Rheological Properties of Plant-tissue Suspensions: Aqueous Suspensions of Potato and Carrot Parenchyma Powders

by

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Acknowledgment

To my loves Ali and Farham

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Abstract

Comprehending the rheological behavior of food-based plant-tissue suspensions, e.g., soups and purees, is critical in terms of production efficiency and final product quality. The rheological behavior of suspensions is governed mainly by the continuous phase properties, the dispersed phase properties, e.g., particle size, solid volume fraction of suspensions, and by processing conditions such as temperature. Therefore, an understanding of how these parameters influence the rheological properties of food-based plant-tissue suspensions is helpful for development of novel foods and process design. In this study, the rheological properties of suspensions of potato and carrot powder were investigated at six solid volume fractions (Φ), three temperatures and two particle sizes. Corn and potato starch granule suspensions were used as model systems due to an anticipated minimal level of interactions among their components. A concentrated sucrose solution was used as the continuous phase to prevent sedimentation of particles. Rheological measurements were carried out using a rotational rheometer with a concentric cylinder geometry via shear flow and oscillatory shear tests. Starch granule suspensions exhibited essentially Newtonian behavior at all Φ. The potato and carrot powder suspensions showed shear-thinning behavior at similar Φ, obeying either a power-law equation or the Herschel-Bulkley equation. Differences in the rheological properties of the potato and carrot powder suspensions compared to starch granule suspensions are due to intra- and inter-cellular components in potato and carrot parenchyma that migrate from the dispersed to the continuous phase. The viscosity or consistency factor data of all the suspensions conformed well to the Krieger-Dougherty equation. Oscillatory shear testing indicated the presence of viscoelastic properties in the potato and carrot powder suspensions. Higher consistency factor and yield stress, more shear-thinning behavior, and lower loss factor were observed in the carrot powder suspensions compared to potato powder

suspensions. The greater amount of soluble solids content in carrot compared to potato is postulated to be the cause of the differences observed in the rheological properties of carrot and potato suspensions. Comparing the rheological behavior of carrot and potato powder suspensions revealed the dominant role of the continuous phase in the rheological properties of carrot powder suspensions.

1. General Introduction

Suspensions, in which solid particles are dispersed in a continuous phase, account for a variety of foods produced throughout the world (Walstra 2002; Shewfelt, Orta-Ramirez, and Clarke 2016). For instance, most commercially prepared baby foods are suspensions of different kinds of plant tissue (Ahmed and Ramaswamy 2006; Ahmed and Ramaswamy 2007; Alvarez, Canet, and Fernández 2007). Food-based plant-tissue suspensions are manufactured by various processes to produce a multitude form of products, e.g., soups, sauces and purees (Ahmed and Ramaswamy 2006; Gundurao, Ramaswamy, and Ahmed 2011; Rao 2013; Ahmed, Ptaszek, and Basu 2017). Understanding the rheological properties of these suspensions helps one achieve a highly efficient process and a desired quality of the final products (Alvarez, Fernández, and Canet 2004; Moelants, Cardinaels, Van Buggenhout, et al. 2014). In this regard, it is critical to determine the parameters influencing the rheological properties of suspensions in order to be able to manipulate the rheological properties based on the processing needs. The rheological properties of suspensions are influenced mainly by the continuous phase properties, solid volume fraction of suspensions, particle properties such as size and shape, and processing conditions such as temperature (Saravacos 1970; Caradec and Nelson 1985; Tanglertpaibul and Rao 1987b; Qiu and Rao 1988; Yoo and Rao 1994; Beresovsky, Kopelman, and Mizrahi 1995; Yang and Rao 1998; Bourne 2002; Cepeda and Gomez 2002; Moelants, Jolie, et al. 2013).

In plant-tissue suspensions, plant-tissue particles are dispersed in an aqueous continuous phase (Moelants, Cardinaels, Van Buggenhout, et al. 2014). The dispersed phase usually consists of single cells, clusters of unbroken cells, broken cell fragments as well as insoluble inter- and intra-cellular components, while the continuous phase is a solution of all soluble intra- and inter-cellular components (Zdunek and Umeda 2005; Day, Xu, Øiseth, Lundin, et al. 2010; Moelants, Cardinaels, Jolie, et al. 2014). The properties of plant-tissue particles in the dispersed phase vary

greatly in different suspensions depending on the plants used and the suspensions' preparation conditions (Walstra 2002). For instance, a wide range of shapes and sizes of cells can be observed in different plants, e.g., polyhedral cells in potato (Zdunek and Umeda 2005; Lopez-Sanchez and Farr 2012), that may be observed in the dispersed phase. In addition to differences in plant tissues, preparation processes such as size reduction and heat treatment influence the properties of the particles in the dispersed phase of plant-tissue suspensions (Ng and Waldron 1997; Lemmens et al. 2010; Lopez-Sanchez, Svelander, et al. 2011). Upon applying these processes, not only are the size and shape of the particles affected, but also soluble and insoluble inter- and intra-cellular components will be released into the suspensions (Caradec and Nelson 1985; Moelants, Cardinaels, Van Buggenhout, et al. 2014).

The liberation of soluble inter- and intra-cellular components, which are mostly macromolecules, organic acids and sugars, affects the continuous phase properties which in turn influences the rheological properties of the suspensions (Caradec and Nelson 1985; Tanglertpaibul and Rao 1987b; Den Ouden and Van Vliet 2002; Santiago et al. 2016). The soluble inter- and intra-cellular components in the continuous phase play different roles in a plant-tissue suspension, such as alteration of the interaction between particles in the dispersed phase (Walstra 2002). The main inter- and intra-cellular components affecting the rheological properties of plant-tissue suspensions have been confirmed to be pectin polymers (Ross-Murphy 1994; Ross-Murphy 1995; Christiaens et al. 2016). Other than pectin polymers, starch granules are another important intracellular component in plant-tissue suspensions which can affect the rheological properties of the suspensions (Ross-Murphy 1995). The starch granules may be liberated from the cells during the preparation of suspensions, e.g., as a result of the comminution process (Moelants, Cardinaels, Van Buggenhout, et al. 2014).

There have been extensive studies to investigate the rheological properties of food-based plant-tissue suspensions, such as carrot suspensions (Lopez-Sanchez, Nijsse, et al. 2011; Lopez-Sanchez, Svelander, et al. 2011; Moelants, Jolie, et al. 2013; Kyomugasho et al. 2015), tomato suspensions (Lopez-Sanchez, Nijsse, et al. 2011; Lopez-Sanchez, Svelander, et al. 2011; Moelants, Jolie, et al. 2013; Moelants, Cardinaels, Jolie, et al. 2014), and apple suspensions (Qiu and Rao 1988; Kunzek, Opel, and Senge 1997; Cantu-Lozano, Rao, and Gasparetto 2000; Espinosa et al. 2011). Although, considerable research has been conducted on the rheology of food-based plant-tissue suspensions, a systematic analysis of the contribution of the dispersed phase and the continuous phase on the overall rheological properties of these suspensions is limited. This is believed to be due to the fact that the preparation methods for plant-tissue suspensions have not been well defined making it difficult to determine the extent to which each phase affects the rheological properties of a suspension. Preparing suspensions with well-defined continuous and dispersed phases will be helpful for clearly specifying the contribution of the dispersed phase and the continuous phase to the overall rheological properties of a plant-tissue suspension.

Various methods have been employed in the preparation of plant-tissue suspensions, e.g., blending, mixing, sieving, high-pressure homogenization and heating (Rao and Cooley 1992; Day, Xu, Øiseth, Lundin, et al. 2010; Day, Xu, Øiseth, Hemar, et al. 2010; Lemmens et al. 2010; Lopez-Sanchez, Svelander, et al. 2011; Moelants, Cardinaels, et al. 2013). For instance, in the preparation of carrot suspensions, Moelants, Cardinaels, et al. (2013) heated carrot pieces in a temperature-controlled water bath at 95 °C for 5 min and mixed with deionized water in a blender. The carrot blend was further disintegrated with a high- pressure homogenizer and then a wet sieving technique with a set of sieves of different pore sizes was used to separate fractions of

different particle sizes (Moelants, Cardinaels, et al. 2013). In studies concerning the effect of particle size on the rheological properties of plant-tissue suspensions, wet sieving is a typical technique which has been widely used (Qiu and Rao 1988; Yoo and Rao 1994; Lemmens et al. 2010; Kyomugasho et al. 2015; Mutsokoti et al. 2016). Wet sieving techniques have been used for powders that have a tendency to aggregate during dry sieving (Ortega-Rivas 2012). However, the cell contents may be lost during wet sieving of plant-tissue suspensions. To avoid the loss of inter- and intra-cellular components, dry sieving should be used. Preparing a plant-tissue powder via the use of a dry sieving technique to separate its fractions based on different particle sizes is helpful in producing suspensions with a well-defined dispersed phase.

In this study, a dry sieving technique has been used to prepare suspensions with a well-defined dispersed phase. Having a well-defined dispersed phase allows more insight into the role of the dispersed phase on the rheological properties of suspensions. Potato and carrot, which contain an abundant amount of starch granules and a large amount of pectin polymers in their parenchyma, respectively (Simon et al. 2008; Singh and Kaur 2016), are chosen as the plant tissue materials. Prior to the dry sieving process, powders of carrot and potato parenchyma were prepared using a Retsch ZM200 mill (Retsch GmbH, Haan, Germany) with a mesh size of 80 µm. The preparation procedures led to production of potato and carrot powders with well-defined particle properties (particularly size) which allowed systematic rheological measurements on suspensions with increasing solid volume fractions of the dispersed phase. The production of potato and carrot powders via dry sieving separates this study from other studies on plant-tissue suspensions that are reported in the literature (Tanglertpaibul and Rao 1987a; Rao and Cooley 1992; Yoo and Rao 1994; Lemmens et al. 2010; Moelants, Cardinaels, et al. 2013; Moelants, Cardinaels, Jolie, et al. 2014; Kyomugasho et al. 2015; Mutsokoti et al. 2016).

To prepare potato and carrot powder suspensions, one major challenge was to prevent particle sedimentation. To do this, a highly concentrated sucrose solution is used as the continuous phase, based on the procedure followed by Pabst, Gregorová, and Berthold (2006). Then, each suspension is prepared by adding an appropriate amount of powder to this highly concentrated sucrose solution to attain a given volume fraction.

In this work, the focus will be on the effect of solid volume fraction, particle size and temperature on the rheological properties of carrot and potato powder suspensions. In this regard, six different solid volume fractions are chosen to represent dilute, semi-dilute and concentrated regimes. In addition, in the present work, all the rheological properties are measured with shear flow and shear oscillatory tests. Therefore, the rheological properties of carrot and potato powders suspensions, including their flow behavior and viscoelastic properties, are studied and the effects of solid volume fraction, size and temperature on these properties are investigated.

To simplify the complexity of the potato and carrot powder suspensions, corn and potato starch granule suspensions are selected as model systems as the level of interactions among their components is remarkably lower than that in potato and carrot powder suspensions. The rheological properties of corn and potato starch granule suspensions are compared as model system to attain an explicit insight into the role of starch granules properties as the dispersed phase. In addition, a better understanding of the rheological behavior of potato powder suspensions (that are rich in starch granules) can be achieved by comparing the rheological properties of the suspensions of potato starch granules with those of potato powder. Such a comparison is expected to reveal the role of inter- and intra-cellular components, other than starch granules, on the rheological properties of potato powder suspensions. Moreover, the rheological properties of potato powder suspensions with an abundant amount of starch granules

are compared to those of carrot powder suspensions with an abundant amount of soluble inter- and intra-cellular components. Consequently, a clearer understanding of the role of soluble components (originally present in the dispersed phase) on the rheological behavior of the continuous phase of the suspensions will be obtained.

In the first study (Chapter 3), the rheological behavior of corn and potato starch granule suspensions is described. Then the rheological properties of potato powder suspensions, wherein potato starch granules are abundant, are presented in Chapter 4 and 5. In Chapter 6, the rheological properties of carrot powder suspensions are presented and compared with those of potato powder suspensions. This comparison provides an understanding of the role of greater migration of components from the dispersed to the continuous phase, as carrot powder suspensions have lower starch content but larger amounts of soluble components, particularly pectin polymers. Overall, four major purposes are defined for this thesis:

1) To describe the rheological properties of suspensions containing different solid volume fractions (Φ), and with particles of different sizes

2) To determine the role of dispersed and continuous phase on the rheological properties of suspensions with increasing degree of interaction between components of the dispersed phase and the continuous phase

3) To examine the effect of temperature on suspension rheology, through its influence on the properties of the continuous and the dispersed phase

4) To analyze whether the rheological properties of suspensions reveal themselves differently depending on the mode of rheological assessment

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2. Literature Review

2.1. Introduction to Plant Tissue

Plant-tissue-based food suspensions, such as different soups and sauces, are important food products that are widely produced and consumed. Accordingly, there has been much interest in determining the effect of different parameters on the rheological properties of these suspensions. The most important parameters influencing the rheological properties of suspensions, such as particle concentration and properties of the solid particles, have been discussed widely in the literature and will be introduced in this chapter in detail. Furthermore, plant anatomy, which has an important role in the determination of the rheological properties of plant-tissue-based food suspensions, is an important parameter influencing both the continuous phase as well as the particulates. In this section, the structure of plant tissues will be introduced with some basic and simplified concepts prior to embarking on the main focus of this chapter, which is an understanding of the flow behavior of plant-tissue suspensions.

2.1.1. Plant Tissue Cells

Various edible vegetables and fruits are made mainly from parenchyma tissue (Vaclavik and Christian 2014). Parenchyma tissue is made of simple thin-wall cells that are almost similar in appearance and function. In a plant tissue, cellular structure arises from a collection of closely fitting cells. The cells contain liquid-like materials, such as water, sugars or water-soluble vitamins, and a variety of solid sub-cellular structures (Fig. 2.1). All of this is enclosed by the plant's cell walls (Fig. 2.1) (Walstra 2002; Vaclavik and Christian 2014). The spatial arrangement, the geometrical parameters, such as shape and size of cells or the orientation of cells within the tissue, vary in different plants. For example, potato cells are bigger than carrot cells. In addition, the cellular structure in carrot tissue is more heterogeneous than in potato tissue (Zdunek and Umeda 2005; Fuentes et al. 2014).

Fig. 2.1. Simplified schematic representation of a plant cell
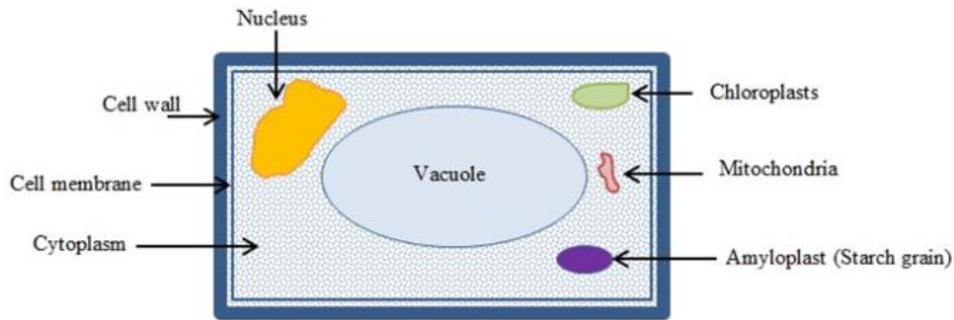
2.1.1.1. Cell Wall

One of the most important parts of the plant cell is its wall. The cell wall is important for the survival and functionality of the cell (Vaclavik and Christian 2014). It protects all cell contents and controls almost all biophysical and biological processes of a cell (Popper 2011). The cell wall can be destroyed by different process such as dehydration, thermal treatment or size reduction. When the wall is destroyed, the intracellular materials are released into the surrounding environment (Vaclavik and Christian 2014). The components of cell walls are mainly polymeric compounds: cellulose, pectic substances, hemicellulose, lignin and proteins (Bateman and Basham 1976; Jackman and Stanley 1995; Popper 2011).

Cellulose is the world's most abundant polysaccharide compound. It is an unbranched polymer of D-glucopyranose residues joined by $\beta - (1 \rightarrow 4)$ linkages, i.e., $\beta - (1 \rightarrow 4) - D - glucan$ (Fry 1988; Kutschera and Heiderich 2002). Cellulose is not water soluble (Jackman and Stanley 1995) and approximately 20 to 30% of the dry weight of the wall is comprised of cellulose microfibrils (McNeil et al. 1984). The role of cellulose microfibrils is to provide a skeleton, giving shape and strength to the cell wall (Fry 1988; Theander et al. 1989; Tungland and Meyer 2002).

Hemicellulose is the other abundant cell wall polysaccharide, and this is built up from a variety of different sugars. This polymer has some degree of structural similarity to cellulose and can form hydrogen bonds with cellulose microfibrils (Jarvis 2009). This polysaccharide is mostly insoluble in water but can be solubilized in alkali (Fry 1988; Varner and Lin 1989; Pedersen 2009).

The other important cell wall constituent is pectin, which is considered as an important polysaccharide with a great ability to form gels and is favored in food products as a thickening and gelling agent (da Silva and Rao 2006). Therefore, more discussion on pectin polymers is provided here.

2.1.1.1.1. Pectin Polymers

Pectin has been described as a "block" polymer which helps the creation of the cellulose-hemicellulose network. Two main roles of pectin polymers are in cell-cell adhesion and in mechanical strength of the cell wall (Jarvis 2011; Vaclavik and Christian 2014). Pectin is a linear polymer of D-galacturonic acid joined by α-1,4-glycosidic linkages where the main galacturonan chain is interrupted and bent by frequent occurrence of rhamnose units (Axelos, Thibault, and Lefebvre 1989; Jackman and Stanley 1995; Vaclavik and Christian 2014). The structure of pectin polymers varies due to different parameters such as plant species and maturity (Stein and Brown 1975; Seymour et al. 1987). In general, pectin polymers are classified into two different groups by their degree of methoxylation (DM): high-methoxylated pectin (HM) (DM>50%) and low-methoxylated pectin (LM) (DM < 50%). The methoxylation degree is an important parameter affecting various properties of pectin polymers such as the gelling properties of pectin (Thakur et al. 1997).

Enzymatic and chemical conversion reactions may change pectin's structural features. Demethoxylation and depolymerization are the two main reactions in pectin polymers which can occur with the aid of enzymes or as chemical conversion reactions that take place under specific conditions of temperature and pH (Varner and Lin 1989; Tungland and Meyer 2002; Vincken et al. 2003).

Altering pectin structure mainly occurs with the help of two different enzymes: polygalacturonase and pectin methylesterase, which exist in most fruits and vegetables causing depolymerization and demethylation of the pectin polymers, respectively (Vaclavik and Christian 2014). Results of a study on pectin solubilization in kiwi fruit showed that polygalacturonase played a role in degrading solubilized pectin polymers and was responsible for cell wall structural changes (Redgwell, Melton, and Brasch 1992).

2.1.1.1.2. The Effect of Temperature on Pectin Polymers

Pectin structural features can be altered by non-enzymatic and enzymatic conversion reactions; both types of reactions are sensitive to temperature (Sila et al. 2009). The non-enzymatic reactions of pectin polymers are a beta-elimination reaction or acid hydrolysis (Greve et al. 1994; Sila et al. 2009). Beta-elimination occurs at neutral or weakly acidic pH (as low as 3.5) and increases with increasing pH and temperature (Moelants, Cardinaels, Van Buggenhout, et al. 2014). On the other hand, acid hydrolysis will degrade pectin polymers under acid conditions (Krall and McFeeters 1998; Sila et al. 2009).

Also, temperature has been shown to affect enzymatic pectin conversion reactions (Duvetter et al. 2009). As an example, different heat treatments can be used to inactivate or activate specific enzymes with the capacity to convert pectin polymers, i.e., pectin

methylesterase (PME) and polygalacturonase (PG) (Duvetter et al. 2009). An optimal temperature for PG and PME activity has been reported around 50 and 60 °C, respectively (Verlent et al. 2007). Both PG and PME are rather readily destroyed or inactivated above 70°C. For instance, a heat treatment process around 77 to 95 °C can inactivate both PG and PME (Bartolome and Hoff 1972; Ormerod et al. 2004).

2.1.1.2. Cytoplasm

Cytoplasm is the region inside the cell wall, Fig. 2.1, where the main physiological functions occur. This region contains different organelles such as chloroplasts and amyloplasts. There is a large central vacuole in a completely developed plant cell (Nobel 1970). It contains a relatively simple aqueous solution. The solutes are mainly organic acids or inorganic ions, a small amount of sugars and dissolved salts (Nobel 1970; Brown 1974; Roshchina and Roshchina 2012). Amyloplasts, such as the amyloplasts of potato tuber, are specialised for starch granule synthesis and storage, i.e., they usually contain one or more starch granules (Parker 1985; Okita 1992; Bechtel and Wilson 2003; Wise and Hoober 2007). Due to the importance of starch granules in terms of production and consumption and how they can influence the rheological properties of plant-tissue suspensions, their characteristics are introduced in more detail in the following section.

2.1.1.2.1. Starch Granules

Starch granules are important biomass ingredients with unique properties and with a wide range of applications (Okechukwu and Rao 1995; Jobling 2004; Yoon and Deng 2006; Gregorová, Pabst, and Bohačenko 2006; BeMiller 2007). Amylose and amylopectin, which are two structurally different polysaccharides of D-glucose, are the main starch granule components.

Other constituents of the starch granule, e.g., fats and proteins, are present at very low concentrations (Jane 2000; Vaclavik and Christian 2014).

Amylose is primarily a linear molecule containing hundreds to thousands of glucose units connected by α 1-4 linkages. In contrast to amylose, amylopectin is a highly branched gigantic molecule, containing up to hundreds-of-thousands of D-glucose units (Mischnick and Momcilovic 2010). Although, the amount of amylose and amylopectin varies in different starches, most starches contain 20–30% amylose and 70–80% amylopectin (Jane et al. 1999; Gupta, Bawa, and Semwal 2009).

Starch granules mainly contain amorphous and crystalline domains. These domains are arranged in alternating concentric rings by which a semicrystalline environment within the granule is created. The crystalline domains are mainly composed of amylopectin, while amorphous domains are made up of amylose traversed by noncrystalline regions of amylopectin (Svihus, Uhlen, and Harstad 2005; Gupta, Bawa, and Semwal 2009). Therefore, the architecture or structure of a starch granule is influenced by the ratio of amylose and amylopectin molecules (Bertolini 2009).

The morphology of starch granules is mainly related to the biochemistry of the amyloplast and the physiology of the plant (Badenhuizen 1969; Singh and Singh 2001). Different sources of starches, e.g., maize and potato, will produce starches with different characteristics, such as granule size and shape. There is a wide range of sizes and shapes for starch granules. For example, potato starch granules are mostly oval while maize starch granules are more angular (Fannon, Hauber, and Bemiller 1992; Singh et al. 2003). The size of starch granules varies in

different starches, e.g., potato has the biggest starch granules (1 to 110 μm), followed by wheat, maize and rice (Gupta, Bawa, and Semwal 2009).

2.1.1.2.2. Heating of Starch in Excess Water (water: starch ratio > 1.5)

Many changes in starch granules occur when they are subjected to a thermal treatment. Researchers have found that water availability and temperature are the two important factors affecting the thermal changes. Water availability is categorized into two regimes: excess water in which the ratio of water to starch is higher than 1.5, and limited water in which the ratio is usually less than 1 (Singh et al. 2009; Zavareze and Dias 2011; Karaman, Yilmaz, and Kayacier 2013).

Upon heating the starch granules in excess water, three distinct phenomena take place in the granules: 1) first phase swelling, 2) gelatinization and 3) pasting (Henríquez et al. 2008; Ratnayake and Jackson 2009; Singh et al. 2009; Colonna and Buleon 2010; Zavareze and Dias 2011).

At temperatures below the gelatinization temperature, the starch granule is stable via van der Waals forces and hydrogen bonds. When a starch-water system is subjected to a gradually increasing temperature below the gelatinization temperature, starch granules slowly and reversibly absorb water and swell to a limited extent (Ratnayake and Jackson 2009). In this stage, the hydrogen bonds present between amylose and amylopectin are broken and new hydrogen bonds are created between water molecules and the exposed hydroxyl groups of amylose and amylopectin. This results in an increase in granule swelling (Bao and Bergman 2004).

By increasing the temperature to around 60 °C in an excess amount of water (depending on the botanical source of starch), a large amount of water will be absorbed by the starch granules and they swell to a larger extent than in the first phase swelling. This swelling mostly occurs in the more water-accessible amorphous regions where mostly amylose molecules exist and the intermolecular bonding is weak. As a result of this swelling, the amount of stress at the interface between the crystalline (high in amylopectin) and amorphous regions increases. As a result of an increase in the stress, at a certain point, the crystalline regions are irreversibly and rapidly disrupted and gelatinization begins. Upon gelatinization, the disruption of molecular order within the starch granule takes place and amylose and amylopectin are partly separated (Keetels, Oostergetel, and Van Vliet 1996; Keetels, van Vliet, and Walstra 1996; Singh et al. 2003; Crochet et al. 2005; Buleon and Colonna 2007; Liu et al. 2009; Colonna and Buleon 2010).

Upon increasing the temperature above the gelatinization temperature, pasting as the third phase of swelling will occur. In this stage, total disruption of the granules takes place. Gupta et al. (2009) studied the pasting properties of some starch granules and reported the pasting temperatures of native barley, maize, rice and wheat starches as about 77°C, 70°C, 75°C and 66°C, respectively (Gupta, Bawa, and Semwal 2009). Jane et al. (1999) showed that pasting properties depend mostly on the length and distribution of the chains of amylopectin branches. The authors also showed that increasing amylose content increased starch pasting temperature (Jane et al. 1999). In addition to temperature, starch paste properties are sensitive to stirring rate, i.e., showing shear dependency with mostly shear thinning behavior. Subramanian et al. (1994) showed that the hot pastes of sorghum starches thinned more than maize starches when they were sheared at high speed (Subramanian, Hoseney, and Bramel-Cox 1994). Therefore, two

important parameters, i.e., heating and stirring rates, are the most important parameters affecting the properties of starch pastes (Doublier, Llamas, and Le Meur 1987; Bahrani et al. 2012).

2.1.1.2.3. Heating of Starch in Limited Water (water: starch ratio <1)

Thermal behavior of starch at low water content depends on the botanical source of starch and its amylose content (Zavareze and Dias 2011). For instance, changes in the structure of tuber starches are more sensitive to the amount of water than legume or cereal starches (Jacobs and Delcour 1998; Gunaratne and Hoover 2002). The amount of water affects starch behavior mainly by influencing swelling and gelatinization temperatures; however, the pattern of changes in starch structure is the same as the changes in excess water. Most studies on starch-water systems with low water contents showed that swelling and gelatinization temperatures increase with decreasing water content. The reason for such an observation is a decrease in molecular mobility of starch components, such as amylose, with a decrease in water availability (Zeleznak and Hoseney 1987; Liu and Lelievre 1991; Kalichevsky et al. 1992; Perdon, Siebenmorgen, and Mauromoustakos 2000; Fukuoka, Ohta, and Watanabe 2002; Sun et al. 2002; Svihus, Uhlen, and Harstad 2005; Liu et al. 2009; Colonna and Buleon 2010).

2.1.1.2.4. Heating of Starch in the Presence of Other Ingredients

The presence of an excess ingredient, e.g., salts and sugars, in the starch-water system can change the behavior of starch granules during their thermal transitions. These ingredients can affect the starch-water system mainly by two different mechanisms: Firstly, by reducing the amount of leached amylose from the starch granules and secondly, by competing with the granules for the available water. In general, the presence of an excess ingredient, e.g., salts and sugars, increases the gelatinization temperature (Kohyama and Nishinari 1991; Kelly et al. 1995;

Farhat et al. 1997; Ahmad and Williams 1999; Ikeda et al. 2001; Pongsawatmanit, Thanasukarn, and Ikeda 2002; Zhang and Hamaker 2003; Bertolini et al. 2005; Buleon and Colonna 2007; Gunaratne, Ranaweera, and Corke 2007). For example, oligosaccharides increase the gelatinization temperature and reduce starch swelling by competing with starch granules for the available water (Chungcharoen and Lund 1987; Eliasson 1992; Ahmad and Williams 1999). However, it is shown that different sugars increased gelatinization temperature to different extents (Spies and Hoseney 1982; Gunaratne, Ranaweera, and Corke 2007). Gunaratne, Ranaweera, and Corke (2007) showed that gelatinization temperature of wheat and potato starches was increased by sucrose, glucose and glycerol in the order of sucrose > glucose > glycerol. This can be related to water activity and also the molecular size of the sugars, i.e., sugars with longer chain length increased gelatinization temperature to a larger extent compared to sugars with shorter chain length (Spies and Hoseney 1982).

2.1.2. Comminution of Plant Tissue

Comminuted plant tissue is present in a lot of food products, e.g., carrot purees. The comminution process is assigned to the size-reduction operations employed to produce small particles from larger ones (Ortega-Rivas 2012). For example, in the manufacturing of different tomato products, such as tomato paste and juice, size reduction is a necessary process (Thakur, Singh, and Nelson 1996). Table 2.1 shows some common comminution machines used in the food industry (McCabe, Smith, and Harriot 2005; Jankovic, Dundar, and Mehta 2010; Cardu and Seccatore 2016; Saravacos and Kostaropoulos 2016).

Table 2.1. Some size reduction machines used in the food industry (Ortega-Rivas 2012)

Equipment	Reduction Range	Type of Equipment	Applications
Ultrafine grinders	Fine	Agitation mills, Fluid-energy mills, Hammer mills with internal classification	For production of different powder of different materials such as ginger, green tea, cornstalk and wheat (Zhao et al. 2009; Hu, Chen, and Ni 2012; Zhao et al. 2013; Niu et al. 2014)
Grinders	Intermediate	Roller mills, Hammer mills, Tumbling mills, Disc grinders, Sharp bladed mill	Wheat flours, cereal grains, fruits, vegetables, starch, sugar, spices and cocoa (Maroulis and Saravacos 2003; Niu et al. 2014; Saravacos and Kostaropoulos 2016)
Crushers	Coarse	Gyratory crushers, Jaw crushers, Roll crushers	Grinding of maize, coffee and frozen products (Saravacos and Kostaropoulos 2016)

For comminution of plant tissue, different techniques are used, such as conventional blending, i.e., a sharp bladed mill (Day, Xu, Øiseth, Hemar, et al. 2010), and high-pressure homogenization (Pickardt, Dongowski, and Kunzek 2004). Day, Xu, Øiseth, Hemar, et al. (2010) used a kitchen blender for size reduction of carrot tissues and showed that particles with different microstructures and sizes were produced depending on different thermal conditions. The authors showed cell clusters, single cells and cell fragments were present in the average particle size of approximately 200 μm, 70 μm and 40 μm, respectively (Day, Xu, Øiseth, Hemar, et al. 2010).

Generally, in the comminution process, plant tissue will be ruptured into a broad range of particles depending on the processing conditions (Lopez-Sanchez, Nijsse, et al. 2011). The plant tissue is broken into several clusters of unbroken cells, single cells, and broken cell fragments in addition to the release of intercellular and intracellular materials, such as pectin and starch granules, as shown in Fig. 2.2 (Bayod et al. 2005; Lemmens et al. 2010; Lopez-Sanchez, Svelander, et al. 2011; Augusto and Vitali 2014). However, the comminution processing

conditions are important factors influencing final product properties. For example, Lopez-Sanchez et al. (2011) demonstrated that carrot tissue required higher shear input for disruption into cells and cell fragments than tomato tissue (Lopez-Sanchez, Svelander, et al. 2011).

Fig. 2.2. Schematic representation of different particles produced by comminution of plant tissue
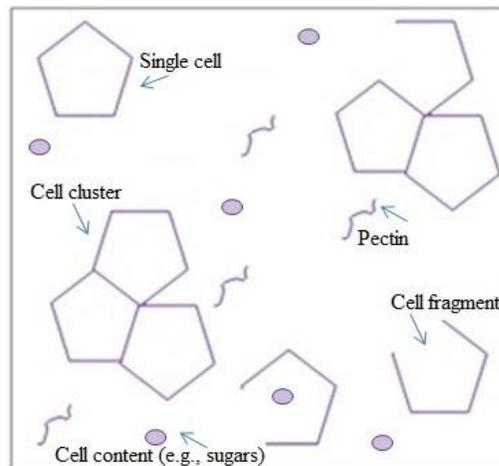
Reeve (1956) did a microscopic examination on comminuted apricot pulp. The author showed that most of the tissue particles consisted of intact and single cells while a minor portion consisted of clusters of unseparated and intact cells. In addition, a small amount of cells were believed to be crushed or reduced to cell wall fragments releasing intercellular and intracellular materials to the surroundings (Reeve 1956).

Tornberg and Bengtsson (2011) compared the different final products of tomato, apple, carrot and potato tissues in a comminution process. They showed that tomato tissue was easily degraded into cell fragments while apple tissue was not. The authors related this difference to the higher content of insoluble pectin in apple tissue compared to tomato tissue. For carrot and

potato tissues, only the cell clusters disintegrated while the whole cells did not. This was believed to be due to the fact that carrot and potato tissues had the highest contents of insoluble pectin among the samples (Tornberg and Bengtsson 2011).

2.2. Plant Tissue Suspensions

Many food products including plant-tissue foods, e.g., different purees, soups and sauces, are suspensions. An increase in the demand for healthy prepared foods has resulted in attention to the manufacturing of the plant tissue suspensions (Alvarez and Canet 2001; Alvarez, Canet, and Fernández 2007; Moelants, Cardinaels, Van Buggenhout, et al. 2014). Basic concepts of suspensions will be introduced in this section with an emphasis on the fundamental aspects of suspensions and the interactions between and within their constituent phases. Then, viscosity and viscoelasticity as two important rheological properties of plant tissue suspensions will be discussed.

2.2.1. Classification of Suspensions

In general, a suspension is a two phase system in which solid particles (dispersed phase) are suspended in a fluid (continuous phase). The size range for the suspended particles is usually assumed as 10^{-3} to 10^{2} μm (Genovese 2012). Suspensions containing particles smaller than 10^{-3} μm are called sub-nanometer-size suspensions and may be considered as one phase systems (Mewis and Wagner 2012). In addition, when the dispersed phase particle size ranges from 10^{-3} to 1 μm, i.e., the colloidal size range, the term 'dispersion' is used (Tadros 1986; Genovese 2012; Mewis and Wagner 2012).

Classification of suspensions is based on the type of dominant particle interactions. In this regard, two main groups can be considered. First, suspensions in which there are no

interparticle forces while there is an infinite repulsion at contact (Genovese 2012). These suspensions are mostly hard-sphere suspensions in which particles are assumed to be spherical, inert and rigid. Second, suspensions in which there is repulsive or attractive forces between particles which are mainly classified into two groups: 1) dispersed or stabilized suspensions in which particles are kept separate by net repulsive forces, 2) aggregated suspensions in which the attractive forces, such as the van der Waals attractions, play a significant role and the net effect of repulsion and attraction results in the aggregation of particles, Fig. 2.3 (Peker and Helvaci 2008; Genovese 2012). In both stabilized and aggregated suspensions, the structure of the suspensions depends on the magnitude of the interaction forces (Quemada and Berli 2002).

Fig. 2.3. Schematic diagram of hard sphere, stabilized and aggregated suspensions
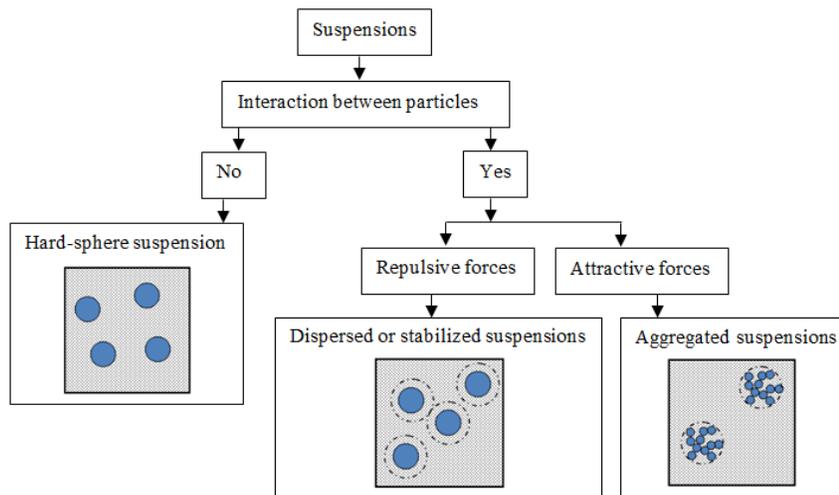
The hard sphere suspensions are the simplest suspensions to consider. Therefore, they have been used widely as a benchmark to compare the behavior of other suspensions. However, experimentally, it is challenging to make ideal hard spheres with negligible interaction forces between particles (Tadros 1986; Shewan and Stokes 2015).

2.2.2. Interactions between Particles

The rheological properties of suspensions depend on the existence and the amount of forces between particles and also between particles and the continuous phase. Three main forces exist with different magnitudes in a flowing suspension: 1- hydrodynamic forces, 2- Brownian forces, 3- interparticle attractive or repulsive forces. These forces are affected mainly by the solid volume fraction of the suspension, and by the shape and size distribution of the particles (Tadros 1986; Tadros 2010; Matveenko and Kirsanov 2011; Tadros 2011; Genovese 2012).

2.2.2.1. Hydrodynamic Forces

Hydrodynamic (or viscous) forces are the most common forces present in all flowing suspensions. These forces are the result of the relative motion of the suspended particles in the liquid phase and cause the dissipation of energy and an increase in viscosity (Genovese 2012; Mewis and Wagner 2012). Hydrodynamic forces are affected by the viscosity of the continuous phase, solids content, and the distribution of particle sizes and shapes. For instance, as the solids content of a suspension increases, the hydrodynamic interactions between particles increase (Tadros 2010). In non-colloidal particle suspensions, hydrodynamic forces dominate Brownian forces and interparticle forces, particularly for suspensions with particles bigger than ~10 μm (Zhou, Scales, and Boger 2001; Genovese 2012).

In a plant tissue, cells have a wide range of size from 50 to 500 μm (Aguilera and Stanley 1999). The size of plant tissue cells is changed during the processing for preparation of plant tissue suspensions. Different particle sizes of plant tissue suspensions have been reported in the literature based on the preparation procedure (Day, Xu, Øiseth, Hemar, et al. 2010; Lopez-Sanchez, Nijsse, et al. 2011; Moelants, Cardinaels, et al. 2013). In most studies of the rheological

properties of plant tissue suspensions, the reported particle sizes are higher than 10 µm. Therefore, it can be concluded that hydrodynamic forces play an important role in the rheological behavior of plant tissue suspensions.

The hydrodynamic forces on a particle in a fluid can be related to the particle Reynolds number (Re_p). This dimensionless parameter is the ratio of the inertia forces to the viscous forces (Barnes, Hutton, and Walters F.R.S. 1993):

$$Re_P = \frac{\rho_0 a^2 \dot{\gamma}}{\eta_0}$$

Eq. 2.1

where ρ_0 is the density of the suspending liquid, a is the particle radius, $\dot{\gamma}$ is the shear rate and η_0 is the viscosity of the suspending liquid (Stickel and Powell 2005; Mueller, Llewellin, and Mader 2009).

2.2.2.2. Brownian Forces

Brownian forces are always present in a suspension as thermal randomizing forces. These forces help to break down any structure in the suspensions and oppose the particles' aggregation (Tadros 1986; Peker and Helvaci 2008). Both rotational and translational movements of the particles result from Brownian forces. The Peclet number (P_e) is used as a dimensionless parameter to investigate the Brownian forces in suspensions. This number relates the shear rate to the particle's diffusion rate (Wagner and Brady 2009):

$$P_e = \frac{6\pi a^3 \eta_0 \dot{\gamma}}{k_B T}$$

Eq. 2.2

where $k_B T$ is the thermal energy. When $P_e > 1$, hydrodynamic forces are the dominant forces which may lead to nonlinear rheological phenomena such as shear-thinning, i.e., $P_e \approx 1$, and

shear-thickening, i.e., $P_e \gg 1$. In contrast, when $P_e \ll 1$, the Brownian forces are the dominant forces in the system, helping disperse the particles and hence stabilize the suspensions (Wagner and Brady 2009; Eberle et al. 2014). Based on Eq. 2.2, the size of particles plays an important role in determining the effect of Brownian forces on the properties of a suspension. That is, the magnitude of the Brownian forces in the suspensions increases (P_e decreases) with decreasing size of particles (Barnes, Hutton, and Walters F.R.S. 1993; Mewis and Wagner 2012).

2.2.2.3. Interparticle Forces

Attractive or repulsive interparticle forces, which can be used to classify suspensions, are determined based on the interactions between the particles (Tadros 1986). Attractive forces are electrostatic attractive (unlike charges on different parts of the particle), hydrophobic, depletion, bridging and van der Waals. Repulsive forces are mainly electrostatic repulsive, i.e., similarly charged surfaces (Zhou, Scales, and Boger 2001).

When interparticle forces dominate over hydrodynamic and Brownian forces in suspensions, the particles form a structure. The type of the formed structure depends on whether the overall forces are repulsive, i.e., dispersed or deflocculated, or attractive, i.e., aggregation (Barnes, Hutton, and Walters F.R.S. 1993). The net interaction between the particles is influenced and controlled by a variety of factors (Shih et al. 1990; Zhou, Scales, and Boger 2001). For instance, smaller particles have a larger surface to interact with other particles at the same volume fraction when compared to larger particles (Yoo and Rao 1994; Moelants, Cardinaels, Jolie, et al. 2014).

In plant-tissue-based food suspensions, particles may interact with each other via different interparticle forces (Moelants, Cardinaels, Van Buggenhout, et al. 2014). Some plant

tissue suspensions form aggregates, for example, tomato suspensions (Bayod and Tornberg 2011). Pectin polymers play an important role in the interactions between particles (Beresovsky, Kopelman, and Mizrahi 1995). Beresovsky, Kopelman, and Mizrahi (1995) showed that depolymerization of the soluble, and especially the insoluble, pectin greatly affected the interaction between particles in tomato juice. Pectin polymers are able to create flocculation in a suspension via pectin-pectin and pectin-particle interactions (da Silva and Rao 2006).

2.2.3. Flow Properties

Viscosity is the parameter which has been used to describe the differences between the flow ability of different food materials. This physical parameter is related to "internal friction" in a fluid and is a measure of "resistance to flow" (Barnes, Hutton, and Walters F.R.S. 1993). Mathematically, viscosity (η) [Pa.s] is defined as the constant of proportionality between the applied stress (σ) [Pa] and the velocity gradient or shear rate ($\dot{\gamma}$) [s^{-1}]:

$$\sigma = \eta \dot{\gamma} \hspace{4cm} \text{Eq. 2.3}$$

This simple concept of viscosity was introduced for the first time by Isaac Newton. If a fluid obeys Eq. 2.3, it is called a Newtonian fluid. Based on Eq. 2.3, the viscosity of a Newtonian fluid does not change with shear rate (Barnes 2000). However, this is an ideal situation which is not the case for many fluids, i.e., non-Newtonian fluids, so that the "viscosity" varies with the shear rate. Therefore, the apparent viscosity has been defined as a function of the shear rate, i.e., $\eta = f(\dot{\gamma})$, for non-Newtonian fluids. Based on the trend of changes in viscosity with shear rate, non-Newtonian fluids are classified into two major groups: shear-thickening and shear-thinning (Barnes, Hutton, and Walters F.R.S. 1993; Barnes 2000; Roussel 2012; Genovese 2012).

2.2.3.1. Shear-thickening and Shear-thinning

In shear-thinning (or pseudoplastic) fluids, e.g., tomato pastes, the apparent viscosity decreases with increasing shear rate (Rao and Cooley 1992). On the other hand, the apparent viscosity of shear-thickening (or dilatant) fluids, e.g., cornstarch and water suspensions, increases with increasing shear rate (Barnes, Hutton, and Walters F.R.S. 1993; Barnes 2000; White, Chellamuthu, and Rothstein 2009).

Materials such as polymer solutions, emulsions and semi-dilute suspensions have mostly shear-thinning behavior (Barnes 2000). In these materials, at low shear rates or shear stresses, the viscosity is constant, i.e., zero-shear viscosity (η_0), and then by increasing shear rates or stresses, the viscosity begins to decrease until it reaches a constant viscosity, i.e., infinite shear viscosity (η_∞). Therefore, in most shear-thinning fluids, there are two plateau regions, i.e., Newtonian viscosities η_0 and η_∞, occurring at low and high shear rates, respectively, separated by a descending curve. However, sometimes it is difficult to see η_0 and η_∞ and only the descending curve region is observed (Ackerson and Clark 1983; Chen et al. 1994; Barnes 2000; Zhou, Scales, and Boger 2001).

Several simple equations have been presented to mathematically describe non-Newtonian flow behavior. One of the well-known models is the power-law model given by:

$$\sigma = k\dot{\gamma}^n \ or \ \eta = k\dot{\gamma}^{n-1} \tag{Eq. 2.4}$$

where k [Pa.s^n] is the consistency and n [-] is the power-law index. In a shear-thinning liquid, the n value is below 1 and in a shear-thickening fluid, the n value is higher than 1. Another well-known model for defining non-Newtonian flow behavior is the Cross model in which the viscosity has been related to η_0, η_∞ and shear rate:

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + (K\dot{\gamma})^m}$$

<div align="right">Eq. 2.5</div>

where m [-] and K [s] are constants. In shear-thinning fluids, the m value is between zero, i.e., more Newtonian behavior, and unity, i.e., more shear-thinning behavior, while for a shear-thickening liquid, the m value is higher than unity (Cross 1965; Barnes 2000).

Shear-thinning behavior in a suspension is mostly of two origins: alignment of dispersed particles in the direction of flow and/or breakdown of structure (Cross 1979; Gallegos, Franco, and Partal 2004; Moelants, Cardinaels, et al. 2013; Augusto and Vitali 2014). A structure can be formed in a suspension as result of aggregation or orientation of particles (Malkin, Semakov, and Kulichikhin 2010; Marín-Santibáñez, Pérez-González, and de Vargas 2010). For instance, by shearing a pectin dispersion the rearrangement of the pectin polymers' chains results in shear-thinning behavior (da Silva and Rao 2006; Wüstenberg 2015).

2.2.3.2.   Time Dependent vs. Time Independent

In shear-thinning or shear-thickening fluids, the apparent viscosity is only a function of the shear rate. However, some materials show time-dependent properties and are known as thixotropic or rheopectic materials (Cheng and Evans 1965). Thixotropy and rheopecty are used for time-dependent shear-thinning and shear-thickening materials, respectively (Barnes, Hutton, and Walters F.R.S. 1993). Both phenomena may be irreversible, reversible or partially reversible. They occur due to the changes in the internal structure of fluids (Roussel 2012).

2.2.3.3.   Yield Stress

Many food products have two different characteristics. They behave as solid materials below a critical stress, i.e., they can keep the shape they have been given, and as liquid materials at

stresses higher than the critical value, i.e., they are able to flow (Roussel 2012). The critical stress at which solid-like behavior is changed to liquid-like behavior is called the yield stress (σ_0) (Coussot 2014). Many plant-tissue-based food suspensions have a yield stress, e.g., tomato and carrot suspensions (Bayod et al. 2007; Day, Xu, Øiseth, Hemar, et al. 2010). It has been concluded that the existence of a yield stress in these suspensions is due to the network structure formed as a result of the net attractive forces between particles (Bayod et al. 2007). The magnitude of the yield stress in suspensions is affected by different parameters such as solids content and particle size. For instance, it has been shown in the literature that the yield stress increases with increasing solids content of suspensions (Marangoni and Rogers 2003; Achayuthakan, Suphantharika, and Rao 2006). Also, particle size effects on yield stress have been discussed in several studies (Qiu and Rao 1988; Missaire, Qiu, and Rao 1990; Zhou et al. 1995; Moelants, Cardinaels, Jolie, et al. 2014). Both an increase and a decrease in yield stress with increasing particle size of suspensions have been reported in different studies. For example in tomato-derived suspensions (Moelants, Cardinaels, Jolie, et al. 2014) and apple sauces (Schijvens, Vliet, and Dijk 1998), the yield stress has been shown to increase with increasing particle size. However, there are a few studies demonstrating an increase in the yield stress of plant tissue suspensions with decreasing particle size (Qiu and Rao 1988; Yoo and Rao 1994). Therefore, variations in the magnitude of the yield stress as a result of changes in the particle size are not completely clear (Schijvens, Vliet, and Dijk 1998). This is due to the complicated relationships between particle size, size distribution, shape and surface properties which all influence the rheological properties of plant tissue suspensions (Moelants, Cardinaels, et al. 2013).

Generally, different models have been proposed to mathematically describe the flow behavior of fluids with a yield stress. For example, in the Bingham model, a yield stress (σ_0) is followed by Newtonian flow of the material (Bingham 1922):

$$\sigma = \sigma_0 + \eta\dot{\gamma} \qquad\qquad \text{Eq. 2.6}$$

For non-Newtonian fluids, the Bingham model is modified to the Herschel-Bulkley equation where a power-law function is included in the equation (Herschel and Bulkley 1926):

$$\sigma = \sigma_0 + k\dot{\gamma}^n \qquad\qquad \text{Eq. 2.7}$$

Based on Eq. 2.7, the structure, which is responsible for the yield behavior at low shear stress, may become weaker or stronger gradually during shearing, leading to the shear-thinning or shear-thickening behavior of the material, respectively (Nguyen and Boger 1992). This model has been extensively used for describing the flow behavior of different food products, such as apricot puree (Duran and Costell 1982), tomato thin pulp samples (Sharma et al. 1996), mixed systems of inulin and waxy maize starch (Zimeri and Kokini 2003), dairy desserts (Tarrega, Duran, and Costell 2004), sweet potato puree (Ahmed and Ramaswamy 2006b), tamarind juice concentrate (Ahmed, Ramaswamy, and Sashidhar 2007), basil seed gum (Hosseini-Parvar et al. 2010), peach purees (Massa et al. 2010), and tomato-derived suspensions (Moelants, Cardinaels, Jolie, et al. 2014).

