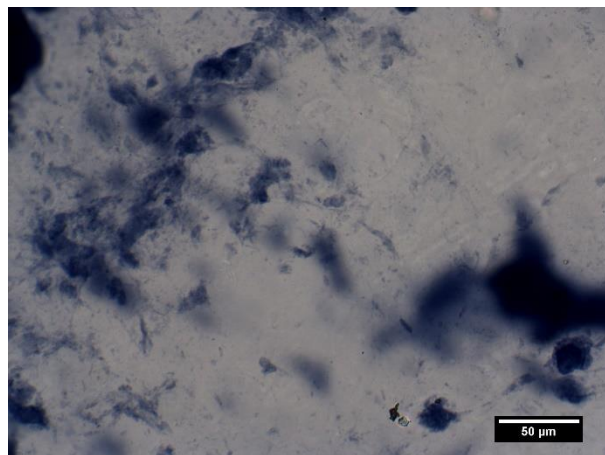
**POTATO STARCH
5% MCC
SHORT PASTING**



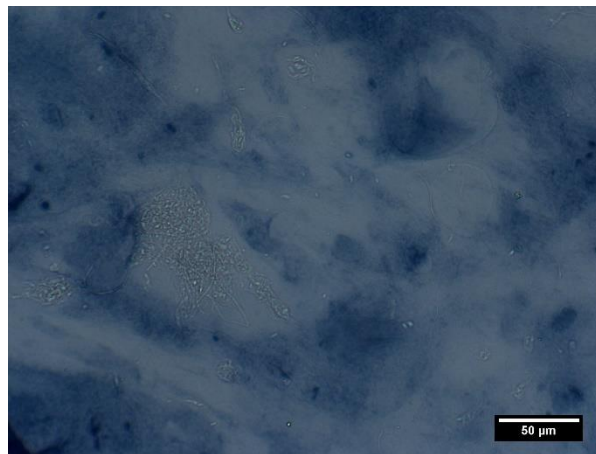
**POTATO STARCH
5% CNF
SHORT PASTING**



**POTATO STARCH
CONTROL
EXTENDED PASTING**



**POTATO STARCH
5% MCC
EXTENDED PASTING**



**POTATO STARCH
5% CNF
EXTENDED PASTING**

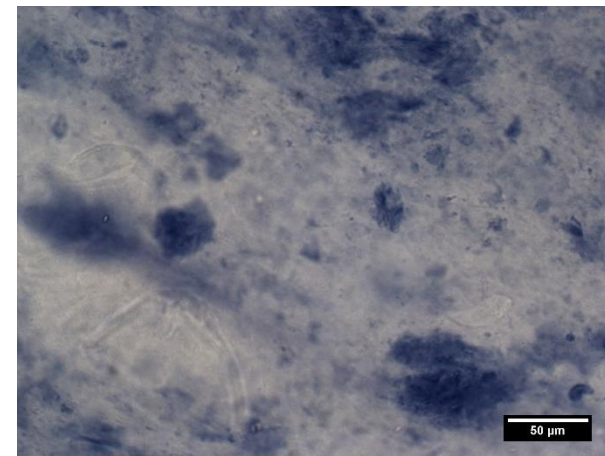


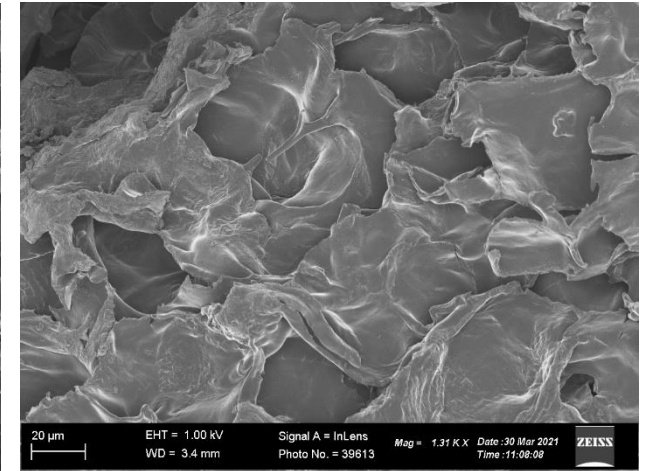
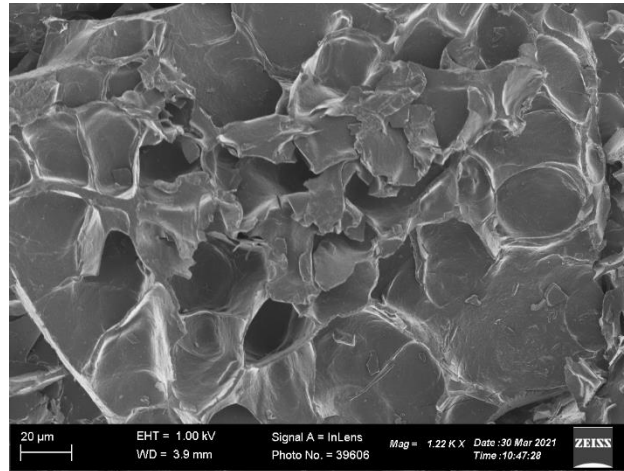
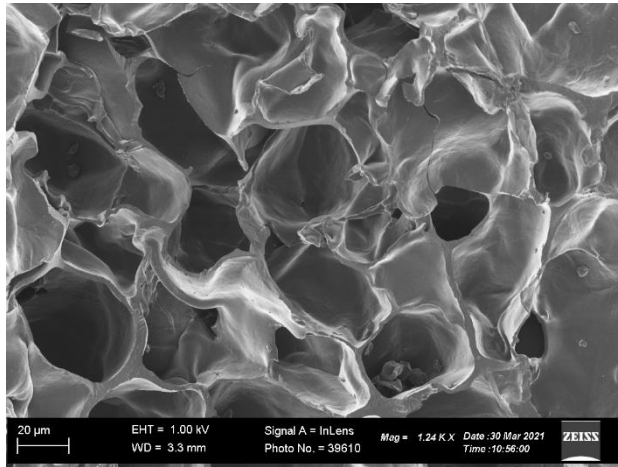
Figure 5.11: Micrographs showing the effect of treating potato starch with cellulose nanofiber (CNF) and microcrystalline cellulose (MCC) on starch granules after short and extended pasting cycles

After Short pasting

Control

MCC 5%

CNF 5%



After Extended pasting

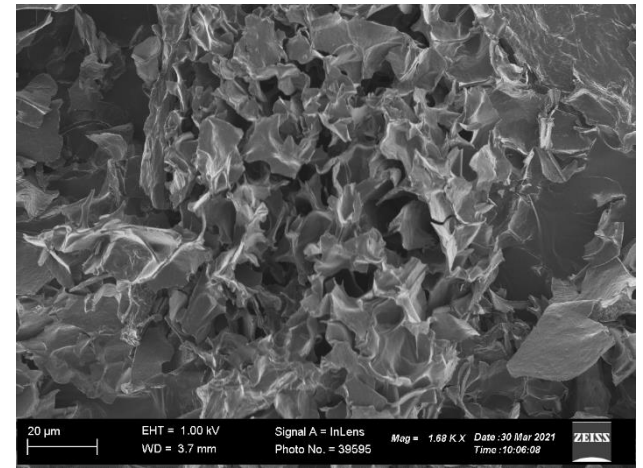
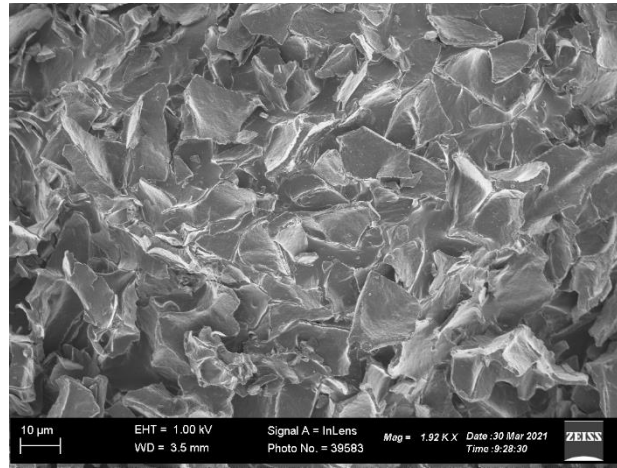
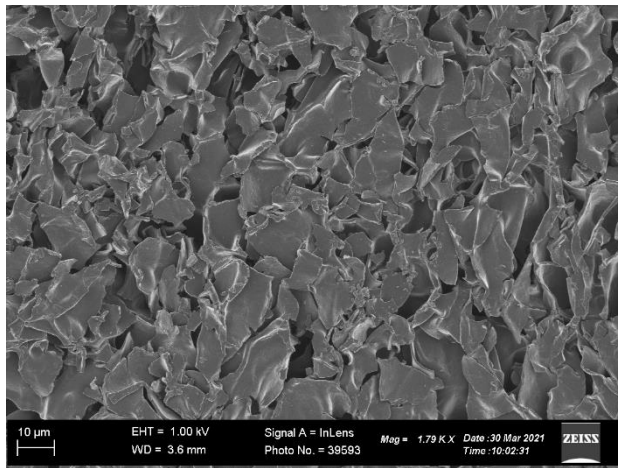


Figure 5.12: Scanning Electron Microscopy (SEM) micrographs of freeze-dried maize starch pastes

5.5 Gelling properties

Tables 5.8 and 5.9 show the effect of treating teff, maize, and potato starches with CNF and MCC on the gelling properties of the starches. After both short and extended pasting cycles, the starch pastes were allowed to cool overnight at about 25 °C to form gels. Gels formed by treating teff and maize starches with CNF and MCC were observed to be opaque and rigid while those formed by treating potato starch with CNF and MCC were translucent and soft and wobbly (Figures 5.13). As a result of the soft and wobbly nature of potato starch gel, gels formed by treating this starch with CNF and MCC could not be analyzed using the compression method. They were harder to cut, handle and fix onto the texture analyzer.

Generally, when CNF and MCC were added to teff and maize starches, gel strength decreased significantly ($P \leq 0.05$) with increasing hydrocolloid concentration.

Treatments of maize and teff starch with CNF generally had lower gel strength than those with MCC. This effect was more significant ($P \leq 0.05$) with gels prepared from extended pasting cycles. Figures 5.14 and 5.15 show the stress-stress curves of teff and maize starch gels prepared after short and extended pasting cycles. Generally, the stress-strain curves show that for all the starch gels, the stress experienced by the gels increased exponentially with an increase in the applied strain. However, as a confluence with the above gel strength results, treatments with CNF had lower stress during compression. Also, starch gels with CNF from extended pasting cycles had even much lower stress when compared to those treated with MCC during the compression test. These results were most evident at higher hydrocolloid concentrations of 5% (w/w) with maize starch.

Table 5.8: Effect of Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) addition on the gel hardness of teff, maize potato starches after short pasting cycles.

TREATMENTS	GEL HARDNESS (Force, N)					
	TEFF STARCH		MAIZE STARCH		*POTATO STARCH	
	MCC	CNF	MCC	CNF	MCC	CNF
0%	1.42a ± 0.02	1.42a ± 0.02	1.76a ± 0.08	1.76a ± 0.08	Soft gel	Soft gel
0.2%	1.38a ± 0.02	1.42a ± 0.04	1.52b ± 0.06	1.65a ± 0.02	Soft gel	Soft gel
0.5%	1.38a ± 0.07	1.40a ± 0.04	1.52b ± 0.07	1.37b ± 0.05	Soft gel	Soft gel
2%	1.37a ± 0.09	1.37a ± 0.02	1.52b ± 0.03	1.36b ± 0.09	Soft gel	Soft gel
5%	1.36a ± 0.06	1.36a ± 0.07	1.41b ± 0.04	1.35b ± 0.01	Soft gel	Soft gel

*Potato starch formed a soft gel that could not be easily diced for analysis using the compression test.
Means within the same column with the different letters are significantly different ($P \leq 0.05$)

Teff starch gels



Maize starch gels



Potato starch gels



Figure 5.13: Appearance of gels formed by teff, maize, and potato starches.

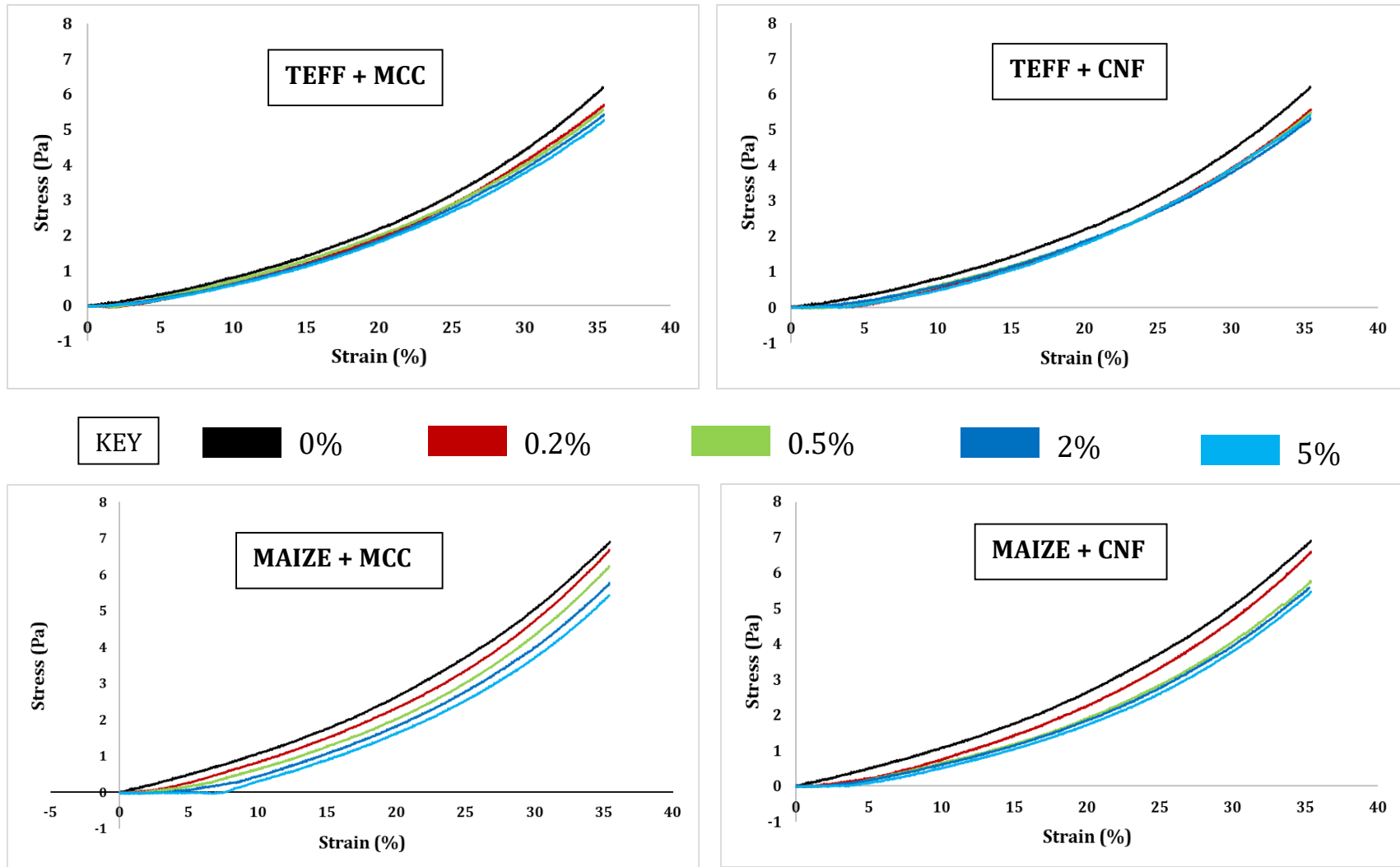


Figure 5.14: Stress-strain curves of teff and maize starch gels treated with Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) after short pasting cycles.

