

**UNIVERSITY OF GAZİANTEP  
GRADUATE SCHOOL OF  
NATURAL & APPLIED SCIENCES**

**EFFECT OF OZONATION  
ON SELECTED PROPERTIES OF STARCHES**

**Ph.D THESIS  
IN  
FOOD ENGINEERING**

**BY  
HATİCE ÇATAL  
MAY 2012**

**Effect of Ozonation on Selected Properties of  
Starches**

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in  
Food Engineering  
University of Gaziantep**

**Supervisor  
Prof. Dr. Şenol İBANOĞLU**

**by  
Hatice ÇATAL  
May 2012**

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**T.C.**  
**UNIVERSITY OF GAZİANTEP**  
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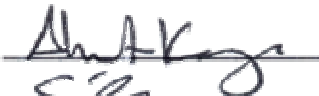


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**Hatice ÇATAL**

## ABSTRACT

### EFFECT OF OZONATION ON SELECTED PROPERTIES OF STARCHES

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Ph.D in Food Engineering

Supervisor: Prof. Dr. Şenol İBANOĞLU

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Corn starch-water, potato starch-water and rice starch-water mixtures were prepared in the ratio of 1:9 (dry sample to water) and ozonated at a concentration of 4.2 mg dissolved ozone L<sup>-1</sup> water for 60 min. A wheat starch-water mixture was also ozonated for 15, 30 and 60 min. Onset, peak and conclusion temperatures of wheat, corn and potato starches increased while the corresponding gelatinization enthalpies were reduced after ozonation, except the wheat starch. Ozone has more distinct effect on the birefringences of corn and potato starch samples under polarized light microscopy. Changes in the granule shape under SEM are visually distinct for ozonated corn and potato starches. Ozonation changed starch pasting characteristics causing a significant reduction in peak, trough, breakdown and final viscosities of all starch samples. A significant reduction was observed in values of pasting parameters of wheat starch with increasing ozonation time. Shear-thinning behaviour was observed for the control and all ozonated wheat starch samples. Longer ozonation time resulted in more gelatinized starch molecules. Significant increases in brightness and whiteness for ozonated wheat, corn and potato starch samples were observed. The ozonation process caused significant decrease in pH and in both total bacteria and mold/yeast counts for all wheat, corn, potato and rice starch samples studied.

**Key words:** Ozone, starch, gelatinization, morphology, rheology, color

## ÖZ

### OZONLAMA İŞLEMİNİN NİŞASTALARIN BAZI ÖZELLİKLERİNE OLAN ETKİSİ

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Mısır, patates ve pirinç nişastaları 1:9 oranında suyla karıştırılarak ozonlandı. Ozon konsantrasyonu 1 litre suda 4.2 mg suda çözülmüş ozon olacak şekilde sabit tutuldu. Buğday nişastası-su karışımı aynı şartlarda 15, 30 ve 60 dakika ozonlandı. Ozonlama sonrasında buğday, mısır ve patates nişastalarının başlangıç, pik ve son sıcaklıkları artarken, buna tekabül eden entalpileri, buğday nişastası hariç, azaldı. Polarize ışık mikroskobu altında, ozonun, mısır ve patates nişastalarının çiftkırımları üzerine daha belirgin etkisi olduğu gözlemlendi. Ozonlanmış mısır ve patates nişastalarının granül şekil ve yüzeylerinin SEM altında incelendiği zaman belirgin bir şekilde değiştiği görüldü. Ozonlama işlemi çalışılan tüm nişasta örneklerinin akışkanlık özelliklerinde önemli ölçüde azalmaya neden oldu. Ozonlama süresi arttıkça, buğday nişastasının çiriş parametre değerlerinde önemli ölçüde bir azalma gözlemlendi. Ozonlama süresinin uzaması nişasta moleküllerinin daha çok jelatinize olmasına neden oldu. Ozonlanmış buğday, mısır ve patates nişasta örneklerinin beyazlık ve parlaklık değerlerinde anlamlı artışlar gözlemlendi. Ozonlama işlemi çalışılan nişastalarının pH'sını, toplam bakteri ile küf/maya sayısını anlamlı bir şekilde azalttı.

**Anahtar Kelimeler:** Ozon, nişasta, jelatinizasyon, morfoloji, reoloji, renk

*TO MY ANGEL (DAUGHTER)*

*ECE NİSA ÇATAL*



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## ABBREVIATIONS

ANOVA	Analysis of variance
DSC	Differential scanning calorimetry
RVA	Rapid Visco Analyser
SEM	Scanning Electron Microscope
SPSS	Statistical package for social science
$\sigma$	Shear stress
$\gamma$	Shear rate
K	Consistency index
n	Flow behaviour index
A	Absorbance of total gelatinized starch
B	Absorbance of a mixture of partially gelatinized after 30 min enzymatic hydrolysis
C	Absorbance of a mixture of partially gelatinized after 60 min enzymatic hydrolysis
k	Absorbance of 1% of intact starch digested in 30 min and is a constant for each variety or specially treated starch
Y	Gelatinized starch percentage
L	Brightness coefficient from dark to bright
a	Coefficient from green to red
b	Coefficient from blue to yellow
To	Onset temperature
Tp	Peak temperature
Tc	Conclusion temperature
$\Delta H$	Gelatinization enthalpy

## **CHAPTER I**

### **INTRODUCTION**

Ozone (the triatomic form of oxygen) is a powerful oxidant due to its high reactivity, penetrability, and spontaneous decomposition to a non-toxic product. There are many applications of ozone in water treatment throughout the World. Ozone has been used not only to treat drinking water but also to improve wastewater treatment units, such as sedimentation, chemical or biological oxidation.

In the mid-1990s, ozone (O<sub>3</sub>) was approved as a strong antimicrobial agent for food processing in Japan, France, and Australia and then approved as generally recognized as safe (GRAS) by the Food and Drug Administration (FDA) of the U.S. in 1997. Now, the food industry is greatly interested in using ozone to prolong the shelf-life and safety of food products. However, to date only a limited number of research studies have been conducted on ozone usage on food materials, particularly cereals and cereal-based products.

In the past studies, ozonated water (washing) and ozone gas (storage) were generally used to inactivate microorganisms or prevent the growth of microorganisms of cereal (wheat, barley, maize) grains and flours. Further research is needed to understand other benefits and limitations of ozone applications in the cereal industry especially the changes in quality parameters of ozonated cereal products if there is an improvement or not.

