Thermal and Rheological Properties of Batter Systems

by

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ABSTRACT

Batters are highly complex systems with wide ranging ingredients including flours, water, flavorings, and spices. Interactions between the ingredients determine the performance of batters and the final quality of coated products. Addition of hydrocolloids into batters of different types of flour provides special effects on batter performance. The functionalities of hydrocolloids-flour mixtures in terms of the thermal and rheological properties of the resulting batter systems were investigated in this study.

The rheological properties of the batter were determined using a strain/stress control rheometer. A steady state method was used to measure the viscosity as a function of the shear rate varying from 0.5 to 150 s^{-1} at 15 °C. The resulting data was then fitted to the Herschel-Bulkley Model. The viscoelastic properties were monitored as a function of temperature and were determined using a dynamic oscillatory test. Two different temperature profiles were used to simulate cooking and storage processes. Differential scanning calorimetry (DSC) was used to determine thermal properties (namely glass transition temperature, gelatinization temperature, ice melting temperature, and enthalpy) and to describe the phase transitions that occur during heating and cooling processes.

The rheological and thermal properties varied for different types of flours and their combination ratios, as well as different types of hydrocolloids at different concentrations. The replacement of corn flour greatly altered the viscosity and viscoelastic properties of wheat based and rice based batter systems. Using 100% corn flour based batter showed highest yield stress, whereas 100% rice flour based batter did not show any yield stress. Higher temperatures and longer times were required to gelatinize starch at the higher

levels of rice flour for each batter system flour mix combination. The various combination ratios of the flours apparently did not significant influence the gelatinization temperatures of the batter systems. However they significantly influence the total enthalpies (ΔH_G) of the various samples. Wheat flour based batters showed the lowest glass transition temperatures. Thermal properties of wheat-based batters were influenced by the replacement of wheat with rice or corn flours. Corn flour based batters required considerably more energy for gelatinization during the cooking process.

Hydrocolloids lowered flow behavior index (n) and increased the consistency index (k) of all batters. The gums also changed the onset temperature of structure development and the storage and loss moduli of the batter systems. Hydrocolloids greatly influenced the thermal properties of batter systems. The gums shifted gelatinization temperature and depressed glass transition temperature of resulting batter systems. Further, MC increased the melting temperature (T_m) for the test batter systems as compared with the values for the control system without methylcellulose (MC). Carboxymethylcellulose (CMC) did not show statistically significant effects on the total enthalpies of ice melting for all samples. However, MC and CMC showed more pronounced effects on rice, corn, and their combined flour based batters than it did on wheat flour based batters. However, this characteristic does not show in batter systems containing xanthan gum.

RESUME

Les pâtes lisses sont des systèmes complexes comportant de nombreux ingrédients comme les farines, l'eau, les arômes et les épices. Les interactions entre les différents ingrédients déterminent la performance de la pâte lisse et la qualité finale des produits enrobés.

L`ajout d` hydrocolloïdes dans les pâtes lisses constituées de différentes farines agit sur la performance de la pâte. Les fonctionnalités des mélanges hydrocolloïdes -farine en terme de propriétés thermiques et rhéologiques de la pâte lisse résultante ont été recherchées dans cette étude.

Les propriétés rhéologiques de la pâte lisse ont été déterminées en utilisant un rhéomètre contrôlant la contrainte et la force appliquée. Une analyse à ei état régulier a permis de mesurer la viscosité en fonction des taux de cisaillement compris entre 0.5 et 150.0 s^{-1} à 15 °C. Les données obtenues ont ensuite été comparées àcllesdu modèle de Herschel-Bulkley. Les propriétés viscoélastiques ont été enregistrées en fonction de la température et déterminées en utilisant un test oscillatoire dynamique. Deux profiles de température ont été utilisés afin de simuler les procédés de cuisson et de stockage. La calorimétrie à balayage différentiel (DSC Differential Scanning Calorimetry) a été utilisée pour déterminer les propriétés thermiques (telles la température de transition vitreuse, la température de gélatinisation, le point de fusion, et l`enthalpie) et pour décrire les transitions de phases qui ont lieu pendant lacuissou et ls nef à gination.

Les propriétés rhéologiques et thermiques ont varié en fonction du type de farine et de son ratio au sein du mélange mais aussi en fonction du type et de la concentration en

hydrocolloide. Le remplacement de la farine de maïs par de la farine de blé ou de riz a fortement altéré la viscosité et les propriétés viscoélastiques de la pâte. Unefocére entièrement à doués la plus grande déformation de la pâte lisse alors que l` utilisation de 100 % de farine de riz n` a montré aucune déformation. Des températures plus élevées et des temps plus longs ont été requis afin de gélatiniser l` amidon dans les systèmes de pâtes lisses utilisant de grandes concentrations dn farine of de riz. Les différents ratios de farine n`ont apparemment pas influencé les températures de gélatinisation des systèmes de pâtes lisses. Cependant ils ont significativement affecté les enthalpies totales des différents échantillons (ΔH_G). Les pâtes lisses utilisant de la farine de blé ont montré les températures de transition vitreuse les plus basses. Les propriétés thermiques de ces pâtes ont été modifiées en remplaçant la farine de blé par des farines de riz ou de maïs. Les pâtes lisses utilisant la farine de maïs ont nécessité beaucoup plus d`énergie pour la gélatinisation au cours du procédé de cuisson.

Les hydrocolloïdes ont abaissé l`indice d`écoulement (n) et augmenté l`indice de consistance (k) de toutes les pâtes lisses. Les gommes ont aussi modifié la température initiale, G` et G``. Les hydrocolloides ont largement influencé les propriétés thermiques des systèmes de pâtes lisses. L'ajout de gommes a décalé les températures de gélatinisation et abaissé la température de transition vitreuse des pâtes lisses résultantes. Par ailleurs l` space ajout de méthylcellulose (MC) a augmenté le point de fusion ($T_m$) comparativement aux valeurs obtenues avec le système contrôle sans méthylcellulose. La carboxyméthylcellulose (CMC) n`a pas montré d`effet significatif sur l'enthalpie totale et sue point de fusion des échantillons. Cependant, MC et CMC ont montré des effets plus prononcés dans le cas des systèmes comportant de la farine de riz ou de maïs ou encore un mélange des deux. Mais cette propriété n`a pas été retrouvée dans les systèmes contenant de la gomme de xanthane.

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CONTRIBUTION OF AUTHORS

The role and contribution made by different authors are as follows: The principal author is Ms. Xue Jun. She is the Ph.D candidate who planned, designed, and executed all the experiments, data analysis, and wrote the manuscript for scientific publications. Dr. Michael O. Ngadi is the thesis supervisor, who guided the candidate in planning, design, and execution of the experiments and analysis of the data during the course of the entire program. He corrected, edited, and reviewed all the manuscripts sent for publication.

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I. GENERAL INTRODUCTION

1.1 BACKGROUND

Batters, or/ and breadings serve many functions as food coatings by adding value to food products and improving their flavour and texture. Also they provide many opportunities to reduce oil absorption during deep-frying (Pinthus et al., 1993; Mohamed et al., 1998; Fiszman et al., 2003). Batter is a liquid mixture comprised of water, flour, starch, flavoring, and seasonings into which food products are dipped prior to cooking. Batters can be classified into one of two categories namely interface/adhesion batters or puff/tempura batters (Loewe, 1990). An adhesive batter is typically used with a supplemental breading, and it serves primarily as an adhesive layer between the food surface and the breading. Chemical leavening is not normally used in an adhesive batter. A tempura batter is chemically leavened, and by itself can serve as the outside coating of the food. Both wheat and corn flours play important roles in tempura batters.

Batters are highly complex systems in which the nature of the ingredients is very wide-ranging, and interactions between ingredients determine the performance quality of the final product. However, the functionalities of ingredients in terms of their influence on thermal and rheological properties of batter systems are not yet fully understood. These functionalities directly influence process conditions as well as coated products quality. For instance, the use of one type flour or combination of flours may provide special effects on the thermal and rheological batter (Mukprasirt et al., 2000; Dogan et al., 2004) properties. Therefore, in order to formulate and apply batter-breading coatings to a wide variety of products, investigation of those properties will continue to be a challenge to workers in this area. A fundamental basic knowledge is needed to advance the science of batter formulation for products.

Rheological properties are among the most important physical properties that define batter behaviour. The viscosity of batter affects the quantity and quality of batter pick-up, appearance, texture, and the handling property of a coated product (Mukprasirt et al., 2000). The quality of a coated product is influenced by changes in batter coating properties associated with the structural phase transition from the liquid to the solid state. The flow behaviors and dynamic viscoelastic properties of a batter may provide information that characterizes the influence of temperature, water content, and various ingredients on a coating's structural behavior during process (Steffe, 1996). Rheological data provide information useful for any coating application.

The thermal properties and phase transition characteristic of batter systems change during cooking (e.g. deep fat frying) and freezing (e.g. frozen storage). They have combined effects on the overall characteristics of the finished coated foods. Several chemical and physical changes such as starch gelatinization and water evaporation occur during heating. The thermal properties (heat capacity, enthalpy, onset temperature and gelatinization temperature) reflect those changes, which directly influence the texture characteristic and quality of finished coated products (Arenson, 1969; and Meste, 2002). Thermal properties are critical in defining heat and mass transfer behaviors of coated product during heating (frying, baking, etc) and storage. They are important parameters in predicting the effect of freezing and thawing on coated product adhesion and quality. It is necessary to understand phase transitions, including glass transitions, occurring in coatings at sub-zero temperatures during storage, since glass transition may control rates of recrystallization of ice and diffusion-controlled reactions (Slade et al., 1995, Lee et al., 2002). Consequently, different batter formulations and their components may affect cooking quality and frozen state stability through their effects on thermal and phase state properties. Researchers and food processors are interested in developing further-processed coated products as a means of providing foods with high nutritional quality and lower fat contents. Understanding phase and state transition of batter system may hold the key to improving coating performance during cooking and maintaining overall product quality during storage.

Many food ingredients can be used to improve functionality (e.g., viscosity, crispness, distinctive flavor, crunchy texture) in batters and coatings. Recently, hydrocolloids represent a category of functional ingredients that have been incorporated into batter formulations, and have shown their effectiveness in improving batter performances and reducing oil absorption in fried coated foods (Meyer al et. 1990; Hsia et al., 1992; Balasuramaniam et al., 1997; Annapure et al., 1999; Holownia et al., 2000; Susanne et al., 2001; Mellma, 2003; and Sanz et al., 2004).

Hydrocolloids are water-soluble polymers, generally carbohydrates, with the ability to thicken and/or gel aqueous systems. Each type of hydrocolloid has a different contribution to the batter system due to different structures resulting from different degrees of substitution with different branch compounds. However, they play an important role on viscosity, film-forming, and barrier properties in batter system (Meyers, 1990, and Albert, 2002). Hydrocolloids as functional ingredients may change the rheological, texture and thermal properties of batter system and lead to an influence on the final quality of the end products. Besides, hydrocolloids and other ingredients may cause interaction resulting in synergistic effects on those properties of batter systems during processing (Ferrero and Zaritzky, 2000; Sanz et al., 2005; Kim and Yoo, 2005; Cao and Vodovot, 2005; Guadalupe et al., 2005)

Although the majority of fried food products are batter and breading coated, formulation of batter system has evolved from an art into a science. In the last decade, research on batter systems has focused mainly on comparing their functionality with respect to fat absorption. Not much work has been done on understanding the fundamental properties such as rheological properties and thermal transition behavior and properties, especially for different combinations of flour blends containing hydrocolloids. Moreover, understanding how these properties change with the formation of flour-hydrocolloids batter systems during heating and cooling process, and the interaction between hydrocolloids, flour base, and other ingredients, will be helpful for optimizing processing and storage conditions as well as in selecting and formulating appropriate batter systems for various types of battered products thus resulting in nutritional foods for healthier living.

1.2 HYPOTHESIS OF THE RESEARCH PROJECT

The present study will significantly extend the current knowledge on the effects of hydrocolloids on thermal and rheological properties of batter systems formulated with hydrocolloids and different combinations of flour blends. Several studies have shown that thermal and rheological properties of batter systems are largely determined by their constituent flour type. The hypothesis of this study is that in addition to the type of flours, combination of different flours, and addition of hydrocolloids such as methylcellulose (MC), carboxymethylcellulose (CMC) and xanthan gum (XG) may have special functional effect on batter systems. It is assumed that the effects of water content, salt, and leavening on thermal properties, phase transition behavior and rheological properties of batter system during cooking and freezing storage will be the same for all samples since the amount of these ingredients will be fixed for all samples. Therefore, the changes on the properties of batter will be considered as due to the effect of different combinations of flour and combination ratios of blends, as well as the addition of different concentrations of hydrocolloids.

1.3 OBJECTIVES

The overall objective of this study was to determine the thermal and rheological changes as well as the phase transitions in batters containing hydrocolloids and different combinations of flour blends during heating processes or during frozen storage. The information can be useful in selecting and formulating appropriate systems for various battered foods. Thus, the knowledge will be critical in designing process and storage conditions resulting in improved and higher quality coated food products.

To contribute to the overall objectives set for this study, three flours (wheat, rice and corn) and three hydrocolloids (MC, CMC, and Xanthan gum) have been identified as the focus materials. Therefore, the following specific objectives were set for the proposed research.

1. To study the flow behavior and viscoelastic properties of batters formulated using wheat flour, rice flour, corn flour and their various combinations.

2. To evaluate the influence of incorporating methylcellulose (MC) or xanthan gum at different concentrations on the flow and viscoelastic properties of wheat, rice and corn based batters.

3. To evaluate the influence of incorporating carboxymethylcellulose (CMC) and xanthan gum at different concentrations on the flow and viscoelastic properties of wheat, rice and corn based batters.

4. To determine changes in the thermal properties (enthalpy, onset temperature and gelatinization temperature), and phase transition (glass transition temperature, ice melting temperature, and enthalpy) during the heating and cooling processes of batters formulated using wheat, rice, and corn flours and their various combinations.

5. To investigate the effects of methylcellulose or xanthan gum on thermal properties (enthalpy, onset temperature, and gelatinization temperature), and phase transition (glass transition temperature, ice melting temperature and enthalpy) of wheat, corn, and rice based batter systems during the heating and cooling processes.

6. To study the effects of carboxymethylcellulose on thermal properties (enthalpy, onset temperature, and gelatinization temperature), and phase and state transition (glass transition temperature, ice melting temperature and enthalpy) of wheat, corn, and rice based batter systems during the heating and cooling processes.

II. LITERATURE REVIEW

Surface properties of foods are very important in influencing fat uptake as well as in defining the physical characteristics of products during deep fat frying. The coating provides promising opportunities to develop flavor and to reduce fat uptake in coated fried foods. The mechanism of the action is not fully understood. However, the ingredients in the coating may have certain functionalities that are related to specific properties. As a result, during the last decade, research on battered products has focused mainly on reducing the quantity of oil absorbed during frying. Modified starch, rice flour, and other ingredients also contribute to the reduction of oil content in fried coated foods. Certain hydrocolloids that have been incorporated in formulations have shown their effectiveness as oil absorption barriers.

During the recent years of rapid growth in the batter and breading industry, many technological advances and breakthroughs have occurred in batter formulation, breading manufacture, frying oils, and production equipment engineering. As a result, many food companies now operate and fund their own research programs for batters and breadings, and their applications to various food products. Along with these changes, improved quality assurance practices, appropriate and practical food regulatory laws, and revolutionary approaches to product development has been needed to provide better technical service to the customers and ultimately to the final consumers.

Batter and breading are complex systems comprising of water, flour, starch, and seasonings with which food products are coated prior to cooking. Different functionalities of the systems apply to different categories of food.

2.1 BATTER SYSTEMS

Batters are the common and vital component of all successful food coating systems. Batters link the fundamentals of food science with the product needs. The proper selection and application of batters influence the flavour, appearance, eating characteristics, performance and cost effectiveness of the final coated product. In addition to the obvious benefits of taste, colour, and texture, batter systems also improve the yield and keeping qualities to withstand the demands of processing, distribution and final preparation for the table.

Batter can be defined as liquid dough, being a thick but pourable mixture, into which a product is dipped before it is breaded or fried. Loewe (1993) classified batter systems into two broad categories: Interface/adhesion and puff/tempura. Normally, interface or adhesion batters serve as "glue" and are used with an added breading, serving primarily as the adhesive layer between the product's surface and the breading. The interface/adhesion batter's main function is to provide a base so the bread crumbs, when used, will adhere to a product. Adhesive batters gained the name for a very simple reason - like Mom's egg and milk dip; they provide an adhesive layer between substrate and outer breading layer. They can be formulated with wheat flour, corn flour or starch.

The characteristic of adhesive batters is a low to medium viscosity, intended mostly to achieve breading adhesion. Typically, they are high in starch and quite thin. The heavier the batter, the more crumb will adhere. They may carry flavors, and the thicker batters can be used as stand-alone coatings. Starch-based batters, also considered adhesion batters, act as the glue in a coating system. They are usually thin and need to be stirred frequently to keep the starch in suspension. Starch-based batters bind themselves quite strongly to protein-based products and can be used as an outer coating on the products in order to increase their crispiness and improve holding time. Flour-based batters can also serve as the product's final outer coating without breading. Since these batters are thicker than starch-based batters, they adhere coarser breadcrumb that may not stick to a thin, starch-based batter. A flour batter can also contain leavening agents that will make the batter more "puffy" when fried. Examples of this are tempura and beer batters. Both starch-based and flour-based batters can be modified with a wide array of flavorings and spices to obtain the desired sensory profile. Viscosity is very important in regulating the amount of pickup or thickness of batter, depending on the flour/water ratio and the batter temperature.

Tempura batter, which includes raising or leavening agents to generate gas and "puff" the product, has a high viscosity to provide a thick coating with minimum requirement for mixing or pumping in order to prevent loss of the leavening gas. Cooked immediately, it is designed to brown and expand the batter (w/gas) into an open, honey-comb-like texture. No breading is required to form a thick coating on the product when a tempura type batter is used.

Batter and breading act as a moisture barrier, and provide a promising route to develop flavor and to reduce fat uptake (Wills et al., 1981; Lamberg et al., 1990; Pinthus et al., 1993; Moreira et al., 1997; Saguy et al., 1998; Fiszman et al., 2003). However, both the convenience food industry and consumers increasingly desire even more sophisticated foods and variety with more juiciness while absorbing less oil.

2.2 FUNCTIONAL INGREDIENTS

Ingredients serve numerous important functions in batter systems to give coatings their unique characteristics and functionalities. The selection of appropriate ingredients directly influences quality of the finished products

2.2.1 Flours

Flour is the key ingredient in batter and breading system. Some flours such as wheat flour provide viscosity and may promote adhesion through the formation of gluten. Gluten provides structure and texture and can act as a barrier to fat absorption. Flour contains some reducing sugars that caramelize during frying, contributing to the color and flavor of the coating (Mohamed et al., 1998). Flour is also the main component of most breadings. It can be used as is or first baked into a crumb. The porosity of the resulting products affects oil absorption - the more porous the material, the more oil is absorbed.

Wheat flour is the most common flour used in batters and breadings (Loewe, 1993). However, rice, corn, soy, malted barley and potato flours have also been used. Wheat flour with higher protein levels will increase batter viscosity and produce darker, crisper fried foods. Corn flour generally produces a yellowish color due to the carotene pigment in corn. It serves as a source of natural yellow color in order to reduce the influence of sugars and milk powder in batter (Salvador et al., 2003). Corn flour is added more often for viscosity control as the higher starch level affects the batter's ability to absorb water. Corn flour in batter systems increases crispness and decreases high levels of puffing due to decreased moisture retention in the coating (Salvador et al., 2002). Corn contains higher crude lipids than wheat and rice flour (USDA Handbook # 8). Suderman (1993) reported that a corn starch based batter required continuous mixing during processing because the solids had a tendency to settle out easily, resulting in changes in batter viscosity throughout the production period, leading to non-uniform batter pickup by substrates. Therefore corn flour based batter requires the addition of a thickener to keep the solids in suspension to solve this problem.

Rice flour shows its potential to be served as an alternative to wheat flour in battered and breaded foods. Rice flour-based batter might be a commercially feasible new product in the food industry. Shih et al. (1999), Dogan et al. (2000) and Mukprasirt et al. (2000) found that proteins and starch in rice flour are chemically different from those in wheat flour. They reported that rice flour resisted oil absorption better but was less effective as a thickening agent than wheat flour. Their results showed a 69% oil reduction with rice flour batter on shrimp products. A high ratio of rice flour provided roughness to the crust (Shih, 1999). However, rice flour-based batters form thin slurries and require additives to develop viscosity and other desirable batter properties. A good strategy is to use rice-based thickening agents as additives. For example, gelatinized long grain rice flour and phosphorylated long grain rice starch ester can be effective in enhancing the batter viscosity and the oil–lowering properties of rice flour batters. Mukprasirt et al. (2000) also studied the effects of ingredients used in a rice flour-base on the adhesion characteristics for deep fat fried chicken drumsticks. They found that batter formulated with a 50:50 mixture of rice and corn flours adhered better to drumsticks than did batter with other rice flour ratios (30:70, 70:30 – rice flour: corn flour). As rice flour ratio increased from 50 to 70%, the binding force decreased. They suggested that rice flour should be combined with other ingredients. For example, methylcellulose, oxidized starch, and xanthan gum increased the amount of batter pick-up before frying by increasing viscosity, and they led to finished products with lower fat content. However, combining different flours may provide special effects and produce desired characteristics in the coated products.

2.2.2 Starch

Starches have traditionally been used for adhesion in batters. The two main components of starch are amylopectin and amylose. Starches with higher amylose content are generally selected for better film-forming properties. They produce a crisper, stronger film, which stays intact through the fryer. Oxidized starches are used for their basic adhesion and coating, while high-amylose starches help reduce fat pickup. Batters typically contain starch levels of 5 to 30% of the dry mixture (Mukprasirt, 2001).

Several specialty ingredients for batters and breadings have been developed. One new development in the starch line is dextrins (Shinsato et al., 1999), which have superior film-forming properties. These products also can increase shelf life on a foodservice line. Since fried items typically sit for 15 minutes or more under heat lamps, the challenge is to keep them just as crunchy as the minute they came out of the fryer. Special hydrophobic starches with less water affinity can also improve adhesion and crispness. A variety of starches can be used in batters and breadings. These include common corn starch, potato starch, wheat starch, tapioca starch, and high-amylose corn starch. The amylose portion improves film forming. Waxy corn starch is not used extensively in batters and breadings because of its high amylopectin content. A modified starch also can add freeze/thaw stability to a par-fried product (Bertram, 2001). However, in most frozen battered items, the starch is not cooked until the product is fried, so it has little to no contribution during frozen storage.

2.2.3 Protein

Adding protein helps the structure or changes the texture of the final coated product. Proteins might be added at a level of 10 to 15% by dry weight base (Robert, 1996). Research with protein ingredients showed that products with higher protein contents are generally more effective as binding agents. Protein has been used to improve the water absorption capacity of flour, which in turn increases the viscosity of the system (Hoseney, 1994). It is also used to strengthen the structure and texture, retard moisture loss, and enhance crust color and flavor development. The level of flour protein used had a major effect on batter pickup, ranging from 11 to 28% when measured at equal water-solids ratios (Loewe, 1993). In general, a higher level of protein increased crispness of the fried product and produced a darker color. As the protein level increased, there was a gradual increase in roughness of texture and brittleness of the fried coating. The pancake-like inner structure was no longer present in the high-protein (12.1%) flour coatings (Loewe, 1993).

2.2.4 Chemical leavening

Typical leavenings used in batters include sodium acid pyrophosphate (SAPP), sodium aluminum phosphate (SALP), and combinations of SALP and monocalcium phosphate (MCP) (Dubois, 1981). The gas-release characteristic of the specific leavening affects the texture. If the release is too early, the product texture will be coarse and the coating will absorb excess oil (Loewe, 1996). Additional leavening may be able to change the color and texture of a fried product, for example a corn-dog (a sausage) coating needs a leavening system that releases gas very rapidly so that the coating can expand very quickly. The batter becomes more brittle as the amount of leavening is increased (Dubois, 1981). The leavening system can be tailored for a specific application by varying the type of leavening acids incorporated. The amount of gas generated, and its rate of production determine the effect of leavening in the batter.

2.2.5 Shortening and oil

Shortening plays a key role in the mouth-feel or eating quality of battered and breaded food. Shortening and oil have specific functions in coatings, such as being carriers of fat-soluble vitamins and contributing to food flavor and palatability as well as to the feeling of satiety after eating. Other fatty materials with potential use in batters and breading include emulsifiers and staling inhibitors (Fennema, 1976). The melting point and solids content are functions of the source of oil selected for the frying shortening. Proper selection of shortening is important to assure the quality of coated products because it would affect flavor, eating quality, nutrition, solid/liquid form, and fry life economics (Crosby & Kincs, 1990). Ang (1993) reported that cellulose had a greater effect in shortening. The research results showed the decreasing in fat and increasing in moisture when 1% powdered cellulose (fiber length in excess of 100 microns) was incorporated into the batter. It could be due to hydrogen bonds forming between water moluecules and cellulose fibers. Results from water and oil retention capacities indicate that powdered cellulose is more hydrophilic than tipophilic. This could also restrict the displacement of water by fat frying (Ang, 1993).

2.2.6 Egg and milk

Eggs are used widely, both as a batter ingredient and as pre-dips. Egg contains albumin, a heat-coagulable protein that is useful in binding the breading /batter to the substrate. The white's protein improves adhesion, while the yolk's phospholipids provide increased emulsification. Egg whites may create some microbiological issues, especially if the product sits on a line at a room temperature of 70 to 90°F. The addition of eggs to a batter tends to darken the final product (Loewe, 1993). Dairy ingredients contribute flavor, adhesion and color. Typical pre-dips include milk, evaporated milk and buttermilk. Some producers select buttermilk for its unique flavor profile in many coating food recipes, including "rock shrimp cones," "crispy fried chicken" and "fried okra." Monhame et al. (1998) reported that amongst the proteins (egg yolk, skimmed milk and ovalbumin) studied, ovalbumin was able to reduce oil absorption and improve the crispness of the fried batter.

2.2.7 Flavoring and seasoning

One way to improve the value-added perception of battered and breaded products is to incorporate additional flavorings and seasonings. Donahoo (1970) suggested that the seasoning level varies considerably though the average is 3 - 5% of a batter mix. Spices and herbs are dry ground plant materials that possess a characteristic taste and contain many aromatic and flavor constituents. They are usually used at a rate of 0.5 - 1.0% in finished food products (Suderman, 1993). At the same time, spices may contribute specks and colors that are unacceptable (i.e. paprika). Also, it takes time to reach flavor equilibrium with their medium (Suderman, 1993). Essential oils offer many advantages that include high flavor concentration, no off colors or specks, instant flavor equilibration and easy blending and quality control. Essential oils are used in food products at a level of 0.01 - 0.10% of the finished weight (Pangborn and Russell, 1976).

Flavor components are released from the coated food (substrate, predust, and batter-breading complex). All flavor components have a volatility spectrum, and it is conceivable that some flavor components are steam stripped from the foods as water converted to steam and exits the food surface. Flavor components are also imparted to the coated food product by the frying oil or heat stable flavors contained in the frying oil. In the commercial batter and breading mix, garlic is one of the popular ingredients that improve the flavor of the product (Suderman, 1996). From a food safety standpoint it should be kept in mind that spices are an occasional source of microbial contamination.

Another factor to consider when selecting the correct batter or breading included texture, crispness, color, flavor, appearance, functionality, cooking characteristics (i.e. baking, frying, microwaving, or convection oven preparation), compatibility, interaction of batter with other ingredients in the system. It is essential to know these principles because most flavor development work is supplemental to the basic development of batters. However, in some situations, structural changes in batters and breading are necessary to achieve highly technical flavor development objectives.

2.2.8 Hydrocolloids

Hydrocolloids are high molecular weight water-soluble carbohydrate biopolymers with the ability to form gel or thickening aqueous system. Hydrocolloids generally contain many hydroxyl groups linked in different configurations. Hydrocolloids can be categorized according to their origin, isolation or derivation methods, major functionality, and the presence of ionic charges. From the structural point of view, hydrocolloids can be classified (Figure 2.1) as: linear (e.g., cellulose, amylose), substituted linear (e.g., guar gum, methylcellulose) or branch-on-branch (e.g., Arabic gum, amylopectin). The structural conformation and degree of substitution also can play an important role to provide different functional properties to food products (Meyers, 1990). Gum and starch are the most important types of hydrocolloids (Meyers, 1990).

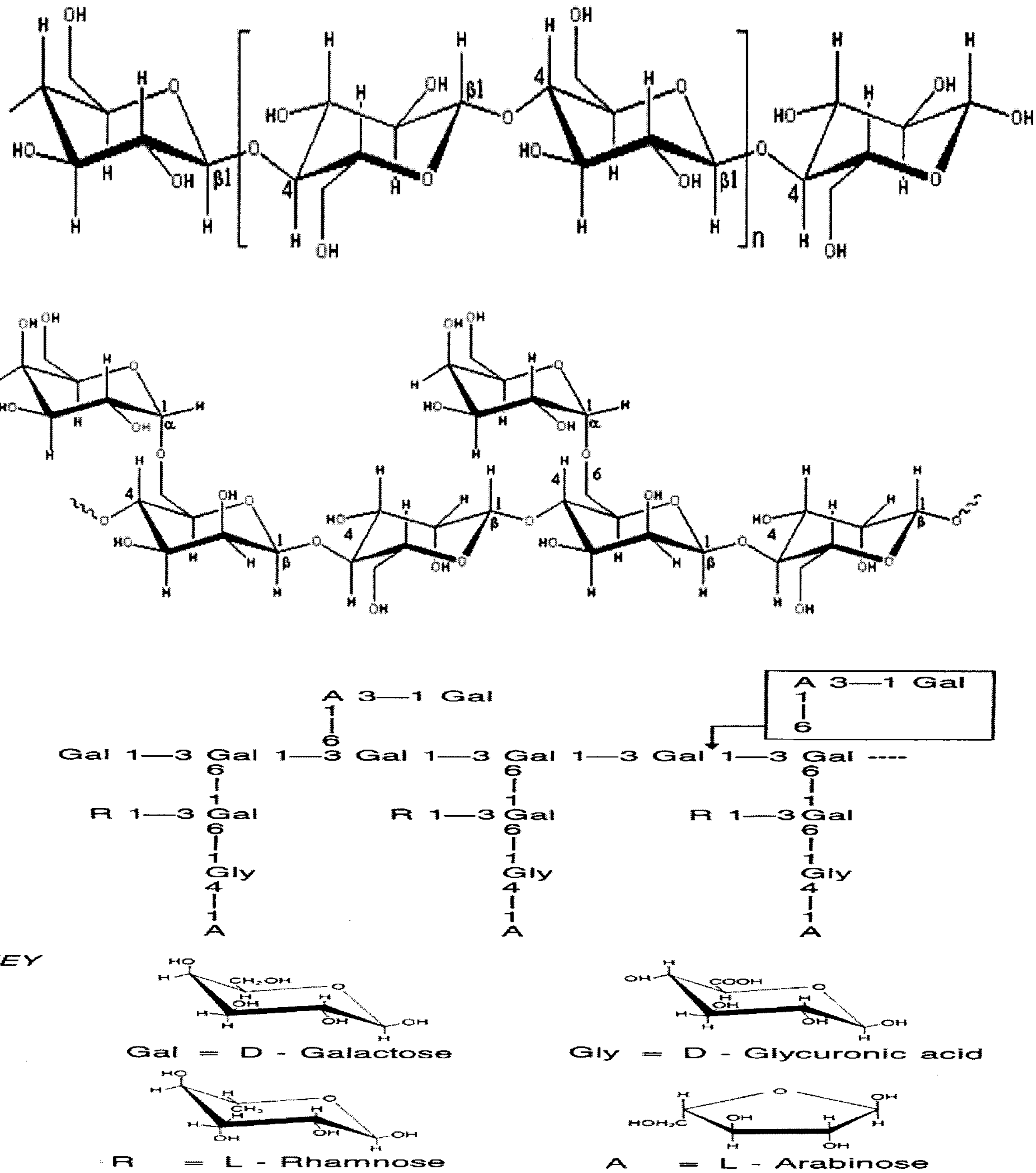

Figure 2.1. Structures of hydrocolloids. (A, linear, cellulose; B, substituted linear, guar gum C, branch-on-branch, Arabic gum.)

Hydrocolloids are currently widely used in a variety of industrial sectors to perform a number of functions including thickening and gelling aqueous solutions, stabilizing foams, emulsions and dispersions, inhibiting ice and sugar crystal formation and the controlled release of flavors. Recently, it has been popularly used in the formulation of batters to cover pieces of food which are to be fried. Traditionally, the primary use of hydrocolloids for this application has been based on their capacity to immobilize water and control viscosity of batters (Fiszman et al., 2005). Carboxymethyl cellulose (CMC) has been used to increase moisture retention and control rheological properties of cereal batters and doughs, and protect against leavening losses in cake mixes, improve the volume and structural uniformity of baked products, and increase the shelf-life of cereal products (Dziezak 1991; Sindhu and Bhawa 2000). Kayacier and Singh (1999) used CMC to obtain low-fat tortilla chips with rheological properties similar to regular chips. The addition of hydrocolloids is generally effective at levels as low as 1% of the formulation's dry weight or less (Meyers,1996). Bell and Steinke (1991) reported increase in volume of microwave-baked cakes on addition of 1-2% methylcellulose gums due to improved distribution of moisture by the gum. Xanthan gum (XG) is used to improve the texture and moisture retention in cake batters and dough, increase the volume and shelf life of cereal foods by limiting starch retrogradation, improve their eating quality and appearance, and enhance the effectiveness of other hydrocolloids (Lee et al., 1982; Miller and Hoseney, 1993; Hanna et al., 1997; Lee et al., 2002). The gel-forming capacities of certain hydrocolloids have been showed their ability to reduce the oil absorption in the cereal product or batter-coated products during the frying process. This has been one of the main applications over the past two decades (Stypula and Bckholz, 1989; Meyers and Cockling, 1990; Chalupa & Sanderson, 1994) and is possibly that of greatest value added. Selecting the appropriate hydrocolloid(s) requires not only an understanding of their physical properties but also an understanding of the foods themselves. It is difficult to ascribe defined exact characteristics and functions to the broad class of hydrocolloids.