Table 5.9: Effect of Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) addition on the gel hardness of teff, maize, and potato starch gels after extended pasting cycles.

TREATMENTS	GEL HARDNESS (Force, N)					
	TEFF STARCH		MAIZE STARCH		*POTATO STARCH	
	MCC	CNF	MCC	CNF	MCC	CNF
0%	1.27a ± 0.03	1.27a ± 0.03	1.78a ± 0.02	1.78a ± 0.02	Soft gel	Soft gel
0.2%	1.26a ± 0.05	1.24ab ± 0.07	1.44b ± 0.01	1.52b ± 0.06	Soft gel	Soft gel
0.5%	1.24a ± 0.02	1.15b ± 0.03	1.34c ± 0.07	1.37c ± 0.03	Soft gel	Soft gel
2%	1.23a ± 0.01	1.10b ± 0.05	1.21d ± 0.02	1.28d ± 0.02	Soft gel	Soft gel
5%	1.21a ± 0.01	0.94c ± 0.02	1.16e ± 0.01	1.03e ± 0.02	Soft gel	Soft gel

*Potato starch formed a soft gel that could not be easily diced for analysis using the compression test.
 Means within the same column with the different letters are significantly different ($P \leq 0.05$)

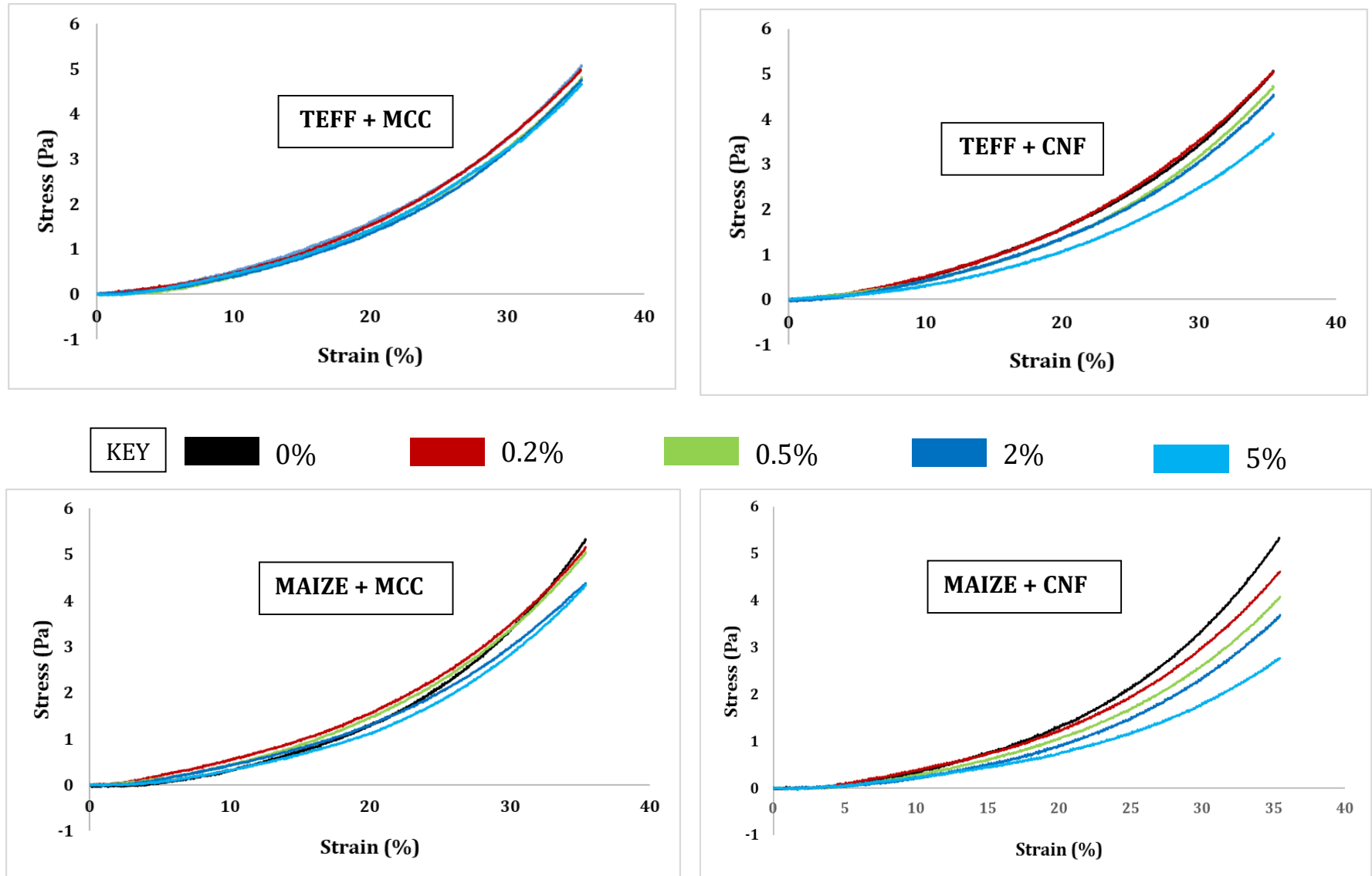


Figure 5.15: Stress-strain curves of teff and maize starch gels treated with Microcrystalline cellulose (MCC) and Cellulose Nanofiber (CNF) after extended pasting cycles.

5.6 Viscoelastic properties

The results of the effect of CNF and MCC on the viscoelastic properties of teff, maize, and potato starches are presented in Figures 5.15, 5.16, and 5.17. Teff starch treatments with CNF started with higher storage modulus (G') and complex viscosity (η^*). But as temperatures decreased from 85 °C to 23 °C with time, the G' and η^* of control and MCC treatments overlapped and increased above those with CNF. By the end of the experiment, The G' and η^* of CNF treatments were lower than those of MCC and the control. The loss moduli (G'') and tan delta of CNF and MCC treatments were higher than those of the control. However, G'' and tan delta of CNF treatments were higher than those of MCC and Control.

With regards to maize starch, the G' and η^* of control, CNF, and MCC treatments started relatively at the same point when the temperature was still at 85 °C. Just like with teff starch, a decrease in temperatures from 85 °C to 23 °C also decreased both G' and η^* of CNF. However, the decrease in G' and η^* with maize starch and CNF was higher than with teff starch. The G'' of MCC and CNF treatments with maize starch started higher than the control but later followed a similar path as the control with the decrease in temperature. As with teff starch, the tan delta of the maize starch and CNF treatment was higher than those of MCC and Control.

Potato starch G' , G'' and η^* started low and increased as temperatures increased from 85 °C to 23 °C. Potato starch treated with MCC has higher G' , G'' and η^* profiles followed by the control and CNF treatments respectively. Potato starch tan delta profile started high and then decreased with the decrease in temperature. The control had the highest tan delta followed below by treatments with CNF and MCC respectively. The potato starch treatment with MCC had a much lower tan delta than the control and CNF treatments.

Overall, maize starch had higher final G' , G'' and η^* profiles than teff and potato starch respectively. Potato starch had higher tan delta profiles than maize and teff starch respectively.

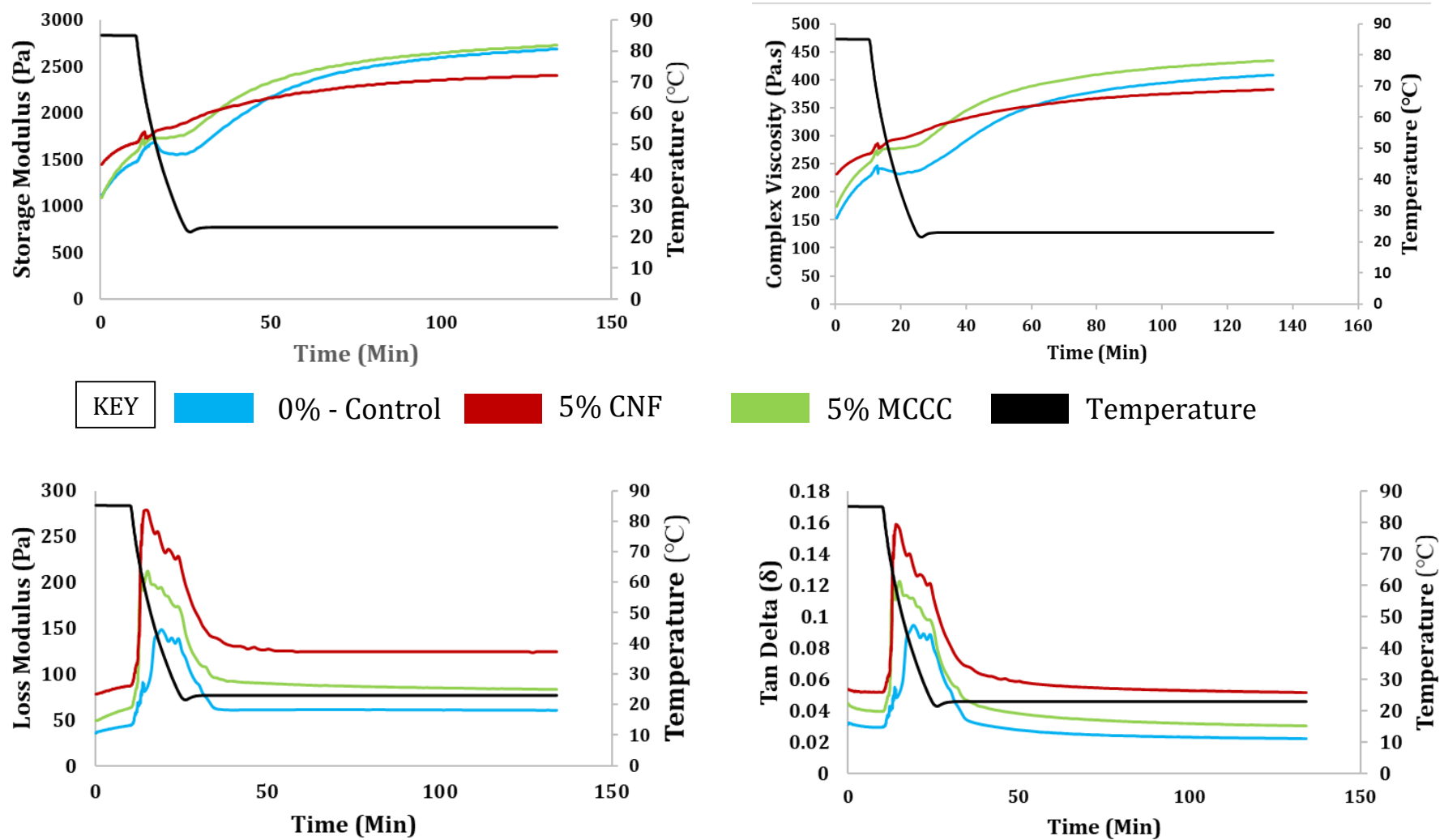


Figure 5.16: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of teff starch during cooling.

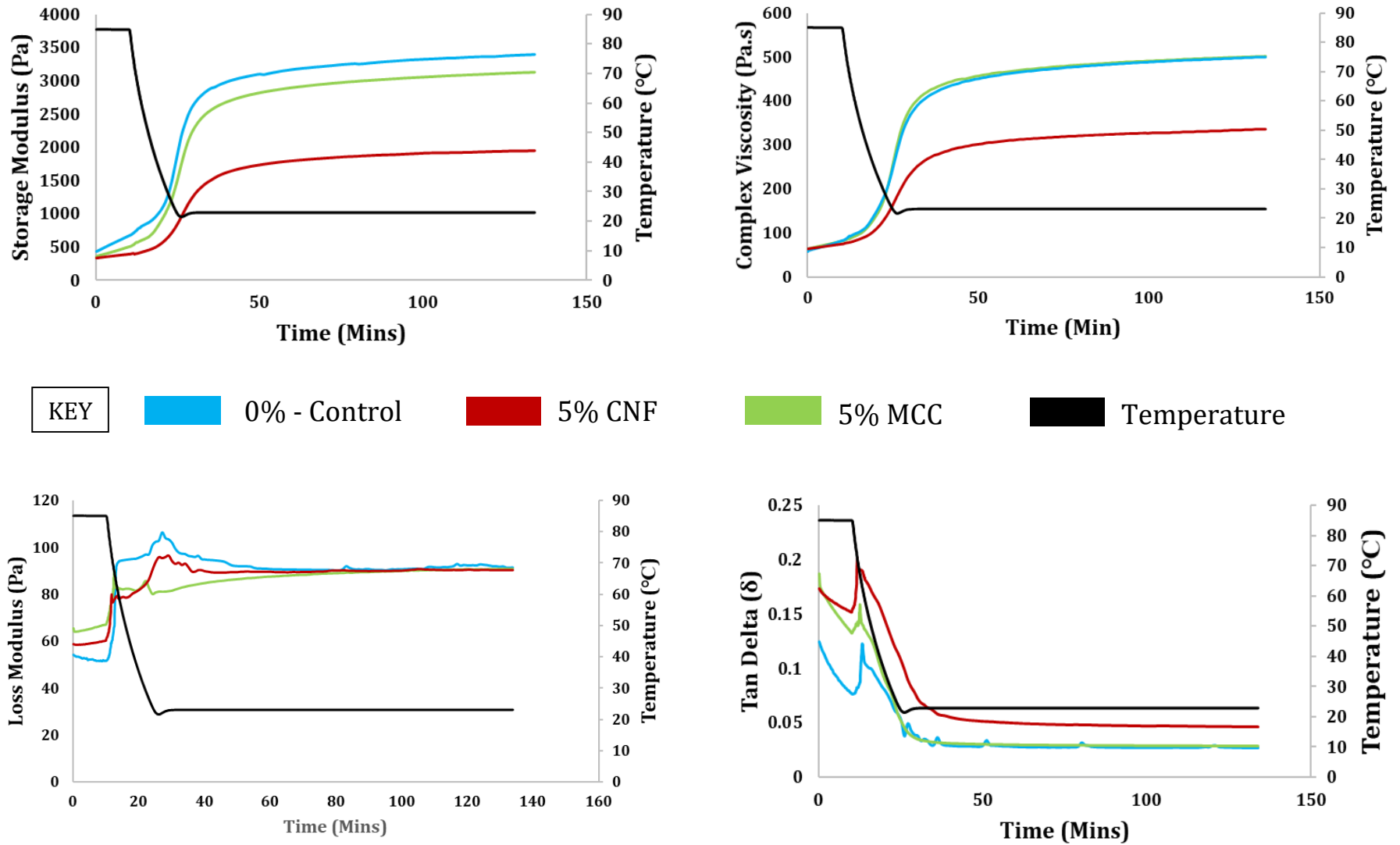


Figure 5.17: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of maize starch during cooling.