Starch, an important natural macromolecule, is an essential component of cereals and widely used in food, paper, textile and pharmaceutical industries. Starch modifications have been used to eliminate or reduce undesirable characteristics of this biopolymer. In recent times, chemical modifications such as acid hydrolysis, oxidation, acetylation, esterification, etherification and cross-linking have been attracted. Especially, oxidized starch use in food industry is increasing because of its low viscosity, high stability, clarity, film forming and binding properties, which has

been applied in food coatings, sealing agents in confectionery and as emulsifiers. There are several methods to oxidize starch by oxidizing agents such as hydrogen peroxide, air, oxygen, ozone, bromine, chromic acid, permanganate and nitrogen dioxide. Since there is no available data about the effect of the reaction of ozone with starch, the effects of ozonation on the physico-chemical properties (color and pH), microbiological properties (total bacteria and yeast/mold counts), pasting properties, rheological properties, structure properties and gelatinization properties of certain types of starch (i.e. wheat starch, corn starch, potato starch and rice starch) were investigated in the present work.

## CHAPTER II

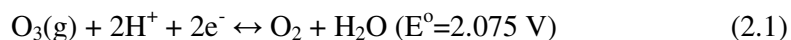
### LITERATURE SUMMARY

#### 2.1. Ozone

##### 2.1.1. General Properties of Ozone

Ozone is a natural substance found in our atmosphere, but it can also be produced synthetically. Ozone is a form of oxygen that includes 3 atoms (O<sub>3</sub>) compared to the standard 2 (O<sub>2</sub>) in a molecule of oxygen. Structurally, the three atoms of oxygen are in the form of an isosceles triangle with an angle of 116.8 degree between the 2 O-O bonds. The distance between the bond oxygen atoms is 1.27 angstroms. Ozone is derived from the Greek word “Ozein” which means “to smell.” Ozone as a gas is blue; both liquid (-111.9°C at 1 atmosphere) and solid ozone (-192.7°C) are an opaque blue-black color (Hunter, 1995).

It is relatively unstable gas at normal temperatures and pressures, is partially soluble in water, has a characteristic pungent odour, and is the strongest disinfectant currently available for contact with foods (Muthukumaparan et al., 2000). The relatively high (+2.075 V) electrochemical potential (E<sup>o</sup>, Volt) indicates that ozone is a very favorable oxidizing agent (Eqn. 2.1). The various physical properties of ozone are summarized in Table 2.1 (Mahapatra et al., 2005).



Ozone was discovered by C.F. Schonbein in 1839 and was first used commercially in water supply treatment in 1907 (Kogelschatz, 1988). Ozone was approved as generally recognized as safe (GRAS) as a disinfectant for foods by the Food and Drug Administration (FDA) of the U. S. in 1997 and the FDA allowed for the use of ozone as a direct contact food sanitizing agent in 2001 (Mahapatra et al., 2005).

Table 2.1. Physical properties of ozone (Mahapatra et al., 2005)

Physical properties	Value
Boiling point, °C	-111.9
Density, kg/m <sup>3</sup>	2.14
Heat of formation, kj/mole	144.7
Melting point, °C	-192.7
Molecular weight, g/mole	47.9982
Oxidation strength, V	2.075
Solubility in water, ppm (at 20 °C)	3
Specific gravity	1.658

### 2.1.2. Production and Reactivity of Ozone

Ozone is generated by the exposure of air or another gas containing normal oxygen to a high-energy source. High-energy sources convert molecules of oxygen to molecules of ozone (Figure 2.1). Ozone must be manufactured on site for immediate use, since it is unstable and quickly decomposes to normal oxygen. The half-life of ozone in distilled water at 20°C is about 20 to 30 min (Khadre et al., 2001).

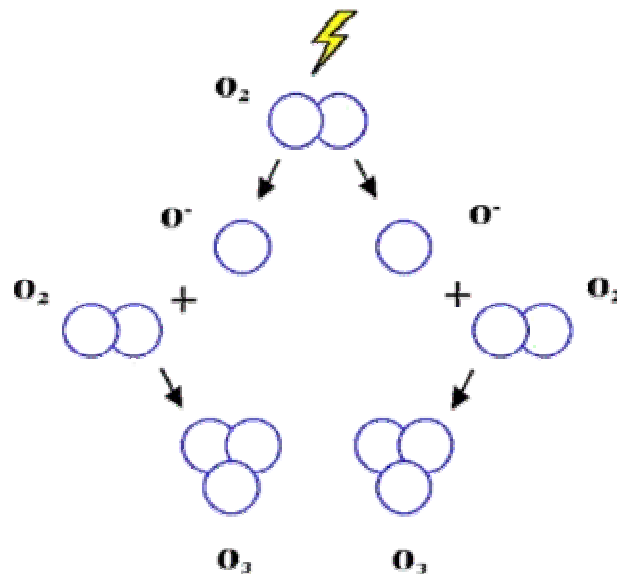


Figure 2.1. Generation of ozone molecule (O'Donnel et al., 2012)

Ozone production is predominantly achieved by one of three methods: electrical (corona) discharge, electrochemical, and ultraviolet (UV) radiation. Electrical discharge methods (Figure 2.2) , which are the most widely used commercial methods, have relatively low efficiencies (2–10%) and consume large amounts of electricity. The other two methods (electrochemical and UV) are less cost effective (Mahapatra et al., 2005).

Ozone is a powerful antimicrobial agent that is suitable for application in food in the gaseous and aqueous states. Molecular ozone or its decomposition products (for example, hydroxyl radical) inactivate microorganisms rapidly by reacting with intracellular enzymes, nucleic material and components of their cell envelope, spore coats, or viral capsids (Khadre et al., 2001).

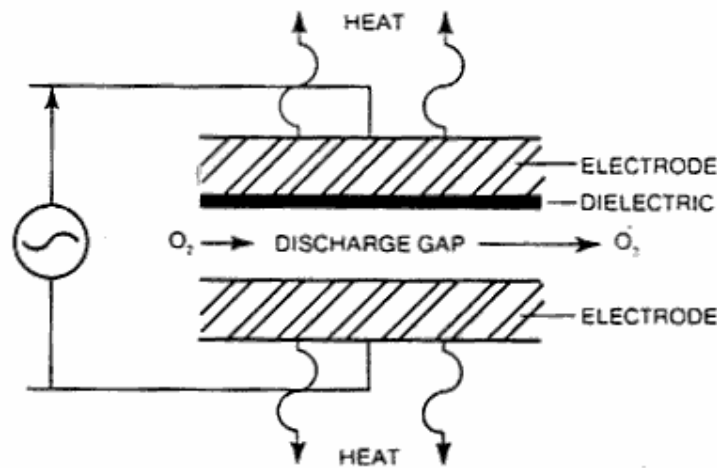


Figure 2.2. Typical corona cell configuration (Rice et al., 1981)

### 2.1.3. Safety Requirements for Ozone Application

Ozone is a toxic gas and can cause severe illness, and even death, if inhaled in high quantity. The ozone exposure levels as recommended by the Occupational Safety and Health Administration (OSHA) of U.S. are shown in Table 2.2 (Mahapatra et al., 2005).