2.2.4. Viscoelasticity

In the previous section, the liquid-like behavior of suspensions was discussed. However, both liquid-like and solid-like behaviors have been observed in many suspensions. The combination of these two types of behavior is called viscoelasticity. Viscoelastic properties are observed in

many food products, for example commercial vegetable (pea, maize and wax bean) puree-based baby foods (Ahmed and Ramaswamy 2006a).

By definition, an ideal liquid has been defined as a material with no definite shape which can flow irreversibly under an external force following Newton's law, Eq. 2.3. On the other hand, a solid is a material with definite shape and an external force can deform it to a new equilibrium shape. Upon removal of the external force from an ideal solid it will revert to its original shape (Ward and Sweeney 2013). Oscillatory tests are used to measure the viscoelastic properties of suspensions. In an oscillatory test, the solid-like and the liquid-like behavior are characterized by two components, i.e., the loss modulus (G'') and the storage modulus (G') (Barnes 2000; Gunasekaran and Ak 2000):

$$G'' = \frac{\sigma}{\gamma}\sin(\delta)$$ Eq. 2.8

and

$$G' = \frac{\sigma}{\gamma}\cos(\delta)$$ Eq. 2.9

where σ is the stress, γ is the strain amplitude, and δ is the loss angle ($\tan\delta = {G''}/{G'}$). In a suspension, G' and G'' may behave differently at different angular frequencies (ω). At low frequency, the behavior corresponds mainly to the terminal zone in which $G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$ (Mewis and Wagner 2012).

Also, in an oscillatory test, G'' is related to the real part of a dynamic viscosity (η′) while G' is defined by an imaginary viscosity (η″) through the angular frequency (ω):

$$\eta' = \frac{G''}{\omega}$$ Eq. 2.10

and

$$\eta'' = \frac{G'}{\omega}$$ Eq. 2.11

The combination of both dynamic and imaginary viscosities is defined by a complex viscosity (η^*) (Bourne 2002; Rao 2013):

$$\eta^* = \eta' - i\eta''$$ Eq. 2.12

The empirical Cox-Merz rule is usually used to compare the similarity between the complex viscosity and the shear viscosity (Cox and Merz 1958):

$$|\eta^*(\omega)| = \eta(\dot{\gamma}), (\omega = \dot{\gamma})$$ Eq. 2.13

However, most food products show a deviation from the Cox-Merz relationship due to the high possibility of aggregation of the particles in the sample (Bistany and Kokini 1983; Rao and Cooley 1992; da Silva, Gonçalves, and Rao 1993; Ikeda and Nishinari 2001).

In suspensions, the transition from predominantly liquid-like to solid-like behavior, i.e., when G' becomes greater than G'', may occur as a result of different factors, including an increase in solids content (Harini and Deshpande 2009). Where this transition happens, the suspensions show the behavior of gels in which G' is higher than G'' and both moduli are largely independent of frequency (Ross-Murphy 1995). Gels can be classified as strong and weak depending on their resistance to break under stress (Ross-Murphy and Shatwell 1992).

2.3. The Rheology of a Comminuted Plant-tissue Suspension

This section is built on the knowledge of plant tissue anatomy and suspensions introduced in sections 2.1 and 2.2, respectively, to develop a rational understanding of the rheological behavior of comminuted plant-tissue suspensions. In general, the rheological behavior of a suspension is influenced by several parameters related to the properties of both continuous and dispersed phases, and the interactions between the dispersed particles, Fig. 2.4.

Fig. 2.4. Most important parameters affecting the rheological behavior of a suspension
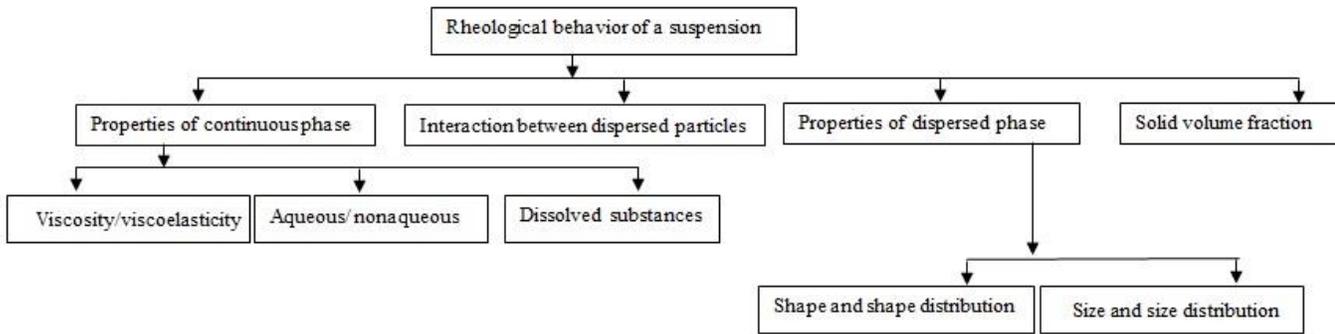
The rheological properties of plant-tissue suspensions are affected by both the properties of the continuous phase and the properties of the dispersed phase (Tanglertpaibul and Rao 1987b). In this regard, the most important parameters are classified as: a) the viscosity (η_0) of the continuous phase, b) the solid volume fraction (Φ), c) particle size (d) and shape (P_a) distributions, d) interparticle interaction forces. In addition to these factors, temperature T and pressure P are important. For instance, the simplest suspensions in which no interparticle forces are involved, the equation of state for a suspension's viscosity (η_s) can be written as (Tadros 1986; Barnes 2000; Tropea, Yarin, and Foss 2007; Rao 2013):

$$\eta_s = f(\eta_0, \Phi, d, P_a, T, P) \hspace{3cm} \text{Eq. 2.14}$$

2.3.1. The Effect of the Continuous Phase

The properties of the continuous phase can greatly affect the rheological behavior of a suspension. These can be classified as: 1) viscosity/ viscoelasticity, 2) aqueous (consisting of water) / nonaqueous (organic solvent), and 3) the type and amount of dissolved substances (Chander 1998; Tropea, Yarin, and Foss 2007). For example, if the continuous phase is a Newtonian liquid, the deviation from Newtonian behavior in a suspension is related to the presence of solid particles (Tropea, Yarin, and Foss 2007). On the other hand, a non-Newtonian

continuous phase can change the interparticle interactions in suspensions and affect particle movement (Tropea, Yarin, and Foss 2007).

In almost all proposed models for the viscosity of suspensions, it is assumed that the viscosity is directly related to the viscosity of the continuous phase. For instance, if the viscosity of the continuous phase is doubled, then the viscosity of the suspension will be doubled. This proportionality is present in the theoretical study of Albert Einstein who proposed the simplest model for predicting the viscosity of a dilute suspension (Barnes, Hutton, and Walters F.R.S. 1993):

$$\eta = \eta_0(1 + 2.5\Phi)$$
Eq. 2.15

To achieve a good understanding of the role of the continuous phase in the rheology of suspensions, there is a need to study the parameters affecting the rheological properties of the continuous phase. The continuous phase of plant-tissue food suspensions is mostly an aqueous solution containing solubilized cell components and cell-wall materials, particularly pectin polymers, sugars, salts, and organic acids (Tanglertpaibul and Rao 1987b; Anthon, Diaz, and Barrett 2008). The soluble constituents of plant cells can greatly affect the properties of the continuous phase. In addition to the soluble components, in general, the viscosity of the continuous phase is sensitive to temperature. Therefore, in this section, the effect of the addition of soluble components of plant cells and temperature on the properties of the continuous phase will be discussed.

2.3.1.1.   The Effect of Addition of Pectin Polymers

Pectin polymers are the most important soluble component of the plant cell affecting the continuous phase properties (Moelants, Cardinaels, Van Buggenhout, et al. 2014). Pectin exists

in plant-tissue-based particle suspensions in a large amount. For example, approximately 55 to 60% of potato cell wall dry weight is pectin (Singh and Kaur 2016). In the cell wall, there are different types of interactions between pectin polymers and other cell wall polysaccharides and also some intermolecular interactions within the pectin polymer chains. These interactions are mostly ionic or non-ionic interactions, covalent bindings or weak noncovalent interactions and intermolecular hydrogen bonds (Selvendran and O'Neill 1987).

The solubility of these polymers depends on the type and magnitude of interactions that are present. For instance, pectin polymers interacting with other cell wall constituents through covalent bonds are less soluble than those that interact with cell wall components via noncovalent and non-ionic bonds which are known as weak bonds (Moelants, Cardinaels, Van Buggenhout, et al. 2014). Otherwise, pectin polymers will remain insoluble with no influence on the continuous phase of the suspension. The first step for pectin solubilization occurs when pectin polymer segments are surrounded by water molecules rather than by other polymer segments (Al-Shammari et al. 2011; Rodriguez et al. 2014). These water-soluble pectin polymers are of interest here since they will be present in the continuous phase of plant-tissue suspensions.

Pectin polymers enter the continuous phase during preparation of the plant-tissue-based particle suspensions, e.g., during size reduction or thermal treatment, and become solubilized. The solubilized pectin polymers affect the rheological properties of the suspension by influencing the characteristics of the continuous phase (Caradec and Nelson 1985; Tanglertpaibul and Rao 1987b; Sharma et al. 1996; Anthon, Diaz, and Barrett 2008). The main characteristics of pectin polymers which affect the rheological behavior of a suspension are the length and size of the polymers, degree of branching, degree of methoxylation, pattern of methoxylation and molar mass distribution (Tanglertpaibul and Rao 1987b; Beresovsky,

Kopelman, and Mizrahi 1995; Anthon, Diaz, and Barrett 2008; Moelants, Jolie, et al. 2013). For instance, depolymerization and solubilization of pectin led to a decrease in the viscosity of the continuous phase (Luh and Daoud 1971; Hurtado, Greve, and Labavitch 2002; Anthon, Diaz, and Barrett 2008; Moelants, Jolie, et al. 2013). In general, it has been shown that by dissolving a small amount of polymeric material into a solvent, the viscosity of the resulting solution will increase noticeably (Steffe 1996; Barnes 2000; Al-Shammari et al. 2011). This is also confirmed for the effect of pectin polymers on the flow behavior of suspensions in which pectin solubility leads to an increase in the viscosity of the continuous phase (Errington, Tucker, and Mitchell 1998).

Pectin solution viscosity is affected by pectin concentration. Dilute pectin solutions, i.e., up to approximately 0.5%, show mostly Newtonian behavior (da Silva and Rao 2006). Chou, Pintauro, and Kokini (1991) analyzed the viscoelastic properties of a dilute pectin solution. Based on the results, the authors suggested that pectin polymers have a compact random coil conformation in dilute solutions (Chou, Pintauro, and Kokini 1991). By increasing the pectin concentration, pectin solutions have been demonstrated to exhibit shear-thinning behavior (da Silva and Rao 2006). This could be explained by the alignment of the pectin polymer chains in the solution under the application of shear (da Silva and Rao 2006; Wüstenberg 2015). This molecular alignment will allow easier flow of the molecules and reduce the viscosity at higher shear rates (McCrum, Buckley, and Bucknall 1997; Al-Shammari et al. 2011; Rodriguez et al. 2014). Kjøniksen et al. (2003) reported the viscoelastic properties of a semi-dilute solution of pectin, i.e., 1.5 wt %. The authors showed that even at the start of the experiment, the elastic modulus was higher than the loss modulus ($G' > G''$). Also, the dynamic moduli (G' and G'')

increased with time, demonstrating the development of gel-like behavior as time passes (Kjøniksen et al. 2003)

2.3.1.2. The Effect of Addition of Other Cell and Cell-wall Materials

In most studies of the flow behavior of plant-tissue suspensions, only pectin has been considered as the main soluble ingredient in the cell wall which influences the continuous phase properties (Ross-Murphy 1995; Hill, Ledward, and Mitchell 1998). The other constituents of plant tissue cell walls, such as protein and cellulose, contribute to the viscosity of the continuous phase, and consequently the viscosity of plant-tissue suspensions, only under certain conditions, e.g., in the presence of enzymes or at specific temperatures.

As mentioned in section 2.1.1.1, the main polysaccharides of the cell wall, i.e., cellulose and hemicelluloses, are insoluble in water. Their solubility and the characteristics of their solutions are influenced by different factors including molecular weight and the extent of intermolecular hydrogen bonding between molecules (McCormick, Callais, and Hutchinson 1985; Bochek 2003). By addition of these polysaccharides to a suspension, at room temperature with no enzyme activity, the characteristics of the continuous phase of the suspension will not change. Compared to polysaccharides, proteins exist in smaller amounts in plant tissue cell walls. Proteins have low solubility in aqueous solvents due to a large hydrophobic character of certain amino acids (Walstra 2002; Harrison et al. 2015).

If protein and cellulose as insoluble cell wall materials become soluble under specific conditions, e.g., partial enzymatic digestion of cellulose or degradation of proteins, the viscosity of the continuous phase increases (McCormick, Callais, and Hutchinson 1985; Liu et al. 2005). However, there is no obvious relationship between the protein level or total polysaccharides with

the continuous phase viscosity (Errington, Tucker, and Mitchell 1998; Moelants, Cardinaels, Van Buggenhout, et al. 2014).

In addition to the cell-wall constituents, in a plant tissue cell, there is the cytoplasm region containing different organelles and a solution of organic acids or inorganic ions, sugars and salts (Nobel 1970; Brown 1974; Roshchina and Roshchina 2012). The concentration of each of these components is an important factor influencing the viscosity of the continuous phase (Moelants, Cardinaels, Van Buggenhout, et al. 2014). In addition, each of the cytoplasm components can affect the viscosity of the continuous phase differently. For example, sodium salts increase the viscosity of a solution while some salts of potassium decrease the viscosity of a solution at low concentrations (Mewis and Wagner 2012). Therefore, drawing a firm conclusion on the influence of cytoplasm addition on the viscosity of plant tissue suspensions is difficult.

2.3.1.3.   The Effect of Temperature

In the simplest case, the dependence of a suspension's viscosity on temperature is attributable to the effect of temperature on the viscosity of the continuous phase. In this regard, with increasing temperature, an increase in Brownian motion of the constituent molecules of the continuous phase causes a decrease in the viscosity. The rate of the viscosity decrease is greater in more viscous liquids (Barnes 2000; Tadros 2010; Fani, Abbassi, and Kalteh 2015). The most well-known approach used to describe the relationship between the viscosity and the temperature of a liquid is the Arrhenius relation (da Silva, Gonçalves, and Rao 1994):

$$\eta = \eta_{\text{ref}} \exp(^{E_a}/_{RT}) \qquad\qquad \text{Eq. 2.16}$$

where η_{ref} [Pa.s] is the viscosity at a reference temperature, E_a is the activation energy [J mol $^{-1}$], R [J mol^{-1} K^{-1}] is the universal gas constant and T [K] is the absolute temperature (Rao and Kenny 1975; Speers and Tung 1986; Rao 2013). According to the Arrhenius equation, a plot of log η vs. (1/T) is a straight line with a slope of (E_a/R).

da Silva, Gonçalves, and Rao (1994) showed that the viscosity of pectin solutions is sensitive to temperature changes, i.e., the viscosity of pectin solutions decreases by increasing the temperature. Also, the authors showed that pectin solutions had a deviation from the Arrhenius model at low pH when the aggregation of pectin chains occurred. They assumed that the deviation from the Arrhenius model was attributable to increase in intermolecular interactions led to a higher degree of chain stiffening in pectin solutions caused by the increase in temperature (da Silva, Gonçalves, and Rao 1994).

2.3.2. The Effect of the Dispersed Phase

The dispersed phase of a plant-tissue suspension is mostly clusters of cells, single cells and cell fragments (Bayod et al. 2005; Lopez-Sanchez, Nijsse, et al. 2011; Augusto and Vitali 2014). When these solid particles are added to a liquid, they begin to interact with each other and with the liquid. Hence, a study on the parameters which affect the rheological properties of suspensions mostly begins with an investigation of the effect of solids content. In addition to solids content, particle properties (such as shape and size distribution) influence the rheology of suspensions (Barnes 2000). Therefore, the focus of this section is the effect of solids content and the dispersed phase properties, mainly size and shape of particles, on the rheological behavior of suspensions.

2.3.2.1.   Particle Concentration

Physically, the presence of particles in a liquid can influence the rheological properties in different ways. For instance, the diversion and distortion of streamlines in the flow fields occur as a result of the presence of regions that are occupied by particles, Fig 2.5. Consequently, the dissipation of mechanical energy increases, leading to an increase in the viscosity. In addition, collisions between particles, which increase with increasing particle concentration, lead to a higher viscosity of the suspension (Genovese 2012; Mewis and Wagner 2012).

Fig. 2.5. Streamlines around a particle in a flow field
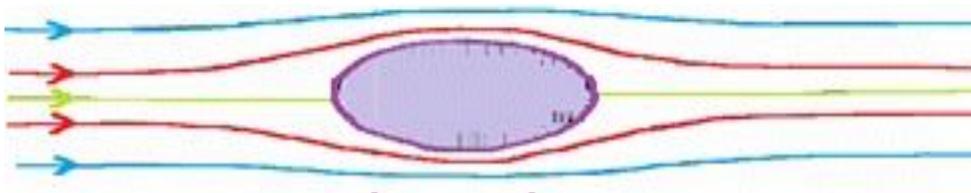
Food scientists have defined different parameters to define the particle concentration in a plant-tissue suspension based on their preparation method. These parameters include solid volume fraction, pulp content, water-insoluble solids, and total solids content (Yoo and Rao 1994; Sharma et al. 1996; Sanchez et al. 2002; Espinosa et al. 2011). It has been shown that with increasing particle concentration the rheological parameters apparent viscosity, yield stress and storage modulus (G') increase (Rani and Bains 1987; Den Ouden and Van Vliet 2002; Nindo et al. 2007; Espinosa et al. 2011). This increase in the rheological parameters can be described by different empirical mathematical models, such as linear, power law and exponential (Rao and Cooley 1983; Tanglertpaibul and Rao 1987b; Qiu and Rao 1988; Yoo and Rao 1994; Beresovsky, Kopelman, and Mizrahi 1995; Sharma et al. 1996; Schijvens, Vliet, and Dijk 1998;

Sanchez et al. 2002; Bayod et al. 2007; Day, Xu, Øiseth, Hemar, et al. 2010; Lopez-Sanchez and Farr 2012; Moelants, Cardinaels, Jolie, et al. 2014).

In addition, by increasing the particle concentration in plant tissue suspensions, shear-thinning behavior and the consistency factor (k) increase (Bhamidipati and Singh 1990; Bayod et al. 2005; Gundurao, Ramaswamy, and Ahmed 2011). The power-law model has been used widely to describe the increase of k with increasing particle concentration (Alviar and Reid 1990; Barbana and El-Omri 2012). Also, it has been shown that by increasing particle concentration, the dependence of the storage modulus (G') of plant tissue suspensions on angular frequency decreases, demonstrating the development of gel-like behavior with a yield stress (Gundurao, Ramaswamy, and Ahmed 2011; Moelants, Cardinaels, et al. 2013).

Systematic study of the effect of particle volume fraction on the viscosity of suspensions has been mostly carried out by considering three different regimes: the dilute, semi-dilute and concentrated regimes which are discussed below.

2.3.2.1.1. Dilute Suspensions

Dilute suspensions are used in theoretical studies as the simplest suspensions in which the calculation of all particle interactions is possible. In these suspensions, there are few particles and the distance between the particles is large compared to the range of the interaction forces. Therefore, hydrodynamic interactions can be ignored and Brownian diffusion dominates (Tadros 1986; Tadros 2011; Mewis and Wagner 2012).

Einstein studied the viscosity of dilute suspensions for the first time in 1906 and proposed his equation (Eq. 2.15) which became the most well-known equation for dilute suspensions. Based on his equation, in the dilute regime of spherical particles (solid volume fractions up to

about 0.1), the total increase in the viscosity is the sum of the contributions of each particle. Also, based on Einstein's equation, the size of particles is not involved in the viscosity (Peker and Helvaci 2008). It has been shown by several researchers that Einstein's equation can well predict the flow behavior of dilute Brownian hard spheres, a model situation that applies to only a few food suspensions (De Kruif et al. 1985; Van der Werff and De Kruif 1989; Van der Werff, De Kruif, and Dhont 1989; Jones, Leary, and Boger 1991; Rao 2013)

2.3.2.1.2.   Semi-dilute Suspensions

By increasing the particle concentration of a suspension, the volume of space occupied by the particles increases and the distance between the particles decreases (Mewis and Wagner 2012). As a consequence, probable interactions between particles increase. Therefore, in these suspensions, the interaction forces between the particles and between the particles and continuous phase become important. In this regard, the effect of other particles and hydrodynamic interactions should be considered and Einstein's equation, Eq. 2.15, is no longer valid. Many researchers have attempted to modify Einstein's equation for higher concentrations of particles. One of the proposed models is the modified Einstein's equation:

$$\eta = \eta_0 (1 + [\eta]\Phi) \hspace{6cm} \text{Eq. 2.17}$$

where $[\eta]$ is the intrinsic viscosity which describe the characteristics of non-spherical particles, defined as 2.5 for rigid spheres (Genovese 2012).

Another well-known model is the semi-empirical equation of Krieger and Dougherty. This equation has been proposed for monodisperse spherical particles (Krieger and Dougherty 1959):

$$\eta = \eta_0 (1 - \frac{\Phi}{\Phi_m})^{-[\eta]\Phi_m} \qquad \text{Eq. 2.18}$$

where Φ_m is the maximum packing fraction of particles (at which the viscosity is infinite). The magnitude of the maximum packing fraction (Φ_m) depends on different parameters, including the particle size and shape distribution (Barnes 2000; Willett 2001; Genovese 2012). Also, the Maron–Pierce relation is another model which is used widely. This model is a modification of Krieger and Dougherty's equation for practical conditions where it has been shown that the value of $[\eta] \Phi_m$ is often around 2:

$$\eta = \eta_0 (1 - \Phi/\Phi_m)^{-2} \qquad \text{Eq. 2.19}$$

Yoo and Rao (1994) derived a model similar to the Maron-Pierce relation for tomato particle suspensions by replacing the solid volume fraction with the pulp weight:

$$\eta = \eta_0 (1 - P/_A)^{-2} \qquad \text{Eq. 2.20}$$

where P is the pulp weight fraction of solids (instead of Φ) and A is a constant that has the meaning of a maximum packing fraction and is adapted as a function of particle shape (Yoo and Rao 1994).

Cepeda and Gomez (2002) used a modified Krieger–Dougherty model to explain the rheological properties of pimento puree in which there is electrostatic repulsion between particles. They showed that the electrostatic repulsion affected the zero shear viscosity (η_0). The apparent viscosity of the pimento puree increased with increasing pulp content. This behavior was explained by the following modified Krieger–Dougherty model:

$$\eta = \eta_0(1 - {}^P\!/_B)^{-2} + C \hspace{6cm} \text{Eq. 2.21}$$

where B is a constant and C is a constant related to the electrostatic contribution.

2.3.2.1.3.   Concentrated Suspensions

Further increase in the particle concentration leads to crowding of particles and causes a more rapid increase in suspension viscosity. Using the proposed models for semi-dilute suspensions is challenging for concentrated suspensions since there are huge amounts of hydrodynamic interactions that must be taken into account here. However, no exact method is known to determine all body interactions. Therefore, precise prediction of the viscosity of concentrated suspensions is not an easy task even for the simplest suspensions, i.e., hard sphere suspensions. For non-Brownian particles, more difficulties arise since there are no Brownian forces to form or restore a well-defined isotropic equilibrium structure (Tadros 1986; Mewis and Wagner 2012).

2.3.2.2.   Particle Size and Size Distribution

The size and size distribution of the particles are important factors affecting the flow behavior of suspensions (Barnes 2000; Tropea, Yarin, and Foss 2007). Several studies showed the effect of particle size on the flow behavior of plant tissue suspensions, such as tomato concentrate (Tanglertpaibul and Rao 1987a), apple sauce (Qiu and Rao 1988), tomato puree (Yoo and Rao 1994), tomato paste suspensions (Bayod et al. 2007), and tomato-derived suspensions (Moelants, Cardinaels, Jolie, et al. 2014). Particle size and size distribution affect the viscosity of suspensions in two different ways. First, at a given solids content, reducing the particle size leads to an increase in the number of particles in a specific volume. As a consequence, a decrease in the distance between the particles and changes in the interparticle interactions and the viscosity will occur. Second, by altering the size and size distribution of the particles the maximum

packing fraction (Φ_m) will change (McGeary 1961; Farris 1968; Yoo and Rao 1994; Senapati, Mishra, and Parida 2010). The maximum packing fraction of suspensions of polydisperse particles is higher than that of suspensions of monodisperse particles. The reason is that, in the former, small particles are entrapped between large particles and occupy the space between the large particles. Consequently, based on the proposed models for the viscosity of suspensions, such as the Maron-Pierce equation, by increasing the maximum solid volume fraction the viscosity of the suspension decreases (Hahn et al. 2015).

The effect of the size and size distribution on flow behavior is a multifold issue, since by changing the size of the particles the other properties of the particles such as shape are altered (Moelants, Cardinaels, Van Buggenhout, et al. 2014). Therefore, the results of studies investigating the effect of particle size and size distribution on the viscosity of suspensions are not in good agreement. Some researchers reported that the viscosity of suspensions increased with a decrease in the particle size (Saunders 1961; Parkinson, Matsumoto, and Sherman 1970) while some others observed that the viscosity increased with increasing particle size (Tanglertpaibul and Rao 1987a). For instance, Qiu and Rao (1988) and Cantu-Lozano et al. (2000) showed that the apparent viscosity and the yield stress increased with decreasing particle size in apple sauce and apple dispersion, respectively. However, Schijvens, Vliet, and Dijk (1998) and Espinosa et al. (2011) reported that the apparent viscosity and the yield stress decreased with decreasing particle size in apple sauce and apple puree, respectively.

2.3.2.3. Particle Shape

Real particles are not spherical and a wide range of shapes are possible. There are some expressions that can be used to define particle shape such as acicular (needle-shaped), crystalline

(geometric shape), angular (sharp-edged), flaky (plate-like), dendritic (branched crystalline shape) and spherical (global shape). However, in the study of the flow behavior of a suspension, the shape of solid particles is assumed to be limited to simple shapes such as axisymmetric particles, i.e., those with rotational symmetry. These shapes include rotational ellipsoids, i.e., prolate spheroids, and circular cylinders, i.e., disks and rods (Fig. 2.6) (Barnes 2000; Mewis and Wagner 2012).

Fig. 2.6. Basic geometries of particles: (a) prolate spheroid, (b) disk and (d) rod or fiber
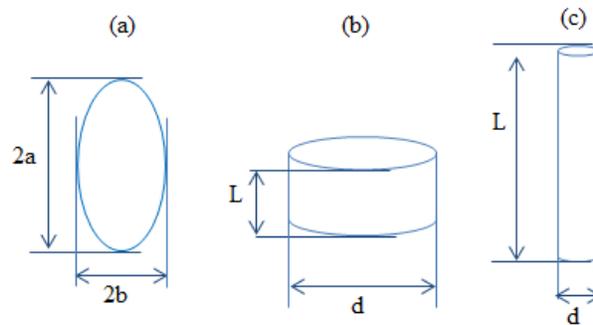
The shape of a particle can be described by different parameters such as roundness and aspect ratio. By definition, the aspect ratio is the major to the minor dimension ratio of a particle, e.g., a/b in Fig. 2.6 (a) (Jennings and Parslow 1988; Gantenbein et al. 2011). Aspect ratio is used widely to describe the effect of shape of particles on the flow behavior of suspensions. It should be noted that two particles with different shapes may have the same aspect ratio, while they display different flow behavior. As per Mewis and Wagner (2012), particles with sharp edges move differently than other particles in a flow field due to a strong effect of sharp edges on the drag force acting on the particle (Mewis and Wagner 2012).

In order to investigate the effect of particle shape on the flow behavior of suspensions, most theoretical works have been carried out for dilute suspensions with a Newtonian continuous

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phase. In general, almost all studies have shown that increasing aspect ratio causes an increase in energy dissipation, poorer space-filling, lower Φ_m , and consequently an increase in the viscosity. As per Barnes (2000), at the same volume fraction, the increase in relative viscosity (η_r) of suspensions of non-spherical particles is in the descending order of rods > plates > cubes/grains > spheres. The relative viscosity (η_r), which is used widely in proposed models for flow behavior of suspensions, is defined as:

$$\eta_r = {}^{\eta}/_{\eta_0}$$

Eq. 2.22

where η is the viscosity of suspension and η_0 is the viscosity of the continuous phase. There are some proposed equations that can be used over a limited solid volume fraction range for non-spherical particles. For example, an equation given by Shaqfeh and Fredrickson (1990):

$$\eta_r = 1 + \frac{4\Phi q^2}{3\ln(^1/_\Phi)}\left[1 - \frac{\ln\ln(^1/_\Phi)}{\ln(^1/_\Phi)} + \frac{C_c}{\ln(^1/_\Phi)}\right]$$

Eq. 2.23

where q is the aspect ratio of the particles: long radius/short radius, C_c =0.663 for slender cylinders and C_c =−0.202 for slender spheroids (Shaqfeh and Fredrickson 1990). However, in most proposed models, the effect of particle shape on the viscosity is shown by the intrinsic viscosity, for instance in the modified Einstein's equation (Eq. 2.17). The intrinsic viscosity may be obtained by different formulae for different particle shapes. For prolate ellipsoids it can be obtained by (Barnes 2000; Genovese 2012):

$$[\eta] = \frac{14}{15} + \frac{q^2}{15(\log 2. q - 3/2)} + \frac{q^2}{5(log2. q - \frac{1}{2})}$$

Eq. 2.24

for oblate ellipsoids:

$$[\eta] = \frac{16}{15} \frac{q}{tan^{-1}q}$$

<div align="right">Eq. 2.25</div>

for rod-like particles:

$$[\eta] = 0.07q^{5/3}$$

<div align="right">Eq. 2.26</div>

and for disc-like particles:

$$[\eta] = 0.3q$$

<div align="right">Eq. 2.27</div>

Kitano, Kataoka, and Shirota (1981) proposed an empirical model to describe the effect of particle shape on the relative viscosity of fiber-filled suspensions:

$$\eta_r = (1 - \Phi/D)^{-2}$$

<div align="right">Eq. 2.28</div>

where D is a constant related to the packing geometry of the filler and corresponds to the maximum packing fraction of particles (Φ_m) in Maron-Pierce's equation (Kitano, Kataoka, and Shirota 1981). The value of D decreases as the aspect ratio of suspended particles increases, e.g., the magnitude of D was reported to be 0.68 and 0.44 for particles with an aspect ratio of 1 and 6-8 (rough crystal) (Metzner 1985). Yoo and Rao (1994) used this model for describing the flow behavior of tomato suspensions. Based on the D values, they showed that the particle shape in tomato puree samples appears to be close to an irregular spherical shape (Yoo and Rao 1994).

Moelants, Cardinaels, Jolie, et al. (2014) showed that the yield stress increases in tomato suspensions containing broken cells with irregular shape particles compared to those containing particles with more regular shape (Moelants, Cardinaels, Jolie, et al. 2014). Due to the irregular shape of plant particles, they can interact with each other even at low particle concentrations in plant tissue suspensions (Bayod, Willers, and Tornberg 2008).

2.4.   Knowledge gap

Based on this literature review, the following knowledge gaps have been found in a systematic understanding of how the rheological properties of plant tissue suspensions arise from their components. Accordingly, this thesis is aimed at addressing these concerns through a comprehensive experimental study of potato and carrot powder suspensions.

1. Systematic analyses of the contribution of the dispersed phase and the continuous phase on the overall rheological properties of plant-tissue suspensions are limited.

2. The dry sieving technique has not been used for plant tissue powders to prevent loss of the cell contents and to generate suspensions with a well-defined dispersed phase.

3. A clear role for the soluble components in the continuous phase (originally present in the dispersed phase) on the rheological behavior of plant tissue suspensions has not been reported.

3. Flow Behavior of Native Corn and Potato Starch Granules in Aqueous Suspensions[1]

Abstract

The flow behavior of native corn and potato starch granule suspensions prepared in a concentrated sucrose solution has been investigated. Measurements were performed using a rotational rheometer with a concentric cylinder geometry. Starch suspensions were dilute to semi-concentrated (1% to 25% by volume). Shear and dynamic viscosity were measured by shear flow and dynamic oscillatory testing at 20, 50 and 80°C. The starch suspensions exhibited essentially Newtonian behavior at all solid contents, although at higher solid volume fractions there was evidence of slight shear thickening. The relative viscosity of suspensions increased with increasing starch granule content, and the data conformed well to Maron-Pierce's equation. An increase in maximum packing fraction and gravitational depletion of the starch granules with increasing temperature resulted in lower relative viscosities at higher temperatures. Also, the relative viscosities of potato starch granule suspensions with bigger, more oval and anisometric particles were lower than those of corn starch suspensions where granules were closer to sphericity but were angular in shape. Oscillatory shear testing results showed the presence of viscoelastic properties at intermediate solid volume fractions at low frequencies; in addition, the relative shear viscosity was higher than the relative dynamic viscosity, probably due to the formation of shear-induced structures during the shear flow test.

Keywords: Corn starch, potato starch, suspension, viscosity, solid volume fraction, temperature

3.1. Introduction

Starch is the most widely consumed carbohydrate food ingredient, providing 75%-80% of the total caloric intake of human beings (Bertolini 2009). This natural material is used in different applications, such as a thickener and stabilizer for control of food consistency, and as a texture enhancer in the food industry, mostly in the form of a suspension (Okechukwu and Rao 1995; Jobling 2004). It is also used extensively in other industries including the paper, petroleum and ceramics sectors (Gregorová, Pabst, and Bohačenko 2006; Yoon and Deng 2006) where its unique properties, such as low cost, availability, biodegradability and renewability, make it an attractive industrial material (BeMiller 2007). Therefore, different aspects of starch properties have been investigated by many researchers.

Starch suspensions with low to intermediate solid volume fractions are regularly encountered in manufacturing processes. Achieving desirable flow properties for these suspensions is therefore important, for instance, in process design and selection of process equipment (e.g., pump selection) since appropriate matching of equipment to suspension properties critically affects the quality of the final product (Karaman et al. 2011; Smith 2011).

Viscosity is the primary physical characteristic of the flow behavior of suspensions and is governed by the following factors: (i) viscosity of the suspending medium η_0; (ii) shape, and often the size, of the particles; (iii) volume fraction of particles in the suspension, Φ; (iv) thermodynamic conditions of the system, i.e., temperature T and pressure P. Then, the general state equation for the viscosity of a suspension can be written as (Barnes 2000; Rao 2013):

$$\eta = f(\eta_0, P_a, d, \Phi, T, P) \hspace{4cm} \text{Eq. 3.1}$$

where the aspect ratio, P_a, is used to define the shape of a particle of size d.

This work has a threefold purpose: first, to describe the viscosity changes in starch suspensions containing particles with different solid volume fractions, and with granules of different shapes and sizes. Second, to analyze the effect of temperature, through its effect on the properties of the suspending medium, and thirdly, to evaluate whether suspension structure effects manifest themselves differently depending on the mode of viscosity measurement.

We used shear flow and dynamic oscillatory shear experiments for measuring the viscosity of starch suspensions. Shear flow experiments provide useful information for control of real processes because the suspension is subject to large deformations. During a shear flow test the native structure of the suspension is disrupted, changing any understanding of how the structure of the suspension might be affected by the presence or absence of shear stresses (Ahmed and Ramaswamy 2007; Augusto and Vitali 2014). Dynamic oscillatory shear tests were therefore also used to characterize our starch suspensions with the focus on the properties of the suspensions assessed by an oscillatory shear deformation rather than a continuous shearing process.

3.2. Theoretical

3.2.1. Relative Viscosity Models

The relative viscosity (η_r) is the viscosity of a suspension (η) divided by the viscosity of the continuous phase (η_0):

$$\eta_r = {}^{\eta}/_{\eta_0} \qquad \text{Eq. 3.2}$$

Many models have been presented for describing how the relative viscosity (η_r) depends on the suspension's concentration. The most simple description of the η_r of a suspension is the theoretical equation of Einstein valid for low particle concentrations in which the effects of other

particles are neglected and where particle size has no effect (Barnes, Hutton, and Walters F.R.S. 1993):

$$\eta_r = 1 + 2.5\Phi$$

Eq. 3.3

Another well-known expression that is valid for monodisperse spherical particle distributions is the semiempirical equation of Krieger and Dougherty, which is mostly used for non-dilute suspensions (Krieger and Dougherty 1959):

$$\eta_r = (1 - \frac{\Phi}{\Phi_m})^{-[\eta]\Phi_m}$$

Eq. 3.4

where Φ_m is the maximum packing fraction of particles (where the viscosity of the suspension reaches an infinite value), and $[\eta]$ is the intrinsic viscosity (which is a function of particle aspect ratio). The intrinsic viscosity $[\eta]$ is defined as (Pabst, Gregorová, and Berthold 2006; Genovese 2012):

$$[\eta] \equiv \lim_{\Phi \to 0} \frac{\eta_r - 1}{\Phi}$$

Eq. 3.5

The maximum packing fraction (Φ_m) depends on the particle size and shape distribution, particle deformability, and the flow conditions (Barnes 2000; Willett 2001; Genovese 2012). For instance, polydispersity increases the value of Φ_m because the smaller particles can reside in gaps between larger ones (Zhou, Scales, and Boger 2001; Genovese 2012). For monodisperse spherical particles, the maximum possible packing is close to 74% (Pabst, Gregorová, and Berthold 2006). The maximum achievable packing in real disordered suspensions is lower and a value of 64% is reported for random close-packing of monodisperse spheres (Rintoul and Torquato 1996; Pabst, Gregorová, and Berthold 2006; Mueller, Llewellin, and Mader 2009).

Experimental data shows that for a variety of situations, the product of $[\eta]\,\Phi_m$ is often around 2 (Barnes 2000). Then, Krieger and Dougherty's equation (Eq. 3.4) can be simplified to the Maron–Pierce relation (Barnes 2000; Pabst, Gregorová, and Berthold 2006; Genovese 2012):

$$\eta_r = (1 - \frac{\Phi}{\Phi_m})^{-2} \qquad\qquad \text{Eq. 3.6}$$

In the Maron–Pierce relation for a given suspension system where Φ is varied, the only constitutive parameter is Φ_m; therefore, it can be used when the intrinsic viscosity $[\eta]$ is not known. Many researchers in the fiber suspensions field have used and recommended this equation for its suitability (Kitano, Kataoka, and Shirota 1981; Phan-Thien and Pham 2000; Pabst, Gregorová, and Berthold 2006).

3.2.2. Particle Shape and Size

The shape of a particle can be characterized by its aspect ratio (P_a), which is the most common shape descriptor in flow behavior studies. Particle shape is characterized by this parameter as the ratio of the major dimension to the minor dimension of the particle (Jennings and Parslow 1988; Gantenbein et al. 2011).

In a real system, the shapes of particles are polydisperse, so that there is a distribution in the aspect ratios, and this is not always easy to define. For this reason, an average aspect ratio ($\overline{P_a}$) is calculated for the suspension (Pabst, Berthold, and Gregorová 2006; Pabst, Gregorová, and Berthold 2006). Also, since sharp edges have a strong influence on the drag on a particle, two different particles (such as cylinders and spheroids) with an identical aspect ratio will not move in the same way in a flow field (Mewis and Wagner 2012).

In addition to the shape of particles, the size and size distribution of particles can affect the flow behavior of a suspension. In real systems, the particle size distribution may be highly polydisperse and the maximum packing fraction (Φ_m) is very sensitive to it (Barnes 2000). A precise definition of particle size with one parameter is therefore not easy. For defining size where there is a distribution of sizes, the median size is the most common and convenient parameter. The median size (D_{50}) in a distribution is that size that splits the distribution into two equal parts with half above and half below this diameter (Hna and Fuerstenau 2003).

3.3. Materials and Methods

3.3.1. Suspension Preparation

The viscosity of starch suspensions was assessed considering the effective factors on the viscosity. Differences in starch granule properties were created by using two different starches: corn starch and potato starch. Unmodified food grade corn and potato starch with ambient moisture content purchased locally were used for preparing starch granule suspensions. The apparent particle size distribution of the starch granules was measured with a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK).

As the continuous phase, 60 grams of sucrose were dissolved in 40 grams of water, i.e., a 60% w/w sucrose solution was used instead of water in order to prevent sedimentation of starch granules under the influence of gravity and to prevent their gelatinization when suspensions were heated. Sucrose was purchased locally. The viscosity values of our sucrose solutions were measured at 20, 50 and 80°C as 0.07, 0.02 and 0.01 Pa.s, respectively (see below for details). Various amounts of starch granules were dispersed in the sucrose solution to create six types of suspensions. Freshly made suspensions (less than 1 hr old) were first hand mixed with a spatula and then stirred with a magnetic stirring bar for 15 minutes at room temperature to form a

homogeneous and well dispersed suspension prior to being poured carefully into the rheometer's concentric cylinder geometry.

The six different solid volume fractions (Φ) of the starch granule suspensions were 1%, 5%, 10%, 15%, 20% and 25% to represent dilute and semi-dilute regimes. Starch volume fractions were calculated based on the density values of 1.49 g cm^{-3} for corn starch and 1.47 g cm^{-3} for potato starch (Talou et al. 2011).

3.3.2. Rheological Measurements

Flow behavior of the starch granule suspensions was studied using a rotational rheometer (AR 2000; TA Instruments, New Castle, DE, USA). The suspensions were tested in a concentric cylinder (stator radius: 15mm, rotor radius: 14 mm, and set gap (the distance between the bob and bottom): 5.92 mm). For each solid volume fraction, approximately 20 ml of suspension was loaded into the sample cup.

Rheological measurements were carried out by applying shear flow followed by dynamic oscillatory shear on the same sample. The shear flow measurements were conducted in a continuous ramp with shear rate increasing from 0.1 to 143.1 s^{-1}. Oscillatory shear tests were conducted as a frequency sweep with angular frequency ranging from 0.6 to 50 rad s^{-1} and a fixed oscillatory stress of 1 Pa (to ensure a reliable response for the low viscosity suspensions).

For characterizing the temperature dependence of suspension flow behavior, all measurements were performed at three different temperatures: 20, 50 and 80 °C. Temperature control was achieved via a Peltier system installed by the manufacturer in the Couette cell. Therefore, a flow of water through the Peltier heat exchanger jacket allows all desired temperatures to be achieved accurately. We carried out the measurements of viscosity on a given

suspension with the following protocol: (i) shear flow at 20°C (ii) dynamic oscillatory shear testing at 20°C (iii) shear flow at 50°C (iv) dynamic oscillatory shear testing at 50°C (v) shear flow at 80°C (vi) dynamic oscillatory shear testing at 80°C. All suspensions were prepared and analyzed in two replications.

3.4. Results and Discussion

We begin by showing the shear rheology of native corn and potato starch granule suspensions as a function of applied shear stress at 20 °C. We note that with the AR 2000, the viscosities measured at stresses lower than 0.1 Pa were not completely reliable since the results between replicates showed high deviation i.e., coefficient of variation more than 10%.

The shear rheology of the suspensions at 20°C is shown in Fig. 3.1 (as an example, the flow curve of some of potato and corn starch granule suspensions are shown in the Appendix). The standard deviations between replicates were very small; therefore, most error bars are too small to be visible relative to symbol size. Each data point in Fig. 3.1 is the average of the corresponding shear stress and viscosity for the two replications and then the standard deviation is calculated for these data. The relative viscosity of suspensions is clearly affected by the volume fraction of starch granules (Fig. 3.1).

Fig. 3.1. Relative shear viscosity of corn starch (a) and potato starch (b) suspensions at 20 °C as a function of the applied shear stress. Solid volume fractions are: 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■).
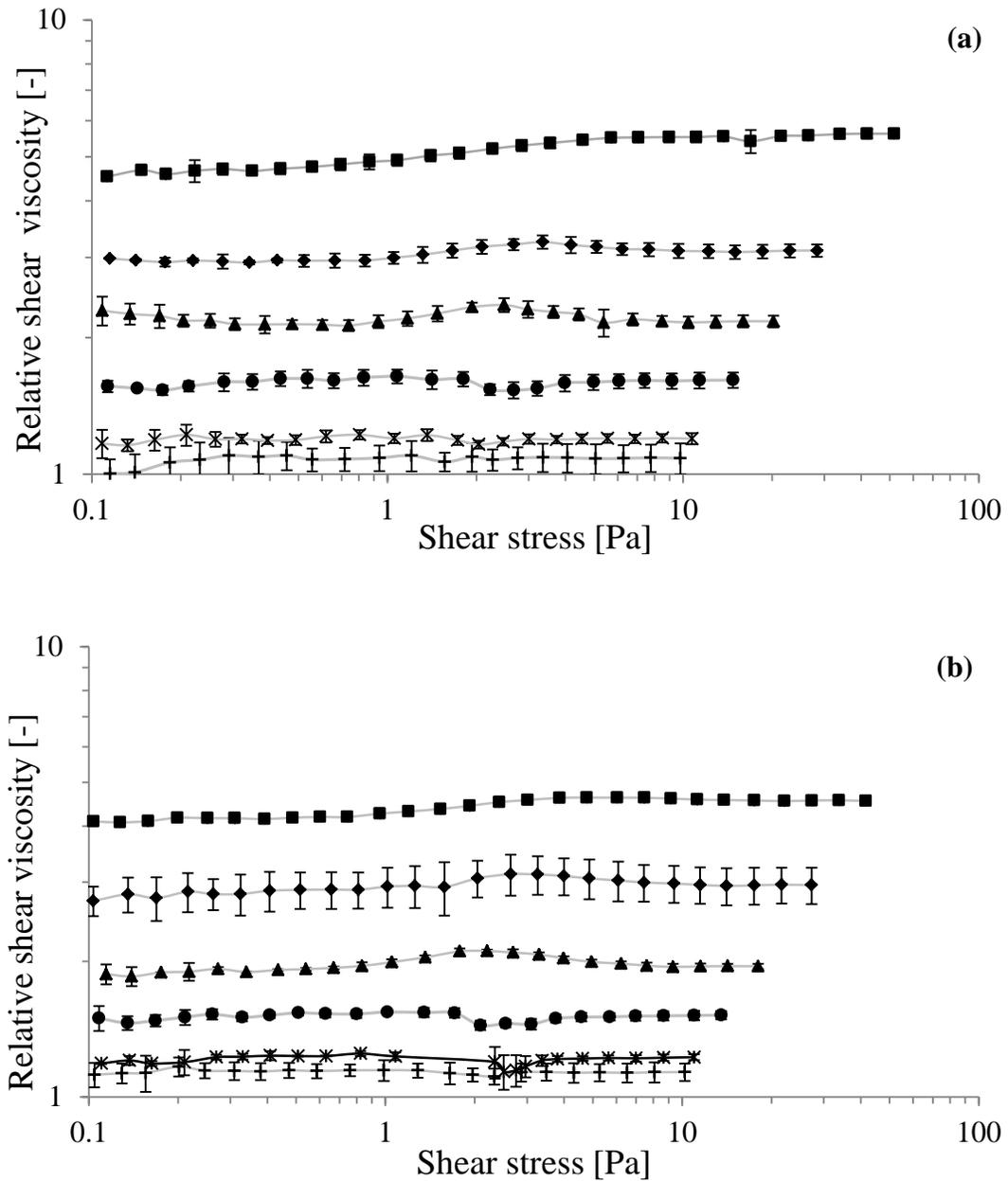
Based on Fig. 3.1, the suspensions show almost linear behavior, i.e., the viscosity remained essentially constant, although upon increasing the volume fraction there is evidence of

shear thickening behavior. Other researchers, see for example (Crawford et al. 2013), have reported that a suspension of starch particles, at sufficiently high concentrations, exhibits shear-thickening behavior, i.e., the viscosity increases with increasing shear stress. From a comparison of Fig. 3.1a and 1b, it is apparent that corn starch suspensions at intermediate solid volume fraction showed shear-thickening to a greater extent than potato starch suspensions. Corn starch granule suspensions at 25% solid volume fraction showed an increase of 24% in relative viscosity over the range of shear stress from 0.1 to 42 Pa while the relative viscosity of potato starch suspensions of the same concentration increased by only 11% over the same range of shear stress. This has been related to effects caused by starch granule properties, such as size and shape, since the nature of shear thickening depends on the properties of the dispersed phase and is governed by hydrodynamic interactions (Barnes, Hutton, and Walters F.R.S. 1993; Okechukwu and Rao 1995; Mewis and Wagner 2012). The more pronounced shear thickening in the higher solid volume fraction corn starch suspensions, where granule size is smaller than in potatoes, is consistent with the observations of others who have reviewed the role of particle size on shear thickening, see for example (Keller and Keller Jr. 1991). Very similar patterns were observed for suspensions tested at 50 and 80 °C, but shear thickening at intermediate solid volume fractions was not as evident.