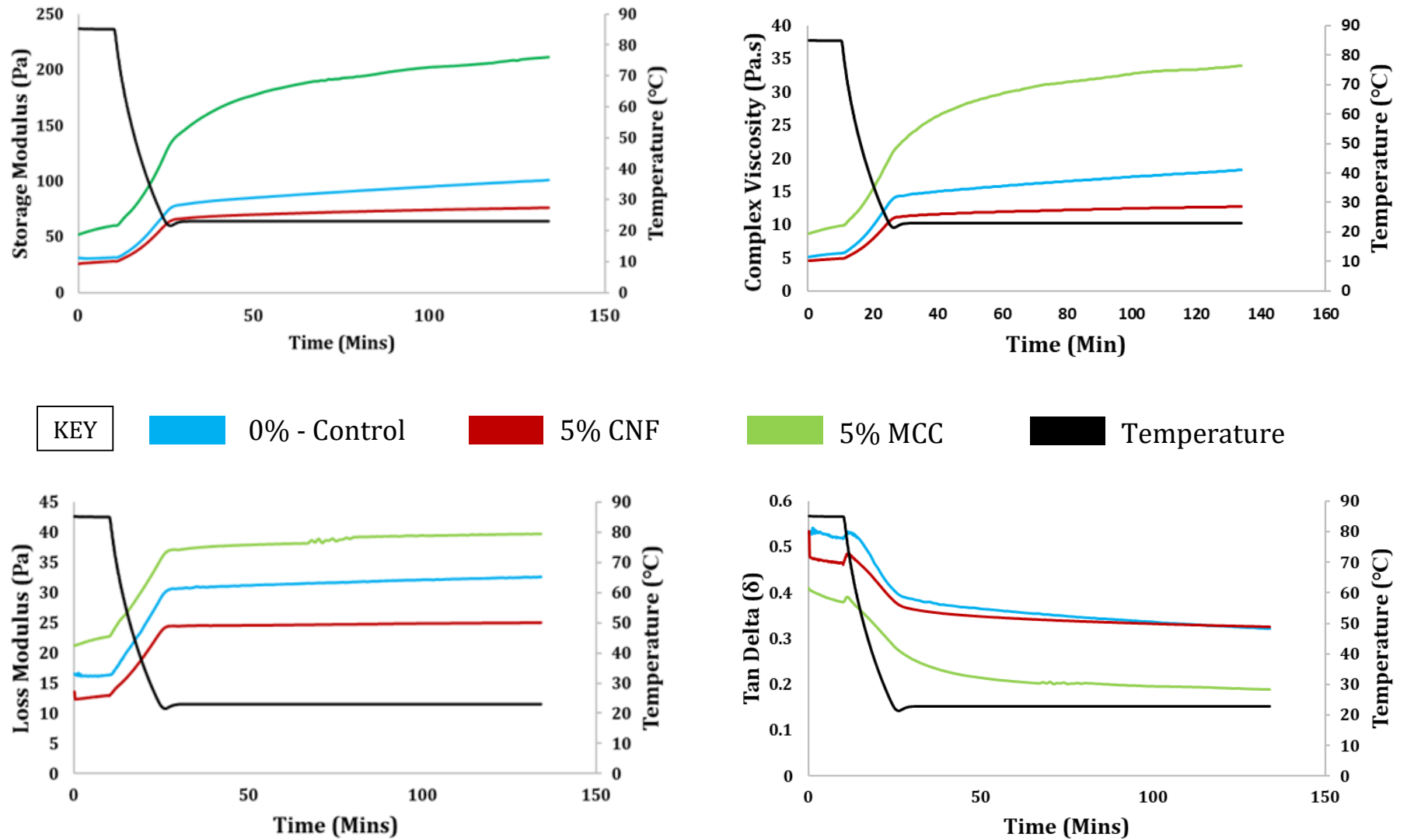


Figure 5.18: Effects of Cellulose Nanofiber (CNF) and Microcrystalline cellulose (MCC) addition on the storage modulus, complex viscosity, loss modulus, and tan delta of potato starch during cooling

6. GENERAL DISCUSSION

This chapter is divided into two sections. The first section reviews the research methodology, highlighting the strengths and weaknesses of the different methods employed in this research. The second section discusses the major finding of this research accompanied by scientific explanations of the effect of microcrystalline cellulose and cellulose nanofiber on the pasting properties of teff, maize, and potato starches.

6.1 Methodological consideration

6.1.1 Teff starch extraction

The extraction of teff starch was done without the aid of chemicals such as lactic acid (Singh *et al.*, 1997), sodium hydroxide (Yang *et al.*, 2000), or sodium metabisulphite (Du *et al.*, 1996). This entire research ensured to minimize the use of chemicals in the process to produce “clean label” starches. As a result, distilled water was utilized in the teff starch extraction process which however resulted in a final teff starch with higher protein content (1.37%,) than the other commercial starches used; maize starch (0.14%) and potato starch (0.10%). This important difference in protein content is worth consideration because it can affect the pasting properties of the starch (Sayar *et al.*, 2005). This difference can probably explain why teff starch had no breakdown viscosity because proteins can coat the starch granule surface thus stabilizing them against breakdown (Costa *et al.*, 2019). Future studies could consider the extraction of teff starch with either lactic acid, sodium hydroxide, or sodium metabisulphite to determine their effect on the pasting properties of teff starch in the presence of hydrocolloids.

6.1.2 Pasting properties

Initially, the pasting of the hydrocolloid and starch suspensions was done by mixing both the hydrocolloid and the starch in a solid state and later suspended in distilled water. However, upon pasting in the rheometer, the suspension formed lumps which are likely caused by the insufficient wetting of the hydrocolloids during dispersion (Phillips & Williams, 2009). This also created noisy pasting curves.

Thereafter, it was discovered that dispersing the hydrocolloid and starch separately in distilled water and later mixing them before pasting would eliminate the noise generated by the earlier technique because it allows for sufficient hydration of both the hydrocolloids and starch. This

technique was adopted from Ma *et al.* (2019). von Borries-Medrano *et al.* (2017) reported that the presence of water “activates” the hydrocolloids. Future studies working with solid-state hydrocolloids in the modification of starches should thus consider the above when determining the pasting properties of starch food systems.

The reason for heating to 91 °C and not 95 °C beyond was to prevent boiling, as the water boils at approximately 95 °C in Pretoria because of the high altitude (approximately 1400 m) which implies boiling can take place at lower temperatures than 100 °C (Teklehaimanot, 2011). Boiling would lead to excessive moisture loss from the starch paste thus concentrating the suspension which would adversely affect the rheological properties by making the starch system thicker than usual.

6.1.3 Gelling and Viscoelastic properties

A compression test was used to determine the gelling properties. However, unlike teff and maize starch which form rigid gels, potato starch formed very soft gels after 24 hours of storage which can be attributed to the bulky phosphate groups which can affect its functionality (Singh *et al.*, 2016). As a result, potato starch gels could not be diced for analysis because of their wobbly nature. This limited the chosen method’s ability to analyze the gel strength of potato starch. Therefore, statistical data for the gel hardness of potato starch was not obtained. Although potato starch gelling properties could not be determined by compression test, rheometry was used to understand these properties.

Initially, a starch paste to be used for determining gelling properties was prepared by heating a starch suspension to 90 °C while stirring on a magnetic stirrer hot plate and then immediately transferred to the rheometer for further analysis. However, this was not an exact simulation of the actual pasting process of the rheometer and the resulting viscoelastic curves were typically not as repeatable (Figure 6.1).

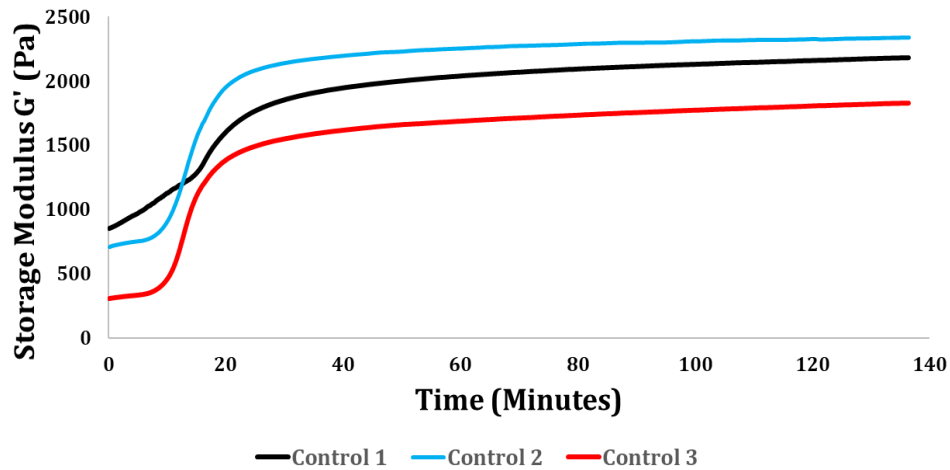


Figure 6.1: Changes in storage modulus of maize starch paste prepared using a magnetic stirrer hot plate (Own work)

Therefore, to simulate the exact pasting process before viscoelastic measurements, starch suspensions were pasted using the exact pasting profile used for determining pasting properties with the rheometer. Once the process was completed, the rheometer paddle was immediately removed and replaced with the measuring bob used to determine the viscoelastic properties. The starch paste was allowed to equilibrate at 85 °C to achieve thermal equilibrium. There was a possibility of moisture loss during the swapping of the paddle with the measuring bob. However, based on the repeatability of the obtained viscoelastic curves, the moisture loss was negligible (Figure 6.2). To minimize and avoid further moisture loss, the top of the bob and cup system was sealed with Paraffin oil.

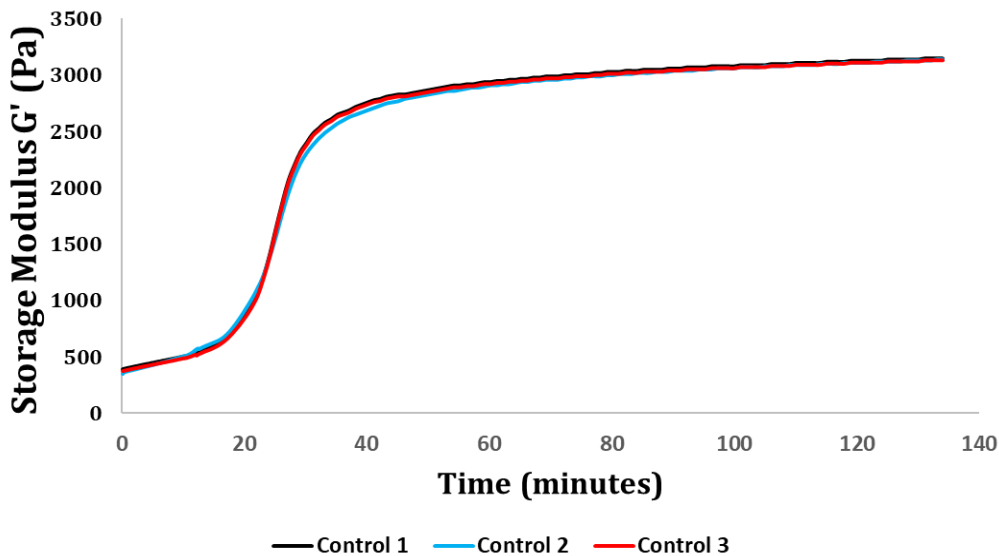


Figure 6.2: Changes in storage modulus of maize starch paste prepared using the rheometer (Own work).

6.1.5 Microscopy

The Linkam CO 102 thermostat and light microscope were used to determine the changes in the microstructure of starch suspensions as temperatures increased from 50 °C to 90 °C in the presence of hydrocolloids. The sample for hot stage analysis is placed in between the glass slide and coverslip and then placed on top of the heating element. As a result, the sample is not heated directly which can lead to some heat loss in the process. This can affect the accuracy of the thermostat and if not carefully monitored, temperature transitions can be difficult to implement. Therefore, when using this particular thermostat, a temperature gun can be used to monitor and confirm the relative temperature values displayed by the thermostat.

Light microscopy was used to observe the changes in starch granule structure after pasting in the presence of microcrystalline cellulose and cellulose nanofiber. Other than identifying starch granules, the obtained micrographs could not be used to clearly identify other components within the system. Therefore, there was insufficient evidence generated to understand and discuss the interaction of hydrocolloids and starch on a micro-level. Therefore, future studies can employ Transmission Electron Microscopy (TEM) to obtain high-resolution nanometric image data which can aid in the identification of micro and nanomaterials and their distribution within the gel structure (Gopiraman *et al.*, 2018). Due to a lack of access to such equipment and expertise, we could not undertake this analysis.

Scanning electron microscopy (SEM) was used to investigate the changes in the surface morphology of starch granules when starch is treated with hydrocolloids. The starch pastes were freeze-dried immediately after pasting to maintain the structural integrity of the starch system. The process of freeze-drying samples can lead to the formation of artifacts that tend to form during the growth of ice crystals (Miller *et al.*, 1983). These artifacts formed during freeze-drying can affect the quality of micrographs produced after microscopy by producing “porous” structures. Also, SEM can only provide surface details and also cannot easily contrast the different components within the system. Because of this limitation, it is difficult to understand how the different components are interacting with each other. Therefore, atomic force microscopy (where necessary coupled with TEM) can be used with specific stains to identify and contrast the distribution of the different nanomaterials within the system (Lahiji *et al.*, 2010).

6.2 Results discussion

6.2.1 Pasting properties

The addition of microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) to teff and maize starch system increased the peak and final viscosity of these starches. The following studies reported similar results where cellulose derivative hydrocolloids have been used to modify starches; wheat treated with hydroxypropyl methylcellulose (HPMC) (Rojas *et al.*, 1999), maize, rice, and tapioca starches treated with carboxymethylcellulose and HPMC (Shi & BeMiller, 2002), rice starch treated with methylcellulose (Mukprasirt *et al.*, 2002). All these studies showed an increase in peak and final viscosities of the starches used.