Table 2.2. Approved levels of ozone application (Mahapatra et al., 2005)

Exposure	Ozone level, ppm
Detectable odour	0.01-0.05
OSHA 8 h limit	0.1
OSHA 1.5 minute limit	0.3
Lethal in few minutes	>1700

#### **2.1.4. Ozone Applications in Food Industry**

The application of ozone in water treatment is widespread throughout the world. Ozone has been shown to be a powerful oxidant and disinfectant in water treatments. So far, ozone has been applied mainly to the treatment of drinking water (Chand et al., 2007; Kasprzyk-Hordern et al., 2006; von Gunten, 2003a; 2003b). However, previous laboratory works have also shown that ozonation may be recommended as a technology to improve wastewater treatment units, such as sedimentation, chemical or biological oxidation (Beltrán et al., 2001).

In recent years, there has been a significant application of ozone in wastewater treatment, such as disinfection applications (Dahl, 1976; Diao et al., 2004; Orta de Velásquez et al., 2006; Xu et al., 2002), removal of phenolic compounds present in wastewater (Beltrán et al., 2000a; 2000b), wine-distillery and molasses fermentation (Beltrán et al., 2001; Benitez et al., 2003; Coca et al., 2007; Sangave et al., 2007), table-olive and olive oil industry (Beltrán et al., 1999; Beltran-Heredia et al., 2000a; 2000b; Benitez et al., 2000; Cañizares et al., 2007; Monteagudo et al., 2005), designation of ozonators (Heng et al., 2007; Lei and Snyder, 2007; Lin and Wang, 2003) etc. These applications improve the reusability of processing water and allows for environment-friendly processing operations.

In the mid-1990s, ozone was approved as a strong antimicrobial agent for food processing in Japan, France, and Australia and it was approved in the U.S. as generally recognized as safe (GRAS). For a considerable time the food industry has shown a great interest in using ozone to enhance the shelf-life and safety of food products (Çatal and İbanoğlu, 2010; Graham, 1997; Kim et al., 1999; Kim et al., 2003; Rice et al., 1982). The antimicrobial spectrum and sanitary applications of



ozone in the food industry are summarized in Table 2.3 (Muthukumarappan et al., 2000).

Table 2.3. Antimicrobial spectrum and sanitary applications of ozone in the food industry (Muthukumarappan et al., 2000)

Sanitation	Dosage	Susceptible microorganisms
Animal	>100 ppm	HVJ/TME/Reo type 3/murine hepatitis virus
Black berries	0.3 ppm	<i>Botrytis cinerea</i>
Cabbage	7-13 mg/m <sup>3</sup>	Shelf life extension
Carrot	5-15 mg/m <sup>3</sup>	Shelf life extension
	60µl/L	<i>Botrytis cinerea/Scerotinia sclerotiorum</i>
Dairy	5 ppm	<i>Alcaligenes faecalis/P. fluorescens</i>
Fish	0.27 mg/L	<i>P. putida/B. Thermospacta/L. Plantarum/Shewanella putrefaciens / Enterobacter sp.</i>
	0.111 mg/L	<i>Enterococcus seriolicida</i>
	0.064 mg/L	<i>Pasteurella piscicida/Vibrio anguillarum</i>
Media	3-18 ppm	<i>E. coli</i> O157:H7
Peppercorn	6.7 mg/L	3-6 log reduction of microbial load
Potatoes	20-25 mg/m <sup>3</sup>	Shelf life extension
Poultry	0.2-0.4 ppm	<i>Salmonella sp./Enterobacteriaceae</i>
Shrimp	1.4 ml/L	<i>E. coli/Salmonella typhimurium</i>
Water	0.35 mg/L	<i>A. hyrophila/B. subtilis/E. coli/V. cholerae/ P. aeruginosa/L. monocytogenes/ Salm.typhi/Staph.aureus/Y. enterocolitica</i>

Ozone can replace traditional sanitizing agents such as chlorine and provide other benefits in the washing, sanitizing, and storage of produce (Wei et al., 2007). Areas where ozone can be used include the washing process and storage of fruit and vegetable. Spores of many types of bacteria, fungi and pathogens causing spoilage of fruits and vegetables could be destroyed by ozone treatment and shelf-life of fruit and vegetables could be increased; while also ensuring a safer product for consumers without any toxic residues (Brown et al., 2004; Gao et al., 2006; Hur et al., 2005; Naito and Takahara, 2006; Palou et al., 2001; Palou et al., 2002; Palou et al., 2003; Smilanick et al., 1999; Smilanick et al., 2002; Xu, 1999).

Ozonation is also tried in many applications as an alternative method to prevent the microbial action in red meat, poultry meat, their products and disinfection of waste

water and knives during processing (Chen et al., 1992; Diaz and Law, 1997; Diaz et al., 2001; Naito and Takahara, 2006; Nieto et al., 1984; Rodriguez-Romo et al., 2007; Sheldon and Brown, 1986; Uradzinski et al., 2005; Wu and Doan, 2005; Yang and Chen, 1979a; 1979b).

In addition, ozone has being used widely in the degradation and removal of pesticide (insecticides, herbicides, fungicides, etc.) residues on many produces (Benitez et al., 2007; Brillas et al., 2004; Kearney et al., 1987; Lafi et al., 2006; Ong et al., 1996; Wu et al., 2007a; 2007b).

In the food industry, much attention is given to the cleaning and sanitizing operations of food-processing equipment, both in preventing contamination of products and in maintaining the functionality of equipment. Since ozone is a strong oxidant, it can be used for the disinfection of processing equipment (Dosti et al., 2005; Khadre and Yousef, 2001; Mahapatra et al., 2005; Pascual et al., 2007).

The antimicrobial efficacy of ozonation can be enhanced considerably when it is combined with other chemicals (e.g. H<sub>2</sub>O<sub>2</sub>) or physical (e.g. UV-C radiation) treatments (Sun, 2005).

#### **2.1.5. Ozonation of Cereals and Cereal Products**

In the grain processing industry, safe storage of food grains is essential in order to minimize qualitative and quantitative losses. Ozone is becoming an alternative method of grain disinfection which is environmentally friendly resulting in no toxic residues.

The effectiveness of ozone depends on several factors including the amount of ozone applied, various environmental factors such as grain mass temperature, moisture and the surface characteristics. Ozone offers unique advantages for food grain processing with minimal or desired effects on the physicochemical properties (Tiwari et al., 2010).

Ozone treatment of grain is generally applied in silos or vessels. Ozone moves through the grain slowly because the gas reacts with the chemical constituents

present in the outer layer of grain (seed coat). Diffusion of ozone into the grain depends upon the grain characteristics. Movement of ozone within a silo or column filled with grain can be in either of 3 directions (Figure 2.3); namely movement in the transverse direction ( $x,z$ ) or movement in the vertical direction ( $y$ ) under the influence of ozone gas velocity ( $v_f$ ) and adsorption of ozone by the grain surface and possible reactions leading to degradation of ozone (Tiwari et al., 2010).