There are several factors to consider when choosing a hydrocolloid for specific application. One of these is the specific requirement for correct hydration of the different hydrocolloids. In this regard, when different alternatives are available the preferred gums will be those that can be incorporated into the batter by dry blending. Correctly selecting hydrocolloids for a specific function should also consider that other ingredients in the batter system might affect hydrocolloids performance, so the compatibility of the hydrocolloids with those components must also be checked (Gnarder et al., 2004). For instance, a high concentration of soluble solids (i.e. sugar, salt, etc) can reduce the solubility of hydrocolloids because of competition for the available water (Grover, 1982, 1990).

2.3 FUNCTIONALITY OF HYDROCOLLOIDS IN BATTER SYSTEMS

Many of the hydrocolloids substances are used as ingredients in batters to serve three functions in batter system. The primary two functions are viscosity control of the batter and control of its water-holding capacity (Mallikarjunan et al., 1997; Ford, 1998). The third function is to control water loss and oil uptake. This is attributed to the unique thermal gelation abilities of some hydrocolloids, which form gels and provide a resistant-barrier coating during heating (Meyers, 1990; Balasuramaniam et al., 1997; Susanne et al., 2001; Albert, 2002; Mellema, 2003).

Methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) are the only food gums that can thermally gel (Henderson, 1988; Sanz et al., 2005) and that are reversible and repeatable. A number of studies have reported that the addition of MC and HPMC in batter systems has successfully reduced oil uptake in coated fried products (Meyer et al., 1990; Annapure et al., 1999; Susanne et al., 2001; Mellema, 2003). Thermogelling can also lead to a stronger but more brittle coating that promotes the formation of a relatively small number of wide punctures with low capillary pressure, resulting in low oil uptake during deep fat frying (Holownia et al., 2000). The temperatures at which the gelation process starts and the strength of the gel formed are dependent upon the type and the degree of substitution, molecular weight, and concentration of hydrocolloids (Nishinari et al., 1997; Sanz et al., 2004). Priyea et al. (1996) reported that adding Carboxymethylcellulose (CMC) to the formulation of "boondis", a deep-fried batter-based legume snack food popular in India, reduced the amount of oil in the final product. This study analyzed the effect of different concentrations of CMC in the range of 0.5 - 3%, by adjusting the proportion of water to obtain adequate viscosity .The greatest barrier efficiency was obtained at a concentration of 2%. The higher concentration of 3% was found to be non effective for oil absorption.

Gums are mostly used for cold-batter viscosity adjustment (Davis, 1983). It contributes to variations in viscosity often attributable to other ingredients such as starches and flours in batter systems. Meyers (1990) reported that some gums (e.g. xanthan and tragacanth) could also provide a yield value to the batter. Yield value is the initial resistance to flow under stress. This yield value enables the suspension of heavy particles at low gum concentrations (0.01-0.25% w/w). Suderman et al. (1981) indicated that carboxymethylcellulose (CMC) was able to improve adhesive strength in batters. Gao and Vodovot (2005) reported that CMC changed the rheological and thermal properties of masa (dough) and the resulting tortilla's shelf-life. Andres et al. (2005) found that CMC greatly influenced the rheological and functional properties of dried nixtamalised (alkaline-cooked) maize masa.. The use of flour as batter base that does not develop much viscosity, such as rice flour, makes it necessary to incorporate a xanthan or guar gum to ensure quality similar to a classic formulation (Mukprasirt et al., 2000).

Apart from providing viscosity, hydrocolloids help to keep solids suspended in solution. This property especially has been related particularly to xanthan gum and tragacanth gum, which also provide yield value and are able to suspend heavy particles under shear conditions at low concentration (0.10 - 0.255 w/w) (Hsia et al., 1992). Generally, the effectiveness of a gum in providing adhesive strength in a batter system will be increased with an increase in its gel strength, concentration, and molecular weight, as well as its viscosity in the batter (Meyers, 1990). Also the highly hydrophilic nature of hydrocolloids retards ice crystal growth during frozen product storage and reduces water migration to the coating from the substrate. This improves the freeze/thaw stability (Fiszman et al., 2003).

Hydrocolloid performance can also be affected by the complexity of other ingredients in the batter system and the compatibility of hydrocolloids with those components. Most food gums are non-digestible polysaccharides that have a profound effect on the available free water and the rheology of liquid batter systems (Meyers, 1990). At high concentrations (greater than approximately 60% by weight), soluble solids such as sugars and salts can reduce the solubility of hydrocolloids because they are competing for the available water (Meyers, 1990). The application of these novel hydrocolloid ingredients in batter systems is still largely in the laboratory stage, and their mechanism and properties are not yet fully understood. However, hydrocolloids show a high potential ability to provide consumers with healthy food products if they could be incorporated into batters on a commercial scale.

2.4 RHEOLOGICAL PROPERTIES OF BATTER SYSTEMS

Batter is a complex system with wide variance of ingredients inside the system. The rheological properties of the batter system affect the pickup and quality of the batter that adheres, the handling properties of the battered product, and its appearance and final texture. Control of viscosity, degree of adhesion, and porosity of the batter system is important to control the quality of final products. Changes in rheological properties of a material reveal changes in its molecular structure. Consequently, the rheological properties of a material influence the flow process and are themselves influenced by the structural changes generated during the process. Those changes in their structure could directly affect the appearance and final texture of the finished products. Therefore, rheological measurements can provide a means of monitoring changes in product structure during process.

The incorporation of hydrocolloids makes the flow behaviour of batters more complex. Fiszman et al. (2005) reported that only single shear rate rheological measurements are usually performed in industrial plants and they do not provide complete information. Also a rheological characterization of batter behavior over a range of shear stresses and time give more complete information for optimizing the processes of mixing, pumping and coating, with a view to keeping the batter properties, pickup and adhesion uniform (Fiszman and Salvador, 2003). However, the determination of rheological properties by using sophisticated rheometers make it possible to study the rheological behavious of batter in depth, although their use is generally confined to the field of research (Sanz et al., 2004).

Batter viscosity is a critical coating characteristic. It affects the pick up and quality of the batter that adheres, and an end product's appearance and texture (Hsia et al., 1992; Shih et al., 1999; and Mukprasirt et al., 2000). Steady shear measurement is commonly used to determine fluid behavior such as the apparent viscosity of batter. Numerous studies showed that batter generally presented shear-thinning behaviour, time dependency and thixotropy. Therefore the rheological characterization of a batter's flow behaviour over a range of shear stresses and time gives more complete information for optimization of the process of mixing, pumping, and coating, with a view to keep the batter properties, pickup, and their adhesion uniform (Hsia et al., 1992; Balasubramaniam et al., 1997; and Mukprasirt et al., 2000). The composition and proportion of the ingredients, the water-solids relationship and temperature are considered factors that affect the rheological properties of a batter. An increase in temperature resulted in lower consistency index values (Ostwald-deWale model) in several tempura batter formulations (Baixauli et al., 2003 and Salvador et al., 2003).

The incorporation of hydrocolloids makes predicting their flow behaviour even more complicated. Christianson et al. (1981) reported that viscosity of wheat starch was significantly increased by the addition of a small amount of xanthan, guar, and cellulose gums. At the initial stage of gelatinization, those gums and their inherent viscosity magnified the effect of swelling so that the viscosity increase was apparent. Sanz et al. (2004) studied the effect of concentration and temperature on properties of MC-added batters. Their results showed that MC produced a significant increase in the consistency (Ostwald-de Waele model) and shear-thinning behaviour of the wheat flour based batter, and this effect was more evident at high levels of MC addition (2%). Sanz et al. (2005) observed that methylcellulose influenced the rheological behaviour of wheat starch and modified corn starch. Marcotte, Hoshahili, and Ramaswamy (2001) studied the concentration and temperature dependencies of rheological characteristics were determined for selected hydrocolloids. In their results, higher gum concentrations resulted in an increase of both Newtonian and apparent (at 50 s^{-1}) viscosities. Xanthan was found to be the most pseudoplastic and the least temperature dependent of all hydrocolloids studied. Hsia et al. (1992) also found guar and xanthan gum to increase shear thinning behaviour in wheat flour based batter and corn flour based batter, but CMC did not increase batter consistency significantly in either wheat or corn flour based batters. Mukprasirt et al. (2000) reported a higher consistency index for rice based batter containing MC at the low temperature of 5 °C compared to either 15 or 25 °C, and that the shear-thinning behavior decreased with temperature increase. Kim and Yoo (2005) showed that the results of the increase in rate constant (k) in the gelatinization of rice starch-xanthan gum mixtures was a function of xanthan gum concentration.

Sanz et al. (2005) studied the thermogelation properties of MC and its effect on wheat flour based batter formulas containing 1, 1.5, or 2% MC. Their results showed that MC solutions tested at 15 to 60 °C clearly showed a transition from a fluid-like to a gel-like behaviour. The evolution of the G' (storage modules) and G" (loss modules) with an upward temperature ramp showed the transition of sol state and gel state that to occur at approximately 52 °C. Increasing temperature of MC batters resulted in a transition from a soft gel at 15 °C to a stronger although still soft gel at 60 °C. Both G' and G" increased with MC concentration, although MC did not seem to qualitatively influence the viscoelastic behaviour.

A limited number of studies were conducted on the fundamental rheological properties of batters formulated by using different combination flour blends containing hydrocolloids designed for food coatings. This is an area of great importance and potential use and the rheological data provide information that is useful for coating applications.

2.5 THERMAL PROPERTIES OF BATTER SYSTEMS

Knowledge of thermal properties (e.g. specific heat C_p , and enthalpy, ΔH) of food may help to predict heat transfer rates in food. Specific heat indicates how much heat is required to change the temperature of a material. It depends strongly on the temperature and composition (such as moisture content, fat content, and the nature of the solid component, such as carbohydrate and protein) of the product (Ngadi et al., 2000). Enthalpy is the heat content or energy level of a material. It can be very complicated for frozen foods because it is difficult to separate the latent and sensible heats in frozen foods. They often contain both frozen and unfrozen water, even at very low temperatures. Therefore, enthalpy depends upon the amount of unfrozen water in addition to the proximate composition of the food (Dickerson, 1981).

The coatings are produced from batters which are coated food substances in which flour is a major functional ingredient. Therefore, gelatinization properties of starch are the paramount properties in processing battered food. Because they are based on gelatinized starch, which may undergo important textural changes during the process which may directly influence the final quality of the particular products. The gelatinization properties are useful to determine the amount of heat and time required for cooking and processing raw material (ingredients) into finished products. Both water and thermal energy play indispensable roles in the process of gelatinization of starch in a batter system containing other ingredients (Sweat et al., 1984; Billiaderis et al., 1986; Saif et al., 2003).

In general, starch gelatinization is greatly influenced by protein and lipid contents, amylose and amylopectin contents, and amount of available water in the system (Hoseney,1994). The availability of water is determined by the formula or recipe used and by the presence of ingredients or components such as proteins, pentosans (naturally present hydrocolloids), or sugars, which compete with starch for the water. The amount of moisture available for gelatinization is also affected by the degree of protection against water absorption that fat provides to the starch particles (Kaletunç et al., 2001). Granule size also affects starch gelatinization behaviors due to their water absorbing and holding capacity during cooking process (Hoseney, 1994).

Many processes and properties encountered in food science are affected by, or changed by, the glass transition phenomena (Levine et al., 1990; Schenz, 1995). Glass transition (phase or state transition) is the name given to a phenomenon observed as a change from a brittle glassy or crystalline state to a rubbery behavior at temperature Tg. At a sufficiently low temperature, or with a limited content of plasticizer such as water, molecular motion becomes restricted as a glassy solid is formed. On heating or plasticizer addition, the mobility of the amorphous polymers increase and the material becomes flexible or rubbery. The glass transition temperature (Tg) depends on molecular characteristics, composition, and compatibility of the components in the amorphous matrix (Kalichevsky et al., 1992). Therefore, the glass transition behavior affects many types of food properties related to molecular mobility, including texture and shelf-life (Mizuno et al., 1998).

Variability in composition of batter system formulas is reflected in their thermal properties and phase transition characteristics exhibiting similar magnitude. Various flours and hydrocolloids change the thermal properties and phase transition characteristics of batter systems. Ferrero et al. (2000) reported that the low hydrocolloid concentrations used (10 g/kg) did not significantly affect corn starch gelatinization temperature as compared to the systems without hydrocolloids in starch-sucrose system. However, small differences were detected among the systems containing alternatively guar, xanthan, or alginate gums. Also small quantities of hydrocolloids did not shift the glass transition temperature, but they played an important role in minimizing structural damages. This was verified in their research by rheological viscoelastic tests where an increase in the dynamic moduli G' (storage module) and G" (loss module) after slow freezing and during storage at -19°C was observed in starch-sucrose system.

Sarkar (1979) and Ford (1999) studied the thermal gelation properties of methylcellulose and hydroxypropyl methylcellulose as a function of molecular weight, degree of methyl and hydroxypropyl substitution, concentration, and the presence of additives. The results of these studies showed that the precipitation temperature of these polymer solutions decreased initially with increasing concentration until a critical concentration was reached, above which the precipitation temperature was minimally affected by concentration changes. The incipient gelation temperature decreases linearly with concentration (Sanz et al., 2005). The strength of these gels is time dependent, increases with increasing molecular weight, decreases with increasing hydroxypropyl substitution, and depends on the nature of additives (Grover, 1982).

Starch and hydrocolloids may provide synergistic effects on thermal properties and phase transition on batter system during processing. However, studies on these properties in the coatings system have not been extensively reported in the current scientific literature.

CONNECTION TEXT

In order to approach the development of batter systems with novel functional properties, it is necessary to start with an understanding of the batter's basic composition, such as flour and its behavior during processing. In many cases, understanding has relied upon empirical experience. Also, a comprehensive review of literature demonstrated the need for further studies regarding the effect of different flour types and combination ratios upon the rheological properties of batter systems, and addition of effects of salt behavior in batter systems during processing.

III. THERMAL PROPERTIES OF BATTER SYSTEMS FORMULATED BY COMBINATIONS OF DIFFERENT FLOURS

3.1 ABSTRACT

There is an increasing consumer preference for reduced oil content in fried food products. The amount of fat absorbed by deep fried foods can be modified using appropriate coatings such as batter and breading systems. Coatings also change the heat transfer characteristics of the composite products. The goal of this study was to determine some thermal properties of selected batter mixes that are commonly used for deep fat frying of chicken products. Three types of flour based batter mixes were used. These were mixtures of wheat and rice (WR), wheat and corn (WC), and corn and rice (CR) flours with salt and different methylcellulose (MC) levels. The differential scanning calorimeter (DSC) was used to measure glass transition temperature (T_g), gelatinization temperature (T_G), ice melting temperature (T_m) and enthalpy (ΔH_G) of the different batter formulations. Salt and MC greatly influenced the thermal properties of batter systems as they increased T_G, but depressed T_m. Adding rice and corn flours to wheat flour based batters apparently changed their thermal properties. Corn flour based batters required considerably more energy for gelatinization during the cooking process.

Keywords: Thermal properties; Batter coating; Fried products; Flour; Deep-fat frying

3.2 INTRODUCTION

Consumers' preference for lower fat products continues to increase and there is significant pressure on processors to reduce fat in fried food products. The application of batter and breading provides many opportunities to develop unique flavors and modify textures in fried products. It also promises to reduce fat uptake if a suitable coating system can be used. Certain hydrocolloids have been incorporated into batter formulations and have shown their effectiveness as oil absorption barriers (Lee & Han, 1988; Hsia, Smith, & Steffe, 1992; Annapure, Sighal, & Kuldarni, 1999; Sanz, Salvador, & Fiszman, 2004a). A number of studies have reported that the addition of methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) in batter systems has successfully reduced oil uptake in coated fried products such as chicken pieces, fish, vegetables, cheese, and cereal products (Meyers, 1990; Albert & Mittal, 2002; Fiszman & Salvador, 2003). The functionalities of the MC and HPMC are attributed to their film-forming properties and unique thermal gelation abilities. Williams and Mittal (1999) also reported that as a film-forming agent, MC was found to reduce fat on fried products more than gellan gum and HPMC. Very little information is currently available about the thermal properties of batter systems for coated fried poultry products formulated using different flour combinations with hydrocolloids.

Wheat flour is the most common flour used in batter systems (Loewe, 1993). However, rice, corn, and soy flours have also been used (Robert, 1990). Shih and Daigle (1999) observed a 69% reduction in oil absorption by using rice flour batter on shrimp products, compared to using wheat flour. Rice flour resulted in a rough crust on the coating due to its less effective role as a thickening agent. However, it still showed some potential as an alternative to wheat flour in batter formulations. Corn flour generally produces a yellowish color due to the carotene pigment in the corn, and may be useful as a source of natural yellow color (Salvador, Sanz, & Fiszman, 2003). In general, higher levels of corn increase crispness and decrease puffing in batter systems due to decreased moisture retention in the coating. Corn is also often added to control viscosity as its higher starch level affects the batter's ability to absorb water (Roger, 1990). Combining different flours may provide special effects.

Batters are complex systems that may undergo various changes in phase transition during processing and storage. The thermal properties of batter systems reflect these changes, and they have combined effects on the overall characteristics of the finished fried products. Batter systems are composed of flour base, water, and other ingredients. They may exhibit different phase behaviors and variations in thermal properties because they may contain components that are or may become phase separated. For instance, carbohydrates, lipids, proteins, salt, water and other functional ingredients may all exist in different phases or in phases separated from each other (Roos, 1995). Water is a key factor that greatly influences the phase transition phenomena such as gelatinization during the cooking process and the glass transition during frozen storage. Batter compositions greatly affect water available for starch gelatinization during heating and the unfrozen water during cooling. However, phase transition behaviors and thermal properties of batters are important in designing a process to achieve a desired functionality as well as for the manipulation of coated food products to meet storage stability requirements and consumer expectations. Nevertheless, characterizations of these properties on batter systems formulated from different flour blends containing hydrocolloids have not been adequately reported in the literature.

The goals of this study were to evaluate the thermal phase transition characteristics, namely the glass transition temperature (T_g), gelatinization temperature (T_G), change in enthalpy (ΔH), and the heat capacity (c_p) of batter systems formulated using different blends of wheat, rice, and corn flours, and to determine the influence of adding salt and a hydrocolloid such as methylcellulose (MC) to the different flour mixes. Results of the study will provide useful information on factors influenceing processing conditions and storage of fried products. It will also assist in the selection and formulation of appropriate batter systems for a given product.

3.3 MATERIALS AND METHODS

The study was conducted using a complete block experimental design method. The first block was to determine the thermal properties of batter containing only blends of flour. The second block was designed to investigate the influence of added ingredients such as salt and methylcellulose (MC) on properties of the batter system.

3.3.1 Batter systems

Commercial wheat flour (Five Roses All Purpose Flour, Les Cuisines Five Roses Kitches, QC), rice flour (Club House Gluten Free Rice Flour, McCormick Canada Inc, ON), and corn flour (CLIC Import Export Inc., Montreal, QC, Canada) were used in the study. Moisture, crude protein, lipid, and ash contents of flours were measured using appropriate AACC methods (1995). The nitrogen to protein conversion factors used were

5.7, 6.25 and 5.95 for wheat, corn and rice flour, respectively. Proximate analyses were conducted to compare compositions of the different flours with typical values as reported in the USDA Handbook. The particle sizes of the flours were determined by using the Fisher Subsieve Particle Size Analyzer (Fisher Scientific, Nepean, ON). The Method involved packing a small plug of flour into a tube to a controlled bulk density, and then pumping air through it. The pressure drop is a function of the average particle size. The values are reported in "Fisher Microns", and represent average particle sizes.

Three blends of flours were obtained by mixing two flours, namely wheat and rice (WR), wheat and corn (WC), and corn and rice (CR) to use in this study. The two flours in each blend were mixed at five different ratios (w/w g/100g) namely 0:100; 30:70; 50:50; 70:30 and 100:0. For instance, there were five levels of WR blends containing wheat and rice flours mixed in the ratios of 0:100; 30:70; 50:50; 70:30 and 100:0. Similar mixtures were prepared for the WC and CR blends. The samples containing 100% of a given flour (i.e. either the so called 0:100 or 100:0 blends) were considered as the control samples. Thus a total of 12 flour samples (9 blends and 3 controls) were used for the first block of experiments. In the second block of experiments, batters were formulated by adding different combinations of salt and methylcellulose (MC, A15C, Dow Chemical Company, MI, US) as ingredients to the flour samples. The fixed quantity of 2.5% (flour weight basis) salt was used in all cases, whereas the different amounts of MC used were 0, 0.5, 1.0, and 1.5% (flour weight basis). To formulate batters, the dry ingredients consisting of flour, salt and MC were first mixed thoroughly before adding cold distilled water at 8 ± 2°C. The water temperature was chosen since it had been reported to enhance the gelling ability of MC (Sanz, Salvador, & Fiszman, 2004b). All batter was constituted with water to dry-mix proportion (w/w) of 1.3 :1. The moisture content of the batter sample was confirmed to be about 55.58 g/100g (wet basis) by drying in an oven set at 105 °C. Batter samples were kept for about 20 minutes at 15 °C (± 2 °C) in a water bath to allow the MC to develop a gel, and then kept at room temperature (20 ± 2 °C) for another 10 min. before commencing the thermal property measurements.

3.3.2 Determination of thermal properties

Thermal properties, namely glass transition temperature (T_g), gelatinization temperature (T_G), melting temperature (T_m), ice crystallization onset temperature (T_i), enthalpy (ΔH), and heat capacity (c_p) of the batters were determined using a differential scanning calorimeter (DSC, TAQ 100, TA Instruments, Delaware, USA). Samples (10 – 15 mg) were placed in aluminum pans and hermetically sealed. Two different temperature profiles were used. To determine T_g, T_m, and the melting enthalpy change (ΔH_m), the samples were first cooled to – 40 °C at 10 °C/min in a DSC chamber and then subsequently heated to 30 °C at 5 °C/min heating rate. However, to determine T_G, and the enthalpy change for gelatinization (ΔH_G), samples were heated from 20 to 100 °C at 5°C/min.

3.4 STATISTICAL ANALYSIS

All measurements were replicated at least twice. Analyses of variance (ANOVA) of the results were performed using the multiple comparison tests, and statistical significance was determined at $P < 0.05$ using the SAS program PROC ANOVA.

3.5 RESULTS AND DISCUSSION

3.5.1 Chemical composition and particle size of the raw material

Table 3.1 shows the moisture, protein, ash, and crude fat contents, and the Fisher microns of the wheat, corn, and rice flours used in the study. The compositions of the flours used in this study were close to the typical values reported by the USDA (USDA Handbook # 8, 2002). Corn flour had lower protein content indicating that it may have higher starch content. Also corn flour had a higher fat content, probably indicating that more germs were in the flour (Hoseney, 1994). Rice flour was relatively low in fat and contains fewer calories. Thus rice could possibly be healthier than traditional batters from the point of view of fat content. However, is should be noted that the initial fat content in batter is usually low, compared to the expected normal fat pick-up during deep fat frying. Rice flour was coarser, as compared with the wheat and corn flours.

Table 3.1 Chemical composition and particle sizes of wheat, rice and corn flours

Flour type	**Wheat flour**	**Rice flour**	**Corn flour**
Moisture (g/100g)	12.60 (12)*	11.78 (12)	10.85 (12)
Protein (g/100g)	11.87 (11.8)	6.78 (6.0)	3.86 (7.8)
Ash (g/100g)	0.41 (0.44)	0.49 (0.2)	0.55 (0.8)
Crude fat (g/100)	0.73 (1.1)	0.41 (0.3)	2.23 (2.6)
Particle size (microns)	24	38	25

* The values in parenthesis are 'typical' values for each type of flours as report by USDA(USDA handbook #8)

Protein, lipid, starch, and moisture contents were different for each flour samples. However, the moisture contents were adjusted in the final batter slurry to be approximately the same for all samples.

3.5.2 Effect of different flours and their combination ratios

The basic batters used in this study consisted of flour and distilled water. Changes in the thermal properties of the batter systems during freezing and cooking processes were observed by the DSC. All samples exhibited a single endothermic transition over the temperature range from 50 to 85 °C during the heating process as shown in Figure 3.1. The temperature range corresponds to the range expected for starch gelatinization.

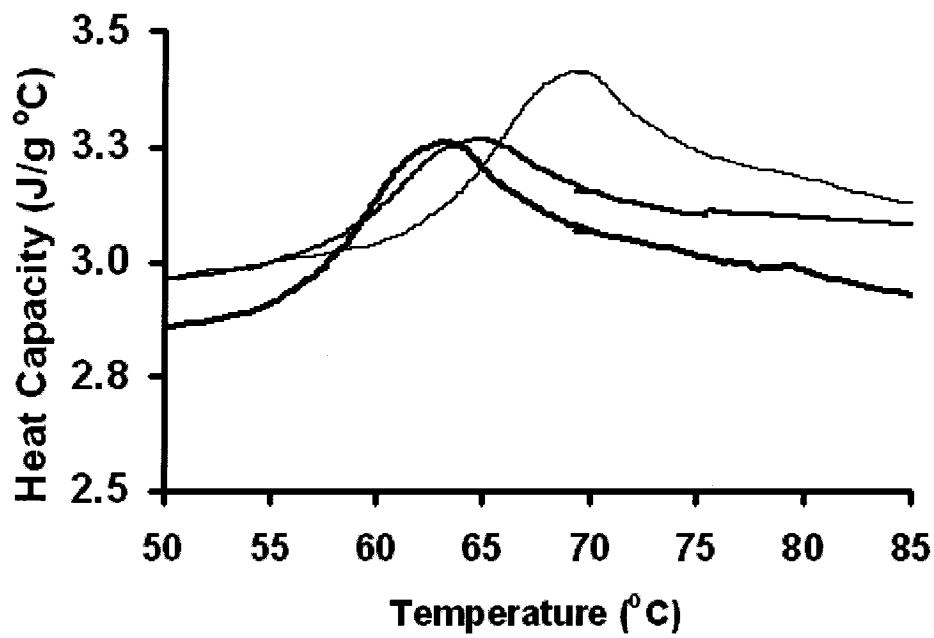

Figure 3.1 Differential scanning calorimetry thermograms corresponding to gelatinization process of wheat, corn and rice flour solution (wheat ——, corn ——; rice ▬▬)

Table 3.2 Gelatinization temperature, total enthalpies of gelatinization, glass transition temperature, ice melting temperature and total enthalpies of melting on flour-water suspension.

Flour	T_G (°C)	ΔH_G (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
Wheat	65.54 [a b c]	2.26 [a]	-10.31 [a]	4.17 [a]	102.80 [a]
Corn	68.97 [a b c]	4.38 [b]	-8.75 [b]	2.54 [d]	74.96 [c]
Rice	61.80 [a b]	3.34 [c]	-7.29 [f]	2.90 [c]	61.52 [f]
C3R7	63.50 [a b c]	2.08 [f]	-7.97 [d]	3.30 [b]	69.20 [d]
C5R5	70.56 [a]	2.56 [e]	-9.21 [b]	1.80 [f]	58.91 [g]
C7R3	64.13 [a b c]	4.13 [d]	-8.06 [d]	1.90 [f]	66.91 [e]
W3C7	62.49 [b c]	2.39 [I]	-7.81 [d]	1.99 [f]	42.15 [I]
W5C5	60.04 [b c]	2.30 [h]	-8.13 [c]	1.08 [g]	55.97 [h]
W7C3	61.55 [b c]	1.62 [g]	-8.56 [c]	2.27 [e]	81.02 [b]
W3R7	61.25 [b c]	2.07 [l]	-7.69 [e]	3.23 [b]	64.15 [f]
W5R5	63.26 [a]	1.71 [k]	-7.77 [e]	2.29 [e]	66.69 [d]
W7R3	63.04 [a b c]	1.38 [j]	-7.86 [d]	3.38 [b]	70.80 [d]

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. The mean with the same letter in any given column are not significant different. T_G = starch gelatinization temperature, ΔH_G = total enthalpies of gelatinization, T_g = glass transition temperature, T_m = ice melting temperature, ΔH_m = total enthalpies of ice melting.

The corresponding gelatinization temperatures (T_G) as peak temperatures, total enthalpies for gelatinization (ΔH_G), glass transition temperatures (T_g), ice melting temperatures T_m (peak temperature) and total enthalpies for melting are shown in Table 3.2. ANOVA analysis and mean comparisons did not show clear statistical difference

($P<0.05$) between the T_G of the different batter samples. The various combination ratios of the flours apparently did not greatly influence the gelatinization temperatures of the batter systems. However, the ANOVA results showed significant differences among the total enthalpies (ΔH_G) of the various samples.

It is known that change in the total enthalpy of gelatinization is influenced by several factors including the distribution of water between gluten and starch, starch granule size, hydration rates, and other possible interactions between the various components (Kaletunç and Breslauer, 2001). Corn based batters showed the highest ΔH_G. Increasing the proportion of corn flour in any batter mixture increased ΔH_G. This result could be attributed to the high starch and the fat contents in the corn flour that required more energy to open the starch helix structure. Hydrophobic fats tend to coat the starch granules and they interfere with the ability of water to enter the starch helix by some sort of a "blocking action", leading to the reduction in the available free water required to interact with starch (Pomeranz, 1987). Starch will not normally be gelatinized if starch crystallinity is not disrupted.

For the wheat and rice flour combination blend based batters, ΔH_G increased with increasing rice flour content due to the reducing proportion of wheat gluten content in the batter mixture. The resulting reduction in gluten content apparently led to a larger amount of water being available for starch gelatinization. A similar effect was observed when the proportion of corn flour was increased in a combination of wheat and corn flour based batters. The results suggest that corn and rice flours exerted diluting effects on wheat gluten, increasing the amount of water available to react with wheat starch during the heating process. Similar results have been reported by other researchers (Liu et al., 2002;

Fukuoka, Ohta, and Watcoonabe, 2002; Wang, Choil, and Kerr, 2004). Wang, Choil, and Kerr (2004) reported the gelatinization temperature to be affected by water and gluten contents in the dough. It is suggested that the heated gluten gel showed a greater binding of water than the starch gel in the dough. This was attributed to less water being available to starch in the presence of gluten.

The glass transition behavior of the starch-water system in a freeze-concentrated phase depends on ice formation. The T_g and ΔH_m are influenced dramatically by the amount of available water in the system (Addo, Xiong, and Blanchard, 2001; Chung, Lee, and Lim, 2002; Hsu, et al., 2003). Roorda (1994) indicated that glass transition occurs at or close to the temperature of water melting (and freezing) in hydrogels. Thermal properties, such as T_g, the peak temperature for ice melting T_m, and the melting enthalpy of ice ΔH_m of the batter systems, indicate that there is freezable water in the batter systems. The ANOVA model showed statistically significant differences in T_g, T_m and ΔH_m for all samples. Thus, the different combination of flours and their combination ratios influenced the changes in glass transition temperature, enthalpy and ice melting temperatures in a starch-water matrix.

The batter system with 100% wheat flour showed the lowest T_g (-10.31 ^oC), T_m (4.17 ^oC), and ΔH_m (102.8 J/g). This is possibly because wheat gluten tightly binds water and protects it from freezing. This apparently led to increasing unfrozen water content in the system resulting in the depressed glass transition temperature. Wang, Choil, and Kerr (2004) reported that water molecules more easily diffuse in starch-water mixtures than in gluten-water mixtures. Reid (1997) demonstrated that water comes out from the food product to form ice during the freezing process. The diffusion of water in mixtures can be complicated, and depends on a number of parameters including type of mixtures, their compositions and particle size. Rice flour has a higher amount of free water than corn flour in the batter system. This difference is because the rice starch granule size is smaller than in corn and it absorbed less water. Also, rice flour has no gluten to hold water in the manner that wheat flour does. Free water can easily be frozen in batter systems during the freezing process. Therefore, rice flour has a higher T_g (-7.29 °C) and lower ΔH_m (61.52 J/g), compared with 100% wheat flour based (-10.31 °C and 102.8 J/g) or 100% corn flour based (-8.75 °C and 74.96 J/g) batter systems.

The thermal property behaviors of wheat based batters were greatly influenced by replacement of either corn or rice flour compared with 100% wheat flour based batter. The glass transition temperatures of the batter systems were raised and T_m values decreased. The ΔH_m values were reduced when the proportion of corn or rice flour in batter systems was increased. It can be explained that reducing the gluten level in the blended flour resulted in increasing free water in the batter systems.

There was a significant difference in T_g, T_m, and ΔH_m for the combinations of corn and rice flour based batters because different compositions and amounts of free water remained in the batter system. C5R5 showed a lower T_g (-9.21 °C) than C3R7 (-8.06 °C) and C7R3 (-7.97 °C), indicating a synergistic effect on the thermal properties of batter systems when the proportions of corn and rice flours were nearly equal.