For the purpose of showing the dependence of the viscosity on solid volume fraction at the three temperatures, relative viscosities were plotted against volume fractions of starch granules (Fig. 3.2). The reported values of η_r for each of the volume fractions in Fig. 3.2 were the average of all corresponding relative shear viscosity values, such as those shown in Fig. 3.1. Therefore, linear behavior was assumed for all Φ despite the slight shear thickening behavior

evident at higher volume fractions. The effect of various parameters on the relative viscosity of the corn and potato starch granule suspensions is discussed in the following subsections.

Fig. 3.2. Relative shear viscosity as a function of solid volume fraction for corn (solid symbols) and potato (open symbols) starch suspensions at 20 °C (■, □), 50 °C (♦,◊) and 80 °C (▲, ∆). Predicted values from Einstein's equation (Eq. 3.3) and Maron-Pierce's equation (Eq. 3.6) at different Φ_m (from Table 3.1), are also shown.
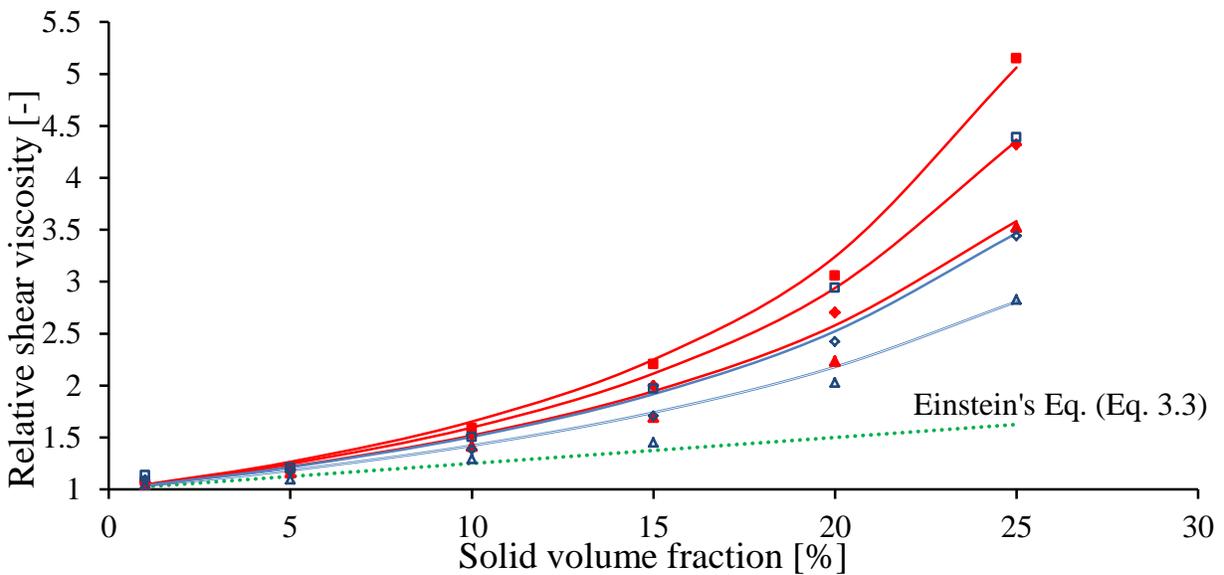
3.4.1. Effect of Solid Volume Fraction

According to Fig. 3.2, for both corn and potato starch granule suspensions, η_r increased with increasing Φ. Generally, the flow field is disturbed by the presence of solid particles, so that the energy dissipation, and thus the viscosity, increases (Willett 2001; Genovese 2012). In addition, collisions between particles are more frequent with increasing Φ and this also increases the viscosity (Mewis and Wagner 2012).

The relative viscosities predicted by Eq. 3.3 and 3.6 are shown in Fig. 3.2. The determination of Φ_m in Eq. 3.6 either by experiment (e.g., sedimentation technique) or by analytical prediction has its limitations in providing reliable values for Φ_m (Liu 2000). We chose a method used by Liu (Liu 2000) to determine Φ_m directly from the shear flow data measured experimentally in our suspensions. To obtain Φ_m, the corresponding relative viscosity data for given volume fractions were inserted into the Maron–Pierce model (Eq. 3.6). By doing this and extrapolating the value of $1 - \eta_r^{-\frac{1}{2}}$ to 1, a value of Φ_m is obtained for each type of starch evaluated at the three temperatures (Table 3.1).

Table 3.1. Maximum packing fractions of corn and potato starch at different temperatures

| | Temperature [°C] | | |
	20	50	80
Corn starch	45%	48%	53%
Potato starch	48%	54%	62%

The values of Φ_m for starch suspensions in Table 3.1 are consistent with those determined by other techniques. Willett (2001) used a tapping method to measure Φ_m for corn and potato starch dispersed in either hexane or ethanol and also in the dry state. Values measured in the liquids were larger than Φ_m values measured on the dry starches. For the dry state, Φ_m values were 37% and 57% for corn and potato starch, respectively. Values measured in ethanol and hexane for potato starch were similar in magnitude at $\Phi_m = 60\%$. For corn starch, values differed depending on the solvent: in ethanol the value of Φ_m was 57% and in hexane 55%.

Based on differences between the thermal expansion of starch particles and the continuous phase, temperature influenced Φ_m. Greater thermal expansion of the continuous

phase relative to the expansion of the starch phase effectively creates a larger volume for the same amount of solid particles. This increases the total volume of a suspension, resulting in an increase in the volume of particles that can pack into it before jamming. This thermal expansion was not due to starch expansion since starch granules do not swell in our high sucrose content continuous phase; the onset temperature of swelling of the granules is noticeably delayed (Bean and Yamazaki 1978; Kohyama and Nishinari 1991; Chiotelli, Rolée, and Le Meste 2000; Gonera and Cornillon 2002).

As shown in Fig. 3.2, the agreement of η_r values from experimental data and the predictions of the Maron–Pierce equation is fairly good. On the other hand, as expected because of its dilute regime applicability, the measured viscosity of suspensions showed obvious deviation, even at $\Phi = 10\%$, from Einstein's equation (Eq. 3.3).

3.4.2. Effect of Temperature

In an examination of temperature effects on the relative viscosities of the starch granule suspensions, we performed experiments at three different temperatures: 20, 50 and 80 °C. A suspension was tested first at 20 °C and then at 50°C and then 80 °C. The temperatures were selected after preliminary experimentation. For example, the selected temperature was not so high to cause thermally induced damage, e.g., gelatinization, to the starches in these low-free water suspensions. Thermal damage to starch is governed by both temperature and moisture content so water availability affects the thermal processing of starch (Bertolini 2009). The presence of sucrose affects water availability, retarding gelatinization and swelling of starch granules in the aqueous system (Chiotelli, Rolée, and Le Meste 2000; Bertolini 2009). In our 60% w/w sucrose solution, the concentration is such that the properties of starch granules were not altered even at temperatures as high as 80 °C. Bean and Yamazaki (Bean and Yamazaki

1978) reported that starch swelling in 60% sucrose solution occurred at about 95 ℃. Hence, all temperature effects on the viscosity of the suspensions are primarily related to changes in the continuous phase.

From Fig. 3.2, it can be observed that the relative viscosity in both corn and potato starch granule suspensions decreases with increasing temperature. As a result of the temperature change, the density of the 60% w/w sucrose solution drops from 1286.61kg m^{-3} at 20°C to 1270.61 kg m^{-3} at 50°C and 1251.99 kg m^{-3} at 80°C (ICUMSA 1990). Although at 20°C, the suspensions are neutrally buoyant, the shift in density of the 60% w/w sucrose solution to slightly lower values results in a loss of density matching in the suspension so that there is a propensity for sedimentation of the particles. In this work, all tests on a single suspension for all three temperatures took less than 45 minutes. We found that this time scale is not sufficient for an obvious sedimentation at the two higher temperatures. However, the slight particle-fluid density mismatch is enough that at 50°C, after 1.5 hours some sedimentation was apparent and after almost 8 hours complete sedimentation occurred, while the starch particles sediment at a faster rate at 80°C, so that initial sedimentation was noticeable by 45 minutes and complete sedimentation was achieved after 3 hours. Therefore, during the course of experiments at 50 and 80 °C, some degree of depletion of starch particles in the annulus containing the suspension may have occurred. This slight depletion will lead to a local difference in granule concentration. Since the measured stress for calculating the viscosity would come from shearing of the somewhat thinned volume of fluid in the annulus (Brown and Jaeger 2012), the true volume fraction of the particles at 50°C is likely slightly smaller than the values used to create the plots of Fig. 3.2, and perhaps more so for measurements at 80°C.

3.4.3. Effect of Starch Granule Morphology

As shown in Fig. 3.2, the relative viscosities of corn starch suspensions were always higher than those of potato starch suspensions. The shape of particles is an important variable which affects the viscosity of suspensions (Barnes 2000; Pabst, Gregorová, and Berthold 2006; Mewis and Wagner 2012). The important effect of particle shape on the viscosity of a suspension is its influence on particle interactions, the most effective factor influencing the viscosity (Mueller, Llewellin, and Mader 2009). An extensive literature about the effect of particle shape on the viscosity of suspensions exists, see for example (Pabst, Gregorová, and Berthold 2006; Gregorová, Pabst, and Bouchet 2009; Fu et al. 2012). The effect of particle shape is basically related to the interactions between particles, with greater interactions for non-spherical particles compared to spherical particles. Therefore, in the suspensions containing particles with greater deviation from sphericity, more energy is dissipated during shearing and consequently the relative viscosity of the suspension increases.

Based on Fig. 3.3 (Willett 2001), it can be seen that corn starch granules are more polyhedral and more isometric, i.e., corn starch has an average aspect ratio very close to 1 while potato starch is more oval and anisometric with an average aspect ratio of 1.3–1.4. Therefore, based on aspect ratio, these two starches are not substantially different (Gregorová, Pabst, and Bohačenko 2006). However, it has been shown that a single number such as aspect ratio is not sufficient for defining the shape of a particle and the full effect of particle shape on suspension viscosity has yet to be explored in detail. Skripkiunas et al. (2005) found that sharp-edged particles increased the viscosity of suspensions of various types of cements, since sharp edges have a strong influence on the drag on a particle and therefore the viscosity of the suspension (Mewis and Wagner 2012). As can be observed in Fig. 3.3, corn starch has more sharp edges,

which leads to greater energy dissipation so that these suspensions exhibit higher viscosity compared to potato starch suspensions.

Fig. 3.3. Scanning electron micrographs of corn (a) and potato (b) starch. Reprinted from American Association of Cereal Chemists (Willett 2001)

(a)   **(b)**
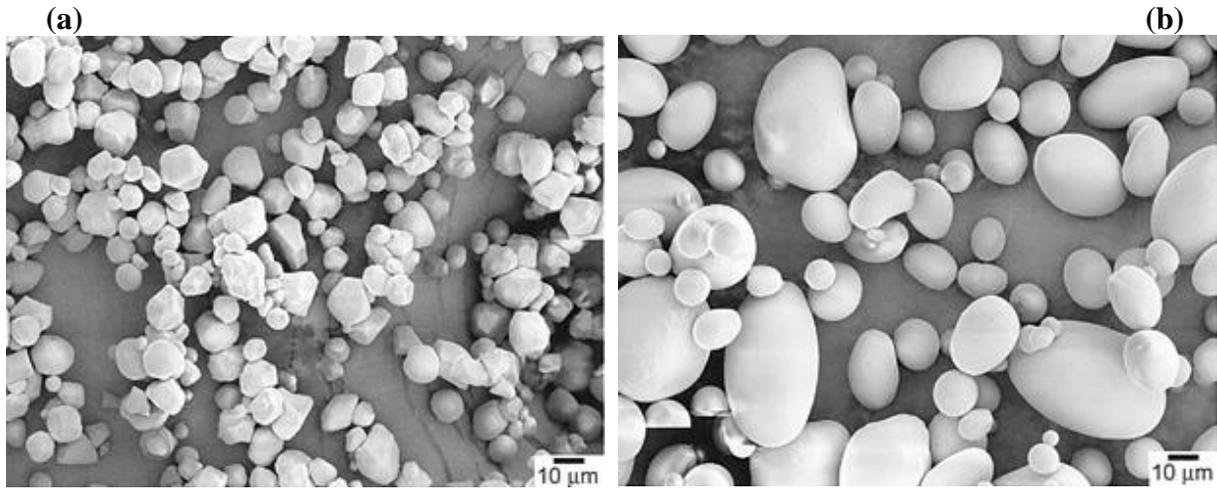
In addition to shape, the flow behavior of concentrated starch granule suspensions is strongly influenced by the particle size and size distribution (Barnes 2000; Genovese 2012). Based on results from size distribution measurements, the median sizes, D_{50}, for corn and potato starch are 13 and 39 µm, respectively (Fig. 3.4). The size distribution of starch granules was defined by an overall polydispersity index (PDI) which is calculated using the formula (Peker and Helvaci 2008):

$$PDI = \frac{\sum_i N_i |R_i - \bar{R}|}{N_T} \qquad \text{Eq.3.7}$$

where N_i is the number of particles of radius R_i, N_T is the total number of particles, and $\bar{R}$ the average radius of particles in the sample. The PDI for corn and potato starch granules was 4 and

16, respectively. This result shows that potato starch granules were more polydisperse and consequently the maximum packing fraction of potato starch granule suspensions was higher at all corresponding temperatures (Table 3.1). Also, corn starch granules are significantly smaller than potato starch granules (see Fig. 3.4). Thus, in addition to particle shape effects, corn starch suspensions with lower D_{50} and lower polydispersity exhibit higher relative viscosity at the same solid volume fraction. The decrease in viscosity of the potato starch granule suspensions associated with differences in size and distribution is due to the decrease in attractive interparticle forces (Pal 1996; Garcia, Le Bolay, and Frances 2003). Similar observations for other particles were made by other researchers while characterizing the rheological behavior of suspensions, see for example (Senapati, Mishra, and Parida 2010; Conrad et al. 2011).

Fig. 3.4. Particle size distribution of (a) corn starch (dashed line) and (b) potato starch (solid line)

Corn starch:
d(0.1): 8 µm
d(0.5): 13 µm
d(0.9): 21 µm

Potato starch:
d(0.1): 20 µm
d(0.5): 39 µm
d(0.9): 70 µm
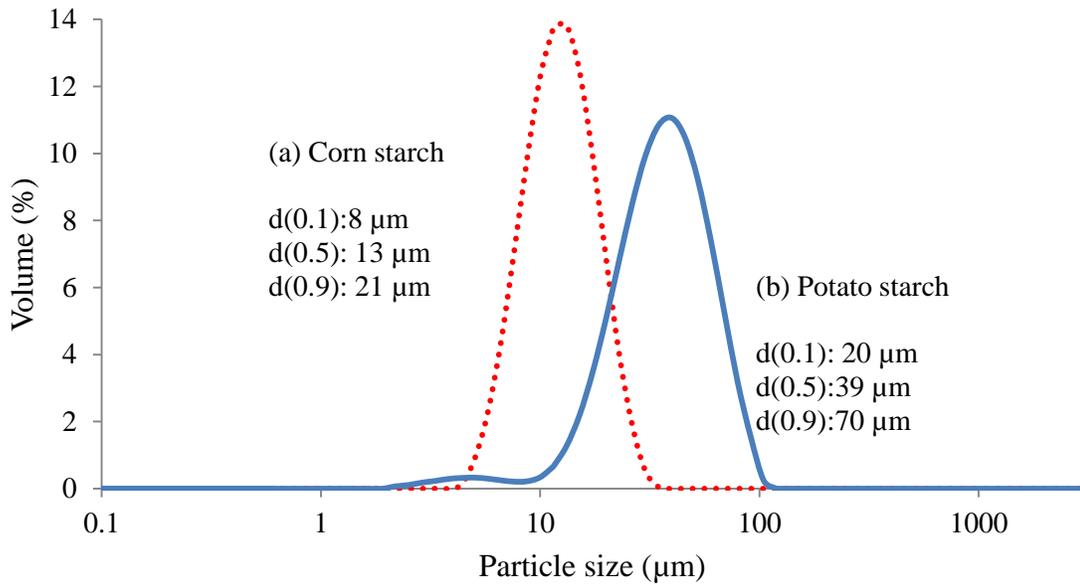
3.4.4. Dynamic Oscillatory Viscosities

The rheology of the corn and potato starch granule suspensions was studied with both shear flow and dynamic shear oscillatory tests so that viscosity could be compared under different types of deformation to probe any effects of structure induced by deformation type in more detail. For the oscillatory shear analysis, two components can be defined: (1) the imaginary, or loss, modulus (G'') and (2) the real, or storage, modulus (G'). The loss modulus (G'') measures the viscous dissipation per cycle of sinusoidal deformation of a suspension:

$$G''(\omega) = \frac{\sigma}{\gamma}\sin(\delta)$$

Eq. 3.8

where ω is angular frequency, σ is the stress, γ is the strain amplitude, and δ is the loss angle. In these dynamic mechanical experiments, G'' can be related to the real part of a dynamic viscosity (η') through the angular frequency:

$$\eta' = \frac{G''}{\omega}$$

Eq. 3.9

In more concentrated particulate suspensions, this viscosity may be affected by an elastic response, which can be quantified through an imaginary viscosity (η'') defined by:

$$\eta'' = \frac{G'}{\omega} = \frac{\sigma}{\gamma\omega}\cos(\delta)$$

Eq. 3.10

In such a situation, both the elastic component and the viscous component contribute to a complex viscosity (η^*) that is defined (Barnes 2000; Bourne 2002; Rao 2013), in a similar manner to the definition of a complex modulus:

$$\eta^* = \eta' - i\eta''$$

Eq. 3.11

The relative dynamic viscosity data of corn and potato starch suspensions are shown in Fig. 3.5 (a)-(d). Fig. 3.5(a) and (c) only show the real part of the dynamic viscosity, whereas in Fig. 3.5(b) and (d), the scale is expanded so that the imaginary viscosities are shown on the same scale. Very weak elasticity is evident, but only for high volume fractions of granules.

Fig. 3.5. Relative imaginary (hachure symbols) and dynamic viscosity vs. ω of corn (solid symbols) and potato (open symbols) starch suspensions with Φ: 1% (+), 5% (*), 10% (○), 15% (Δ), 20% (◊) and 25% (□).
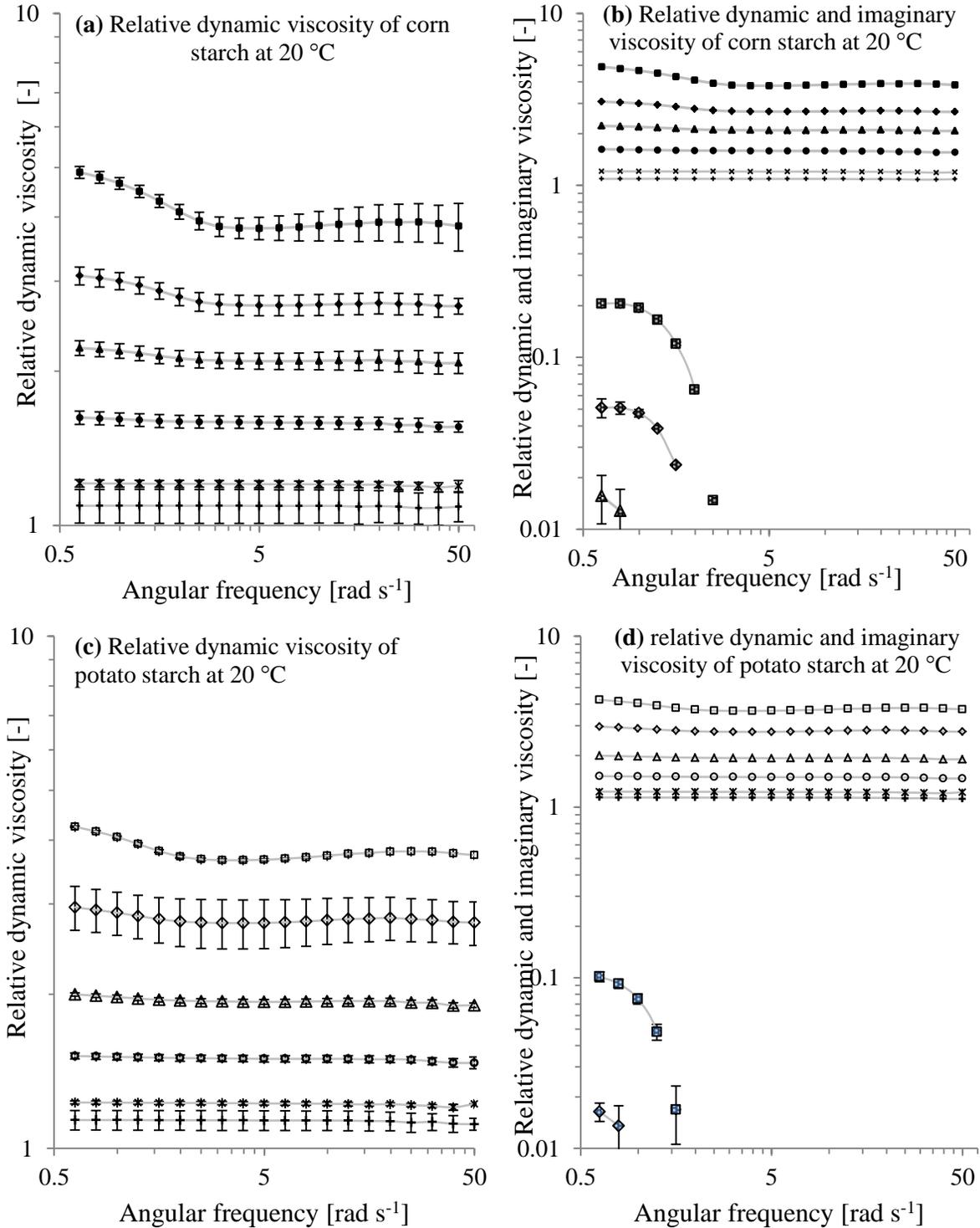
At low volume fractions, for both types of suspensions, viscosity is unaffected by increasing angular frequency. But, at the higher volume fractions, there is evidence that the viscosity is greater at lower angular frequencies, dropping to a lower common value at higher angular velocities. As shown in Fig. 3.5(b) and (d), at the three highest solid volume fractions for corn starch and the highest two for potato, meaningful values for the imaginary viscosity are evident (albeit small). However, these only exist for the lowest values of the angular velocity. This is most likely due to the formation of weak structures in the suspensions arising from relaxation following the preceding shear flow step or the formation of shear-induced structure during this large deformation analysis (Grizzuti et al. 1993). Similar structural changes upon evaluation of dynamic properties after completion of shear flow experiments have been observed for a lyotropic liquid crystalline solution (Valdes et al. 1993). Therefore, in the more concentrated starch granule suspensions, the existence of weak structures gave rise to a weak elastic response and a resistance to flow. For validating this result in more concentrated suspensions, the oscillatory test was applied on fresh suspensions (10% and 25%) in which the shear flow test was not applied before the oscillatory test. Additionally, the oscillatory test was conducted from high to low frequency after the shear test. Identical results were obtained (not reported here). The higher viscosity seen in Fig. 3.5(a) and (c) at low ω is also associated with this structure. The dynamic viscosity of the suspensions gradually approaches a constant value for a specific solid volume fraction so that the suspensions show a constant value for dynamic viscosity similar to that observed in the steady shear tests.

The changes in the dynamic viscosity of starch suspensions with angular frequency were similar at 20, 50 and 80 °C. However, measurable imaginary viscosities at 50 °C existed only for Φ of 20% and 25%, with lower values than those at 20 °C. No imaginary viscosities were

measurable at 80 °C, indicative of creation of more space for movement of particles in the more concentrated starch suspensions at this temperature so that weak elasticity from structuring of starch granules is absent.

3.4.5. Comparison between Relative Shear and Dynamic Viscosities

In Fig. 3.6 we show the shear viscosity vs. the dynamic viscosity for corn and potato starch suspensions analyzed at the three temperatures. The solid symbols were obtained by calculating the average for all relative shear viscosity and dynamic viscosity data in Fig. 3.1 and 3.5. The relative viscosity results from shear flow and oscillatory tests are in very good agreement except at the higher solid volume fractions at the two lower temperatures.

Fig. 3.6. Shear viscosity vs. dynamic viscosity for corn starch (▲) and potato starch (●) suspensions. Average of all measured viscosity data (solid symbols), average of first two data points (low frequency) for dynamic viscosity (open symbols)
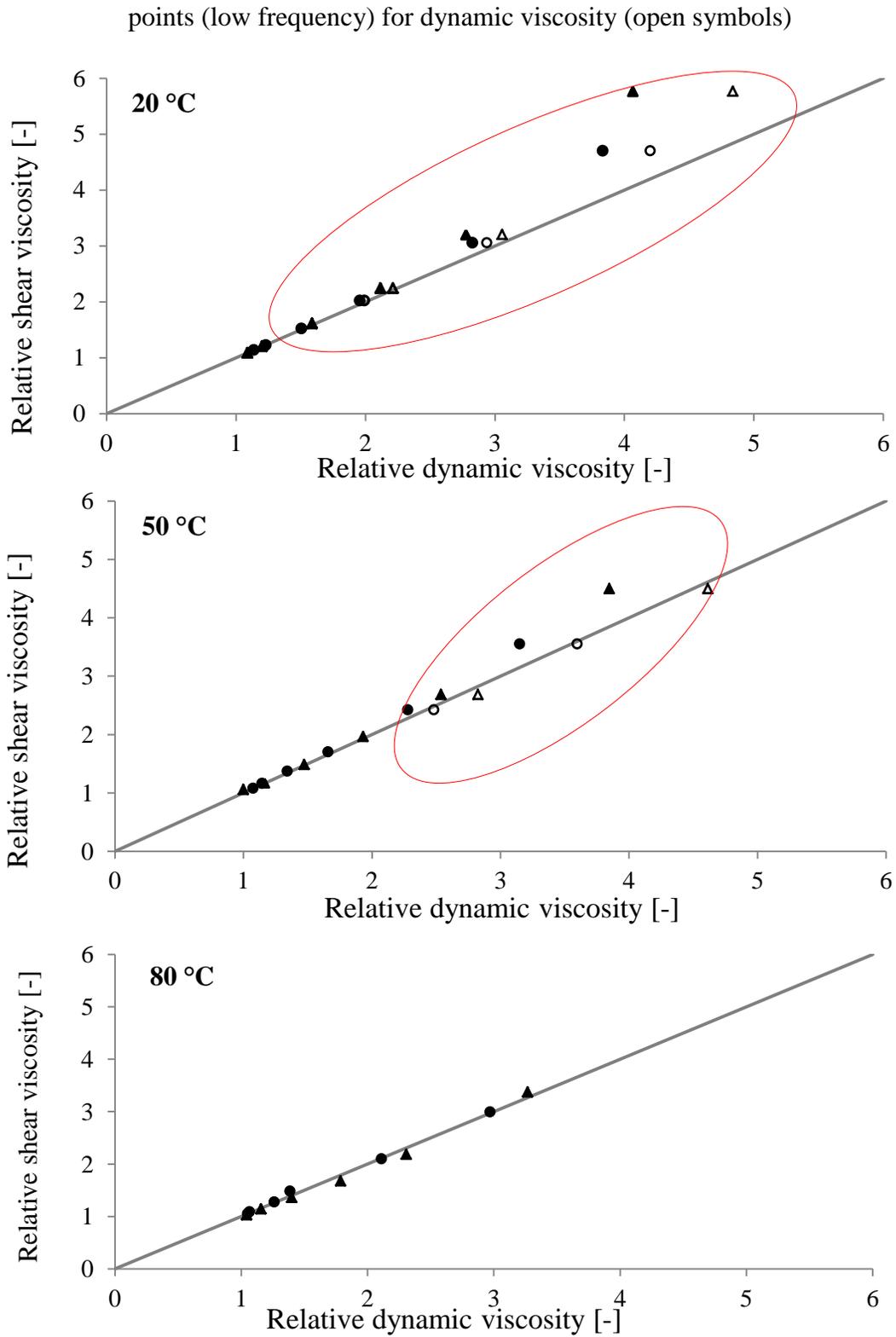
At the intermediate solid volume fractions of both starch suspensions at 20 and 50 °C, the relative shear viscosity is higher than the relative dynamic viscosity. A potential hypothesis relates this behavior (a slope greater than 1 in Fig. 3.6) to the temporary, flow-induced structuring of starch suspensions by the action of shear flow (Grizzuti et al. 1993) . The formation of shear-induced structures in a suspension at large deformation can result in shear thickening behavior (Valdes et al. 1993). This behavior was shown in Fig. 3.1, where shear thickening at intermediate solid volume fractions, i.e., 20% and 25%, was observed. Therefore, the difference between shear and dynamic viscosities is potentially due to the structural alterations that take place during shear testing. An interpretation of the structural alterations can be associated with the shape of the starch particles. Solid particles in a suspension rotate when subjected to a shear flow, and for non-spherical particles such as starch, the viscosity is dependent on particle orientation with respect to the direction of flow. At intermediate solid volume fractions, the rotational motion of non-spherical particles will be limited (Mewis and Wagner 2012). Therefore, it is plausible that the restricted motion of non-spherical starch particles in the concentrated regimes leads to the formation of shear-induced structures and results in a higher shear viscosity compared to the dynamic viscosity where the oscillatory nature of testing limits the rotational orientation.

Upon cessation of shear flow, i.e., before the dynamic oscillatory test begins, the suspension still preserves much of this shear-induced character. As a result, no significant difference would be observed between the shear viscosity and the dynamic viscosity of the suspension at the beginning of dynamic testing, i.e., at the low frequencies. To illustrate this, the average of the dynamic viscosity at the two lowest frequencies (0.63 and 0.79 rad s^{-1}) was calculated (shown in Fig. 3.6 by open symbols). As a result, the dynamic viscosities of corn and

potato starch suspensions are much closer to their corresponding shear viscosities when measured in their start-up condition instead of being averaged over the whole frequency range.

3.5. Conclusions

This paper presents a comprehensive study on the flow behavior of native corn and potato starch aqueous suspensions at low to medium concentrations. It has been shown how key parameters, i.e., the morphology of the starch granules and their volume fraction, and the temperature of the continuous phase influence the viscosity, as measured by two different techniques. Starch suspensions exhibited essentially Newtonian behavior at all solid contents up to 25%, with the relative viscosity as a function of solid volume fraction being described well by the Maron-Pierce equation. Even at intermediate volume fractions of particles, the formation of weak structures and their elastic effects on the viscosity of suspensions was evident, so that a direct comparison of viscosities from shear flow tests and their oscillatory shearing counterparts needs to consider these structural features and how they arise.

3.6. References

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Concentrated Metal Oxide Suspensions." *Chemical Engineering Science* 56 (9): 2901–20.

4. Shear Flow Behavior of Aqueous Suspensions of Potato Parenchyma Powder

Abstract

The shear flow behavior of plant tissue suspensions is an important topic in many food process technologies. A rotational rheometer equipped with concentric cylinders was employed to study aqueous suspensions of potato parenchyma. Potato powder suspensions were prepared from two different particle sizes, i.e., d(0.5)= 34 and 79µm, and with a range of solid volume fraction (Φ), from the dilute to the more concentrated, i.e., Φ=1% to 25%. A concentrated sucrose solution (60% w/w) was used as the continuous phase to maintain particle buoyancy. The shear flow properties were measured at T= 20, 50 and 80 °C. Potato powder suspensions obeyed a power-law equation in the dilute regime while the Herschel-Bulkley equation was the best fit for almost all semi-dilute and more concentrated suspensions. With increasing Φ, particle size and temperature, a gradual development of shear-thinning behavior was evident, i.e., $0.4 <$ power-law index (n) < 1, which coincided with an increase in the consistency factor ($0.01 < k < 38$ Pa.s^n) and the development of a yield stress ($0 < \sigma_y < 7.5$ Pa). Changes in the flow behavior of potato powder suspensions are the results of an alteration in the properties of both the continuous phase and the dispersed phase. A plausible mechanism is proposed in which pectin polymers play an important role in the flow behavior of potato powder suspensions in terms of their solubilization into the continuous phase from the dispersed phase particles. The potato powder suspensions therefore behaved very differently to potato starch suspensions. The flow behavior of these suspensions is dominated by the effect of intracellular and intercellular components in the potato powder particles, particularly pectin polymers, that alter the properties of the continuous phase.

Keywords: Potato parenchyma powder, suspension, viscosity, solid volume fraction, temperature, particle size

4.1. Introduction

Many foods are suspensions in which solid particles are dispersed in a liquid phase (Walstra 2002). The main parameters affecting the flow behavior of suspensions are the viscosity of the continuous phase, the volume fraction of solids in the suspension, temperature, and particle morphology such as shape and size (Barnes 2000; Alvarez, Fernández, and Canet 2004; Fischer et al. 2009). The manufacture of fluid-like plant-tissue-based food suspensions, e.g., different purees, soups and sauces, is in high demand for pre-prepared and convenience foods (Alvarez and Canet 2001; Alvarez, Canet, and Fernández 2007; Moelants, Cardinaels, Van Buggenhout, et al. 2014). Understanding, the flow behavior of these suspensions is important in different aspects of production, such as process performance, and in design of equipment (Alvarez, Fernández, and Canet 2004).

A highly simplified structure of a plant at various size scales is shown in Fig. 4.1. Cell properties such as size and shape vary in different plants. In most plants, the size of the cell ranges from 50 to 500 µm (Walstra 2002). Also a wide range of shapes is observed for the cells in different plants, e.g., polyhedral cells in potato (Bateman and Basham 1976; Carpita and Gibeaut 1993; Jackman and Stanley 1995; Fuentes et al. 2014). These shapes and sizes are affected by processing, particularly by size reduction or heat treatment. By these processes, single cells or clusters of unbroken cells, broken cell fragments and cell wall fragments may be produced. Consequently, intercellular and intracellular materials will be released as soluble or insoluble materials (Bayod et al. 2005; Lopez-Sanchez, Nijsse, et al. 2011; Augusto and Vitali 2014). The intercellular and intracellular materials are mainly biopolymers such as cellulose,

pectin, hemicelluloses, lignin and proteins in addition to aqueous solutions of sugars, amino acids, organic acids or inorganic ions (Nobel 1970; Fry 1988). These biopolymers can play different roles in a suspension, for example, slowing down the sedimentation of particles and affecting interactions between particles in a suspension (Barnes 2000; Walstra 2002).

Fig. 4.1. Highly simplified structure of a plant at various size scales

| 5 cm | 0.5 mm | 50 μm | 1 μm | 0.6 nm |
| Organ | Tissue | Cell | Cell wall | Cellulose |
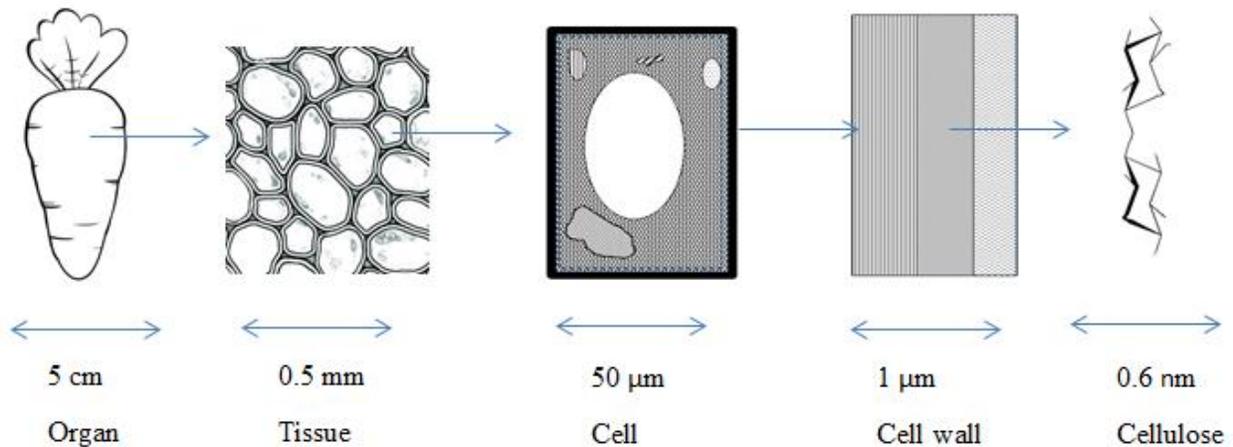
One of the most important intracellular component in potato parenchyma is starch, with approximately 15-20% of potato parenchyma's weight being starch granules while the rest is mostly water (about 80%) (Singh and Kaur 2016). Other than starch granules, the principal remainder of the dry matter in a potato cell is cell wall materials. Potato cell walls are particularly rich in pectin polymers, representing 55 to 60% of the cell wall's dry weight (Singh and Kaur 2016). Both starch granules and pectin polymers will affect the flow behavior of potato parenchyma powder suspensions if they are released from the cells during preparation of the suspensions or upon raising the temperature of the suspension (Moelants, Cardinaels, Van Buggenhout, et al. 2014).

Here, in the first of several articles where the rheological properties of plant-tissue based aqueous suspensions are studied, we describe the flow behavior of aqueous suspensions of potato parenchyma powder with particles of different sizes and different solids volume fractions. The effect of temperature on the flow behavior of these suspensions is also analyzed. The flow behavior of these suspensions is also compared with native potato starch granule suspensions of similar solids content at the same suspension temperature. This comparison has been made to provide insights into how exchange of components from the dispersed phase into the continuous phase affects suspension viscosity.

4.2. Materials and Methods

The flow behavior of potato powder suspensions was analyzed by a shear flow test considering the key factors influencing suspension viscosity: solid volume fraction, particle morphology and temperature.

4.2.1. Preparation of Potato Powder

Fresh potatoes were purchased locally. Potato powder was prepared from the same batch of potato. Potatoes were washed, peeled and cut into small pieces. Then they were reduced in size in a kitchen blender with distilled water, approximately in a 1:3 ratio. The resulting slurries were dried in an oven at 50°C for four days to remove excess water to reach a constant weight. The dried potato cake was disintegrated with a Retsch ZM200 mill (Retsch GmbH, Haan, Germany) with a mesh size of 80 µm.

A dry sieving technique was used to classify the potato powder particle sizes. A sieve shaker equipped with four different aperture sizes (202, 106, 75 and 63 µm) was used for sieving potato powder (960 g). Shaking was done for each 100 g of potato powder for about 40 minutes.

Each fraction retained on the various sieves was manually poured into five different beakers that were stored in a refrigerator until required. For investigating the effect of particle size on the viscosity of potato powder suspensions two different sizes were chosen: the potato particles yielded on the sieve with aperture sizes of 75 μm (75-106 μm), and particles passing through the 63 μm sieve ($<$ 63 μm).

The apparent particle size distribution of the potato powder in both size fractions was measured with a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK). This device measures the size of particles based on apparent sphericity (Moelants, Cardinaels, et al. 2013). Therefore, in potato powder suspensions with different particle shapes, the reported values of particle size are approximate. The particle size measurements of the selected potato parenchyma powder are reported in Fig. 4.2. The median size (d(0.5)) of potato particles retained on the sieve with aperture size of 75 μm, and potato particles passing through the sieve with aperture size of 63 μm were 79 and 34 μm, respectively. Median size is the size that splits the particle size distribution into two equal parts with half above and half below this diameter.

Fig. 4.2. Particle size distribution of potato powder passing the sieve size of 63 µm (solid line a),

and residing on the sieve size of 75 µm (dotted line b)
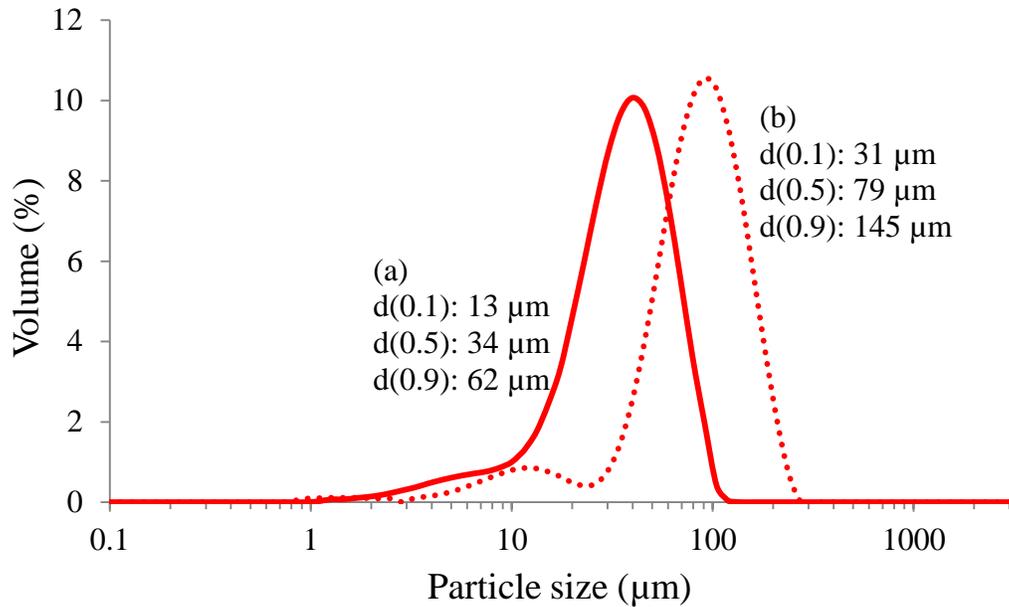
An overall polydispersity index (PDI) has been used to define the size distribution of particles in powder (Peker and Helvaci 2008):

$$PDI = \frac{\sum_i N_i |R_i - \bar{R}|}{N_T}$$

Eq. 4.1

where N_i is the number of particles of radius R_i, N_T is the total number of particles, and $\bar{R}$ the average radius of particles in the sample. Based on this equation, the PDI for potato powder with d(0.5)=34 and 79 µm is 18 and 53 µm, respectively. This means that both systems are highly polydisperse with greater polydispersity for the larger potato powder particles, i.e., d(0.5)=79 µm.

4.2.2. Solid Volume Fraction

Six different solid volume fractions were chosen to represent the dilute, i.e., $\Phi = 1\%$ and 5%, semi-dilute, i.e., $\Phi = 10\%$ and 15%, and more concentrated suspensions, i.e., $\Phi = 20\%$ and 25%.

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To obtain the exact solid volume fraction, the density of the particles was measured with a multivolume helium pycnometer 1305 (Micromeritics, Norcross, GA, USA). The density of potato powder was about 1530 kg m^{-3} for the particles of both sizes, i.e., d(0.5)=34 and 79 µm (Table 4.1). Then, the required weight of potato powder for a specific volume fraction was calculated based on the density value and the definition of Φ, i.e., the volume of a constituent i (Vi) divided by the volume of the suspension (V).

Table 4.1. The density values (kg m^{-3}) of the potato powder

Particles median size	Replication	Duplication 1	Duplication 2
d(0.5)=34µm			
	1	1538	1531
	2	1539	1532
	3	1542	1533
	Average	1539	1532
d(0.5)=79µm			
	1	1527	1526
	2	1526	1532
	3	1531	1529
	Average	1528	1529

4.2.3. Preparation of Potato Powder Suspensions

For the continuous phase, a 60% w/w sucrose solution was used in which 60 grams of sucrose were dissolved in 40 grams of water. This solution was used to create a restricted water environment and also to minimize sedimentation of potato powder particles by increasing the density of the continuous phase. By adding sucrose to water, the density of the solution increased to a value close to the density of the potato powder particles and this minimized the rate of sedimentation of particles under the influence of gravity. Sucrose was locally purchased. The viscosities of the sucrose solutions were 0.07, 0.02 and 0.01 Pa.s at 20, 50 and 80°C, respectively (see below for details).

Suspensions of six different solid volume fractions, i.e., $\Phi = 1\%$, 5%, 10%, 15%, 20% and 25% were prepared by adding appropriate amounts of solid particles. For preparing a homogeneous suspension, all suspensions were first mixed with a spatula. Then they were stirred for 15 minutes with a magnetic stirring bar at room temperature. Fresh suspensions (less than 1 hr old) were used for measurements. All determinations were carried out in duplicate.

4.2.4. Rheological Measurements

Shear flow behavior of the potato powder suspensions was characterized with a rotational rheometer (AR 2000; TA Instruments, New Castle, DE, USA). The suspensions were poured carefully into a concentric cylinder geometry comprised of a cup and bob. The concentric cylinder geometry had a stator and rotor radius of 15 and 14 mm, respectively, and a set gap at the bottom, i.e., the distance between the bob and bottom was 5.92 mm. Approximately 20 ml of prepared suspensions was loaded into the sample cup.

Shear flow behavior was studied by applying a shear flow test (a continuous ramp with shear rate from 0.2 to 143.1 s^{-1}). The effect of temperature was characterized by performing the measurements at three different temperatures: 20, 50 and 80°C. The measurements of flow behavior on a given suspension were carried out in the following manner: (i) shear flow at 20°C (ii) dynamic oscillatory shear at 20°C (iii) shear flow at 50°C (iv) dynamic oscillatory shear at 50°C (v) shear flow at 80°C and (vi) dynamic oscillatory shear at 80°C. The results of the dynamic oscillatory shear testing are not shown in this paper. All preparations and measurements were done in two replications.

4.2.5. Flow Behavior Analysis

A general flow curve can be described by equations relating shear stress σ and shear rate γ̇. The most simple equation is Newton's equation in which the shear stress (σ) is directly related to shear rate ($\dot{\gamma}$) via a constant number (the viscosity, η) (Barnes, Hutton, and Walters F.R.S. 1993; Barnes 2000):

$$\sigma = \eta\dot{\gamma} \qquad \text{Eq. 4.2}$$

When shear stress and shear rate data can be fitted to Eq. 4.2, the flow behavior is called Newtonian. In suspensions of hard-sphere particles at low solids content, the flow is generally Newtonian (Mueller, Llewellin, and Mader 2009), as has been illustrated for starch granules suspensions except at higher solid volume fractions (Sinaki and Scanlon 2016).

For describing non-Newtonian flow behavior, a well-known equation is the Power-law model given by:

$$\sigma = k\dot{\gamma}^{n} \qquad \text{Eq. 4.3}$$

where k [Pa.s^{n}] is the consistency factor and n [-] the power-law index. The power-law index n is equal to 1 for Newtonian fluids and ranges from 0 to 1 for fluids that are shear-thinning and higher than 1 for shear-thickening fluids (Barnes 2000).

Many different suspensions, including food product suspensions, show a yield stress, σ_y. The yield stress is the minimum required stress at which flow will begin in a suspension (Mullineux 2008). The Herschel–Bulkley model is a well-known model for describing flow behavior in a suspension with a yield stress (Steffe 1996; Ahmed and Ramaswamy 2006b; Moelants, Cardinaels, et al. 2013; Rao 2014):

$$\sigma = \sigma_y + k\dot{\gamma}^n \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \text{Eq. 4.4}$$

All the flow curves of potato powder suspensions were fitted to one of these equations (Eq. 4.2 to 4.4). The trend-line function in Microsoft Excel was used for Eq. 4.2 and 4.3, while for the Herschel-Bulkley equation (Eq. 4.4), the solver function in Microsoft Excel was employed.

4.3. Results and Discussion

4.3.1. Shear Flow Behavior

The shear stress vs. shear rate curves of potato powder suspensions of the two particle sizes with different solid volume fractions are shown in Fig. 4.3 (a-f) at three different temperatures. Each marked point in Fig. 4.3 represents the average values of the corresponding shear stress and shear rate data for the two replications. As shown in Fig. 4.3 (a-f), the standard deviations between replicates are smaller in the suspensions of smaller particles at the same temperature and solids content. This can be related to the particle sizes and the gap size between the stator and rotor. Based on the 1 mm gap between the two cylinders, there should be no edge effects on the measured flow properties if the maximum particle size is 100 µm or less. However, based on Fig. 4.2, the size measurements show that in the potato powder suspensions of the bigger particles, i.e., d(0.5)=79 µm, there is a small portion of particles above the 100 µm limit (90% of particles were smaller than 145 µm). Therefore, in the suspensions of d(0.5)= 79 µm, there was a portion of the particles that transgress the appropriate particle size for the apparatus. Phenomena associated with the particle size and the gap between the two cylinders can cause scatter in the data (Savage and Mckeown 1983). These phenomena are reported as the creation of rigid no-flow zones, locking and jamming of the particles and sudden alterations in the arrangement of particle arrays during a shear test in concentric cylinders (Cheng and Richmond 1978; Savage

and Mckeown 1983). These effects are particularly manifest for the more concentrated volume fractions.