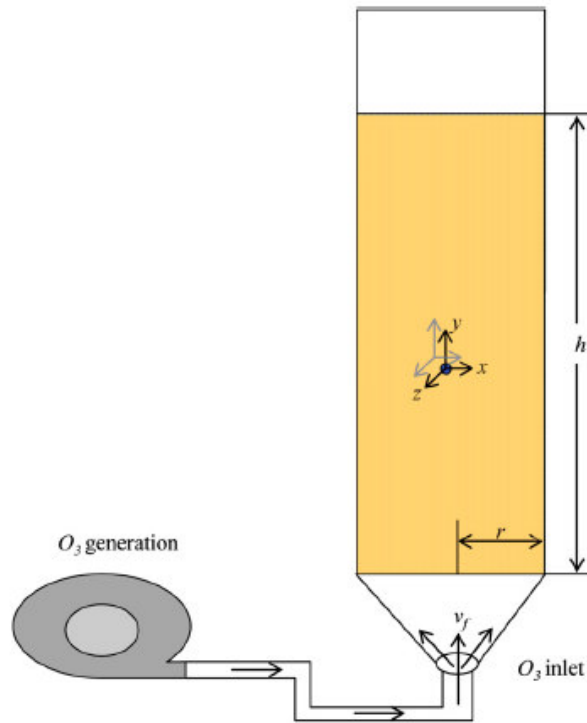


Figure 2.3. Schematic diagram showing movement of ozone in grain column (Tiwari et al., 2010)

Tiwari et al. (2010) demonstrated that ozone is an effective greener alternative against a range of pests, micro-organisms and mycotoxins. Table 2.4 lists reported applications of ozone for the control of insects. Within the grain processing industry, ozone is employed as a replacement for the existing fumigants such as methyl bromide and phosphine for the control of storage pests. Ozone as a fumigant is reported to kill stored-grain insects such as *Tribolium castaneum*, *Rhizopertha dominica*, *Oryzaephilus surinamensis*, *Sitophilus oryzae*, and *Ephestia elutella* (Sousa et al., 2008).

Table 2.4. Effects of ozone treatment on storage insects (Tiwari et al., 2010)

Food grain	Insects	Conditions	Mortality rate
Maize	RFB ( <i>Tribolium castaneum</i> )	50 ppm for	94.5% IMM
	MW ( <i>Sitophilus zeamais</i> )	3 days	100% MW
	IMM ( <i>Plodia interpunctella</i> )		92.2% RFB
Maize	RFB ( <i>T. Castaneum</i> )	25 ppm for	77.0% IMM
	MW ( <i>Sitophilus zeamais</i> )	5 days	99.9% MW
	IMM ( <i>P. Interpunctella</i> )		91.4% RFB
Wheat	<i>Ephestia kuehniella</i> and <i>Tribolium confusum</i>	Ozone conc. of 13.9 mg/L	<i>T. confusum</i> , 72.6% (Larvae) 1.3–22.7% (Adult) 90–100% (larvae, adult)
Stored products	<i>Tribolium castaneum</i>	50 ppm 30°C	50% mortality 11.39–20.10 h (TC)
	<i>Rhyzopertha dominica</i>	and 70% RH	9.22–12.19 h (RD)
	<i>Oryzaephilus surinamensis</i>		6.1–9.66 h (OS) 95% mortality 22.17–37.9 h (TC) 21.85–35.17 h (RD) 11.03–18.72 h (OS)
Maize	<i>T. castaneum</i>	50 ppm	50% mortality (71.4 h) at 20°C 95% mortality (151.8 h) at 20°C

IMM: Indian meal moth; MW: Maize weevil; RFB: Red flour beetle; RD: *Rhyzopertha dominica*; OS: *Oryzaephilus surinamensis*.

Ozone in gaseous or aqueous form is reported to reduce levels of the natural microflora, as well as bacterial, fungal and mold contamination in cereals and cereal products, including spores of *Bacillus*, Coliform bacteria, *Micrococcus*, *Flavobacterium*, *Alcaligenes*, *Serratia*, *Aspergillus* and *Penicillium* (Naito and Takahara, 2006).

The use of gaseous ozone as a fungicide to preserve stored barley and stored wheat was studied. The effects of the applied ozone dose, ozonation time, water activities of barley and wheat, temperatures of barley and wheat on the fungicidal efficacy of ozone and the effect of ozonation on germination of barley and wheat were examined. The experimental results showed that ozone was very effective in the inactivation of fungi associated with both barley and wheat. With 5 minutes of

ozonation, 96% of inactivation were achieved for spores as well as for mixtures of spores and a small amount of mycelia by applying 0.16 and 0.10 mg of ozone/(g barley).min. 96.9% of the fungal spores were inactivated by applying 0.33 mg of ozone (g wheat)<sup>-1</sup> min<sup>-1</sup>. In addition, for sealed storage silos, inactivation of fungi continued when the ozone-containing gas was held inside the silos following a continuous ozone supply. The experimental results also revealed that increases in water activity and temperature of barley and wheat enhanced the fungicidal efficacy of ozone. Results of these studies also indicated that the inactivation processes could be controlled by simply monitoring the exit ozone from the reactor instead of performing the time consuming microbial examination. This finding would make the application of ozone in the preservation of cereal grains easier, simpler, and more practically applicable. The experimental results demonstrated that although ozonation above a certain strength may reduce barley and wheat germination, inactivation of fungi was achieved with ozonation strengths far below the critical point (Allen et al.,2003; Wu et al., 2006).

The surface of a freshly baked loaf of bread is practically free of viable microorganisms but is subject to contamination by mold spores from the air during cooling and before wrapping. During slicing, contamination may take place from microorganisms in the air, on the knives, or on the wrapper. The predominant strains of airborne molds detected in the white bread manufacturing process were *Moniliella suaverolens*, *Cladosporium*, *Aspergillus*, *Penicillium*, *Aureobacidium*. The survival ratio of *M. suaverolens* was found to decrease with increasing dissolved ozone concentration ranging from 1 to 15mg/L and all mold cells were completely killed with ozonated water containing 15mg/L dissolved ozone at 25°C for 5 min. (Naito and Takahara, 2006).

Ozone is also reported to be effective in the detoxification and degradation of commonly occurring mycotoxins such as aflatoxin, patulin, cyclopiazonic acid, secalonlic acid D, ochratoxin A, and ZEN (Lemke et al., 1999; McKenzie et al., 1997). Table 2.5 lists reported effects of ozone treatment on fungal and mycotoxins in food grains.