The starch-hydrocolloid system comprises both a continuous and discontinuous phase (Tecante & Doublier, 1999) (Figure 6.3). Before pasting, the continuous phase contains hydrocolloid polymers dissolved in water while the discontinuous phase contains the intact unswollen starch granules (Heyman *et al.*, 2014). During pasting, some of the starch granules disintegrate leaching out amylose molecules into the continuous phase (Abdulmola *et al.*, 1996). At this point, the continuous phase comprises both the hydrocolloid and leached amylose while the discontinuous phase comprises both the disintegrated and intact starch granules (Tecante & Doublier, 1999). The changes in the starch pasting properties are influenced by a combination of intermolecular associations and phase separation (Zhang *et al.*, 2018)

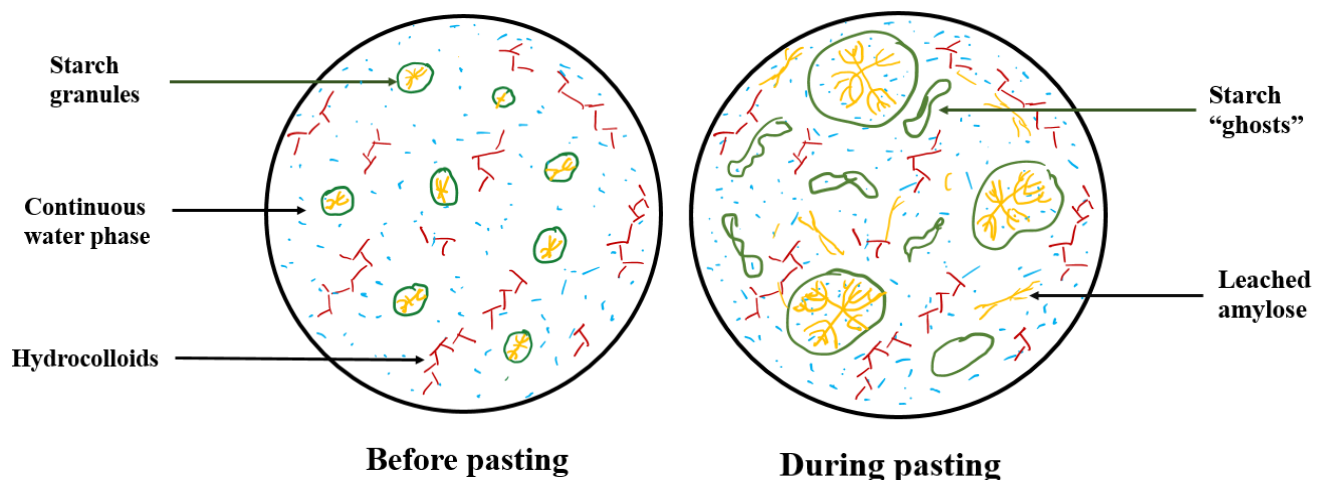


Figure 6.3: Schematic diagram showing the continuous and discontinuous phase components of the starch-hydrocolloid system before and during pasting (Own work).

When hydrocolloids are added to the water-rich continuous phase, their primarily hydrophilic nature enables them to bind water using their free hydroxyl groups via hydrogen bonding within the phase thus forming networks of interconnected polymers (Chaisawang & Supphantharika, 2005). These networks formed within the continuous phase increase the resistance to flow within the starch system. As the concentration of the hydrocolloids increases, the starch-hydrocolloid system becomes more viscous because more water molecules are bound from the continuous phase.

The process by which paste viscosity increases in the presence of CNF and MCC suggests a possible interaction between the starch and non-starch polysaccharides. When hydrocolloids are pasted alone at a 5% (w/w) concentration, both CNF and MCC have a final viscosity of less than 80 mPa.s (Figure 5.1). The final viscosity of maize starch control was about 3000 mPa.s. However, when maize starch is pasted with CNF at 5% (w/w), the final viscosity exponentially increased from about 3000 mPa.s to over 4000 mPa.s. It is also therefore probable that the interactions between hydrocolloids and the starch polymers contribute to the overall increase in starch paste viscosity.

Generally, the peak viscosity of the starch-hydrocolloid system did not increase significantly with an increase in hydrocolloid concentration until a critical concentration (C^*) was reached. The C^* was determined as the lowest concentration at which the increase in peak viscosity transitioned from slow and insignificant to significant (Figure 6.4). It is probable that, below the critical hydrocolloid concentration (C^*), there are sufficient molecular spaces within the continuous phase for the polymers to move freely without forming any significant interactions that can influence the pasting properties of the starch system (Khan & Bhattacharyya, 1987). Saha and Bhattacharyya (2010) reported that thickening or increase in viscosity occurs when the hydrocolloid concentration increases above the critical concentration called overlap concentration.

Using the data that shows changes in the peak viscosity of maize starch with an increase in hydrocolloid concentration, the intercept between the slopes of the peak viscosity curve of the low hydrocolloid concentrations (0-2%) and high hydrocolloid concentrations (2-5%) yielded the critical concentration (C^*) (Goodwin *et al.*, 2000). From Figure 6.4, it is evident that at hydrocolloid concentrations lower than the critical concentration (2% w/w), the increase in starch

paste viscosity was slow or insignificant but it increased linearly beyond C^* because of the same reasons explained above.

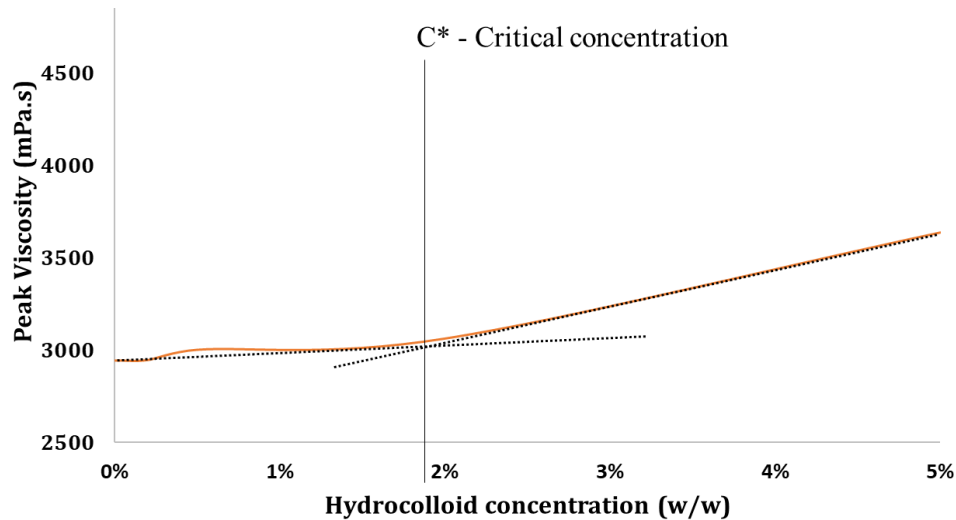


Figure 6.4: Critical concentration (C^*) of microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) in the starch-hydrocolloid system (Own work)

Hot stage microscopy micrographs show that the addition of CNF or MCC to starch temporarily stabilizes several starch granules against breakdown. This can probably be attributed to granule stabilizing hydrocolloid networks around the surface of the granules which insulate the granules against impact forces that lead to a structural breakdown (da Silva Costa *et al.*, 2020). This enables the starch system treated with CNF or MCF to maintain a higher viscosity than the control (Figure 5.4).

The swelling of granules can also influence the paste viscosity by reducing the free space available for mobility within the continuous phase (Kumar & Khatkar, 2017). This phenomenon leads to phase separation which increases the effective concentration of the hydrocolloid within the continuous phase (BeMiller, 2011). As a result of this increased hydrocolloid concentration in the continuous phase, the system becomes more viscous by hydrocolloids forming more intra and inter molecular networks within the continuous phase (Zhang *et al.*, 2018) (Figure 6.5). Therefore, the more swollen granules present in the starch system, the more viscous the system becomes.

Although from Table 5.7 starch treatments with CNF and MCC showed significantly smaller granule sizes than the control ($P \leq 0.05$), they had fewer disintegrated granules which enabled them to maintain a higher viscosity profile than the control.

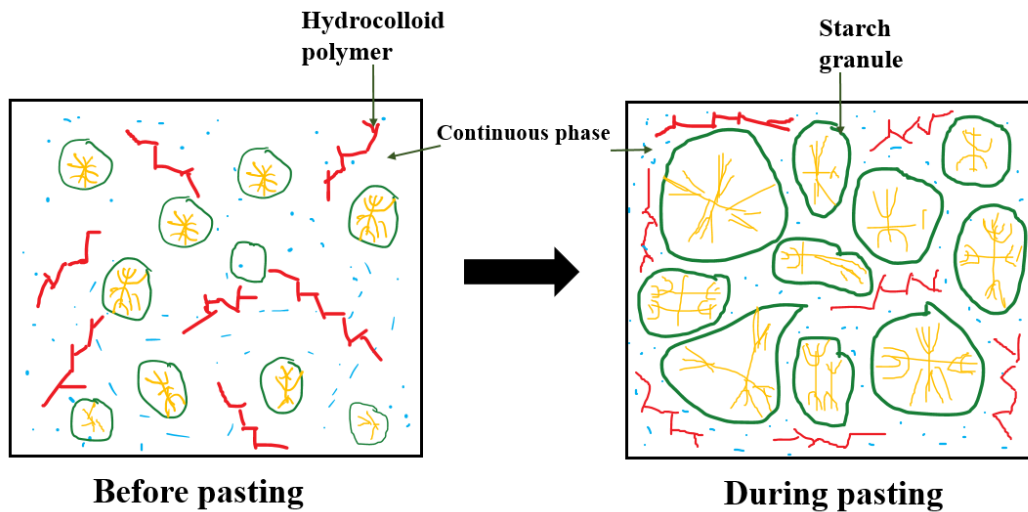


Figure 6.5: Schematic diagram showing the effect of starch granule swelling on the continuous phase (Own work)

When added to the continuous water phase of a starch system, hydrocolloids have been reported to form networks around the surfaces of starch granules within the system (Chaisawang & Suphantharika, 2006). Through inter and intramolecular hydrogen bonds, CNF and MCC form networks within the continuous phase that stabilize the structure of the starch granules (Wüstenberg, 2015). This provides an extra layer of reinforcement that stabilizes and strengthens their structures against shear forces during processing (Aguirre-Cruz *et al.*, 2005) (Figure 6.6). This leads to an increase in the number of rigid, swollen, and unruptured granules in the dispersed phase. These rigid swollen granules reduce the intergranular spaces within the starch system and consequently increase the friction within the system as granules move past each other (Hongsprabhas *et al.*, 2007). This is reflected in the increased starch paste viscosity in the presence

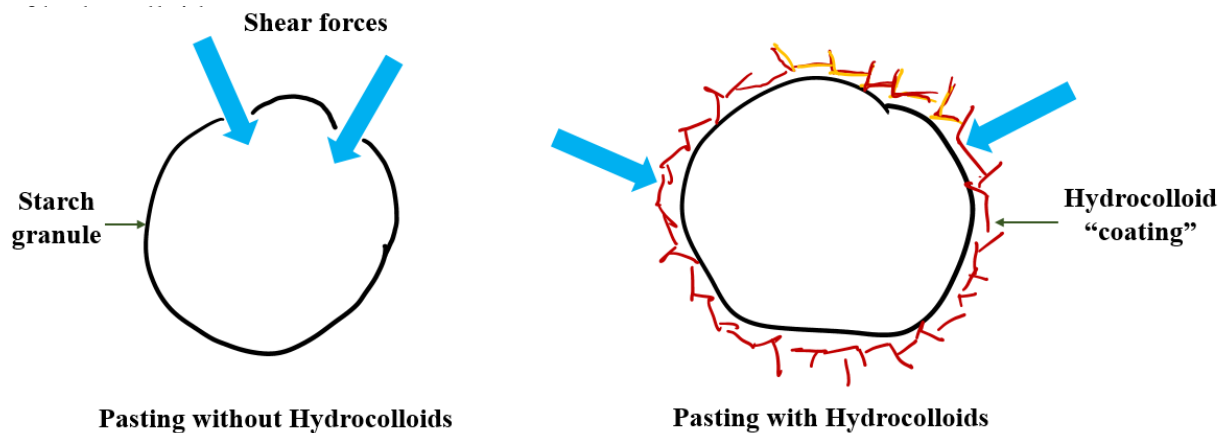


Figure 6.6: Schematic diagram illustrating the stabilizing effect of hydrocolloids during pasting (Own work).

Maize and teff starch treatments with CNF had higher paste viscosities than those with MCC. CNF is a nanomaterial with a diameter of 2-20 nm (Zhang *et al.*, 2019) while MCC has a diameter of 10–50 μm (Hachaichi *et al.*, 2021) which makes MCC larger than CNF. Therefore, MCC has more cellulose biopolymer chains bound within its structure than CNF and thus less of its hydroxyl groups are exposed and available for hydrogen bonding. This lowers the hydrodynamic volume of MCC. On the other hand, the ultrafine nanostructure of cellulose nanofiber results in more hydroxyl groups being exposed and available for more extensive hydrogen bonding with water within the continuous phase (Guan *et al.*, 2020). This gives CNF a higher surface area and hydrodynamic volume than MCC. Also, the highly fibrous nature of CNF also gives it great encapsulation ability of water-soluble polymers such as amylose which further reduces molecular mobility within the continuous phase (Robles-García *et al.*, 2018).

Also, the bulky nature of MCC can hinder its interaction with smaller starch polymers. This molecular incompatibility causes the bulky MCC (micro-sized) and smaller amylose polymers (nano-sized) to undergo mutual exclusion (Eidam *et al.*, 1995). This leads to phase separation which limits any possible interactions between the two polymers. Ahmad and Williams (2001) reported an increase in phase separation when bulky polymers of locust bean gum (LBG) were added to the sago starch solution. Also, phase separation increased as the concentration of the bulky LBG was increased from 0.75% (w/w) to 1.5% (w/w). Phase separation limits intermolecular interactions by mainly favoring associations between like polymers which consequently limits the increase in viscosity (Lui *et al.*, 2003). Xie *et al.* (2018) also reported that although MCC is quite hydrophilic, the surface of the polymer is mostly hydrophobic and this can affect its ability to bind water molecules. As a result of this molecular incompatibility, addition of a less solvent polymer (MCC) to a starch polymer solution can lead phase separation which in turn limits the extent of viscosity increase in the presence of MCC (van Langenhove, 2015).

All these factors combined explain why starch treatments with CNF have higher paste viscosities than those with MCC.

Teff starch did not show any viscosity breakdown, especially during the short pasting cycles. The addition of CNF or MCC to teff starch also increased the plateau viscosity and final viscosity of teff starch just like with maize starch. A study by Sayar *et al.* (2005) on the effects of proteins on pasting properties of chickpea starch suggested proteins stabilize the components of the continuous

phase by coating the starch granules thus reducing the impact of the shear forces on the starch granules. The results of material characterization proved that the extracted teff starch indeed had a higher protein content than the other starches used in this research.

Unlike starch treatments that underwent short pasting cycles, extended pasting did not have any effect on the final starch paste viscosity with or without the hydrocolloids. When pasting with a rheometer, a rotating paddle is used to stir the starch paste homogeneously. Stirring when done continuously (at least 2 hours for extended pasting cycles), generates a lot of friction, impact, and shear forces which cause a massive breakdown of the starch granules in the system (Figures 5.8 – 5.11). When compared with short pasting cycles, micrographs from extended pasting cycles show more structural breakdown at the end of the cycle and this can mainly be attributed to the prolonged shearing experienced during the extended pasting cycles.