Fig. 4.3. Flow properties of aqueous suspensions of potato powder at 20°C (a, b), 50°C (c, d) and 80 °C (e, f) with Φ = 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■)

50°C, d(0.5)=34μm   **(c)**

50°C, d(0.5)=79μm   **(d)**

d(0.5)=34μm, 80°C   **(e)**

Shear stress [Pa]

Shear rate [s⁻¹]

d(0.5)=79μm, 80°C   **(f)**

Shear stress [Pa]

Shear rate [s⁻¹]
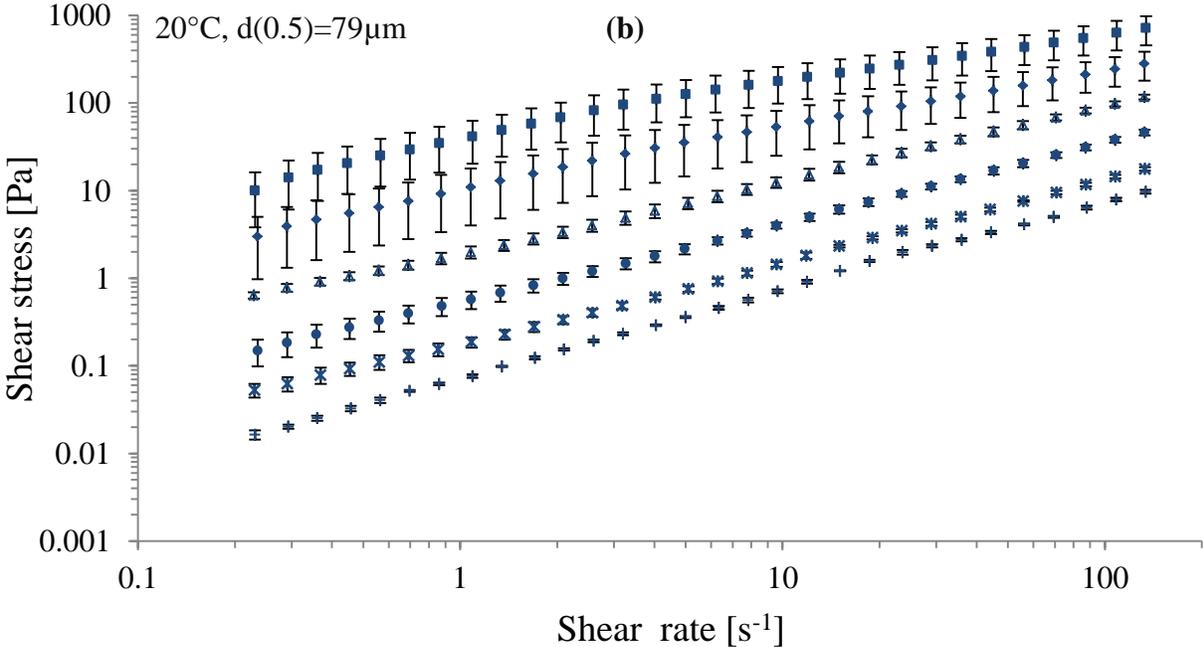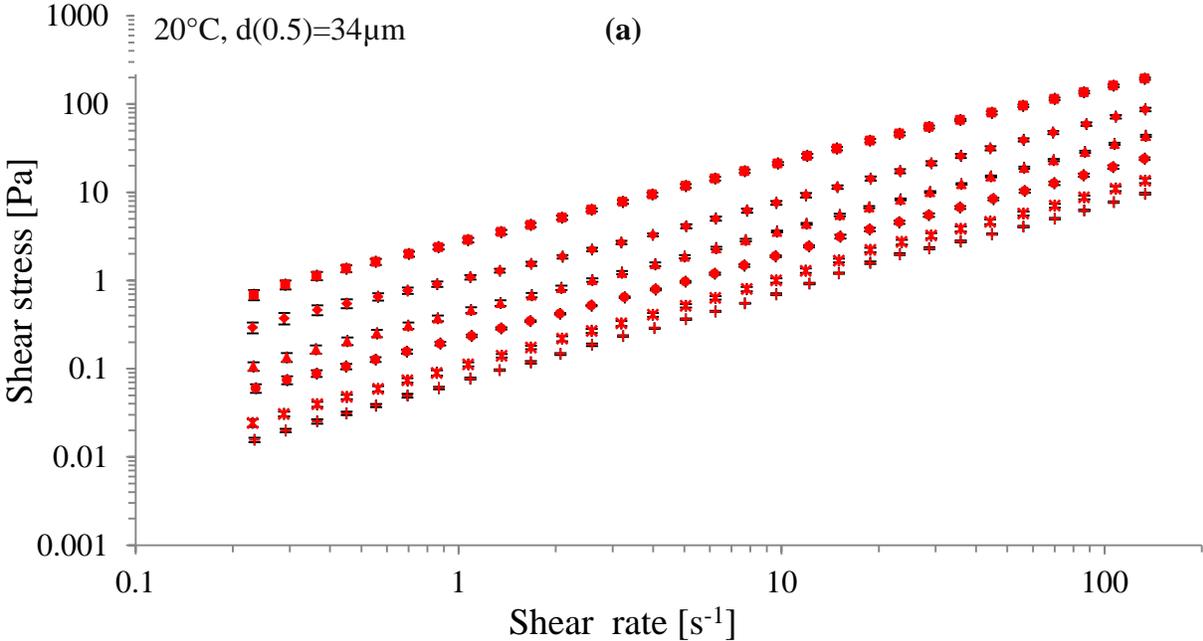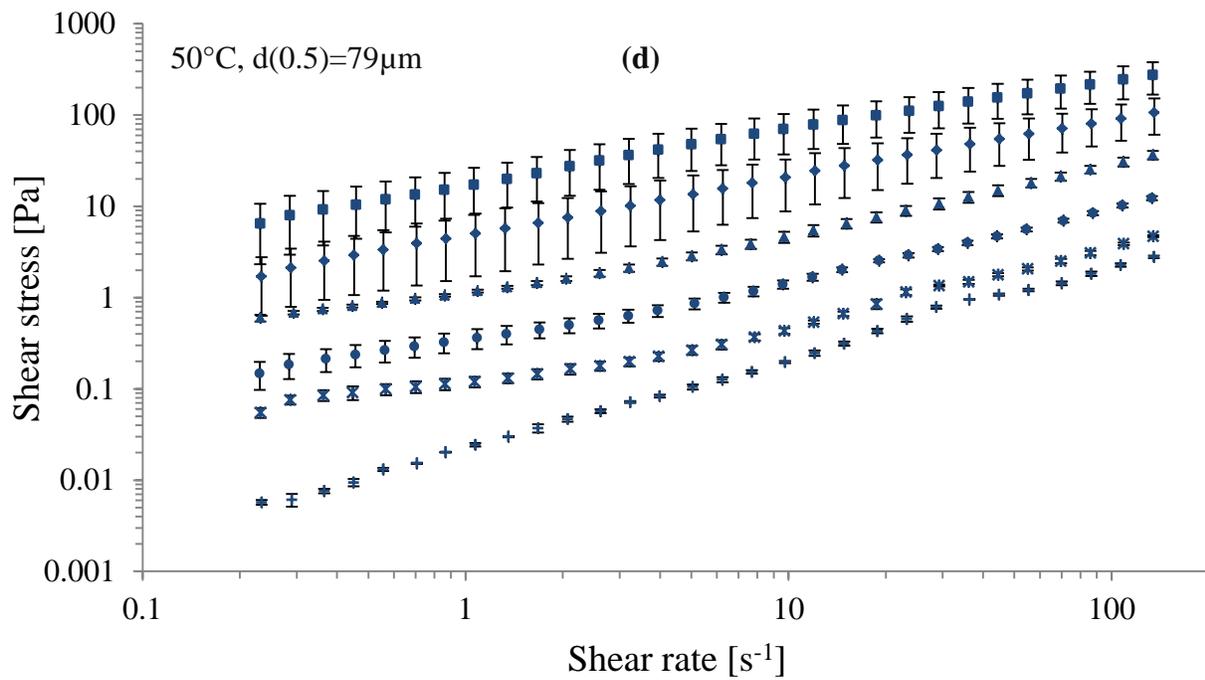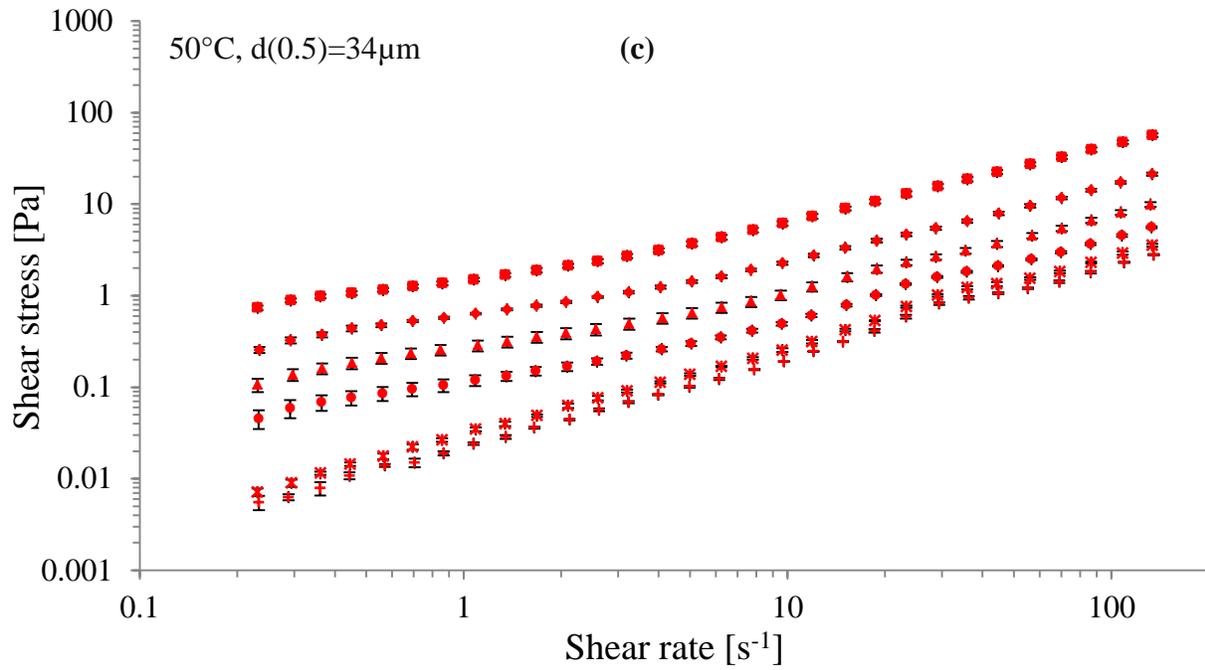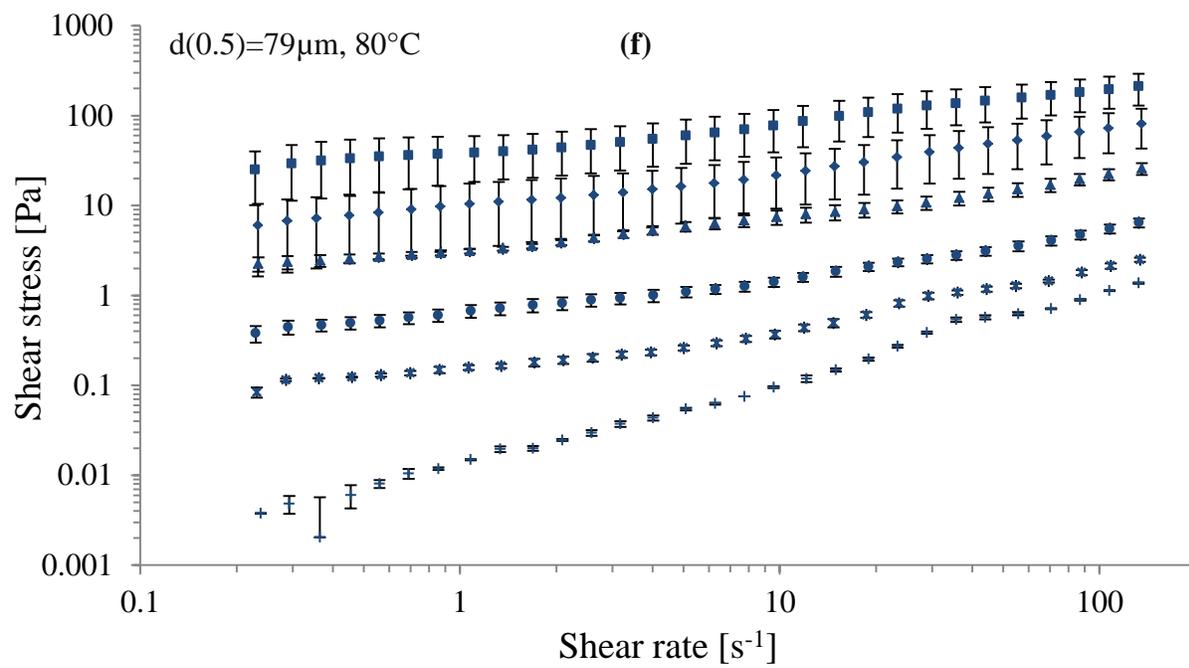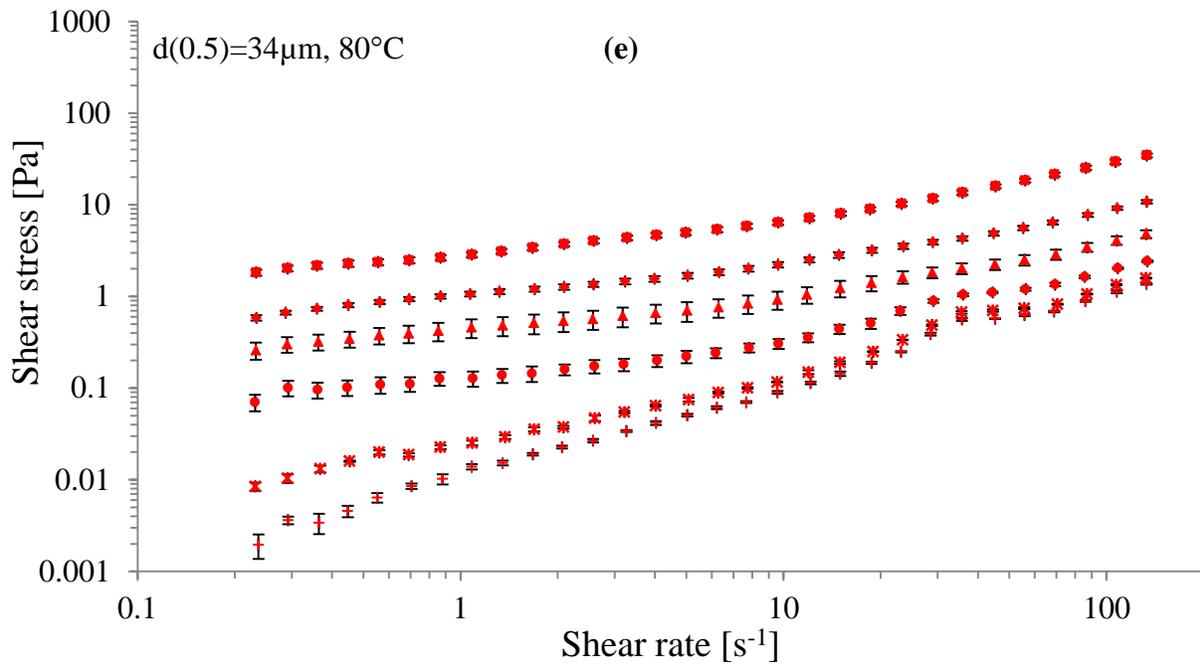
4.3.2. Comparison of Model Predictions and Experimental Data

To quantify the flow behavior of potato powder suspensions as affected by solids content and particle sizes at the three different temperatures, Newtonian, power-law and Herschel-Bulkley models (Eq. 4.2 to 4.4) were applied to all stress and shear rate data. The adequacy of the models was evaluated by the coefficient of determination (R^2) (Table 4.2).

Based on Table 4.2, although R^2 values vary very slightly, the Newtonian model is not the best model for all solid volume fractions of the potato powder suspensions. Also, most suspensions in the dilute regime, i.e., $\Phi=1\%$ or 5%, regardless of particle size and temperature, are shown to obey a power-law equation (Eq. 4.3), although goodness of fit for Newtonian and power-law fits are both very good at low Φ. The Herschel-Bulkley equation is the best fit for almost all semi-dilute and more concentrated potato powder suspensions, regardless of the particle size and temperature (Table 4.2).

Table 4.2. Coefficients of determination (R^2) of Newtonian, power-law and Herschel-Bulkley models for the potato powder suspensions

Temperature (°C)	Model	d(0.5)=34 μm						d(0.5)=79μm					
		Solid volume fraction (%)						Solid volume fraction (%)					
		1	5	10	15	20	25	1	5	10	15	20	25
20													
	Newtonian	0.999	0.999	0.999	0.9996	0.9987	0.992	0.999	0.999	0.999	0.995	0.96	0.93
	Power-law	0.9994	0.999	0.999	0.9999	0.999	0.9996	0.9995	0.9989	0.9996	0.9991	0.996	0.987
	Herschel-Bulkley	0.994	0.996	0.9998	0.9999	0.9999	0.991	0.995	0.9998	0.9999	0.9994	0.993	0.981
50													
	Newtonian	0.994	0.994	0.996	0.997	0.998	0.996	0.994	0.996	0.996	0.993	0.96	0.92
	Power-law	0.998	0.999	0.986	0.987	0.985	0.98	0.998	0.97	0.989	0.987	0.9995	0.997
	Herschel-Bulkley	0.98	0.98	0.998	0.999	0.9997	0.9999	0.98	0.998	0.9997	0.9999	0.996	0.98
80													
	Newtonian	0.986	0.984	0.981	0.981	0.983	0.988	0.988	0.978	0.972	0.954	0.935	0.871
	Power-law	0.995	0.99	0.95	0.97	0.98	0.97	0.988	0.96	0.98	0.985	0.985	0.983
	Herschel-Bulkley	0.97	0.978	0.993	0.999	0.997	0.999	0.97	0.995	0.998	0.996	0.999	0.995

Table 4.3 shows the appropriate power-law or Herschel-Bulkley model parameters for each potato powder suspension. In suspensions obeying the power-law equation, the yield stress does not exist, therefore, the sign (–) has been used for the yield stress.

Table 4.3. Model parameters from power-law and Herschel-Bulkley models for potato powder suspensions

Particle median size	20 °C						50 °C						80 °C					
	Solid volume fraction (%)						Solid volume fraction (%)						Solid volume fraction (%)					
	1	5	10	15	20	25	1	5	10	15	20	25	1	5	10	15	20	25
d(0.5):34 µm																		
n	1	1	0.97	0.96	0.92	0.89	1	0.98	0.89	0.91	0.92	0.87	1	0.82	0.78	0.73	0.75	0.78
σ_y	-	-	0.01	0.02	0.01	-	-	-	0.03	0.15	0.37	0.55	-	-	0.06	0.3	0.76	2.12
k	0.07	0.11	0.21	0.4	0.95	2.73	0.02	0.03	0.07	0.12	0.23	0.82	0.01	0.02	0.05	0.12	0.25	0.72
d(0.5):79 µm																		
n	1.01	0.95	0.93	0.85	0.7	0.63	1	0.9	0.87	0.83	0.64	0.59	0.97	0.74	0.67	0.59	0.54	0.39
σ_y	-	0.01	0.01	0.02	-	-	-	0.05	0.17	0.49	-	-	-	0.07	0.42	1.98	3.93	7.42
k	0.07	0.17	0.48	1.85	10.3	37.8	0.02	0.06	0.17	0.63	4.78	17.14	0.01	0.06	0.22	1.3	5.5	30.16

Units are n [-], σ_y [Pa], k [Pa.s^n].

4.3.2.1. Consistency Factor

The consistency factor *k*, as affected by the solid volume fraction of potato powder suspensions at 20, 50 and 80°C, is plotted in Fig. 4.4. In addition to the potato powder suspensions, the consistency factor for potato starch suspensions obtained from a power-law model is also plotted (data from Sinaki and Scanlon (2016)) so that the flow properties of a major constituent of potato parenchyma can be compared with the potato suspensions.

Fig. 4.4. Consistency factor of aqueous suspensions of potato powder with d(0.5)=34 µm (solid line) and d(0.5)=79 µm (dotted line) and potato starch suspensions (open symbols) at 20°C (■), 50°C (●) and 80°C (▲)
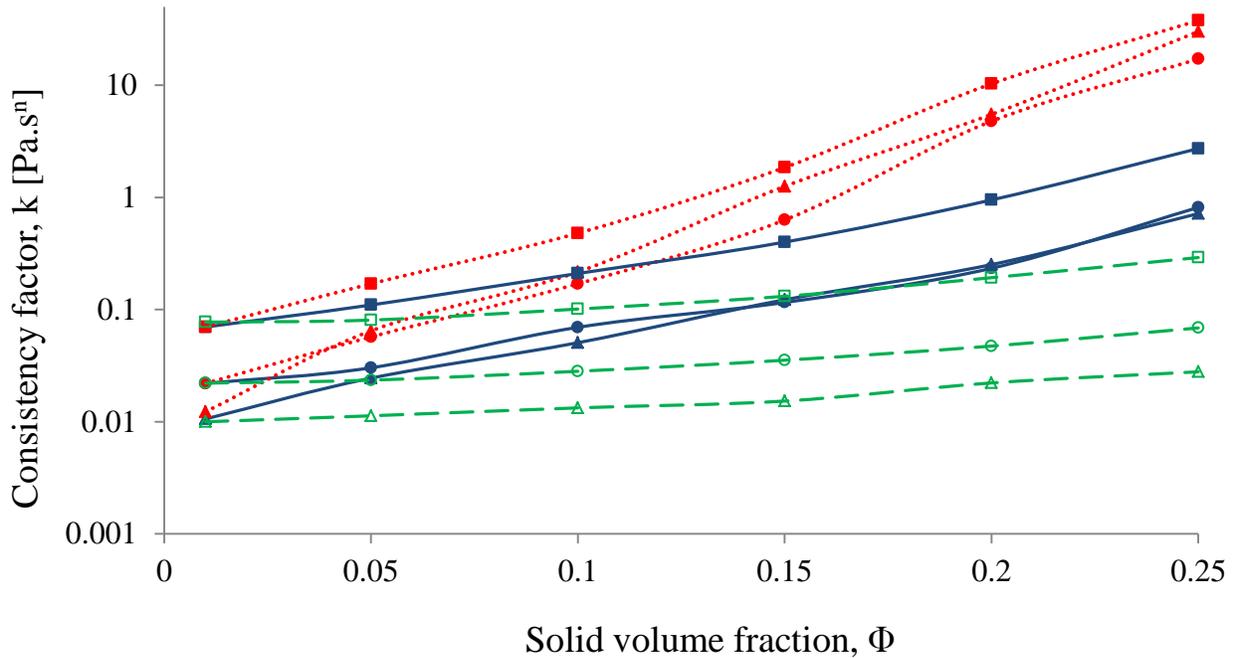
The k values increased with increasing solid volume fraction (Φ) of the potato powder suspensions, regardless of the temperature and particle size (Fig. 4.4). This is due to the fact that the consistency factor of a suspension increases with increasing solids content due to a greater disruption of the flow field as a result of the elevated number of particles (Mewis and Wagner 2012).

According to Fig. 4.4, in suspensions of both particle sizes, k decreased as temperature was increased from 20 to 50 °C, while the trend of changes from 50 to 80 °C was ambiguous. The decrease in consistency factor (k) with increasing the temperature of the suspensions can be related to the effect of temperature on both the continuous phase and the dispersed phase. For the continuous phase, an increase in temperature leads to an increase in molecular motions, which

results in a decrease in the viscosity of the continuous phase (Barnes 2000). In the potato powder suspensions, clusters of cells or single cells and cell fragments exist. These insoluble components make up the dispersed phase. On the other hand, the continuous phase can now contain any soluble intercellular and intracellular materials from the potato parenchyma. One particular effect of increasing temperature is on the depolymerisation and solubility of pectin polymers, which both increase with increasing temperature (Sriamornsak 2003). Therefore, the changes in pectin polymers, as the responsible components for cell-cell adhesion and cell-wall creation, cause alteration in the properties of both the continuous and the dispersed phases (Ormerod et al. 2004; Bayod et al. 2005; Sila et al. 2009). That is, an increase in pectin solubility decreases the solid volume fraction of the suspension, changing the dispersed particle properties, i.e., size and shape, and altering the flow characteristics of the continuous phase.

Although the potato powder particles were neutrally buoyant in the suspensions at 20 °C, the density of the continuous phase decreased with increasing temperature. This loss of density matching results in a tendency for sedimentation of the dispersed particles. In this study, all measurements on a potato powder suspension were done in less than 45 minutes. No obvious sedimentation was observed in this time scale at 50 and 80 °C. However, our observations revealed that some degree of depletion of the dispersed particles may have occurred in the rheometer in the dilute and semi-dilute suspensions as temperature was increased. In the more concentrated regime where greater interactions existed among suspension components, suspensions were gel-like and as a result, no depletion of dispersed particles was observed at 50°C or at 80°C. Hence, in the interpretation of the data, the probability of depletion of particles in the suspensions with low solids contents cannot be ruled out, i.e., for the dilute and semi-dilute suspensions there may have been differences in the dispersed phase concentration in the

measurement annulus. Therefore, the true solids content of the suspensions at 50 and 80 °C will be slightly smaller than the values at 20 °C. Such behavior has been observed for suspensions of starch granules in concentrated sucrose solutions (Chapter 3). Consequently, the measured stress in the rheometer arises from the shearing of a thinned volume of particles in the suspension for dilute and semi-dilute suspensions. All these changes are presumed to lead to the reduction of the consistency factor when temperature is raised, particularly in dilute and semi-dilute suspensions.

Based on Fig. 4.4, the *k* values are higher in the potato powder suspensions of bigger particles, i.e., d(0.5)= 79 µm, than *k* values in the suspensions of smaller particles, i.e., d(0.5)= 34 µm, at a given solid volume fraction. The same result, i.e., an increase in consistency factor with increasing particle size, has been reported for different systems (Tanglertpaibul and Rao 1987; Schijvens, Vliet, and Dijk 1998). In particular, in a study on green chilli puree it has been shown that *k* values increased with increasing particle size (Ahmed, Shivhare, and Raghavan 2000). As mentioned before, based on the particle size measurement results and the gap between the stator and rotor in this study, some phenomena, such as no-flow zones or locking and jamming of the particles during the shear flow test, could be responsible for an increase in the consistency factor in the suspensions of bigger particles, i.e., d(0.5)=79 µm (Cheng and Richmond 1978; Savage and Mckeown 1983).

4.3.2.2. Shear-thinning Behavior

The power-law index (*n*), as affected by solid volume fraction of the potato powder suspensions at 20, 50 and 80 °C, is shown in Fig. 4.5. As with the consistency factor, the power-law index of potato starch suspensions obtained from a power-law model is also plotted.

Fig. 4.5. Power-law index of potato starch suspensions (open symbols) and aqueous suspensions of potato powder with d(0.5)=34 μm (solid line) and d(0.5)=79 μm (dotted line) at 20°C (■), 50°C (●) and 80°C (▲)
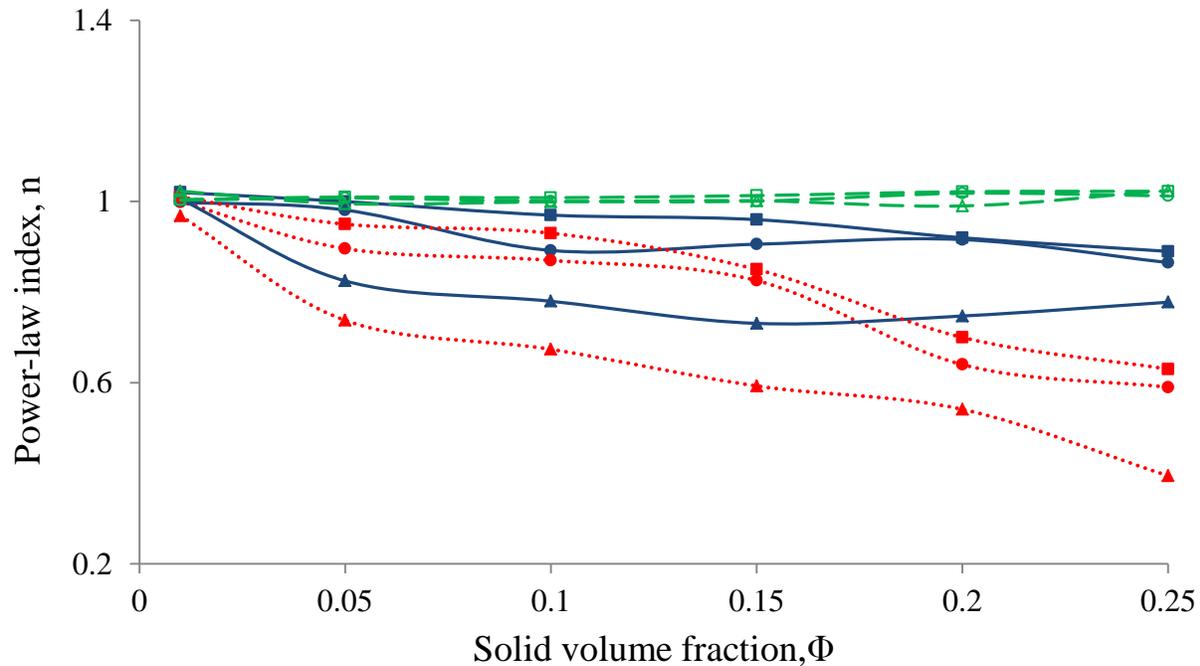
Based on Fig. 4.5, in the very dilute regime, i.e., $\Phi = 1\%$, the power-law index is close to 1.0 in all the suspensions, showing essentially Newtonian behavior. The potato starch granule suspensions maintained their Newtonian behavior (*n* values close to 1.0) over the whole Φ range and at all temperatures. However, an increase in the solids content and the temperature led to a decrease in the power-law index (*n*) of the potato powder suspensions, indicating a gradual development of a greater degree of shear-thinning behavior in these suspensions with increasing Φ and temperature (Fig. 4.5).

The deviation of the flow behavior of the potato powder suspensions from that of the starch granule suspensions implies that in the potato powder suspensions it is the non-starch

granule components that strongly influence the suspension's flow behavior. These components, which can be intracellular and intercellular components, were produced during the preparation process, i.e., the size reduction process on the tissue or upon raising the temperature of the suspension. One of the principal materials is the cell wall components, mostly pectin polymers, that can make up to 60% of the potato cell wall's dry weight (Singh and Kaur 2016). Pectin is a polymer that exhibits great intramolecular interactions as well as intermolecular interactions with other components of a suspension (da Silva and Rao 2006). Pectin polymers affect the flow behavior of plant tissue suspensions in different ways. The most important are effects on the interactions between particles (Beresovsky, Kopelman, and Mizrahi 1995) and the flow properties of the continuous phase when pectin is dissolved (Errington, Tucker, and Mitchell 1998).

Pectin-promoted interactions, i.e., pectin-sucrose, pectin-pectin and pectin-particle interactions, seem to play an important role in the flow properties of our potato powder suspensions. The formation of a pectin-sucrose network (Fu and Rao 2001; Ahmed, Ptaszek, and Basu 2017), pectin gel via pectin-pectin interactions (Sorchan et al. 1971; Sriamornsak 2003; da Silva and Rao 2006; Sila et al. 2009) and flocculation of dispersed particles via pectin-particle interactions (Sorchan et al. 1971; Elimelech et al. 1995; Walstra 2002) have been reported previously. All these phenomena can contribute to large differences between the flow behavior of the potato powder suspensions (shear-thinning) and that of the starch granule suspensions (Newtonian). In general, shear-thinning behavior is a result of either particle alignment in the flow direction or breakdown of structure in suspensions (Cross 1979; Steffe 1996; Gallegos, Franco, and Partal 2004; Stokes, Telford, and Williamson 2005; Moelants et al. 2013; Augusto and Vitali 2014). The presence of pectin-promoted interactions in our potato powder suspensions

is presumed to be responsible for the formation of a structure in these suspensions prior to the measurements. Accordingly, the alignment of particles in the flow direction could not be the responsible mechanism for the shear-thinning behavior of the potato powder suspensions. However, during the shear experiment, and with increasing shear rate in the potato powder suspensions, the structure was broken down leading to a shear-thinning behavior of the suspensions (Mueller, Llewellin, and Mader 2009). A decrease in *n* values of the potato powder suspensions with increasing Φ (Fig. 4.5) suggests a more effective breakage of the structure at larger Φ.

In addition to solid volume fraction, temperature also affected the shear-thinning behavior of the potato powder suspensions. However, no effect of temperature on the properties of potato starch granule suspensions was observed (Fig. 4.5). The high amount of sugar in the continuous phase led to a reduction in water availability which retards any thermally induced changes in the starch granules (Colonna and Buleon 2010). For example, starch swelling, as the first phase of the thermal changes in starch granules, occurs at about 95 ºC in 60% sucrose solution (Bean and Yamazaki 1978). Therefore, even at our highest testing temperature, i.e., 80°C, the starch granules properties were not changed. Consequently, starch granules are not responsible for the changes in the flow behavior of potato powder suspensions when temperature is raised.

An increase in shear-thinning behavior of our potato powder suspensions with increasing temperature can be related to the depolymerization and solubility of pectin polymers in the suspensions at elevated temperatures. In general, with increasing temperature, pectin depolymerization and solubility increase (Sriamornsak 2003). In addition to temperature, enzyme activities can influence the solubility of pectin polymers. The optimum temperatures for pectin

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depolymerizing enzymes are around 50 to 60 °C (Verlent et al. 2007). However, the presence of a large amount of sugar inhibits enzyme activity (Chang, Morita, and Yamamoto 1963). Therefore, the high amount of sucrose in the potato powder suspensions, i.e., 60% sucrose solution as the continuous phase, might eliminate enzyme activity at the testing temperatures.

As mentioned earlier, the flow properties of suspensions are affected by changes in the properties of both the continuous and the dispersed phases. Greater solubility of pectin as a result of increasing temperature leads to changes in the particle properties such as shape and size (Ormerod et al. 2004; Bayod et al. 2005; Sila et al. 2009; Lopez-Sanchez, Nijsse, et al. 2011; Augusto and Vitali 2014; Moelants, Cardinaels, Van Buggenhout, et al. 2014). Accordingly, by increasing the temperature from 20 to 50 °C and then to 80°C, a new set of particles with different geometries might be produced in the suspensions, i.e., changes in particle properties. Moreover, pectin solubilization promoted by increasing temperature could affect the continuous phase by inducing various types of interactions in the continuous phase (Wüstenberg 2015) (Fig. 4.6). Consequently, a greater deviation from Newtonian behavior was observed in the potato powder suspensions as a result of this increase in temperature.

Fig. 4.6. Highly simplified schematic of the effect of temperature on particle properties in plant-tissue suspensions
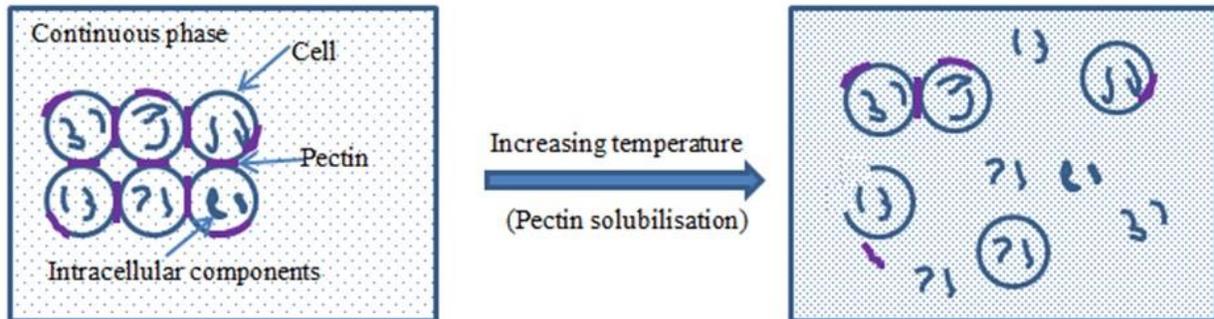
4.3.2.3. Yield Stress

Based on Table 4.3, most of the semi-dilute and concentrated potato powder suspensions obey the Herschel-Bulkley equation, displaying a yield stress. Yield stress is observed in many plant-tissue-based food suspensions, for example tomato suspensions (Bayod et al. 2007) and carrot suspensions (Day, Xu, Øiseth, Hemar, et al. 2010). The presence of a yield stress in these suspensions has been related to a network structure formed by the net attractive forces between particles. The value of the yield stress in the potato powder suspensions (given in Table 4.3) is plotted in Fig. 4.7.

Fig. 4.7. Yield stress from Herschel-Bulkley model of aqueous suspensions of potato powder with d(0.5)=34 µm (dotted lines) and d(0.5)=79 µm (solid lines) at 20°C(■), 50°C (●) and 80°C (▲)
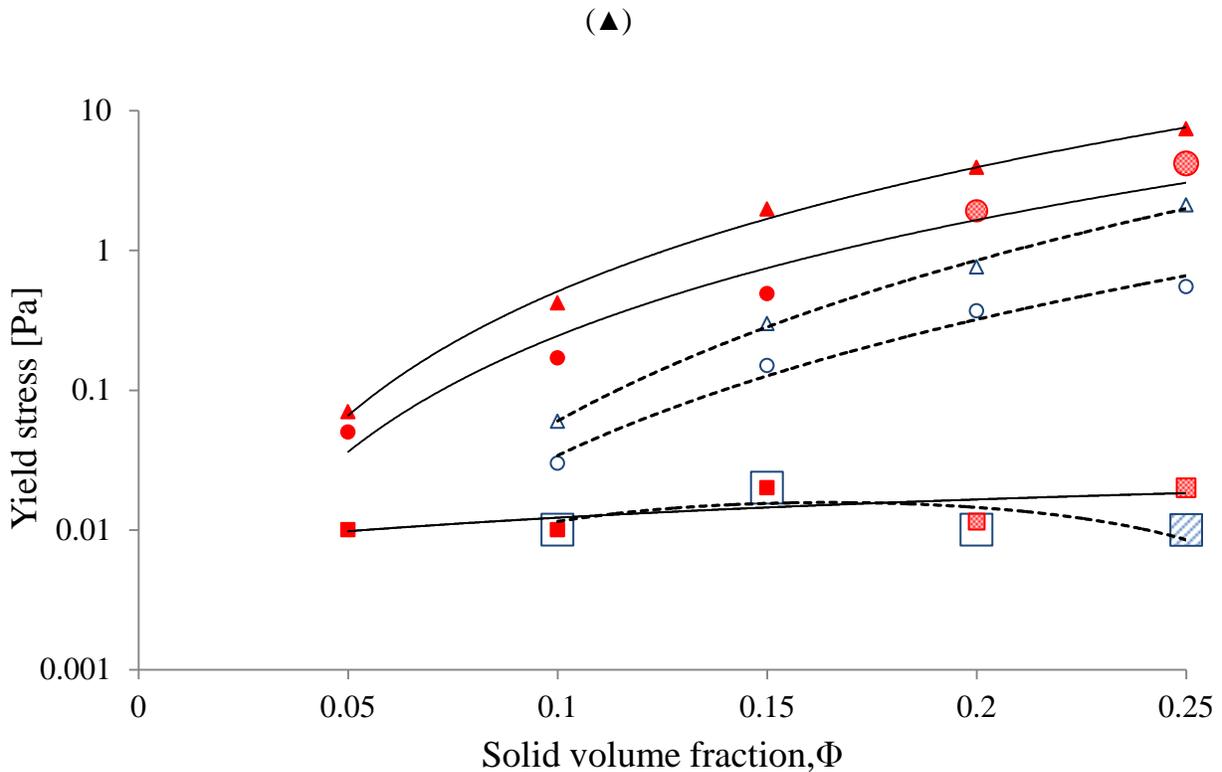
Although based on R^2 values (Table 4.2) the power-law equation was chosen as the best fit for some of the systems in Fig. 4.7, yield stress values determined from the Herschel-Bulkley model are shown with hachure symbols. This is justified because of small differences between the R^2 values of the power-law and Herschel-Bulkley models (see Table 4.2). This allows us to interpret the effects of Φ, particle size and temperature on the yield stress of all the suspensions in a single graph. Based on Fig. 4.7, a general increase in the yield stress values of the potato powder suspensions with increasing Φ, particle size and temperature was observed. However, for the potato powder suspensions at 20 °C essentially no change in their very weak yield stress values with Φ and particle size was observed.

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An increase in the yield stress with increasing solids content and temperature could be attributable to elevated pectin-promoted interactions at high Φ as well as an enhanced solubility of pectin polymers at high temperatures (Sriamornsak 2003). Pectin polymers form a gel when their polymer chains interact with each other through hydrogen bonds or electro-static interactions. Ptitchkina et al. (1994) reported that the magnitude of the yield stress increased non-linearly with increasing pectin concentrations in citrus pectin solutions with pectin concentrations of 0.9-3%. A similar trend was observed for our potato powder suspensions in which yield stress increased with increasing solid volume fraction following a power-law equation:

$$\sigma_y = a\,\Phi^b \qquad\qquad\qquad \text{Eq. 4.5}$$

where a and b are constants which were determined for the potato powder suspensions (Table 4.4).

Table 4.4. Parameters of the power-law equation (Eq. 4.5) fitted to experimental data

Particle median size	Temperature (°C)	a	b	R^2
d(0.5)= 34 μm				
	20	NA	NA	NA
	50	58	3.23	0.980
	80	398	3.82	0.997
d(0.5)= 79 μm				
	20	NA	NA	NA
	50	22	2.04	0.988
	80	454	2.95	0.995

NA: not applicable

Based on R^2 values presented in Table 4.4, experimental data for the effect of solids volume fraction on yield stress values of the potato powder suspensions at 50 and 80 °C conforms well

with a power-law equation. As illustrated in Fig. 4.7 and reflected in Table 4.4, suspensions at 20ºC do not obey the same relationship between yield stress and Φ observed at higher temperatures. This observation could be attributable to negligible pectin-promoted interactions in the potato powder suspensions at 20 °C, i.e., less liberation of pectin polymers into the continuous phase at 20 °C. Regarding the effect of temperature, da Silva, Gonçalves, and Rao (1994) showed that in pectin dispersions there is evidence of a yield stress which increases as temperature increases. Therefore, it can be concluded that the presence of pectin polymers in the continuous phase and their gelation properties are responsible for the yield stress of the potato powder suspensions.

As shown in Fig. 4.7, at a given solids content of potato powder suspensions, the yield stress increased with increasing particle size. The effect of particle size on yield stress has been discussed in several studies, see for example (Qiu and Rao 1988; Missaire, Qiu, and Rao 1990; Zhou et al. 1995; Moelants, Cardinaels, Jolie, et al. 2014). Yield stress has been reported to increase both with increase and decrease in particle size. An increase in yield stress with increasing particle size has been reported in tomato-derived suspensions (Moelants, Cardinaels, Jolie, et al. 2014) and apple sauces (Schijvens, Vliet, and Dijk 1998). To our knowledge, no plausible mechanism has been provided in the literature for this observation. The reason would be attributable to the fact that variations in particle size are always accompanied by variations in particle shape and surface properties, which both affect the rheological properties of the suspensions (Moelants, Cardinaels, Jolie, et al. 2014).

4.4. Conclusion

A comprehensive study on the shear flow behavior of aqueous suspensions of potato powder has been presented for particle concentrations ranging from dilute to more concentrated regimes. It

has been shown how key parameters, i.e., solids content, particle size and temperature influence the flow behavior of these suspensions. Comparison between the flow behaviors of potato powder with potato starch granule suspensions showed that there are completely different flow behaviors in these two types of suspensions. Although potato parenchyma is rich in starch granules, the potato powder suspensions owe their flow properties to the presence of different intracellular and intercellular components, particularly pectin polymers, that are liberated into the continuous phase of the suspensions.

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5. Oscillatory Shear Behavior of Aqueous Suspensions of Potato Parenchyma Powder

Abstract

The viscoelastic properties of potato parenchyma powder aqueous suspensions were studied. A concentrated sucrose solution was used as the continuous phase to maintain particle buoyancy. Suspensions were prepared as two different particle sizes and six different solids contents from dilute to more concentrated, i.e., 1% to 25% by volume. Oscillatory shear testing at 20, 50 and 80 °C was applied on suspensions in a rotational rheometer with a frequency sweep test of angular frequency (ω) ranging from 0.6 to 628 rad s^{-1}. At a given solids content, the magnitude of both loss and storage moduli (G'' and G') decreased with decreasing size of the particles. The viscoelastic properties of the potato powder suspensions corresponded mainly to the terminal zone ($G'(\omega) \propto \omega^2$ and $G''(\omega) \propto \omega$). Based on the loss factor results, with increasing frequency, the viscoelastic behavior of potato powder suspensions showed a transition from liquid-like behavior to solid-like behavior. In addition, the loss factor decreased with increasing temperature. Deviations from the Cox-Merz rule were observed for almost all potato powder suspensions. To gain insights into the role of different components on the viscoelastic behavior of the potato powder suspensions, viscoelastic properties of the samples were compared with those of potato starch granule suspensions. Differences in the viscoelastic properties of the two systems are due to the strong effect of potato parenchyma's other intracellular and intercellular components, specifically pectin.

Keywords: Potato parenchyma powder, suspension, viscoelastic properties, solid volume fraction, temperature, particle size

5.1. Introduction

The potato is a historically staple food around the world. It is used as a cheap primary ingredient for various food products and industrial applications in large volume (Woolfe 1992). Potato-derived products are used in different forms, such as mashed potato and potato puree, or as an additive in the manufacturing of different vegetable purees (Alvarez and Canet 2001; Alvarez, Fernández, and Canet 2004; Ahmed and Ramaswamy 2006a; Ahmed and Ramaswamy 2006b).

Nowadays, developing novel foods and materials and refining conventional technologies and processes are important issues for the food industry. Potato particles as starchy particles have potential applications for manufacturing healthier and cheaper products, e.g., by eliminating the need for stabilisers and thickeners. Therefore, a fundamental understanding of the rheological properties of potato powder suspensions is critical for applications development. The results obtained from the rheological measurements of these suspensions can be used in controlling different fields of process performance and for attaining various final product properties.

Potato powder suspensions are, in general, dispersions of plant-tissue derived particles. The rheological properties of these type of suspensions depend mostly on solid volume fraction, particle size and size distribution, particle shape, surface properties and particle interactions (Gallegos, Franco, and Partal 2004; Pabst, Gregorová, and Berthold 2006; Genovese, Lozano, and Rao 2007; Stokes and Frith 2008; Fischer et al. 2009). For instance, Valencia et al. (2003) showed that the flow properties of tomato paste as a plant-tissue suspension depended mostly on solids content and particle size (Valencia et al. 2003).

Plant-tissue suspensions usually show viscoelastic properties which are a combination of both liquid-like and solid-like responses to external forces (Ward and Sweeney 2013).

Viscoelastic properties can be obtained using an oscillatory test. In an oscillatory test, the solid-like and liquid-like behavior is characterized by the storage modulus (G') and the loss modulus (G''), respectively. The complex viscosity is used to define the viscosity of a sample in an oscillatory test in which both G' and G'' are involved (Barnes 2000; Gunasekaran and Ak 2000; Bourne 2002; Rao 2013). For instance, a study on commercial pea, corn and wax bean purees in the temperature range of 20-80 °C showed that G' was higher than G'', i.e., elastic behavior was predominant at all temperatures (Ahmed and Ramaswamy 2006a). Similar results were observed for sweet potato puree infant food, i.e., $G' > G''$, both moduli decreasing with an increase in temperature (Ahmed and Ramaswamy 2006b). Examination of apple suspensions demonstrated that G' and G'' depend on both frequency and solids content (Kunzek, Opel, and Senge 1997). Vetter and Kunzek (2003) reported that concentrated suspensions of apple cell-wall materials had predominantly solid-like behavior. Solid-like behavior was also observed in a study on cell wall components from carrot at a concentration of 5% (Pickardt, Dongowski, and Kunzek 2004).

In this paper, in a series of studies on the rheological properties of plant tissue aqueous suspensions, we describe the viscoelastic properties of aqueous suspensions of potato parenchyma powder. We used dynamic oscillatory shear experiments for obtaining the viscoelastic properties of these suspensions. In doing so, the effects of the main parameters affecting the viscoelastic properties, i.e., solid volume fraction, particle size and temperature, were investigated.

5.2. Materials and Methods

The viscoelastic properties of potato powder suspensions were analyzed by applying a shear oscillatory test. The effect of three important parameters influencing the viscoelastic properties, i.e., solids content, particle size and temperature, were investigated.

5.2.1. Preparation of Potato Powder

The same batch of fresh local potatoes was used for preparation of potato particles. After washing and peeling potatoes, they were cut into small pieces. Then a kitchen blender was used to reduce the potato pieces in size. Distilled water (approximately in a 1:3 ratio) was used to facilitate comminution. For drying the resulting slurries, an oven at 50°C was employed until a constant weight was attained. Then, the dried potato cake was ground in a Retsch ZM200 mill (Retsch GmbH, Haan, Germany) with a mesh size of 80 μm.

To classify the particle sizes of the potato powder, a dry sieving technique was used and four different aperture sizes (202, 106, 75 and 63μm) were selected. A sieve shaker was employed for sieving potato powder (960 g) in lots of 100 g for about 40 minutes each. Then the retained fractions of potato powder on the different sieves and the throughs of the 63μm sieve were manually collected and poured into five different beakers. These beakers were stored in a refrigerator until required. For this study, two different sizes were chosen to investigate the effect of particle size on the viscoelastic properties of potato powder suspensions: the potato powder particles yielded on the sieve with aperture size of 75 μm, i.e., d(0.5)=79 μm, and particles passing through the 63 μm sieve, i.e., d(0.5)=34 μm (Fig. 4.2). The particle size measurements of these fractions, i.e., d(0.5), were determined by a Mastersizer 2000 in which the size of particles is measured based on their apparent sphericity (Malvern Instruments Ltd., Worcestershire, UK). The details of particle size measurements have been previously described in Chapter 4.