Table 2.5. Effects of ozone treatment on mycotoxins (Tiwari et al., 2010)

Food grain or product	Mycotoxins	Treatment conditions	Degradation
Peanut meals	Aflatoxins	25 mg ozone/min	AFB1 and G1 (100% destruction) AFB2 (78%)
Corn	Aflatoxins	Ozonation (10–12 wt%) reduced	aflatoxin levels by 92%
Corn	Aflatoxin	92 h with O <sub>3</sub> at 200 mg/min	>95% reduction in AFB1
Barley	Fungal spores and mycelia	0.16 mg of ozone (g wheat) <sup>-1</sup> min <sup>-1</sup>	96% fungal spore inactivation
Maize	<i>Aspergillus parasiticus</i>	50 ppm for 3 days	63% reduction
Wheat	Fungal spores and mycelia	0.33 mg of ozone (g wheat) <sup>-1</sup> min <sup>-1</sup>	96.9% fungal spore inactivation
Wheat	Deoxynivalenol	Moist ozone (1.1 mol %) for 1 h	90% reduction
Wheat	Deoxynivalenol	Dry ozone (1.1 mol %) for 1 h	70% reduction
Barley	Fusarium	Gaseous ozone treatment 11 and 26 mg/g for 15 min	24–36% decrease in <i>Fusarium</i> survival
Peanut	Aflatoxin	Gaseous ozone (4.2 wt%) Temp. 25, 50, 75°C	AFB1 (77%): 10 min at 75°C AFB1 (80%): 5–10 min at 75°C

The trichothecene class of mycotoxins consists of naturally occurring metabolites produced by *Fusarium* spp. Fungi on a variety of cereal grains are known to be associated with several diseases in animals and humans. Kells et al. (2001) evaluated the efficacy of ozone as a fumigant to disinfest stored maize. Ozone fumigation of maize had two distinct phases. Phase 1 was characterized by rapid degradation of the ozone and slow movement through the grain. In Phase 2, the ozone flowed freely through the grain with little degradation and occurred once the molecular sites responsible for ozone degradation became saturated. The rate of saturation depended on the velocity of the ozone/air stream. The data in this research demonstrate the potential usefulness of using ozone in managing stored maize and possibly other grains.

Application of ozone at doses that are sufficient for the effective decontamination of grains may affect various quality attributes. The effects of ozone treatment on the quality and physiology of various food grains are reported in Table 2.6. Ozone is not universally beneficial and in some cases may promote oxidation degradation of chemical constituents present in the grains. Surface oxidation, discoloration or development of undesirable odours may occur from excessive use of ozone (Tiwari et al., 2010).

İbanoğlu (2001; 2002) studied the effects of tempering and wheat washing with ozonated water on flour properties. Soft and hard wheat samples were tempered using ozonated water (1.5 and 11.5 mg ozone/l) and washed using ozonated water (1.5 mg ozone/l). Milling (rate of extraction), rheological (farinograph and extensograph characteristics), chemical (protein, falling number, sedimentation volume), color (Hunter Lab values) and microbiological (total bacterial and yeast/moulds) properties of the flours were evaluated. Results indicated the chemical, physical and rheological properties of the flours were not significantly altered by tempering with ozonated water and the same properties of the flours from hard wheat samples were again not altered by washing with ozonated water. However, small but statistically significant differences were observed on extensograph values of flours milled from the soft wheat washed with ozonated water. A statistically significant reduction in the total bacterial and yeast/mold counts were obtained after tempering and washing with ozonated water for both soft and hard wheat samples. Results suggest that ozonated water can be successfully used to wash hard wheat without affecting flour quality and water ozonated up to 11.5 mg ozone/l can be successfully used in the tempering of soft and hard wheat without deterioration in the flour quality.

Table 2.6. Effects of ozone treatment on food grain quality (Tiwari et al., 2010)

Food grain	Conditions	Changes in quality
Wheat	Ozone concentration 10 g kg <sup>-1</sup> Oxygreen® process	Flour yield (~), Milling energy required (↓), bran friability (↑), mechanical properties (√)
Wheat	Ozonated water (1.5 mg L <sup>-1</sup> )	Extensibility (↓); water absorption (~); dough development time (~); dough stability (~); degree of softening (~); overall flour quality (~)
Barley	Gaseous ozone treatment 11 and 26 mg/g for 30 min	Germination energy (↓)
Soybean	50 ppm for 30 days	Fatty acid profile (~); Amino acid profile (~); rancidity (~)
Wheat	50 ppm for 30 days	Fatty acid profile (~); Amino acid profile (~); rancidity (~); bread-making properties (~); Milling performance (~)
Maize	50 ppm for 30 days	Fatty acid profile (~); Amino acid profile (~); popping volume (~)
Rice	50 ppm for 30 days	Adhesiveness (~); cooking quality (~)
Barley	Ozonation (10–12 wt%)	Fatty acid profile (~)
Wheat	0.33 mg of ozone (g wheat) <sup>-1</sup> min <sup>-1</sup>	Germination rate (↓)
Barley	0.16 and 0.10 mg of ozone (g barley) <sup>-1</sup> min <sup>-1</sup>	Germination rate (↓)

(×): Significant difference; (√) Insignificant; (↑): Increases; (↓): Decreases and (~): No change.

In further evaluation, Mendez et al. (2003) investigated the flow characteristics of ozone through a less porous grain than maize such as wheat, and the effects of long exposure to a high ozone concentration (50 ppm) on grain quality for end-users of the grain. Treatment of grains with 50 ppm ozone had no detrimental effect on popping volume of popcorn, fatty acid and amino acid composition of soybean, wheat, and maize, milling characteristics of wheat and maize, baking characteristics of wheat, and stickiness of rice. These data indicate that, if repeated ozone treatments are needed, such treatment should not decrease the quality of grain for end-users.

## 2.2. Starch

Starch (an integral part of cereals) is one of the very important biopolymers widely used in the food industry (Liu et al., 2008). Starch affects texture, viscosity, gel formation, adhesion, binding, moisture retention, film formation and product



homogeneity. It is used mainly in soups, sauces and gravies, bakery products, dairy confectionery, snacks, batters and coatings and meat products (Kaur et al., 2011). Non-food applications of starch include their use in pharmaceuticals, textiles, alcohol-based fuels and adhesives. Other uses of starch include low-calorie substitutes, biodegradable packaging materials, thin films and thermoplastic materials with improved thermal and mechanical properties (Biliaderis, 1998).

Starch is made up of two fractions: amylose (Figure 2.4) which is made up of essentially  $\alpha$ -(1 $\rightarrow$ 4) D-glucopyranosyl units and amylopectin (Figure 2.5) which is made up of a large number of short chains linked together at their reducing end side by a  $\alpha$ -(1 $\rightarrow$ 6) linkage (Biliaderis, 1998).