All the samples showed trends similar to those in Figure 3.1. The heat capacity c_p gradually and consistently increased to the onset temperature of gelatinization, and then it progressively increased more rapidly until gelatinization temperature T_G (peak temperature) was reached. After that, the heat capacity decreased to the endpoint temperature that indicated when the starch was completely gelatinized. The corn flour has a higher heat capacity due to its higher fat and starch contents.

3.5.3 Effect of salt addition on thermal properties

Sodium chloride (NaCl) is an essential ingredient in batter systems and is used as a flavor enhancer and batter stabilizer (Salvador, Sanz, and Fiszman, 2003). Formulations with salt showed dramatically increased starch gelatinization temperatures for all samples (Figure 3.2). This increasing of gelatinization temperature is attributed to the role of salt in maintaining the integrity of the starch granule. The starch granule swells to a greater extent or remains intact for a longer time before fragmentation occurs (Ganz, 1965). Similar results were observed on corn and wheat flours (Evans and Haisman, 1982; Salvador, Sanz, and Fiszman, 2002). Salt lowered the ΔH_G value in all samples due to its strengthening and tightening effect on the gluten (Pyler, 1988). It is a competitor with flour and other components for water, so less water is available to be absorbed by starch. Therefore, more energy was required for starch gelatinization to occur in limited water systems during heating process, and hence an elevation in the gelatinization temperature.

Figure 3.3 shows that salt depressed the glass transition temperature T_g. Results are shown in Table3.3, indicating that salt greatly lowed ice-melting temperature $T_{m,}$ and reduced the ΔH_m value for all samples, because salt dissolved in water lowers the temperature at which the water freezes, or at which the ice melts (Reid, 1997).

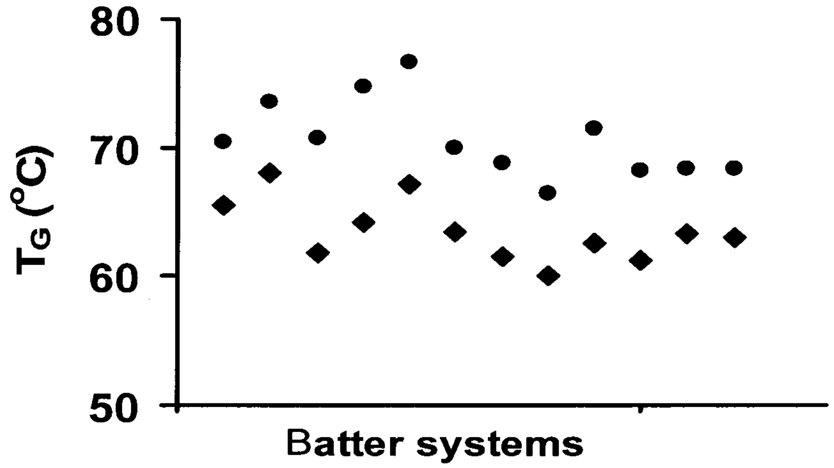

Figure 3.2. Comparison of gelatinization of batter systems with/without salt (from left to right, each dot present the batter systems of 100% wheat, 100% corn, 100% rice, C7R3, C5R5, C3R7, W7C3, W5C5, W3C7, W7R3, W5R5, W3R7, respectively, No salt ♦, with salt ●)

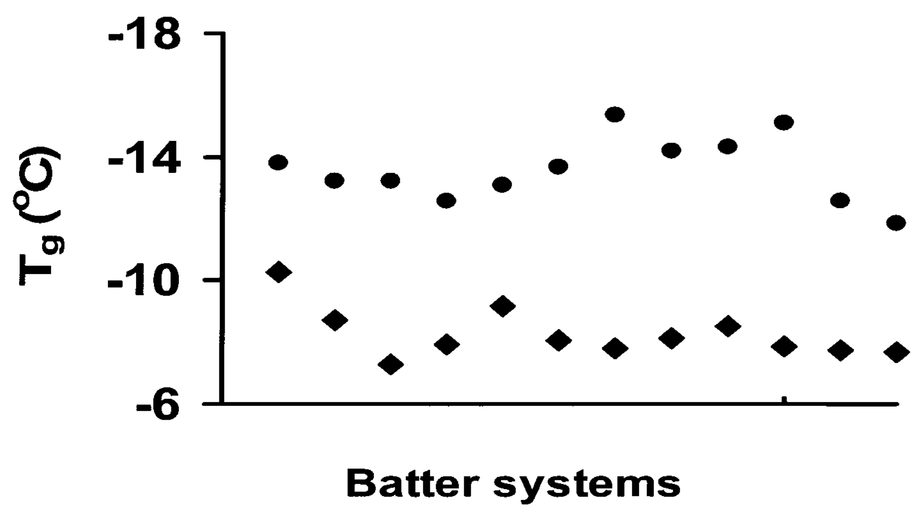

Figure 3.3.Comparision of glass transition temperature of batter systems with/without salt (No salt♦, with salt ●)

Table 3.3 Comparison of Tm and ΔH_m on batter systems with/without salt

Batter System	T_m (°C)		ΔH_m (J/g)	
	Control	Salt	Control	Salt
Wheat	4.17 [a]	0.80 [c]	102.80 [a]	63.75 [a]
Corn	2.54 [e]	-0.74 [i]	74.96 [c]	39.92 [d]
Rice	2.90 [d]	0.72 [d]	61.52 [f]	50.22 [c]
C3R7	3.30 [b]	-0.41 [g]	69.20 [c]	40.80 [d]
C5R5	1.80 [g]	-0.01 [f]	58.91 [f]	52.92 [b]
C7R3	1.90 [g]	0.47 [e]	66.91 [d]	57.20 [a]
W3C7	1.99 [g]	-0.59 [h]	42.15 [h]	35.94 [e]
W5C5	1.08 [h]	1.02 [a]	55.97 [g]	39.21 [d]
W7C3	2.27 [f]	-0.79 [i]	81.02 [b]	52.34 [b]
W3R7	3.23 [c]	0.76 [d]	64.15 [d]	49.29 [c]
W5R5	2.29 [f]	0.91 [c]	66.69 [d]	55.17 [b]
W7R3	3.38 [b]	0.97 [b]	70.80 [c]	58.26 [a]

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. The mean with the same letter in any given column are not significant different. Tm = ice melting temperature, ΔH_m = total enthalpy of ice melting.

3.5.4 Effect of methylcellulose (MC) on thermal properties

The effects of Methylcellulose on the thermal properties of batter systems were determined by DSC at frozen and above thawing temperatures ranging from -40 to 25 °C, and at cooking temperatures from 20 to 100 °C. ANOVA results showed significant differences in all parameters with different levels of MC. MC greatly affected the thermal properties of the batter for all the samples. Figure 3.4 shows that the gelatinization temperatures of all samples have the same trend, increasing with the concentration of MC in batter systems, as compared with the control. This is probably because MC reduced the amount of water available to react with starch during gelatinization. As MC is one of the food gums that can thermally gel, it also started gelation at a lower temperature (52 - 57°C) than starch gelatinization. Another reason could be that MC is a water-soluble polymer that has a higher capacity for absorbing water than does starch (Mukprasirt et al., 2001). Generally, the available free water for starch granule reaction is reduced with an increasing concentration of MC in batter systems. In comparisons of 100% wheat, 100% corn and 100% rice flour based batter, MC greatly increased T_G of 100% wheat flour based batter more than 100% rice or 100% corn flour based batters due to synergistic effect of MC and wheat gluten. Thus the synergistic effect of MC and flour components greatly raised the gelatinization temperature and ΔH_G of the batter systems.

Variations in the thermal properties (T_g, T_m and ΔH_m) of all samples during freezing and thawing processes followed similar trends as shown in Figure 3.5 for combined wheat and corn flour based batter systems. MC increased T_m and depressed T_g, especially at higher MC levels. This is due to the absorption of water by MC to form gel and subsequent reduction of free water in the batter systems (Sanz, Salvador, and Fiszman, 2004b; Sarkar, 1997). MC gel typically binds water tightly during a freezing process, resulting in postponement of freezing of the bound water in MC-flour batter systems. Therefore, lower temperature was required to complete phase transition and glass transition temperature of batter was depressed. On the other hand, more energy was required to melt ice formed in batter system during thawing process. Thus, T_m was raised and the batter system enthalpies (ΔH_m) were increased.

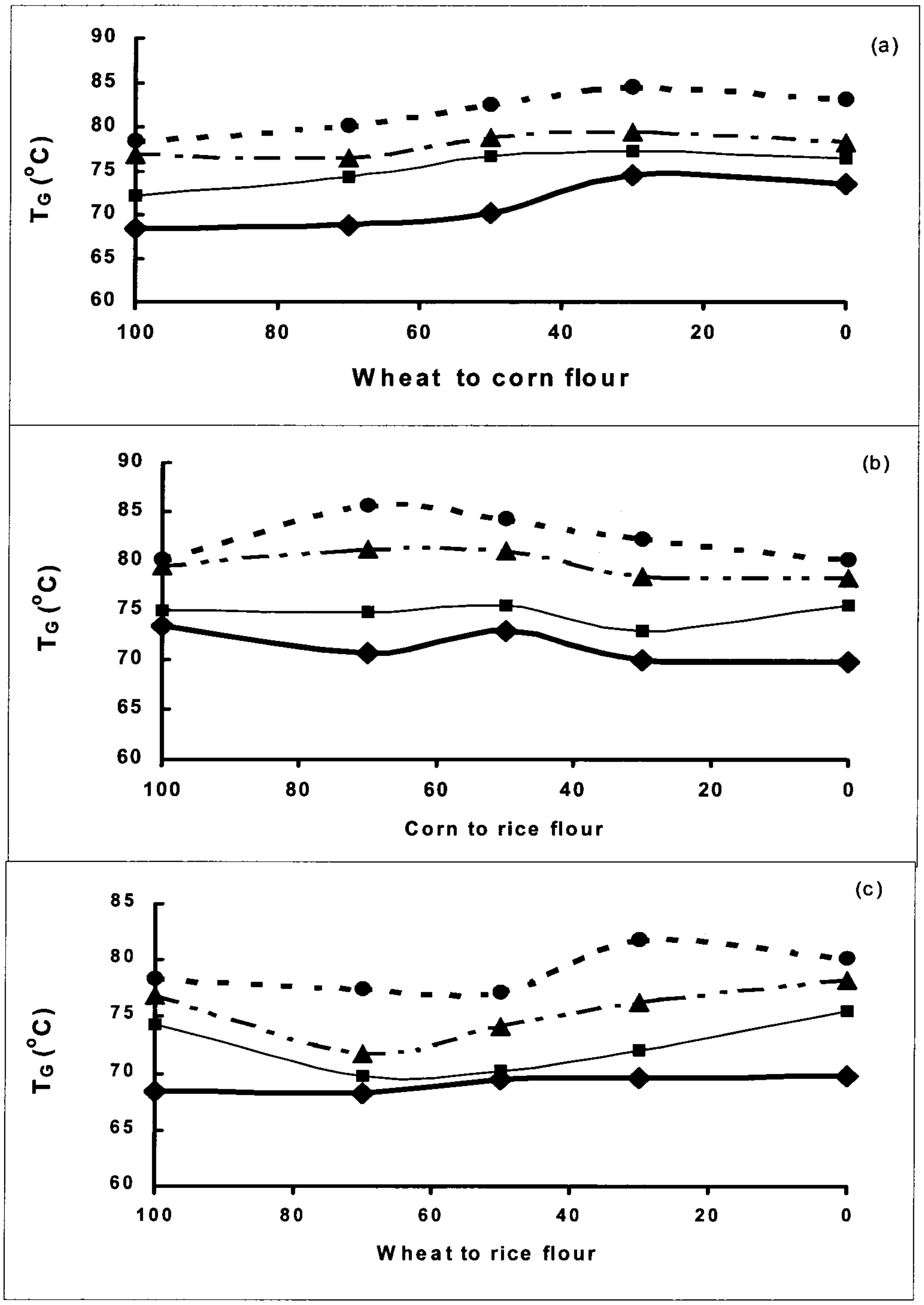

Figure 3.4 Effect of MC on gelatinization of batter system with (a) wheat to corn flour, (b) corn to rice flour, (c) wheat to rice flour (wheat to corn flour means that from left to right, the proportion of wheat flour decrease from 100% to 0% which is 100% corn flour, same as wheat to rice and corn to rice flour).

(0%MC —◆—, 0.5%MC —■— , 1.0% MC – ·▲· · , 1.5% MC ···◆··)

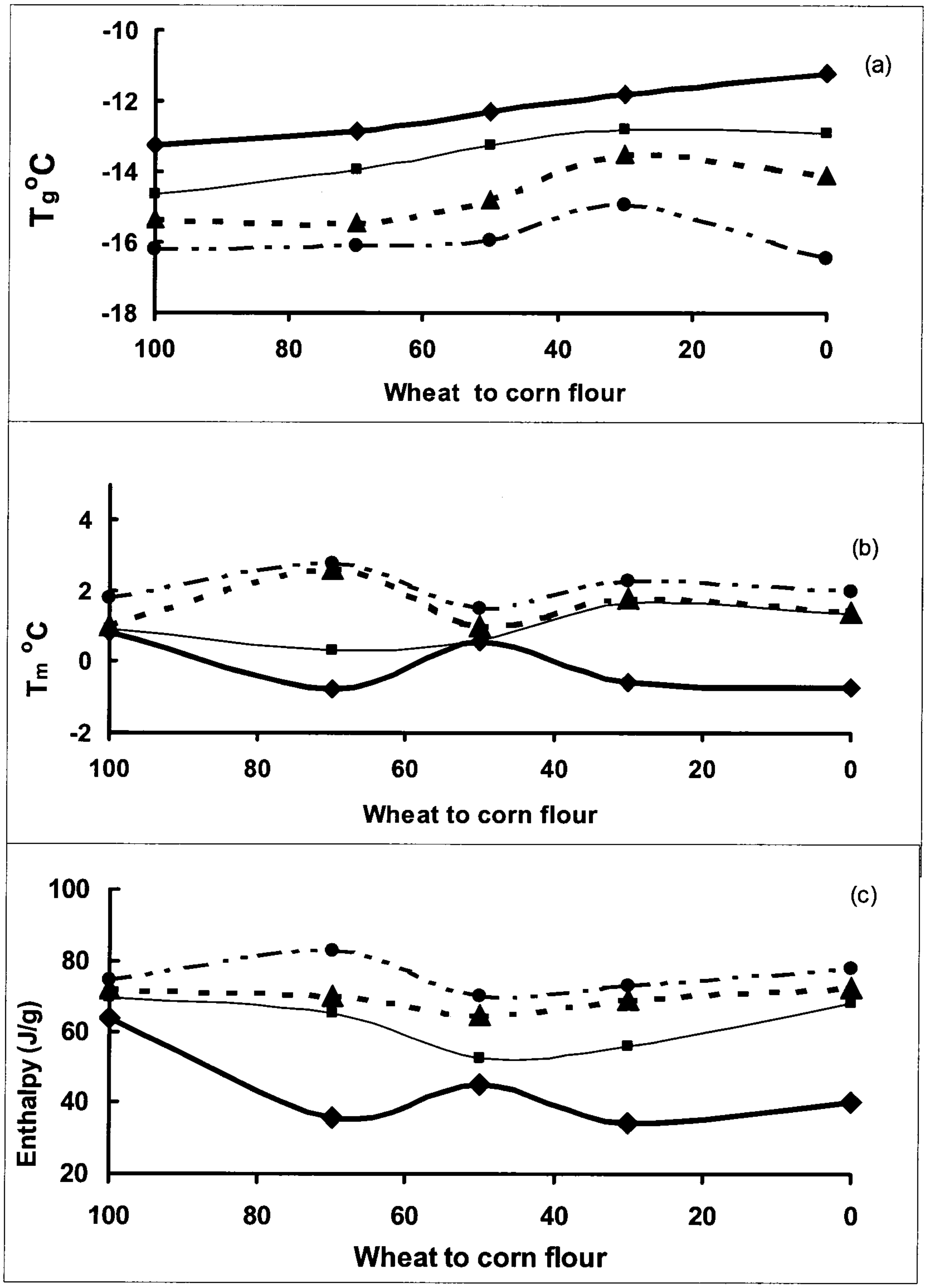

Figure 3.5. Effect of MC concentration on thermal properties of batter system. (a) Tg of combined wheat to corn flour, (b) Tm of combined wheat to corn flour, (c) ΔHm of combined wheat to corn flour. (0%MC —◆—, 0.5%MC —■—, 1.0% MC –▲· · , 1.5% MC ··●··)

3.6 CONCLUSIONS

DSC was used to determine several important thermal parameters such as glass transition and gelatinization temperatures, enthalpy and heat capacity changes in batter systems. The thermal properties varied for different types of flours and their combination ratios. Thermal properties of wheat based batters were greatly influenced by replacement of wheat by rice or corn flours. There was a synergistic interaction resulting in marked change in glass transition temperature when rice and corn flours were mixed in equal proportions. Salt and methylcellulose (MC) each greatly influenced thermal properties. Both of the ingredients increased the gelatinization temperature but depressed the glass transition temperature of the resulting batter. Salt also decreased the total enthalpy of gelatinization ΔH_G and depressed the melting temperature (T_m) for batter systems. MC increased the melting temperature (T_m) for the test batter systems as compared with the values for the control system without MC. A higher enthalpy ΔH_G was required to gelatinize starch at higher levels of corn flour (70%) for each flour mix combination tested.

3.7 IMPLICATIONS FOR BATTER PREFORMANCE

Fried food coatings are most commonly produced from batters in which flour is the major functional ingredient. The selection of different flours, and how they are blended for optimal product quality, depends upon the composition of the particular batter system being used and the characteristics of the specific food product being coated. Information on thermal properties can be used as an aid in formulating batters with better performance during the various processing operations. Thermal properties can also aid in prescribing process parameters such as cooking time, cooking energy, and freezing and thawing conditions (i.e. temperature, time, and required energy). The gelatinization temperature and total enthalpy reflect the temperature and energy required for coating structure development and final solid-like coating layer formation. It is also related to cooking temperature and time requirements. The frying temperature and duration time are two process-controlled factors which affect the amount of oil uptake during deep fat frying.

The gelatinization temperature appeared to be independent of the ratios by which the flours were combined into the batter systems, but the different types of flour have great influence on the energy required to complete the coating's structure formation. More energy is required to cook batters containing higher levels of corn flour. However, substituting some wheat flour in corn based batters might reduce the energy required for coating layer formation. The information on glass transition temperature, ice melting temperature, and total enthalpy for ice melting affect the choice of storage conditions for batters or coated products. Wheat flour showed the lowest glass transition temperature, highest ice melting temperature and total enthalpy (energy) for ice melting. This suggests that products with wheat flour batter might require relatively lower temperature to be stable during frozen storage but they do not thaw as readily as other batters. However, partial replacement of rice or corn flour would reduce the energy required for the freezing and thawing processes of wheat flour based batters. Various food substrates require special batter systems in order to match their characteristics during storage, and to achieve the desired end product quality.

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CONNECTING TEXT

Results reported in chapter III showed that different types of flour and their combination ratio greatly influenced the thermal properties of batter systems. In chapter IV, the effect of hydrocolloids (xanthan gum, methylcellulose, carboxymethylcellulose) on thermal properties such as gelatinization temperature, total enthalpies of gelatinization, glass transition, ice melting temperature, and total enthalpies of ice melting were extensively studied and reported

IV. EFFECTS OF HYDROCOLLOIDS ON THERMAL PROPERTIES OF BATTER SYSTEMS

4.1 ABSTRACT

Batters are highly complex systems containing a wide range of ingredients. Interactions between the ingredients determine batter performance and the final coated product quality. The functionalities of hydrocolloid-flour mixtures, in terms of the thermal properties of the resulting batter systems, were investigated in this study. Differential Scanning Calorimeter (DSC) were used to determine thermal property parameters including gelatinization temperature (T_G), total enthalpies of gelatinization (ΔH_G), glass transition temperature (Tg), melting peak temperature (T_m) and total melting enthalpies (ΔH_m). Hydrocolloids such as methylcellulose (MC), carboxymethylcellulose (CMC) and xanthan gum (XG) greatly influenced the thermal properties of batter systems. The gums shifted gelatinization temperatures and depressed glass transition temperatures of the resulting batter systems. Further, MC increased the melting temperature (T_m) of the test batter systems whereas no significant (at the 0.5% level) effects of CMC and XT were observed on Tm. Different heating processes influenced Tg of the batter systems. Lower Tg were obtained when batters were sequentially cooked, frozen and thawed (CFT process) compared to when batters were frozen and cooked (FC process). The effect of xanthan gum was more pronounced in the batters that were FC processed than in the CFT processed samples. MC and CMC showed more pronounced effects on rice and corn flour based batters than on wheat flour based batters.

Keywords: Batter coating; Thermal properties; Cooking processes; Phase transition, Hydrocolloids.

4.1 INTRODUCTION

Hydrocolloids are widely used as functional ingredients in the food industry to add commercial value to foodstuffs. In addition to the obvious benefits of taste, texture, mouth-feel, moisture control, and water mobility, they also improve the overall product quality, stability in withstanding the demands of processing, distribution, and final preparation for the table. From a health perspective, hydrocolloids have been used in batter and breading systems to block fat absorption during deep-fat frying so that lower fat, more nutritious, coated food products could be created (Meyer, 1990; Hsia et al., 1992; Balasubramaniam et al., 1997; Annapure et al., 1999; Holownia et al., 2000; Garcia et al., 2001, Mellma 2003, Sanz et al., 2004). Batters are complex mixtures of flour and various ingredients. The properties of batter systems are further altered by the addition of hydrocolloids. Therefore, it is important to understand the interactions between flours, hydrocolloids, and other ingredients in batter systems during processing as they relate to the functionalities they impart on fried food products. This would assist in understanding and controlling the functionalities of the ingredients.

Methylcellulose (MC), xanthan gum (XG), and carboxymethylcellulose (CMC) are the hydrocolloids that are most extensively used in batter industries. They are high molecular weight water-soluble carbohydrate biopolymers with the ability to form gels and thickening in aqueous systems. They are greatly attracted to water and absorb it readily (Keller, 1982). MC and CMC are cellulose derivative hydrocolloids. MC can thermally gel (Meyers et al., 1990; Sanz et al., 2005), and CMC forms a three-dimensional network with an ability to link water molecules within the systems (Andrew, 2004). They form and provide a resistant-barrier coating during heating (Meyers, 1990; Khalil, 1999, Susanne et al., 2001; Albert, 2002; Mellema, 2003). Xanthan gum has a linear main chain whose molecular formation appears to allow a high degree of interaction between polymer chains. The results in the formation of network of molecular aggregates held together by a valence force (Pettitt, 1982). Therefore, these gums could change the physical and thermal properties of batter systems. Hydrocolloid performance are affected by the complexity of other ingredients in the batter system and the compatibility of the specific hydrocolloids with those components

Coated food products undergo several physical and chemical changes during processing. Thermal property analyses should reveal possible interactions between hydrocolloids and the other batter constituents. This could partially explain the effects of adding hydrocolloids to complex batter systems. The effects of hydrocolloids on phase transitions are important in examining the molecular interactions involved in developing structural stability during processing of coated products. To an extent, one can generally select a hydrocolloid to use for a product based on its characteristics and its impact during processing. Thus, it is critical to have a conceptual understanding of how the thermal properties of the coating system can be changed by the addition of hydrocolloids and other ingredients. Furthermore, understanding the functionality of ingredients and their interactions in batter systems during thermal processing steps is essential to achieving superior product quality. The thermal properties of batter systems containing hydrocolloids have not yet been studied in detail.

There are limited published studies dealing with the thermal properties of batter systems that were formulated using wheat, rice and corn flours with the addition of MC, CMC and xanthan gum (XG) (Christianson et al., 1981; Hsia et al., 1992; Rojas et al., 1999; Sanz et al 2005; Gao and Vodovot 2005; Xue and Ngadi 2006). In this study, two different processes, simulating cooking and frozen storage, were used to determine thermal properties of the batter systems. The objectives were to achieve a better understanding of the functionality of MC, CMC and xanthan gum in batter systems during processing, and to investigate the synergistic effects of the hydrocolloids and different flour blend combinations on thermal properties of the various batter systems. The knowledge generated by this study could be helpful in designing product development protocols for coating systems with hydrocolloids

4.2 MATERIALS AND METHODS

4.2.1 Batter ingredients and formulations

Wheat flour (Five Roses All Purpose Flour, Les Cuisines Five Roses Kitchens, QC, Canada), rice flour RL-100 (Riviana Foods Inc., Houston, Texas, USA), yellow corn flour (ADM Milling Co., Lincoln, Nebraska, USA), leavening agent (Sodium bicarbonate, H. Cantin Ltd, Quebec, Canada), Methylcellulose (MC, A15C, Dow Chemical Company, MI, USA), xanthan gum (TIC Gums Inc, Maryland, USA), and carboxymethylcellulose (CMC 2500, TIC Gums Inc, Maryland, USA) were used in the study. The characteristics of the flour samples, according to the flour manufacturers, are presented in Table 4.1. Three flour blends were prepared for this study by mixing two flours, namely wheat and rice flours (WR), wheat and corn flours (WC), and corn and rice flours (CR). The two flours in each blend were mixed at five different ratios (w/w %), namely 0:100; 30:70; 50:50; 70:30 and 100:0. Thus a total of 12 flour samples were used.

Table 4.1. Chemical composition of wheat, rice, and corn flours used in the study

Flour type	**Wheat flour**	**Rice flour**	**Corn flour**
Moisture (%)	12.60	11.78	14.0
Protein (%)	11.87	8.2	8.0
Ash (%)	0.41	0.49	0.55
Crude fat (%)	0.73	0.41	2.5
Avg. particle size (μm)	24	26	27

The batter systems were formulated with different combinations of flour and methylcellulose or carboxymethylcellulose (0, 0.5, 1.0, or 1.5%), or xanthan gum (0 or 0.2%). Other ingredients included 2.5% salt, 3.1% leavening agent ($NaHCO_3$, Sodium bicarbonate). All the ingredients were added on a flour dry weight basis. To formulate the batters, the MC, CMC, or xanthan gum powders were first dispersed and mixed in the total amount of cold distilled water required for the batter. Afterward hydrocolloid was totally dissolved, the dry ingredients (flour, salt, and leavening) were added to the hydrocolloid solution and mixed thoroughly until the batter was uniform and free of lumps.

All the samples were prepared with the same water-to-solids ratio. Therefore, their apparent rheological and thermal property values would indicate the functional contribution of the ingredients to the mixture. All batters were prepared with water to dry-mix in the proportion (w/w) of 1.3:1. The moisture content of the batter sample was confirmed to be about 55.6% (wet basis) by drying the samples in an oven set at 105 °C. Batter samples were kept for at least 45 minutes at 10 ± 2 °C to allow all the ingredients to completely hydrate and for the MC or CMC to develop a gel before measuring their thermal and rheological properties.

4.2.2 Determination of thermal properties

The batter systems were characterized thermally using a differential scanning calorimeter (DSC, TAQ 100, TA Instruments, Delaware, USA), previously calibrated with indium and sapphire. For analysis, a sample (10 – 15 mg) was placed in aluminum pans and hermetically sealed. An empty aluminum pan was used as reference. The values of thermal properties, namely gelatinization temperature (peak temperature, T_G), enthalpy for gelatinization (ΔH_G), glass transition temperature (T_g), melting temperature (peak temperature, T_m), and enthalpy for ice melting (ΔH_m) of the batters were obtained directly from the analysis of the software TA instruments OS/2 version 5.5.

Two different temperature profiles were used to simulate cooking and storage processes. To simulate a cooking-freezing-thawing process (CFT process), the samples were first heated to 120 °C at 10 °C/min from 15 °C, which is an initial temperature commonly used for batters in the food industry. Then the samples were rapidly cooled to -50 °C at 20 °C/min to avoid formation large ice crystals which could damage the food's structure. After that, the samples were heated to 25 °C as in a thawing condition. To simulate processing of battered products being first frozen then cooked (namely FC process), the samples were first rapidly cooled to -50 °C at the rate of 20 °C/min, then heated to 120 °C at 10 °C/min. The thermal transition parameters were directly determined from the DSC thermogram curves after measurement.

4.3 STATISTICAL DESIGN AND ANALYSIS

All experiments were conducted using the factorial experimental designs and analyzed in each block experiment. The batter systems were prepared and tested in triplicate in a completely randomized design. A two-way analysis of variance (ANOVA) using the General Linear Model (GLM) was used to study the differences and interaction effects in batter formulations, such as main factors and their combined effects, including the ratio and type of combined flours and the levels of hydrocolloids. The significance of mean comparisons by the Scheffe's least significant difference (LSD) were determined at $P<0.05$ using the SAS software (SAS Institute Inc., Cary, NC, USA).

4.4 RESULTS AND DISCUSSION

4.4.1 Effects of different thermal processes on thermal properties of batter systems

The gelatinization temperature (T_G) of batters varied from 66.9 to 88.2°C during the CFT process, and from 67.2 to 88.6 °C during the FC process as shown in Table 4.2. The ranges of the total enthalpies of batter samples were from 1.52 to 4.57 J/g, and from 1.59 to 4.50 J/g for CFT and FC processes, respectively (Table 4.3). The values varied according to flour type and their combinations and different types of hydrocolloids and their concentrations. ANOVA analysis and mean comparison showed that the different thermal processing (CFT and FC) did not significantly affect the gelatinization temperature and total enthalpies for the batter systems. It appeared that freezing did not affect the function of the component in the raw batter systems (uncooked samples). In this study, the batter samples were rapidly cooled to –50 °C in order to avoid large ice crystal formation during the cooling process. The process conditions apparently maintained the batter system intact during frozen storage.

Table 4.2. Effects of hydrocolloids on gelatinization temperature of batter systems during different thermal processes

Process	Cooking-freezing-thawing (CFT)							
Batter	Control	0.2% XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	66.9(0.69)	69.17(1.02)	72.1(0.72)	76.8(0.69)	78.4(0.98)	70.2(0.23)	72.6(0.72)	72.9(0.98)
Corn	75.7(0.72)	78.68(0.32)	76.5(0.96)	77.2(0.23)	79.1(0.28)	77.8(0.72)	78.5(0.28)	79.1(1.09)
Rice	82.8(1.2)	82.43(0.96)	83.6(0.43)	84.2(0.55)	85.2(0.43)	83.8(0.28)	84.6(0.85)	84.9(0.69)
W3C7	75.5(0.96)	78.37(1.02)	77.3(0.85)	79.5(0.87)	84.6(1.09)	78.9(0.98)	79.3(0.98)	79.4(0.55)
W5C5	79.4(1.56)	80.54(0.63)	80.8(0.43)	81.9(0.69)	82.6(0.55)	81.2(0.43)	81.9(0.87)	82.6(0.43)
W7C3	70.4(0.65)	71.85(0.23)	74.4(0.72)	76.5(0.85)	80.2(0.98)	72.1(0.69)	73.8(0.72)	74.1(0.72)
W3R7	83.6(1.02)	84.63(0.69)	83.9(0.55)	85.6(0.28)	88.2(0.87)	84.5(0.23)	85.2(0.87)	86.1(1.09)
W5R5	71.1(0.96)	85.94(1.030	72.1(1.02)	74.2(0.72)	77.2(0.85)	73.5(0.72)	75.3(0.43)	77.0(0.23)
W7R3	69.5(0.49)	70.58(0.98)	69.8(0.28)	75.7(0.87)	77.5(0.43)	70.7(0.87)	71.5(0.28)	72.5(0.87)
C3R7	82.3(1.36)	82.76(1.32)	82.9(0.98)	84.2(0.55)	85.3(0.98)	82.9(0.69)	84.1(0.72)	84.9(0.69)
C5R5	79.4(0.98)	81.97(0.62)	80.2(0.87)	81.1(0.96)	84.3(0.85)	80.1(0.28)	82.1(0.55)	83.1(0.85)
C7R3	78.1(1.56)	79.83(0.98)	79.1(0.43)	81.3(0.43)	84.7(0.28)	78.8(0.85)	79.9(0.87)	80.6(0.87)
Process	Freezing-Cooking (FC)							
Batter	Control	0.2% XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	67.2(1.02)	69.6(0.36)	72.2(0.43)	77.1(0.85)	78.9(0.65)	70.6(0.85)	72.1(0.23)	72.6(0.96)
Corn	75.3(0.65)	78.8(0.98)	76.9(0.85)	78.3(0.96)	79.2(0.72)	77.4(1.09)	78.7(0.28)	79.6(0.55)
Rice	82.6(0.98)	82.6(1.01)	83.8(0.55)	84.5(0.28)	85.3(0.87)	83.2(0.72)	84.1(0.85)	84.9(0.43)
W3C7	75.6(1.23)	78.7(1.09)	77.6(0.96)	79.7(0.43)	84.9(0.43)	78.9(0.87)	79.5(0.98)	79.6(0.72)
W5C5	79.1(1.36)	80.6(0.36)	80.9(1.01)	82.1(0.87)	82.5(0.55)	81.4(0.69)	81.6(0.87)	82.6(0.69)
W7C3	70.1(0.65)	71.3(0.87)	74.8(0.23)	76.8(0.23)	80.6(0.72)	71.9(0.87)	72.9(0.72)	74.2(0.28)
W3R7	83.3(1.02)	84.0(1.02)	72.1(0.87)	85.9(0.85)	88.6(0.85)	85.5(0.23)	85.6(0.87)	86.1(0.23)
W5R5	71.2(0.69)	85.9(1.02)	70.6(0.69)	74.9(0.28)	77.5(0.43)	73.4(0.99)	75.4(0.23)	76.8(0.87)
W7R3	69.4(0.46)	71.6(0.95)	70.1(0.85)	75.9(0.69)	77.9(1.09)	70.8(0.96)	71.9(0.43)	72.4(0.85)
C3R7	82.4(1.24)	83.2(0.36)	82.7(0.55)	84.9(0.65)	85.7(0.98)	82.6(0.72)	83.9(1.09)	85.0(0.98)
C5R5	79.7(0.69)	81.1(0.97)	80.9(0.98)	81.3(0.43)	84.9(0.28)	80.3(0.72)	82.6(0.85)	83.4(0.28)
C7R3	78.0(0.55)	79.0(1.02)	80.5(0.28)	81.5(0.23)	85.8(0.55)	78.6(0.69)	79.7(0.72)	80.9(0.96)

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. CFT= cooking –frozen-thawing process, FC=frozen-cooking process. Values in parentheses are standard deviations.