The extended pasting cycle of maize and teff starches showed a second peak which suggested the probable formation of complexes within the starch-hydrocolloid system. Wokadala *et al.* (2012) reported the formation of Type II complexes which are mostly formed after pasting starch for a prolonged time (more than 30 minutes). These findings suggest a possible interaction between the endogenous starch lipids with amylose polymers during pasting thus forming complexes that lead to the formation of the second peak (D'Silva *et al.*, 2011).

Treating potato starch with CNF or MCC did not show any observable effect on the pasting properties of the starch. Varela *et al.* (2016) reported similar results when potato starch was treated with hydroxypropylmethylcellulose, pectin, and Arabic gum. This can be attributed to the bulky phosphate group attached to the potato starch chains which probably limited any possible interactions between starch and the hydrocolloids (Singh *et al.*, 2016). These bulky groups also make potato starch granules very fragile and susceptible to a massive breakdown which negates the effects of the added hydrocolloids (Figure 5.10). Also, Gibiński *et al.*, (2006) suggested that potato starch is possibly thermodynamically incompatible with several hydrocolloids and this can be a result of the potato starch's bulky phosphate groups which can hinder its interaction with other molecules.

When compared with teff and maize starches, potato starch had the highest breakdown viscosity even in the presence of CNF and MCC. This can be attributed to the large and fragile potato starch granules which cannot withstand shear forces (Kaur *et al.*, 2002). The potato starch fragility can be attributed to the negatively-charged bulky phosphate groups which cause ionic repulsions amongst starch molecules thus weakening the starch granule structure (Lim *et al.*, 2002).

6.2.2 Gelling properties

The addition of MCC and CNF to teff and maize starches significantly decreased ($P \leq 0.05$) the gel strength of the starches. Several studies have reported a decrease in gel strength when cellulose derivative hydrocolloids were added to starches: maize starch treated with carboxymethylcellulose (Eidam *et al.*, 1995) and wheat starch treated with methylcellulose, and hydroxypropylmethylcellulose (Naruenartwongsakul *et al.*, 2004). These results show that treating these hydrocolloids can inhibit or retard the process of gel formation and consequently retrogradation.

During the cooling stage of starch paste, free amylose molecules leached into the continuous phase during pasting start to rearrange and realign forming junction zones that lead to an ordered three-dimensional gel structure (Klucinec & Thompson, 1999). These ordered structures of amylose helices aligned together result in the formation of firm starch gel structures. However, in the presence of hydrocolloid polymers, amylose molecules leached into the continuous phase have been reported to interact and entangle with the available hydrocolloid polymers via hydrogen bonding (Funami *et al.*, 2005; Shi & BeMiller, 2002). These amylose-hydrocolloid entanglements form randomly arranged complexes/structures within the continuous phase which result in less firm gel structures (Richardson *et al.*, 2004). As a result, these amylose and hydrocolloid entanglements reduce the number of ordered amylose-amylose three-dimension structures formed which consequently results in weaker gel structures (BeMillier, 2011).

Also, as discussed earlier, with the addition of CNF and MCC when added to the continuous water phase, these hydrocolloids form intertwined viscous networks which can cover the surface of starch granules. These networks surrounding the surface of the starch granules can reduce the rate of amylose leaching from the starch granules (Figure 6.6). In a study by Nagano *et al.* (2008), the addition of guar gum to maize starch in increasing concentrations inhibited the leaching of amylose

molecules thus inhibiting retrogradation. The resulting gel structures are weaker in strength. When the rate of amylose leaching is decreased, few amylose molecules are available in the continuous phase to form junction zones thus forming weaker gel structures.

Generally, a critical hydrocolloid concentration of 2% (w/w) was observed to result in a significant decrease in gel strength ($P < 0.05$). At this critical hydrocolloid concentration, significant intermolecular entanglements take place via hydrogen bonding between the hydrocolloid and starch polymers which make amylose unavailable for junction zones formation (Nabilah *et al.*, 2021). This results in weaker gel structures. At hydrocolloid concentrations lower than 2% (w/w), the hydrocolloid polymers move freely within the continuous phase without any significant entanglements with the free leached amylose molecules (Khan & Bhattacharyya, 1987). As the hydrocolloid concentration increases over the critical concentration, the molecular spaces reduce within the continuous phase causing the free amylose and hydrocolloid polymers to eventually entangle and associate via hydrogen bonding (Saha & Bhattacharya, 2010). In this situation, these entangled amylose molecules can no longer rearrange to form junction zones which leads to weaker gel structures.

Findings from the viscoelastic properties of maize and teff starch showed that treating these starches with CNF or MCC increased the tan delta values while storage modulus values (G') decreased (Figures 5.16 & 5.17). According to Varela *et al.* (2016). Starches with higher tan delta values have weaker gel structures than starches with low tan delta values (the viscous behavior dominates more than the elastic behavior). These findings support the earlier observation indicating a reduction in starch gel strength in the presence of CNF and MCC. Eidam *et al.* (1995) also reported a decrease in G' when CMC was added to maize starch. Also, when maize starch was treated with Fenugreek gum, Funami *et al.* (2008) reported an increase in tan delta values and a decrease in G' which was attributed to the interaction between the hydrocolloids and amylose.

Teff and maize starch treatments with CNF generally had significantly lower ($P \leq 0.05$) gel strength than MCC. Results from the viscoelastic properties also showed that CNF treatments had higher tan delta values, lower storage modulus (G'), and complex viscosity η^* . These results show the teff or Maize treatment with CNF showed more viscous behavior than MCC which confirms a decrease in gel strength in the presence of CNF. As earlier described in pasting properties, the ultrafine nanostructure of CNF gives it a higher surface area and hydrodynamic volume than MCC

which results in more of its hydroxyl groups being exposed and available for hydrogen bonding with other hydrophilic polymers such as amylose (Guan *et al.*, 2020). This enables CNF to form more molecular entanglements with the available amylose within the continuous phase which reduces the availability of the leached amylose molecules for amylose-amylose associations. As a result, fewer junction zones are formed between the amylose molecules which results in a less elastic gel structure but with more viscous behavior in the presence of CNF.

Also, because both cellulose nanofiber and amylose polymer exist on a nanoscale, they can perhaps exhibit more molecular compatibility than MCC which exists in micro-dimensions (Kowalski *et al.*, 2008). As a result, less phase separation occurs in the presence of CNF which allows for more associations between amylose and CNF (Jiménez *et al.*, 2012). This makes amylose less available to form junction zones in the presence of CNF which leads to weaker gel structures. Due to molecular incompatibility between MCC and amylose polymers, both polymers interact less leading to phase separation which “frees” several amylose polymers (Eidam *et al.*, 1995). This increases the effective concentration of amylose in the continuous phase leading to the formation of more junction zones (BeMiller, 2011). Therefore, starch gels formed in the presence of MCC exhibit more elasticity and solid like properties than those with CNF because of the formation of more amylose junction zones facilitated by microphase separation.

Potato starch gels (even those with CNF or MCC treatments) were soft and wobbly. Potato starch has been reported in other studies to form soft gels (Whittenberger & Nutting, 1948; Gunaratne & Corke, 2007). This can be attributed partly to its low amylose content compared to teff and maize starches (Table 2.1). As a result, fewer junction zones are formed leading to softer gels. It is also probable that bulky phosphate groups attached to the potato starch molecules limit the formation of junction zones through steric hindrance (Singh *et al.*, 2016).

Unlike teff and maize starches, treating potato starch with CNF only slightly decreased the G' of the treatment while its $\tan \delta$ was generally similar to that of the control. Potato starch treatments with MCC had higher G' and η^* values and lower $\tan \delta$ values than the control thus showing a resulting gel structure with more elastic behavior. Shahzad *et al.* (2019) also reported an increase in G' and a decrease in $\tan \delta$ when potato starch was treated with cress seed, fenugreek, and flaxseed gums in increasing hydrocolloid concentrations. In a review of the pasting properties of the different starches with hydrocolloids by Mahmood, *et al.* (2017), it was suggested that

microphase separation often occurs between certain hydrocolloids and starches which increases the concentration of the amylose in the continuous phase. The increased amylose polymer concentration within the continuous phase increases the extent of amylose-amylose associations via hydrogen bonding which leads to the formation of more junction zones. Yoshimura *et al.*, 1998 observed an increase in short term retrogradation when maize starch was treated with konjac-glucomannan. This effect was attributed to the molecular incompatibility of starch polymers and konjac-glucomannan which increases the effective concentration of amylose in the continuous phase. Consequently, these increased junction zones lead to the formation of firmer starch gels with higher G' and lower $\tan \delta$ values which explains why potato starch exhibited more elasticity in the presence of MCC. CNF when added to potato starch did not exhibit any major effect on the G' and $\tan \delta$ of potato starch which also signified an absence of interaction between the two polymers. This molecular incompatibility exhibited by potato starch in the presence of the hydrocolloids was probably contributed in part by the bulky phosphate groups of potato starch which hindered potential interactions between the hydrocolloid and amylose molecules (Muhamedbegović *et al.*, 2012) This resulted in phase separation as described above by increasing the concentration of amylose in the continuous phase which promoted junction zone formation.

7. CONCLUSIONS

The treatment of Teff and maize starches with microcrystalline cellulose (MCC) and cellulose nanofiber (CNF) produces starches with high peak and final paste viscosities and are non-gelling properties which suggest a possible interaction between the hydrocolloids and starches. The increase in peak and final viscosities can be attributed to the interconnected networks formed in the continuous phase when hydrocolloids interact with the free amylose and water molecules via hydrogen bonding. The ability of the hydrocolloids to inhibit the gelling process can be attributed to the molecular entanglement between the hydrocolloids and leached amylose molecules which makes the amylose unavailable for junction zone formation. This leads to starches with non-gelling properties.

The high paste viscosity and non-gelling properties were more pronounced with CNF than MCC. The ultrafine nanostructure of CNF gives it a high surface area and hydrodynamic volume which exposes more of its hydroxyl groups for hydrogen bonding with free amylose and water molecules. Therefore, CNF forms more extensive networks via hydrogen bonding within the continuous phase which gives the CNF-starch systems more pronounced peak and final viscosities than the MCC-starch systems. The more pronounced non-gelling properties of starch in the presence of CNF can also be attributed to the above CNF properties which enable CNF to entangle more amylose molecules which leads to lesser junction zones being formed in the continuous phase than with MCC. Therefore, CNF can be used with normal teff and maize starches to produce soft gel starches with high viscosities similar to substituted starch but with no chemical residues that can pose health concerns to the consumers.

This study shows that due to their increased viscosity and non-gelling properties, modified starches produced by the addition of MCC and CNF to starch are a possible environmentally safe and “clean-label” replacement for chemically and physically modified starches. This will improve the consumer acceptability of foods with modified starches on the market that are interested in less chemically modified food options.

8. REFERENCES

- Abdel-Aal, E.S.M. and Gallagher, E., 2009. 11 Functionality of Starches and Hydrocolloids in Gluten-Free Foods. *Gluten-free food science and technology*, pp.200.
- Abdulmola, N.A., Hember, M.W.N., Richardson, R.K. and Morris, E.R., 1996. Effect of xanthan on the small-deformation rheology of crosslinked and uncrosslinked waxy maize starch. *Carbohydrate Polymers*, 31(1-2), pp.65-78.
- Aguirre-Cruz, A., Méndez-Montealvo, G., Solorza-Feria, J. and Bello-Pérez, L.A., 2005. Effect of carboxymethylcellulose and xanthan gum on the thermal, functional and rheological properties of dried nixtamalised maize masa. *Carbohydrate Polymers*, 62(3), pp.222-231.
- Ahmad, F.B. and Williams, P.A., 2001. Effect of galactomannans on the thermal and rheological properties of sago starch. *Journal of Agricultural and Food Chemistry*, 49(3), pp.1578-1586.
- Aho, J., Boetker, J.P., Baldursdottir, S. and Rantanen, J., 2015. Rheology as a tool for evaluation of melt processability of innovative dosage forms. *International journal of pharmaceutics*, 494(2), pp.623-642.
- Alloncle, M., Lefebvre, J., Llamas, G. and Doublier, J.L., 1989. A rheological characterization of cereal starch-galactomannan mixtures. *Cereal Chemistry*, 66(2), pp.90-93.
- Anastas, P. and Eghbali, N., 2010. Green chemistry: principles and practice. *Chemical Society Reviews*, 39(1), pp.301-312.
- Ansari, F. and Berglund, L.A., 2016. *Multifunctional Polymeric Nanocomposites Based on Cellulosic Reinforcements*, Cambridge, MA: William Andrew Publishing. pp.115-130.
- Arendt, E.K. and Dal Bello, F., 2008. *Technology of functional cereal product*, Cambridge, EN: Woodhead Publishing. pp.446-475.
- Ashogbon, A.O. and Akintayo, E.T., 2014. Recent trend in the physical and chemical modification of starches from different botanical sources: A review. *Starch-Stärke*, 66(1-2), pp.41-57.
- Bahnassey, Y.A. and Breene, W.M., 1994. Rapid visco-analyzer (RVA) pasting profiles of wheat, corn, waxy corn, tapioca and amaranth starches (*A. hypochondriacus* and *A. cruentus*) in

- the presence of konjac flour, gellan, guar, xanthan and locust bean gums. *Starch-Stärke*, 46(4), pp.134-141.
- Baldwin, P.M., Adler, J., Davies, M.C. and Melia, C.D., 1998. High resolution imaging of starch granule surfaces by atomic force microscopy. *Journal of Cereal Science*, 27(3), pp.255-265.
- Bao, J. and Bergman, C.J., 2004. The functionality of rice starch. *Starch in food: Structure, function and applications*, pp.258-294.
- Baranowska, H.M., Sikora, M., Kowalski, S. and Tomasik, P., 2008. Interactions of potato starch with selected polysaccharide hydrocolloids as measured by low-field NMR. *Food Hydrocolloids*, 22(2), pp.336-345.
- BeMiller, J.N. and Whistler, R.L., 2009. *Starch: chemistry and technology*. 3rd Edition, London, UK: Academic Press. pp.745-767.
- BeMiller, J.N., 2011. Pasting, paste, and gel properties of starch–hydrocolloid combinations. *Carbohydrate polymers*, 86(2), pp.386-423.
- Berski, W., Ptaszek, A., Ptaszek, P., Ziobro, R., Kowalski, G., Grzesik, M. and Achremowicz, B.J.C.P., 2011. Pasting and rheological properties of oat starch and its derivatives. *Carbohydrate polymers*, 83(2), pp.665-671.
- Bertoft, E., 2017. Understanding starch structure: Recent progress. *Agronomy*, 7(3), pp.56.
- Biliaderis, C.G., Arvanitoyannis, I., Izydorczyk, M.S. and Prokopowich, D.J., 1997. Effect of hydrocolloids on gelatinization and structure formation in concentrated waxy maize and wheat starch gels. *Starch-Stärke*, 49(7-8), pp.278-283.
- Bultosa, G. and Taylor, J.R., 2004. Paste and gel properties and in vitro digestibility of tef [Eragrostis tef (Zucc.) Trotter] starch. *Starch-Stärke*, 56(1), pp.20-28.
- Bultosa, G., Hall, A.N. and Taylor, J.R., 2002. Physico-chemical characterization of grain tef [Eragrostis tef (Zucc.) Trotter] starch. *Starch-Stärke*, 54(10), pp.461-468.