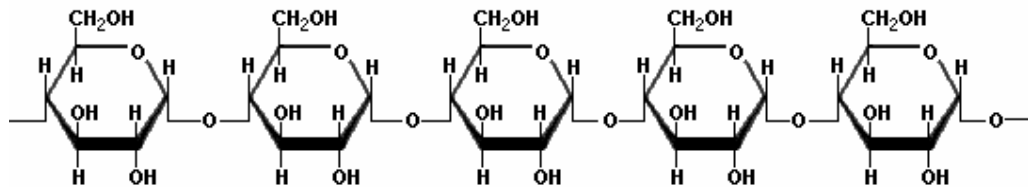


Figure 2.4. Structure of amylose (Tester et al., 2004)

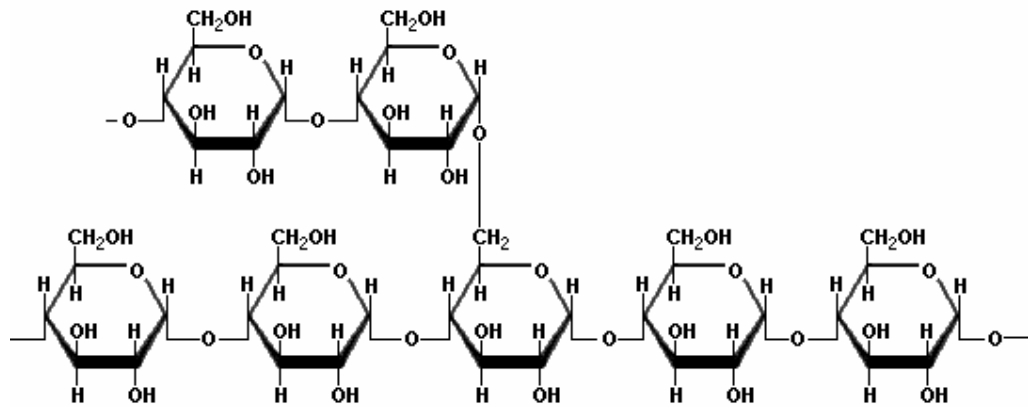


Figure 2.5. Structure of amylopectin (Tester et al., 2004)

### 2.2.1. Physico-Chemical Properties of Starch

Starches are obtained from various plant sources, such as corn, potato, wheat, rice, etc. The most basic of the physical properties of starch granules are their size and amylose content as exemplified in Table 2.7 (Pilla, 2011).

Table 2.7. Granule size distribution and amylose content of various starches (Pilla, 2011)

Starch species	Granule size range ( $\mu\text{m}$ )	Average size ( $\mu\text{m}$ )	Amylose (%)
Waxy rice	2-13	5.5	0
High amylose corn	4-22	9.8	70
Corn	5-25	14.3	28
Cassava	3-28	14	17
Waxy sorghum	3-27	16	0
Wheat	3-34	6.5, 19.5	26
Sweet potato	4-40	18.5	18
Arrowroot	9-40	23	21
Sago	15-50	33	26
Potato	10-70	36	20

Color is an important attribute to the food industry. Consumers frequently look at a product and make a judgement decision largely based on overall appearance including color. Often color and flavour are directly related. The color scales that are most widely used by the food industry are the Hunter L,a,b. These are 3-dimensional scales. The L, a, b type of scales simulate this as: L (lightness) axis – 0 is black, 100 is white; a (red-green) axis – positive values are red, negative values are green and 0 is neutral; b (yellow-blue) axis – positive values are yellow, negative values are blue and 0 is neutral (İbanoğlu, 2002).

The color of starch due to the presence of polyphenolic compounds, ascorbic acid and carotene has an impact on its quality. Any pigmentation in the starch is carried over to the final product. This reduces the quality, hence acceptability of the starch product. A low value for chroma and a high value for lightness are desired for the starch to meet the consumer preference (Gani et al., 2010; Ikegwu et al., 2010).

pH value is one of the physico-chemical properties of starch. The concentration of hydrogen ions in a solution is very important. As the hydrogen ions are positively charged, they alter the charge environment of other molecules in solution. By putting different forces on the molecules, the molecules can change shape from their normal shape and alter related properties of starch (binding, color, pasting, structure, gelatinization and microbial properties).

### **2.2.2. Microbial Properties of Starch**

There are many types of bacteria and fungi in grain, flour and starch including spores of *Bacillus*, Coliform bacteria, *Micrococcus*, *Flavobacterium*, *Alcaligenes*, and *Serratia*. Mold spores are chiefly those of *Aspergillus* and *Penicillium*, with also some of *Alternaria*, *Cladosporium* and other genera (Naito and Takahara, 2006). Chlorine and hydrogen peroxide are probably the most commonly used sanitizer in food industry, but ozone and a combination of ozone with initiators (UV or H<sub>2</sub>O<sub>2</sub>) or advanced oxidation processes (AOPs) are also potent sanitizers against a wide spectrum of microorganisms (Khadre et al., 2001).

### **2.2.3. Gelatinization Properties of Starch**

Starch gelatinization is a very complex combined process consisting of the hydration of an amorphous region and subsequent melting of crystalline arrays. The stabilities of the crystalline domains vary within and between granules. At high water contents, the amorphous regions of the granules imbibed water and swelled, resulting in stripping or separation of the starch chains from the crystallites. When all crystals were stripped at high moisture levels, no crystallites remained to be melted at high temperatures (Zaidul et al., 2008).

The crystalline order in starch granules is often the basic underlying factor influencing functional properties. Collapse of crystalline order within the starch granules manifests itself as irreversible changes in properties, such as granule swelling, pasting, loss of optical birefringence, loss of crystalline order, uncoiling and dissociation of the double helices, and starch solubility. The order–disorder transitions that occur on heating an aqueous suspension of starch granules have been extensively investigated using DSC. Starch transition temperatures and gelatinization enthalpies by DSC may be related to characteristics of the starch granule, such as

degree of crystallinity. This is influenced by chemical composition of starch and helps to determine the thermal and other physical characteristics of starch. Starches from different botanical sources, differing in composition, exhibited different transition temperatures and enthalpies of gelatinization (Singh et al., 2003).

Gelatinization starts at the hilum of the granule and swells rapidly to the periphery. Gelatinization occurs initially in the amorphous regions, as opposed to the crystalline regions, of the granule, because hydrogen bonding is weakened in these areas. Gelatinization temperatures and enthalpies associated with gelatinization endotherms vary between the starches from different sources (Table 2.8). The differences in transition temperatures between the different starches may be attributed to the differences in the degree of crystallinity. High transition temperatures have been reported to result from a high degree of crystallinity, which provides structural stability and makes the granule more resistant towards gelatinization (Singh et al., 2003).