5.2.2. Solid Volume Fraction

For analysing the effect of solids content on the viscoelastic properties of the potato powder suspensions, the suspensions were prepared in six different solid volume fractions (Φ). These solid volume fractions represent dilute to more concentrated regimes, i.e., $\Phi = 1\%$ and 5% for dilute regime, $\Phi = 10\%$ and 15% for semi-dilute regime and $\Phi = 20\%$ and 25% for the more concentrated regime. To obtain the exact required amount of potato powder for making a suspension with a specific solid volume fraction, the density of the particles was measured, which has been previously described in Chapter 4.

5.2.3. Preparation of Potato Powder Suspensions

Potato powder suspensions were prepared by adding the appropriate amount of potato powder to a 60% w/w sucrose solution as the continuous phase. The sucrose solution was made by dissolving 60 grams of sucrose in 40 grams of water. Then, all suspensions were mixed with a spatula and stirred for 15 minutes with a magnetic stirring bar at room temperature. Fresh suspensions (less than 1 hr old) were used for measurements. All measurements were done in duplicate.

5.2.4. Rheological Measurements

Viscoelastic properties of the potato powder suspensions were characterized by a rotational rheometer (AR 2000; TA Instruments, New Castle, DE, USA). A concentric cylinder geometry was used with a stator and rotor radius of 15 and 14 mm, respectively, and a set gap of 5.92 mm for the lowered rotor.

Viscoelastic properties were studied by applying a shear oscillatory test on the potato powder suspensions. In this test, at a fixed oscillatory stress of 1 Pa (Sinaki and Scanlon (2016)),

a frequency sweep, i.e., angular frequency ranging from 0.6 to 628 rad s^{-1}, was used. Three different temperatures, i.e., 20, 50 and 80°C, were used to probe the effect of temperature on the viscoelastic properties of potato powder suspensions. Then, the measurements of the viscoelastic properties on a given suspension were done in the following manner: (i) shear flow at 20°C (ii) dynamic oscillatory shear at 20°C (iii) shear flow at 50°C (iv) dynamic oscillatory shear at 50°C (v) shear flow at 80°C and (vi) dynamic oscillatory shear at 80°C. The results of the shear flow tests are shown in Chapter 4.

5.3. Results and Discussion

5.3.1. Viscoelastic Properties

5.3.1.1. Mechanical Moduli

The viscoelastic properties of the potato powder suspensions were investigated using a frequency sweep test. The loss (G'') and storage (G') moduli of the potato powder suspensions containing particles of d(0.5)= 34 μm and d(0.5)=79 μm are shown in Fig. 5.1 (a-f) and Fig. 5.2 (a-f), respectively. Each data point in Fig. 5.1 (a-f) and Fig. 5.2 (a-f) is the average of the corresponding G' and G'' of two replications.

Fig. 5.1. The frequency dependence of the storage and loss moduli of potato powder suspensions (d(0.5)=34 µm) at 20°C (a-b), 50°C (c, d) and 80°C (e, f) with $\Phi = 1\%$ (+), 5% (*), 10% (●), 15%(▲), 20% (♦), 25% (■)

d(0.5)=34 μm, 50°C

(c)

d(0.5)=34 μm, 50°C

(d)

Fig. 5.2. The frequency dependence of the storage and loss moduli of potato powder suspensions (d(0.5)=79 μm) at 20°C (a-b), 50°C (c, d) and 80°C (e, f) with $\Phi = 1\%$ (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■)

d(0.5)=79μm, 50°C **(c)**

G'[Pa]

Angular frequency [rad s⁻¹]

d(0.5)=79μm, 50°C **(d)**

G'' [Pa]

Angular frequency [rad s⁻¹]
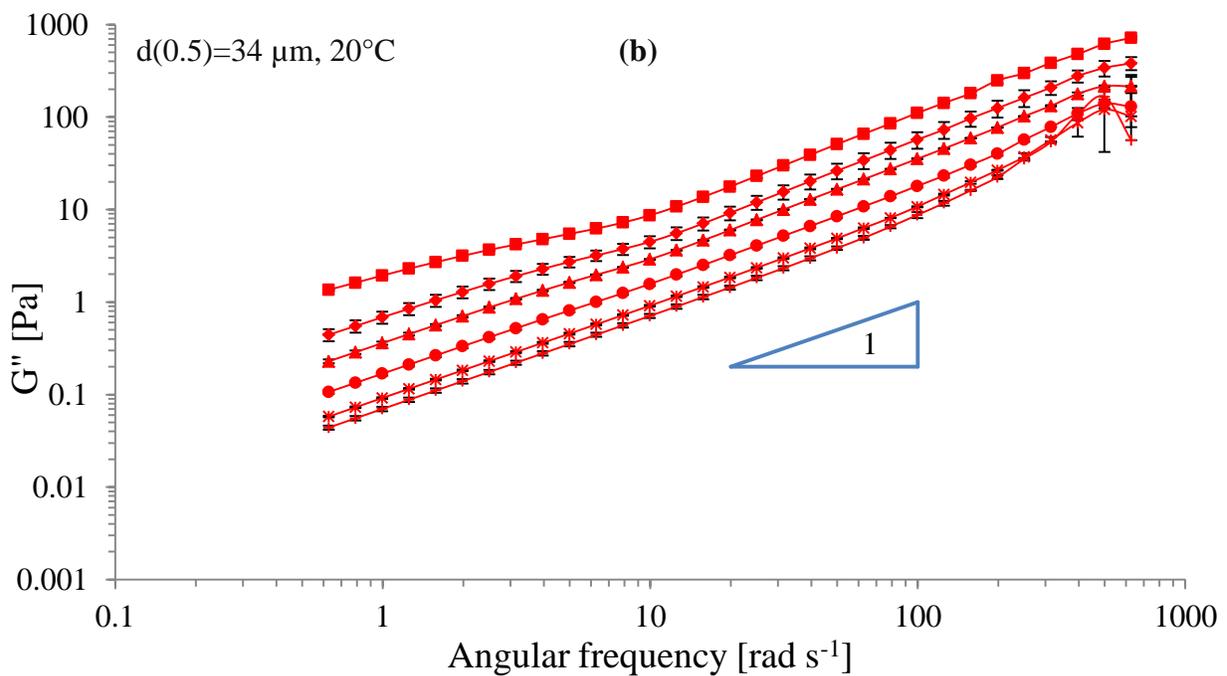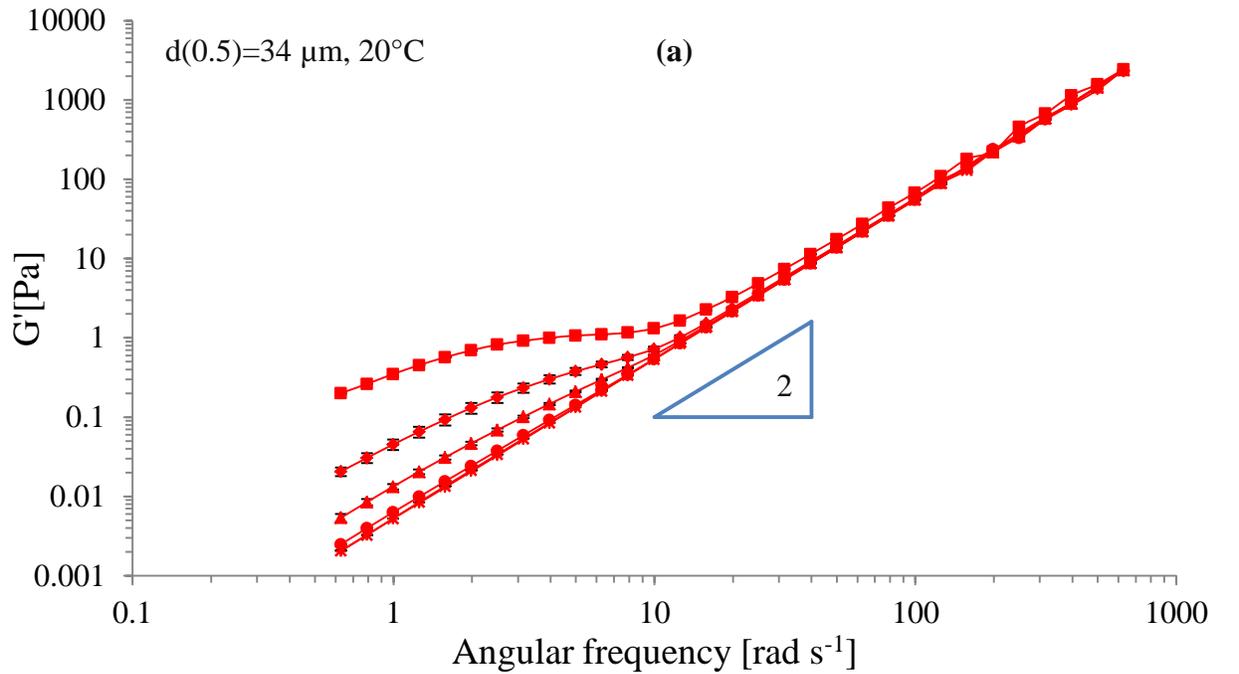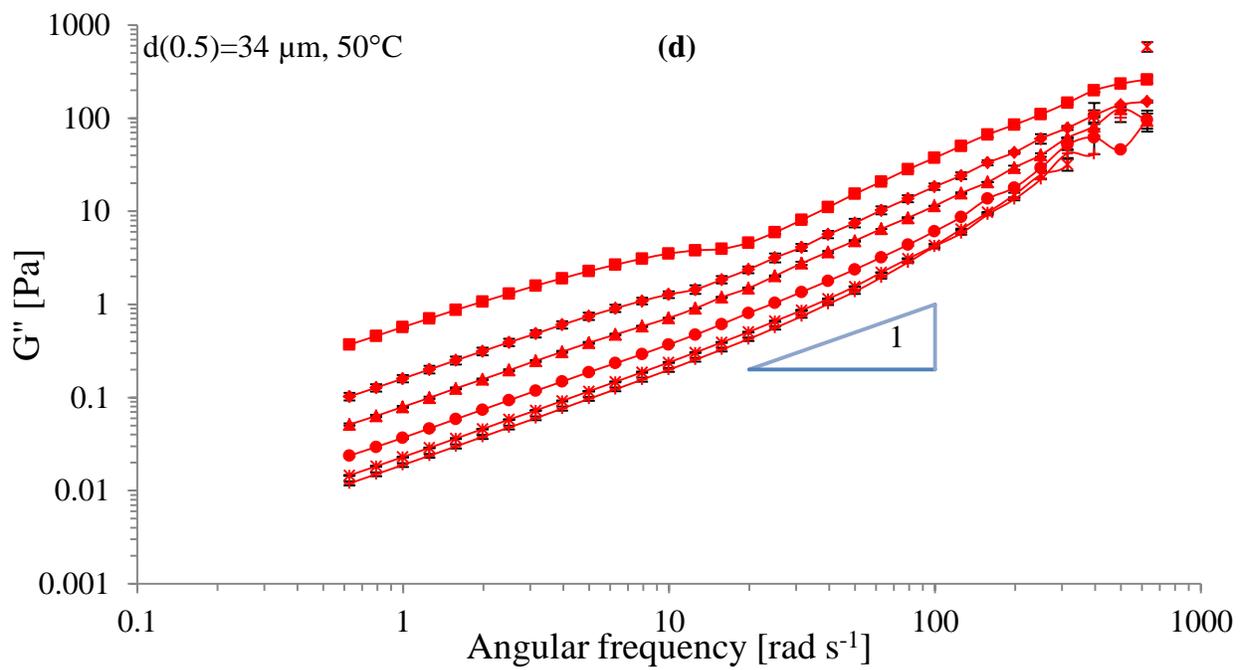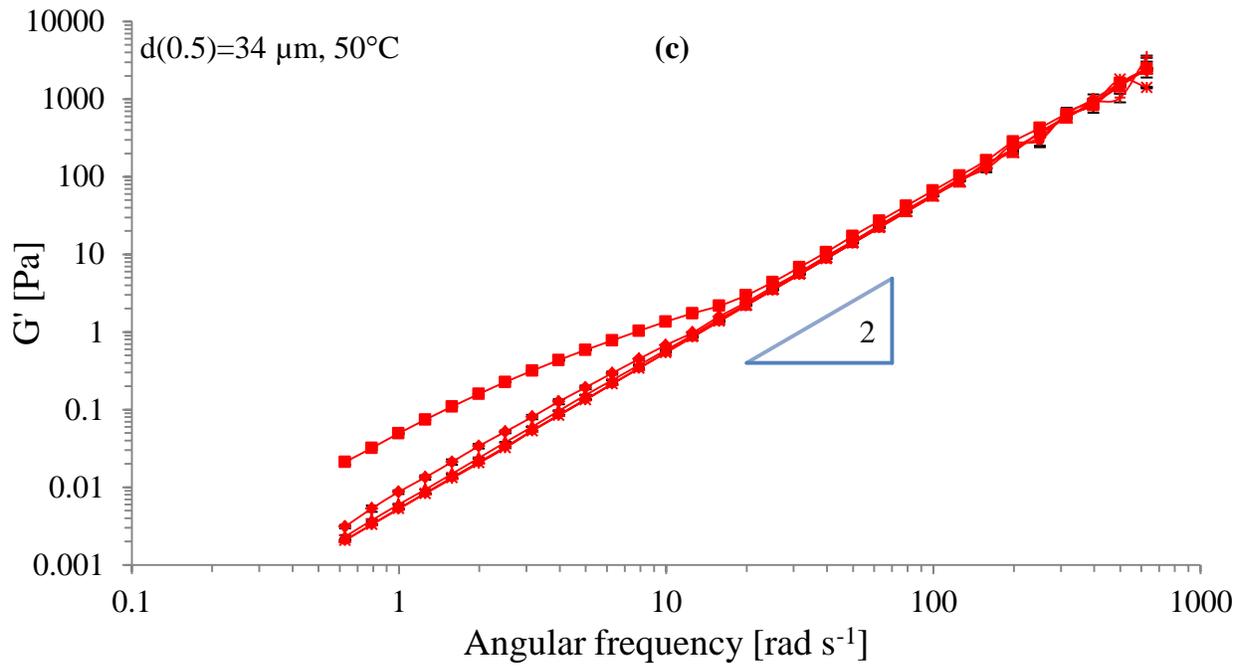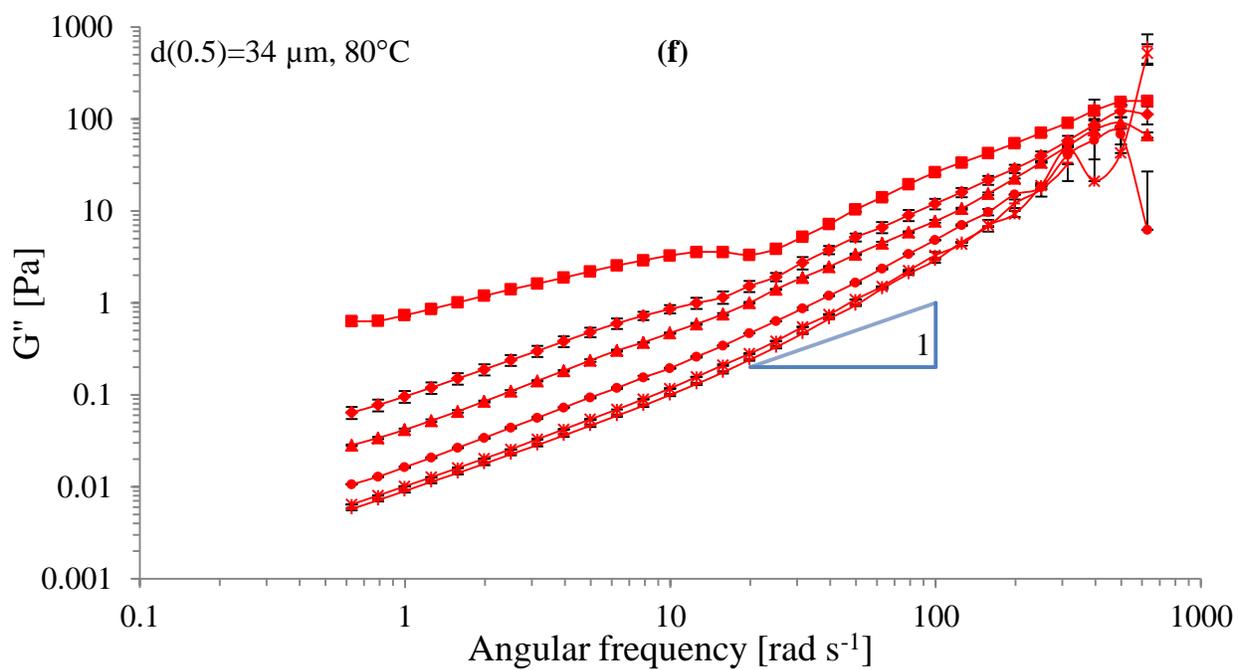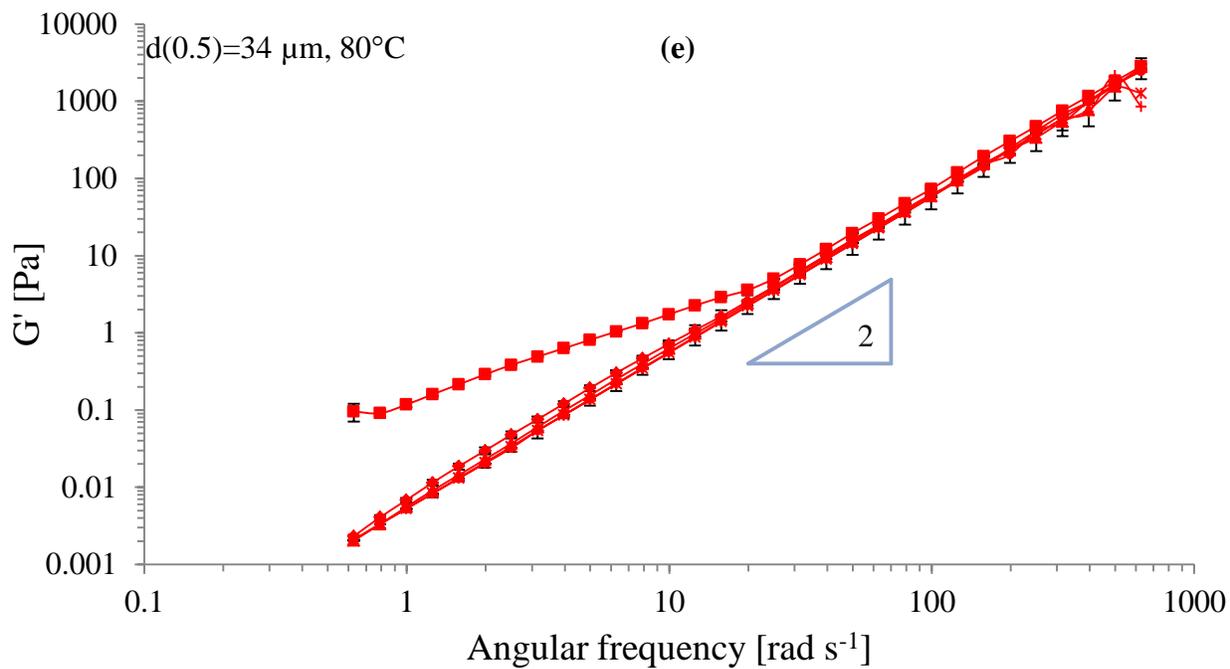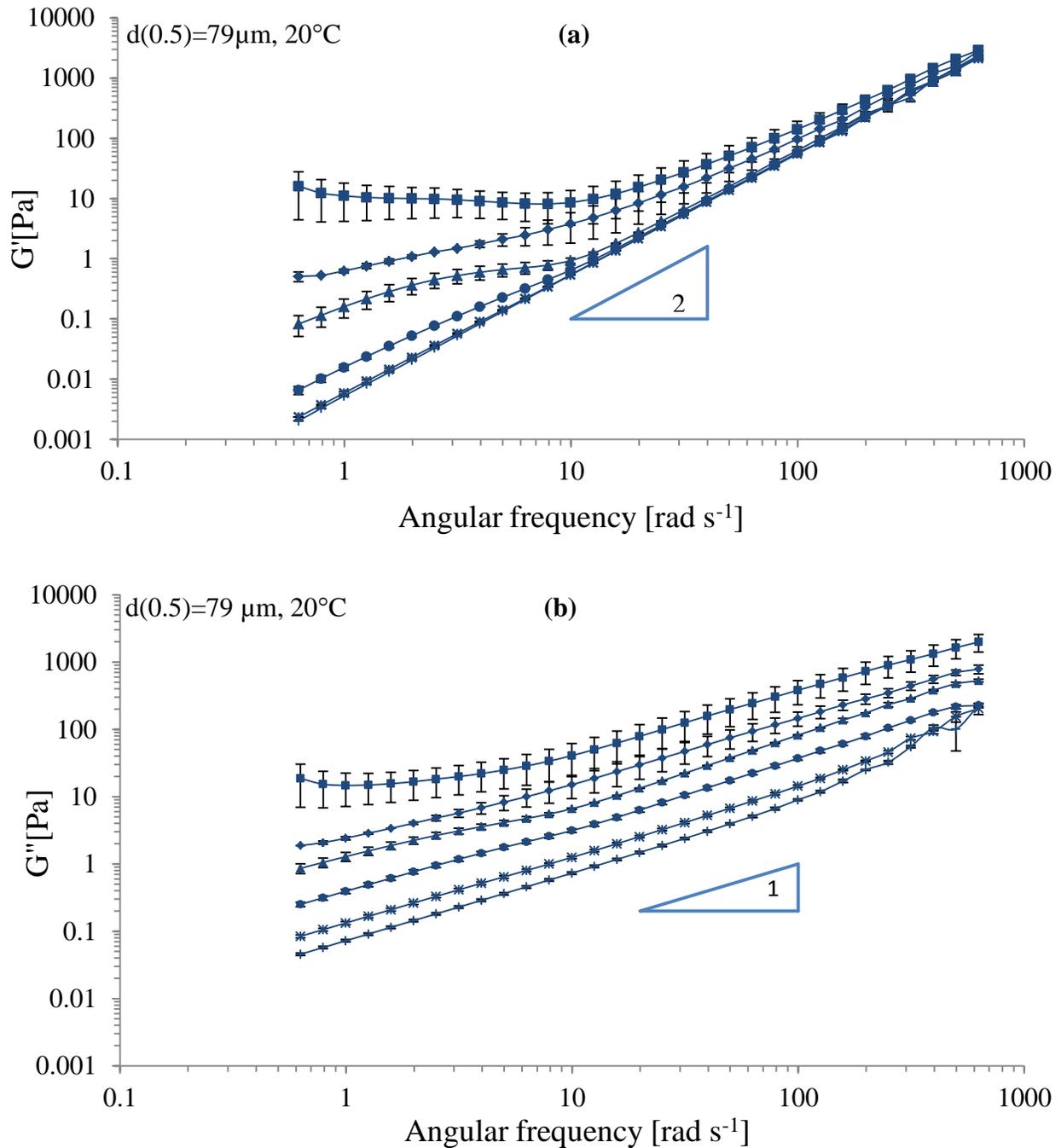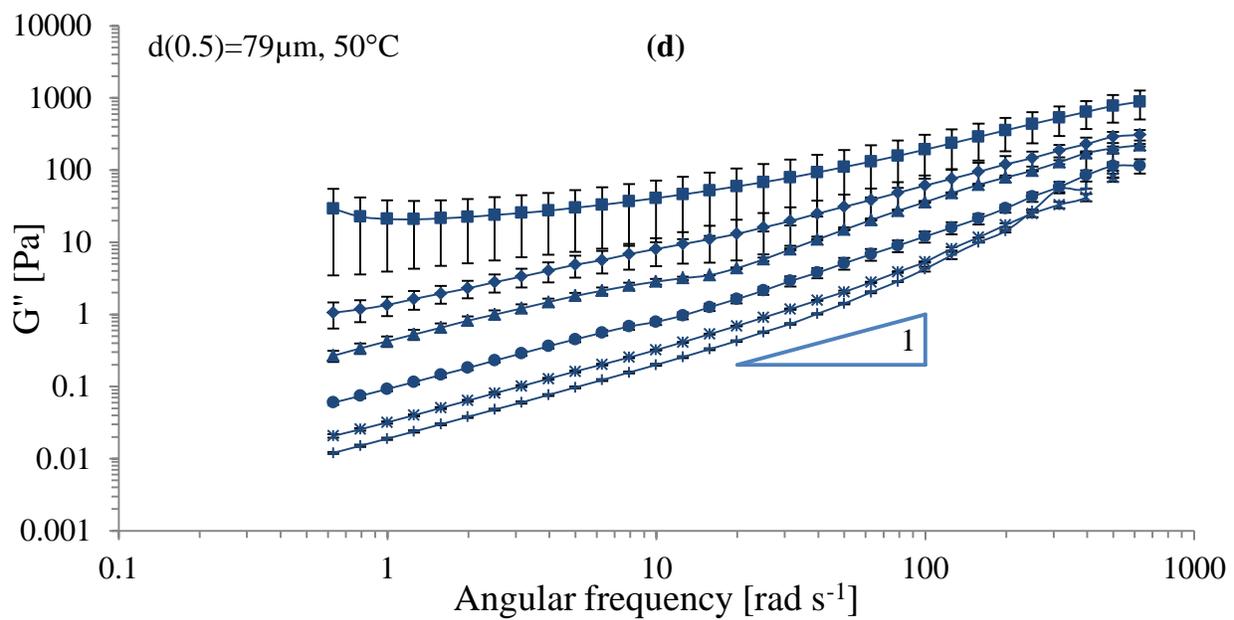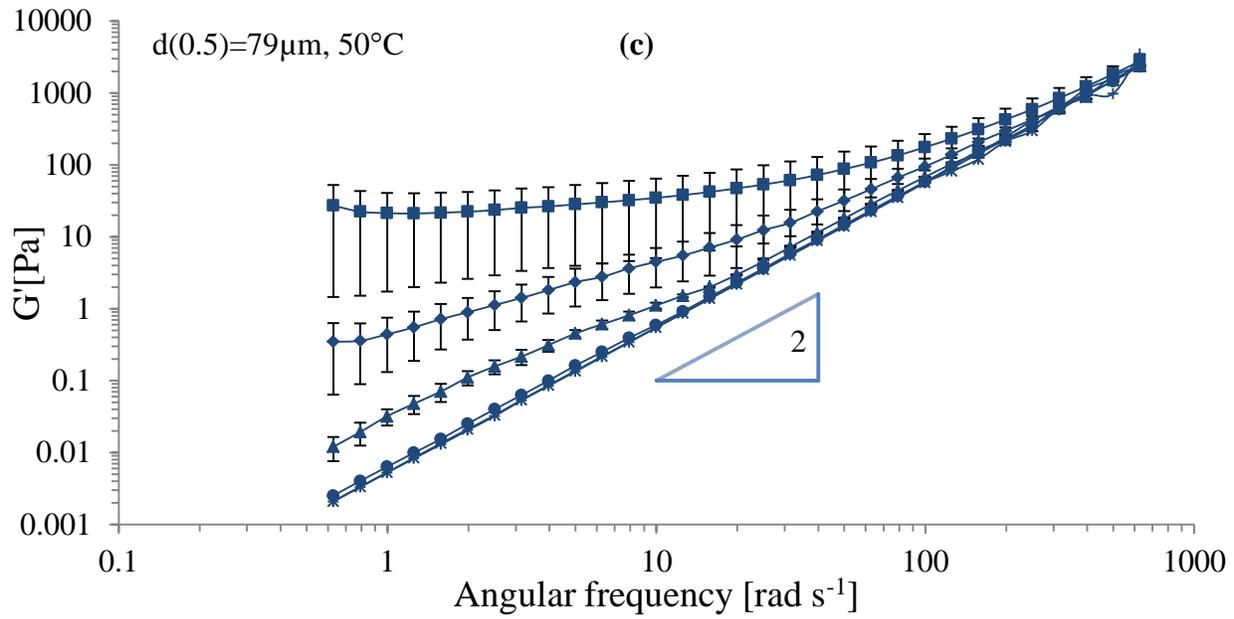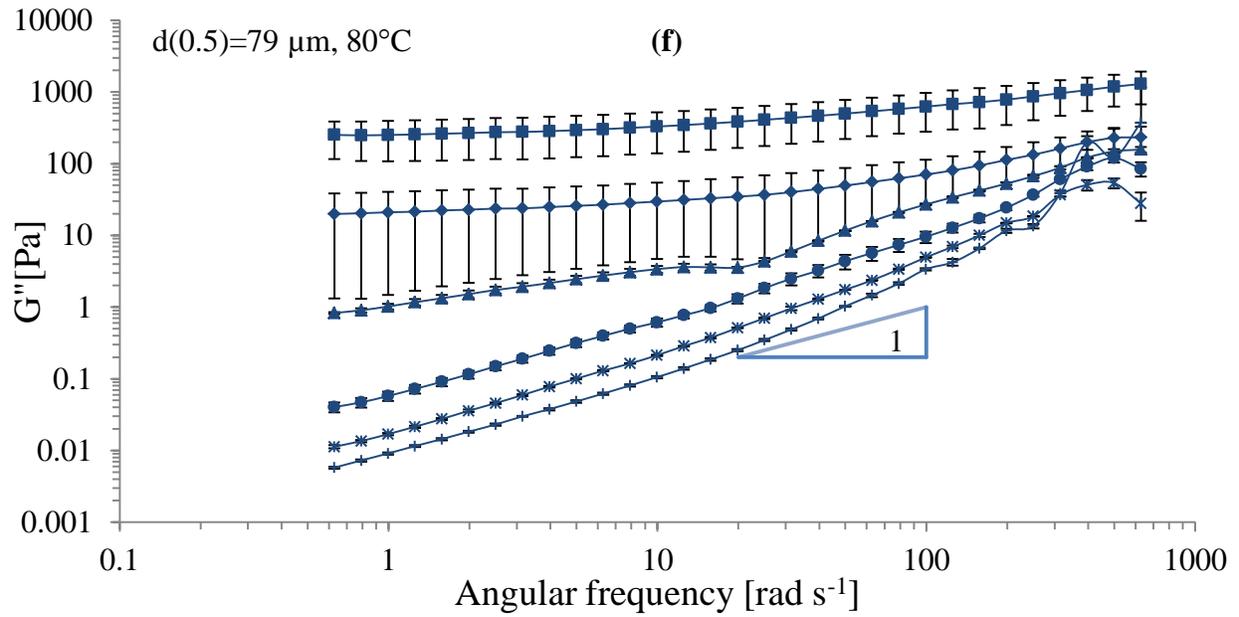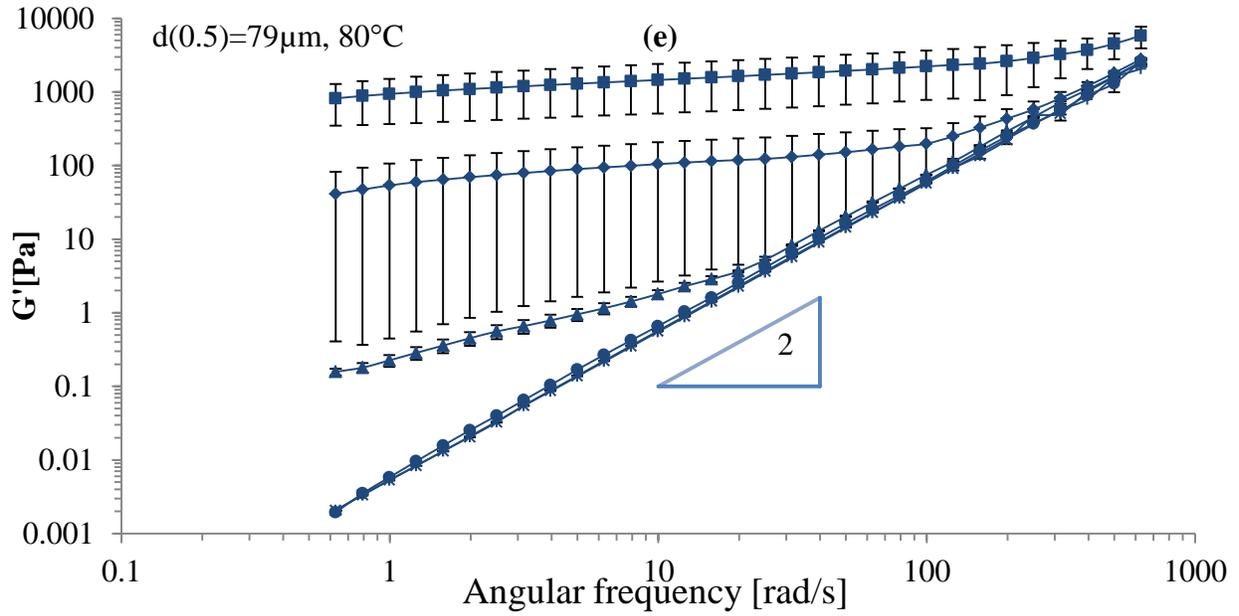
As shown in Fig. 5.1 (a-f) and Fig. 5.2 (a-f), regardless of the particle size and temperature, the loss modulus (G'') increased with increasing Φ due to an increase in the dissipation of viscous energy in an elevated solid volume fraction of particles (Aral and Kalyon 1997). However, increases in storage modulus (G') with increasing Φ were less pronounced compared to changes in G'', particularly at dilute regimes (Φ=1 and 5%).

Based on Fig. 5.1 (a-f) and Fig. 5.2 (a-f), the slope of the G'-ω and G''-ω curves changed over the angular frequency range, i.e., smaller slopes at low ω and larger slopes at high ω. For further investigation, the following relationships between the moduli (G' and G'') and the angular frequency (ω) are assumed (Rao and Cooley 1992; Ahmed and Ramaswamy 2006a):

$$G' = K'\omega^{n'}$$ Eq. 5.1

$$G'' = K''\omega^{n''}$$ Eq. 5.2

where K', K'', n' and n'' are regression coefficients relating G' and G'' to ω. The values of n' and n'' were obtained by determining the slopes of $\ln G'$-$\ln \omega$ and $\ln G''$-$\ln \omega$ curves, respectively (Table 5.1). Since the slopes of the G' and G'' curves vs. ω are not constant over the whole range of angular frequency for all of the solids volume fractions, two values for n' and n'' are reported in Table 5.1 (one at low frequency and one at high frequency). Values of n' and n'' at low and high frequency were determined based upon the changes in the coefficient of determination (R^2) of the trend lines drawn for $\ln G'$-$\ln \omega$ and $\ln G''$-$\ln \omega$ curves. Wherever the highest value of the R^2 for trend lines was obtained, regardless of the number of points considered, slopes were determined. For example, at low frequencies, values of R^2 for the trend lines drawn for the first 2, 3 or more points were compared and the slope of a line with highest R^2 was considered as

n′ or n″ values for each curve. At high frequencies, R^2 values for the trend lines drawn for the last 2, 3 or more points were compared to derive n′ or n″ values for each curve.

Table 5.1. $\boldsymbol{n'}$ and $\boldsymbol{n''}$ for potato powder suspensions at different $\boldsymbol{\Phi}$ and temperatures

Particle median size	Temperature (°C)	ω range	n'						n''					
			Solid volume fraction (%)						Solid volume fraction (%)					
			1	5	10	15	20	25	1	5	10	15	20	25
d(0.5)=34μm	20													
		Low ω	2	2	2	1.72	1.6	1.18	1	1	1	0.97	0.93	0.75
		High ω	2	2	2	2	2	1.95	1	1	1	1.1	1	1.1
	50													
		Low ω	2	2	2	1.99	1.96	1.76	1	1	1	0.97	0.96	0.9
		High ω	2	2	2	1.99	1.99	1.99	1.7	1.6	1.4	1.3	1.3	1.3
	80													
		Low ω	2	2	2	2	1.98	1.27	1	1	1.1	1	1	0.67
		High ω	2	2	2	2	1.98	1.98	1.6	1.4	1.4	1.3	1.3	1.1
d(0.5)=79μm	20													
		Low ω	2	2	1.8	1.4	0.78	-0.1	1	0.99	0.97	0.87	0.73	0.3
		High ω	2	2	2	2	1.8	1.7	1.3	1.1	1.1	1.1	0.98	0.87
	50													
		Low ω	2	2	2	2.1	1	0.12	1	1	0.96	1	0.77	0.16
		High ω	2	2	2	1.9	1.6	1.7	1.77	1.2	1.3	1.2	0.96	0.84
	80													
		Low ω	2	2	2	1	0.57	0.26	1	1	1	0.57	0.12	0.09
		High ω	2	2	2	1.9	1.77	0.99	1.4	1.3	1.2	1.4	0.5	0.4

Based on Table 5.1, by increasing the solid volume fraction of the potato powder suspensions, the breakpoints in the slope of $\ln G'$- $\ln \omega$ and $\ln G''$- $\ln \omega$ curves over the range of angular frequency are more pronounced. Where different slopes were apparent, smaller values of n' and n'' were observed at lower frequencies compared to those at higher frequencies indicating an increase in the dependence of mechanical moduli on angular frequencies with increasing frequency. The smaller slope of $\ln G'$ vs. $\ln \omega$, i.e., less frequency dependency of $\ln G'$ at lower frequencies, can be explained by the formation of temporary agglomerates of particles under low frequency conditions (Aral and Kalyon 1997). At high angular frequencies, the extent of the

agglomeration of particles decreased presumably due to an insufficient time, associated with high frequencies, for particles to agglomerate which led to an increase in the n′ values.

In general, the overall behavior of G' and G'' vs. ω in a suspension can be classified into different regions as shown in Fig. 5.3. At low angular frequency, i.e., long observation time, the viscous or terminal zone is defined at which the slope of $\ln G'$ and $\ln G''$ vs. ω equals 2 and 1, respectively (Mewis and Wagner 2012). Then by increasing the frequency, the two moduli cross over and G' dominates over G'' and a transition region can be defined as the observation time decreases (Ferry 1980; Giboreau, Cuvelier, and Launay 1994; Barnes 2000). As reported in Table 5.1, in most of the potato powder suspensions, the values of n' and n'' are close to 2 and 1, respectively. This shows that these suspensions are mostly in the terminal zone in which G'' is higher than G', i.e., liquid-like behavior prevails.

Fig. 5.3. Various regions in the viscoelastic spectrum of non-Newtonian liquids. Reprinted by permission from Barnes (2000)
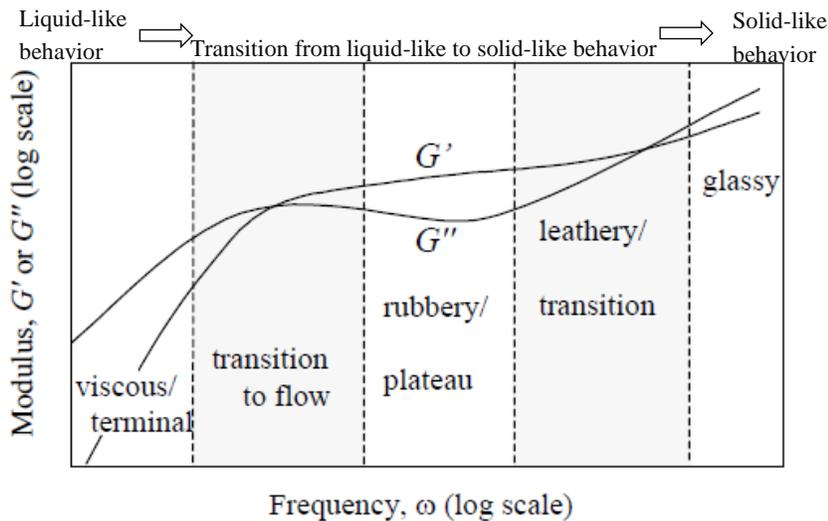
The n' and n'' of potato starch suspensions obtained from Eq. 5.1 and Eq. 5.2 are shown in Table 5.2 (data from Sinaki and Scanlon (2016) for comparison). Potato powder suspensions

are compared to potato starch suspensions based on the fact that potato has a large amount of starch granules, i.e., approximately 15-20% of potato parenchyma's weight is starch granules (Singh and Kaur 2016), i.e., about 75% of the solids content of these samples is starch.

Based on Table 5.2, measurable n' values, which indicate the presence of a solid-like behavior, exist only for the more concentrated potato starch granule suspensions, and this was only apparent at low angular frequencies. Also, by increasing the temperature this weak elasticity totally disappeared.

Table 5.2. n' and n'' for potato starch suspensions at low ω and different Φ and temperatures

Temperature (°C)	n'						n''					
	Solid volume fraction (%)						Solid volume fraction (%)					
	1	5	10	15	20	25	1	5	10	15	20	25
20	-	-	-	-	-3.32	-0.84	1	1	1	1	1	1
50	-	-	-	-	-	0.63	1	1	1	1	0.98	0.97
80	-	-	-	-	-	-	1	1	1	1	1	1

The comparison between the n' and n'' values of the potato powder suspensions and potato starch granule suspensions shows that the viscoelastic properties differ considerably in these two types of suspensions. There is a measurable elastic response in all potato powder suspensions over the whole range of ω, while a very weak solid-like behavior is only observed at low frequencies and high solids content for the potato starch granule suspensions. Therefore, it can be concluded that the starch granules are not the predominant factor in the rheological properties of potato powder suspensions, but instead the elastic character is due to other intracellular and intercellular components in the potato parenchyma.

The most important component affecting the rheological properties of plant-tissue suspensions is confirmed to be pectin polymers (Ross-Murphy 1995; Hill, Ledward, and Mitchell 1998). Pectin content is high in potato cell walls, i.e., 55-60% of the cell wall dry weight (Singh and Kaur 2016). Accordingly, it can be presumed that the rheological properties of the potato powder suspensions are influenced by four different types of interactions: particle-particle interactions, pectin-sucrose interactions, pectin-pectin interactions and particle-pectin interactions. First, the particle-particle interactions promoted by attractive interparticle forces among neighboring particles result in the formation of aggregates (Mewis and Wagner 2012), which typically leads to the presence of solid-like behavior in suspensions (Genovese 2012). This type of interactions is evident in starch granule suspensions, particularly at high solid volume fractions (Sinaki and Scanlon 2016). Second, pectin-sucrose interactions are presumed to exist in our potato powder suspensions. An interaction between pectin polymers and sucrose in the continuous phase is believed to promote the formation of a pectin-sucrose network (Fu and Rao 2001) by providing additional hydroxyl groups (Ahmed, Ptaszek, and Basu 2017). Sucrose is used as an effective modifier of the properties of pectin solutions (da Silva and Rao 2006), decreasing the water activity and increasing hydrogen bonding formation (Evageliou, Richardson, and Morris 2000; Ahmed, Ptaszek, and Basu 2017). Third, there are interactions between pectin polymers which lead to the formation of gels in pectin aqueous solutions (Sorchan et al. 1971; Sriamornsak 2003; da Silva and Rao 2006; Sila et al. 2009). Fourth, particle-pectin polymer interactions can induce flocculation of dispersed particles (Sorchan et al. 1971; Walstra 2002; Gregory and Barany 2011). As per Elimelech et al. (1995), flocculation is the term used when the aggregation of particles is induced by addition of polymers. Flocculation occurs when several particles are connected by a polymer chain (bridging) (Elimelech et al.

1995). Based on Koch et al. (2016), even in a dilute suspension, particles can flocculate in the presence of polymers causing solid-like behavior in suspensions (Koch, Lee, and Mustafa 2016). In conclusion, the presence of solid-like behavior in the potato powder suspensions over the whole frequency range, even in dilute suspensions, i.e., $\Phi=1\%$, is believed to be due to the presence of all four of these interactions.

Furthermore, G' and G'' were observed to be affected by temperature (Fig. 5.1 (a-f) and Fig. 5.2 (a-f)). In almost all suspensions, G'' decreased while G' values did not change significantly with increasing temperature, regardless of the particle size. The only exception was in suspensions of d(0.5)= 79 μm at $\Phi=20\%$ and 25% where both G' and G'' increased with increasing temperature. The difference in the effect of temperature on G' and G'' values of suspensions with d(0.5)=34 μm and d(0.5)= 79 μm, might imply a particle size-related phenomenon, which will be discussed in section 5.3.1.2.

5.3.1.2. Loss Factor

To demonstrate the transition from liquid-like to solid-like behavior in the suspensions due to changes in Φ and to show the effect of temperature on the balance between suspension components in two phases, the loss factor (G''/G') values of samples are plotted in Fig. 5.4 (a-f). As a dimensionless parameter, the loss factor is a measure of the ratio of the energy lost to the energy stored in a material in oscillatory testing (Ferry 1980).