Table 4.3. Effects of hydrocolloids on total gelatinization enthalpies of various batter systems during different processes

Process	Cooking-freezing-thawing (CFT)							
Batter	Control	0.2%XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	2.98(0.12)	2.87(0.09)	2.16(0.17)	1.94(0.09)	1.61(0.22)	2.92(0.25)	2.83(0.17)	2.63(0.09)
Corn	3.58(0.25)	3.14(0.31)	3.38(0.27)	2.46(0.16)	2.03(0.31)	3.34(0.08)	3.29(0.08)	3.09(0.31)
Rice	4.57(0.09)	4.17(0.08)	4.38(0.08)	3.10(0.11)	3.04(0.16)	4.46(0.17)	4.39(0.22)	4.21(0.09)
W3C7	2.89(0.12)	2.67(0.27)	2.70(0.16)	2.30(0.22)	1.92(0.09)	2.81(0.25)	2.69(0.11)	2.51(0.27)
W5C5	2.71(0.23)	2.40(0.22)	2.31(0.22)	2.03(0.09)	1.64(0.22)	2.59(0.16)	2.49(0.16)	2.34(0.22)
W7C3	2.72(0.11)	2.950.19)	2.50(0.17)	2.19(0.16)	1.57(0.09)	2.57(0.17)	2.49(0.31)	2.35(0.17)
W3R7	3.47(0.23)	2.97(0.17)	3.17(0.08)	2.73(0.27)	1.73(0.31)	3.21(0.27)	2.89(0.27)	2.21(0.25)
W5R5	3.34(0.09)	2.82(0.21)	3.02(0.31)	2.65(0.11)	2.39(0.08)	3.29(0.08)	3.14(0.08)	2.87(0.09)
W7R3	2.61(0.12)	2.31(0.08)	2.19(0.16)	1.90(0.22)	1.52(0.31)	2.59(0.22)	2.56(0.16)	2.19(0.31)
C3R7	4.00(0.04)	3.65(0.19)	3.79(0.31)	3.12(0.17)	2.14(0.09)	3.72(0.17)	3.69(0.22)	3.50(0.08)
C5R5	3.98(0.31)	3.57(0.31)	3.73(0.22)	3.22(0.27)	2.72(0.22)	3.68(0.11)	3.48(0.17)	3.29(0.17)
C7R3	3.82(0.22)	3.22(0.08)	3.32(0.17)	2.82(0.08)	1.56(0.27)	3.48(0.09)	3.21(0.27)	3.14(0.09)
Process	Freezing-Cooking (FC)							
Batter	Control	0.2%XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	2.94(0.17)	2.93(0.04)	2.17(0.09)	1.92(0.25)	1.65(0.22)	2.91(0.09)	2.81(0.27)	2.67(0.22)
Corn	3.57(0.15)	3.24(0.16)	3.32(0.27)	2.41(0.08)	2.01(0.27)	3.38(0.08)	3.27(0.16)	3.11(0.25)
Rice	4.50(0.08)	4.34(0.22)	4.28(0.11)	3.09(0.22)	2.99(0.11)	4.51(0.11)	4.31(0.22)	4.23(0.11)
W3C7	2.91(0.22)	2.40(0.09)	2.64(0.25)	2.34(0.16)	1.93(0.17)	2.79(0.22)	2.70(0.17)	2.53(0.08)
W5C5	2.71(0.17)	2.71(0.08)	2.32(0.22)	2.11(0.31)	1.59(0.09)	2.61(0.31)	2.50(0.31)	2.38(0.31)
W7C3	2.71(0.22)	2.41(0.31)	2.54(0.11)	2.07(0.11)	1.60(0.22)	2.56(0.09)	2.48(0.22)	2.34(0.17)
W3R7	3.41(0.25)	3.10(0.17)	3.21(0.22)	2.64(0.08)	1.62(0.27)	3.26(0.08)	2.84(0.08)	2.23(0.25)
W5R5	3.38(0.11)	2.90(0.25)	3.12(0.17)	2.59(0.22)	2.31(0.25)	3.27(0.22)	3.19(0.25)	2.91(0.22)
W7R3	2.59(0.04)	2.32(0.11)	2.09(0.25)	1.94(0.17)	1.62(0.08)	2.57(0.17)	2.54(0.08)	2.21(0.08)
C3R7	4.01(0.09)	3.44(0.22)	3.75(0.08)	3.02(0.04)	2.01(0.25)	3.78(0.09)	3.68(0.11)	3.51(0.11)
C5R5	4.01(0.22)	3.38(0.27)	3.71(0.09)	3.21(0.31)	2.73(0.04)	3.61(0.22)	3.49(0.17)	3.31(0.09)
C7R3	3.67(0.08)	3.27(0.31)	3.21(0.25)	2.96(0.27)	1.62(0.17)	3.51(0.25)	3.24(0.22)	3.19(0.11)

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. CFT= cooking –frozen-thawing process, FC=frozen-cooking process. Values in parentheses are standard deviations.

The different thermal processes greatly influenced the phase transition properties of batter systems during the cooling process. The glass transition temperatures of uncooked samples (FC process) varied from –10.2 to –13.1 °C, and for cooked samples

(CFT process) from –16.6 to –23.8 °C, respectively. The cooked samples (CFT process) showed lower glass transition temperatures than uncooked samples (FC process) irrespective of the flours used in formulating the batter (Fig. 4.1). The glass transition behaviors of starch-water system in the freeze-concentrated phase depend upon ice formation, and are dramatically influenced by the amount of available water in the system (Addo et al., 2001, Chung et al., 2002, Hsu et al., 2003). A fraction of water existed compartmentalized and/or was trapped within the network structure of the cooked batter (CFT process). Apparently water was bound more tightly in the cooked samples making it difficult to freeze the trapped water into an ice crystal form. Therefore, the Tg was lower for the cooked samples (CFT process) than for the uncooked batters (CF process).

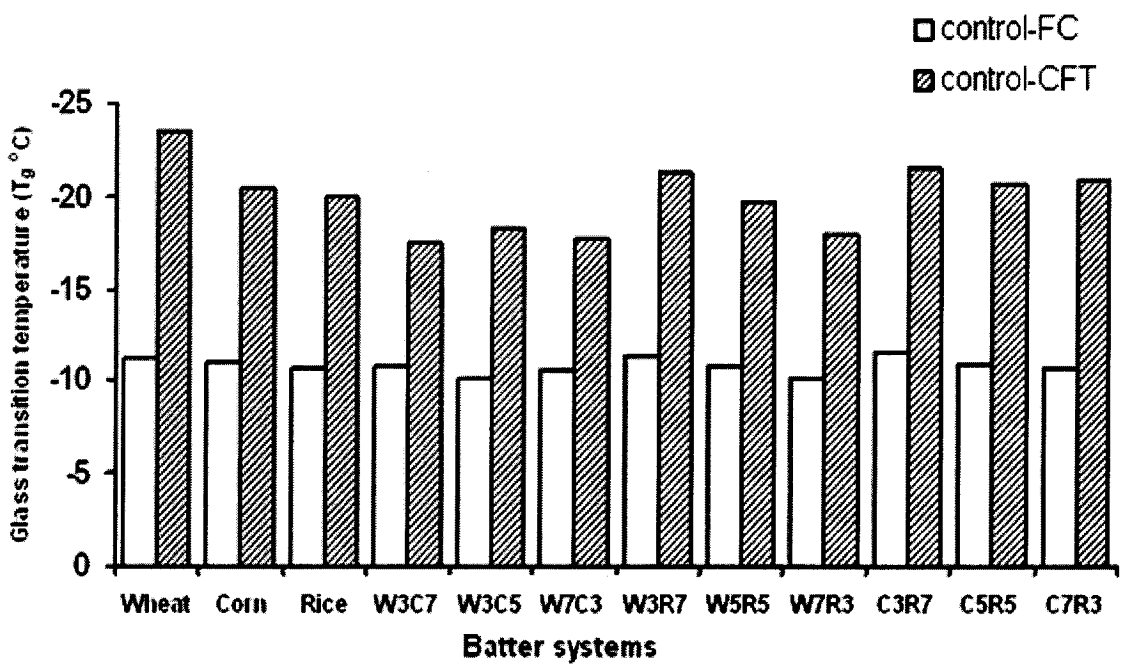

Figure 4. 1. Glass transition temperature of control batters in different thermal processes.

The melting temperatures (peak temperature T_m) for all the batter systems were in the range from 1.8 to 4.3 °C and from 2.0 to 4.8 °C for the cooked and uncooked samples, respectively. There were no significant differences in the melting peak temperatures (T_m) of batter systems containing CMC or 0.2% xanthan gum. ANOVA analysis results showed statistically significant differences in the melting peak temperatures of batter systems to which MC had been added. However, significant differences were observed in the total enthalpy for ice melting (ΔH_m) across all samples (Table 4.4). The ΔH_m values for the uncooked samples (FC process) were higher as compared with those for the cooked samples (CFT process). The differences in thermal properties between these two thermal profiles could be due to the structures formed during processing. The batter samples were cooked and formed to the structure of a solid-like coating in the CFT process, thus less free water content remained as compared with the raw batters in which the batters were not cooked and more water remained. They apparently required different latent heats to melt ice crystals at a similar temperature. Therefore, resulting higher enthalpy was required to melt the ice in uncooked samples compared with cooked samples during the thawing process.

Table 4.4. Effects of hydrocolloids on ice melting peak temperature of various batter systems at different thermal processes

Process	Cooking-freezing-thawing (CFT)							
Batter	Control	0.2%XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	2.1(0.22)	2.29(0.29)	2.2(0.25)	3.0(0.62)	3.5(0.21)	2.2(0.39)	2.4(0.29)	2.7(0.23)
Corn	2.0(0.31)	3.49(0.17)	2.1(0.32)	3.7(0.24)	4.0(0.35)	2.2(0.55)	2.5(0.62)	2.6(0.39)
Rice	1.9(0.49)	2.17(0.11)	2.0(0.19)	3.2(0.35)	3.7(0.19)	2.3(0.29)	2.6(0.42)	3.1(0.17)
W3C7	2.2(0.27)	3.06(0.23)	2.4(0.25)	3.7(0.19)	4.0(0.45)	2.3(0.19)	2.4(0.34)	2.7(0.55)
W5C5	2.3(0.22)	2.88(0.41)	2.6(0.34)	2.6(0.29)	3.5(0.53)	2.5(0.48)	2.6(0.23)	2.7(0.48)
W7C3	1.8(0.31)	2.71(0.55)	1.7(0.36)	4.3(0.31)	4.7(0.32)	1.9(0.23)	2.4(0.11)	2.6(0.39)
W3R7	2.1(0.25)	3.19(0.12)	2.3(0.28)	3.6(0.23)	3.8(0.29)	2.5(0.31)	2.8(0.29)	3.4(0.29)
W5R5	2.3(0.19)	3.44(0.39)	2.5(0.48)	3.1(0.65)	3.6(0.62)	2.6(0.17)	2.7(0.31)	2.8(0.28)
W7R3	2.2(0.36)	3.08(0.43)	2.4(0.34)	3.6(0.42)	4.0(0.39)	2.3(0.28)	2.5(0.39)	2.7(0.62)
C3R7	2.3(0.28)	2.88(0.62)	2.4(0.29)	3.3(0.23)	3.7(0.41)	2.5(0.48)	2.6(0.42)	2.9(0.19)
C5R5	2.3(0.17)	2.85(0.23)	2.3(0.42)	2.3(0.19)	2.6(0.24)	2.4(0.37)	2.6(0.48)	2.6(0.23)
C7R3	2.2(0.43)	3.04(0.59)	2.6(0.32)	3.4(0.33)	3.6(0.36)	2.2(0.29)	2.4(0.31)	2.5(0.11)
Process	Freezing-Cooking (FC)							
Batter	Control	0.2%XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	2.3(0.48)	2.39(0.62)	2.4(0.55)	2.9(0.62)	3.2(0.55)	2.3(0.19)	2.5(0.28)	2.6(0.55)
Corn	2.1(0.34)	3.58(0.55)	2.3(0.28)	2.6(0.48)	3.8(0.62)	2.2(0.62)	2.6(0.48)	2.8(0.31)
Rice	2.1(0.39)	2.31(0.28)	2.4(0.29)	2.4(0.17)	3.3(0.29)	2.5(0.55)	2.8(0.53)	3.4(0.11)
W3C7	2.2(0.11)	3.09(0.42)	2.6(0.17)	2.3(0.34)	3.5(0.62)	2.4(0.53)	2.6(0.29)	2.9(0.23)
W5C5	2.2(0.48)	2.96(0.23)	2.5(0.62)	2.8(0.39)	2.6(0.62)	2.4(0.39)	2.7(0.42)	2.8(0.34)
W7C3	2.0(0.29)	2.69(0.17)	2.3(0.48)	2.1(0.11)	4.8(0.34)	2.1(0.62)	2.5(0.39)	2.7(0.19)
W3R7	2.3(0.34)	3.23(0.39)	2.5(0.55)	3.5(0.23)	3.2(0.23)	2.5(0.31)	2.8(0.17)	3.3(0.48)
W5R5	2.2(0.29)	3.49(0.34)	2.4(0.42)	2.9(0.11)	1.5(0.11)	2.4(0.48)	2.5(0.23)	3.0(0.62)
W7R3	2.1(0.42)	3.12(0.19)	2.2(0.28)	2.2(0.19)	4.0(0.55)	2.4(0.34)	2.6(0.34)	2.8(0.23)
C3R7	2.6(0.19)	2.91(0.28)	2.5(0.39)	3.0(0.42)	2.4(0.31)	2.6(0.62)	2.8(0.29)	2.9(0.42)
C5R5	2.4(0.55)	2.89(0.55)	2.6(0.34)	3.4(0.29)	2.7(0.17)	2.6(0.48)	2.8(0.39)	2.9(0.11)
C7R3	2.1(0.11)	3.12(0.62)	2.3(0.23)	3.2(0.19)	3.8(0.23)	2.5(0.19)	2.7(0.23)	2.8(0.48)

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. CFT= cooking –frozen-thawing process, FC=frozen-cooking process. Values in parentheses are standard deviations

There was a significant effect of adding hydrocolloids on the Tg of batter system. Hydrocolloids depressed the Tg of batters. Figure 4.2 shows the effect of 0.2% xanthan gum on Tg. The effect of xanthan gum was more pronounced in the raw batter systems (i.e. FC process) than in the cooked samples (CFT process). It is suggested that xanthan gum absorbed water, and increased the viscosity of batter system at low temperatures. However, xanthan gum did not show a significant effect on the different flours and their combination blends in raw batters. These characteristics might be explained as due to the lower concentration of xanthan gum used in the batter system to stabilize suspension and viscosity in the systems. The xanthan gum at the lower concentration required less water to develop its properties as compared with CMC or MC used in this study in the limited water systems. None-the-less, xanthan gum showed more effects on Tg values of batter with rice and corn flour compared to batter with the wheat flour during the CFT process.

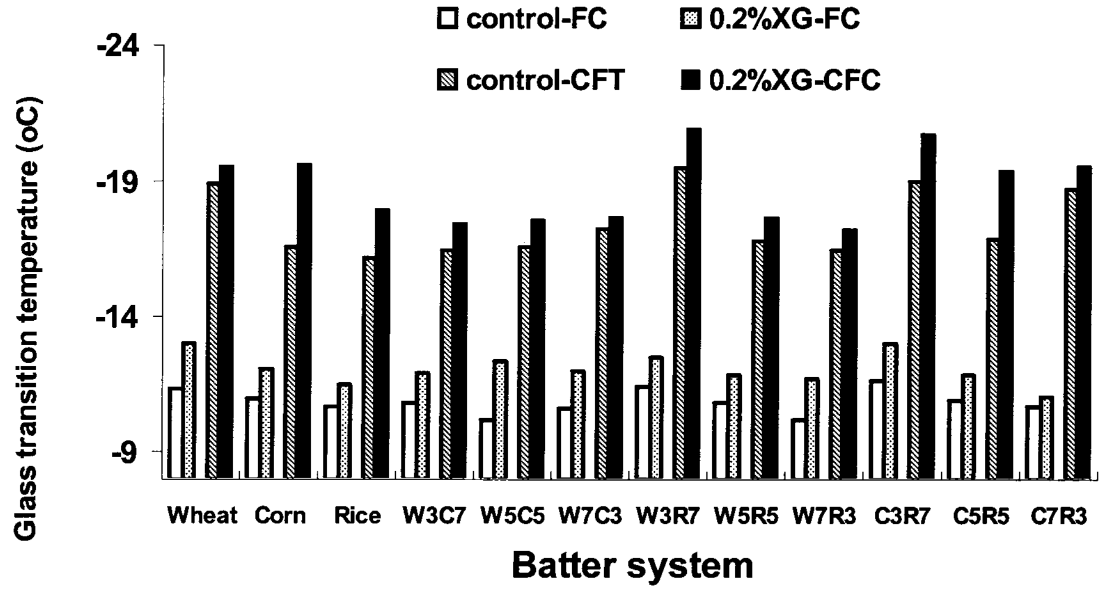

Figure 4. 2. Effects of xanthan gum (XG) on glass transition temperature of various batter systems

4.4.2 Effect of hydrocolloids on thermal properties of batter systems

Xue and Ngadi (2006) reported that the thermal properties of batter systems varied depending on the types of flours used in their formulation. Addition of hydrocolloids significantly increased T_G of batter samples (Table 4.2). The results indicate that the interaction of starch-hydrocolloids in the system produced a more stable structure and needed a higher temperature for disorganization (Christianson et al., 1981; Rojas et al., 1999). The observed effect of MC on the T_G of the batter systems was more pronounced than the effect of CMC and XG. This may be attributed to the ability of MC to gel during heating, resulting in blocked or reduced water being available to react with starch. In that case, there was not enough water available to completely gelatinize the starch at low temperatures, as would be expected for starch gelatinized in the absence of hydrocolloids (Wang et al., 1991, Xue and Ngadi 2006). Hydrocolloids are also water-soluble polymers, causing them to compete for water with other components in the batter systems thus delaying temperature required for starch granules being to become completely swollen. Also, the polymer increased the viscosity of batter systems causing reduction in the heat transfer rate. Therefore, the addition of hydrocolloids shifted T_G toward higher temperatures. Increasing hydrocolloid concentration led to increased in T_G for all of samples.

Total gelatinization enthalpies were significantly influenced by different samples (Table 4.3). They decreased with increasing hydrocolloid concentrations in the batter systems. Gimeno et al. (2004) found that a higher interaction of hydrocolloids and starch retained more water molecules, causing a higher mobility of water during heating, increasing the kinetic energy and decreasing the enthalpy value. Therefore, the symbiotic effects of hydrocolloids and starch increased the starch gelatinization temperature but reduced the total enthalpies of gelatinization of the batter systems during the heating process.

Figure 4.3 shows variation in Tg with respect to different concentrations of MC and different batters. Figure 4.4 shows similar data for CMC. There were no significant differences in the glass transition temperatures of the control samples (0% CMC/ MC) and 0.5 % CMC or MC samples during the CFT process, but it showed that the statistical effect of CMC or MC concentration was more pronounced in the glass transition of samples in the FC process (Fig. 4.3 and 4.4). The different behaviors of the batters can be attributed to their ability to form structures during the different thermal processes. Although similar CMC-flour or MC-flour interactions may have occurred at the 0.5% level, but it was not sufficient to cause large differences in the structure of the coating formed by heating during CFT processing.

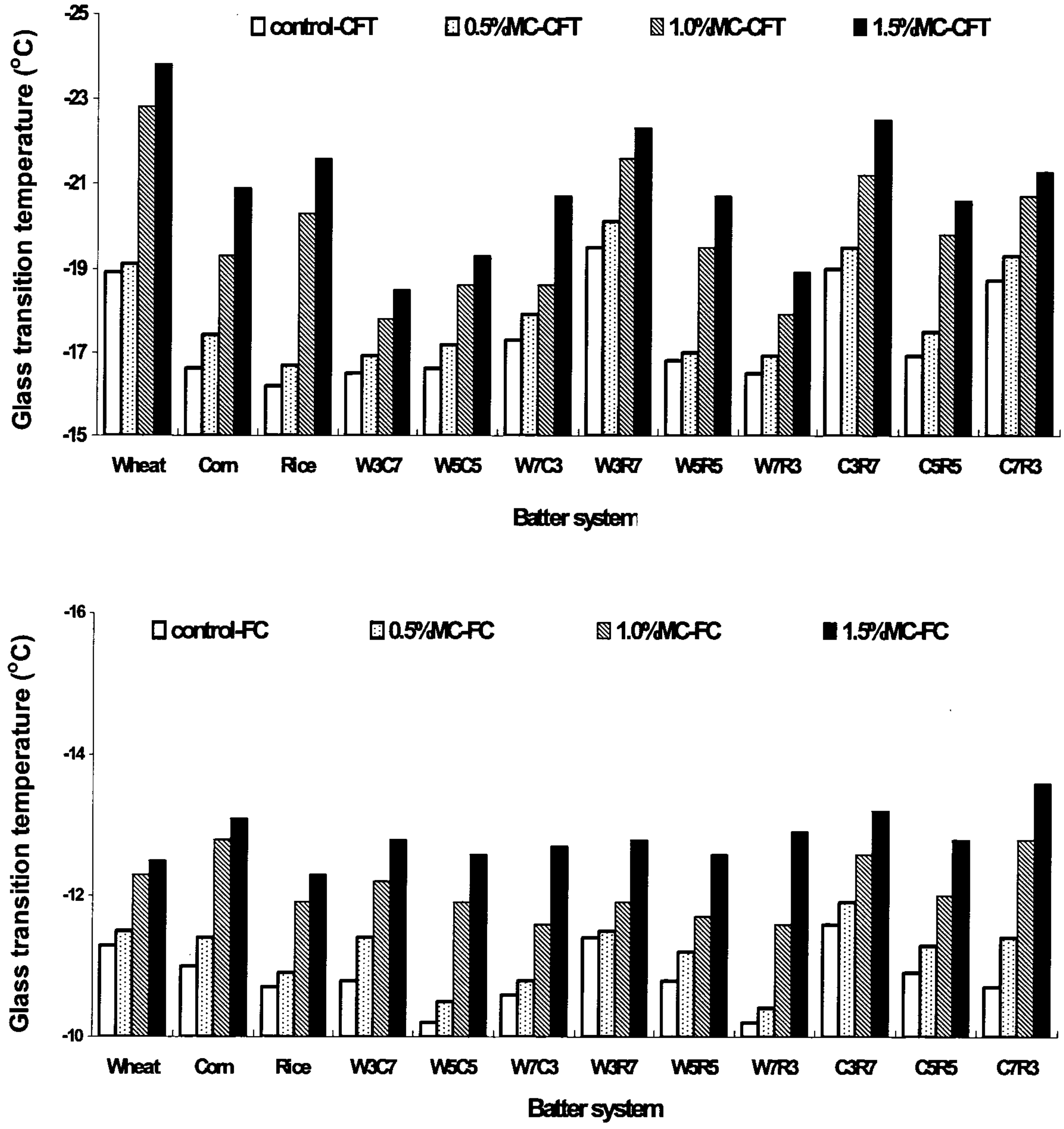

Figure 4.3. Effects of methylcellulose (MC) on glass transition temperature of various batter systems.

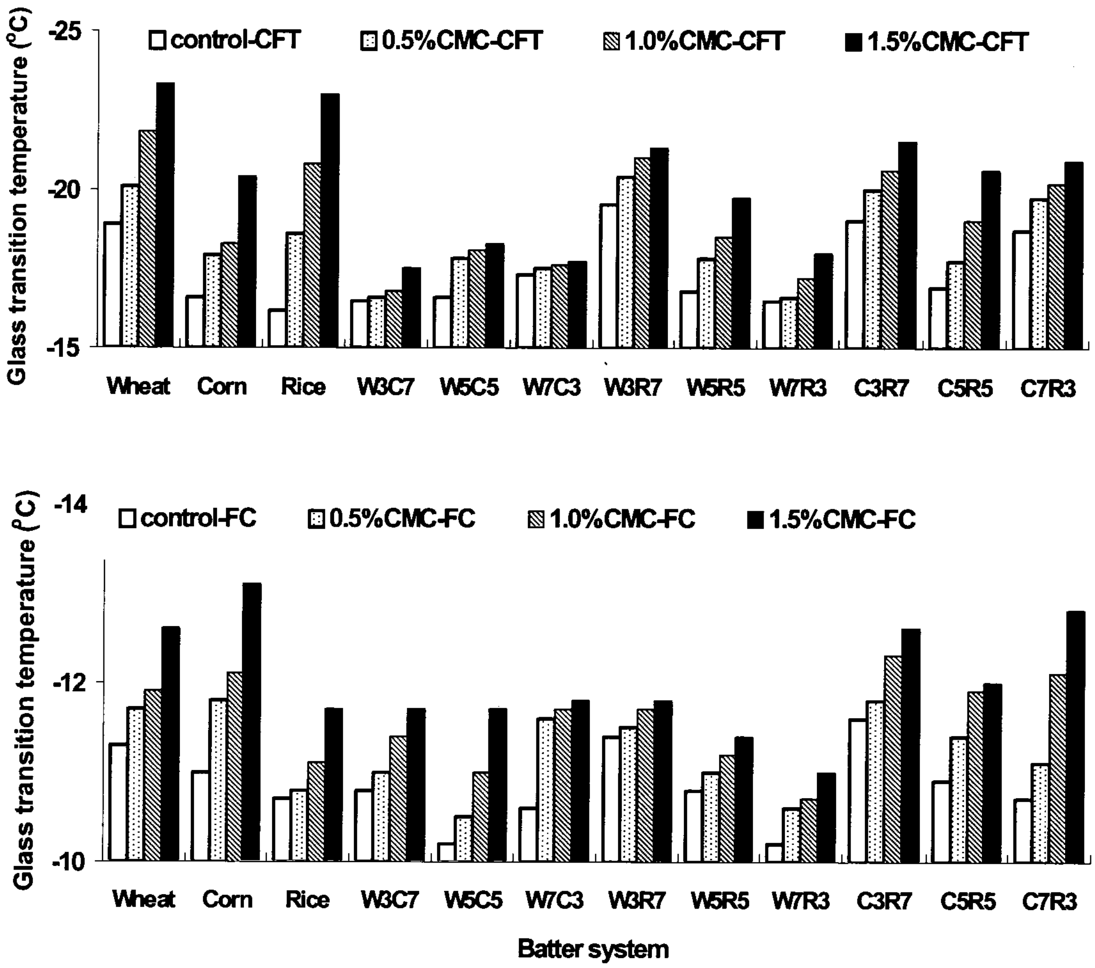

Figure 4.4. Effects of carboxymethylcellulose (CMC) on glass transition temperature of various batter systems

Free water is easily frozen as compared with bound freezable water, and it crystallizes during cooling (Bhaskar et al., 1998). . In raw batter systems, MC and CMC typically bind water tightly, reducing the amount of free water in the batter systems. The effect of MC or CMC is to cause a postponement in the freezing of the bound freezable water in hydrocolloid-batter systems. Therefore, lower temperatures were required to complete the phase transition for the batters containing the addition of MC or CMC. Also, the MC or CMC concentration had a significant effect on the glass transition temperatures in all raw batter systems.

In a cooking-freezing-thawing (CFT) process, MC or CMC greatly influences the structure formation of the coating during heating, and the final water content of the cooked samples (Nakamur et al., 2004, Gao and Vodovot, 2005). This seemed to correlate with the interactions between starch and hydrocolloids in reorganization, creating a higher number of crosslink structures which retain a larger amount of water molecules during the process (Gimeno et al., 2004). Thus, MC or CMC increases the water content of the final cooked samples, and it consequently influences phase transition behavior such as glass transition, ice melting temperature, and total enthalpies of ice melting during cooling and thawing. The absorbed water inside a hydrocolloid-cooked sample that is mostly bound freezable water sets with the unfreezable water fraction, and water content of cooked samples would be increased with increasing MC or CMC concentrations. A lower temperature is required to form ice crystals in order to attain the glass state from the rubber state in the systems.

During the thawing process, the DSC thermograph showed that endothermic transitions occurred due to the melting of ice crystal within the batter systems. The range of ice melting temperatures was from 1.8 to 4.8°C while the range of total enthalpies was from 110 to 155.6 J/g for the various batters system. ANOVA results showed statistically similar effects of hydrocolloids on the ice melting peak temperatures in the various batter systems (Table 4.4). Xanthan gum and MC greatly increased the ice melting temperatures and total enthalpies of ice melting across all batter systems for both thermal processes, but no significant differences were observed on the total enthalpies of ice melting in batter systems containing CMC for either CFT or FT processing (Table 4.5).

Table 4.5. Effects of hydrocolloids on total enthalpies of ice melting in various batter systems

Process	Cooking-freezing-thawing (CFT)							
Batter	Control	0.2% XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	136.8(0.81)	145.4(1.02)	138.2(0.72)	142.6(0.96)	146.2(1.72)	141.2(1.23)	145.6(0.92)	145.9(1.14)
Corn	126.5(1.14)	136.8(0.85)	129.6(0.69)	135.2(0.85)	142.3(1.43)	129.6(0.98)	134.5(1.02)	139.6(0.97)
Rice	110.5(1.86)	135.8(1.43)	112.3(1.56)	116.2(1.02)	121.3(0.87)	115.8(1.04)	128.9(1.31)	134.8(1.02)
W3C7	120.7(1.02)	140.7(1.20)	126.1(0.72)	130.2(0.87)	136.2(0.98)	129.4(0.78)	144.0(0.86)	145.8(0.98)
W5C5	133.0(0.42)	135.0(0.72)	138.2(0.96)	140.3(0.72)	143.6(0.72)	137.9(1.03)	145.2(1.03)	149.2(0.78)
W7C3	126.9(0.84)	141.0(1.56)	128.2(1.32)	129.6(1.09)	132.3(1.02)	134.2(0.98)	138.6(0.98)	143.2(1.02)
W3R7	119.4(1.03)	137.0(0.96)	120.9(0.55)	123.6(0.72)	127.6(0.85)	126.2(1.03)	138.2(1.85)	142.8(1.09)
W5R5	129.8(1.25)	134.7(0.85)	130.1(0.63)	135.2(0.69)	139.2(1.36)	134.6(1.15)	139.2(0.85)	142.5(0.98)
W7R3	132.9(0.61)	146.3(1.36)	135.1(0.87)	135.9(0.87)	139.6(0.98)	136.8(1.43)	143.2(0.87)	146.4(0.67)
C3R7	112.8(1.20)	137.9(0.55)	117.8(0.96)	124.5(0.98)	132.1(1.03)	115.5(0.95)	124.8(1.00)	130.1(1.02)
C5R5	122.2(0.14)	137.5(1.09)	126.9(1.23)	129.2(1.28)	135.2(0.98)	133.8(0.87)	139.8(1.06)	141.7(0.98)
C7R3	128.9(0.65)	134.3(0.98)	129.9(0.55)	131.2(0.69)	136.2(1.09)	134.5(0.81)	137.5(0.92)	140.3(1.00)
Process	Freezing-Cooking (FC)							
Batter	Control	0.2% XT	0.5%MC	1.0%MC	1.5%MC	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	149.3(0.95)	141.5(1.02)	150.1(0.98)	153.6(1.09)	154.6(0.72)	150.1(0.73)	150.9(0.23)	151.6(0.81)
Corn	144.6(1.02)	133.8(1.28)	146.2(1.43)	148.3(1.02)	147.5(1.28)	144.8(1.12)	145.2(0.89)	145.4(0.79)
Rice	139.2(1.03)	138.3(0.96)	140.2(0.69)	143.6(0.97)	144.5(0.87)	140.6(2.04)	140.9(1.03)	141.2(1.02)
W3C7	140.6(1.06)	132.4(0.85)	141.2(0.87)	146.2(0.98)	147.6(0.43)	141.5(0.84)	141.9(0.97)	142.5(1.06)
W5C5	145.8(0.64)	129.7(0.69)	147.2(0.28)	149.6(1.28)	150.3(0.98)	146.7(1.20)	147.7(1.02)	148.2(0.73)
W7C3	146.1(0.25)	137.8(0.87)	148.9(0.98)	151.2(1.02)	151.9(0.87)	146.7(2.03)	147.5(0.98)	147.9(0.98)
W3R7	143.2(0.89)	133.5(1.09)	145.2(1.23)	148.3(0.85)	149.8(0.72)	143.6(1.32)	147.2(0.78)	148.2(1.12)
W5R5	146.5(1.04)	127.0(1.07)	147.2(0.69)	150.3(0.87)	152.3(1.01)	146.1(0.98)	146.8(0.69)	147.2(1.86)
W7R3	151.0(0.98)	134.6(1.01)	152.3(1.07)	155.6(1.02)	157.2(1.24)	151.8(0.98)	152.0(1.02)	152.4(0.86)
C3R7	146.4(1.75)	122.5(0.87)	146.8(0.65)	150.3(0.69)	151.3(1.72)	146.5(1.12)	148.5(0.99)	148.2(0.14)
C5R5	141.7(0.45)	132.4(1.08)	142.3(0.98)	146.2(0.95)	149.6(0.55)	142.1(1.09)	142.1(0.67)	143.2(1.23)
C7R3	142.5(1.38)	137.3(1.25)	146.3(0.55)	149.2(1.43)	152.3(0.85)	143.7(1.46)	144.8(1.23)	144.6(1.09)

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. CFT= cooking –frozen-thawing process, FC=frozen-cooking process.