The gelatinization and swelling properties are controlled in part by the molecular structure of amylopectin (unit chain length, extent of branching, molecular weight, and polydispersity), starch composition (amylose to amylopectin ratio and phosphorus content), and granule architecture (crystalline to amorphous ratio).  $T_p$  (peak temperature) gives a measure of crystallite quality (double helix length). Enthalpy of gelatinization ( $\Delta H_{gel}$ ) gives an overall measure of crystallinity (quality and quantity) and is an indicator of the loss of molecular order within the granule (Singh et al., 2003).

Table 2.8. Gelatinization parameters of the starches from different botanical sources (Singh et al., 2003)

Source	Methodology	To (°C)	Tp (°C)	Tc (°C)	ΔHgel (J/g)
Potato	DSC:S:W 1:2:3	59.72–66.2	62.9–69.6	67.28–75.4	12.55–17.9
Potato	DSC:S:W 1:3:3	57.0–68.3	60.6–72.4	66.5–78.0	13.0–15.8
Potato	DSC:S:W 1:1:5	57.2	61.4	80.3	17.4
Normal corn	DSC:S:W 1:1:5	62.3	67.7	84.3	14.0
Normal corn	DSC:S:W 1:3	64.1	69.4	74.9	12.3
Normal corn	DSC:S:W 1:9	65.7	71.0	–	12.0
Waxy corn	DSC:S:W 1:9	66.6	73.6	–	14.2
Waxy corn	DSC:S:W 1:3	64.2	69.2	74.6	15.4
High amylose corn	DSC:S:W 1:9	66.8	73.7	–	13.7
Rice	DSC:S:W 1:1:5	62.0	67.4	97.5	11.0
Rice	DSC:S:W 1:9	57.7	65.1	–	11.5
Rice	DSC:S:W 1:2:3	66.0–67.26	69.74–71.94	74.08–78.04	8.16–10.88
Rice	DSC:S:W 1:3	70.3	76.2	80.2	13.2
Waxy rice	DSC	66.1–74.9	70.4–78.8	–	7.7–12.1
Wheat	DSC:S:W 1:1:5	51.2	56.0	76.0	9.0
Wheat	DSC:S:W 1:2:3	46.0–52.4	52.2–57.6	57.8–66.1	14.8–17.9
Wheat	DSC:S:W 1:3	57.1	61.6	66.2	10.7

Enthalpy values are expressed in J/g of the dry starch; S, starch; W, water. To=onset temperature, Tp=peak temperature; Tc=final temperature; ΔHgel=Enthalpy of gelatinization (dsb, based on dry starch weight).

Yamin et al. (1999) stated that a starch with low To (onset temperature) and broad gelatinization range might have irregularly shaped granules. Singh and Singh (2001) and Kaur et al. (2002) also reported lower transition temperatures and higher ΔHgel (enthalpy of gelatinization) for large and irregular or cuboidal potato starch granules. The variation in To, ΔHgel and gelatinization temperature range in starches from different cultivars may be due to difference in the amounts of longer chains in amylopectins. These longer chains require a higher temperature to dissociate completely than that required for shorter double helices (Yamin et al., 1999). Noda et al., (1996) also reported that DSC parameters are influenced by the molecular architecture of the crystalline region, which corresponds to the distribution of amylopectin shorter chains. The higher transition temperatures for corn and rice starch may result from the more rigid granular structure and the presence of lipids

(Singh and Singh, 2003). Because amylopectin plays a major role in starch granule crystallinity, the presence of amylose lowers the melting point of crystalline regions and the energy for starting gelatinization (Flipse et al., 1996).

#### **2.2.4. Morphological Characteristics of Starch**

The variation in the size and shape of starch granules is related to the biological origin (Svegmark and Hermansson, 1993). The granular structures of potato, corn, rice and wheat starches show significant variations in size and shape when viewed by SEM. Scanning electron micrographs of the starch granules from various plant sources are illustrated in Figure 2.6. The granule size is variable and ranges from 1 to 110  $\mu\text{m}$  (Hoover, 2001).

The extent of variation in the granular structure of starches from cultivar to cultivar is significantly higher in potatoes. Potato starch granules have been observed to be oval and irregular or cuboidal in shape. The starch granules are angular-shaped for corn, and pentagonal and angular-shaped for rice. At maturity, wheat endosperm contains two types of starch granules: large A- and small B-type. A-type granules are disk-like or lenticular in shape with diameters ranging from 10 to 35  $\mu\text{m}$ . On the other hand, B-type starch granules are roughly spherical or polygonal in shape, ranging from 1 to 10  $\mu\text{m}$  in diameter. When observed under a scanning electron microscope, the surfaces of the granules from corn, rice and wheat appear to be less smooth than potato starch granules (Singh et al., 2003).

Starch granules show birefringence in the form of the typical ‘‘maltese cross’’, which is due to the high degree of molecular order in starch granules when viewed under polarized light (Hoseney, 1998). In starch granules, the partial crystalline structure contributes partly to the high degree of molecular order. Figure 2.7 shows birefringence of native corn, wheat and potato starches (Liu et al., 2008).

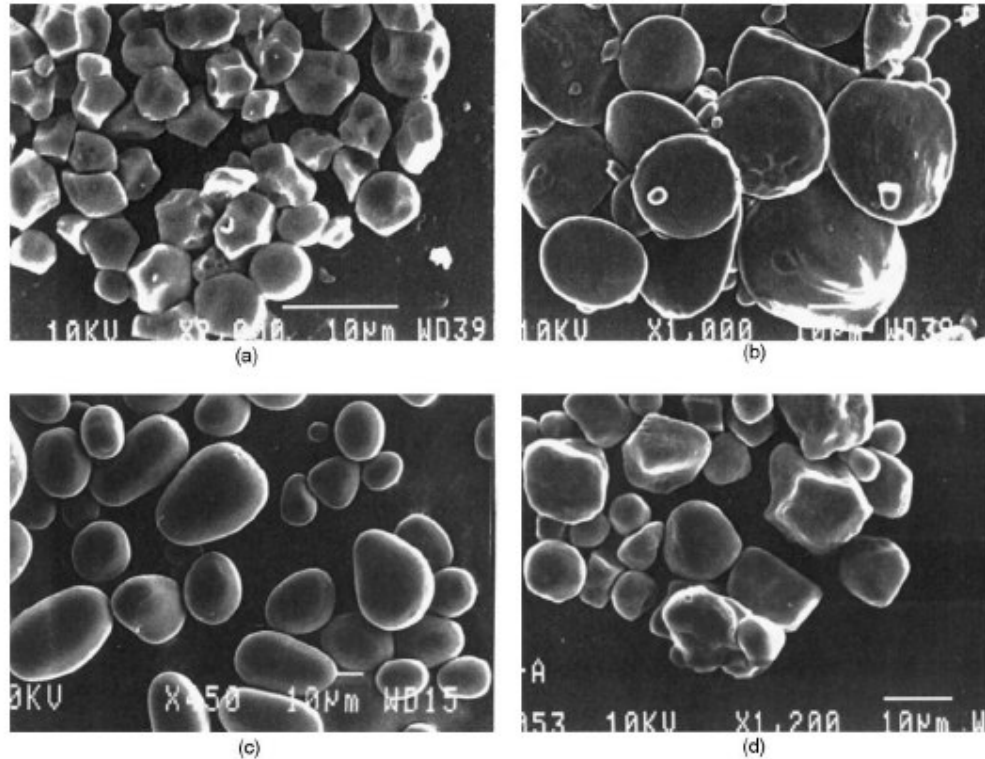


Figure 2.6. Scanning electron micrographs (SEM) of starches separated from different sources: (a) rice, (b) wheat, (c) potato, (d) corn (bar=10 µm) (Singh et al., 2003)