Fig. 5.4. Loss factor as a function of angular frequency for potato powder suspensions at 20°C (a-b), 50°C (c, d) and 80°C (e, f): Φ = 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■)

(c)   d(0.5)=34 μm, 50 °C

(d)   d(0.5)=79 μm, 50 °C

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(e) d(0.5)=34 μm, 80 °C

(f) d(0.5)=79 μm, 80 °C
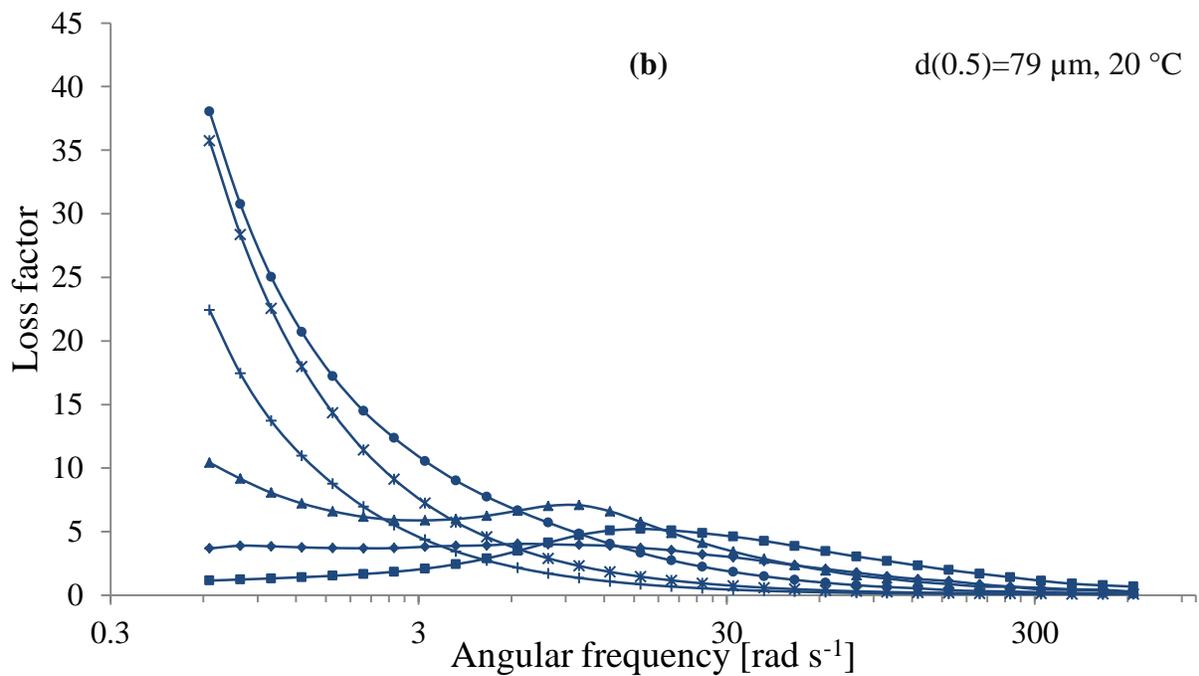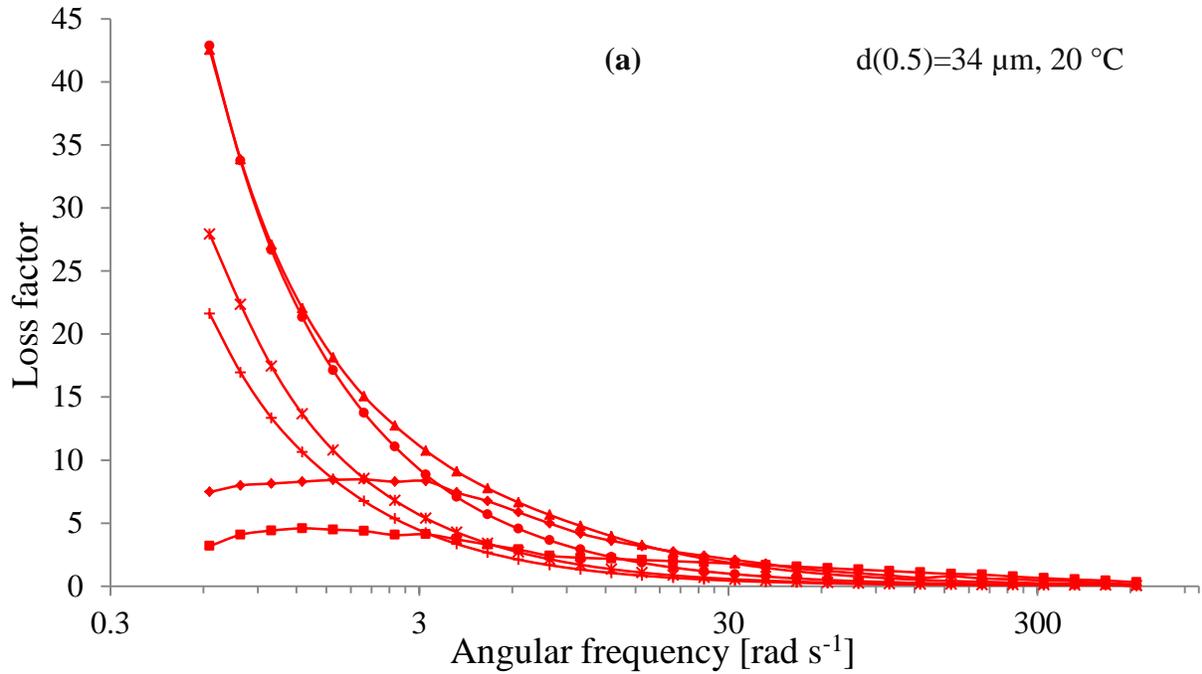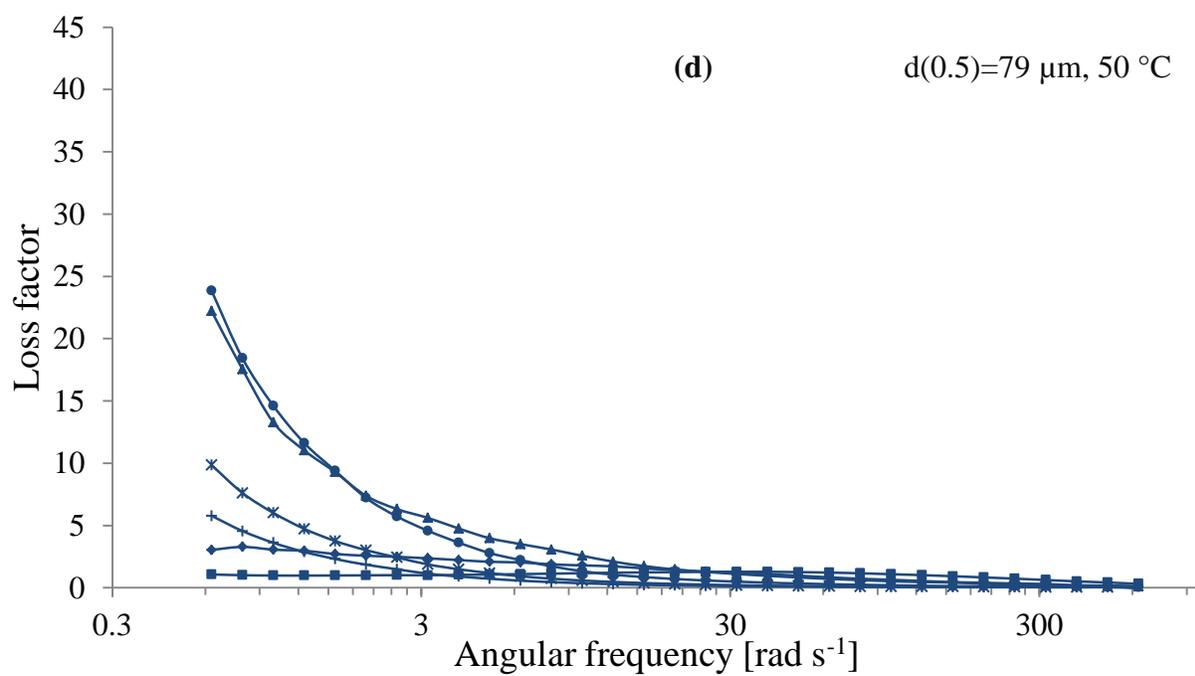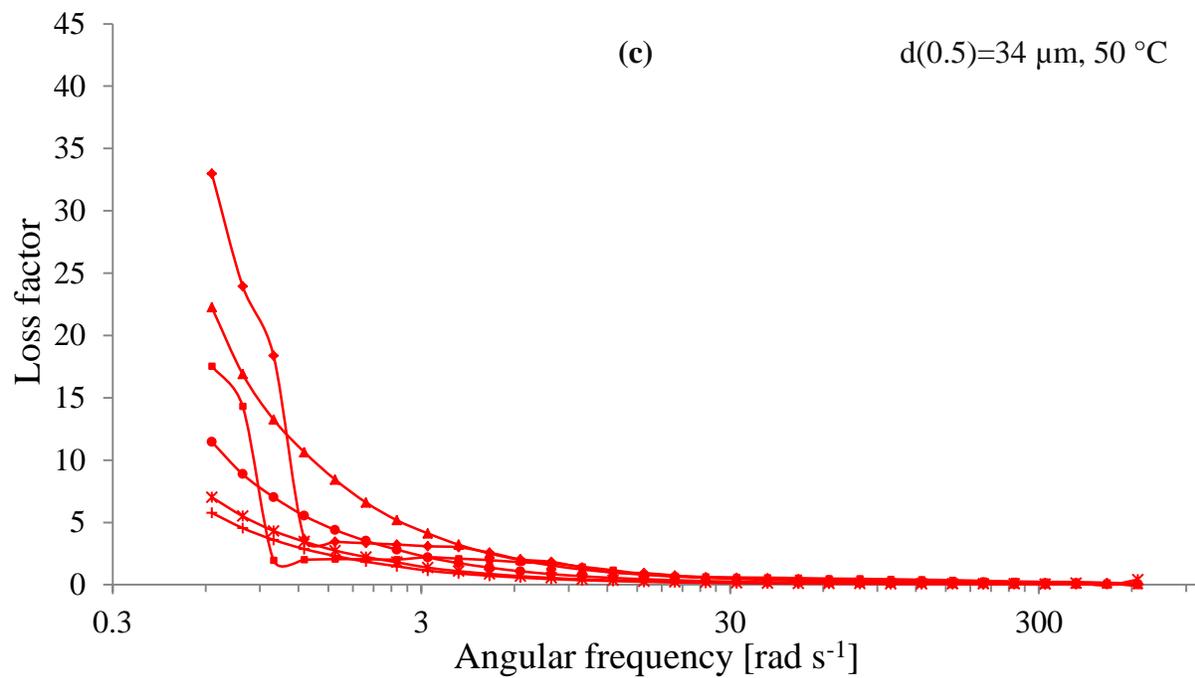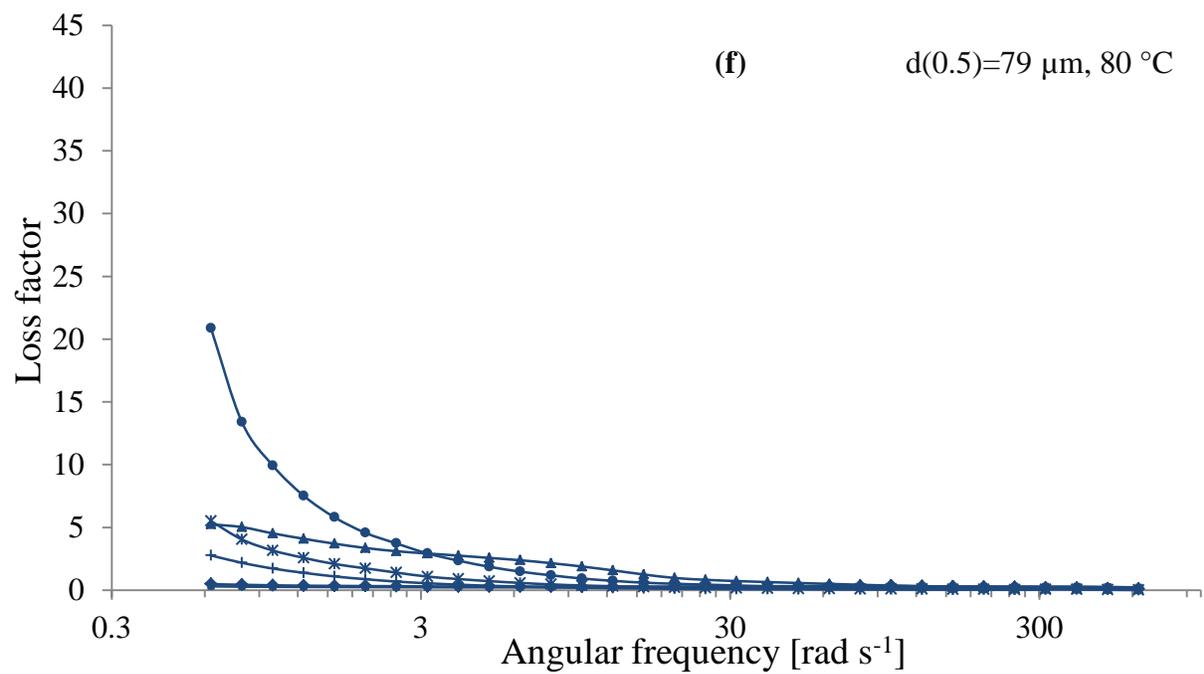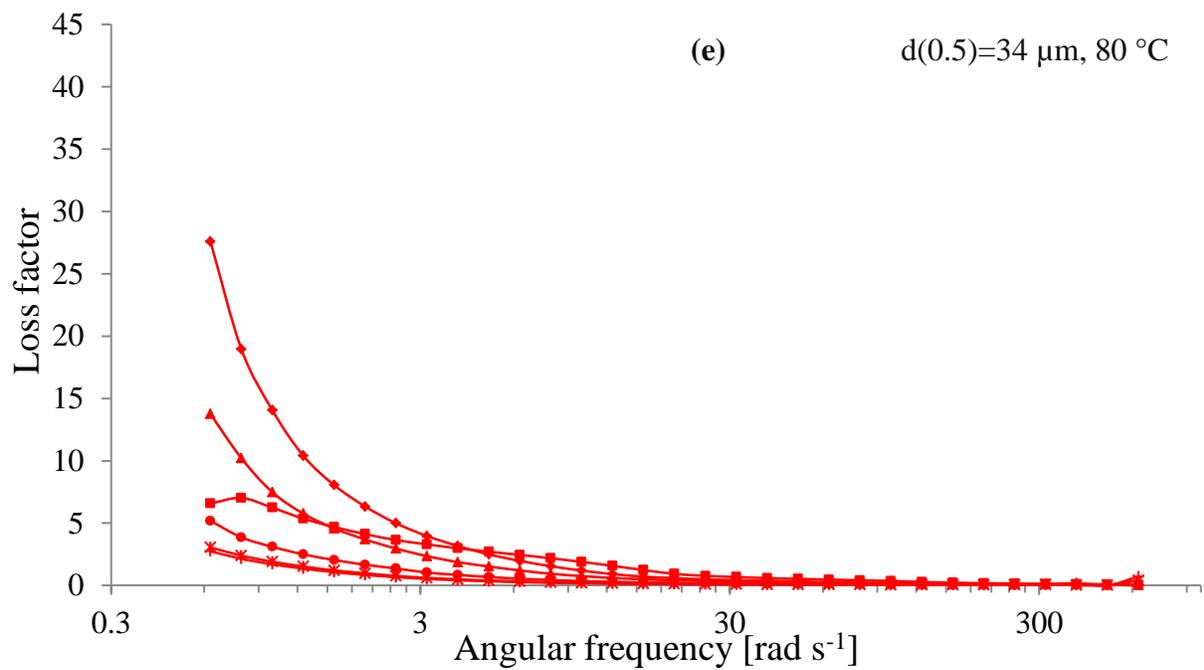
As shown in Fig. 5.4 (a-f), at low angular frequencies, the loss factor values are substantially larger than 1 ($G'' \gg G'$) for most suspensions regardless of the solid volume fractions and particle size, indicating a liquid-like behavior of the potato powder suspensions. With increasing ω, loss factor values decreased, with the loss factor falling exponentially against $\ln \omega$ for some volume fractions, indicative of a loss factor that scales inversely with angular frequency. The reason might be attributable to a decrease in the time for deformation with increasing ω, which resulted in less energy dissipation in the potato powder suspensions (Aral and Kalyon 1997). This decrease in loss factor values of potato powder suspensions with increasing ω indicated a transition from a liquid-like ($G'' > G'$) to a solid-like ($G' > G''$) behavior in the suspensions. The loss factor curves for more concentrated suspensions, i.e., $\Phi = 20\%$ and 25%, are almost flat and unchanged over the whole frequency range (Fig. 5-4 a-f). However, at $\Phi = 15\%$, 20% and 25% in suspensions of d(0.5)=79 µm at 20ºC (Fig. 5.4 b), there is a small peak in the curve of loss factor vs. angular frequency, $3 < \omega < 30$. This peak might be an indication of changes in the structure (disruption and formation) as a result of a slow relaxation of the entangled network of pectin polymers within a specific angular frequency range (Jurczuk, Galeski, and Piorkowska 2014; Jurczuk and Galeski 2016). No such small peak was observed in the curves of loss factor vs. angular frequency for suspensions of d(0.5)=34 µm as well as suspensions of d(0.5)=79 µm at 50 and 80 ºC.

Moreover, comparing the loss factor values of suspensions prepared at different Φ revealed a decrease in loss factor values with increasing Φ in the potato powder suspensions at all temperatures. An enhanced solid-like behavior of suspensions at higher Φ might be due to elevated particle-particle interactions promoted by attractive interparticle forces among neighboring particles with increasing Φ (Mewis and Wagner 2012). That is, more concentrated

suspensions had larger and/or more aggregates than dilute suspensions, leading to smaller values of loss factor in the former compared to the latter (Ikeda and Nishinari 2001; Jurczuk, Galeski, and Piorkowska 2014). In other words, a gradual transition from liquid-like to solid-like behavior of the suspensions was observed as a result of an increase in Φ.

At most solid volume fractions, the loss factor for suspensions of bigger particles, i.e., d(0.5)= 79 μm, is lower than that for suspensions of particles with d(0.5)= 34 μm, showing a greater solid-like behavior of the former compared to the latter (Fig. 5-4 a-f). However, the particle size could not be considered as the only responsible factor for such observation. The reason is that the shape and surface properties of the dispersed particles were changed as a result of changes in the size of the potato powder particles (Moelants, Cardinaels, Jolie, et al. 2014). Therefore, the extent to which the particle size per se influenced the viscoelastic properties of the potato powder suspensions is unknown.

Furthermore, the loss factor was observed to be affected by temperature. As an example, the loss factor values for suspensions of Φ= 15% at three different temperatures are shown in Fig. 5.5. As demonstrated in Fig. 5.5, the loss factor is lower at a higher temperature for a given Φ. The same trend was also observed for the potato powder suspensions prepared at various solid volume fractions (not shown here).

Fig. 5.5. Loss factor as a function of angular frequency for potato powder suspensions of d(0.5)=

34μm and Φ=15% at temperatures= 20°C (■), 50°C (▲), 80°C (●)
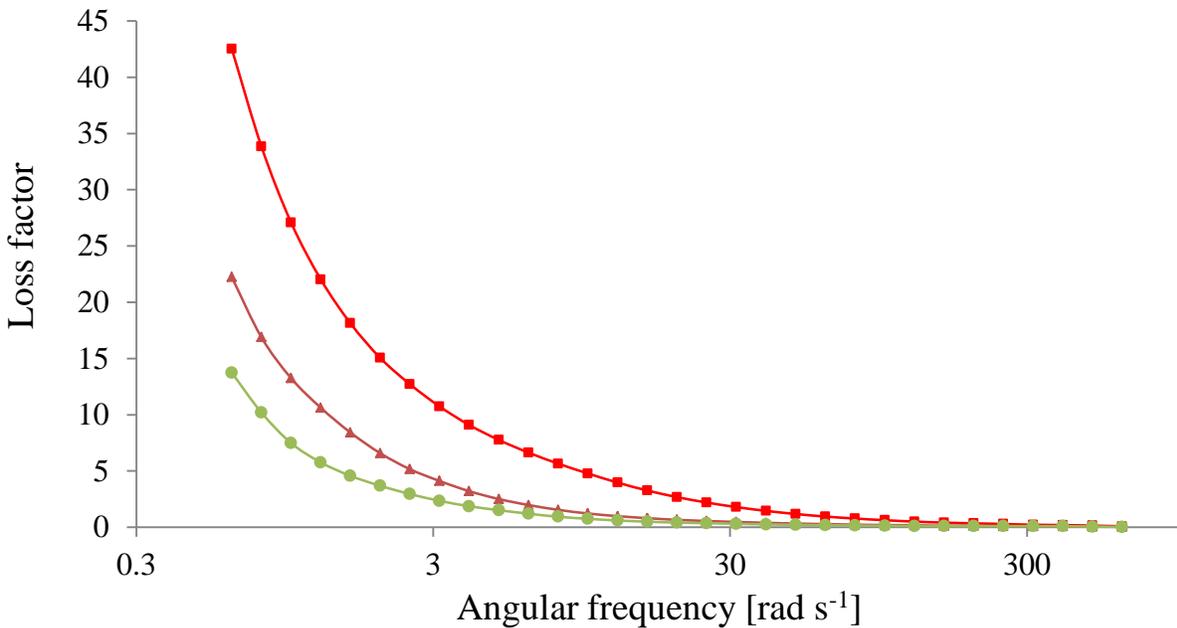
The decrease in loss factor values of suspensions with increasing temperature is attributable to the role of temperature in promoting the solubility of intracellular and intercellular components, particularly pectin polymers (Sriamornsak 2003). Consequently, greater interactions, e.g., pectin-promoted interactions, existed at elevated temperatures resulting in more solid-like behavior in the suspensions (Fig. 5.5). To examine whether this enhanced solid-like behavior at elevated temperatures was associated with gelation in the suspensions, the existence of gel properties in the suspensions is investigated here. Gel properties are considered to exist in suspensions when G' does not depend on ω and the loss factor is smaller than one (Ross-Murphy 1995). Based on Figs. 5.1, 5.2 and 5.4, suspensions of d(0.5)= 79 μm at Φ=20% and 25% are the only suspensions exhibiting gel properties, and only at 50 and 80 °C. This was not the case for suspensions with d(0.5)= 34 μm, which impute a particle size-related phenomenon occurred at elevated temperatures, for which the following hypothesis is suggested.

The hypothesis is related to the jamming of dispersed particles which is promoted at elevated temperatures. Based on Fig. 4.2, in the potato powder suspensions of d(0.5)=79 µm, there is a small portion of particles that exceeds the upper particle size limit of the recommended range for the concentric cylinder geometry, i.e., d(0.9) = 145 µm > gap/10. This transgression could result in locking and jamming of the particles in concentric cylinders (Cheng and Richmond 1978; Savage and Mckeown 1983). This was not the case for potato powder suspensions of d(0.5)= 34 µm in which d(0.9)= 62 µm. Jamming, which is particularly exhibited at more concentrated volume fractions, is one of the scenarios for gelation (Trappe et al. 2001; Lu et al. 2008). Gelation is observed here to be more prevalent at elevated temperatures, i.e., 50 and 80 °C, due to the effect of temperature on different components of the potato powder suspensions. However, increasing gel behavior with increasing temperature was not observed in potato powder suspensions of d(0.5)=34 µm. A closer look at the strain values for potato powder suspensions of d(0.5)=34 µm and d(0.5)=79 µm subjected to the frequency sweep test is helpful in understanding the effective role of jamming in the gel behavior of suspensions of d(0.5)=79 µm. For this purpose, strain values of these suspensions tested at a typical angular frequency (ω=6.284 rad s^{-1}) and temperatures of 20, 50 and 80 °C are shown in Table 5.3.

Table 5.3. Strain values for potato powder suspensions at ω=6.284 rad s^{-1}

	Φ (%)	Temperature(°C)		
		20	50	80
d(0.5)=34 μm				
	1	0.91	0.99	1.0
	5	0.86	0.99	1.0
	10	0.71	0.97	0.99
	15	0.46	0.92	0.99
	20	0.31	0.77	0.91
	25	0.16	0.37	0.39
d(0.5)=79 μm				
	1	0.90	0.99	1.0
	5	0.78	0.98	1.0
	10	0.43	0.90	0.97
	15	0.21	0.45	0.37
	20	0.11	0.19	0.13
	25	0.04	0.06	0.0010

Based on the strain results (Table 5.3), potato powder suspensions of d(0.5)=79 μm at 20ºC were deformed remarkably less than those of d(0.5)= 34 μm at Φ > 5%. Additionally, at Φ >15%, significantly smaller deformations in suspensions of d(0.5)=79 μm, compared to those of d(0.5)= 34 μm, was observed at all temperatures. These observations implied the direct effect of Φ on the jamming of particles, as previously demonstrated by Trappe et al. (2001).

Additionally, an increase in the temperature will result in specific intercellular and intracellular interactions which might be responsible for enhanced solid-like behavior of the potato powder suspensions at elevated temperatures. These interactions are mostly induced by

pectin, including pectin-particle interactions, pectin-sucrose interactions and pectin-pectin interactions (Fu and Rao 2001; da Silva and Rao 2006).

Pectin polymers and starch granules are the two important intracellular and/or intercellular components in the dispersed phase which affect the properties of plant-tissue suspensions (Ross-Murphy 1995; Hill, Ledward, and Mitchell 1998). Lopez-Sanchez, Nijsse, et al. (2011) showed that the effect of temperature on the disruption of tomato, carrot and broccoli is different, which they related to the amount of pectin in these vegetables. In general, by increasing the temperature, the release of pectin from the particulates increases, and more depolymerization and solubilization of pectin occurs (Ormerod et al. 2004; Sila et al. 2009; Moelants, Cardinaels, Van Buggenhout, et al. 2014). These phenomena lead to an increase in pectin-pectin and pectin-sucrose interactions in the suspension, which in turn, affect the gel properties of pectin polymers (da Silva and Rao 2006). Generally, the structure of a gel owes its physical properties to the properties of a network of polymer molecules (Flory 1995). In pectin gels, the structure is stabilized by hydrogen bonds and hydrophobic interactions of the ester methyl groups (Walkinshaw and Arnott 1981; da Silva, Gonçalves, and Rao 1995; Thakur et al. 1997; Chan et al. 2017). The stability of hydrophobic interactions can be improved by increasing the temperature (0- 50 °C) and adding different sugars (Oakenfull and Scott 1984). Oakenfull and Scott (1984) demonstrated that by increasing the temperature, hydrophobic interactions increase. Evageliou, Richardson, and Morris (2000) showed that the storage modulus (G') at 90 °C for pectin-sucrose solutions at sucrose concentrations of 50 and 55 wt% were appreciably higher than the corresponding values at 5 °C. They concluded that this behavior is related to the formation of additional intermolecular associations in the solution as the temperature is increased (Evageliou, Richardson, and Morris 2000).

Furthermore, an increase in pectin solubility will decrease the solid volume fraction of the suspension and change the characteristics of the dispersed particle properties, i.e., size, shape and surface. That is, an increase in temperature will create a new polydispersed system with particles of different shapes and surface properties and smaller size than in the unheated suspensions (Bayod et al. 2005; Lopez-Sanchez, Nijsse, et al. 2011; Augusto and Vitali 2014; Moelants, Cardinaels, Van Buggenhout, et al. 2014).

In addition to pectin, thermal changes in the starch granules, which are quantitatively the most abundant component of potato parenchyma, should be considered in an investigation of the viscoelastic properties of potato powder suspensions. As shown in many studies, the thermal changes in starch granules are affected by both the temperature and the moisture content of the aqueous suspension (Colonna and Buleon 2010). The use of a 60% sucrose solution as the continuous phase for the potato powder suspensions highly restricts the availability of free moisture. This restriction increases the temperature required for thermal changes to occur in the starch granules, such as gelatinization and swelling (Chiotelli, Rolée, and Le Meste 2000; Colonna and Buleon 2010). For 60% sucrose solutions, thermal changes in starch granules did not occur in the potato powder suspensions even at our highest chosen temperature, i.e., 80°C. Therefore, it can be concluded that the alteration in the properties of the continuous phase and pectin polymers, i.e., depolymerization and solubilization, are the main factors which contribute to the decrease in G'' and G' with increasing temperature.

5.3.2. Correlation between Complex Viscosity and Shear Viscosity

Complex viscosity (η^*) is used to characterize the properties of a viscoelastic suspension which is defined as (Barnes 2000; Gunasekaran and Ak 2003):

$$\eta^* = \eta' + i\eta'' \tag{Eq. 5.3}$$

where

$$\eta' = {}^{G''}\!/_{\omega} \tag{Eq. 5.4}$$

and

$$\eta'' = {}^{G'}\!/_{\omega} \tag{Eq. 5.5}$$

The empirical Cox-Merz relationship is usually employed to show the similarity between the complex viscosity and the shear viscosity. In this rule, a curve of complex viscosity vs. angular frequency is often numerically close to a curve of shear viscosity vs. shear rate (Cox and Merz 1958):

$$|\eta^*(\omega)| = \eta(\dot{\gamma}), (\omega = \dot{\gamma}) \tag{Eq. 5.6}$$

The curves of complex viscosity ($|\eta^*|$) versus angular frequency (ω) and those of shear viscosity (η) versus shear rate ($\dot{\gamma}$), from chapter 4, for the potato powder suspensions are compared in Fig. 5.6 (a-f).

Fig. 5.6. Steady shear viscosity (η) (solid lines) and oscillatory complex viscosity (|η*|) (dotted lines) versus the shear rate ($\dot{\gamma}$) and angular frequency (ω) for potato powder suspensions at 20°C (a, b), 50°C (c, d) and 80°C (e, f) with Φ = 1% (+), 5% (*), 10% (●), 15%(▲), 20% (♦), 25% (■)

(c)   d(0.5)=34μm, 50 °C

Complex and shear viscosity [Pa.s]

Angular frequency [rad s⁻¹] and shear rate [s⁻¹]

(d)   d(0.5)=79μm, 50 °C

Complex and shear viscosity [Pa.s]

Angular frequency [rad s⁻¹] and shear rate [s⁻¹]

(e) d(0.5)=34μm, 80 °C

Complex and shear viscosity [Pa.s]

Angular frequency [rad s⁻¹] and shear rate [s⁻¹]

(f) d(0.5)=79μm, 80 °C

Complex and shear viscosity [Pa.s]

Angular frequency [rad s⁻¹] and shear rate [s⁻¹]
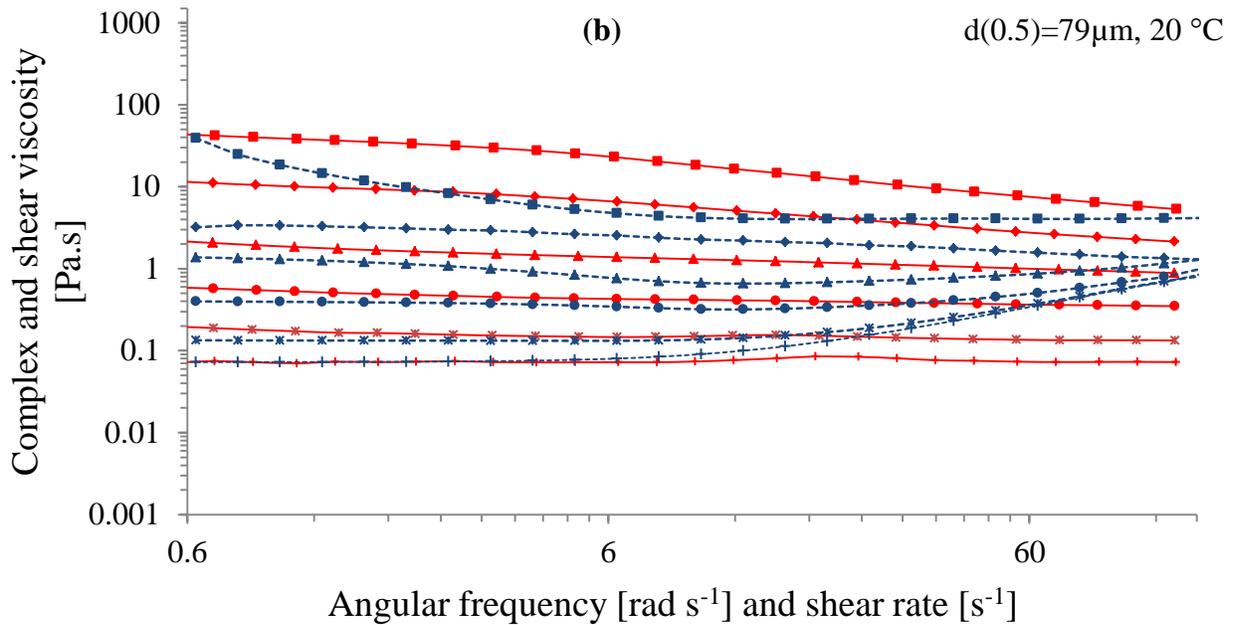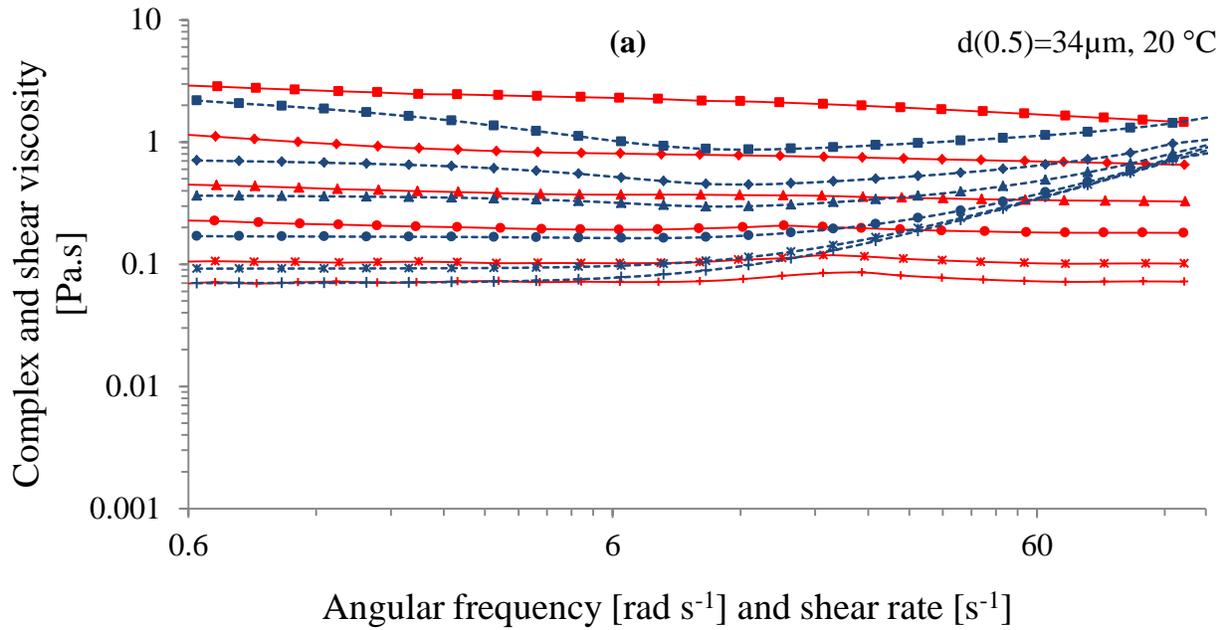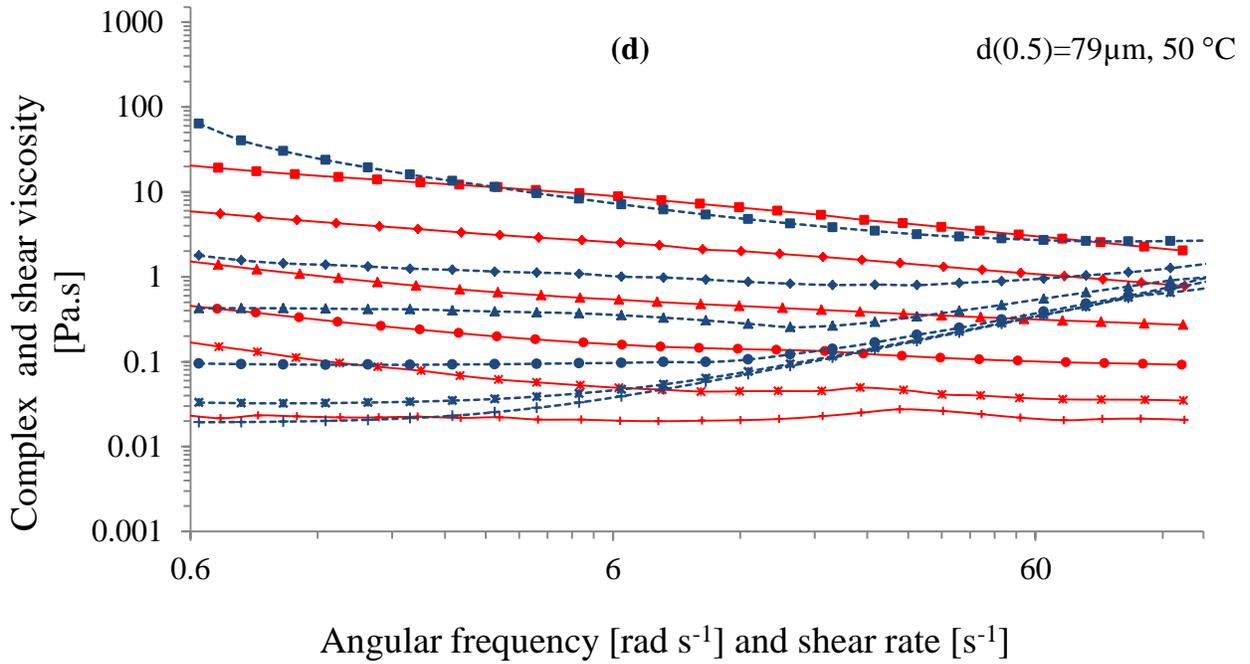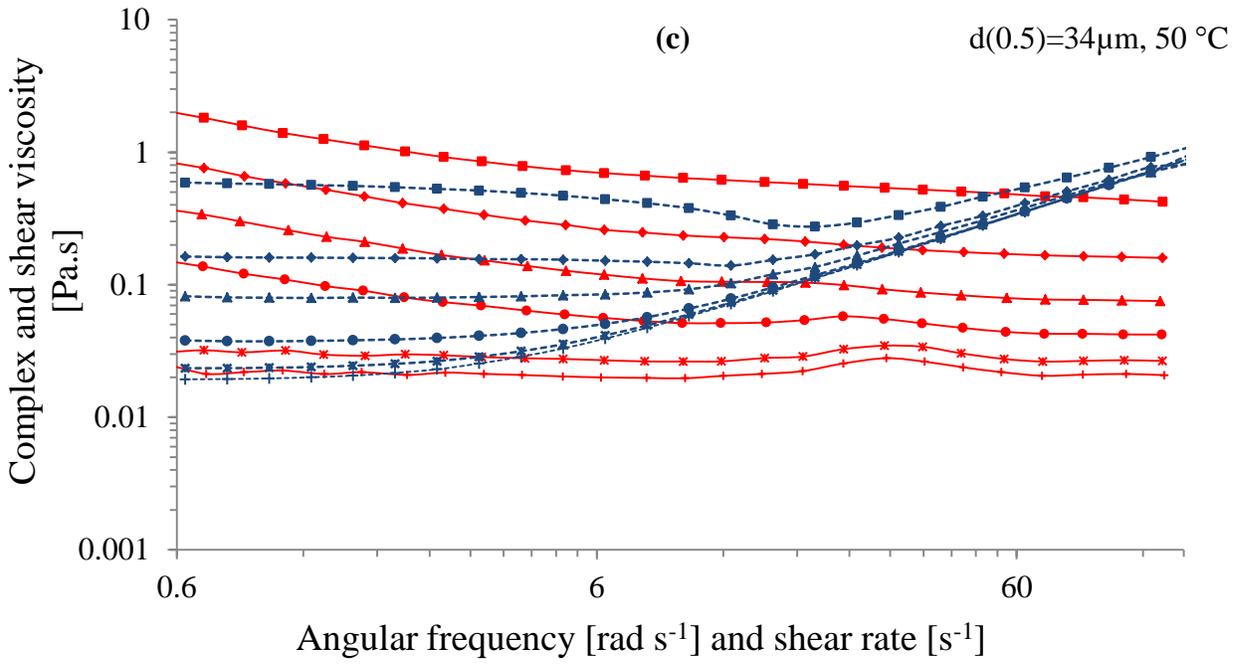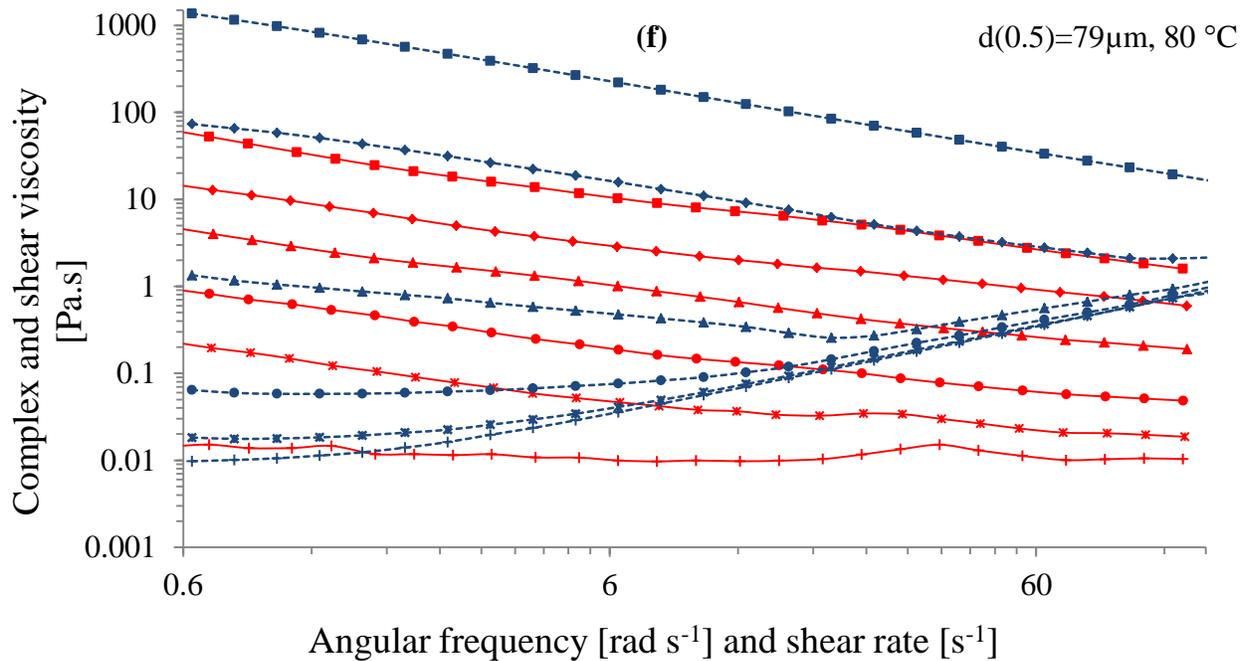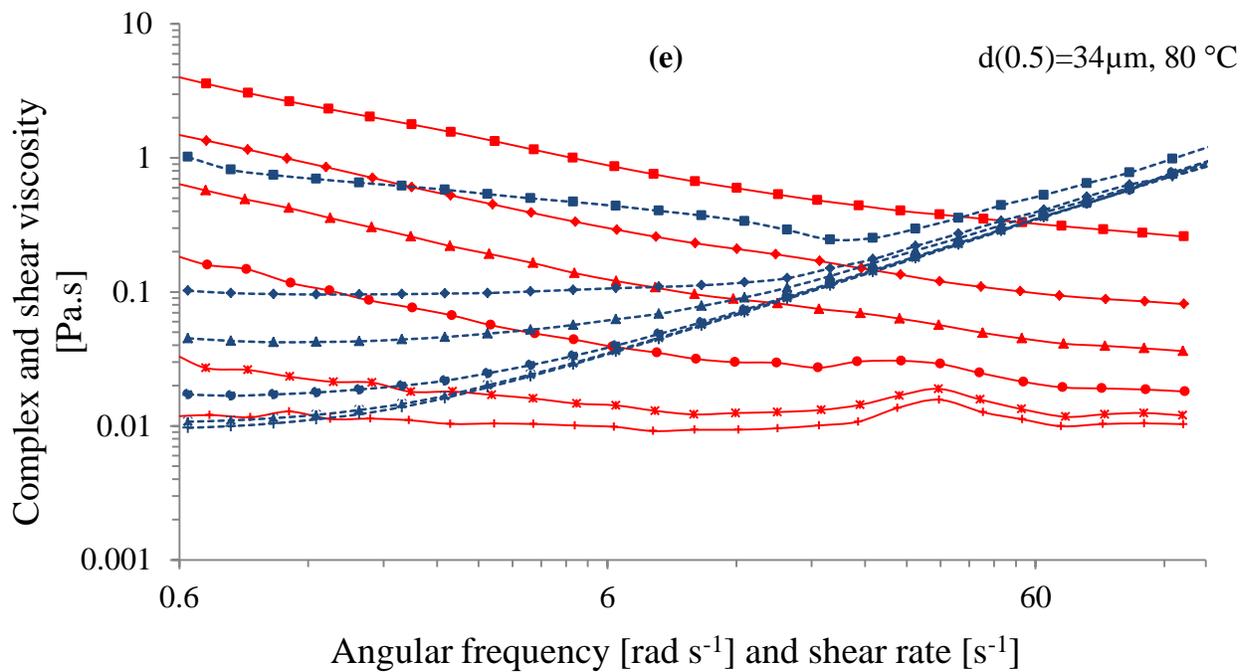
Based on Fig. 5.6 (a-f), deviations from the Cox–Merz relationship are observed for almost all potato powder suspensions for the whole range of $\dot{\gamma}$ (or ω), regardless of the temperature and the particle size of the suspensions. The only exception is the potato powder suspensions of $\Phi=1\%$ in which the η^*-ω and η-$\dot{\gamma}$ curves coincide at low values of $\dot{\gamma}$ (or ω) at 20 °C. Deviation from the Cox-Merz rule has been reported for most complex food systems, e.g., tomato concentrates (Bistany and Kokini 1983; Rao and Cooley 1992), and for biopolymer dispersions, e.g., pectin dispersions (da Silva, Gonçalves, and Rao 1993). The failure of the Cox-Merz rule has been related mostly to the aggregation of the particles in a suspension (da Silva, Gonçalves, and Rao 1993; Ikeda and Nishinari 2001). A deviation from the Cox–Merz rule could be considered as an indication of the non-linear, i.e., time-dependent, viscoelastic behavior of the suspension (Gleissle and Hochstein 2003). It has been stated that he Cox–Merz rule should only be employed if the rheological properties of a suspension are studied in a linear viscoelastic region (Han, Zhao, and Wang 2016). Nevertheless, despite a difference between the values of the complex and shear viscosities in most of the suspensions, the complex and shear viscosities show the same behavior to an increase in $\dot{\gamma}$ (or ω) up to a certain point, e.g., $\dot{\gamma}$ (or ω)$\cong$10 for suspensions at 20 °C. Beyond this point, the trends in the complex and shear viscosities vary, i.e., there is a transition from shear-thinning to shear-thickening behavior of suspensions with increasing ω, i.e., decreasing time, in the shear oscillatory test (Han, Zhao, and Wang 2016).

A clear understanding of the underlying factors behind the contradiction between the results obtained by the shear flow test and the shear oscillatory test could be achieved by looking at the relationship between $\dot{\gamma}$ in the shear test and ω in the oscillatory test. According to AR2000 Rheometer operator's manual (AR 2000; TA Instruments, New Castle, DE, USA) for the

concentric cylinder geometry (Fig. 5.7), $\dot{\gamma}$ in the shear flow test is related to the angular frequency (ω) by the following equation:

$$\dot{\gamma} = F_{\dot{\gamma}}\omega \qquad\qquad \text{Eq. 5.7}$$

where $F_{\dot{\gamma}}$ (shear rate factor) is determined by equation 5.8.

$$F_{\dot{\gamma}} = \frac{1}{\tan\alpha} \qquad\qquad \text{Eq. 5.8}$$

Fig. 5.7. Concentric cylinder geometry
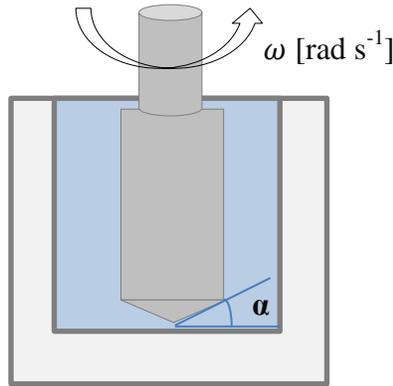
Based on the data acquired from the AR2000 rheometer for the concentric cylinder geometry used in this study, the shear rate factor ($F_{\dot{\gamma}}$) value was 14.52, i.e., α=0.069 rad. Consequently, the range for the angular frequency values in the shear flow test of the potato powder suspensions was 0.02-9.4 rad s^{-1} which fell within the low ω region of the oscillatory test. In other words, there was agreement between the results of shear flow and oscillatory tests, as both tests indicated shear-thinning behavior for most potato powder suspensions at low frequencies (ω <10 rad s^{-1}). The difference between the trends of the complex and shear viscosities with ω observed only at low solid volume fractions, i.e., Φ=1% and 5%, might be attributable to artefacts due to a variety of factors, e.g., inertia (Spagnolie 2015). To demonstrate

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the good agreement between the changes in the complex and shear viscosities of potato powder suspensions with ω, a plot of complex and shear viscosity versus ω for a typical sample is shown in Fig. 5.8.

Fig. 5.8. Complex (dotted lines) and shear (solid lines) viscosity of suspensions of d(0.5)=34µm at 20 °C with $\Phi = 1\%$ (+), 5% (*), 10% (●), 15%(▲), 20% (♦), 25% (■)
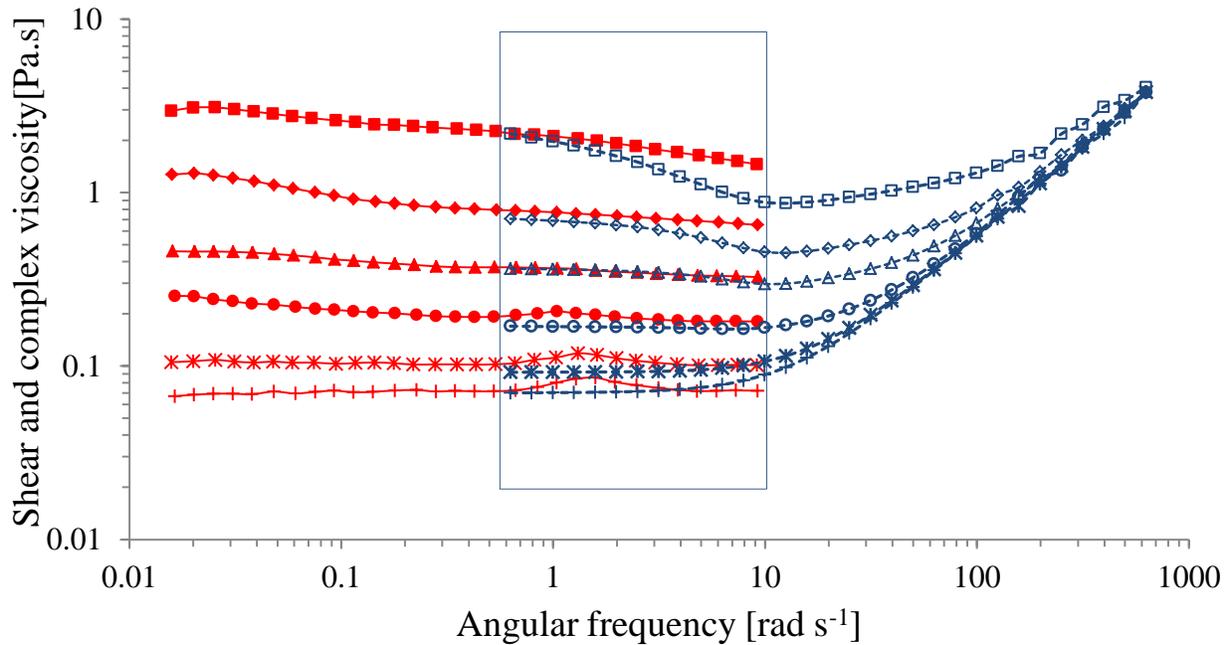
Moreover, a comparison between viscosity curves of Fig. 5.6 at different temperatures shows that the $\dot{\gamma}$ (or ω) value at which the suspensions display a non-linear viscoelastic behavior decreases with increasing temperature. According to changes in the dependence of the shear and complex viscosities on $\dot{\gamma}$ (or ω) shown in Fig. 5.6, the viscosity curves can be divided into two regions: linear and non-linear viscoelastic regions. The curves in Fig. 5.6 (a-f) show that in non-linear viscoelastic regions for most of the potato powder suspensions the complex viscosity increases with increasing angular frequency, showing a thickening behavior. The presence of this thickening behavior at high frequencies might be attributable to an increase in the solid-like

response of the suspensions with an increase in angular frequency (Boersma, Laven, and Stein 1992; Lee and Wagner 2003). Furthermore, an increase in temperature widened the thickening frequency window in the potato powder suspensions, i.e., thickening behavior started at lower frequencies in suspensions with increasing temperature (Fig. 5.6). The effect of temperature increase on increasing thickening behavior in suspensions at high frequencies confirmed the influence of temperature on the solid-like response of the suspensions illustrated by the loss factor results (Fig. 5.5). That is, by increasing the temperature, various interactions such as particle-pectin polymer and pectin-pectin interactions, were promoted leading, to more solid-like responses in the suspensions.