- Cai, X., Hong, Y., Gu, Z. and Zhang, Y., 2011. The effect of electrostatic interactions on pasting properties of potato starch/xanthan gum combinations. *Food Research International*, 44(9), pp.3079-3086.
- Chaerunisaa, A.Y., Sriwidodo, S. and Abdassah, M., 2019. *Pharmaceutical formulation design-recent practices*, London, UK: IntechOpen. pp.41-55.
- Chaisawang, M. and Supphantharika, M., 2005. Effects of guar gum and xanthan gum additions on physical and rheological properties of cationic tapioca starch. *Carbohydrate Polymers*, 61(3), pp.288-295.
- Chaisawang, M. and Supphantharika, M., 2006. Pasting and rheological properties of native and anionic tapioca starches as modified by guar gum and xanthan gum. *Food Hydrocolloids*, 20(5), pp.641-649.
- Chandanasree, D., Gul, K. and Riar, C.S., 2016. Effect of hydrocolloids and dry heat modification on physicochemical, thermal, pasting and morphological characteristics of cassava (*Manihot esculenta*) starch. *Food Hydrocolloids*, 52, pp.175-182.
- Chen, P., Liu, X., Zhang, X., Sangwan, P. and Yu, L., 2015. Phase transition of waxy and normal wheat starch granules during gelatinization. *International Journal of Polymer Science*, 2015.
- Christianson, D.D., 1982. Hydrocolloid interactions with starches. *Food carbohydrates*, pp.399-419.
- Chun, J.Y., Hong, G.P., Surassmo, S., Weiss, J., Min, S.G. and Choi, M.J., 2014. Study of the phase separation behaviour of native or preheated WPI with polysaccharides. *Polymer*, 55(16), pp.4379-4384.
- Chung, H.J., Jeong, H.Y. and Lim, S.T., 2003. Effects of acid hydrolysis and defatting on crystallinity and pasting properties of freeze-thawed high amylose corn starch. *Carbohydrate Polymers*, 54(4), pp.449-455.
- Ciolacu, D.E., 2018. *Biomass as renewable raw material to obtain bioproducts of high-tech value*, Cambridge, MA: John Feder. pp.315-350.

- Cirillo, G., Spizzirri, U.G. and Iemma, F. eds., 2015. *Functional polymers in food Science: From technology to biology, Volume 1: Food packaging*. John Wiley & Sons. Pp.168
- Copeland, L., Blazek, J., Salman, H. and Tang, M.C., 2009. Form and functionality of starch. *Food hydrocolloids*, 23(6), pp.1527-1534.
- Corrêa, A.C., de Morais Teixeira, E., Pessan, L.A. and Mattoso, L.H.C., 2010. Cellulose nanofibers from curaua fibers. *Cellulose*, 17(6), pp.1183-1192.
- Costa, C., Medronho, B., Filipe, A., Mira, I., Lindman, B., Edlund, H. and Norgren, M., 2019. Emulsion formation and stabilization by biomolecules: The leading role of cellulose. *Polymers*, 11(10), p.1570.
- Cui, S., Li, M., Zhang, S., Liu, J., Sun, Q. and Xiong, L., 2018. Physicochemical properties of maize and sweet potato starches in the presence of cellulose nanocrystals. *Food Hydrocolloids*, 77, pp.220-227.
- D'Silva, T.V., Taylor, J.R. and Emmambux, M.N., 2011. Enhancement of the pasting properties of teff and maize starches through wet-heat processing with added stearic acid. *Journal of Cereal Science*, 53(2), pp.192-197.
- da Silva Costa, R.A., Bonomo, R.C.F., Rodrigues, L.B., Santos, L.S. and Veloso, C.M., 2020. Improvement of texture properties and syneresis of arrowroot (*Maranta arundinacea*) starch gels by using hydrocolloids (guar gum and xanthan gum). *Journal of the Science of Food and Agriculture*, 100(7), pp.3204-3211.
- David, D.J., 1996. Polymer interactions and the influence of molecular structure on polymer miscibility. *Advances in Polymer Technology*, 15(4), pp.315-326.
- de Oliveira Maior, L., de Almeida, V.S., Barretti, B.R.V., Ito, V.C., Beninca, C., Demiate, I.M., Schnitzler, E., Carvalho Filho, M.A.D.S. and Lacerda, L.G., 2020. Combination of organic acid and heat-moisture treatment: impact on the thermal, structural, pasting properties and digestibility of maize starch. *Journal of Thermal Analysis and Calorimetry*, pp.1-9.
- de Oliveira, C.S., Bet, C.D., Bisinella, R.Z.B., Waiga, L.H., Colman, T.A.D. and Schnitzler, E., 2018. Heat-moisture treatment (HMT) on blends from potato starch (PS) and sweet potato starch (SPS). *Journal of Thermal Analysis and Calorimetry*, 133(3), pp.1491-1498.

- Díaz-Calderón, P., MacNaughtan, B., Hill, S., Foster, T., Enrione, J. and Mitchell, J., 2018. Changes in gelatinisation and pasting properties of various starches (wheat, maize and waxy maize) by the addition of bacterial cellulose fibrils. *Food Hydrocolloids*, 80, pp.274-280.
- Dickinson, E., 1998. Stability and rheological implications of electrostatic milk protein–polysaccharide interactions. *Trends in Food Science & Technology*, 9(10), pp.347-354.
- Du, L.I.N.G., Li, B.I.H.U.A., Lopes-Filho, J.F., Daniels, C.R. and Eckhoff, S.R., 1996. Effect of selected organic and inorganic acids on corn wet-milling yields. *Cereal chemistry*, 73(1), pp.96-98.
- Dufresne, A., 2013. Nanocellulose: a new ageless bionanomaterial. *Materials Today*, 16(6), pp.220-227.
- Eidam, D., Kulicke, W.M., Kuhn, K. and Stute, R., 1995. Formation of maize starch gels selectively regulated by the addition of hydrocolloids. *Starch-Stärke*, 47(10), pp.378-384.
- Eliasson, A.C., 1994. Interactions between starch and lipids studied by DSC. *Thermochimica Acta*, 246(2), pp.343-356.
- Eliasson, A.C., 2017. *Carbohydrates in food*, New York, NY: CRC Press. pp.501-600.
- Fang, Y., Li, L., Inoue, C., Lundin, L. and Appelqvist, I., 2006. Associative and segregative phase separations of gelatin/ κ -carrageenan aqueous mixtures. *Langmuir*, 22(23), pp.9532-9537.
- Franco, T.S. and de Muniz, G.I.B., 2015. Nanocellulose in food science and technology-potential, advantages and gaps of research. *Interfaces*, 29, pp.83-95.
- Funami, T., Kataoka, Y., Noda, S., Hiroe, M., Ishihara, S., Asai, I., Takahashi, R., Inouchi, N. and Nishinari, K., 2008. Functions of fenugreek gum with various molecular weights on the gelatinization and retrogradation behaviors of corn starch—2: Characterizations of starch and investigations of corn starch/fenugreek gum composite system at a relatively low starch concentration; 5 w/v%. *Food Hydrocolloids*, 22(5), pp.777-787.

- Funami, T., Kataoka, Y., Omoto, T., Goto, Y., Asai, I. and Nishinari, K., 2005. Effects of non-ionic polysaccharides on the gelatinization and retrogradation behavior of wheat starch. *Food Hydrocolloids*, 19(1), pp.1-13.
- Furia, T.E., 1973. *CRC handbook of food additives*, 2nd Edition, London, UK: CRC Press. pp.8-44.
- Gallant, D.J., Bouchet, B. and Baldwin, P.M., 1997. Microscopy of starch: evidence of a new level of granule organization. *Carbohydrate polymers*, 32(3-4), pp.177-191.
- Gebremariam, M.M., Zarnkow, M. and Becker, T., 2014. Teff (*Eragrostis tef*) as a raw material for malting, brewing and manufacturing of gluten-free foods and beverages: a review. *Journal of Food Science and Technology*, 51(11), pp.2881-2895.
- Gelardi, G., Mantellato, S., Marchon, D., Palacios, M., Eberhardt, A.B. and Flatt, R.J., 2016. *Science and technology of concrete admixtures*, Cambridge, UK: Woodhead Publishing. pp.149-218.
- Gibiński, M., Kowalski, S., Sady, M., Krawontka, J., Tomasik, P. and Sikora, M., 2006. Thickening of sweet and sour sauces with various polysaccharide combinations. *Journal of Food Engineering*, 75(3), pp.407-414.
- Gill, A.N., Iftikhar, A., Rashid, A., Amin, M., Khan, R.R.M., Rafique, H.M., Jelani, S. and Adnan, A., 2018. Lipase-catalyzed green synthesis of starch–maleate monoesters and its characterization. *Journal of the Iranian Chemical Society*, 15(9), pp.1939-1945.
- Goodwin, J.W., Hughes, R.W., Kwaambwa, H.M. and Reynolds, P.A., 2000. The phase separation behaviour and the viscoelastic properties of particles with non-adsorbing polymers:: Part I—Experimental study. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 161(2), pp.339-359.
- Gopiraman, M., Deng, D., Saravanamoorthy, S., Chung, I.M. and Kim, I.S., 2018. Gold, silver and nickel nanoparticle anchored cellulose nanofiber composites as highly active catalysts for the rapid and selective reduction of nitrophenols in water. *RSC advances*, 8(6), pp.3014-3023.

- Grinberg, V.Y. and Tolstoguzov, V.B., 1997. Thermodynamic incompatibility of proteins and polysaccharides in solutions. *Food Hydrocolloids*, 11(2), pp.145-158.
- Guan, Q.F., Yang, H.B., Han, Z.M., Zhou, L.C., Zhu, Y.B., Ling, Z.C., Jiang, H.B., Wang, P.F., Ma, T., Wu, H.A. and Yu, S.H., 2020. Lightweight, tough, and sustainable cellulose nanofiber-derived bulk structural materials with low thermal expansion coefficient. *Science advances*, 6(18), pp.1-8.
- Gularte, M.A. and Rosell, C.M., 2011. Physicochemical properties and enzymatic hydrolysis of different starches in the presence of hydrocolloids. *Carbohydrate Polymers*, 85(1), pp.237-244.
- Gunaratne, A. and Corke, H., 2007. Influence of prior acid treatment on acetylation of wheat, potato and maize starches. *Food chemistry*, 105(3), pp.917-925.
- Gupta, R., Mauri, R. and Shinnar, R., 1999. Phase separation of liquid mixtures in the presence of surfactants. *Industrial & engineering chemistry research*, 38(6), pp.2418-2424.
- Hachaichi, A., Kouini, B., Kian, L.K., Asim, M., Fouad, H., Jawaid, M. and Sain, M., 2021. Nanocrystalline cellulose from microcrystalline cellulose of date palm fibers as a promising candidate for bio-nanocomposites: isolation and characterization. *Materials*, 14(18), p.5313.
- Han, J.A., Lee, B.H., Lim, W.J. and Lim, S.T., 2005. Utilization of hydroxypropylated waxy rice and corn starches in Korean waxy rice cake to retard retrogradation. *Cereal chemistry*, 82(1), pp.88-92.
- Hari, P.K., Garg, S. and Garg, S.K., 1989. Gelatinization of starch and modified starch. *Starch-Stärke*, 41(3), pp.88-91.
- Helle, S., Bray, F., Putaux, J.L., Verbeke, J., Flament, S., Rolando, C., D'hulst, C. and Szydlowski, N., 2019. Intra-sample heterogeneity of potato starch reveals fluctuation of starch-binding proteins according to granule morphology. *Plants*, 8(9), p.324.
- Heyman, B., De Vos, W.H., Van der Meeren, P. and Dewettinck, K., 2014. Gums tuning the rheological properties of modified maize starch pastes: Differences between guar and xanthan. *Food Hydrocolloids*, 39, pp.85-94.

- Hizukuri, S., ABE, J.I., Mizowaki, N., Koizumi, K. and Utamura, T., 1986. Synthesis of branched cyclodextrins with Pseudomonas isoamylase. *Journal of the Japanese Society of Starch Science*, 33(2), pp.119-126.
- Hon, D.N.S., 2001. *Encyclopedia of Materials: Science and Technology*, 2nd Edition, New York, NY: IntechOpen. pp.1039-1045.
- Hongsprabhas, P., Israkarn, K. and Rattanawattanaprakit, C., 2007. Architectural changes of heated mungbean, rice and cassava starch granules: effects of hydrocolloids and protein-containing envelope. *Carbohydrate Polymers*, 67(4), pp.614-622.
- Hoover, R., Vasanthan, T., Senanayake, N.J. and Martin, A.M., 1994. The effects of defatting and heat-moisture treatment on the retrogradation of starch gels from wheat, oat, potato, and lentil. *Carbohydrate Research*, 261(1), pp.13-24.
- Horikawa, Y., Tsushima, R., Noguchi, K., Nakaba, S. and Funada, R., 2020. Development of colorless wood via two-step delignification involving alcoholysis and bleaching with maintaining natural hierarchical structure. *Journal of Wood Science*, 66, pp.1-9.
- Horstmann, S.W., Belz, M.C., Heitmann, M., Zannini, E. and Arendt, E.K., 2016. Fundamental study on the impact of gluten-free starches on the quality of gluten-free model breads. *Foods*, 5(2), pp.30.
- Huang, M., Kennedy, J.F., Li, B., Xu, X. and Xie, B.J., 2007. Characters of rice starch gel modified by gellan, carrageenan, and glucomannan: A texture profile analysis study. *Carbohydrate Polymers*, 69(3), pp.411-418.
- Immel, S. and Lichtenthaler, F.W., 2000. The hydrophobic topographies of amylose and its blue iodine complex. *Starch-Stärke*, 52(1), pp.1-8.
- Ioelovich, M. and Leykin, A., 2008. Structural investigations of various cotton fibers and cotton celluloses. *BioResources*, 3(1), pp.170-177.
- Islam, M.N. and Rahman, F., 2019. *Green composites for automotive applications*, 1st Edition, Cambridge, MA: Woodhead Publishing. pp.115-141.
- Jane, J.L., 2009. *Starch*, 3rd Edition, London, UK: Academic Press. pp.193-236.