Values in parentheses are standard deviations.The concentration of MC had a noticeable effect on the melting peak temperature of samples for both thermal processes. CMC only showed a noticeable effect on the melting peak temperature of uncooked batter systems during the FC process. It might be explained that the MC could thermally gel during heating; thus it could greatly influence the structure formation of a coating during heating. It also affected the amount of available free water in the raw batter systems during cooling due to its water-binding capacity. When CMC absorbed water, it leads to an increase in the viscosity of the batter systems. This affected the heat transfer in the batter, thus causing a slight shift to a higher melting temperature, as compared with the control samples. However, in cooked samples (i.e. CFT process), the results showed no significant differences in ice melting peak temperatures between the control samples and batter systems with addition of 0.5% CMC. But the results apparently did show effects on the melting peak temperature, and it increased with increasing concentration from 1.0 to 1.5 % CMC in the CFT process. It might be explained that the high concentration of CMC more strongly influences the structure of coating formation during heating than does a lower concentration.

In comparison with the effects of hydrocolloids in different flour blend combination batter systems, the results showed that the effect of CMC or MC was more pronounced in rice, corn, and their combination blend batters as compared with wheat flour based batter systems. This may be due to water limitations to MC or CMC developing their maximum efficiency in batter systems. Also, wheat gluten may have diluted the effect of CMC on wheat flour based batters. However, this special behavior did not show-up in batter systems containing xanthan gum.

4.5 CONCLUSIONS

This study investigated and monitored the thermal properties of different flour combinations in conjunction with different types of hydrocolloids in batter systems. It was found that the thermal properties varied with the different types of flours, their combination ratios, and with the different types of hydrocolloids. Two different thermal processes for cooking and frozen storage were used to determine the thermal properties of batter systems formulated using different flour combinations with the addition of hydrocolloids at different levels. Although the different thermal processes did not show effects on gelatinization or total enthalpies of gelatinization in all samples, they affected the phase transition of batter systems during cooling. Hydrocolloids increased the gelatinization temperatures but depressed the glass transition temperatures of the resulting batters. MC increased the melting temperature (T_m) for the test batter systems as compared with the values for the control system without MC. CMC did not show statistically significant effects on the total enthalpies of ice melting for all samples. However, MC and CMC showed more pronounced effects on rice, corn, and their combined flour based batters than it did on wheat flour based batters. However, this characteristic does not show in batter systems containing xanthan gum.

4.6 IMPLICATIONS FOR BATTER PREFORMANCE

Hydrocolloids are incorporated into batter systems to improve their performance and end product quality. Moreover, interactions between the flours, hydrocolloids, and the other ingredients present can change the thermal properties as the food passes through the processes. It was observed in this study that hydrocolloids extend the starch gelatinization process and require lower temperatures to maintain satisfactory frozen properties. Therefore, high temperature and more energy might be require for coating structure development, but lower temperatures are required to freeze battered food products.

Hydrocolloids influence the freeze/thaw stability of batters. The results suggest that 0.2% xanthan gum might be more suitable for batters than MC and CMC from the point of view of their resulting glass transition temperatures, when cooked batters are kept in frozen storage. However, MC and CMC with 0.5% (higher glass transition temperatures) might be more suitable when raw batters are to be kept in frozen storage.

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CONNECTING TEXT

The results of the investigation in chapter IV confirm the existence of a relationship between different types of flours and combination ratios on the thermal properties of batter systems. In Chapter V, the effects of different combination flour blends at different combination ratios on the flow behavior & viscoelastic properties of batter systems were investigated.

V. RHEOLOGICAL PROPERTIES OF BATTER SYSTEMS FORMULATED USING DIFFERENT FLOUR COMBINATIONS

5.1 ABSTRACT

Battered foods are popular due to their crispy texture, more desirable color, and flavour. The quality of batter coated products is influenced by the rheological properties of the batter materials and by changes in their properties associated with their transition from liquid to solid states. The rheological properties of combinations of rice and wheat, rice and corn, and wheat and corn flour based batters at different combination ratios were studied. The batters were formulated using different flour combinations and 2.5% (w/w) salt. The rheological properties varied with different types of flours and their combination ratios. The replacement of corn flour greatly altered the viscosity and viscoelastic properties of wheat based and rice based batter systems. Salt significantly lowered the viscosity and decreased G'_{max} and G''_{max} of batter. Higher temperatures and longer times were required to gelatinize starch at the higher levels of rice flour for each batter system flour mix combination.

Keywords: Batter coating; Fried products; Flour; Rheological properties; Viscoelastic properties

5.2 INTRODUCTION

Most fried products incorporate coatings that are used to add value to the products by improving their texture, flavour, weight, and volume. Coatings can take the form of a batter and/or breading and often these coatings are applied in combination to produce a desired effect. Food batters are complex systems comprised of water, flour or starch, and seasonings into which food products are dipped prior to cooking. No exact recipes exist for batter systems. Formulations can be extremely flexible to allow for maximum adaptability to the product development process, depending on the food substance and the desired coating appearances.

Wheat flour is the most common flour used in batter systems (Loewe, 1993). However, rice, corn, and soy flours have also been used (Robert, 1990). Rice flour is often used as a substitute for wheat flour and corn flour for batter system because of its perceived healthier properties, and it contains fewer calories. Rice flour reduces oil absorption better than wheat flour although it is less effective as a thickening agent (Shih and Daigle, 1999; Dogan, Sahin, and Sumnu, 2005). Corn flour is often used to provide natural yellow color and to increase crispness in coated fried products because it has decreased moisture retention in the coating. It is also often added to control viscosity since its higher starch level affects the batter's ability to absorb water (Roger, 1990). Traditional batter basically consists of flour, salt and water, although the proportions of the basic ingredients are variable. It would be of interest to know how each of the ingredients contributes to the overall characteristics and more importantly to the final texture of the fried products. Combination of different flours may provide special effects on quality of coated products.

The viscosity of a batter plays a major role in the quality of the coating. It is also one of the most important factors in determining a batter's performance during frying (Shih and Daigle, 1999; Dogan et al., 2005). The factors that affect rheological properties of batters include composition and proportion of the ingredients, the solid-water relationship, and temperature. Other important factors are shear rate and duration, and previous thermal and shear histories. A temperature increase resulted in lower consistency index values (Ostwald-deWale model) in tempura batter formulations (Baixauli, Sanz, Salvador, and Fiszman, 2003). Structural changes that took place during the batter cooking process corresponding to the transition from fluid to gelled state could be clearly followed by studying their mechanical spectra at three different temperatures (65, 75 and 85°C). Pasting or gelatinization is another property of flour starch that affects batter viscosity during cooking. As heating disrupts the crystalline structure of starch granules, they begin to absorb water and swell with a consequent increase in viscosity. The peak viscosity of gelatinized starch is reduced by the action of α - amylase, which disrupts the starch granules during the frying operation. The swollen starch granules provide a film barrier that inhibits oil penetration into the food substrate, and prevents water loss from the substrate (Gibney, Butler, and Dwyer, 1999). Gelatinization and the film formed play a significant role in providing crispness and texture to the finished fried product.

Therefore, the rheological properties of a batter system directly determine the quantity, quality, appearance, texture, and handing properties of the coated product. The viscosity of the batter applied to deep fat fried products is a critical coating characteristic, which affects the pick up and adhesion of the batter and breading, as well as the quality of the final product. Viscosity and rheological data provide information that may be useful for many coating applications.

Few studies have considered the rheological properties of batters containing different combinations of ingredients blended at different ratios (Dogan et al., 2005; Sanz, et al., 2005). These studies show that the type of ingredient and their combinations not only influence the consistency of the batter mix but it also affects critical quality parameters of fried product. Not much work has been reported on wide combination of flour blends at different ratios. The purpose of this study is to evaluate the rheological properties of batter system formulations using blends of wheat, rice and corn flours and also to show how flow behavior and viscoelastic properties change as one type of flour is partially replaced with either of the other types. This study also investigates the effect of salt on the rheological properties of these batter systems.

5.3 MATERIALS AND METHODS

5.3.1 Composition and particle size analysis

Commercial wheat flour (Five Roses All Purpose Flour, Les Cuisines Five Roses Kitchens, QC, Canada), rice flour (Club House Gluten Free Rice Flour, McCormick Canada Inc, ON, Canada), and corn flour (CLIC Import Export Inc., Montreal, Canada) were obtained from a local grocery and used in the study. Moisture, crude protein, lipid, and ash contents of flours were measured as described in chapter III.

5.3.2 Batter formulations

Experimental design was conducts as block experimental design. In the first block experiment, flour blends suspense was prepared according the procedure outlined in chapter III.

In the second block of experiments, batters were formulated by adding salt to the flour samples. A fixed quantity of 2.5% (by weight) salt was used in all cases. To formulate batters, the dry ingredients consisting of flour and salt were first mixed thoroughly before adding cold distilled water at 8 ± 2 °C. The water temperature was chosen since it had been considered necessary to maintain a fairly tight control on the cold-water viscosity of the mix. All batters were constituted with water to dry-mix in the proportion (w/w) of 1.3:1. The moisture content of the batter sample was confirmed to be about 55.6% (wet basis) by drying in an oven set at 105 °C. All mixed batter samples were allowed to rest for about 15 min at 15 °C before their rheological properties were measured.

5.3.3 Thermo-rheological measurements

A strain/stress control rheometer (Advanced Rheometer 2000, TA Instruments, Delaware, USA) equipped with 4 cm diameter parallel plates was used in the study. The gap between the plates was set to 1 mm, which was considered large enough with regard to the flour particle size. Rheological characterization was carried out using both stationary shear flow and oscillatory tests. The free surface of the sample edges was covered with silicone oil and a steel cover was used to minimize the water loss during the measurements.

5.3.3.1 Flow behavior

Shear measurements (flour curves) were performed to evaluate the flow behavior of the batter systems. Apparent viscosity was measured as a function of shear rate over the range 0.5 to 150 s^{-1} at 15 °C. Apparent viscosity was reported as the mean of three replicates on each sample.

5.3.3.2 Viscoelastic behaviors

In order to study the changes due to the effect of cooking temperature on the batters, the storage modulus (G') and loss modulus (G") were monitored as functions of temperature and were determined using dynamic oscillatory test.

Preliminary tests were run in frequency sweep mode by varying the strain amplitude from 0.05 to 100%, which indicated that the selected strain (2.65%) was within the linear viscoelastic region. After equilibration at the initial temperature of 15 °C for 5 min, the samples were heated continuously at 2.5 °C/min to a final temperature of 100 °C. During the heating process, the samples were sheared at a fixed frequency of 1 Hz with maximum strain amplitude of 2.65%. The storage modulus (G', a measure of elastic response) and the loss modulus (G", a measure of viscous response) were continuously monitored during the dynamic rheological testing.

5.4 STATISTICAL ANALYSIS

All batter systems were prepared and tested at least in duplicate in a completely randomized design. An analysis of variance (ANOVA) using the General Linear Models (GLM) procedure (SAS software) was conducted to study the differences in batter formulations using the multiple comparison test, and the significance was determined at $P \leq 0.05$ using the SAS software.

5.5 RESULTS AND DISCUSSION

5.5.1 Chemical composition and particle size of the raw material

The chemical composition and particles size of the flours was reported in chapter III, and summarized in Table 3.1. The corn flour also had a higher fat content and the rice flour was coarser than the wheat and corn flours.

5.5.2 Flow behaviors

Batter viscosity decreased with increasing shear rate, revealing the shear thinning characteristics of the batters. The ANOVA results showed significant differences in viscosity for all the samples (Table 5.1). Sample viscosities varied from 1.08 to 7.41 Pa.s at different shear rates. Batter viscosity is a function of several variables including materials (especially their protein, starch, and pentosan contents), particle size, the amount of water present (solids concentration), and temperature. Free water might play a critical role in the viscosity value because starch granules are not soluble in cold water. Generally a higher viscosity is caused by lower water content.

The batter containing 100% wheat flour showed higher viscosity than the batter containing either 100% corn or 100% rice flour. This could be attributed to the ability of wheat gluten to absorb water, resulting in decreased free water in the batter system. Corn and rice flours tend to feel more "gritty" because their proteins do not absorb water easily at lower temperatures. Their particles also do not hydrate as fully, do not swell, and do not interact with each other as much. Therefore, the viscosities of batter systems containing corn and rice flours do not rise as rapidly as systems containing wheat flour. Rice flour batters had higher viscosities (4.46 Pa. s) as compared to corn flour (1.08 Pa. s) systems. This may be attributed to differences in their particle diameters and size distributions.

Generally, viscosity has been reported to increase with increased particle size (Mukprasirt, Herald, & Flores, 2000). The value of apparent viscosity obtained in this study is higher than the value of 3.52 Pa.s reported by Dogan et al. (2005) for a 100% rice flour based batter. An average rice flour particle size of 38 μm was used in the work by the authors whereas in this study, the average particle size was measured as 25.7 μm. The difference in apparent viscosity values reported in the two studies may be attributed to the particle sizes of the rice flour samples used in the different studies. In addition, the discrepancy could also be explained by noting that apparent viscosity was measured in this study at a lower temperature of 15 °C.

Flow curves of the different batter formulations using wheat and corn (WC) flour, wheat and rice (WR) flour, and corn and rice (CR) flour at a temperature of 15 °C are presented in Figures 5.1, 5.2, and 5.3, respectively. For the wheat and corn flour blends, batter viscosity decreased with an increasing proportion of corn flour in the batter. Corn flour apparently dilutes the strengthening influence of wheat flour gluten (Navickis, 1987). Rice flour also exerted a diluting effect on wheat flour gluten, increasing the available free water in the batter system. This free water could lubricate particles, enhance flow, and result in a lower viscosity value (Mukprasirt et al., 2000). However, the effect of increasing the proportion of rice flour from 30 to 70% was not significant (Table 5.1).

Table 5.1. Average viscosities of batter systems formulated using different combinations of flour and salt

Batter system	Viscosity (Pa.s)	
	Without salt	With 2.5% (w/w) salt
Wheat	7.41 ± 0.5 [a]	5.14 ± 0.4 [b]
Rice	4.46 ± 0.5 [b]	3.10 ± 0.3 [cd]
Corn	1.08 ± 0.5 [d]	0.68 ± 0.3 [fg]
W3C7	1.87 ± 0.4 [d]	1.34 ± 0.3 [fg]
W5C5	2.71 ± 0.4 [cd]	2.45 ± 0.3 [de]
W7C3	4.26 ± 0.4 [bc]	3.29 ± 0.3 [cd]
W3R7	4.01 ± 0.4 [bc]	2.98 ± 0.3 [cd]
W5R5	3.90 ± 0.5 [bc]	2.63 ± 0.4 [cd]
W7R3	4.36 ± 0.4 [bc]	3.99 ± 0.3 [a]
C3R7	2.24 ± 0.4 [b]	1.59 ± 0.3 [ef]
C5R5	1.75 ± 0.5 [d]	0.87 ± 0.3 [fg]
C7R3	1.85 ± 0.5 [d]	0.32 ± 0.3 [g]

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. Means with the same letter are not significantly different.

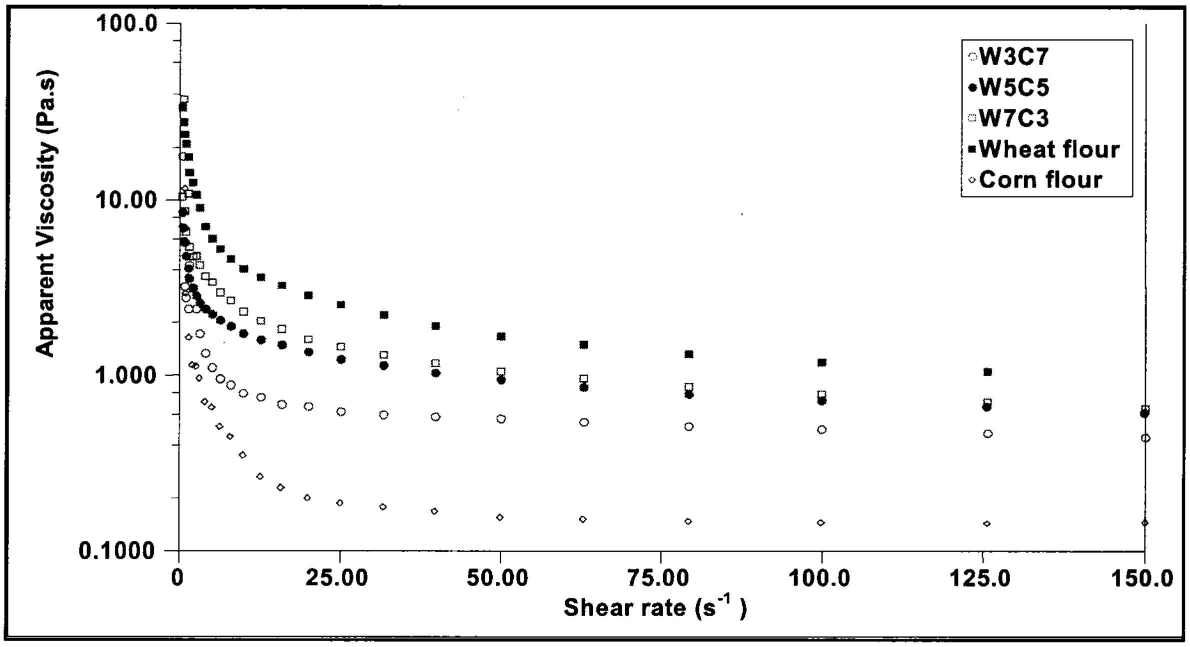

Figure. 5.1 Viscosity of batter system formulated using wheat, corn flour, and their blends

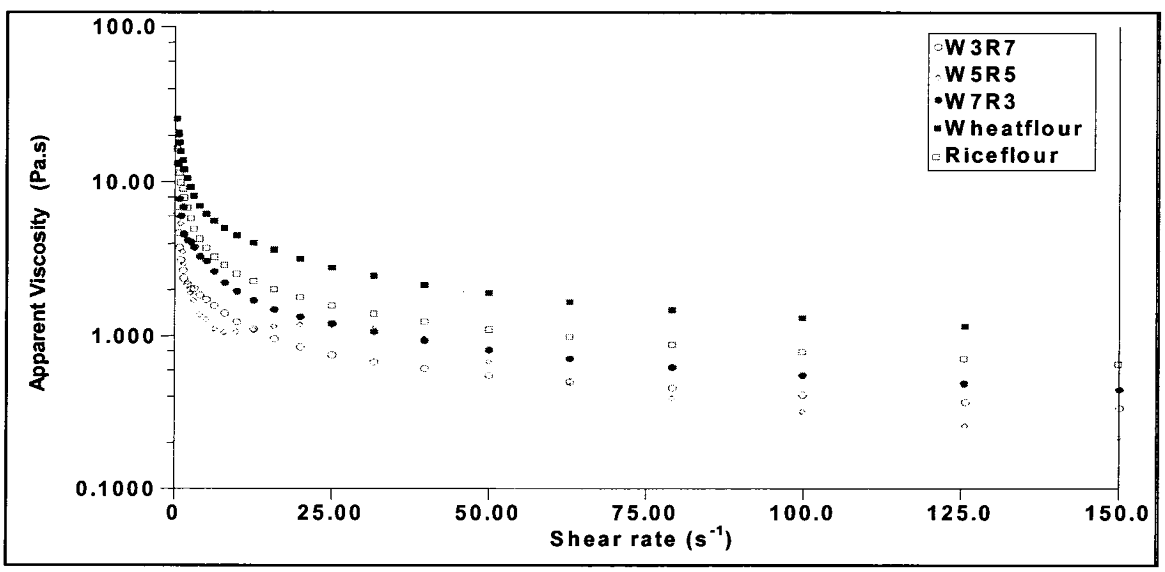

Figure 5.2. Viscosity of batters formulated using wheat, rice, and their blends

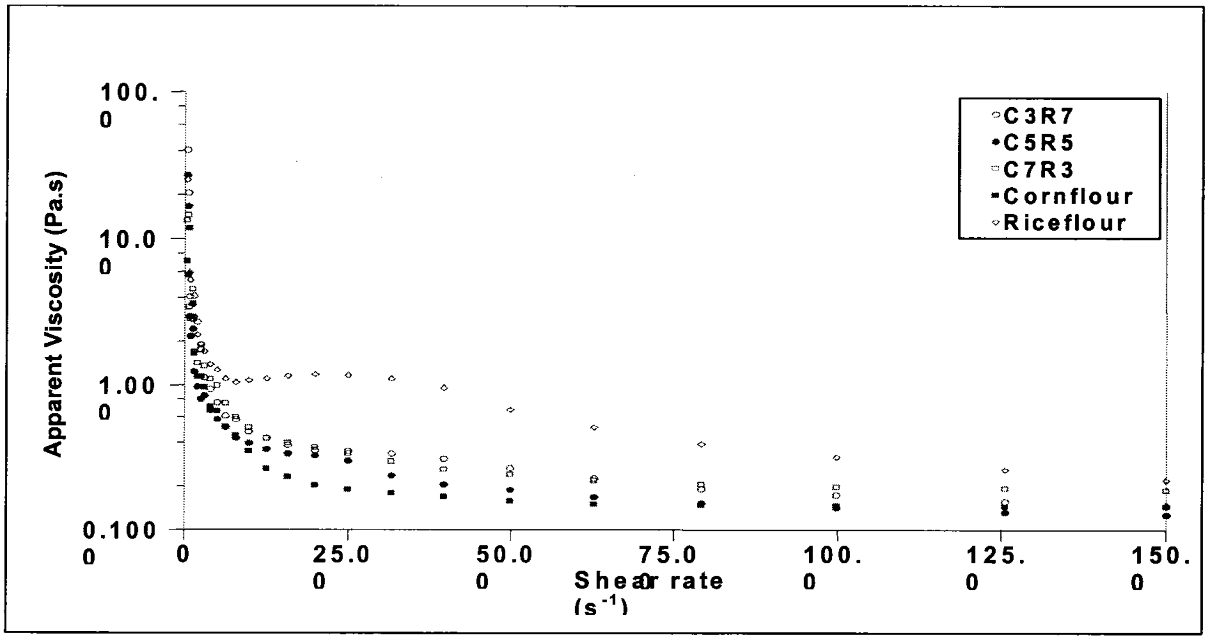

Figure 5.3. Viscosity of batters formulated using corn, rice, and their blends

The viscosities of batters with 100% corn flour was not significantly different from those for batters formulated either with 70% corn flour and 30% rice flour (C7R3) or with 50% corn flour and 50% rice flour (C5R5). However, further increases in the proportion of rice flour in the corn and rice flour mixtures resulted in significant increases in batter viscosity (Table 5.2). In the C7R3 batter, corn flour was the major flour base and the viscosity behavior of the batter system tended towards corn flour, which had the lowest viscosity (1.08 Pa.s), whereas in C3R7 batter the behavior tended to rise to a higher viscosity. The results indicate that replacement of corn flour by up to 50% rice flour did not influence the viscosity of corn flour based batters. On the other hand, replacement of rice flour by 30% corn flour in a rice-based batter significantly lowered the viscosity of the system. Therefore, corn flour showed a stronger influence on viscosity of corn – rice batter than did rice flour. Both corn and rice flours significantly reduced the viscosity of wheat based batter systems.

Adding salt to the batter formulations slightly lowered their viscosities (Table 5.2). Salt binds water tightly and increases the water-holding capacity of batter systems. Changala, Susheelamma, and Tharanathan (1989), also reported similar results as salt caused a decrease in the consistency index and an increase in the flow behavior index for both native and fermented black gram flour dispersions.

5.5.3 Thermo-rheological properties

Onset temperature of structure development (T_{onset}), G'_{max} (measured at peak) and G''_{max} were used to monitor changes in the batter systems rheological properties as functions of temperature for different flour combinations and proportions. These values are shown in Table 5.2.

The storage and loss moduli for different batter systems exhibited similar trends for all samples. None of the samples showed a significant elastic response (G') during the dynamic shearing test at temperatures below 50 °C (Figure 5.4). However, a rapid increase in G' was observed for all batters between from 58 to 68 °C, after which G' increased rapidly, indicating an increase in elastic properties. This increase was attributed to starch gelatinization resulting in the onset of structure formation during which the fluid-like batter transforms into a solid-like coating. The storage modulus of samples reached maximum values (G'_{max}) but subsequently decreased steadily with further heating at higher temperatures due to molecules of soluble starch orienting themselves in the direction that the system is being sheared, causing a decrease in the viscosity (Hoseney, 1994b). Changes in the loss modulus (G") of the different batter systems generally followed patterns similar to those observed for G' (Figure.5.4).

Table 5.2. Dynamic rheological characteristics of batter systems at different formulations

Batter	T_{onset} (°C)	G' (Kpa)	$T_{G'max}$ (°C)	G" (kpa)
Wheat	58.7^{a}	30.53± 0.94 ^{cd}	69.5	7.24± 2.1 ^{g}
Rice	68.0^{bc}	25.65± 0.98 ^{d}	78.6	3.57± 2.2 ^{h}
Corn	67.6^{bc}	44.59± 1.01 ^{ab}	71.8	10.40± 2.3 ^{ef}
W3C7	67.1^{bc}	51.18± 1.03 ^{a}	73.6	24.01± 2.3 ^{a}
W5C5	63.4^{ab}	43.83± 1.04 ^{ab}	73.9	18.85± 2.4 ^{c}
W7C3	62.3^{ab}	38.21± 1.05 ^{bc}	73.3	13.16± 2.4 ^{d}
W3R7	67.4^{bc}	46.34± 1.05 ^{ab}	80.9	21.23± 2.4 ^{b}
W5R5	63.7^{ab}	37.33± 1.06 ^{bc}	81.4	14.88± 2.4 ^{d}
W7R3	62.4^{ab}	30.08± 1.06 ^{cd}	70.9	10.76± 2.4 ^{ef}
C3R7	66.6^{bc}	39.83± 1.06 ^{ab}	76.7	6.56± 2.4 ^{g}
C5R5	68.2^{bc}	36.02± 1.06 ^{bc}	74.1	6.17± 2.4 ^{g}
C7R3	64.8^{ab}	43.50± 0.9 ^{bc}	72.3	8.38± 2.1 ^{fg}

C7R3 = 70% corn and 30% rice flour, C5R5 = 50% corn and 50% rice flour, C3R7 = 30% corn and 70% rice flour, W7C3= 70% wheat and 30% corn flour, W5C5 = 50% wheat and 50% rice flour, W3C7 = 30% wheat and 70% corn flour, W7R3 = 70% wheat and 30% rice flour, W5R5 = 50% wheat and 50% rice flour, W3R7= 30% wheat and 70% rice flour. The mean with the same letter are not significant different.

ANOVA results showed significant differences between onset temperatures (T_{onset}) for 100% wheat flour batter and other batter samples used in the study. The onset temperatures for batters containing rice and corn flours were not significantly different. Onset temperature indicates the onset of structure development related to initialization of starch gelatinization or other structure related processes during heating. The different result obtained with wheat flour is attributed to gluten gelation which occurred at a lower temperature than starch (Olewink and Kulp, 1993). There was a significant difference between G'_{max} for corn and rice, and corn and wheat flour based batters. The corn based batter showed higher G'_{max}, whereas rice flour showed lower G'_{max}. Corn flour has higher fat and starch contents compared to the other flours. This may have been an explanation for the increased elastic characteristics. Rice flour has more free water than wheat flour resulting in lower elastic behaviour, and only reached the G'_{max} at a higher temperature (78.6 °C). This implied that rice based batters require more time for complete gelatinization than corn and wheat based ones do. Corn based batters showed higher G" than rice and wheat based since corn flour has a higher flow characteristic than rice and wheat based. Wheat flour greatly influence G' and G'' of either corn or rice based batters. G' and G" were reduced with increasing wheat flour proportion in batter systems. Similar results were reported by Sanz et al. (2005) who showed that both storage and loss moduli were higher in batters where wheat flour was partially replaced by corn starch.

Corn flour with higher G' and G" values dominated the viscoelastic behavior in combined flour systems. There were also synergistic effects of combined flours on properties of batter systems.

Figures 5.5 and 5.6 show the effect of salt on storage and loss modules of the batter systems, respectively. Salt lowered the storage moduli G and the loss moduli G'' in all samples. This is due to the influence of salt on the dynamic properties, which apparently resulted in a distinctly more viscous behavior. Llorca et al. (2001) explained that salt affected the solubilization of gluten proteins in wheat flour resulting in decreasing consistency coefficients. Similar results were also described by Salvador, Sanz, and Fiszman, (2003). The results indicate that salt containing products would be less elastic than those samples that do not contain salt.

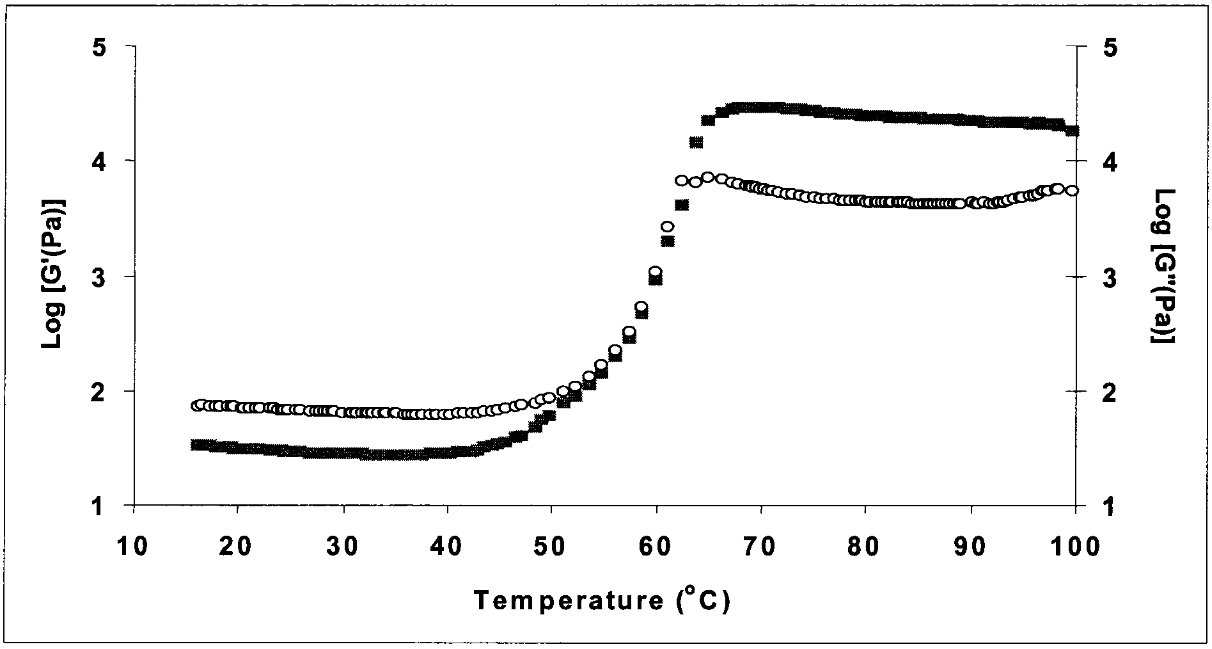

Figure 5.4 Dynamic oscillatory rheological curve on storage modulus and loss modulus of wheat flour. Legend: The solid square (■) refers to storage modulus (G') whereas the open circle (○) refers to loss modulus (G'').