5.4. Conclusion

In this chapter, an oscillatory test was used to evaluate the viscoelastic properties of potato powder aqueous suspensions. In particular, this work shows the important role of the solid volume fraction, particle size and temperature on the viscoelastic properties of potato powder suspensions. Increases in solid volume fraction and temperature serve as two important parameters that promote interactions in the suspensions, i.e., particle-particle and pectin-promoted interactions. These interactions are responsible for a liquid-like to solid-like transition in the potato powder suspensions at elevated solid volume fraction and temperature. The deviation from the Cox-Merz rule was believed to be attributable to the complex nature of the potato powder suspensions in which the rheological behavior was found to be sensitive to the rate of testing. At a comparable time-scale (or frequency) employed in the shear flow and shear oscillatory deformation, the results of the two tests were in agreement. A comparison of the viscoelastic properties of potato powder suspensions with those of potato starch granule suspensions shows the influence of different intracellular and intercellular components,

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particularly pectin polymers, on the behavior of potato powder suspensions. Pectin-promoted interactions dictate the overall viscoelastic properties of the potato powder suspensions.

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6. Rheological Behavior of Aqueous Suspensions of Carrot Parenchyma Powder as Affected by Solids Volume Fraction and Temperature

Abstract

Carrot is widely used in the processing of different commercially prepared foods. Therefore, an understanding of the rheological behavior of its suspensions is of interest for high efficiency and low price production of commercial carrot-based foods. In this chapter, the relationship between the rheological behavior of carrot parenchyma powder aqueous suspensions with varying solids volume fraction (Φ) was studied at various temperatures. A solids volume fraction range of Φ= 1-25% was used to represent dilute, semi-dilute and more concentrated regimes. All suspensions were prepared by dispersing the carrot parenchyma powder particles in a 60% (w/w) sucrose solution to prevent particle sedimentation under the effect of gravity. Rheological behavior was studied using shear flow and oscillatory shear tests at 20, 50 and 80 °C in a rotational rheometer. The results showed an increase in the consistency factor and the yield stress, as well as shear-thinning behavior and a decrease in the loss factor, with increasing Φ. Suspensions of Φ=25% were highly shear-thinning (n~0.2) with a large yield stress (>100 Pa). Loss factor results indicated that the more concentrated suspensions, i.e., Φ=20% and 25%, were mostly gels. By increasing the temperature from 20 to 80 °C, the shear-thinning behavior and yield stress increased while the consistency factor and the loss factor decreased. To further investigate the role of different interactions among components on the rheological properties of the carrot powder suspensions, their rheological properties were compared with those of potato powder suspensions. Differences in the rheological properties of the carrot and potato powders suspensions are attributable to the difference in the extent of pectin-induced interactions and particle-particle interactions present in these suspensions.

Keywords: Carrot parenchyma powder, suspension, rheology, solid volume fraction, temperature

6.1. Introduction

Although a daily intake of fruit and vegetables of about 600 g has been recommended by most health organizations, most people consume lower than this amount (Lopez-Sanchez, Nijsse, et al. 2011). In this regard, the food industry has attempted to meet consumer needs and has paid great attention to producing healthier and more natural fruit and vegetable food products. Among all different vegetables, carrots, which are grown throughout the world, are an important vegetable based on the rate of production and market value (Rubatzky, Quiros, and Simon 1999; Simon 2000; Simon et al. 2008). This vegetable with high nutrient content is widely used for producing a number of natural and healthier products and ready-to-eat foods. Carrot is a major source of natural antioxidants in addition to the anticancer activity associated with β-carotene (a precursor of vitamin A) (Speizer et al. 1999). Carrot tissue contains mostly water, i.e., approximately 86 to 89%, as well as carbohydrates (6-10%), sugars (5-6%), crude fiber (1-2%), protein (less than 1%) and fat (less than 1%) (Simon 2000; Sharma et al. 2012).

Many vegetable food products, including products derived from carrots, are suspensions. Understanding the rheological behavior of these suspensions is critical for designing an appropriate production line with the lowest price and the highest efficiency. In general, the rheological properties of a suspension depend on the properties of both continuous and dispersed phases. The properties of the dispersed phase can be classified according to the surface properties of the particles, particle size and shape (Lapasin, Grassi, and Pricl 1996; Snabre and Mills 1996; Barnes 2000; Tropea, Yarin, and Foss 2007).

The dispersed phase in plant-tissue suspensions is mostly cell clusters, single cells and cell fragments (Moelants, Cardinaels, Van Buggenhout, et al. 2014). These particles will be affected by different processing regimes, e.g., thermal and mechanical treatments, where the

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intensity and conditions of the processes are important factors. The effect of high-pressure homogenization and heating processes on the microstructure of carrot dispersions in the presence of 5% (w/w) olive oil has been studied by Lopez-Sanchez, Svelander et al. (2011). The authors showed that a high shear input was required for carrot tissue to be disrupted into cells and cell fragments (Lopez-Sanchez, Svelander et al. 2011). Also, after heating a blend of carrot and water at 90°C for 40 minutes, a loss of intercellular adhesion occurred as a result of the solubilization of pectin polymers (Lopez-Sanchez, Svelander et al. 2011). Similar observations were reported by Ormerod et al. (2004), where the solubilization of pectin polymers as a result of thermal treatment caused a decrease in cell-cell adhesion, which in turn affected the particle properties. Any change in the particle properties, such as size, can influence the rheological properties of the suspensions. Moelants, Cardinaels, et al. (2013) studied the effect of particle properties on the rheological characteristics of carrot suspensions. They showed that these suspensions have a non-Newtonian behavior with a yield stress that changed with particle size and type (cell cluster, single cell or cell fragments). However, relationships between rheological parameters and particle properties were not clear since the changes in particle size were accompanied by changes in the particle shape and surface properties (Moelants, Cardinaels, et al. 2013).

The aim of this study, in a series of investigations of the rheological properties of plant-tissue based aqueous suspensions, is to study the rheological behavior of carrot powder aqueous suspensions. The main goal is to determine the effects of solids volume fraction and temperature on the rheological behavior of carrot powder suspensions. For examining these, two different types of deformations, i.e., shear flow and oscillatory shear, were applied on suspensions in a rotational rheometer. In addition, the rheological behavior of the carrot powder suspensions was compared with that of potato powder suspensions of similar solids volume fraction and at the

same temperature. This comparison has been done to gain insights into the role of constituent components on the rheological properties of the carrot suspensions.

6.2. Materials and Methods

6.2.1. Preparation of Carrot Powder Particles

The complete procedure for preparation of carrot powder is shown in Fig. 6.1. One batch of fresh carrot was purchased locally and used for all preparations. As shown in Fig. 6.1, carrots were washed and peeled. Then, they were cut into small pieces and boiled in water at 100 °C for 20 minutes. The resulting liquid was poured out and carrot pieces were put into an oven at 50 °C for approximately 96 hours. This period of time was used to reach a constant weight by removing unbound water in the carrot particles. Afterward, the dried carrot particles were disintegrated with a kitchen blender followed by a grinding in a Retsch ZM200 mill (Retsch GmbH, Haan, Germany) with a mesh size of 80 µm.

Fig. 6.1. Preparation steps of carrot powder

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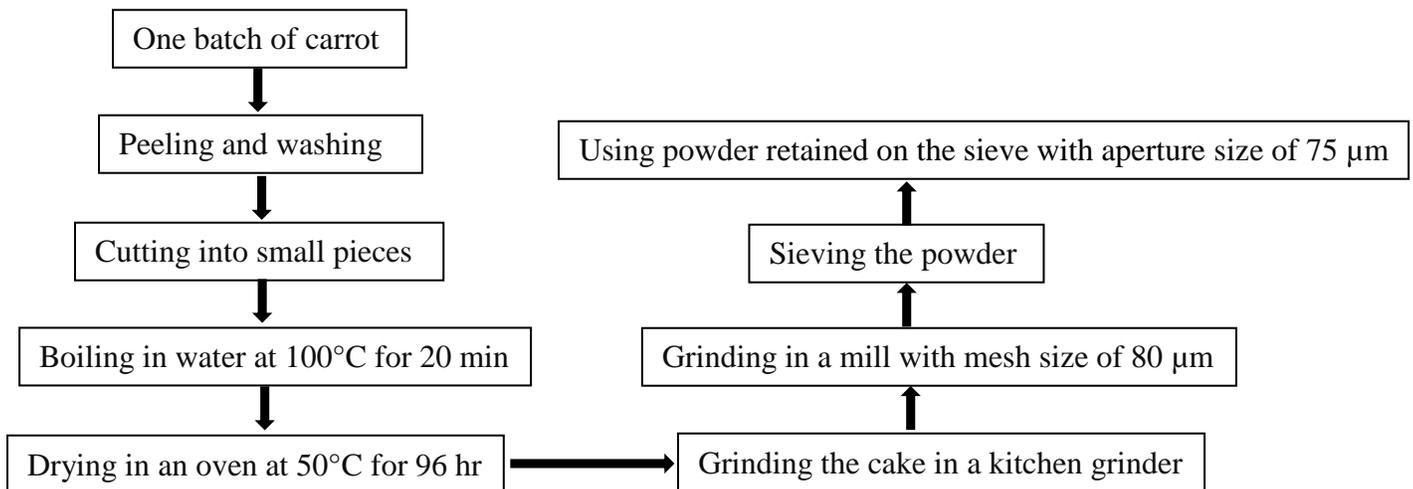
A dry sieving technique was used to classify the carrot powder particle sizes. Four different aperture sizes (202, 106, 75 and 63µm) were chosen for sieving carrot powder (155 g). Sieves were then shaken for 50 minutes on an Endecott test sieve shaker (Endecotts Ltd, London, UK). The carrot powder retained on each sieve size was collected in five different beakers. The beakers remained in a refrigerator until the test date.

The carrot powder particles retained on the sieve with aperture size of 75 µm (75-106 µm) were used for preparation of carrot suspensions. Carrot powder showed a tendency to agglomerate, particularly in the case of fine powder, i.e., greater agglomerations in the sieve with aperture size of 63 µm. This tendency made the sieving process difficult to carry on due to the clogging of the sieve meshes (McGlinchey 2005). Consequently, all the rheological measurements were performed on the carrot powder particles retained on the sieve with aperture size of 75 µm, a size that was also used to prepare the potato powder suspensions. The comparison was carried out between suspensions prepared with carrot and potato powders retained on the sieve with aperture size of 75 µm. However, the mean particle size varied slightly between these two powders, i.e., d(0.5)=79 µm for the potato powder and d(0.5)=60 µm for the carrot powder, on the sieve with aperture size of 75 µm. This difference in mean particle size of the carrot and potato powders was indicative of a greater tendency of carrot powder to agglomerate. For the particle size measurements, a Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK) was used. Fig. 6.2 shows the results of the particle size measurements of the selected carrot powder particles.

Fig. 6.2. Particle size distribution of carrot powder residing on the sieve size of 75 µm

d(0.1): 16 µm
d(0.5): 60 µm
d(0.9): 144 µm
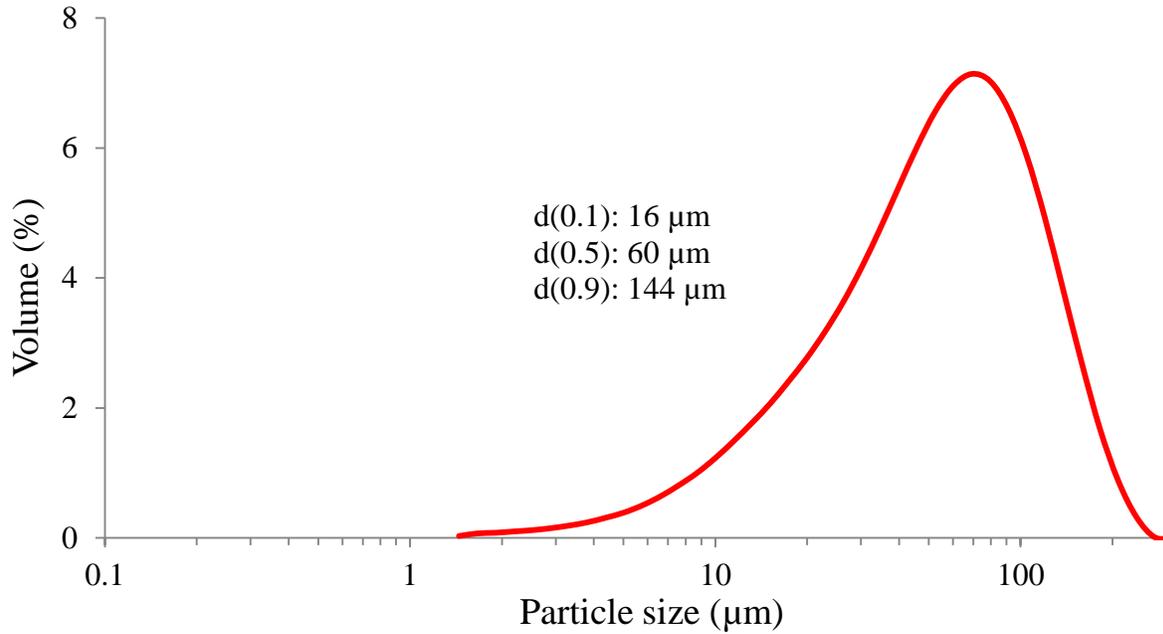
6.2.2. Solids Volume Fraction

For preparing the suspensions at a specific particle concentration, the definition of solid volume fraction was employed and the required amount of powder was calculated based on the powder density and the definition of solid volume fraction. To obtain an accurate solids volume fraction, the density of the carrot particles was measured with a multivolume helium pycnometer 1305 (Micromeritics, Norcross, GA, USA). The density of carrot powder was about 1483 kg m^{-3} (Table 6.1). The density of potato powder was 1530 kg m^{-3}. Consequently, the weight of powder used for preparing the carrot powder suspension with a given solid volume fraction varied slightly from the same solid volume fraction of the potato powder suspension.

Table 6.1. The density values (kg m^{-3}) of the carrot powder

Replication	Duplication 1	Duplication 2
1	1484	1481
2	1486	1480
3	1488	1480
Average	1486	1480

6.2.3. Preparation of Carrot Powder Suspensions

A concentrated sucrose solution, i.e., 60% (w/w), was used as the continuous phase. This solution was prepared by dissolving 60 grams of sucrose in 40 grams of water. This continuous phase was selected to prevent sedimentation of carrot particles by increasing the density of the continuous phase.

By adding appropriate amounts of carrot particles to the sucrose solution, six suspensions were prepared with different solid volume fractions, i.e., $\Phi = 1\%, 5\%, 10\%, 15\%, 20\%$ and 25%, to investigate the effect of solids volume fraction (Φ) on the rheological behavior of carrot powder suspensions. Each solids volume fraction represents a specific regime: for the dilute regime $\Phi = 1\%$ and 5%, for the semi-dilute regime $\Phi = 10\%$ and 15%, and for the concentrated regime $\Phi = 20\%$ and 25%. All suspensions were prepared at room temperature. First, they were mixed with a spatula and then stirred for 15 minutes with a magnetic stirring bar. For all measurements, fresh suspensions (less than 1 hr old) were used. All measurements were performed in duplicate.

6.2.4. Rheological Measurements

The prepared suspensions were poured carefully from a beaker into a concentric cylinder geometry of a rotational rheometer (AR 2000; TA Instruments, New Castle, DE, USA) as described in Chapter 4.

Rheological measurements were carried out by applying two different types of deformation, i.e., shear flow and oscillatory shear. In the shear flow test, a continuous ramp with a shear rate increasing from 0.2 to 143.1 s^{-1} was used. Then, the oscillatory shear measurements were conducted as a frequency sweep with angular frequency ranging from 0.6 to 628 rad s^{-1} at a fixed oscillatory stress of 1 Pa (Sinaki and Scanlon 2016). To characterize the effect of temperature on the rheological behavior of the carrot suspensions, all measurements were run at three different temperatures, i.e., 20, 50 and 80°C. The manner of measurements of rheological properties on a given suspension were: (i) shear flow at 20°C (ii) dynamic oscillatory shear at 20°C (iii) shear flow at 50°C (iv) dynamic oscillatory shear at 50°C (v) shear flow at 80°C and (vi) dynamic oscillatory shear at 80°C. Rheological parameters of carrot powder suspensions, including power-law index (n), consistency factor (k), yield stress (σ_y) and loss factor, were obtained as per Chapters 4 and 5 for potato powder suspensions.

6.3. Results and Discussion

6.3.1. The Effect of Solids Content

6.3.1.1. Shear-thinning Behavior

Analysis of shear stress-shear rate data of carrot powder suspensions (Fig. 6.3) revealed their shear-thinning behavior. This behavior increased dramatically with increasing Φ and with

temperature, such that suspensions at Φ=25% were highly shear-thinning (power low index (n) ~0.2) (Fig. 6.4).

Fig. 6.3. Flow properties of aqueous suspensions of carrot powder particles at three temperatures

and Φ= 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■).
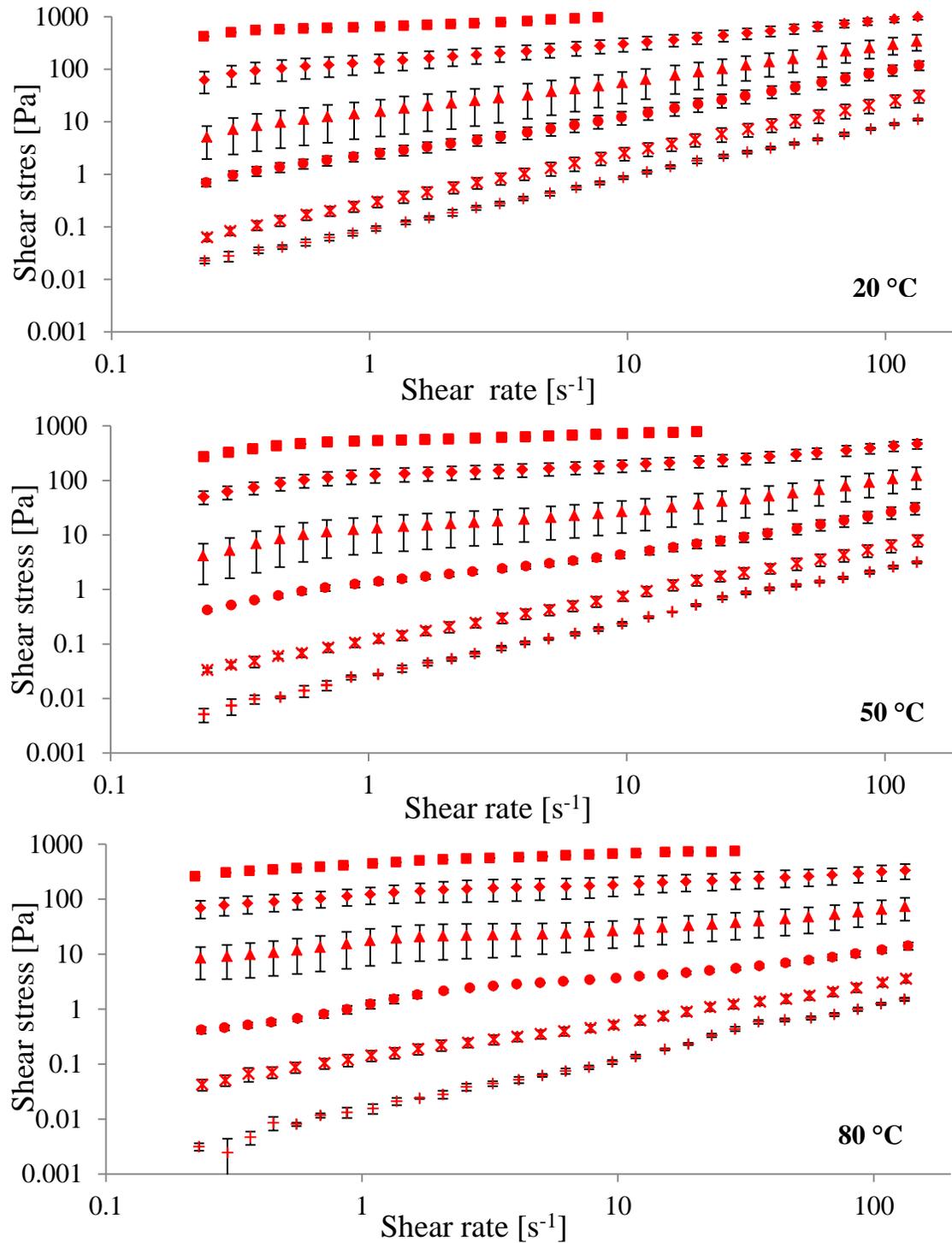
A comparison between power-law index values (n) of aqueous suspensions of carrot and potato powders at three different temperatures, i.e., 20, 50 and 80 ℃, is also presented in Fig. 6.4. Although not as pronounced, similar results to carrot powder suspensions were observed for potato powder suspensions, i.e., greater shear-thinning behavior for the more concentrated regimes (Fig. 6.4).

Fig. 6.4. Power-law index values of aqueous suspensions of carrot powder (solid line) and potato powder (dotted line) at 20 °C (■), 50 °C (●) and 80 °C (▲)
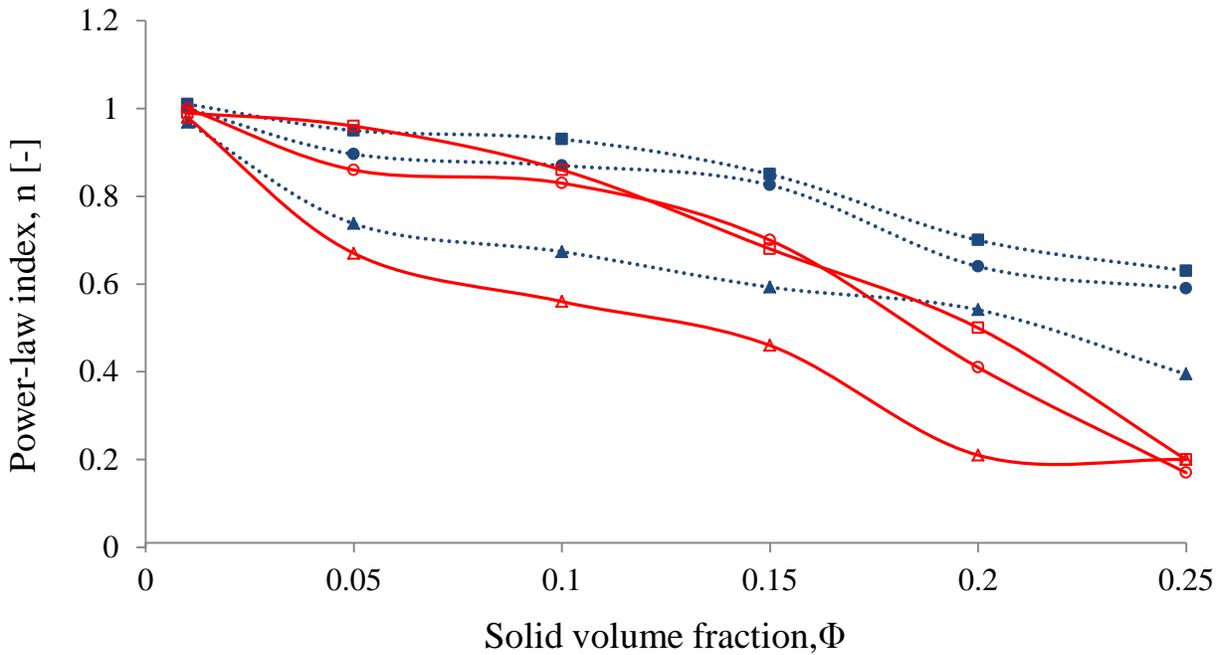
According to Fig. 6.4, at a given solid volume fraction, the shear-thinning behavior is more pronounced (smaller *n*) in carrot powder suspensions than in potato powder suspensions. To find out why at the same Φ, carrot powder suspensions possessed smaller power-law index values than potato powder suspensions, soluble solids content and insoluble solids content of carrot and potato powders were compared. Table 6.2 presents the different components of raw

potato, raw carrot and slightly boiled carrot; the latter is similar to the carrot particles used in this study.

Table 6.2. Different components of carrot and potato (g kg^{-1} dry matter)

	Carrot (Svanberg et al. 1997)			
	Raw	Boiled[1]	Potato	
Total dietary fibre	274	247	111	(Saura-Calixto et al. 2000)
Insoluble dietary fibre	129	116	38	(Saura-Calixto et al. 2000)
Soluble dietary fibre	145	131	73	(Saura-Calixto et al. 2000)
Total sugar[2]	586	524	50	(Singh and Kaur 2016)
Starch	9	not analysed	500	(Singh and Kaur 2016)
Others[3]	131	229	339	

[1]Boiled in lightly salted water (2 g NaCl in 0.5 liter water) for 12 min; [2]Glucose + fructose + sucrose; [3]ash, fat and protein

Based on Table 6.2, carrot powder would have a much greater amount of soluble solids content compared to potato powder, leading to a higher soluble solids content in the suspensions of the former at the same Φ. The soluble solids content influenced the continuous phase properties and consequently the rheological properties of the suspensions (Moelants, Cardinaels, Van Buggenhout, et al. 2014). The most important component of the soluble solids content in playing an important role in the rheological properties of carrot powder suspensions is the pectin (Lopez-Sanchez, Svelander, et al. 2011). Pectin polymer content is almost four times higher in carrot tissue compared to potato tissue, i.e., pectin contents of carrot and potato are 10% and 2.35% of dry matter, respectively (Lisinska and Leszczynski 1989; M. deMan 1999). However, the difference between the amount of pectin polymers in our carrot and potato powders suspensions is likely lower than this due to the fact that in the preparation of the carrot powder suspensions, carrot pieces were boiled in water at 100 °C for 20 minutes. As per Lopez-Sanchez,

Svelander, et al. (2011), heating a blended mixture of water and carrot at 90 °C for 40 minutes leads to solubilization of pectin polymers. This caused liberation and then removal of some soluble pectin polymers from the carrot particles (Fig. 6.1). Based on Fig. 6.4, it seems that the amount of pectin polymers is still sufficiently high in carrot powder that they play a role in the rheological behavior of carrot powder suspensions. An important role of pectin in producing a shear-thinning behavior in pectin-containing fluids has been mentioned in the literature (Fu and Rao 2001; Moelants, Jolie, et al. 2013). For instance, pectin solutions are reported to exhibit shear-thinning behavior due to the rearrangement of pectin polymer chains upon shearing (da Silva and Rao 2006; Wüstenberg 2015). On the other hand, based on Table 6.2, suspensions of potato powder would contain considerably more insoluble solids content than suspensions of carrot powder, leading to higher particle-particle interactions in the former. However, it seems that higher soluble solids content, particularly pectin, of carrot powder suspensions compared to potato powder suspensions, was the responsible factor for greater shear-thinning behavior of the former. This might be considered as an indication of the dominant role of continuous phase properties over dispersed phase properties in the difference between the shear-thinning behaviors of these suspensions.

6.3.1.2. Consistency Factor

A comparison between the consistency factors of the suspensions of carrot and potato powders at various temperatures and solid volume fractions is shown in Fig. 6.5. For both suspensions, the consistency factor increases with an increase in solid volume fraction at all temperatures. The same result, i.e., an increase in consistency factor with increasing Φ, has been reported for different suspensions (Tanglertpaibul and Rao 1987; Yoo and Rao 1994; Schijvens, Vliet, and Dijk 1998; Den Ouden and Van Vliet 2002). Moreover, at a given Φ, the carrot powder

suspensions possessed higher consistency factors compared to the potato powder suspensions (Fig. 6.5). A greater amount of soluble solids content, mostly pectin, in the continuous phase of carrot powder suspensions in comparison to the potato powder suspensions is likely responsible for this observation. That is, a greater amount of interactions, e.g., pectin-promoted interactions, in the continuous phase of the carrot powder suspensions compared to the potato powder suspensions caused a higher resistance to flow, and therefore increased k, in the former. As mentioned in section 6.3.1.1, the role of continuous phase seems to dominate over the role of dispersed phase in generating higher k values in carrot powder suspensions compared to potato powder suspensions for most solid volume fractions.

Fig. 6.5. Consistency factor of aqueous suspensions of carrot powder (solid line) and potato powder (dotted line) at 20°C (■), 50°C (●) and 80°C (▲)
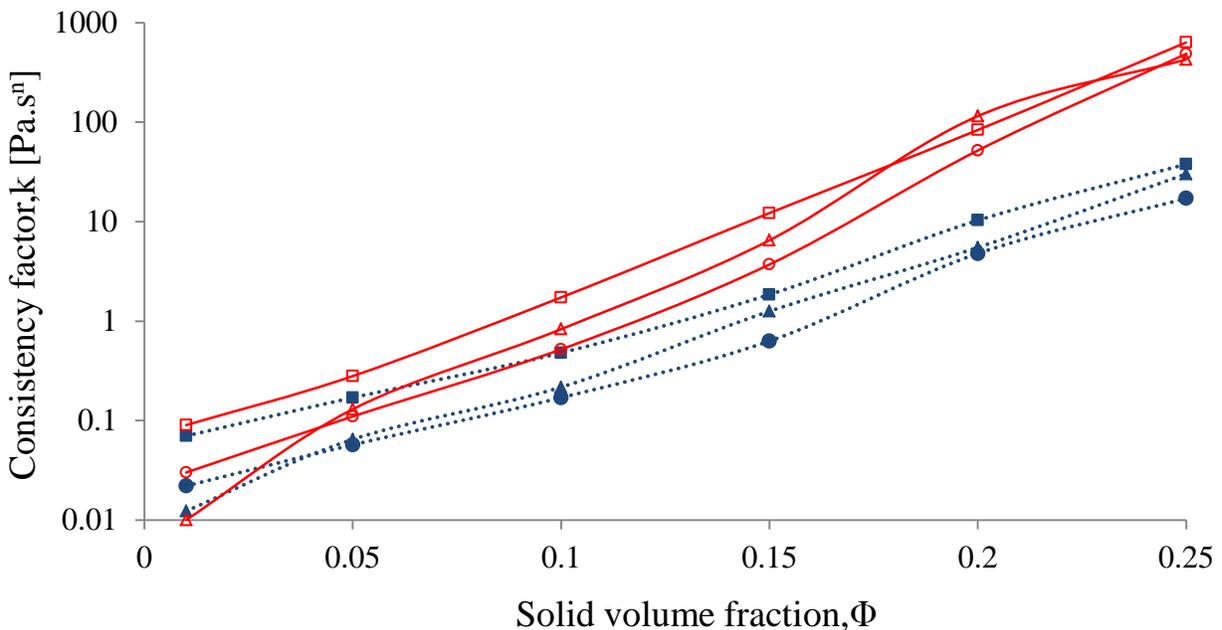
6.3.1.3. Yield Stress

The influence of Φ on the yield stress (σ_y) of the carrot powder suspensions is shown in Fig. 6.6. The yield stress increased with an increase in Φ of the suspensions (Fig. 6.6). An increase in yield stress with increasing solid content has also been reported in different systems, such as apple sauce (Qiu and Rao 1988) and starch–xanthan gum dispersions (Achayuthakan, Suphantharika, and Rao 2006). One underlying factor behind an increase in σ_y with increasing solids content would be elevated interactions among solid particles with increasing solid content of the suspensions (Mewis and Wagner 2012). Another factor would be the role of soluble solids content in promoting interactions between different components of the suspensions, e.g., interactions promoted by pectin polymers dissolved in the continuous phase (Moelants, Cardinaels, Van Buggenhout, et al. 2014).

Fig. 6.6. Yield stress of aqueous suspensions of carrot powder (solid line) and potato powder (dotted line) at 20°C (■), 50°C (●) and 80°C (▲)

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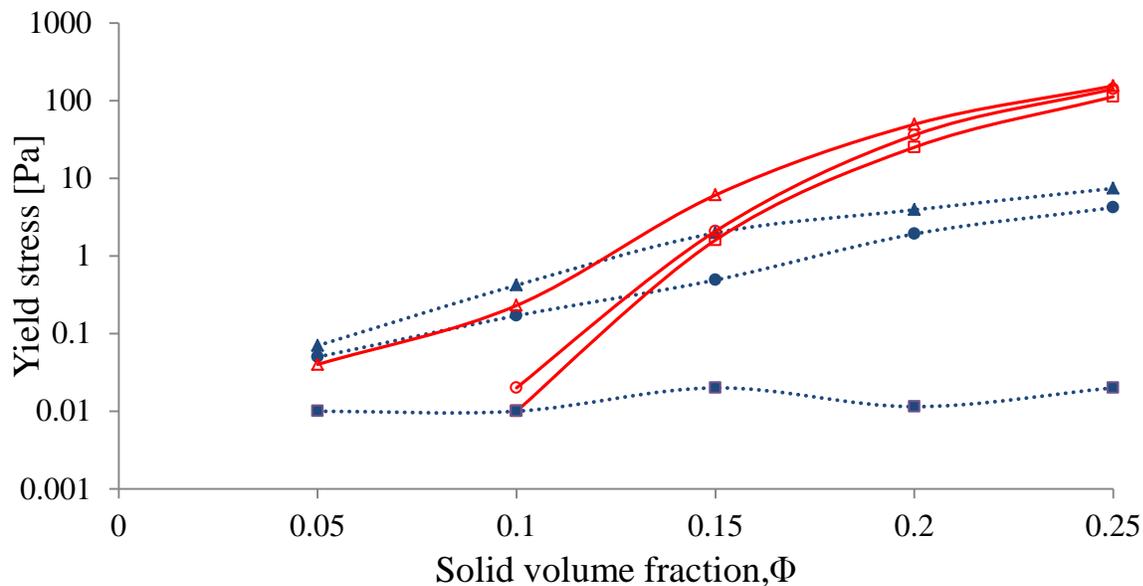
For comparison purposes, yield stress values of the suspensions of potato powder (determined as per Chapter 4) are also plotted in Fig. 6.6. At $\Phi=5\%$, carrot powder suspensions showed a yield stress only at 80 °C, while at $\Phi=10\%$, they exhibited yield stresses at all temperatures. Therefore, there was an effect of temperature on yield stress values of carrot powder suspensions at $\Phi=5\%$, which will be discussed in section 6.3.2. In addition, at $\Phi=5$ and 10%, carrot powder suspensions exhibited smaller yield stress values than potato powder suspensions. As shown in Table 6.2, potato powder suspensions possessed a greater amount of insoluble solids content compared to carrot powder suspensions at a given Φ. Consequently, larger yield stress values of potato powder suspensions compared to carrot powder suspensions indicated the dominant role of insoluble solids content over pectin-promoted interactions in the yield stress values of our suspensions at $\Phi=5$ and 10%.

Within a Φ range of 15-25%, the carrot powder suspensions showed larger σ_y values than potato powder suspensions, indicating an enhanced role of soluble solids content in determining σ_y at $\Phi \geq 15\%$. Based on Table 6.2, at a given Φ, a larger amount of soluble solids content, particularly pectin, is present in the continuous phase of carrot powder suspensions compared to that of potato powder suspensions. Consequently, the extent of interactions promoted by pectin polymers is larger in suspensions of carrot powder compared to those of potato powder. In addition, an increase in Φ of carrot powder suspensions leads to an increase in the concentration of pectin polymers in these suspensions, causing a greater difference between σ_y of carrot and potato powders suspensions at higher Φ. As demonstrated in Fig. 6.6, the difference between σ_y of the carrot and potato powders suspensions became larger with increasing Φ from 15% to 25%. Therefore, it can be concluded that the extent to which the role of pectin polymers dominated over the role of insoluble solids content in the σ_y values of carrot and potato powder suspensions

was enhanced with increasing Φ within the range of 15 to 25%. In other words, the concentration of pectin in the suspension determines which factor, solids content or pectin-promoted interactions, is dominant in affecting the σ_y of our suspensions. As a summary, changes in σ_y of potato and carrot powder suspensions were governed by the dispersed phase at Φ=5 and 10% and by continuous phase at Φ=15-25%, i.e., a transition from dispersed phase-dominance to continuous phase-dominance occurred at Φ=15%.

6.3.1.4. Loss Factor

The loss factor values of the carrot powder suspensions are plotted in Fig. 6.7. The loss factor values of carrot powder suspensions decreased gradually with increasing Φ and reached values lower than 1, indicating a transition from a liquid-like ($G'' > G'$) to a solid-like ($G' > G''$) behavior in these suspensions. The same trend, i.e., a decrease in the loss factor with an increase in Φ, was observed for the potato powder suspensions (Fig. 5.4 b, d and f). The transition from liquid-like to solid-like behavior with increasing Φ is attributable to the elevated interactions, e.g., pectin- induced interactions, in these suspensions. An increase in solidity could be due to the formation of a gel in the suspensions, which could be examined by careful investigation of the changes in G' with ω. The presence of gel properties can be confirmed if the loss factor is smaller than one and G' is almost independent of the angular frequency (Rao and Cooley 1992; Ross-Murphy 1995; Ikeda and Nishinari 2001; Alvarez, Canet, and Fernández 2007). Based on Fig. 6.7, loss factor values of the carrot powder suspensions with Φ ≥ 15% were smaller than one. Additionally, in the carrot powder suspensions with Φ ≥ 15%, G' had a very small slope over the whole range of angular frequencies, i.e., G' was almost independent of ω (Fig. 6.8). Therefore, it can be concluded that a gel was formed in the carrot powder suspensions at Φ ≥ 15%. However, no gel properties were observed in the potato powder suspensions, as the slope

of G'-ω curves for these suspensions changed over the frequency range, particularly at 20 and 50°C (Fig. 5.2 a, c and e).

The presence of gel properties in carrot powder suspensions is presumed to be attributed to pectin-induced interactions in the suspensions, which exist in the potato suspensions to a much smaller extent. Furthermore, an increase in the volume fraction of particles in the suspensions would lead to an increase in the amount of interactions among suspension components. As a consequence, the gel-like behavior in carrot powder suspensions was more pronounced at elevated solid volume fractions, i.e., $\Phi \geq 15\%$.

Fig. 6.7. Loss factor as a function of ω for carrot powder suspensions with Φ = 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■)
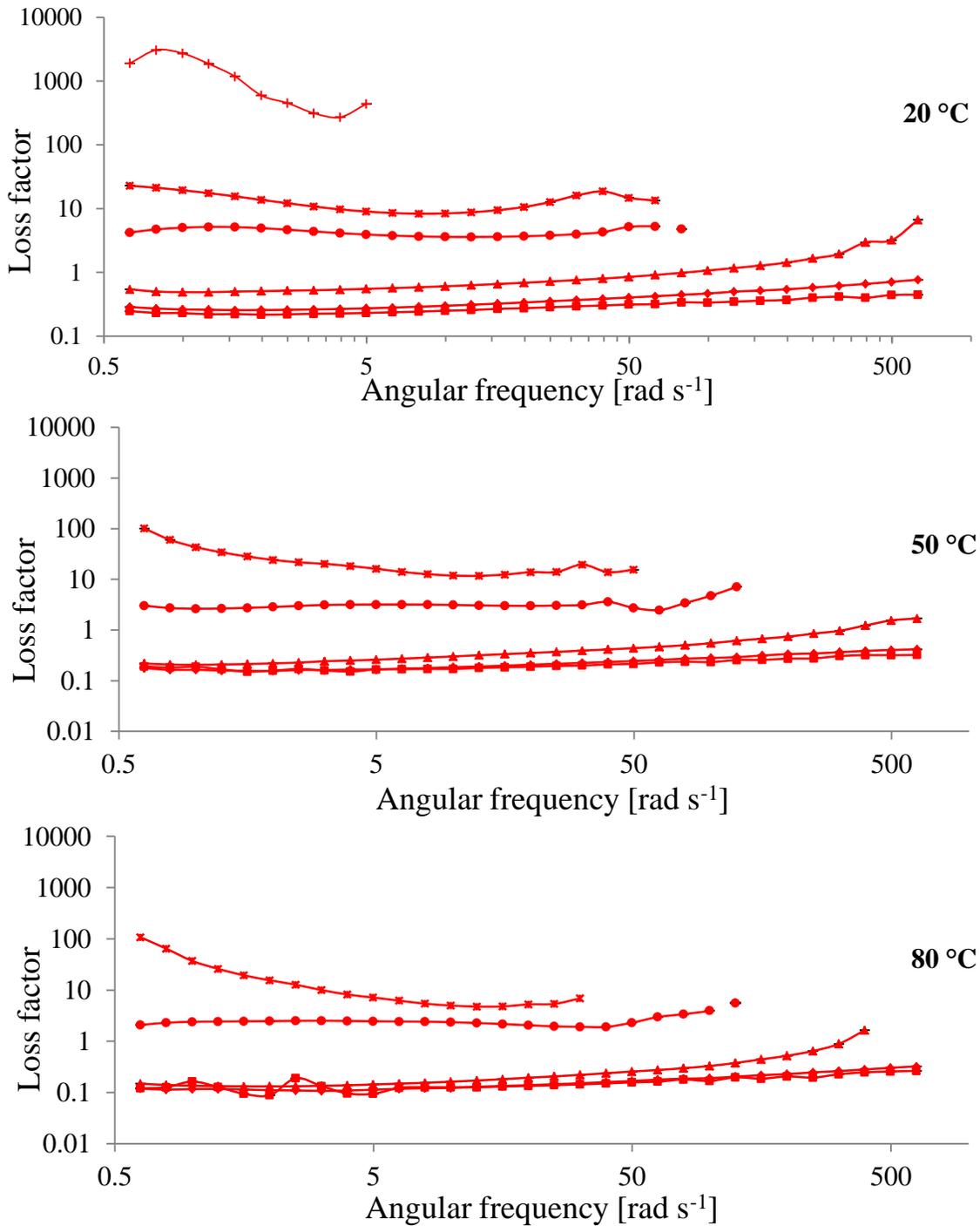
Fig. 6.8. Frequency dependence of the G′ of carrot powder suspensions at 20 °C with Φ = 1% (+), 5% (*), 10% (●), 15% (▲), 20% (♦), 25% (■)
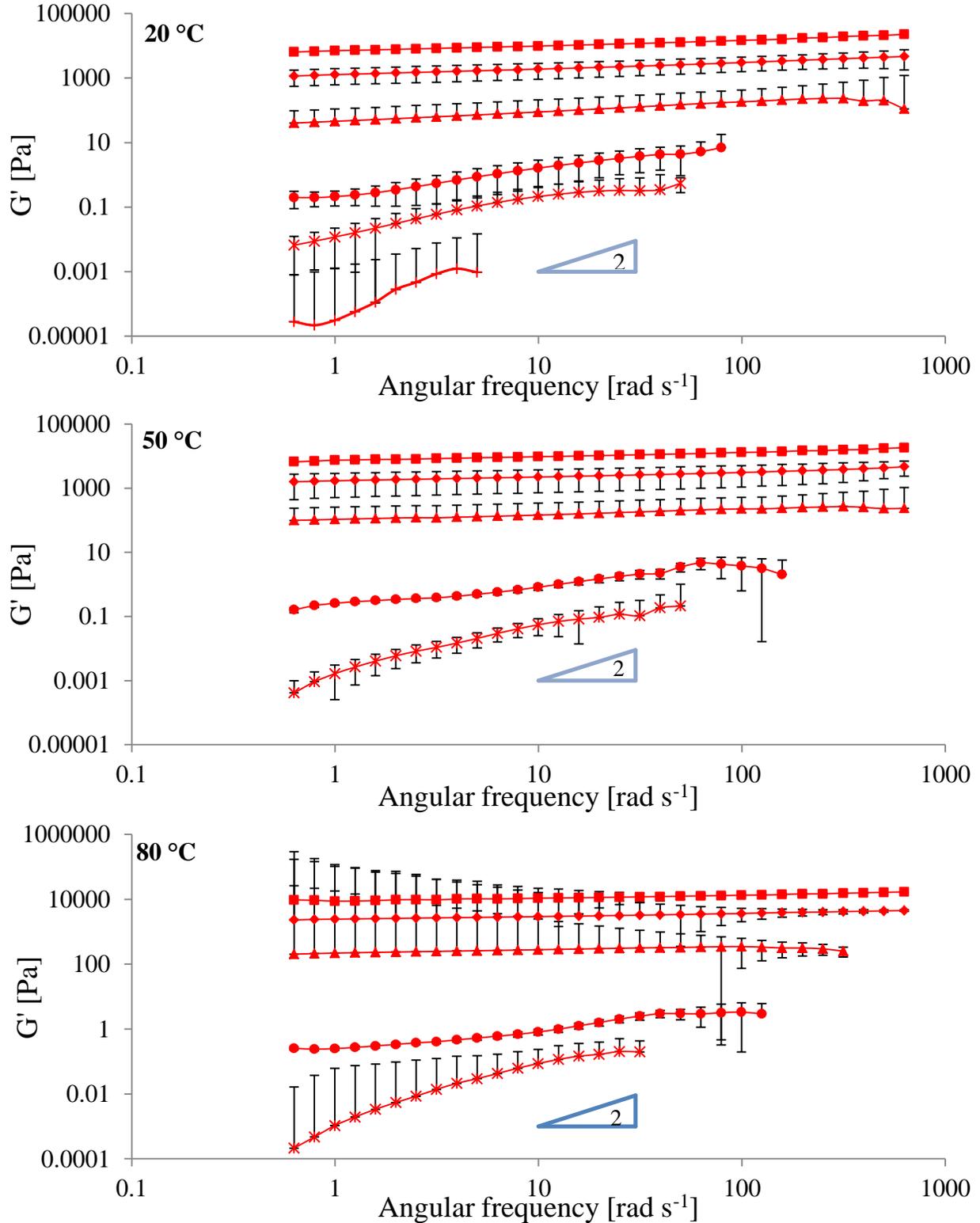
6.3.2. The Effect of Temperature

To investigate the effect of temperature on the rheological behavior of carrot powder suspensions, three different temperatures, i.e., 20, 50 and 80 °C, were used for all rheological measurements. As shown in Fig. 6.5, k values of the carrot powder suspensions decreased with an increase in temperature from 20 ºC to 50 ºC.

In general, a direct relationship exists between the rheological properties of a suspension and the rheological properties of the continuous phase, e.g., a decrease in the viscosity of the continuous phase leads to a decrease in the viscosity of the suspensions. In this regard, by increasing the temperature of a suspension, if the solid particles in the dispersed phase remain unchanged, the continuous phase viscosity decreases, decreasing the viscosity of suspensions (Barnes 2000; Tropea, Yarin, and Foss 2007). The decrease in the continuous phase viscosity by increasing the temperature is due to thermal expansion which leads to an increase in the distance between continuous phase molecules and a decrease in the intermolecular forces (Barnes, Hutton, and Walters F.R.S. 1993; Barnes 2000; Rao 2013). Therefore, the decrease in k values of the carrot powder suspensions with an increase in temperature from 20 ºC to 50 ºC is related to a decrease in the resistance to flow of the continuous phase in these suspensions.

However, one should consider that in the carrot powder suspensions the properties of the particles in the dispersed phase are also affected by an increase in temperature, which in turn, influences the properties of the continuous phase. This manifests itself when the k values of the suspensions showed an increase by increasing the temperature from 50 ºC to 80 ºC (Fig. 6.5). That is, an increase in temperature from 50 ºC to 80 ºC affected the properties of the dispersed phase, leading to a change in the properties of the continuous phase, which was not the case when temperature increased from 20 ºC to 50 ºC. The reason might be attributed to the effect of

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temperature on the extent of solubilized intracellular and intercellular components in the continuous phase (Sriamornsak 2003; Moelants, Jolie, et al. 2013; Moelants et al. 2014). That is, a larger amount of intracellular and intercellular components, e.g., pectin polymers, were solubilized into the continuous phase at 80 ℃ compared to that at 50 ℃. Consequently, a greater increase in the resistance to flow of the continuous phase caused an increase in k values of the carrot suspensions when temperature was elevated from 50 to 80 ℃ compared to when the temperature was increased from 20 to 50 ℃.

In addition, the power-law index (n) decreased with increasing temperature in the carrot powder suspensions (Fig. 6.4 and 6.6). The decrease in n values of the carrot powder suspensions with increasing temperature was more pronounced when the temperature increased from 50 to 80 °C. An increase in the shear-thinning behavior of citrus pectin solutions with increasing pectin concentration has been also demonstrated by Sousa et al. (2015). Changes in the n values of carrot powder suspensions confirms greater solubilization of intracellular and intercellular components when temperature increases from 50 to 80 °C compared to the 20 to 50 °C temperature increase.

The yield stress values of carrot powder suspensions increased with increasing temperature, indicating their greater gel-like behavior at elevated temperatures due to increased solubilization of intracellular and intercellular components, particularly pectin, with increasing temperature. Higher yield stress values at elevated temperatures has been also reported for pumpkin pectin solutions (Ptitchkina et al. 1994). Additionally, carrot powder suspensions at Φ= 5% possessed a yield stress only at 80 °C, which was presumably due to greater solubilization of intracellular and intercellular components, particularly pectin, at 80 °C compared to other temperatures. As a summary, an increase in temperature was presumed to enhance the

interactions induced by intracellular and intercellular components, particularly pectin, solubilized in the continuous phase of the suspensions, leading to an increase in k and σ_y, as well as a decrease in n values of the suspensions.