- Jiang, H., Horner, H.T., Pepper, T.M., Blanco, M., Campbell, M. and Jane, J.L., 2010. Formation of elongated starch granules in high-amylose maize. *Carbohydrate Polymers*, 80(2), pp.533-538.
- Jiménez, A., Fabra, M.J., Talens, P. and Chiralt, A., 2012. Effect of sodium caseinate on properties and ageing behaviour of corn starch based films. *Food Hydrocolloids*, 29(2), pp.265-271.
- Juneja, P., Kaur, B., Odeku, O.A. and Singh, I., 2014. Development of Corn Starch-Neusilin UFL2 conjugate as tablet superdisintegrant: Formulation and evaluation of fast disintegrating tablets. *Journal of drug delivery*, 2014, pp.1-14.
- Karoui, R., Downey, G. and Blecker, C., 2010. Mid-infrared spectroscopy coupled with chemometrics: a tool for the analysis of intact food systems and the exploration of their molecular structure– quality relationships– a review. *Chemical reviews*, 110(10), pp.6144-6168.
- Karwasra, B.L., Gill, B.S. and Kaur, M., 2017. Rheological and structural properties of starches from different Indian wheat cultivars and their relationships. *International journal of food properties*, 20(sup1), pp.S1093-S1106.
- Kasemsuwan, T., 1995. *Characterization and food applications of high amylose and other varieties of starch*. (Doctoral dissertation, Iowa State University).
- Katakojwala, R. and Mohan, S.V., 2020. Microcrystalline cellulose production from sugarcane bagasse: Sustainable process development and life cycle assessment. *Journal of Cleaner Production*, 249, p.119342
- Kaur, L., Singh, N. and Sodhi, N.S., 2002. Some properties of potatoes and their starches II. Morphological, thermal and rheological properties of starches. *Food chemistry*, 79(2), pp.183-192.
- Khan, H.U. and Bhattacharyya, K.K., 1987. Dependence of polymer chain entanglements on the solution concentration. *Journal of Macromolecular Science—Chemistry*, 24(7), pp.841-852.

- Kian, L.K., Saba, N., Jawaid, M. and Fouad, H., 2020. Characterization of microcrystalline cellulose extracted from olive fiber. *International journal of biological macromolecules*, 156, pp.347-353.
- Kim, C., Lee, S.P. and Yoo, B., 2006. Dynamic rheology of rice starch-galactomannan mixtures in the aging process. *Starch-Stärke*, 58(1), pp.35-43.
- Klucinec, J.D. and Thompson, D.B., 1999. Amylose and amylopectin interact in retrogradation of dispersed high-amylose starches. *Cereal chemistry*, 76(2), pp.282-291.
- Knorr, D., Heinz, V. and Buckow, R., 2006. High pressure application for food biopolymers. *Biochimica et Biophysica Acta (BBA)-Proteins and Proteomics*, 1764(3), pp.619-631.
- Kohyama, K. and Nishinari, K., 1992. Cellulose derivatives effects on gelatinization and retrogradation of sweet potato starch. *Journal of food science*, 57(1), pp.128-131.
- Kowalski, S., Sikora, M., Tomasik, P. and Krystyjan, M., 2008. Starch polysaccharide hydrocolloid gels. *Polimery*, 53(6).
- Kraugerud, O.F. and Svihus, B., 2011. Tools to determine the degree of starch gelatinization in commercial extruded salmon feeds. *Journal of the World Aquaculture Society*, 42(6), pp.914-920.
- Krithika, P.L. and Ratnamala, K.V., 2019. Modification of Starch: A Review of Various Techniques. *International Journal of Research and Analytical Reviews*, 6(1), pp.32-45.
- Kumar, R. and Khatkar, B.S., 2017. Thermal, pasting and morphological properties of starch granules of wheat (*Triticum aestivum* L.) varieties. *Journal of food science and technology*, 54(8), pp.2403-2410.
- Lagarrigue, S. and Alvarez, G., 2001. The rheology of starch dispersions at high temperatures and high shear rates: a review. *Journal of Food Engineering*, 50(4), pp.189-202.
- Lahiji, R.R., Xu, X., Reifenberger, R., Raman, A., Rudie, A. and Moon, R.J., 2010. Atomic force microscopy characterization of cellulose nanocrystals. *Langmuir*, 26(6), pp.4480-4488.
- Lawal, M.V., 2019. Modified starches as direct compression excipients—effect of physical and chemical modifications on tablet properties: A review. *Starch-Stärke*, 71(1-2), p.1800040.

- Lawton, J.W., Shogren, R.L. and Tiefenbacher, K.F., 1999. Effect of batter solids and starch type on the structure of baked starch foams. *Cereal chemistry*, 76(5), pp.682-687.
- Li, H., Gidley, M.J. and Dhital, S., 2019. High-amylose starches to bridge the “Fiber Gap”: development, structure, and nutritional functionality. *Comprehensive reviews in food science and food safety*, 18(2), pp.362-379.
- Lim, H.S., BeMiller, J.N. and Lim, S.T., 2003. Effect of dry heating with ionic gums at controlled pH on starch paste viscosity. *Cereal Chemistry*, 80(2), pp.198-202.
- Lim, S.T., Han, J.A., Lim, H.S. and BeMiller, J.N., 2002. Modification of starch by dry heating with ionic gums. *Cereal chemistry*, 79(5), pp.601-606.
- Lindeboom, N., Chang, P.R. and Tyler, R.T., 2004. Analytical, biochemical and physicochemical aspects of starch granule size, with emphasis on small granule starches: a review. *Starch-Stärke*, 56(3-4), pp.89-99.
- Linlaud, N., Ferrer, E., Puppo, M.C. and Ferrero, C., 2011. Hydrocolloid interaction with water, protein, and starch in wheat dough. *Journal of agricultural and food chemistry*, 59(2), pp.713-719.
- Liu, H., Eskin, N.M. and Cui, S.W., 2003. Interaction of wheat and rice starches with yellow mustard mucilage. *Food Hydrocolloids*, 17(6), pp.863-869.
- Liu, Q., Donner, E., Tarn, R., Singh, J. and Chung, H.J., 2009. *Advances in Potato Chemistry and Technology*, London, UK: Academic Press. pp.221-248.
- Liu, S.Q., Lei, P., Cao, Z.P., Lv, Y., Li, J.H. and Cui, X.H., 2012. Nonsuture anastomosis of arteries and veins using the magnetic pinned-ring device: a histologic and scanning electron microscopic study. *Annals of vascular surgery*, 26(7), pp.985-995.
- Liu, X., Liu, S., Xi, H., Xu, J., Deng, D. and Huang, G., 2019. Effects of soluble dietary fiber on the crystallinity, pasting, rheological, and morphological properties of corn resistant starch. *LWT- Food Science and Technology*, 111, pp.632-639.
- Lu, J., Luo, Z. and Xiao, Z., 2012. Effect of lysine and glycine on pasting and rheological properties of maize starch. *Food research international*, 49(1), pp.612-617.

- Ma, S., Zhu, P. and Wang, M., 2019. Effects of konjac glucomannan on pasting and rheological properties of corn starch. *Food Hydrocolloids*, 89, pp.234-240.
- Mahmood, K., Kamilah, H., Shang, P.L., Sulaiman, S. and Ariffin, F., 2017. A review: Interaction of starch/non-starch hydrocolloid blending and the recent food applications. *Food Bioscience*, 19, pp.110-120.
- Maphalla, T.G. and Emmambux, M.N., 2016. Functionality of maize, wheat, teff and cassava starches with stearic acid and xanthan gum. *Carbohydrate polymers*, 136, pp.970-978.
- Miller, K.R., Prescott, C.S., Jacobs, T.L. and Lassignal, N.L., 1983. Artifacts associated with quick-freezing and freeze-drying. *Journal of ultrastructure research*, 82(2), pp.123-133.
- Moberg, T., Sahlin, K., Yao, K., Geng, S., Westman, G., Zhou, Q., Oksman, K. and Rigdahl, M., 2017. Rheological properties of nanocellulose suspensions: effects of fibril/particle dimensions and surface characteristics. *Cellulose*, 24(6), pp.2499-2510.
- Moon, D., Yagishita, T., Minowa, T. and Sun, X.Z., 2013. Evaluation of energy consumption and greenhouse gas emissions in preparation of cellulose nanofibers from woody biomass. *Transactions of the ASABE*, 56(3), pp.1061-1067.
- Mua, J.P. and Jackson, D.S., 1997. Relationships between functional attributes and molecular structures of amylose and amylopectin fractions from corn starch. *Journal of Agricultural and Food Chemistry*, 45(10), pp.3848-3854.
- Mukprasirt, a., Herald, t.j. and Seib, P.A., 2002. Pasting characteristics of rice flour-based batter compared to wheat flour-based batter. *Journal of food quality*, 25(2), pp.139-154.
- Muhamedbegović, B., Šubarić, D., Babić, J., Ačkar, Đ., Jašić, M., Keran, H., Budimlić, A. and Matas, I., 2012. Modification of potato starch. *Technol. Acta*, 5, pp.1-6.
- Nabilah, U.U., Sitanggang, A.B. and Purnomo, E.H., 2021. Rheological method for determination of critical concentration of pectin dispersion—A review. *The Annals of the University Dunarea de Jos of Galati. Fascicle VI-Food Technology*, 45(2), pp.180-202.
- Nagano, T., Tamaki, E. and Funami, T., 2008. Influence of guar gum on granule morphologies and rheological properties of maize starch. *Carbohydrate Polymers*, 72(1), pp.95-101.

- Naruenartwongsakul, S., Chinnan, M.S., Bhumiratana, S. and Yoovidhya, T., 2004. Pasting characteristics of wheat flour-based batters containing cellulose ethers. *LWT-Food Science and Technology*, 37(4), pp.489-495.
- Neelam, K., Vijay, S. and Lalit, S., 2012. Various techniques for the modification of starch and the applications of its derivatives. *International research journal of pharmacy*, 3(5), pp.25-31.
- Ng, H.M., Sin, L.T., Tee, T.T., Bee, S.T., Hui, D., Low, C.Y. and Rahmat, A.R., 2015. Extraction of cellulose nanocrystals from plant sources for application as reinforcing agent in polymers. *Composites Part B: Engineering*, 75, pp.176-200.
- Noda, T., Tsuda, S., Mori, M., Takigawa, S., Matsuura-Endo, C., Kim, S.J., Hashimoto, N. and Yamauchi, H., 2006. Determination of the phosphorus content in potato starch using an energy-dispersive X-ray fluorescence method. *Food Chemistry*, 95(4), pp.632-637.
- Nsor-Atindana, J., Chen, M., Goff, H.D., Zhong, F., Sharif, H.R. and Li, Y., 2017. Functionality and nutritional aspects of microcrystalline cellulose in food. *Carbohydrate polymers*, 172, pp.159-174.
- Nyakabau, T., Wokadala, O.C. and Emmambux, M.N., 2013. Effect of steeping additives on tef starch extraction and its quality. *Starch-Stärke*, 65(9-10), pp.738-746.
- Oates, C.G., 1997. Towards an understanding of starch granule structure and hydrolysis. *Trends in Food Science & Technology*, 8(11), pp.375-382.
- Oh, H.E., Hemar, Y., Anema, S.G., Wong, M. and Pinder, D.N., 2008. Effect of high-pressure treatment on normal rice and waxy rice starch-in-water suspensions. *Carbohydrate Polymers*, 73(2), pp.332-343.
- Onyango, C., Unbehend, G. and Lindhauer, M.G., 2009. Effect of cellulose-derivatives and emulsifiers on creep-recovery and crumb properties of gluten-free bread prepared from sorghum and gelatinised cassava starch. *Food Research International*, 42(8), pp.949-955.
- Osorio, M., Cañas, A., Sanchez, D., Naranjo, T., Gañán, P., Zuluaga, R., Ortiz, I., Rojas, O.J. and Castro, C., 2020, *Lignocellulosics*, Cambridge, MA: Suasn Dennis. pp.209-248.

- Panaras, G., Moatsou, G., Yanniotis, S. and Mandala, I., 2011. The influence of functional properties of different whey protein concentrates on the rheological and emulsification capacity of blends with xanthan gum. *Carbohydrate Polymers*, 86(2), pp.433-440.
- Parker, R. and Ring, S.G., 2001. Aspects of the physical chemistry of starch. *Journal of Cereal Science*, 34(1), pp.1-17.
- Pathak, J., Priyadarshini, E., Rawat, K. and Bohidar, H.B., 2017. Complex coacervation in charge complementary biopolymers: Electrostatic versus surface patch binding. *Advances in Colloid and Interface Science*, 250, pp.40-53.
- Pennells, J., Godwin, I.D., Amiralian, N. and Martin, D.J., 2020. Trends in the production of cellulose nanofibers from non-wood sources. *Cellulose*, 27(2), pp.575-593.
- Pérez, S. and Bertoft, E., 2010. The molecular structures of starch components and their contribution to the architecture of starch granules: A comprehensive review. *Starch-Stärke*, 62(8), pp.389-420.
- Pérez, S., Baldwin, P.M. and Gallant, D.J., 2009. Structural features of starch granules I. In *Starch* (pp. 149-192). Academic Press.
- Petri, D.F., 2015. Xanthan gum: A versatile biopolymer for biomedical and technological applications. *Journal of Applied Polymer Science*, 132(23).
- Phillips, G.O. and Williams, P.A., 2009. *Handbook of hydrocolloids*, 2nd Edition, Cambridge, UK: CRC Press. pp.1-22.
- Pongsawatmanit, R. and Srijunthongsiri, S., 2008. Influence of xanthan gum on rheological properties and freeze–thaw stability of tapioca starch. *Journal of Food Engineering*, 88(1), pp.137-143.
- Ptaszek, P. and Grzesik, M., 2007. Viscoelastic properties of maize starch and guar gum gels. *Journal of Food Engineering*, 82(2), pp.227-237.
- Ptaszek, A., Ptaszek, P. and Łukasiewicz, M., 2015. Rheological Properties of Non-starch Polysaccharides in Food Science. *Functional Polymers in Food Science*, p.99.

- Qi, X. and Tester, R.F., 2016. Effect of native starch granule size on susceptibility to amylase hydrolysis. *Starch-Stärke*, 68(9-10), pp.807-810.
- Rao, M.A. and Tattiyakul, J., 1999. Granule size and rheological behavior of heated tapioca starch dispersions. *Carbohydrate Polymers*, 38(2), pp.123-132.
- Rasheed, M., Jawaid, M., Karim, Z. and Abdullah, L.C., 2020. Morphological, physiochemical and thermal properties of microcrystalline cellulose (MCC) extracted from bamboo fiber. *Molecules*, 25(12), p.2824.
- Ratnayake, W.S. and Jackson, D.S., 2006. Gelatinization and solubility of corn starch during heating in excess water: new insights. *Journal of Agricultural and Food Chemistry*, 54(10), pp.3712-3716.
- Ravindran, G. and Matia-Merino, L., 2009. Starch–fenugreek (*Trigonella foenum-graecum* L.) polysaccharide interactions in pure and soup systems. *Food Hydrocolloids*, 23(3), pp.1047-1053.
- Richardson, G., Kidman, S., Langton, M. and Hermansson, A.M., 2004. Differences in amylose aggregation and starch gel formation with emulsifiers. *Carbohydrate Polymers*, 58(1), pp.7-13.
- Rincón-Londoño, N., Vega-Rojas, L.J., Contreras-Padilla, M., Acosta-Osorio, A.A. and Rodríguez-García, M.E., 2016. Analysis of the pasting profile in corn starch: Structural, morphological, and thermal transformations, Part I. *International journal of biological macromolecules*, 91, pp.106-114.
- Robles-García, M.Á., Del-Toro-Sánchez, C.L., Márquez-Ríos, E., Barrera-Rodríguez, A., Aguilar, J., Aguilar, J.A., Reynoso-Marín, F.J., Ceja, I., Dórame-Miranda, R. and Rodríguez-Félix, F., 2018. Nanofibers of cellulose bagasse from Agave tequilana Weber var. azul by electrospinning: preparation and characterization. *Carbohydrate polymers*, 192, pp.69-74.
- Rojas, J.A., Rosell, C.M. and De Barber, C.B., 1999. Pasting properties of different wheat flour-hydrocolloid systems. *Food hydrocolloids*, 13(1), pp.27-33.