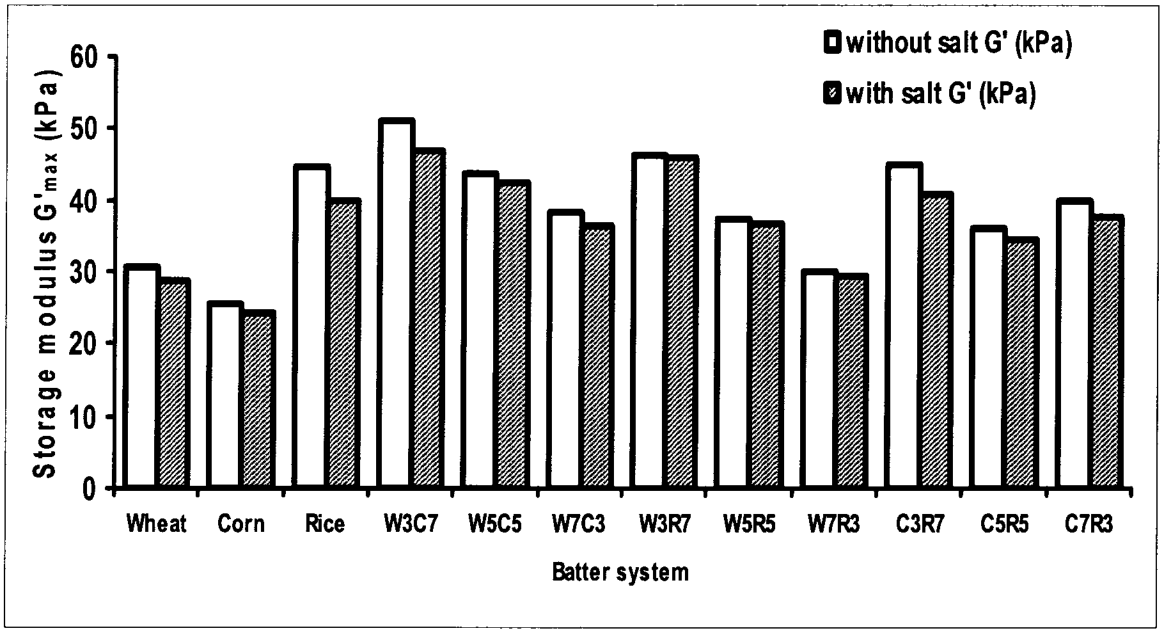

Figure 5.5 Effect of salt on storage modulus of batter systems

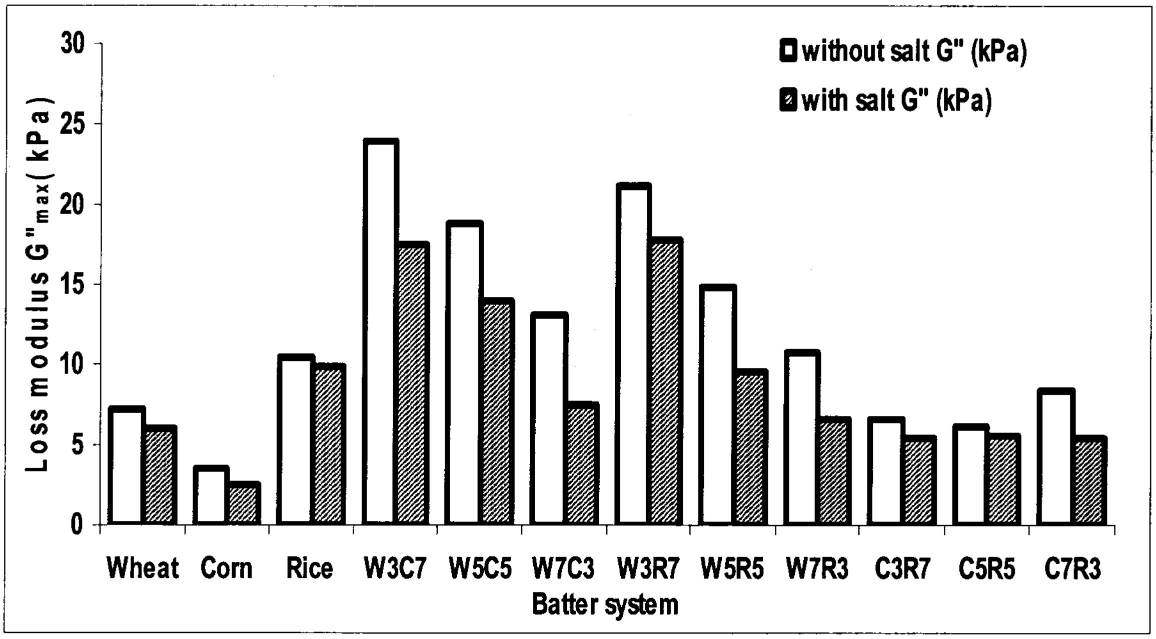

Figure 5.6 Effect of salt on loss modulus of batter systems

5.6 CONCLUSIONS

This study investigated and monitored the rheological properties of different flour combinations, with and without salt in batter systems. It was found that the rheological properties varied with the different types of flours and their combination ratios. The addition of corn flour greatly influenced viscosity and viscoelastic properties of wheat based and rice based batter systems as viscosity decreased with an increase of the corn flour proportion in the batter system. Both corn and rice reduced the viscosity and increased the onset temperature (T_{onset}), storage module (G'_{max} Peak value) and loss module (G''_{max} peak value) of wheat flour based batter systems. Salt significantly influenced the flow properties of batter systems by lowering the viscosity and decreasing G'_{max} and G''_{max} as well as increasing the onset temperature. A higher temperature and longer time was required to gelatinize starch at higher proportions of rice flour (70%) for each flour mix combination in the batter systems tested in this study.

5.7 IMPLICATIONS FOR BATTER PREFORMANCE

A thin, low viscosity batter capable of releasing a large quantity of water produces a porous coating that absorbs a lot of oil. There is a strong positive relationship between oil uptake and water removal. Moreover, a coating layer that is too thin (eg. a 100% rice flour based batter) is difficult to handle during processing, and the coating (batter) maybe easily blown off from the food substrate during the frying. That directly affects the product's yield and quality, as well as providing a poor fat barrier effect during frying. Rice and corn flour batters have very low viscosities, and partial replacement with wheat flour could adjust the viscosity of these batters to an appropriate requirement for batter handling or coating processing. A layer that is too thick (eg. a 100% wheat flour based batter) can lead to an incompletely cooked final product, lack of crispness, high fat content, and a generally hard, lumpy, unattractive appearance. This may be in part attributed to the high viscosity of batters that reduced the heat transfer rate during thermal processing. On the other hand, the reduced viscosity occurring when rice or corn is used to replace wheat flours can also have some advantages.

A batter with a high yield stress value (eg. a 100% corn flour based batter) requires continuous mixing to maintain the solids in suspension during processing due to the tendency for the batter solids to settle out, and sediment in the bottom of the tank. This requires additional equipment (blender) and energy to operate in order to maintain a uniform batter. Also, the viscosity of the batter tends to change throughout the production period, again resulting in irregular batter pickup and inferior end product quality. Therefore, some replacement with wheat flour can be used for stabilizing corn flour solids in suspension, due at least in part to the wheat gluten effects. Rice flour does not have the ability to stabilize solids in suspension because it lacks wheat-type gluten and adhesion properties. Therefore, the adjustment of the amount of flour replacement in batter system is very important to maintain optimum batter functionality and performance.

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CONNECTING TEXT

The changes in the rheological properties of batter systems that depended on the different types of flour and combination ratios were observed in chapter V. Chapter VI describes how xanthan gum (XG) and methylcellulose influence the flow behavior and viscoelastic properties of various batter systems. The Herschel-Bulkley model was used to describe the flow characteristics of batter systems. The linear viscoelastic properties were monitored during heat processing.

VI. RHEOLOGICAL PROPERTIES OF BATTER SYSTEMS CONTAINING DIFFERENT COMBINATIONS OF FLOURS AND HYDROCOLLOIDS

6.1 ABSTRACT:

The rheological properties of batters formulated using different combinations of wheat, corn, and rice flours with two types of hydrocolloids, namely methylcellulose (0.5, 1 and 1.5%) or xanthan gum (0.2%), were studied. Control samples were formulated with combinations of flours without the added hydrocolloids. The effects of hydrocolloids on the rheological flow characteristics of the batter systems were measured using a controlled stress rheometer at a temperature of 15°C. The effects of hydrocolloids on dynamic viscoelastic parameters as functions of temperatures were evaluated. All the batters showed shear thinning behavior with flow behavior indices in the range from 0.34 to 0.67. Addition of xanthan gum lowered the flow index values, imparting a higher degree of pseudoplasticity to the batter samples compared to methylcellulose. The consistency index of the control batter samples varied from 0.46 to 69.2 $Pa.s^n$. Addition of xanthan gum or MC significantly increased the batter consistency index value. The gums changed the onset temperature of structure development, and the storage (G'_{max}) and loss moduli (G''_{max}) of the batter systems. However, no statistically significant effects were observed on the peak temperature of batter systems in which the G' reached maximum value. Xanthan gum increased both G'_{max} and G''_{max}, whereas at higher concentrations, methylcellulose increased G'_{max} but lowered G''_{max}.

6.2 INTRODUCTION

Batters are among the common and vital components of most successful food coating systems. Batters link the fundamentals of food science with the product needs. The proper selection and application of batters influences the flavour, appearance, eating characteristics, performance, and cost effectiveness of final coated product. In addition to the obvious benefits of taste, colour and texture, batter systems also improve the yield and keeping qualities and withstand the demands of processing, distribution, and final preparation for the table.

Tempura type batters are chemically leavened, and they normally form a crispy, light, and puffy texture on seafoods and vegetables. The most common flour used in batter system is wheat flour. However, wheat flour absorbs more oil during deep-fat frying compared with rice flour (Shih and Daigle, 1999; Mukprashirt et al., 2000). Mukprasirt et al. (2000) reported that batters formulated with rice flour alone would produce an inferior product due to the absence of gluten that contributes to viscoelasticity. Thus, rice flour batters do not develop high viscosity like batters made with wheat flour. Studies have shown that apparent viscosity was highly correlated with batter adhesion (Cunnigham and Tiede, 1981; Lane et al., 1986). Corn flour is cheap, and could provide a natural golden color and increase crispness (Burge, 1996; Fiszman and Salvador, 2003) but it has a high crude fat content and it is difficult to maintain solids in suspension during processing (Fiszman and Salvador, 2003). Therefore, combining different types of flours may provide special effects. Also some functional ingredients can be used to enhance these effects to produce more appealing and healthy food products. However, the behaviors of these combination flours with the addition of functional ingredients in batter systems during processing have not been studied at a superstructure level.

Hydrocolloids are water-soluble, high molecule weight polymers with the ability to thicken or gel in aqueous solutions. Hydrocolloids are used in batter systems as functional ingredients in order to improve batter performance by controlling viscosity and increasing adhesive strength, stabilizing solids suspension, and increasing the water holding capacity to obtain specific textural characteristics (Ferrero and Zaritzky, 2000; Kruger et al., 2003). They are also used as a barrier to prevent water loss and oil uptake during frying because some gums can create gel films during heating (Meyers, 1997; Hsia et al., 1992; Balasubramaniam et al., 1997; Annapure et al., 1999; Holownia et al., 2000; Albert and Mittal, 2002; Mellema, 2003 and Sanz et al., 2004). Methylcellulose (MC) has unique thermal gelation abilities and it is mostly used in the batter industry for reducing oil uptake (Meyers and Conklin, 1990; Sanz et al., 2005). Xanthan gum (XG) is widely used in the food industry. Its popularity could be attributed to its unique properties such as uniform viscosity over a wide temperature range (0-100 ^{o}C), and its compatibility and stability in salt solutions (Peettitt, 1982, Urlacher, 1997). However, xanthan gum has been reported to impart an adverse effect on product quality such as a chewy texture when it is used at more than 0.2% (Kuntz, 1995).

Rheological properties are among the most important physical properties that define batter behaviour. It is also important to determine how the batter system behaves as it moves from a static to a dynamic environment. Changes in the rheological properties of a material reveal changes in its molecular structure. Consequently, the rheological properties of a material influence its flow process and are themselves influenced by the structural changes generated during the process. These structure changes could directly affect the appearance and final texture of the finished products. Ferrero and Zaritzky (2000) reported the effects of certain hydrocolloids in retarding or inhibiting starch retrogradation. The highly hydrophilic characteristics of these gums may decrease water availability causing decreased starch dispersion and gelatinization. Sanz et al. (2005) observed that methylcellulose influenced the rheological behaviors of wheat starch and modified corn starch. Kim and Yoo (2005) showed that the results of the increase in rate constant (*k*) in the gelation of rice starch-xanthan gum mixtures were a function of xanthan gum concentration. Therefore, as a consequence, addition of hydrocolloids should modify the rheological properties of batter systems.

However, there have been only a limited number of studies on fundamental rheological properties of batters formulated by using different combination flour blends containing hydrocolloids designed for food coatings. This is an important area due to its obvious applications in the food product formulations. In order to achieve a better understanding of the hydrocolloid-flour interactions, the main objectives of this study were to investigate the effects of methylcellulose and xanthan gum on the flow behaviour of batter system composed of different combinations of wheat, rice, and corn flours during a steady shear process, and to determine the changes in their viscoelastic properties during the heating process. This knowledge could be helpful in the development of new batter formulations.

6.3 MATERIALS AND METHODS

6.3.1 Batter ingredients and formulations

Wheat flour (Five Roses All Purpose Flour, Les Cuisines Five Roses Kitchens, QC, Canada), rice flour RL-100 (Riviana Foods Inc., Houston, Tex., USA), yellow corn flour (ADM Milling Co., Lincoln, Nebr., USA), leavening agent (Sodium bicarbonate, H. Cantin Ltd, Quebec, Canada), Methylcellulose (MC, A15C, Dow Chemical Company, MI, USA), and xanthan gum (TIC Gums Inc, Maryland, USA) were used in the study. The characteristics of the flour samples, according to the flour's manufacturers, are presented in Table 4.1.

The flour blends were prepared in this study as described in an earlier study (Xue and Ngadi, 2006). The batter systems were formulated with different combinations of flour, methylcellulose (0, 0.5, 1.0, or 1.5%) or xanthan gum (0 or 0.2%) on a flour dry weight basis Other ingredients included 2.5% salt, 3.1% leavening agent ($NaHCO_3$, Sodium bicarbonate). All ingredients were added on a flour dry weight basis (expressed as a percentage of g ingredients kg^{-1} dry flour). To formulate batters, the MC or xanthan gum powder was first dispersed in the total amount of cold distilled water (8 ± 2 °C) required for the batter, and mixed. This water temperature was chosen because it has been reported to enhance the gelling ability of MC (Sanz et al., 2004). After the hydrocolloid was totally dissolved, the dry ingredients (flour, salt, and leavening) were added to the hydrocolloid solution and mixed thoroughly until the batter was uniform and free of lumps. All the samples were prepared with the same water-to-solids ratio. Therefore, their apparent rheological property values would indicate the functional contribution of the ingredient to the mixture. All batters were prepared with water to dry-mix in the proportion (w/w) of 1.3:1. The moisture content of the batter sample was confirmed to be about 55.6% (wet basis) by drying the samples in an oven set at 105 °C. Batter samples were kept for at least 45 min. at 10 ± 2 °C to allow the hydrocolloids to completely hydrate and to develop a gel before measuring the rheological properties.

6.3.2 Rheological measurement

Measurements of the rheological properties of batters were performed using a strain/stress control rheometer (Advanced Rheometer 2000, TA Instruments, Delaware, USA). The 4 cm diameter parallel plate was used in the study because parallel plate geometry allowed gap flexibility. The gap between the plates was set to 1 mm, which was considered large enough with regards to the flour particle size. Rheological characterization was carried out using both stationary shear flow and oscillatory tests. The free surface of the sample edges was covered with silicone oil and a steel cover to minimize dehydration of the samples during the measurements. Before conducting any rheological measurements, the samples were allowed to rest in the measurement position for 5 min equilibration time to allow the stresses induced during sample loading to relax.

6.3.2.1 Flow behavior

To determine the flow behavior of the batters, apparent viscosity was measured as a function of shear rate over the range 0 to 150 s^{-1} at temperature of 15°C. The temperature was chosen since it had been considered necessary to maintain a fairly tight control on the cold-water viscosity of batter out of the mixer and onto the batter applicator. Normally, pseudoplastic behavior describes many fluids and is characterized using the general power law model. The power law model with the yield stress is called

Herschel–Bulkley (Mukprashirt, 2000). Therefore, in order to describe the variation in rheological properties of samples under steady shear, the data was fitted to the Herschel-Bulkley.

6.3.2.2 Viscoelastic properties

The linear viscoelastic properties were monitored as a function of temperature and were determined using a dynamic oscillatory test. After equilibration at the initial temperature of 15°C for 5 min, the samples were continuously heated to 100 °C at 4°C/min. During the heating process, the samples were sheared at a fixed frequency of 1 Hz with maximum strain amplitude of 1.074% which was selected from preliminary test to guarantee the existence of a linear viscoelastic response. The preliminary test performed in strain sweep mode, and the tests were made by varying the strain amplitude from 0 to 100%. At least two replications of each oscillatory shear test were conducted TA rheometer Data Analysis Software (Version VI. 2.5) was used to obtain the experimental data and to calculate the storage modulus (G') and the loss modulus (G") that are used to describe the batter viscoelastic behaviors. Also, the onset temperature (T_{onset}) that indicates when the structure of the batter system starts to change by G' or G" increased dramatically, and the peak temperature ($T_{G'}$) was measured at the point that the storage modulus reached its maximum value.

6.4 STATISTICAL DESIGN AND ANALYSIS

All experiments were conducted using factorial experimental designs and analyses. The batter systems were prepared and tested in triplicate in a completely randomized design. An analysis of variance (ANOVA) using the General Linear Model

(GLM) was used to study the differences in batter formulations, such as the main factors and their combined effects including: ratio and type of combined flours, and the levels of methylcellulose and xanthan gum. The significance of mean comparisons by the Scheffe's least significant difference (LSD) were determined at $P<0.05$ using the SAS software (SAS Institute Inc., Cary, NC, USA).

6.5 RESULTS AND DISCUSSION

6.5.1 Effect of hydrocolloids on flow behavior properties of batter systems

Flow behavior of the batters was determined by changing shear rate from 0 to 150 s^{-1}. The Herschel-Bulkley Model (Equation 1) adequately described the experimental data for the flow curves of all samples (R^2 varied from 0.87 to 0.98).

$$\sigma = \sigma_o + \kappa \dot{\gamma}^n \quad (1)$$

Where σ is shear stress (Pa); σ_o is yield stress (Pa); κ is the consistency coefficient (Pa s^n); $\dot{\gamma}$ is shear rate (1/s), and n is the flow behavior index (dimensionless). Three replications of each flow curve gave good reproducibility since the difference between duplicates was less than 5%. All batters showed shear thinning behavior with the flow behavior index less than one as shown in Table 6.1. Analysis of variance (ANOVA) showed that the types of flour and hydrocolloids used in formulating a batter significantly influenced variations in the flow behavior index (n) of the batter system. Addition of xanthan gum consistently lowered the flow behavior index of batter. Thus, xanthan gum induced increased shear-thinning characteristics to the batter. This may be attributed to xanthan gum's unique rigid, rod-like conformation that is more responsive to shear and the required progressive alignment of the rigid molecules during shearing (Peettitt, 1982; Urlacher and Noble, 1997). Kim and Yoo (2005) reported increasing shear-thinning behavior with increasing xanthan gum concentration in rice starch–xanthan gum mixtures. These results are also consistent with observations in other systems, namely wheat starch–xanthan gum mixtures (Sajjan and Rao, 1987) and corn starch–xanthan gum mixtures (Sudhakar et al., 1996). A lower concentration of xanthan gum, compared to methylcellulose (MC), was required to lower n values, indicating its higher degree of pseudoplasticity.

Comparison of means indicated that there was no significant difference between the n values for control samples and 0.5% MC batters samples. However, increasing MC concentrations from 0.5 to 1.5% significantly lowered n values and increased shear-thinning behavior of batter. The degree of shear thinning pseudoplasticity typically increases with increasing MC concentration in a solution (Grover, 1982). Similar results have been reported by Sanz et al. (2004) and Mukprashirt et al. (2000) in their wheat flour batters and rice flour batters, respectively. The influence of MC was more pronounced in batters formulated with various combinations of rice and corn flours. There was no significant difference between n values obtained for control batter samples (100% wheat flour), W7C3 (combination of 70% wheat and 30% corn flour) and W7R3 (combination of 70% wheat and 30% rice flour). It is known that rice flour absorbs less water (thus it leaves more available water) than corn flour with the same solid content (Hoseney, 1994). Wheat flour absorbs more water (therefore leaving less available water) than the other flours due to its higher gluten content. There is apparently more free water available for MC hydration in rice based batters. The influence of MC in batter is attributed to its intrinsic gelation properties. It may also be related to the availability of free water in the batter necessary for the gum to hydrate adequately (Hoseney, 1994; Ribotta et al., 2005).

Table 6.1. Effect of xanthan gum (XG) and methylcellulose (MC) on flow behavior index (n) of the batter systems

Batters	**Control**	**0.2% Xanthan**	**0.5%MC**	**1.0%MC**	**1.5%MC**
Wheat	0.46 ± 0.02	0.35 ± 0.01	0.47 ± 0.01	0.45 ± 0.01	0.45 ± 0.02
Corn	0.58 ± 0.01	0.48 ± 0.02	0.68 ± 0.02	0.56 ± 0.02	0.51 ± 0.01
Rice	0.71 ± 0.03	0.51 ± 0.01	0.65 ± 0.01	0.53 ± 0.01	0.49 ± 0.01
W3C7	0.60 ± 0.03	0.36 ± 0.01	0.51 ± 0.02	0.53 ± 0.02	0.53 ± 0.01
W5C5	0.48 ± 0.01	0.35 ± 0.02	0.50 ± 0.02	0.53 ± 0.01	0.53 ± 0.01
W7C3	0.48 ± 0.02	0.37 ± 0.01	0.48 ± 0.01	0.51 ± 0.01	0.49 ± 0.01
W3R7	0.52 ± 0.02	0.38 ± 0.01	0.49 ± 0.01	0.49 ± 0.01	0.55 ± 0.01
W5R5	0.50 ± 0.02	0.33 ± 0.01	0.45 ± 0.01	0.47 ± 0.01	0.48 ± 0.02
W7R3	0.49 ± 0.01	0.35 ± 0.01	0.45 ± 0.01	0.46 ± 0.01	0.50 ± 0.01
C3R7	0.57 ± 0.02	0.53 ± 0.02	0.57 ± 0.02	0.56 ± 0.02	0.52 ± 0.01
C5R5	0.65 ± 0.03	0.48 ± 0.01	0.61 ± 0.01	0.55 ± 0.01	0.51 ± 0.01
C7R3	0.66 ± 0.01	0.55 ± 0.02	0.64 ± 0.01	0.60 ± 0.01	0.47 ± 0.02

Wheat = 100% wheat flour, Corn = 100% corn flour, Rice = 100% rice flour, W3C7 = 30% wheat and 70% corn flour, W5C5 = 50% wheat and 50% corn flour, W7C3= 70% wheat and 30% corn flour, W3R7= 30% wheat and 70% rice flour, W5R5 = 50% wheat and 50% rice flour, W7R3 = 70% wheat and 30% rice flour, C3R7 = 30% corn and 70% rice flour, C5R5 = 50% corn and 50% rice flour, C7R3 = 70% corn and 30% rice flour.

Consistency index (k) of the control batter samples varied from 0.46 to 69.2 Pa.s^n. These values are in the range (4.35 to 22.66 Pa.s^n) reported by Mukprasirt et al. (2000) for rice flour based batters containing methylcellulose. The values varied according to flour type and their combinations as was also reported by Xue and Ngadi (2006). Addition of hydrocolloids significantly increased the consistency index of all batter systems.

The effect of xanthan gum on batter consistency index (k) for different batter system formulations at 15 °C is shown in Figure 6.1. Addition of xanthan gum increased the consistency index value in the rice flour based batters much more than in the wheat or corn flour based batters. There was also a pronounced effect of xanthan gum on batters formulated with combined corn and rice flour batters. This could again be attributed to availability of more free water in the rice and corn based batters, allowing the gum to develop its viscosity in the batter systems. It is responsible for the effectiveness of xanthan gum in stabilizing suspensions against separation as rice and corn flours easily sediment in flour suspensions (Fiszman and Salvador, 2003; Peettitt, 1982). Similar results were obtained when MC was added in the batter as shown in Figure 6.2. Increasing the concentration of MC from 0.5 to 1.5% increased the value of consistency index. These results are in agreement with the work of Mukprasirt et al. (2000), Sanz et al. (2004), Wang et al. (2001), Kim and Yoo (2005) in different systems.

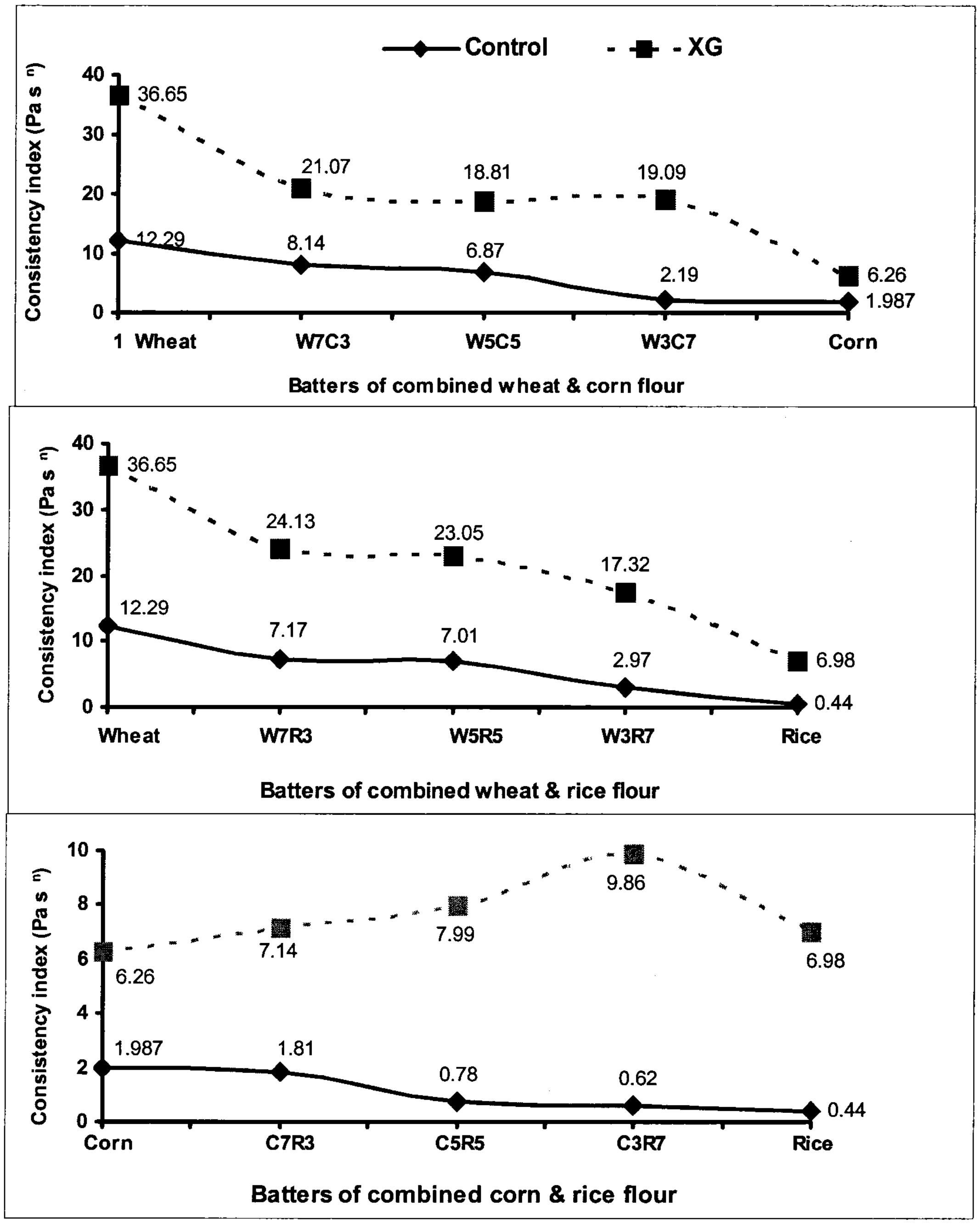

Figure 6.1 . Effect of 0.2 % xanthan gum (XG) on the consistency index of batter systems with (a) wheat to corn flour, (b) corn to rice flour, (c) wheat to rice flour (wheat to corn flour means that from left to right, the proportion of wheat flour decrease from 100% to 0% which is 100% corn flour. The meaning of wheat to rice flour and corn to rice flour is same as wheat to corn flour).

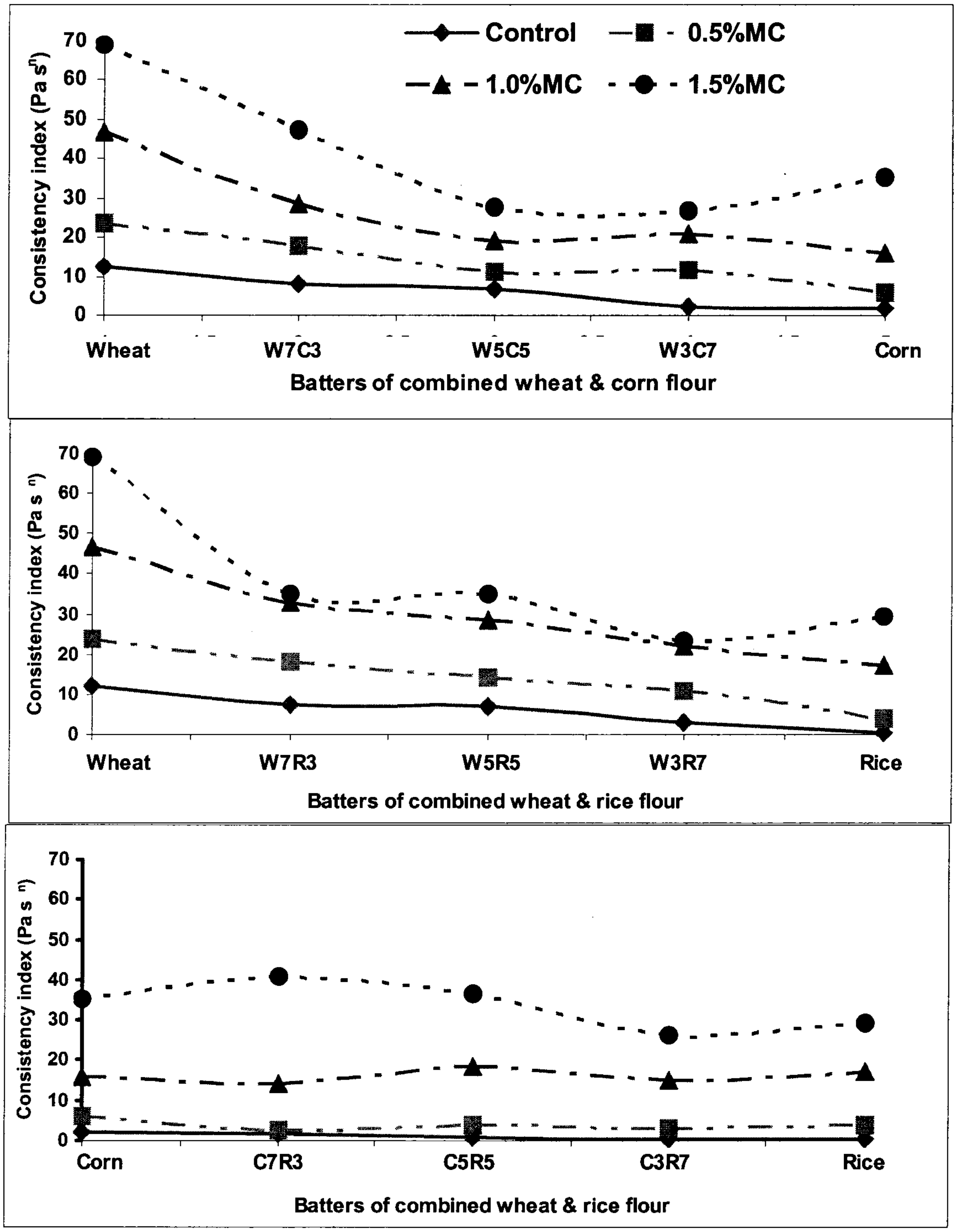

Figure 6.2 Effect of methylcellulose (MC) on the consistency index of batter systems with (a) wheat to corn flour, (b) corn to rice flour, (c) wheat to rice flour (wheat to corn flour means that from left to right, the proportion of wheat flour decrease from 100% to 0% which is 100% corn flour. The meaning of wheat to rice flour and corn to rice flour is same as wheat to corn flour).

In the case of the control batters that did not contain hydrocolloids, the yield stress values varied from 0 to 2.58 Pa. The 100% corn flour based batter showed the highest yield stress, whereas the 100% rice flour batter did not show a yield stress. Also, its flow behavior parameters fit the power law model very well, with $R^2 = 0.93$, as compared with the Herschel-Bulkley model fit ($R^2 = 0.87$). This might be attributed to there being more free-water in rice flour based batter systems, and the free water could lubricate the particles, enhancing their flow, resulting in a lower yield stress. It is also known that rice starch granules are small and have different surface characteristics, which may affect their interaction with each other and the surrounding water. Suderman (1993) reported that corn-starch solids have a tendency to settle out easily, which changes the viscosity of the batter throughout the production period. This observation could be used to support the suggestion that corn starch solid sediments require more force to initiate the desired flow rate of batters during processing, resulting in a higher yield stress, even though there may be more free water in the 100% corn flour based batters as compared with wheat flour based batters.

The ANOVA results (Table 6. 2) showed that the addition of xanthan gum or MC resulted in significantly higher yield stress values as compared with the control samples. However, no statistically significant differences were observed in the yield stress between batters containing high levels of corn flour (50 to 100%) with or without the addition of 0.5% MC. Xanthan gum or methylcellulose developed viscosity in batter systems and reduced the amount of available free water, subsequently increasing the yield stress required to initiate flow in the batter systems.