To examine the effect of temperature on the viscoelastic behavior of the suspensions, the changes in loss factor values with varying temperature were investigated (Coffin and Fishman 1993; Hsu, Lu, and Huang 2000; Ahmed and Ramaswamy 2006b). Based on Fig. 6.7, at 20 °C, the carrot powder suspensions with $\Phi =1\%$ possessed large loss factor values (>100) at low ω (up to 5 rad s^{-1}), indicating their liquid-like behavior in the dilute regime. At elevated temperatures, i.e., at 50 °C and 80 °C, there were no measureable loss factor values for the carrot powder suspensions with $\Phi =1\%$, as shown in Fig. 6.7. That is, the carrot powder suspensions at $\Phi =1\%$ did not possess any measurable storage modulus (G$'$) values at 50 °C and 80 °C. As mentioned in section 6.3.1.3, at $\Phi < 15\%$ the role of insoluble solids content dominates over that of the pectin-promoted interactions in the rheological behavior of the suspensions. On the other hand, an increase in temperature would enhance the solubility of soluble solids content in the continuous phase (Rao 2013; Moelants et al. 2014). As a result, carrot powder suspensions with $\Phi =1\%$ at 50 and 80 °C contained less particle-particle interactions than those at 20 °C (with G$'$ <0.001 Pa), resulting in liquid-like behavior with no measurable G$'$. In addition to temperature, enzyme activities can influence the solubility of pectin polymers (Sanchez et al. 2002; Sousa et al. 2015). The optimum temperature for pectin depolymerizing enzymes in carrot are around 50°C (Ly-Nguyen et al. 2002). However, the presence of a large amount of sucrose in the carrot powder suspensions, i.e., the use of 60% (w/w) sucrose solution as the continuous phase, highly restricted water activity. Consequently, enzyme activity which is directly related to the water activity is eliminated in these suspensions (M. deMan 1999).

Finally, a clearer view on the important role of temperature on the viscoelastic behavior of the carrot and potato powders suspensions, via its effect on pectin-induced interactions, could be achieved by comparing the loss factor values of these suspensions. For this purpose, loss factor values of potato and carrot powders suspensions at a typical Φ (20%) are plotted against angular frequencies in Fig. 6.9.

Fig. 6.9. Loss factor as a function of ω for suspensions of carrot powder (solid lines) and potato powder (dotted lines) with Φ=20% at 20°C (■), 50°C (●), 80°C (▲)
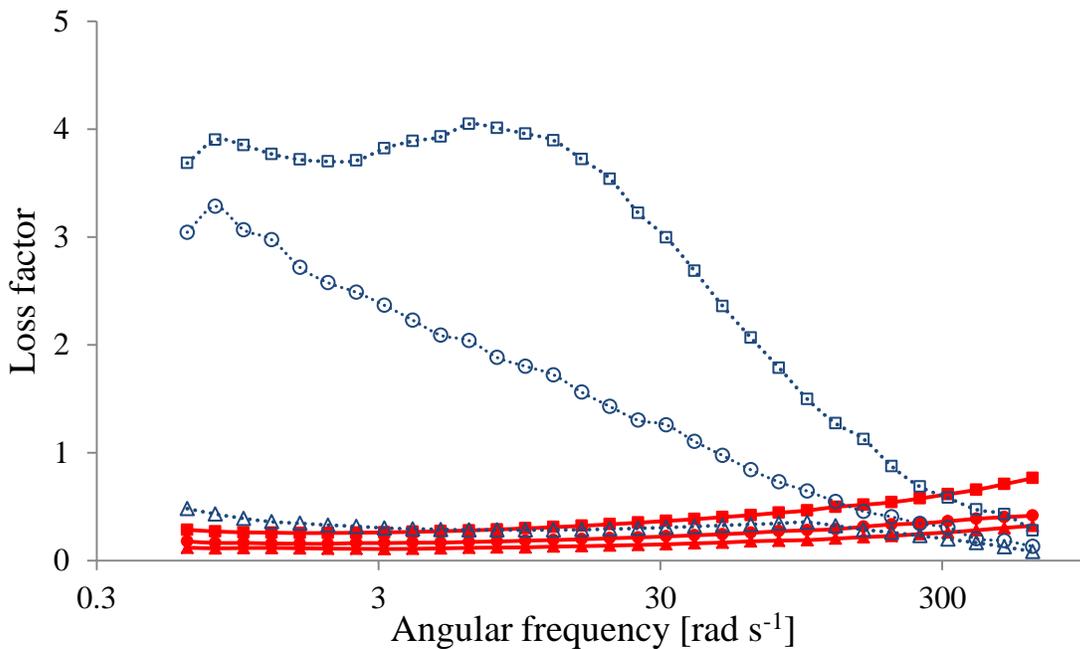
As mentioned before (and demonstrated in Fig. 6.9), the promoted pectin-induced interactions at higher temperatures are believed to be responsible for an increase in the solid-like behavior of these suspensions with increasing temperature (Sorchan et al. 1971; Fu and Rao 2001; Sriamornsak 2003; da Silva and Rao 2006; Ahmed, Ptaszek, and Basu 2017). On the other hand, greater solid-like behavior (smaller loss factor values) of the carrot powder suspensions compared to the potato powder suspensions was an indication of the greater pectin-induced

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interactions in the former. This observation was expected, as carrot powders contained considerably greater amount of soluble inter- and intra-cellular components than the potato powders (Table 6.2). As a summary, a noticeable role of the continuous phase in the viscoelastic behavior of carrot powders suspensions, due to the presence of pectin-induced interactions, was evident.

6.4. Conclusion

In this chapter, the rheological behavior of aqueous suspensions containing particulates of carrot powder has been studied. By increasing the solid volume fraction and the temperature of the carrot powder suspensions, the yield stress and shear-thinning behavior increased and the loss factor decreased. The consistency factor increased by increasing the solid volume fraction and decreased by increasing the temperature from 20 to 50°C, but increased by increasing the temperature from 50 to 80°C. To find out the role of different interactions present in the carrot suspensions, potato powder suspensions (with a significantly lower amount of soluble solids such as pectin) were compared to the carrot powder suspensions. A greater amount of pectin-induced interactions, particularly at elevated Φ and temperatures, in carrot suspensions compared to potato suspensions was responsible for a higher consistency factor, yield stress and shear-thinning behavior in the former. Moreover, a greater contribution of the continuous phase, as affected by component migration from the dispersed phase, led to solid-like behavior of carrot powder suspensions at $\Phi \geq 15\%$.

6.5. References

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7. General Discussion and Conclusions

The objective of this work was to show how food model suspensions behave with increasing levels of complexity. To start with the possibly simplest suspensions with the lowest level of interactions among the components, the rheological properties of native corn and potato starch granules suspensions, as model systems, were investigated (Chapter 3). An understanding of the rheological behavior of native starch granules suspensions was thought to be helpful in comprehending the rheological behavior of suspensions of plant tissue rich in starch granules. As the next step, potato parenchyma which contains an abundant amount of starch granules was chosen as the raw material for the plant-tissue suspensions of this study. The potato parenchyma was comminuted and the potato powder suspensions were prepared using the same procedure employed for preparation of the starch granule suspensions. Based on a comparison between the rheological properties of the potato powder suspensions and the potato starch granule suspensions (Chapters 4 and 5), the effects of other intercellular and intracellular components in the former were evident. As per the literature concerning the effects of intercellular and intracellular components on the rheology of suspensions, pectin polymers were hypothesized to play an important role in the rheological properties of the potato powder suspensions. In order to examine this hypothesis, carrot parenchyma which has a significantly higher amount of pectin polymers than potato parenchyma was selected as the raw material for plant-tissue suspensions in the third study of this work (Chapter 6). Then, a comparison between the rheological properties of carrot and potato powders suspensions was conducted to draw a conclusion on the role of pectin polymers in the rheology of plant-tissue suspensions.

Two types of shear deformation, i.e., shear flow and oscillatory shear, were employed to evaluate the effects of key parameters including solid volume fraction (Φ), particle size and temperature on the rheological properties of the suspensions of this study. In addition, various

models, such as power law and Herschel-Bulkley equations, were employed to describe the flow behavior of the suspensions.

This chapter draws general conclusions on the rheological properties of plant-tissue suspensions. The chapter starts with the role of dispersed phase and continuous phase in plant-tissue suspensions by considering the simplest equation for the viscosity of a suspension, i.e., the Einstein equation. This is the bare necessity for establishing a systematic study of plant-tissue suspensions. Then, the rheology of plant-tissue suspensions with increasing levels of complexity is treated systematically by exploring the importance of solid volume fraction in plant-tissue suspensions. Additionally, the important role of temperature on the properties of plant-tissue suspensions is demonstrated. The effects of temperature on the maximum packing fraction of plant-tissue suspensions as well as on liquid-like and solid-like behavior of plant-tissue suspensions are discussed.

7.1. The Role of Dispersed Phase and Continuous Phase in Plant-tissue Suspensions

By comparing the rheological properties of starch granule suspensions (Chapter 3), potato powder suspensions (Chapter 4 and 5) and carrot powder suspensions (Chapter 6), it was concluded that three rheological behaviors existed in these suspensions: (1) viscous; (2) viscoelastic liquid-like; and (3) viscoelastic solid-like. Viscous behavior, where the storage modulus (G') was not measurable, was observed for most of the starch granule suspensions at all temperatures (Chapter 3). Viscoelastic liquid-like ($G'' > G'$) and solid-like ($G'' < G'$) behaviors were observed for potato and carrot powders suspensions depending on the Φ, temperature and angular frequency (ω), as discussed in Chapter 5 and 6.

For starch granule suspensions which showed viscous behavior, the simplest equation describing the viscosity- Φ relationship is the Einstein equation. According to the Einstein equation, for suspensions of hard spheres at dilute regime ($\Phi \leq 0.05$) where no interactions exist between particles, the relative viscosity can be determined by:

$$\eta_r = 1 + [\eta]\Phi \qquad\qquad \text{Eq. 7.1}$$

where [η] is the intrinsic viscosity which is a function of particle shape (Genovese 2012). To determine [η] for the starch granule suspensions, the fitting process was performed using the Minitab software version 16 (Minitab, State College, PA). The [η] values determined by the Einstein equation for potato starch granule suspensions and the standard error of the regression (S) used by Minitab as an indication of how close the actual data points are to the fitted line, are shown in Table 7.1. Minitab uses S (with the unit of the parameter of interest) as a means of demonstrating the non-linear regression line precision, i.e., S value of a regression is the average distance of the data points from the fitted line. For example, a given S value (e.g., 0.51) for regression line of the η_r versus Φ means that 95% of the actual data points fall within $\pm 2 \times S$ ($\pm 2 \times 0.51 = \pm 1.1$) from the fitted line.

Table 7.1. [$\boldsymbol{\eta}$] from Einstein equation for potato starch granule suspensions

Temperature	Φ=0.01-0.25		Φ=0.01-0.05	
	[η]	S	[η]	S
20°C	9.64	0.51	3.34	0.07
50°C	7.62	0.35	3.77	0.07
80°C	5.89	0.26	2.5	0.03

To examine the applicability of the Einstein equation for starch granule suspensions, two sets of data were taken into account: data for all suspensions, i.e., Φ=1%-25%, and data for suspensions in the dilute regime, i.e., Φ= 1%-5% (Table 7.1). As shown in Table 7.1, better fitting was achieved when dilute regime suspensions were only used for the regression, i.e., smaller values of S for dilute regime regression compared to regression for all suspensions. The reason for such an observation was an increase in the interactions between particles with increasing Φ, leading to the deviation of the rheological behavior of suspensions from Einstein equation. Given no alteration of starch granule in the suspensions (Sinaki and Scanlon 2016), it can be concluded that the rheology of starch granule suspensions is governed only by the dispersed phase of these suspensions.

The presence of a viscoelastic liquid-like and solid-like behavior in potato and carrot powders suspensions suggests that there is the potential for energy storage over a measureable timescale in these suspensions (Peker and Helvaci 2008). The viscoelasticity can be a result of different origins, such as the viscoelasticity of the continuous phase of a suspension (Aral and Kalyon 1997). The viscoelasticity in the continuous phase is mostly a result of the presence of polymers which influence the hydrodynamic interactions of particles (Mewis and Wagner 2012). Different polymers, particularly pectin polymers, existed in our potato and carrot powders suspensions (Lopez-Sanchez, Nijsse, et al. 2011; Moelants et al. 2014). Upon addition of the dry powders of potato and carrot to the continuous phase, a part of these polymers are solubilized, leading to an enhanced role of the continuous phase in the rheological behavior of the suspensions. Given the greater amount of pectin polymers in carrot parenchyma compared to potato parenchyma, the role of the continuous phase in the rheology of our suspensions is believed to be greater for carrot powder suspensions compared to potato powder suspensions.

Higher consistency factor and yield stress, more shear-thinning behavior and lower loss factor were observed in the carrot powder suspensions compared to potato powder suspensions (Chapter 6). These differences in rheological properties of these suspensions are believed to be mostly governed by the important role of the continuous phase in these suspensions.

7.2. The Importance of Solid Volume Fraction in Plant-tissue Suspensions

It was demonstrated in Chapters 3, 4 and 6 that the rheological properties of starch granules and potato and carrot powders suspensions were greatly affected by the solid volume fraction (Φ) of the suspensions. As discussed in 7.1, the flow behavior of viscous suspensions at dilute regime can be predicted by the Einstein equation. However, an increase in Φ, which leads to an increase in the interparticle interactions, was shown to result in a deviation from this equation. In such cases, the Maron-Pierce and Krieger–Dougherty equations are used to describe the solid volume fraction (Φ) dependence of the relative viscosity (η_r) of suspensions. However, for suspensions exhibiting non-Newtonian behavior, the relative consistency factor (k_r) can be employed based on the definition of the relative viscosity (η_r) (Mueller, Llewellin, and Mader 2009):

$$k_r = \frac{k}{\eta_0}$$
<div align="right">Eq. 7.2</div>

where η_0 is the viscosity of the continuous phase of the suspension. We followed the procedure used by Mueller, Llewellin and Mader (2009) to introduce the relative consistency factor (k_r) in the proposed $\eta_r - \Phi$ models to study the flow behavior of the suspensions of their study. The k values for each suspension were obtained as explained in Chapters 4 and 6. Also, the viscosity of the continuous phase, i.e., 60% sucrose solution, (η_0) was determined as explained in Chapter 3.

The one-parameter Maron-Pierce equation (Eq. 7.3) was employed to find out the relationship between k_r and Φ in the potato and carrot powders suspensions:

$$k_r \equiv \eta_r = (1 - \Phi/\Phi_m)^{-2}$$ Eq. 7.3

where Φ_m is the maximum packing fraction at which η_r (or k_r) approaches infinity. The fitting process was performed using the Minitab software version 16 (Minitab, State College, PA). The Φ_m values determined from Eq. 7.3 and the standard error of the regression (S) used by Minitab as a measure of closeness of the actual data to the regression line, are shown in Table 7.2.

Table 7.2. Φ_m of potato starch and potato and carrot powder suspensions at various temperatures from the Maron-Pierce equation

Temperature	d(0.5) [µm]	Φ=0.01-0.25		Φ=0.01-0.2		Φ=0.01-0.15	
		Φ_m	S	Φ_m	S	Φ_m	S
20°C							
Potato starch	39	0.49	0.11	-	-	-	-
Potato	34	0.3	1.89	-	-	-	-
Potato	79	0.24	45.88	0.18	1.42	-	-
Carrot	60	0.25	480.85	0.19	69.97	0.16	10.4
50°C							
Potato starch	39	0.55	0.09	-	-	-	-
Potato	34	0.3	1.24	-	-	-	-
Potato	79	0.24	84.5	0.21	9.35	0.18	2.15
Carrot	60	0.25	1052.06	0.2	77.23	0.14	8.07
80°C							
Potato starch	39	0.62	0.09	-	-	-	-
Potato	34	0.28	7.13	-	-	-	-
Potato	79	0.25	218.40	0.19	47.42	0.14	5.34
Carrot	60	0.25	4694.55	0.2	285.35	0.16	43.9

Based on the S values in Table 7.2, the relative viscosity of potato starch granule suspensions and the relative consistency of potato powder suspensions of d(0.5)=34 µm conform well to the Maron-Pierce equation at all temperatures. However, in the potato powder

suspensions with particles of d(0.5)= 79 μm and in the carrot powder suspensions, the Maron-Pierce equation showed a high standard error of regression (S) when all solid volume fractions were considered. For further analysis of the data in these two suspensions, multiple regressions were carried out in two steps using Minitab: first by omitting the Φ=25% and second by omitting Φ= 20% and 25%. As a result, shown in Table 7.2, the standard error of regression (S) decreased, i.e., better fitting was achieved by removing the data of more concentrated regimes from the fitting process. Therefore, it can be concluded that when Φ= 20% and 25% were taken into account, the Maron-Pierce equation fails to accurately predict the trend of changes in the $k_r - \Phi$ curves.

Hence, a better description for the $k_r - \Phi$ data of the potato and carrot powders suspensions was sought by using the Krieger–Dougherty equation as a widely used two-parameter model to predict the flow behavior of suspensions (Barnes 2000; Tropea, Yarin, and Foss 2007):

$$k_r \equiv \eta_r = (1 - \frac{\Phi}{\Phi_m})^{-[\eta]\Phi_m}$$
<div align="right">Eq. 7.4</div>

Table 7.3 shows the results obtained for Φ_m and [η] from the Krieger–Dougherty equation used to analyze potato starch granule suspensions as well as carrot and potato powders suspensions.

Table 7.3. Φ_m and [η] from Krieger–Dougherty equation in potato starch, carrot and potato powder suspensions at different temperatures

Temperature	d(0.5) [µm]	Φ=0.01-0.25			Φ=0.01-0.2		
		Φ_m	[η]	S	Φ_m	[η]	S
20 °C							
Potato starch	39	0.37	3.43	0.065	-	-	-
Potato	34	0.41	9.47	0.112	-	-	-
Potato	79	0.65	21.7	200	0.34	16.5	0.170
Carrot	60	0.65	28.9	134	0.65	29.8	21.6
50 °C							
Potato starch	39	0.38	3.01	0.038	-	-	-
Potato	34	0.35	8.33	0.550	-	-	-
Potato	79	0.80	22.7	38.3	0.30	16.6	0.611
Carrot	60	0.65	34.0	109E+2	0.36	26.9	1.66
80 °C							
Potato starch	39	0.41	2.68	0.093	-	-	-
Potato	34	0.75	14.1	1.08	-	-	-
Potato	79	0.65	25.4	64.9	0.65	26.7	28.4
Carrot	60	0.90	38.2	149E+2	0.47	35.8	15.9

Based on *S* values in Table 7.3, the Krieger–Dougherty equation can predict the relative viscosity/consistency factor of starch granules and potato powder suspensions of d(0.5)=34 µm over the whole range of Φ. However, this was not the case for the potato powder suspensions of d(0.5)=79 µm and the carrot powder suspensions. To find out if large Φ values contributed to high *S* values for the suspensions of potato powder of d(0.5)=79 µm and the carrot powder, another regression analysis was carried out with Φ=25% excluded from the data set. As shown in Table 7.3, the *S* values for the potato powder suspensions of d(0.5)=79 µm and carrot powder suspensions decreased when the data corresponding to suspensions of Φ=1-20% were fitted to the Krieger–Dougherty equation. According to the aforementioned analysis, the Krieger–Dougherty equation approximated the experimental data with a better accuracy in a rather larger

range of Φ, i.e., Φ=1-20%, compared to the Maron-Pierce equation which could only predict the data for Φ=1-15%.

To achieve a clearer view on the applicability of the aforementioned equations, the η_r of potato starch granule suspensions and the k_r of potato and carrot powders suspensions predicted by the Maron-Pierce and Krieger–Dougherty's equations are plotted in Fig. 7.1. For comparison purposes, the experimental η_r of the potato starch granule suspensions and the experimental k_r of the potato and carrot powders suspensions are also plotted in Fig. 7.1. As discussed before, the experimental values for k_r and η_r of the carrot and potato powders suspensions were reasonably well fitted to the Krieger–Dougherty equation.

The results showed that the Krieger-Dougherty equation is more successful, particularly at elevated Φ. The two-parameter Krieger–Dougherty equation was developed for suspensions of spherical rigid particles (Rao 2013). Therefore, the deviation of this equation from the experimental data of this study is not surprising, as the potato and carrot powders were polydisperse in size and shape. On the other hand, the low quality of fit for the Maron–Pierce equation indicated that the relationship $[\eta]\Phi_m \approx 2$ is not valid for carrot and potato powders suspensions where various interactions exist between the dispersed phase and the continuous phase.

Fig. 7.1. k_r for suspensions of carrot powder (●), potato powder of d(0.5)= 79 μm (▲) and potato powder of d(0.5)= 34 μm (♦), and η_r for potato starch granule suspensions (■) as a function of Φ at 20, 50 and 80 °C. Dashed lines: best-fit of Maron-Pierce equation; solid lines: best fit to Krieger–Dougherty equation
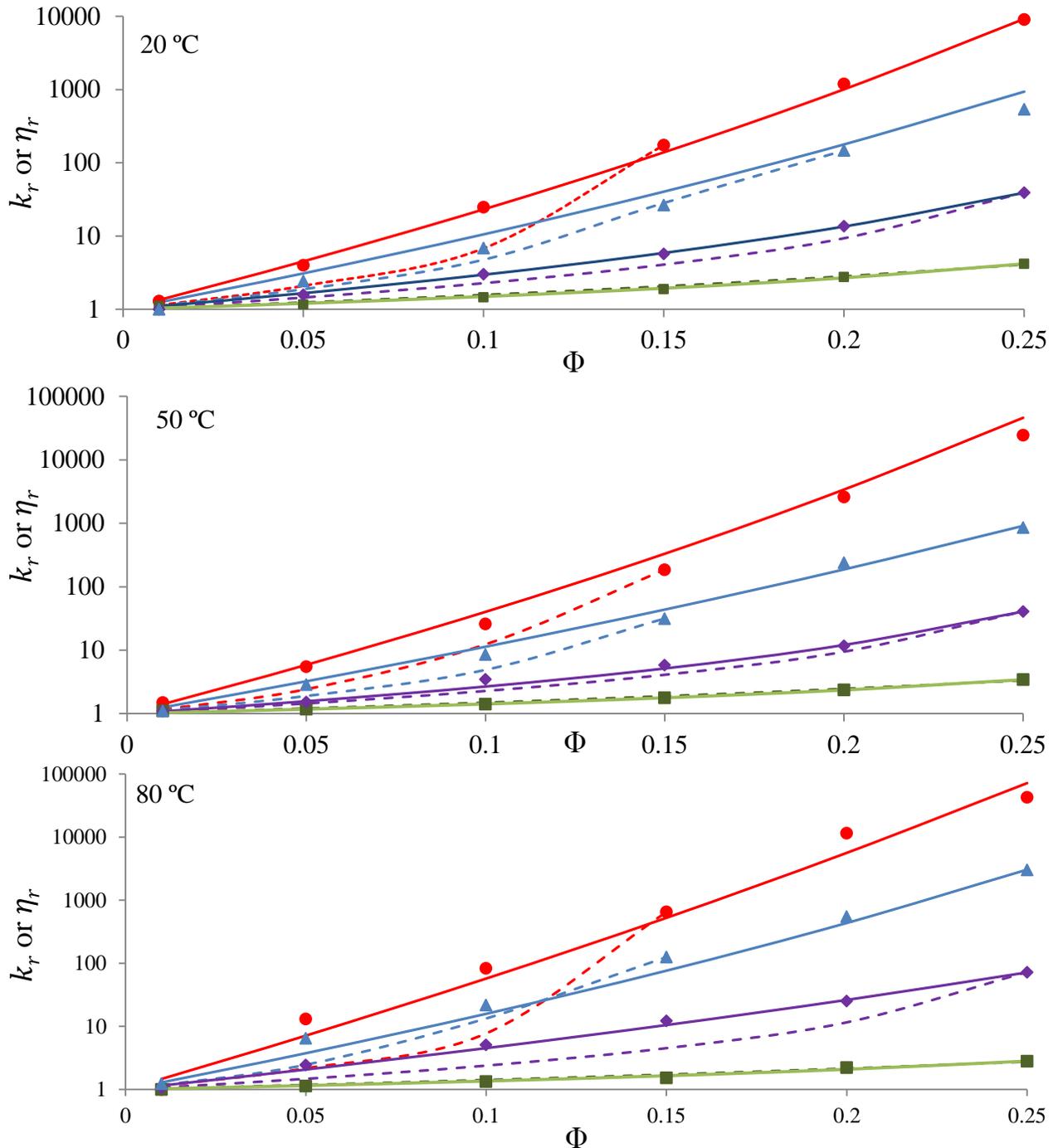
7.3. The Importance of Temperature in Plant-tissue Suspensions

One of the major challenges associated with the manufacturing of plant-tissue suspensions is to understand the relationship between the temperature and the rheological behavior of the suspensions. The results of this study revealed that changes in temperature influenced the consistency factor, shear-thinning behavior, yield stress and loss factor in potato and carrot powders suspensions (Chapters 4-6).

The use of the Arrhenius equation could help us achieve an insight into the effect of temperature on the viscosity/consistency factor (k) of the suspensions of potato starch granules, carrot and potato powders (da Silva, Gonçalves, and Rao 1994; Hosseini-Parvar et al. 2010). The Arrhenius equation is described as:

$$k = k_\infty \exp(E_{ak}/RT) \qquad \text{Eq. 7.5}$$

where k_∞ is the frequency factor, E_{ak} is the activation energy [J mol^{-1}], R [J mol^{-1} K^{-1}] is the universal gas constant and T [K] is the absolute temperature. Taking the natural logarithm of the Arrhenius equation yields:

$$\ln k = \frac{E_{ak}}{R}\left(\frac{1}{T}\right) + \ln k_\infty \qquad \text{Eq. 7.6}$$

A plot of ln k vs. (1/T) results in a straight line where E_{ak} equals the slope multiplied by R, and k_∞ is the exponential of the intercept (Rao and Kenny 1975; Speers and Tung 1986; Rao 2013). The magnitudes of the parameters of the Arrhenius equation for the suspensions of potato starch granules, potato powder and carrot powder are given in Table 7.4.

Table 7.4. Parameters of Arrhenius equation for suspensions of potato starch granules, potato

powder and carrot powder

	Φ	k_∞	E_{ak} (kJ mol^{-1})	R^2
Potato starch granule suspensions				
	0.01	4.18E-07	29.55	0.99
	0.05	6.85E-07	28.34	0.99
	0.10	5.88E-07	29.26	0.99
	0.15	3.79E-07	30.99	0.99
	0.20	4.98E-07	31.19	0.99
	0.25	2.64E-07	33.79	0.99
Potato powder suspensions, d(0.5)=34μm				
	0.01	9.63E-07	27.19	0.99
	0.05	1.17E-05	21.96	0.89
	0.10	3.93E-05	20.68	0.94
	0.15	2.55E-04	17.5	0.76
	0.20	2.45E-04	19.64	0.75
	0.25	7.68E-04	19.57	0.86
Potato powder suspensions, d(0.5)=79μm				
	0.01	2.19E-06	25.13	0.98
	0.05	3.95E-04	14.37	0.70
	0.10	2.98E-03	11.94	0.59
	0.15	1.06E-01	6.33	0.16
	0.20	1.94E-01	9.37	0.64
	0.25	6.42E+00	3.83	0.11
Carrot powder suspensions				
	0.01	2.33E-07	31.43	1
	0.05	2.17E-03	11.46	0.64
	0.10	1.35E-02	11.24	0.42
	0.15	1.71E-01	9.78	0.33
	0.20	3.58E+02	-4.02	0.12
	0.25	6.06E+01	5.69	0.98

Based on Table 7.4, the viscosity of the potato starch granule suspensions at all solid volume fractions as well as the consistency factor of potato and carrot powders suspensions at Φ=1% could be well modeled by the Arrhenius Equation ($R^2 \geq 0.98$). However, this was not the case for potato and carrot powders suspensions at Φ >1% where viscoelastic properties were particularly evident in the suspensions, especially for solid-like characteristics.

Moreover, the activation energy of suspensions (E_{ak}) was in the range of 3-34 kJ mol^{-1}, with its magnitude depending on Φ and the type of suspension, i.e., starch granules, potato and carrot powders suspensions (Table 7.4). E_{ak} decreased with increasing Φ in most suspensions, which is similar to observations for purees of apple, pear and peach by Saravacos (1970) and guava puree by (Vitali and Rao 1982). In general, the highest values of E_{ak} were observed for the potato starch granule suspensions and the lowest for carrot suspensions at all Φ, except for $\Phi=1\%$, where carrot powder suspensions had the highest E_{ak} values (Table 7.4). By definition, higher activation energy corresponds to a greater influence of temperature on the viscosity (Cepeda and Gomez 2002; Bertuzzi, Armada, and Gottifredi 2007).

Therefore, it can be concluded that the viscosity of potato starch granule suspensions was affected by temperature to a larger extent than the consistency factor of potato and carrot powders suspensions. In addition, the consistency factor of carrot powder suspensions was less affected by temperature than the large particle size potato powder suspensions, followed by potato powder suspensions of d(0.5)=34 µm. The reason might be attributable to a greater solid-like behavior in carrot powder suspensions, e.g., higher amount of pectin-induced interactions, compared to potato powder suspensions. The large extent of pectin-induced interactions in the carrot and potato powders suspensions also led to the onset of gel properties in some of these suspensions at elevated temperatures. The presence of gel properties at high temperatures might be due to jamming in these suspensions as a result of the temperature increase. More understanding about jamming and its effect on the rheology of suspensions can be achieved by investigating the effect of temperature on the Φ_m of these suspensions.

7.4. The Effect of Temperature on Maximum Packing Fraction of Plant-tissue Suspensions

The influence of temperature on Φ_m is believed to be attributable to the difference between thermal expansion of the particles in the dispersed phase and that of the liquid in the continuous phase (Wildemuth and Williams 1984). To study the effect of temperature on maximum packing fractions of our suspensions, the Φ_m values of all suspensions predicted by the Krieger–Dougherty equation are plotted at 20, 50 and 80 ℃ in Fig. 7.2. Based on the standard error of regression (S) values (Tables 7.2 and 7.3), the Krieger–Dougherty equation could predict the Φ_m values of the carrot and potato powders suspensions with greater confidence compared to the Maron-Pierce equation. Both the Maron-Pierce and Krieger–Dougherty equations can be employed to predict the Φ_m values of potato starch granule suspensions with comparable s values (Tables 7.2 and 7.3).

Fig. 7.2. Maximum packing fraction of aqueous suspensions of potato starch, carrot powder and potato powder obtained by the Krieger–Dougherty equation
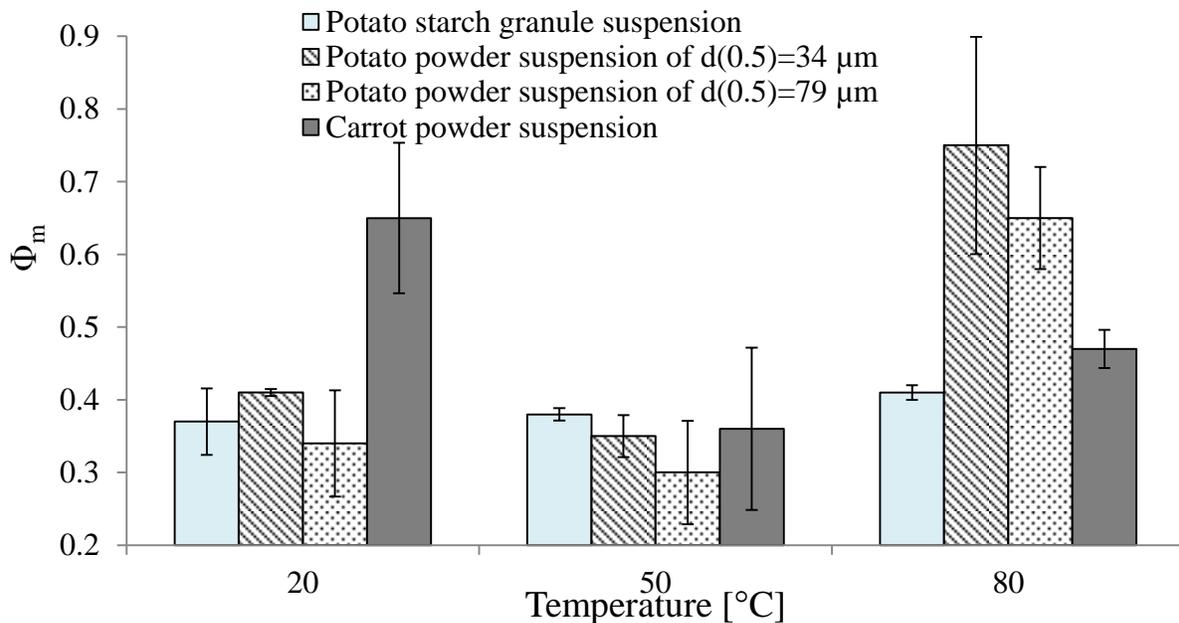
Based on Fig. 7.2, an increase in temperature from 20 to 50 °C led to an increase in Φ_m values of the potato starch granule suspensions. Additionally, Φ_m values of all the suspensions increased with increasing temperature from 50 to 80 °C. An increase in Φ_m of the suspensions with increasing temperature is believed to be attributable to an increase in the volume of suspensions due to the thermal expansion of the continuous phase (Wildemuth and Williams 1984; Sinaki and Scanlon 2016). However, a decrease in the Φ_m values of the suspensions of the carrot powder and potato powder of d(0.5)= 79 µm with increasing temperature from 20 to 50 °C contradicted the role of temperature in increasing Φ_m of the suspensions. This observation was hypothesized to be attributable to the role of intracellular and intercellular components, e.g., pectin polymers, whose amount in the continuous phase of the potato and carrot powders suspensions increased with increasing temperature. That is, the large amount of interactions promoted by these components resulted in the entrapment of the continuous phase by the aggregated and/or flocculated particles which, in turn, reduced the Φ_m of the suspensions (Zhou et al. 1995). Accordingly, a greater amount of intercellular and intracellular components in the suspensions is expected to lead to a greater decrease in Φ_m with increasing temperature. As discussed in Chapter 6, the amount of water-soluble intercellular and intracellular components, e.g., pectin polymers, was greater in carrot powder suspensions than the potato powder suspensions. A 45% decrease in Φ_m of carrot powder suspensions with increasing temperature (20 to 50 °C) compared to 12% and 15% decreases in the Φ_m of potato powder suspensions of d(0.5)=34 and 79 µm, respectively, confirmed the aforementioned hypothesis.

Moreover, the presence of intracellular and intercellular components in the suspensions was also anticipated to affect the extent of increase in Φ_m of suspensions with increasing temperature from 50 to 80 °C as well. That is, the role of thermal expansion of liquid in

increasing Φ_m with increasing temperature from 50 to 80 °C would be greater in suspensions with a greater amount of free liquid, i.e., liquid that was not entrapped by aggregated and/or flocculated particles (Rha 1975). It seems that a further increase in temperature, i.e., from 50 to 80 °C, highlighted the role of thermal expansion of free liquid in the suspensions in increasing Φ_m (Table 7.3) (Shewan 2014). A smaller amount of free liquid in suspensions of carrot powder compared to those of potato powder led to a 31% increase in Φ_m of the former compared to 117% and 114% increase in Φ_m of the latter with d(0.5)=34 and 79 μm, respectively, as temperature increased from 50 to 80 °C.

7.5. Liquid-like and Solid-like Behavior in Plant-tissue Suspensions

A liquid-like to solid-like transition occurred in the potato and carrot powders suspensions with increasing solid volume fractions (Φ) due to promoted particle-particle interactions at elevated Φ. In addition, with an increase in temperature, from 20 to 80 °C, more solid-like behavior in the suspensions was observed. An enhanced solubility of intracellular and intercellular components, particularly pectin polymers, with increasing temperature was thought to be responsible for such an observation (Sriamornsak 2003). That is, a temperature-induced solubilization of intracellular and intercellular components resulted in greater amounts of interactions, e.g., pectin-promoted interactions, in the suspensions, leading to more solid-like behavior of the suspensions at elevated temperatures. Such a conclusion was drawn based on the comparison between the rheological behavior of starch granule suspensions with no intercellular and intracellular components and that of potato and carrot powders suspensions with different amounts of such components.

The transition from liquid-like to solid-like behavior was also observed in the potato powder suspensions as a result of increasing angular frequency (ω). This transition could be attributable to a decrease in the time for deformation with increasing ω, which resulted in less energy dissipation and consequently the presence of more solid-like behavior in the suspensions (Aral and Kalyon 1997).

7.6. Practical Implications

The food industry is always looking for healthier and more natural food products (Vaclavik and Christian 2014). Studying potato and carrot powder suspensions as model systems offers an opportunity to learn whether other food formulations can be processed so that products free of artificial thickeners and gelling agents can be manufactured. For example, carrot powder can be used in food manufacturing as a source of natural pectin polymers with a great ability to form gels and also to increase the nutritional quality of the food products (Sharma et al. 2012). The results of this study showed that solid-like behavior is exhibited in carrot powder suspensions at intermediate solid volume fraction of $\Phi \geq 15\%$. In addition, potato powder suspensions rich in starch granules showed different rheological behavior than starch granule suspensions due to the presence of other intra- and inter-cellular components. Potato powder suspensions showed shear-thinning behavior whereas potato starch granule suspensions had shear-thickening behavior. Shear-thickening behavior is not of interest in industry as more energy is required to maintain flow, e.g., during mixing and pumping (Brown and Jaeger 2009). Therefore, using potato powder in a formulation rather than starch granules alone may remove processing complications which are important in practical applications.

Both potato and carrot powder suspensions showed a yield stress. The yield stress is a very important parameter to consider in practical purposes. For example, in mixing processes flow may be impeded if conditions are such that shear stresses are below the yield stress, and this may lead to bulking or uneven distribution of material in a mixer (Björn et al. 2012). Also, to select an appropriate pump, one should consider the necessary initial stress to cause flow in suspensions (Cheng 1986).

During the processing, storage, transportation and consumption of food products, different temperatures are encountered (Rao 2013). Therefore, understanding the temperature dependence of the rheological properties of the potato and carrot powder suspensions is useful in practical applications and in understanding the mechanism of flow in these suspensions. The practical applications of the findings of this work in regards to the effect of temperature on flow behavior of plant tissue suspensions include minimizing the viscosity at a given solid volume fraction with increasing the temperature. This facilitates pumping, mixing and transportation during processing.

7.7. Potential Future Works

The shape of dispersed particles was hypothesized to influence the rheological behavior of the potato and carrot powders suspensions. To examine the shape of these particles at different temperatures, the use of confocal scanning laser microscope (CSLM), as used by Zdunek and Umeda (2006), may help achieve a better insight on the effect of shape on the rheological properties of the suspensions. Additionally, to fully understand the effect of particle size on the

rheological properties of carrot and potato powders suspensions, it is suggested that a broader range of particle size is chosen for future studies.

In regards to the important role of pectin polymers in the rheological behavior of potato and carrot powders suspensions, follow-up studies are suggested to include the measurement of the amount of pectin in the suspensions at various temperatures, i.e., 20, 50 and 80 °C. The procedure described by Anthon and Barrett (2008) for the measurement of the amount of pectin in suspensions can be followed.

In addition to pectin polymers, other water-soluble and insoluble components of the potato and carrot powders are believed to influence the rheological behavior of the suspensions. Therefore, determination of the amount of total soluble and insoluble components in the suspensions will be helpful. The amount of soluble components, such as different sugars, and insoluble components, which are present in the continuous phase and the dispersed phase of suspensions, respectively, can be measured by following the method of Sharma et al. (1996).

In the processing of many food suspensions, temperatures above 90 °C are used which could result in different phenomena occurring during processing (Rao 2013). For instance, starch gelatinization is a probable phenomenon at sufficiently high temperatures, affecting the rheological properties of starch-containing food suspensions. Given a significantly greater amount of starch in potato compared to carrot, the rheological properties of potato powder suspensions are expected to be affected to a larger extent than those of carrot powder suspensions. However, the exact extent to which high temperatures would affect the rheological properties of our suspensions could only be quantified using a wide temperature range in the study of the rheological properties of potato and carrot suspensions. A follow-up study could

include rheological measurements of carrot and potato powders suspensions at temperatures higher than 80 °C to observe the influence of phenomena such as starch gelatinization on the rheology of these suspensions. Furthermore, the extent to which the role of the dispersed phase and continuous phase in the rheological behavior of plant tissue suspensions would change due to the gelatinization of starch could then be of interest in such study.

Additionally, the shear-thinning behavior of carrot and potato powders suspensions and the microstructural mechanisms responsible for such behavior can be studied using the rheo-microscopy technique employed by Cheng et al. (2011). Using rheo-microscopy, i.e., simultaneous use of fast confocal microscopy and force measurements (Cheng et al. 2011), the inner structure of the suspensions during rheological measurements can be investigated. This methodology would be helpful for interpreting the rheological behavior of the suspensions, particularly at concentrated regimes and elevated temperature, with respect to their internal structures.

8. Conclusions

In this work, the rheological behavior of potato and carrot powders suspensions containing different solid volume fraction with a focus on the effect of increasing structural complexity has been investigated. To create different levels of complexity, potato starch granule suspensions were chosen as the model system in which the lowest amount of interaction exists between components. As the next level of complexity, potato was selected in which starch granules are abundant while other intra- and inter- cellular components exist. To investigate the effect of soluble intra- and inter-cellular components, carrot was selected in which the presence of high amount of soluble components led to substantial complexity in the suspensions.

The Einstein equation was selected as a baseline for the study since there is a direct and linear relationship between the solid volume fraction and the viscosity of a suspension. Therefore, this equation was the closest model for the potato starch granule suspensions. While the Einstein equation could be fitted to potato starch granule suspensions experimental results quite well, there was not a good fit for this equation and the experimental data of the potato and carrot powder suspensions. The Krieger- Dougherty equation was found to be a good fit to the experimental data in all suspensions over the whole range of solid volume fraction.

Potato starch granule suspensions exhibited essentially Newtonian behavior while potato and carrot powder suspensions showed shear-thinning behavior. Non-Newtonian behavior in carrot and potato powder suspensions could be modelled by the Herschel-Bulkley equation. The results show that soluble intra- and inter cellular components play a key role in the rheological properties of potato and carrot powder suspensions. A higher consistency factor and yield stress and more shear-thinning behavior in carrot powder suspensions compared to potato powder suspensions are the results of the liberation of soluble components, particularly pectin polymers, in carrot parenchyma from the dispersed phase to the continuous phase.

The large extent of pectin-induced interactions in carrot powder suspensions led to more solid-like behavior in these suspensions compared to potato powder suspensions. Also, a temperature-induced solubilization of intra-cellular and inter-cellular components resulted in greater amounts of interactions in the suspensions, leading to more solid-like behavior of the suspensions at elevated temperatures.

9. Appendix

Fig. A.1 Examples of flow curves of potato (solid lines) and corn (dotted lines) starch granule suspensions at different temperatures.
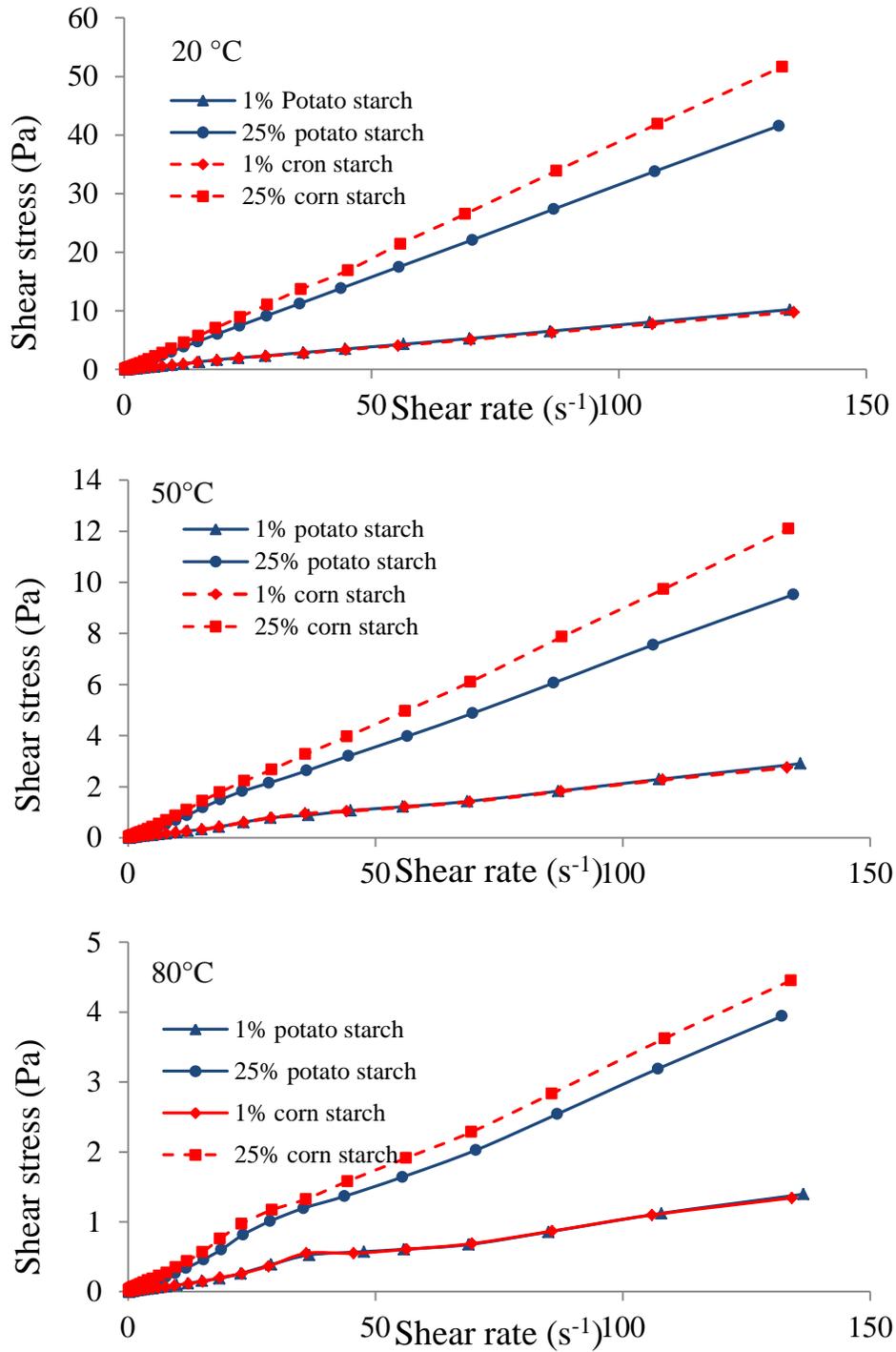
Light microscopy images

To determine the shape of the potato and carrot particles in the suspensions, light microscopy images were taken using a Zeiss Axiocam microscope (Zeiss, Carl Zeiss Ltd, Hertfordshire, UK) equipped with a camera. Suspensions of carrot powder and potato powders at d(0.5) 34 and 79 µm with $\Phi = 5\%$ were prepared based on the suspension preparation method. The images demonstrated a clear difference for the overall microstructures between carrot powder suspensions and potato powder suspensions. Based on Fig. A.2, comminution of carrot led to the creation of large cell clusters with broken edges, similar to the resulted demonstrated by Pickardt, Dongowski, and Kunzek (2004) and Lopez-Sanchez et al. (2011).

The difference in the potato suspensions of two different sizes caused by the disintegration process was also observed (Fig. A.2). In potato powder suspensions with d(0.5)= 34 µm, globular to ellipsoid starch granules were visible.

Fig. A.2 Light microscopy images. From left to right, carrot suspension, potato suspension with d(0.5) 34 µm and potato suspension with d(0.5) 79µm.
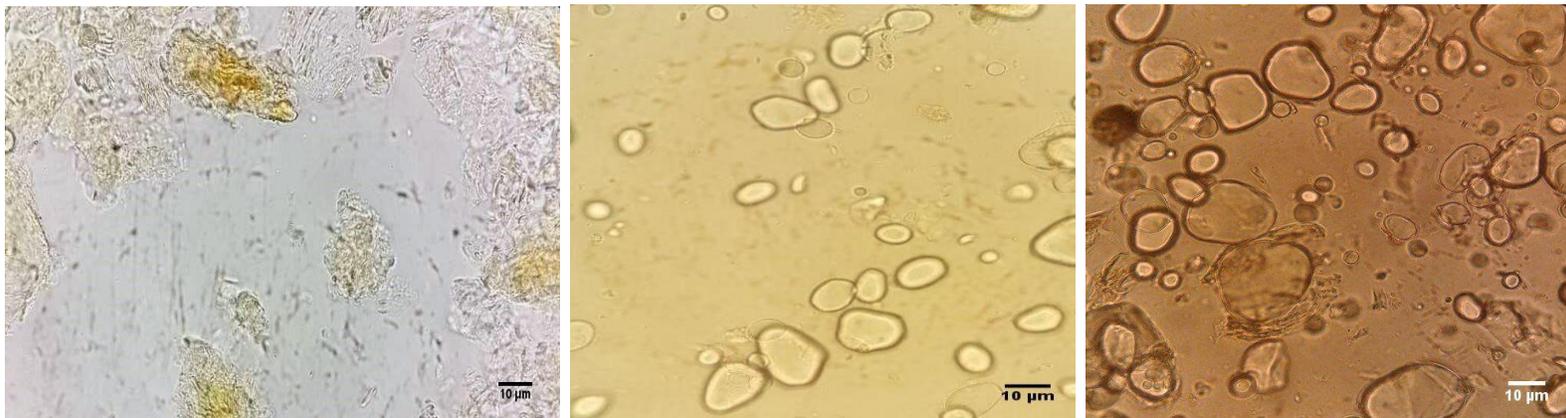
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