- Rosell, C.M., Yokoyama, W. and Shoemaker, C., 2011. Rheology of different hydrocolloids–rice starch blends. Effect of successive heating–cooling cycles. *Carbohydrate Polymers*, 84(1), pp.373-382.
- Saha, D. and Bhattacharya, S., 2010. Hydrocolloids as thickening and gelling agents in food: a critical review. *Journal of food science and technology*, 47(6), pp.587-597.
- Samutsri, W. and Supphantharika, M., 2012. Effect of salts on pasting, thermal, and rheological properties of rice starch in the presence of non-ionic and ionic hydrocolloids. *Carbohydrate Polymers*, 87(2), pp.1559-1568.
- Sandhu, K.S. and Singh, N., 2007. Some properties of corn starches II: Physicochemical, gelatinization, retrogradation, pasting and gel textural properties. *Food Chemistry*, 101(4), pp.1499-1507.
- Sasaki, T., Yasui, T. and Matsuki, J., 2000. Influence of non-starch polysaccharides isolated from wheat flour on the gelatinization and gelation of wheat starches. *Food Hydrocolloids*, 14(4), pp.295-303.
- Satrapai, S. and Supphantharika, M., 2007. Influence of spent brewer's yeast β -glucan on gelatinization and retrogradation of rice starch. *Carbohydrate Polymers*, 67(4), pp.500-510.
- Sayar, S., Koxsel, H. and Turhan, M., 2005. The effects of protein-rich fraction and defatting on pasting behavior of chickpea starch. *Starch-Stärke*, 57(12), pp.599-604.
- Schirmer, M., Höchstötter, A., Jekle, M., Arendt, E. and Becker, T., 2013. Physicochemical and morphological characterization of different starches with variable amylose/amylopectin ratio. *Food Hydrocolloids*, 32(1), pp.52-63.
- Schrieber, R. and Gareis, H., 2007. *Gelatine handbook: theory and industrial practice*, 1st Edition, Eberbach, DE: John Wiley & Sons. pp 130.
- Sekhon, B.S., 2010. Food nanotechnology–an overview. *Nanotechnology, science and applications*, 3, pp.1.

- Serpa, A., Velásquez-Cock, J., Gañán, P., Castro, C., Vélez, L. and Zuluaga, R., 2016. Vegetable nanocellulose in food science: A review. *Food Hydrocolloids*, 57, pp.178-186.
- Shahzad, S.A., Hussain, S., Alamri, M.S., Mohamed, A.A., Ahmed, A.S., Ibraheem, M.A. and Abdo Qasem, A.A., 2019. Use of hydrocolloid gums to modify the pasting, thermal, rheological, and textural properties of sweet potato starch. *International Journal of Polymer Science*, 2019, pp.1-12.
- Shalviri, A., Liu, Q., Abdekhodaie, M.J. and Wu, X.Y., 2010. Novel modified starch–xanthan gum hydrogels for controlled drug delivery: Synthesis and characterization. *Carbohydrate Polymers*, 79(4), pp.898-907.
- Shen, D.K., Gu, S. and Bridgwater, A.V., 2010. The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicellulose. *Carbohydrate Polymers*, 82(1), pp.39-45.
- Shi, X. and BeMiller, J.N., 2002. Effects of food gums on viscosities of starch suspensions during pasting. *Carbohydrate polymers*, 50(1), pp.7-18.
- Singh, A.V., 2011. Biopolymers in drug delivery: a review. *Pharmacologyonline*, 1, pp.666-674.
- Singh, J., Colussi, R., McCarthy, O.J. and Kaur, L., 2016. *Advances in potato chemistry and technology*, London, UK: Academic Press. pp.195-247.
- Singh, J., Singh, N. and Saxena, S.K., 2002. Effect of fatty acids on the rheological properties of corn and potato starch. *Journal of Food Engineering*, 52(1), pp.9-16.
- Singh, V., Haken, A.E., Niu, Y.X., Zou, S.H. and Eckhoff, S.R., 1997. Hybrid-dependent effect of lactic acid on corn starch yields. *Cereal chemistry*, 74(3), pp.249-253.
- Smitha, S., Rajiv, J., Begum, K. and Indrani, D., 2008. Effect of hydrocolloids on rheological, microstructural and quality characteristics of parotta—an unleavened indian flat bread. *Journal of texture studies*, 39(3), pp.267-283.
- Song, J.Y., Kwon, J.Y., Choi, J., Kim, Y.C. and Shin, M., 2006. Pasting properties of non-waxy rice starch-hydrocolloid mixtures. *Starch-Stärke*, 58(5), pp.223-230.

- Sudhakar, V., Singhal, R.S. and Kulkarni, P.R., 1995. Effect of sucrose on starch—hydrocolloid interactions. *Food Chemistry*, 52(3), pp.281-284.
- Tang, H., Mitsunaga, T. and Kawamura, Y., 2006. Molecular arrangement in blocklets and starch granule architecture. *Carbohydrate Polymers*, 63(4), pp.555-560.
- Tecante, A. and Doublier, J.L., 1999. Steady flow and viscoelastic behavior of crosslinked waxy corn starch- κ -carrageenan pastes and gels. *Carbohydrate Polymers*, 40(3), pp.221-231.
- Techawipharat, J., Suphantharika, M. and BeMiller, J.N., 2008. Effects of cellulose derivatives and carrageenans on the pasting, paste, and gel properties of rice starches. *Carbohydrate Polymers*, 73(3), pp.417-426.
- Teixé-Roig, J., Oms-Oliu, G., Velderrain-Rodríguez, G.R., Odriozola-Serrano, I. and Martín-Belloso, O., 2018. The effect of sodium carboxymethylcellulose on the stability and bioaccessibility of anthocyanin water-in-oil-in-water emulsions. *Food and Bioprocess Technology*, 11(12), pp.2229-2241.
- Teklehaimanot, W.H., 2011. *Rheology and microscopy of low calorie mayonnaise-type emulsions made with stearic acid-modified maize and teff starches* (Doctoral dissertation, University of Pretoria).
- Terinte, N., Ibbett, R. and Schuster, K.C., 2011. Overview on native cellulose and microcrystalline cellulose I structure studied by X-ray diffraction (WAXD): Comparison between measurement techniques. *Lenzinger Berichte*, 89(1), pp.118-131.
- Thomas, D.J. and Atwell, W.A., 1999. Gelatinization, pasting, and retrogradation. *Starches: Practical guides for the food industry*, pp.25-29.
- Thompson, L., Azadmanjiri, J., Nikzad, M., Sbarski, I., Wang, J. and Yu, A., 2019. Cellulose nanocrystals: Production, functionalization and advanced applications. *Reviews on Advanced Materials Science*, 58(1), pp.1-16.
- Thoorens, G., Krier, F., Leclercq, B., Carlin, B. and Evrard, B., 2014. Microcrystalline cellulose, a direct compression binder in a quality by design environment—A review. *International journal of pharmaceutics*, 473(1-2), pp.64-72.

- Tosh, B., 2014. Synthesis and sustainable applications of cellulose esters and ethers: A review. *International Journal of Energy, Sustainability and Environmental Engineering*, 1(2).
- Tran, T., Thitipraphunkul, K., Piyachomkwan, K. and Sriroth, K., 2008. Effect of starch modifications and hydrocolloids on freezable water in cassava starch systems. *Starch-Stärke*, 60(2), pp.61-69.
- Tsai, M.L., Li, C.F. and Lii, C.Y., 1997. Effects of granular structures on the pasting behaviors of starches. *Cereal Chemistry*, 74(6), pp.750-757.
- van Langenhove, 2015. *Advances in smart medical textiles*, Cambridge, UK: Woodhead Publishing. pp. 30-67
- Varela, M.S., Navarro, A.S. and Yamul, D.K., 2016. Effect of hydrocolloids on the properties of wheat/potato starch mixtures. *Starch-Stärke*, 68(7-8), pp.753-761.
- Ventura-Cruz, S. and Tecante, A., 2021. | Nanocellulose and microcrystalline cellulose from agricultural waste: Review on isolation and application as reinforcement in polymeric matrices. *Food Hydrocolloids*, 118, pp.1-10.
- Vilarinho, F., Sanches Silva, A., Vaz, M.F. and Farinha, J.P., 2018. Nanocellulose in green food packaging. *Critical reviews in food science and nutrition*, 58(9), pp.1526-1537.
- von Borries-Medrano, E., Jaime-Fonseca, M.R. and Aguilar-Méndez, M.Á., 2017. *Solubility of Polysaccharides*, London, UK: InTech: pp.65-87.
- von Borries-Medrano, E., Jaime-Fonseca, M.R., Aguilar-Méndez, M.A. and García-Cruz, H.I., 2018. Addition of galactomannans and citric acid in corn starch processed by extrusion: Retrogradation and resistant starch studies. *Food Hydrocolloids*, 83, pp.485-496.
- Wang, S., Li, C., Copeland, L., Niu, Q. and Wang, S., 2015. Starch retrogradation: A comprehensive review. *Comprehensive Reviews in Food Science and Food Safety*, 14(5), pp.568-585.
- Wang, Y., Wang, X., Xie, Y. and Zhang, K., 2018. Functional nanomaterials through esterification of cellulose: a review of chemistry and application. *Cellulose*, 25(7), pp.3703-3731.

- Wang, Y.J., White, P., Pollak, L. and Jane, J., 1993. Characterization of starch structures of 17 maize endosperm mutant genotypes with Oh43 inbred line background. *Cereal chemistry*, 70, pp.171-171.
- Wei, C.H., 2007. Statsoft, inc., Tulsa, Oklahoma: Statistica, version 8.
- Whistler, R. L., and BeMiller, J. N. 1997. *Carbohydrate Chemistry for Food Scientists*, St. Paul, MN: Eagan Press. pp.117-151.
- Whittenberger, R.T. and Nutting, G.C., 1948. Potato-starch gels. *Industrial & Engineering Chemistry*, 40(8), pp.1407-1413.
- Williams, P.A., 2007. *Handbook of industrial water soluble polymers*, Oxford, UK: Blackwell Publishing. pp.73-97.
- Winuprasith, T. and Suphantharika, M., 2015. Properties and stability of oil-in-water emulsions stabilized by microfibrillated cellulose from mangosteen rind. *Food Hydrocolloids*, 43, pp.690-699.
- Wokadala, O.C., Ray, S.S. and Emmambux, M.N., 2012. Occurrence of amylose–lipid complexes in teff and maize starch biphasic pastes. *Carbohydrate polymers*, 90(1), pp.616-622.
- Wstenberg, T., 2015. *Cellulose and Cellulose Derivatives in the Food industry Fundamentals and Applications*; Weinheim, DE: John Wiley & Sons. pp.1-68.
- Xie, Y., Cai, S., Hou, Z., Li, W., Wang, Y., Zhang, X. and Yang, W., 2018. Surface hydrophobic modification of microcrystalline cellulose by poly (methylhydro) siloxane using response surface methodology. *Polymers*, 10(12), p.1335.
- Xiong, J., Li, Q., Shi, Z. and Ye, J., 2017. Interactions between wheat starch and cellulose derivatives in short-term retrogradation: Rheology and FTIR study. *Food Research International*, 100, pp.858-863.
- Xu, J., Tan, X., Chen, L., Li, X. and Xie, F., 2019. Starch/microcrystalline cellulose hybrid gels as gastric-floating drug delivery systems. *Carbohydrate polymers*, 215, pp.151-159.
- Xu, X., Liu, F., Jiang, L., Zhu, J.Y., Haagenson, D. and Wiesenborn, D.P., 2013. Cellulose nanocrystals vs. cellulose nanofibrils: a comparative study on their microstructures and

- effects as polymer reinforcing agents. *ACS applied materials & interfaces*, 5(8), pp.2999-3009.
- Yang, D., Peng, X., Zhong, L., Cao, X., Chen, W., Zhang, X., Liu, S. and Sun, R., 2014. “Green” films from renewable resources: properties of epoxidized soybean oil plasticized ethyl cellulose films. *Carbohydrate polymers*, 103, pp.198-206.
- Yang, P., Du, L., Wang, D.L., Li, B.H., Rausch, K.D., Buriak, P. and Eckhoff, S.R., 2000. Effects of alkali debranning, roller mill cracking and gap setting, and alkali steeping conditions on milling yields from a dent corn hybrid. *Cereal chemistry*, 77(2), pp.128-132.
- Ye, L., Wang, C., Wang, S., Zhou, S. and Liu, X., 2016. Thermal and rheological properties of brown flour from Indica rice. *Journal of Cereal Science*, 70, pp.270-274.
- Yoshimura, M., Takaya, T. and Nishinari, K., 1998. Rheological studies on mixtures of corn starch and konjac-glucomannan. *Carbohydrate Polymers*, 35(1-2), pp.71-79.
- Yuris, A., Matia-Merino, L., Hardacre, A.K., Hindmarsh, J. and Goh, K.K.T., 2018. Molecular interactions in composite wheat starch-Mesona chinensis polysaccharide gels: Rheological, textural, microstructural and retrogradation properties. *Food Hydrocolloids*, 79, pp.1-12.
- Zhang, K., Barhoum, A., Xiaoqing, C., Li, H. and Samyn, P., 2019. Cellulose nanofibers: Fabrication and surface functionalization techniques. *Handbook of nanofibers*, pp.409-449.
- Zhang, Y., Gu, Z., Zhu, L. and Hong, Y., 2018. Comparative study on the interaction between native corn starch and different hydrocolloids during gelatinization. *International journal of biological macromolecules*, 116, pp.136-143.
- Zhao, X.P., Yin, J.B. and Tang, H., 2007. New advances in design and preparation of electrorheological materials and devices. *Smart Materials and Structures: New Research*, pp.1-66.
- Zia-ud-Din, Xiong, H. and Fei, P., 2017. Physical and chemical modification of starches: A review. *Critical reviews in food science and nutrition*, 57(12), pp.2691-2705.

Zobel, H.F., 1988. Molecules to granules: a comprehensive starch review. *Starch-Stärke*, 40(2), pp.44-50.