Table 6.2. Effect of xanthan gum (XG) and methylcellulose (MC) on yield stress of batter systems

System	Control	0.2% Xanthan	0.5%MC	1.0%MC	1.5%MC
Wheat	1.47 ± 0.18	5.56 ± 0.46	1.58 ± 0.07	1.94 ± 0.09	2.41 ± 0.12
Corn	2.58 ± 0.48	2.68 ± 0.32	2.29 ± 0.77	2.71 ± 0.14	3.38 ± 0.31
Rice	0.00 ± 0.02	0.60 ± 0.07	0.07 ± 0.01	0.88 ± 0.03	0.64 ± 0.09
W3C7	0.68 ± 0.01	2.94 ± 0.13	0.75 ± 0.12	0.82 ± 0.04	1.15 ± 0.12
W5C5	0.89 ± 0.03	3.42 ± 0.24	0.83 ± 0.32	0.91 ± 0.12	1.06 ± 0.08
W7C3	0.70 ± 0.04	2.85 ± 0.32	1.59 ± 0.41	1.49 ± 0.23	2.32 ± 0.11
W3R7	0.04 ± 0.01	2.58 ± 0.09	0.42 ± 0.06	0.55 ± 0.06	0.76 ± 0.09
W5R5	0.34 ± 0.06	4.50 ± 0.42	0.59 ± 0.08	1.31 ± 0.51	1.39 ± 0.14
W7R3	0.47 ± 0.07	4.65 ± 0.34	1.41 ± 0.13	1.43 ± 0.31	1.61 ± 0.11
C3R7	0.01 ± 0.01	1.13 ± 0.18	0.07 ± 0.01	0.54 ± 0.02	0.62 ± 0.06
C5R5	0.05 ± 0.01	1.25 ± 0.09	0.20 ± 0.03	0.50 ± 0.01	0.61 ± 0.04
C7R3	1.50 ± 0.21	4.60 ± 0.53	1.53 ± 0.09	3.33 ± 0.34	3.94 ± 0.62

Wheat = 100% wheat flour, Corn = 100% corn flour, Rice = 100% rice flour, W3C7 = 30% wheat and 70% corn flour, W5C5 = 50% wheat and 50% corn flour, W7C3= 70% wheat and 30% corn flour, W3R7= 30% wheat and 70% rice flour, W5R5 = 50% wheat and 50% rice flour, W7R3 = 70% wheat and 30% rice flour, C3R7 = 30% corn and 70% rice flour, C5R5 = 50% corn and 50% rice flour, C7R3 = 70% corn and 30% rice flour

ANVOA results showed that MC greatly increased the yield stress for all the samples at high concentration (1.0 and 1.5%), but it had different effects on batter systems at the lower concentration of 0.5%. At 0.5%, it did not show a statistically significant influence on the yield stress of 100% wheat flour based batters. It did however significantly lower the yield stress of the 100% corn flour based batter, but it appeared to increase the yield stress of the rice flour based batter. This might be because the effect of wheat gluten was greater than the influence of 0.5% MC, so the wheat gluten dominated the characteristics of the wheat flour based batters. However, in the corn flour based batters, 0.5% MC stabilized the solids in suspension, leading to reduced resistance and resulting in lowering the yield stress. Xanthan gum showed a higher effect on batter yield stress than did MC. Xanthan gum has previously been used to control viscosity of particulate suspension in systems containing materials such as corn flour that are known to affect yield the stress value (Peettitt, 1982). Similar results have been reported by Mukprasirt et al. (2000) and Ma et al.(1995).

6.5.2 Effect of hydrocolloids on structure of batter systems during the heating

In order to investigate changes in the structure of hydrocolloid containing batter systems during a heating process, a small-amplitude oscillatory test was conducted to determine such rheological properties as the onset temperature of structure development (T_{onset}), peak temperature $T_{G'}$ (measured temperature at peak), storage modulus G'_{max} (measured at peak), and loss modulus G''_{max} (measured at peak), which are functions of temperature. The storage and loss moduli for all the various batter systems exhibited similar trends as shown in Figure 6.3. None of the samples showed a significance difference between G' and G" during the dynamic shearing test at temperatures below 50 °C. However, there was a rapid increase in G' and G" for all batters with /without hydrocolloids between 54 and 64 °C, after which G' and G" increased rapidly, indicating an increase in elastic and viscosity properties. This increase was attributed to starch gelatinization resulting in the onset of structure formation during which the fluid-like batter transforms into a solid-like coating. The storage modulus G' of samples reached maximum values (G'_{max}), but subsequently decreased steadily with further heating at higher temperatures, apparently due to the orientation of soluble starch molecules in the shear direction, causing a reduction in the viscosity (Hoseney, 1994).

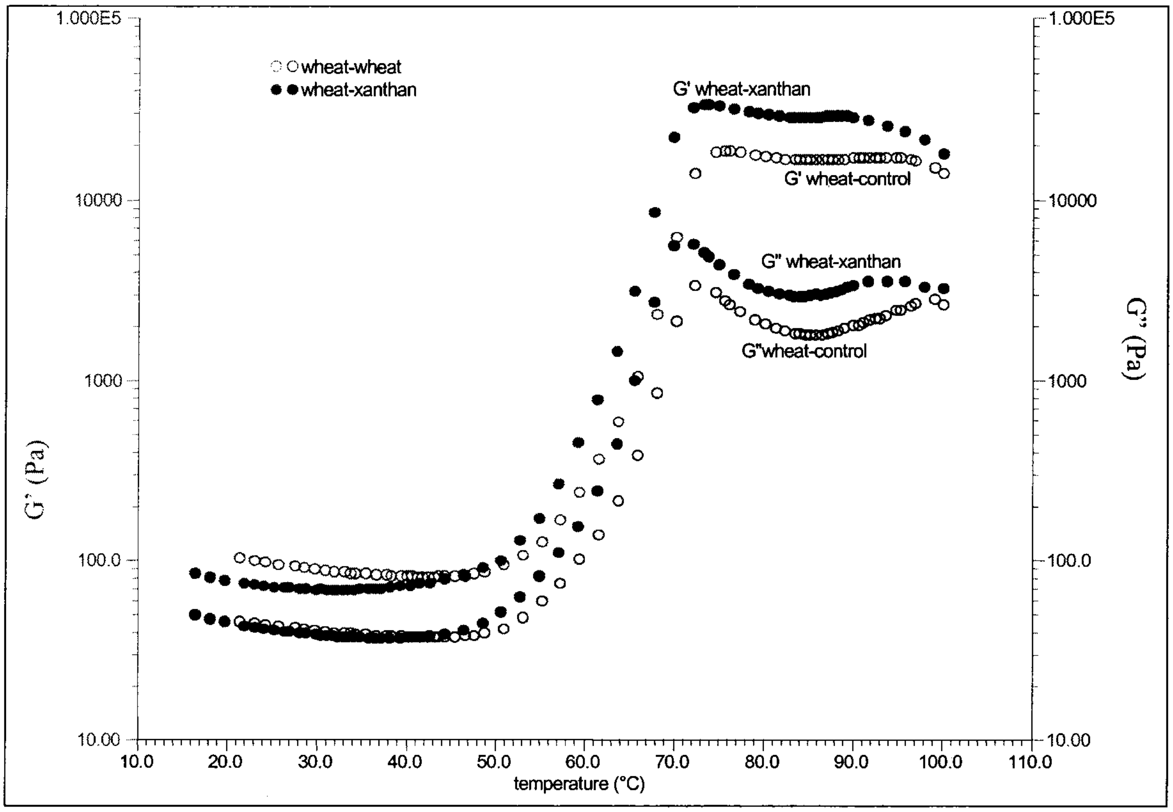

Figure 6.3. Dynamic oscillatory rheological curves of storage modulus and loss modulus of wheat flour and wheat-xanthan batters. Legend: The solid square (■) refers to storage modulus (G') whereas the open circle (○) refers to loss modulus (G'').

ANOVA results showed significant differences between the onset temperatures (T_{onset}) of control and xanthan gum (XG) incorporated batters (Table 6.3). However, the peak temperature $T_{G'}$ did not change significantly among the batters. Onset temperature indicates the onset of structure development related to initialization of starch swelling and readiness to initiate gelatinization or other structure related processes during heating. Peak temperature $T_{G'}$ indicates that the solid structure was formed due to starch gelatinization, achieving maximum values of elastic properties of the material. Xanthan gum absorbs water to develop batter viscosity, apparently resulting in reduced heat transfer, thus greatly influencing the starch swelling process and significantly increasing onset temperature. Consequently, xanthan gum shifted the onset temperature of structure development to higher temperatures. However, it did not influence the peak temperature of structure formation since temperature does not affect its viscosity (Peettitt, 1982). Therefore, a higher temperature and shorter time were required to gelatinize starch when xanthan was added to batter systems.

Xanthan gum significantly increased both the G' and G" of all the batter systems (Table 6.3). This may be attributed to enhancements in overall viscous behavior of flour-XG mixture due to swelling of the starch granules during gelatinization in starch-gum composite system (Alloncle et al., 1989; Adulmola et al., 1996). The increase of elastic behavior of starch in the starch-XG mixture is attributed to the interactions between gelatinized granules enhanced by xanthan gum (Christianson et al., 1981). Alloncle et al. (1989) reported that gum affected the gelatinization and retrogradation of starch through strong association of amylose with gum, resulting in a decrease in the retrogradation of starch. Therefore, xanthan gum influenced batter viscoelastic properties and structure of coating formation during the heating process.

The results of the effect of methylcellulose on structural changes and viscoelastic properties in various batter systems are reported in Table 6.4. Addition of methylcellulose (MC) also significantly increased the onset temperature. However the different MC concentrations did not show any statistical difference for onset temperatures. MC did not affect peak temperatures in any batter samples. This is probably because MC is a food gum that can thermally gel, and thus reduced the amount of water available to react with starch. After MC gelation, dehydration of MC gel apparently caused its molecules to gradually loose their hydrated water as temperature rose and viscosity was reduced (Grover, 1982). This unique thermogelation property of MC significantly affected structure formation during the heating process in which MC delayed the starch swelling and gelatinization process. Thus structure onset temperatures were shifted to higher temperatures. However, structure formation was not affected after starch was gelatinized. Similar results were reported by Mukprasirt et al. (2000)·

Table 6.3. Effect of xanthan gum on dynamic rheological properties of batter systems

	T_{onset} (°C)		T_G (°C)		Storage modulus (G) KPa		Loss modulus(G') KPa	
Batter	Control	Xanthan	Control	Xanthan	Control	Xanthan	Control	Xanthan
Wheat	53.65 ± 0.59	59.35 ± 1.06	73.75 ± 0.81	75.25 ± 1.21	18.97 ± 0.34	27.10 ± 0.21	3.44 ± 0.03	4.71 ± 0.04
Corn	57.13 ± 0.83	66.20 ± 0.87	78.96 ± 0.86	80.10 ± 1.11	42.06 ± 0.28	49.80 ± 0.27	8.25 ± 0.05	9.86 ± 0.04
Rice	67.75 ± 0.71	69.00 ± 1.33	83.60 ± 0.92	84.05 ± 0.28	34.96 ± 0.38	40.00 ± 0.23	5.49 ± 0.06	6.61 ± 0.06
W3C7	53.35 ± 0.62	67.50 ± 0.89	79.10 ± 0.98	80.40 ± 0.93	29.52 ± 0.29	33.24 ± 0.22	5.58 ± 0.01	5.63 ± 0.04
W5C5	59.30 ± 0.62	68.55 ± 0.47	78.90 ± 0.66	79.85 ± 0.98	26.64 ± 0.24	31.11 ± 0.31	5.17 ± 0.02	5.05 ± 0.08
W7C3	56.85 ± 0.46	67.35 ± 0.77	77.95 ± 0.68	78.50 ± 1.25	25.47 ± 0.41	26.73 ± 0.2	4.5 ± 0.03	4.89 ± 0.09
W3R7	61.30 ± 0.35	69.15 ± 0.67	84.20 ± 0.11	84.05 ± 1.19	25.63 ± 0.14	33.39 ± 0.48	3.89 ± 0.06	6.16 ± 0.04
W5R5	61.05 ± 0.53	68.15 ± 0.99	82.65 ± 0.75	84.50 ± 0.62	22.80 ± 0.2	28.77 ± 0.52	3.6 ± 0.02	4.73 ± 0.04
W7R3	61.40 ± 0.7	68.05 ± 0.71	79.20 ± 0.62	76.20 ± 1.38	20.30 ± 0.25	22.59 ± 0.29	3.38 ± 0.03	4.08 ± 0.08
C3R7	58.75 ± 0.79	68.55 ± 0.73	82.50 ± 0.38	83.85 ± 0.2	28.09 ± 0.27	44.75 ± 0.12	4.21 ± 0.02	7.59 ± 0.1
C5R5	62.15 ± 0.58	66.15 ± 0.71	82.30 ± 1.29	82.60 ± 0.51	35.06 ± 0.35	49.44 ± 0.2	5.64 ± 0.03	8.85 ± 0.12
C7R3	63.70 ± 0.37	68.80 ± 0.77	81.80 ± 1.25	80.55 ± 1.24	27.24 ± 0.56	47.02 ± 0.47	4.36 ± 0.03	8.75 ± 0.06

MC significantly increased G' and lowered G'' of batter systems at high concentration of 1.0 and 1.5%. No significant difference was observed between the 0.5% MC and control batter samples, or between batter samples with 1.0 and 1.5% concentrations. This again may be attributed to thermal gelation properties of MC that affect the viscoelastic properties of batter system during heating. Grover (1982) reported that the viscosity of an aqueous solution of MC would initially decrease upon heating. However, there was a substantial increase in viscosity and enhanced development of elastic properties of material resulting in increased G' when the solution gels reached their gelation temperature (52-57°C). Once gelation of MC started, dehydration and association are time-dependent processes in which viscosity decreased with increased time at constant shear rate, resulting in decreased loss modulus G". The concentration did not show any obvious effect after gelation. Therefore, elastic behavior dominated the material's characteristics more than the viscous behavior, for coating formation of batter-MC during the heating process. Sanz et al. (2004) observed similar effect of MC on the viscoelastic behavior of wheat flour batters.

Table 6. 4. Effect of methylcellulose on dynamic rheological properties of batter systems

	T_{onset} (°C)				$T_{G'}$ (°C)			
Batter	Control	0.5%MC	1.0%MC	1.5%MC	Control	0.5%MC	1.0%MC	1.5%MC
Wheat	53.65 ± 0.59	62.80 ± 0.07	63.35 ± 0.92	64.25 ± 1.02	73.75 ± 0.81	74.05 ± 0.59	75.70 ± 0.37	75.50 ± 0.81
Corn	57.13 ± 0.83	64.20 ± 0.02	65.20 ± 0.58	66.34 ± 0.98	78.96 ± 0.86	79.95 ± 0.62	79.25 ± 0.74	78.80 ± 0.66
Rice	67.75 ± 0.71	72.05 ± 0.49	74.75 ± 0.59	75.15 ± 0.78	83.60 ± 0.92	84.70 ± 0.35	84.80 ± 0.62	83.70 ± 0.98
W3C7	53.35 ± 0.62	62.90 ± 0.13	64.25 ± 0.68	65.60 ± 0.69	79.10 ± 0.98	79.50 ± 0.37	79.85 ± 0.72	80.94 ± 0.32
W5C5	59.30 ± 0.62	64.85 ± 0.3	66.10 ± 0.37	67.35 ± 0.58	78.90 ± 0.66	78.15 ± 0.59	78.75 ± 0.58	79.05 ± 0.69
W7C3	56.85 ± 0.46	65.95 ± 1.27	67.10 ± 0.98	68.30 ± 0.74	77.95 ± 0.68	77.90 ± 0.29	78.20 ± 0.12	79.20 ± 1.02
W3R7	61.30 ± 0.35	66.30 ± 0.72	66.35 ± 0.46	69.70 ± 0.45	84.20 ± 0.11	84.40 ± 0.58	85.05 ± 0.69	84.15 ± 0.91
W5R5	61.05 ± 0.53	64.45 ± 0.87	65.35 ± 0.58	69.30 ± 0.87	82.65 ± 0.75	83.20 ± 0.78	84.00 ± 1.02	84.30 ± 0.38
W7R3	61.40 ± 0.7	67.70 ± 0.16	67.98 ± 0.32	68.60 ± 0.69	79.20 ± 0.62	79.15 ± 0.74	79.50 ± 0.53	80.20 ± 0.37
C3R7	58.75 ± 0.79	65.90 ± 0.88	66.25 ± 0.58	67.05 ± 0.24	82.50 ± 0.38	83.65 ± 0.98	83.75 ± 0.29	84.15 ± 0.62
C5R5	62.15 ± 0.58	66.45 ± 0.29	67.15 ± 0.91	67.30 ± 0.72	82.30 ± 1.29	82.45 ± 0.32	82.60 ± 0.58	82.50 ± 0.66
C7R3	63.70 ± 0.37	70.60 ± 0.68	70.50 ± 0.34	71.80 ± 0.69	81.80 ± 1.25	81.25 ± 0.59	82.15 ± 0.91	82.71 ± 0.92

	Storage modulus (G') KPa				Loss modulus(G") KPa			
Batter	Control	0.5%MC	1.0%MC	1.5%MC	Control	0.5%MC	1.0%MC	1.5%MC
Wheat	18.97 ± 0.34	11.41 ± 0.7	15.77 ± 0.05	19.94 ± 0.92	3.44 ± 0.03	3.23 ± 0.02	2.73 ± 0.01	2.16 ± 0.01
Corn	42.06 ± 0.28	40.09 ± 0.29	48.94 ± 0.69	48.84 ± 1.07	8.25 ± 0.05	9.29 ± 0.01	7.21 ± 0.01	7.07 ± 0.02
Rice	34.96 ± 0.38	32.75 ± 0.32	36.45 ± 0.45	39.35 ± 0.32	5.49 ± 0.06	5.99 ± 0.06	4.87 ± 0.02	4.62 ± 0.03
W3C7	29.52 ± 0.29	29.71 ± 0.91	36.23 ± 0.38	37.67 ± 0.2	5.58 ± 0.01	5.97 ± 0.05	4.90 ± 0.03	4.18 ± 0.02
W5C5	26.64 ± 0.24	25.29 ± 1.27	37.18 ± 0.79	38.23 ± 0.26	5.17 ± 0.02	5.90 ± 0.05	4.61 ± 0.02	4.20 ± 0.03
W7C3	25.47 ± 0.41	21.50 ± 0.74	28.05 ± 0.53	27.97 ± 0.74	4.50 ± 0.03	4.62 ± 0.03	3.46 ± 0.01	3.40 ± 0.01
W3R7	25.63 ± 0.14	26.52 ± 0.46	28.88 ± 0.42	29.24 ± 0.53	3.89 ± 0.06	4.02 ± 0.04	3.01 ± 0.03	2.87 ± 0.04
W5R5	22.80 ± 0.2	18.77 ± 0.49	26.07 ± 0.23	27.39 ± 0.45	3.60 ± 0.02	3.26 ± 0.04	2.70 ± 0.02	2.98 ± 0.05
W7R3	20.30 ± 0.25	16.51 ± 0.62	25.00 ± 0.32	34.09 ± 0.38	3.38 ± 0.03	2.78 ± 0.03	2.60 ± 0.02	2.66 ± 0.03
C3R7	28.09 ± 0.27	29.07 ± 0.69	33.15 ± 0.45	36.72 ± 0.69	4.21 ± 0.02	4.73 ± 0.02	3.08 ± 0.03	3.01 ± 0.01
C5R5	35.06 ± 0.35	34.08 ± 0.72	38.08 ± 0.61	38.86 ± 0.7	5.64 ± 0.03	5.62 ± 0.02	4.11 ± 0.03	4.31 ± 0.05
C7R3	27.24 ± 0.56	25.64 ± 0.91	34.93 ± 0.23	44.22 ± 0.05	4.36 ± 0.03	4.78 ± 0.04	3.18 ± 0.01	3.85 ± 0.03

6.6 CONCLUSIONS

This study investigated and monitored the rheological properties of tempura batters formulated using different flour combinations, with and without hydrocolloids. Xanthan gum and methylcellulose significantly influenced the flow behavior, increased the consistency, and lowered the shear-shinning behavior of batters. Xanthan gum showed more pronounced effects on batters containing corn or rice flours or their combined flour blends than on wheat flour based batters. Viscoelastic properties during the heating process were changed with the addition of XG and MC to the batter systems. The gums shifted the onset temperature of structure development to high temperature, but the concentration of MC did not show significant effects on the onset temperature. However, neither xanthan gum nor MC affected the peak temperature. XG and MC significantly influenced the storage and loss moduli of batter systems. Xanthan gum increased both G'_{max} and G''_{max}, whereas MC increased G'_{max} but lowered G''_{max}. A higher temperature and shorter time was required to gelatinize starch when the hydrocolloids were added to batter systems.

6.7 IMPLICATIONS FOR BATTER PREFORMANCE

Xanthan gum and Methylcellulose when incorporated into batter systems greatly increase a batter's viscosity. They also raise the temperature and shorten the time required for the formation of a solids-like structure during heating. When hydrocolloids are used in a formulation, it is important to ensure their effectiveness, complete incorporation and hydration are necessary. The batter uniformity and thickness that is related to the batter's viscosity largely determine the acceptability of the finished products. Corn flour batters are difficult to maintain solids in suspension that they change viscosity during the process and result in non-uniform batter coating systems. The results generated from this study suggested that xanthan gum at 0.2% concentration or 0.5% MC have more effect on stabilizing the solids in suspension than simply its viscosity effect on those batters containing high levels corn flour (greatly than 70% of corn flour, dry basis w/w). However, both of the hydrocolloids increased the yield stress value of all batters formulated with wheat, rice, and their combination flour blends. High yield stress values require more force to initiate flow when mixing or pumping.

The ability of a batter to form a crust is enhanced by the higher initial amount of coating that adheres. There is a linear relationship between coating adhesion and viscosity. Xanthan gum and MC lowered the shear shinning behaviour and increased consistence index. However, it should be noted that high viscosity of batter also has some disadvantages that affect finished products quality such as hard crust and less crispiness. The results generated from this study show that MC has a greater effect on rice or corn flour based batters than on wheat flour batters, possibly because the corn and rice batters have more free water available to interact with the hydrocolloid gums in order to develop their maximum viscosity properties. Wheat flour tends to compete with the hydrocolloid gums for water of hydration. Therefore, the addition of hydrocolloids increases the batter viscosity at a lower temperature, improving the ability of the batter to maintain a uniform consistency and composition during preparation and application. This action should result in a more uniform product coating, but hydrocolloid use may increase the batter costs slightly, and changes the mixing action and power required. Xanthan gum and MC greatly influence solids structure development, which delay the starch swelling process, but they did not show effects on structure formation after the starch gelatinization phase (the G'_{max} temperature that indicates the temperature when G' reaches its maximum value due to starch gelatinization, and develops the higher elastic properties). Therefore, high temperatures and shorter time intervals were required to cook the batters containing hydrocolloids.

Selection a hydrocolloids at properly concentration is very important for batter formulation. The effects of hydrocolloids dependent in which types of flour would be used in batter systems and the batter formulation should match the food substrate that will be coated.

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CONNECTING TEXT

Results reported in Chapter VI showed the synergistic effect of flour and xanthan gum or methylcellulose on the flow behavior of various batter systems such as increased consistency, and lowered shear-shinning behavior of batters. Xanthan gum and methylcellulose also significantly influenced the viscoelastic properties of batter systems during heating. In Chapter VII, the same objectives and parameters as followed in Chapter VI were used to study carboxymethylcellulose's effect on the rheological properties of batter systems, except that the power model was used to describe the flow behavior of the batter systems.

VII. EFFECT OF CARBOXYMETHYLCELLULOSE ON RHEOLOGICAL PROPERTIES OF BATTER SYSTEMS

7.1 ABSTRACT

Batters are highly complex systems with wide ranging ingredients. Interactions between the ingredients determine the performance of batters and the final quality of coated products. Combining different types of flour provide special effects on batter performance. Carboxymethylcellulose (CMC) has been used as a functional ingredient due to its unique properties such as water retention and resistance to oil as well as a certain degree of adhesiveness. The functionalities of CMC-flour mixtures in terms of rheological properties of batter systems were investigated in this study. The combinations of wheat and rice, wheat and corn, rice and corn flours, and CMC at different concentrations of 0, 0.5%, 1.0% or 1.5% were studied. A strain/stress control rheometer was used to determine the rheological properties (flow behaviors and viscoelastic properties) of the mixtures. CMC influenced the flow behavior of batter systems at 15 oC. The viscoelastic properties of the batter systems depended upon formulation and temperatures from 15 to 100 ^{0}C. The higher concentration of CMC also increased the shear thinning behavior of batter systems. CMC greatly influenced the viscoelastic properties of batter systems during heating processes.

7.2 INTRODUCTION

A wide variety of foods can be coated (battered and breaded) before frying. Each product to be coated (substrate) has its particular characteristics in term of structure, size, and cooking parameters. Coatings are normally specialized for each type of food and paired with flavors that match well with each substrate. Initially, batters and breadings were simple: wheat flour, seasonings and water for batters; whereas for breadings, seasoned breadcrumbs affixed with water, milk or egg. However, the technology for these coatings has evolved from its simple early roots. Instead of basic batter, manufacturers have developed a wide variety of batter systems using different flours with functional ingredients such as hydrocolloids to produce delicious and nutritional coated foods to entice the consumer.

Interactions between ingredients determine the performance of batters and the final quality of coated products. Leavened batters are referred to as puff or tempura batters. These light stand-alone batters are typically used for seafoods and vegetables. The industry trend is toward producing lighter batter through selection of batter systems with different flour bases and other ingredients to produce a desired light, crispy and open structure coating form. Ingredients such as hydrocolloids may not directly influence the food taste and flavors, but they may have significant effect on gel formation, water retention, and aroma retention that influence the finished product's quality and consumer appeal (Speers and Tung, 1986; Meyer, 1990; Balasuramaniam, Chinnan, Mallikarjunan, and Phillips, 1997; Annapure, Singha, and Kulkarni, 1999; Holownia, Chinnan, Erickson, and Mallikarjunan, 2000; Sanz, Salvador, and Fiszman, 2004; Sanz et al., 2005). Combining sodium bicarbonate (leavening agent), special hydrocolloids and different flours may also result in different desired flavor, crispy and open texture of coated products.

Carboxymethylcellulose (CMC) is typical of cellulose derivatives that are obtained by chemical modification of cellulose. This ensures their uniform properties such as solubility in cold and hot water, and low to high viscosity in solution, as opposed to hydrocolloids from natural sources that normally have high variability (Guarda, Rosell, Benedito, and Calotto, 2004). CMC has wide applications in food processing as a functional ingredient due to its unique properties such as water retention, resistance to oil as well as certain degree of adhesiveness (Khalil, 1999; Cancela, Alarez, and Maceiras, 2005). Combining different types of flour and incorporating CMC provided special effects on batter performance.

Coated food products undergo several physical and chemical transformations during processing. Gao and Vodovot (2005) reported that CMC changed the rheological and thermal properties of masa (dough) and the resulting tortilla's shelf-life. Andres, Guadalupe, Javier and Luis (2005) also found that CMC greatly influenced the rheological and functional properties of dried nixtamalised (alkaline-cooked) maize masa. However, the applications of CMC in batter systems have not been extensively reported in the scientific literature. Rheological analyses reveal a possible interaction between CMC and the other batter constituents, which could partially explain the effect of this hydrocolloid in complex batter systems. In cooking processing, carboxymethylcellulose (CMC) forms film to keep the batter intact and aid cohesiveness during heating (Keller, 1982). Characterization of CMC and different types of flour behaviors in batter system is important in order to understand their performance and application where they are used jointly.

The objective of this study was to investigate the possible interaction of the CMC with the other batter constituents in order to establish an understanding about the effects of the CMC as a batter improver agent. In this regard, the rheological properties of batters containing different combinations of flours (namely wheat, rice and corn flours) in the presence of CMC, and the resulting batter behaviors during heat processing were studied.

7.3 MATERIALS AND METHODS

Three concentration of carboxymethylcellulose (0, 0.5, 1.0, or 1.5% on a flour weight basis) were used in this study. Batter systems were formulated in this study as described in the chapter VI. The samples that were formulated with no (0%) CMC were considered as the control samples.

The rheological properties of batter were determined using a strain/stress control rheometer (Advanced Rheometer 2000, TA Instruments, Delaware, USA). The 4 cm diameter parallel plate was chosen and the gap between the plates was set to 1 mm. Rheological characterization was carried out using both stationary shear flow and oscillatory tests. To determine the flow behavior of the batters, apparent viscosity was measured as a function of shear rate over the range 0 to 120 s^{-1} at the temperature of 15°C. In order to describe the variation in rheological properties of samples under steady shear, the data was fitted to the power law model (Barnes, Hutton, and Walters, 1989).

The linear viscoelastic properties were carried out by using a dynamic oscillatory test. After equilibration at the initial temperature of 15°C for 5 min, the samples were continuously heated to 100°C at the rate of 4°C/min. During the heating process, the samples were sheared at a fixed frequency of 1 Hz with maximum strain amplitude of 1.074% which was selected from preliminary tests to guarantee the existence of a linear viscoelastic response. The parameters of storage modulus (G'_{max} measured at peak) and the loss modulus (G''_{max}, measured at peak) that were used to describe the batter viscoelastic behaviors. Also, the onset temperature (TR_{onset}) which indicates the temperature at which the structure of the batter system begins to change dramatically, and the peak temperature (T_{peak}) of the storage modulus were determined.

7.4 STATISTICAL DESIGN AND ANALYSIS

All experiments were conducted using factorial experimental designs. The batter systems were prepared and tested in triplicate in a completely randomized design. A Two-way analysis of variance (ANOVA) using the General Linear Model (GLM) was used to study the differences and interaction effect in batter formulations, such as main factors and their combined effects including: ratio and type of combined flours, and the levels of CMC. The significance of mean comparisons by the Scheffe's least significant difference (LSD) were determined at $P<0.01$ using the SAS software (SAS Institute Inc., Cary, NC, USA).

7.5 RESULTS AND DISCUSSION

Flow behaviors of batters were described in terms of consistency coefficient, and flow behavior index, in a power-law model according to the following Equation.

$$\eta = k\left(\dot{\gamma}\right)^{n-1} \qquad (1)$$

where η is the viscosity in Pa s, k is the consistency coefficient in Pa s, $\dot{\gamma}$ is the shear rate expressed in s^{-1}, and n is the flow behavior index. For Newtonian fluid, $n = 1$ that is its viscosity remains constant for different shear stress values. However, viscosity varies ($n \neq 1$) for a non-Newtonian fluid with varying applied stress.

Analysis of variance (ANOVA) showed that CMC significantly influenced the flow behavior index of all samples. All batters were non-Newtonian and exhibited pseudoplastic behavior with flow behavior index less than one (Table 7.1). Wheat flour batter had the lowest flow behavior index compared to corn and rice flour batters. Thus, the apparent viscosity of wheat flour batter was higher at a given shear rate. Wheat flour based batter had more shear thinning behavior than corn or rice flour based batters. This is attributed to the higher ability of the gluten containing wheat flour to bind water in the system resulting in decreased free water for flow (Xue and Ngadi, 2005; Hoseney, 1994). The behavior index of batters decreased with increasing CMC concentration. Thus, increasing concentrations of CMC decreased the shear thinning behavior of batters. It is known that CMC exhibits pseudoplasticity in solution (Keller, 1982). This may be attributed to the orientation of the CMC macromolecules as they align themselves in the direction of the shearing force (Rozema and Beverloo, 1974). Cancela, Alarez, & Maceiras (2005) also observed a similar trend in an aqueous solution of CMC with sucrose.

Table 7.1. Effect of CMC on flow behavior index, n of batter systems

Batter	Control	0.5% CMC	1.0% CMC	1.5% CMC
Wheat	0.46 ± 0.01	0.45 ± 0.01	0.36 ± 0.01	0.34 ± 0.01
Corn	0.59 ± 0.02	0.56 ± 0.02	0.46 ± 0.02	0.41 ± 0.01
Rice	0.71 ± 0.07	0.61 ± 0.02	0.55 ± 0.01	0.52 ± 0.01
W3C7	0.61 ± 0.03	0.51 ± 0.02	0.46 ± 0.01	0.43 ± 0.01
W5C5	0.49 ± 0.01	0.47 ± 0.02	0.40 ± 0.01	0.36 ± 0.01
W7C3	0.48 ± 0.02	0.47 ± 0.02	0.42 ± 0.02	0.38 ± 0.01
W3R7	0.53 ± 0.04	0.48 ± 0.01	0.39 ± 0.01	0.36 ± 0.01
W5R5	0.50 ± 0.02	0.47 ± 0.01	0.43 ± 0.01	0.41 ± 0.01
W7R3	0.49 ± 0.01	0.47 ± 0.01	0.43 ± 0.01	0.39 ± 0.01
C3R7	0.58 ± 0.02	0.57 ± 0.01	0.53 ± 0.01	0.48 ± 0.01
C5R5	0.66 ± 0.02	0.63 ± 0.05	0.54 ± 0.01	0.50 ± 0.01
C7R3	0.67 ± 0.01	0.65 ± 0.01	0.56 ± 0.02	0.53 ± 0.02

Wheat = 100% wheat flour, Corn = 100% corn flour, Rice = 100% rice flour, W3C7 = 30% wheat and 70% corn flour, W5C5 = 50% wheat and 50% corn flour, W7C3= 70% wheat and 30% corn flour, W3R7= 30% wheat and 70% rice flour, W5R5 = 50% wheat and 50% rice flour, W7R3 = 70% wheat and 30% rice flour, C3R7 = 30% corn and 70% rice flour, C5R5 = 50% corn and 50% rice flour, C7R3 = 70% corn and 30% rice flour

There were significant differences in the consistency index of batters containing different levels of CMC concentrations. The effect of CMC on consistency index for different batters formulated at 15°C with different combinations of wheat and corn flour (WC), wheat and rice flour (WR), and corn and rice flour (CR) are shown in Figure 7.1, 7.2, and 7.3, respectively. The results clearly show that CMC increased the consistency index for all batter systems. In other words, increasing the CMC concentration in a batter resulted in more viscous batters. CMC is a linear, long-chain, water-soluble hydrocolloids that can absorb water causing reduced free water in the batter systems. Similar result was reported by Cancela, Alvarez & Maceiraas (2005). Viscosity development in batters is mainly related to the water binding capacity of the ingredients. The consistency indices of batters formulated with only (100%) wheat, corn and rice flour, without addition of CMC were 14.29, 2.14, and 0.46 Pa.s^n, respectively. Addition of 1.5% CMC in these batter systems, increased the consistency indices of the wheat, corn and rice batters to 83.8, 57.4 and 48.7 Pa.s^n (that is 4.86, 25.82 and 104.87% increase), respectively. There was more pronounced effect of CMC on batters formulated with corn or rice, or their combinations than on batters formulated with wheat flour. Among the different ingredients used in this study, wheat flour and CMC have the highest water-binding capacity. The hydroxyl group of CMC enables hydrogen bonding with water whereas wheat flour contains gluten which has a high water binding capacity (Keller, 1982). Thus the consequence of increasing amount of wheat flour and CMC will be less available free water and higher viscosity in a batter system.

Since rice and corn flours absorbed less water compared with wheat flour, there was more free water available for CMC to develop its maximum viscosity as was indicated by the pronounced effect of CMC in these batter systems. However, in wheat flour based batter systems, there was apparently a strong competition for water from wheat gluten, resulting in is less free water available for CMC to develop its high efficiency for viscosity change in the limited water system. Therefore, there was a synergistic interaction between batter flours and CMC on flow behavior of batter systems.

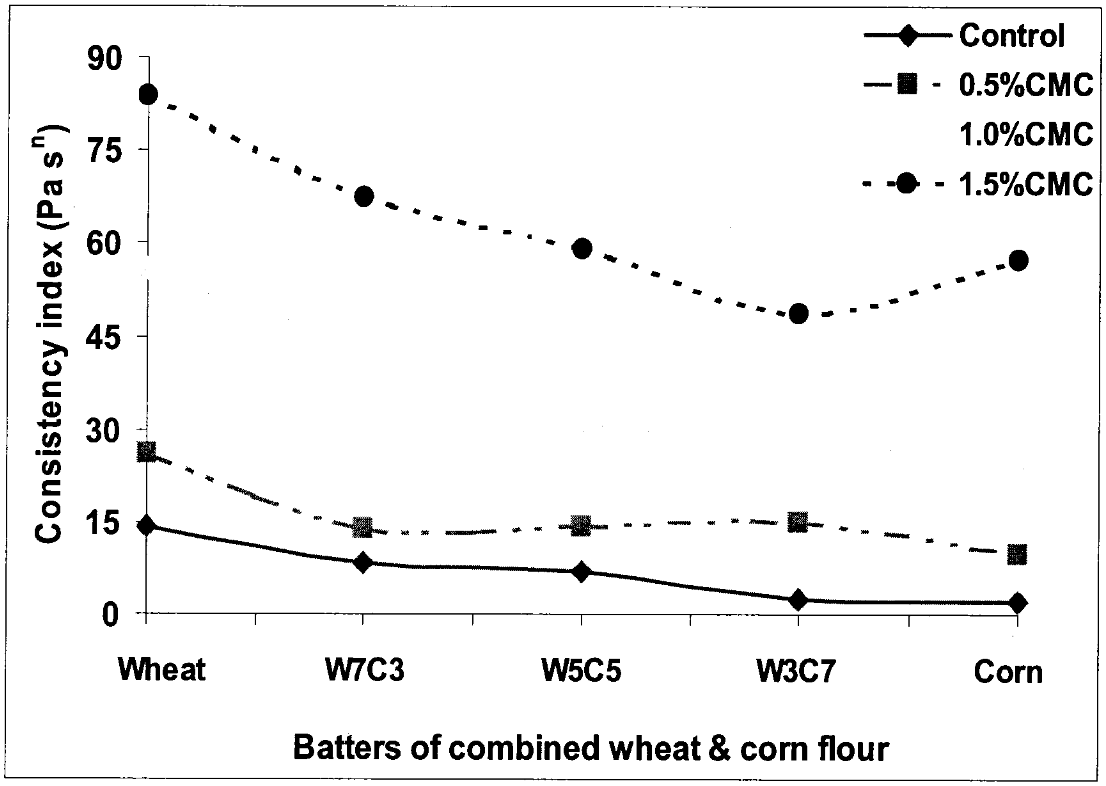

Figure 7.1. Effect of CMC on the consistency index of wheat, corn and their combination flour based batters

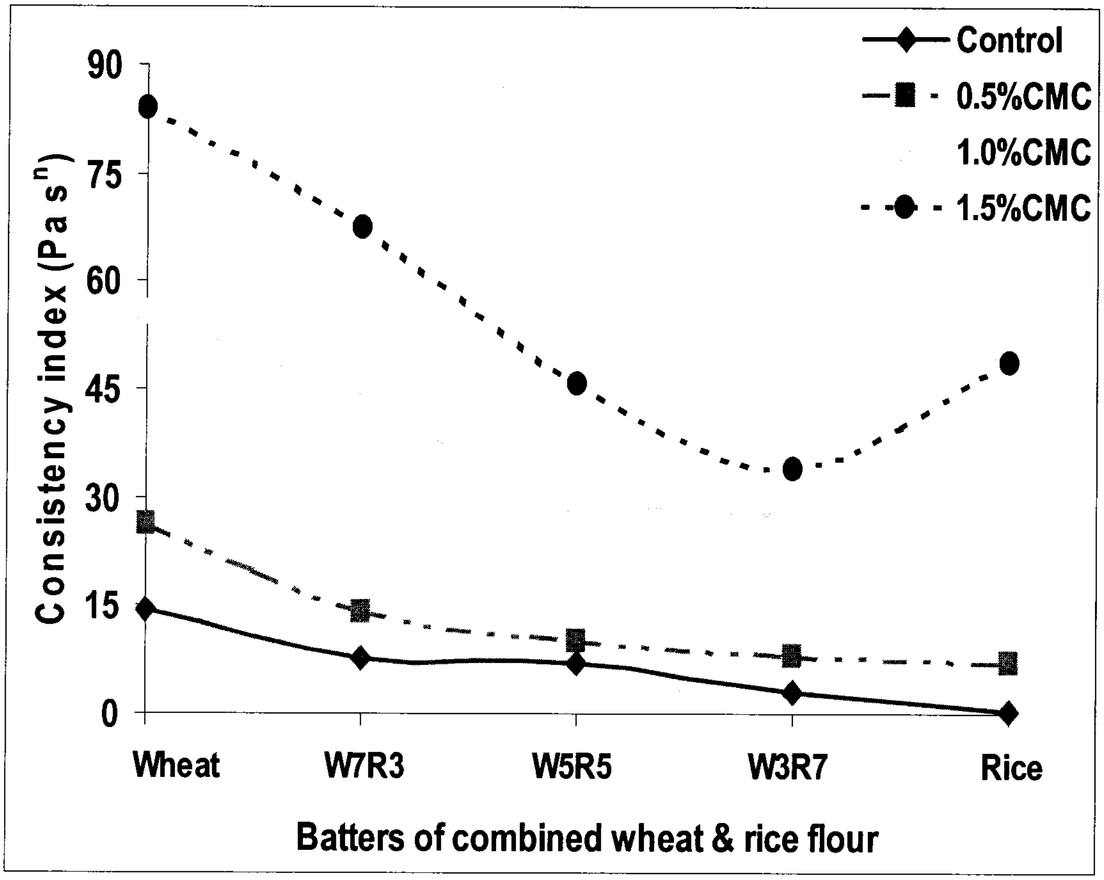

Figure 7.2. Effect of CMC on the consistency index of wheat, rice and their combination flour based batters.

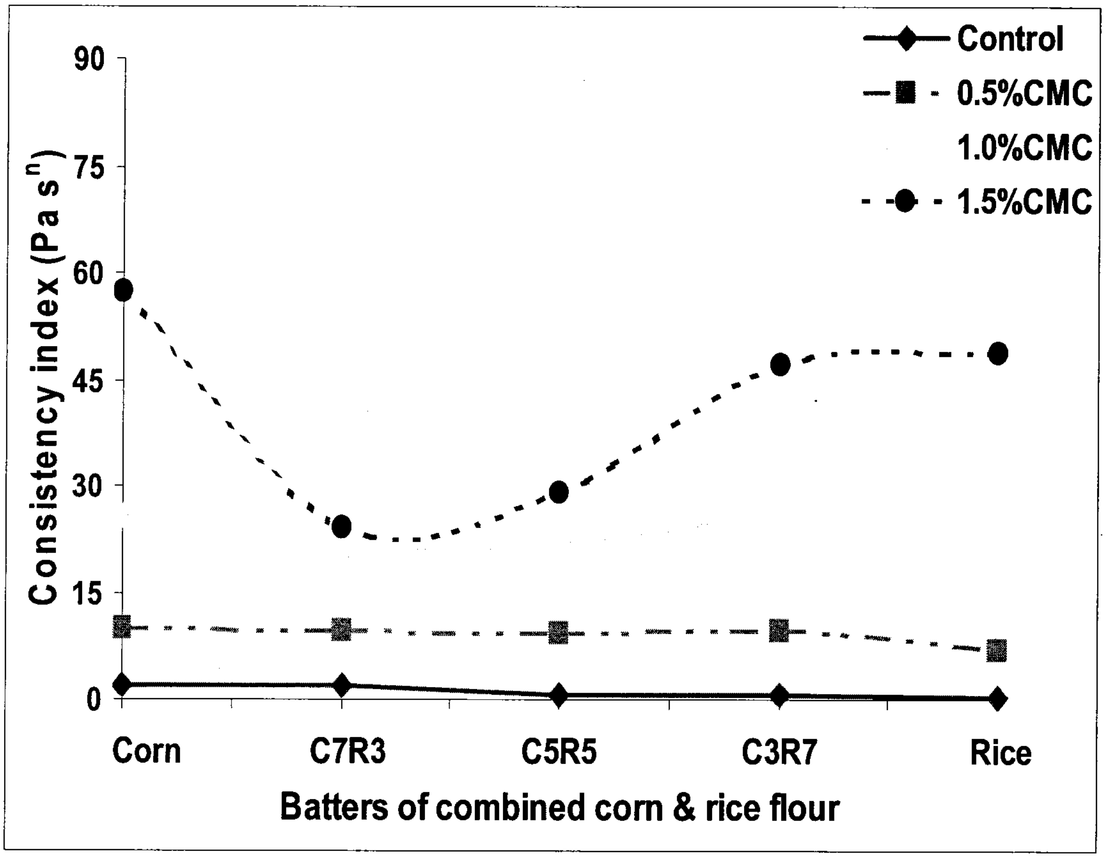

Figure 7.3. Effect of CMC on the consistency index of corn, rice and their combination flour based batters.

Typical changes in storage modulus G' of batter systems containing different concentrations of CMC are shown in Figure 4. Changes in loss modulus (G") of the different batter systems generally followed trends similar to those observed for storage modulus (G') in all samples.

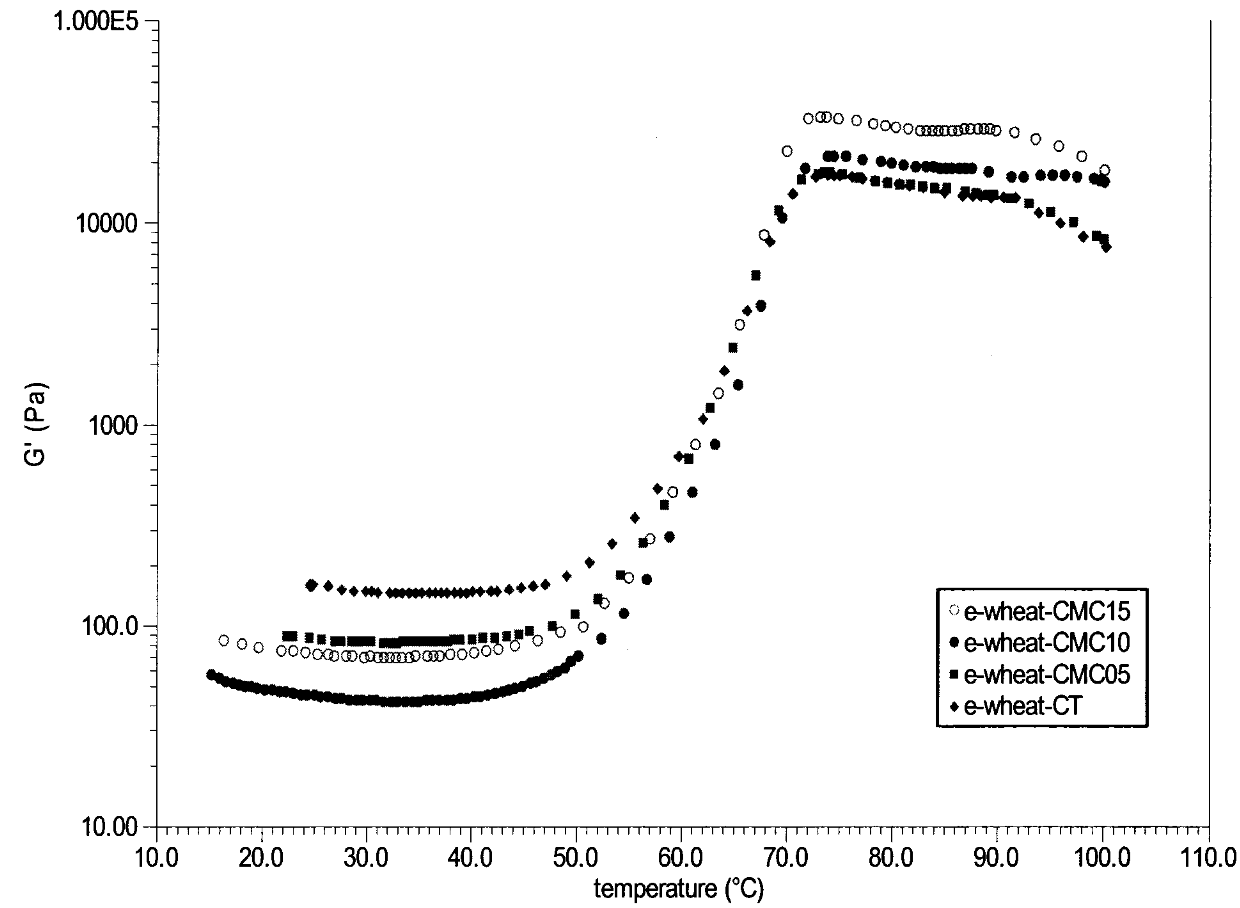

Figure 7.4 Dynamic oscillatory rheological curve on storage modulus of 100% wheat flour and wheat-CMC batter systems. Legend: The (♦) refers to G' of 100% wheat flour based control batter without CMC, the solid square (■) refers to G' of 100% wheat flour based batter with 0.5% CMC, the solid circle (•) refers to G' of 100%wheat flour based batter with addition of 1.0% CMC, the open circle (○) refers to G'of 100% wheat flour based batter with addition of 1.5% CMC.

There was no significant change in G' during the dynamic shearing test at temperatures below 50°C. However, G' increased rapidly for all batters between 58 and 68°C indicating increase in elastic properties. The increase occurred as the starch granules swelled, and started to gelatinize when starch polymer molecules and/or granule fragments reinforced the gel in the formation of a solid-like coating from a fluid-like batter during heating (Liu and Lelievre, 1992). At each corresponding temperatures, the values of G' were higher than the values of G". This implies that the elastic behavior predominated at all temperature in these batter systems (Andres, Guadalupe, Javier and Luis, 2005). Thus, the overall response of the system approached that of a fully formed solid-like structure. The viscoelastic properties of batter systems formulated using different combined flours blends were varied depending on types of flour and combination ratios of the flour blends as was also observed in an earlier study (Xue and Ngadi, 2005).

The onset temperature is the onset of structure development related to how the starch granules swell and initiate gelatinization. Complex reactions between ingredients or flour components may also cause structural changes during heating. The onset temperature was determined at the point where G' started to increase rapidly, whereas peak temperature was determined at the point where G' reached its maximum value. Peak temperature Tpeak indicates the temperature where solid structure was formed due to starch gelatinization, achieving maximum values for the elastic properties of the material. The storage modulus of the samples reached their maximum values (G'max) but subsequently decreased steadily with further heating at higher temperatures due to the molecules of soluble starch orienting themselves in the direction of shear, causing a decrease in viscosity (Hoseney, 1994).

100% of wheat flour based batter had the lowest onset temperatures whereas rice flour only had the highest onset temperature as shown in Table 7.2. This could be attributed to their differences in water absorption characteristics, starch granule sizes, shapes and gelatinization properties of the flours. Rice starch granules are the smallest among the cereals, and absorbed less water compared to corn and wheat flour (Hoseney, 1994; Mukprasirt, Herald, and Flores, 2000). Typical gelatinization temperature range for rice starch is from 68 to 78°C, corn starch is from 62 to 70°C and wheat flour is from 58 to 60°C (Hoseney, 1994).

Table 7.2. Effects of CMC on onset temperature (TR_{onset}, °C) of structure development of batter system during heating

Batter	Control	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	53.7± 0.59	56.4± 0.07	57.8± 0.92	60.6± 0.12
Corn	57.1± 0.32	59.5± 0.72	63.5± 0.58	65.6± 0.98
Rice	65.8± 0.21	67.2± 0.49	68.0± 0.59	68.3± 0.78
W3C7	53.4± 0.62	57.1± 0.13	63.2± 0.68	65.0± 0.69
W5C5	59.3± 0.62	59.2± 0.30	60.5± 0.37	62.7± 0.58
W7C3	53.4± 0.62	57.1± 0.13	59.2± 0.68	62.0± 0.69
W3R7	61.3± 0.35	62.9± 0.72	64.2± 0.46	64.5± 0.45
W5R5	61.1± 0.53	56.3± 0.87	59.9± 0.58	63.3± 0.87
W7R3	61.4± 0.42	62.8± 0.16	61.7± 0.32	60.0± 0.69
C3R7	58.8± 0.19	61.8± 0.88	67.6± 0.58	68.2± 0.24
C5R5	62.2± 0.58	66.0± 0.29	66.2± 0.91	66.6± 0.72
C7R3	63.7± 0.37	67.3± 0.68	67.4± 0.34	68.8± 0.69

CMC significantly influenced the structural onset temperature for all samples (Tables 7.2). The effects of CMC concentration on onset temperature were more pronounced for the batters that were formulated with either wheat or corn and their combination flours based batters. Competition for water between CMC, flour components and other ingredients apparently contributed to the development of structure during heating. There apparently was more water available for reaction with rice starch than with wheat or corn starch in the limited water systems. The interaction between increasing concentration of CMC and wheat protein (gluten), or wheat starch may have produced less available water for starch to be swelled and consequently to be gelatinized. CMC did not significantly change onset temperature of rice flour based batters. Since there was more available water in rice flour, CMC apparently was more efficient in forming gel without increasing elastic behavior of the batter. Keller (1982) reported that viscous behavior of CMC gel was much greater than its elastic characteristics (G'< G"). Shil and BeMiller (2002) reported a carboxymethyl-starch interaction, observing that viscosity of sodium CMC solution dropped gradually when it was heated from 35 to 90°C with agitation speed of 125 rpm, but there was an increase in viscosity at 58°C when corn starch was added to the CMC solution.

Table 7.3 shows that CMC slightly increased the peak temperature of structure formation since temperature does not affect its viscosity after starch gelatinization is completed (Peettitt, 1982). However, elastic properties were changed to form different structures for different flour with added CMC. Rojas, Rosell, and Benedito (1999) and Cameron, Sansom, and Donald (1993) also found that gums had little or no effect on the peak gelatinization temperature of wheat and waxy maize starches but they influenced the onset of gelatinization temperature. Shi and BeMiller (2002) reported a significant viscosity increased before pasting occurred in CMC-maize and CMC-rice suspensions. Therefore, higher temperatures and shorter times were required to gelatinize starch when CMC was added to batter systems.

Table 7.3. Effect of CMC on peak temperature (T_{peak}, °C) of structure development of batter system during heating process

Batter	Control	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	73.8± 0.81	73.8± 0.59	73.8± 0.37	74.6± 0.21
Corn	79.0± 0.86	80.1± 0.62	80.9± 0.74	81.2± 0.36
Rice	83.6± 0.29	84.9± 0.35	84.9± 0.62	85.1± 0.38
W3C7	79.1± 0.28	80.1± 0.37	80.9± 0.72	82.1± 0.32
W5C5	78.9± 0.66	79.6± 0.59	80.6± 0.58	80.9± 0.69
W7C3	78.0± 0.68	79.9± 0.29	80.8± 0.12	81.3± 0.24
W3R7	84.2± 0.11	85.0± 0.58	86.0± 0.69	86.8± 0.19
W5R5	82.7± 0.75	83.2± 0.78	83.9± 0.35	83.8± 0.38
W7R3	79.2± 0.62	78.0± 0.74	80.2± 0.53	80.4± 0.37
C3R7	82.5± 0.38	83.8± 0.98	84.5± 0.29	85.0± 0.62
C5R5	82.3± 0.29	82.4± 0.32	83.2± 0.58	84.5± 0.66
C7R3	81.8± 0.25	82.5± 0.59	83.2± 0.91	83.5± 0.92

CMC significantly increased both the values of G'_{max} and G''_{max} in all samples (Tables 7.4 and 7.5). This can be attributed to the ability of CMC form three-dimensional network and to its ability to link water molecules within the systems (Andrew, 2004). Other authors reported similar finding with corn starch (Gimeno, Moraru, and Kokini, 2004), yam starch (Mali et al., 2003) and dried nixtamalised maize masa (Andres, Guadalupe, Javier and Luis, 2005). Therefore, CMC influences not only the elastic properties, it also influenced the viscous properties and the final structure of batters during heating.

Table 7.4. Effects of CMC on the maximum values of storage modulus (G'_{max} kPa) of batter system during heating process

Batter	Control	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	19.0± 0.34	18.4± 0.52	21.9± 0.7	23.7± 0.05
Corn	42.1± 0.28	41.7± 0.57	44.3± 0.29	46.4± 0.39
Rice	35.0± 0.38	35.6± 0.32	39.6± 0.32	41.0± 0.45
W3C7	29.5± 0.29	31.4± 0.25	33.0± 0.41	35.0± 0.38
W5C5	26.6± 0.24	27.3± 0.26	30.9± 0.27	32.8± 0.59
W7C3	25.5± 0.41	24.0± 0.34	27.7± 0.74	29.5± 0.53
W3R7	25.6± 0.14	26.0± 0.53	28.4± 0.46	29.3± 0.42
W5R5	22.8± 0.20	23.0± 0.45	25.7± 0.49	28.5± 0.23
W7R3	20.3± 0.25	21.0± 0.38	24.6± 0.62	26.3± 0.32
C3R7	28.1± 0.27	27.0± 0.49	30.4± 0.59	31.8± 0.45
C5R5	35.1± 0.35	35.8± 0.67	37.6± 0.72	39.7± 0.61
C7R3	27.2± 0.56	26.4± 0.05	31.1± 0.91	33.2± 0.23

Table 7.5. Effects of CMC on the maximum values of loss modulus (G''_{max} kPa) of batter system during heating process

Batter	Control	0.5%CMC	1.0%CMC	1.5%CMC
Wheat	3.4± 0.32	3.6± 0.28	4.0± 0.18	4.4± 0.21
Corn	8.3± 0.51	6.8± 0.17	6.9± 0.19	7.4± 0.29
Rice	5.5± 0.59	5.8± 0.61	6.2± 0.26	6.5± 0.38
W3C7	5.6± 0.14	6.6± 0.56	6.9± 0.43	7.6± 0.52
W5C5	5.2± 0.23	5.1± 0.52	6.4± 0.32	8.3± 0.32
W7C3	4.5± 0.33	4.8± 0.33	5.4± 0.21	6.5± 0.41
W3R7	3.9± 0.62	5.2± 0.42	5.4± 0.13	5.6± 0.43
W5R5	3.6± 0.23	3.8± 0.43	4.2± 0.25	4.3± 0.52
W7R3	3.4± 0.34	3.4± 0.36	3.6± 0.26	3.7± 0.31
C3R7	4.2± 0.21	4.8± 0.29	5.4± 0.35	5.9± 0.34
C5R5	5.6± 0.33	5.8± 0.21	6.2± 0.53	6.8± 0.51
C7R3	6.4± 0.34	6.2± 0.40	6.5± 0.21	6.7± 0.43

7.6 CONCLUSION

The addition of CMC significantly influenced the flow behavior of batter systems. It increased consistency index and decreased shear-shinning behavior of batter systems. Viscoelastic properties were changed with the addition of CMC in batters. Increasing concentrations of CMC shifted onset temperature of structure development but only slightly increased the peak temperature. Maximum values of elastic and loss moduli increased consistently with increasing CMC concentration. There was more pronounced effect of CMC on corn and rice flour based batters and their combination flour based batters than wheat flour based batter systems.

7.7 IMPLICATIONS FOR BATTER PREFORMANCE

CMC greatly influences the flow behaviour and viscoelastic properties of various batter systems. Wheat flour batters containing CMC showed the highest viscosity. That may affect the batter and the coated piece handling process, as well as the end-product quality. It may cause difficulty in mixing as the batter becomes stickier. A high batter pick up yield would result in uncooked food substrate that required a longer cooking duration and higher energy. The results suggest that, in the case of selecting those ingredients that do not develop much viscosity on their own, such as rice or corn flours, it is advantageous to incorporate CMC to ensure batter characteristics similar to the more classic formulations. Therefore, selecting the proper flour or flour blend and an appropriate hydrocolloid, along with other ingredients, is very important when starting to formulate a batter system. For special or unusual food substrates, the batter system not only affects the character and the quality of the products, but it also influences the processing conditions and bears heavily upon the economic aspect.

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VIII. GENERAL SUMMARY AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 GENERAL SUMMARY

Research conducted in the past decade has demonstrated the effectiveness of hydrocolloids on reduction of fat uptake in deep fat fried food products. This study investigated and monitored the rheological and thermal properties of different flour combinations in conjunction with different types of hydrocolloids in batter systems. It was found that the rheological and thermal properties varied with the different types of flours, their combination ratios, and with the different types of hydrocolloids. In the batter systems containing only flours and water, the addition of corn flour greatly influenced the viscosity and viscoelastic properties of wheat based and rice based batter systems, as the viscosity decreased with an increase in the corn flour proportion in the batter system. Both corn and rice reduced the viscosity and increased the onset temperatures (TR_{onset}), storage moduli (G'_{max}) and loss moduli (G''_{max}) of wheat flour based batter systems. Salt significantly influenced the flow properties of batter systems by lowering the viscosity and decreasing G'_{max} and G''_{max} as well as increasing the onset temperature. A higher temperature and longer time was required to gelatinize starch at higher proportions of rice flour (70%) for each flour mixture combination in the batter systems tested in this study. Also, the thermal properties of wheat based batters were greatly influenced by replacement of wheat by rice or corn flours. There was a synergistic interaction resulting in marked change in glass transition temperature when rice and corn flours are mixed in equal proportions. A higher enthalpy ΔH_G was required to gelatinize starch at higher levels of corn flour (70%) for each flour mix combination tested.

Hydrocolloids greatly influenced the rheological and thermal properties of batter systems. They significantly influenced the flow behavior, increased the consistency, and lowered the shear-shinning behavior of the batters. Viscoelastic properties during the heating process were changed with the addition of XG, MC, or CMC to the batter systems. The gums shifted the onset temperature of structure development but they did not affect the peak temperature. Hydrocolloids significantly influenced the storage and loss moduli of batter systems. A higher temperature and shorter time was required to gelatinize starch when hydrocolloids were added to the batter systems.

Two different thermal processes for cooking and frozen storage were used to determine the thermal properties of batter systems formulated using different flour combinations with the addition of hydrocolloids at different levels. However, different thermal processes did not show effects on gelatinization or total enthalpies of gelatinization in all samples, but it affected the phase transition of batter systems during cooling. They increased the gelatinization temperatures but depressed the glass transition temperatures of the resulting batters. MC increased the melting temperature (T_m) for the test batter systems as compared with the values for the control system without MC. CMC did not show statistically significant effects on the total enthalpies of ice melting for all samples. However, MC and CMC showed more pronounced effects on rice, corn, and their combined flour based batters than it did on wheat flour based batters. However, this characteristic was not evident in batter systems containing xanthan gum.

8.2 RECOMMENDATIONS FOR FUTURE RESEARCH

Further investigation is required to study the phase transitions during the heating and cooling process that result from the interactions arising from different flour combinations when hydrocolloids are added. The design of a system of thermal processes permitting the use of a microstructure image analysis to track phase changes and to provide visible evidence of different combination flours and hydrocolloids involved in the resulting structural changes occurring during this crucial stage is recommended.

A non-invasive imaging technique such as scanning electron microscopy (SEM), or confocal laser scanning microscopy (CLSM) combined with the proper imagine analytical software could be used to study the structure of the coating part of batter products. This method would complement DSC and Rheological techniques and understanding of structural role of batter components and their effect on the overall microstructure of the complex food system. Therefore the effects of the interactions between the different flours and hydrocolloids on the resulting structure should become more evident. The experimental data generated from these tests can facilitate the development of a model to predict moisture loss and oil uptake based on the starch-hydrocolloid matrix networks.

A further study is vital to investigate the effects of hydrocolloids on different types of starches (wheat, corn, or rice starch, etc.) which swell and gelatinize at different temperatures during the heating process. It could also help to understand how cooling conditions affect the structure and quality of the cooked batters during frozen storage. This would provide complementary information on the physical characteristics of batters and their responses to thermal processing. Exploring the effect of different types of flour and their combination ratios, and with addition of hydrocolloids at different concentration on quality of coating such as coating color, texture, fat and moisture contend in the end of coated food products.

IX. CONTRIBUTIONS TO KNOWLEDGE

This is the first time that a comprehensive study has been carried out to investigate the rheological and physical properties of batters formulated by different types of four and their combinations with the addition of different types of hydrocolloids at different concentrations. The results provide more knowledge about interactions between flours, hydrocolloids and other ingredients on rheological and thermal properties that are important during processing. The data on batter properties generated from this work can be used as an aid in proper selection and formulation of batter systems for different food types. The data can also be used in optimizing process and storage conditions. The contributions to scientific knowledge are summarized as follows:

1. The effects of different types of flours and their combination ratios, on thermal properties were determined. Thermal properties of batter systems varied with different types of flour, and with different flour combination ratios. Gelatinization temperatures of batter systems were independent of the ratio by which the flours were combined. However, the different flour type combinations and their blending ratio greatly changed total entropies for gelatinization. More energy was required to gelatinize the batter when they contained high levels of corn flour. Replacement of corn or rice flour in wheat-flour-based batters caused glass transition temperature to increase and should influence product stability during frozen storage.
2. The effects of hydrocolloids on thermal properties of batters formulated using with different blends of flour in different combination ratio were investigated for two different thermal processes. Hydrocolloids increased gelatinization temperature and depressed the glass transition temperature of batter. The two different thermal

processes (cook-freeze-thaw, CFT and freeze-cook, FC) affected glass transition and ice melting processes. Cooked samples (i.e. prepare by CFT process) required lower temperatures to freeze for adequate frozen storage than did uncooked samples (prepared via FC process). Hydrocolloids delayed gelatinization process, especially batters containing MC. A lower temperature was required to freeze either uncooked or cooked samples during cooling process, as compared with the samples that did not contain hydrocolloids. MC had more effect on thermal properties of cooked products during cooling and freezing process, but xanthan gum showed more effect on uncooked samples during cooling. Hydrocolloids showed more pronounced effects on rice, corn, and their combined flour batters than they did on wheat flour based batters.

3. The effects of different types of flour and their combination ratios on rheological properties of batters were examined. Blended flours at different combination ratios greatly influenced flow behavior and viscoelastic properties of batters. Corn flour batters did not show yield stress. Partial corn flour substitution had a larger effect on the viscosity of wheat flour based batters than did rice flour. However, corn and rice flours greatly affected viscoelastic properties of wheat flour based batters. Higher temperature and longer time was required to gelatinize starch at the higher proportions of rice flour (greater than 70%) for each flour mix combination in the batter systems tested in this study.
4. Effect of hydrocolloids on the rheological properties of batter formulated using combined and different types of flour was elucidated in this study. Addition of hydrocolloids greatly increased viscosity and yield stress of batters but lowered their shear shinning behaviour. Hydrocolloids showed more effect on the flow behavior of batters containing rice or corn flours. Xanthan gum at 0.2% concentration in batters

increased yield stress in all batters expects for batter containing high level of corn flours. CMC increased rice flour starch gelatinization process in batters containing high proportional rice flour (greater than 70% of rice flour). Partial replacement of wheat with corn and rice flours greatly changed the rheological properties of wheat-flour-based batters and compounded the action of hydrocolloids.

Batters are complex systems. Although the results obtained in this study can be general, the commercial user will need to weigh carefully the potential benefits of blending flours and adding hydrocolloids. Although addition of hydrocolloids may result in superior performance, storage stability, sensory characteristics, consumer preference, economics and other product specific issues need to be considered.

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