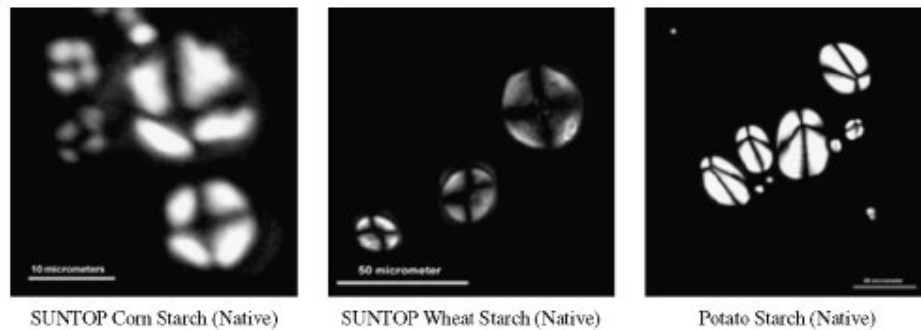


Figure 2.7. Birefringence of native corn, wheat and potato starches (Liu et al., 2008)

### 2.2.5. Rheological and Pasting Properties of Starch

Rheological properties of a material reflect its structure. During gelatinization, starch granules swell to several times their initial volume. Swelling is accompanied by leaching of granule constituents, predominantly amylose, and the formation of a three dimensional network. These changes are responsible for the rheological

characteristics exhibited by starch suspensions during heating and shearing. Rheological/pasting behaviour of starch is governed by amylose content, granule size distribution, granule volume fraction, granule shape, granule-granule interaction and continuous phase viscosity. Starch exhibits unique viscosity behaviour with change of temperature, concentration and shear rate. This can be measured in terms of rheological/pasting curves (plots of viscosity versus temperature) obtained with a Brabender Viscoamylograph or Rapid Viscosity Analyzer (RVA) and rheometer. Information obtained from rheology/pasting curves is vital when considering a starch as a possible component of a food product. The maximum viscosity at a given concentration reflects the ability of the granules to swell freely prior to their physical breakdown. Starches that are capable of swelling to a high degree are also less resistant to breakdown on cooking and hence exhibit significant viscosity decreases after the maximum viscosity is reached (Singh et al., 2007).

Gelatinized starch dispersions have a non-Newtonian, time-independent and viscoelastic behaviour. These gelatinized starch dispersions are usually represented by the power law model (Eqn. 2.2) using shear rate and shear stress data. The consistency index  $K$ , and the flow behaviour index  $n$ , depend on the kind of starch, concentration and temperature (Lagarrigue and Alvarez, 2001).

$$\sigma = K\dot{\gamma}^n \quad (2.2)$$

Typical flow curves, shear stress as a function of shear rate, of starch-in-water pastes heated to 95 °C are shown in Figure 2.8. All exhibited a shear-thinning behaviour; that is a curvature downwards on the shear rate axis (Thebaudin, 1998).



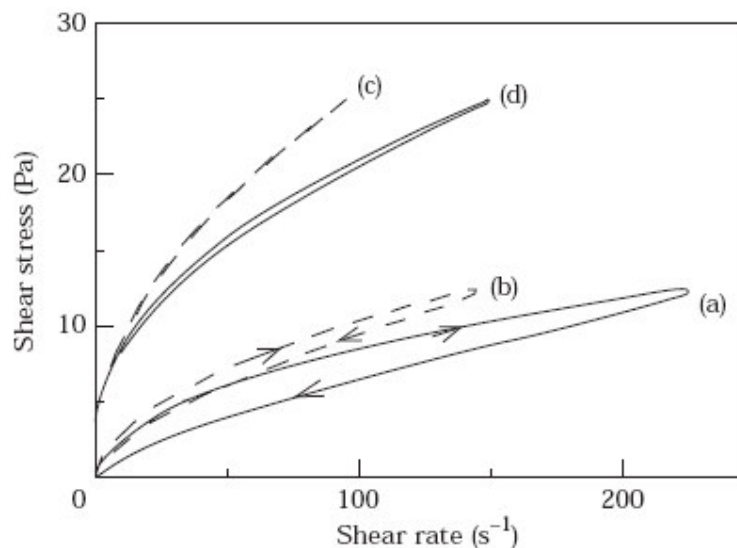


Figure 2.8. Flow curves of starch pastes measured at 60 °C. (a) wheat starch (continuous line); (b) normal maize starch (dashed line); (c) modified waxy starch (dashed line); (d) rice starch (continuous line).

Viscosity changes of starch dispersions during gelatinization are most frequently measured with a Brabender Visco/Amylograph. It is equipped with a rotational cup and a stationary upper element. Similar instruments have been developed as an alternative to the Visco/Amylograph, especially Rapid Visco Analyser (RVA) working on the same principle (Lagarrigue and Alvarez, 2001). Pasting profiles of native wheat, potato and maize starches determined using a Rapid Visco-Analyser (RVA) are presented Table 2.9 (Gunaratne and Corke, 2007).

Table 2.9. Pasting properties of native wheat, potato, and maize starches (Gunaratne and Corke, 2007)

Starch	Peak viscosity	Hot paste viscosity	Breakdown	Cold paste viscosity	Setback
Wheat	153 ± 1.2	114 ± 1.4	39 ± 0.8	216 ± 1.6	101 ± 1.4
Potato	655 ± 1.4	174 ± 1.7	481 ± 1.9	254 ± 1.8	81 ± 1.1
Maize	194 ± 1.1	163 ± 1.4	90 ± 0.8	210 ± 1.8	107 ± 1.6

### **2.2.6. Modification of Starch**

Modification of starch was carried out to overcome shortcomings of native starches and increase the usefulness of starch for industrial applications. Native starches when cooked can easily retrograde and there is a gelling tendency of pastes besides easily undergoing syneresis. Therefore starch modification not only decreases retrogradation, gelling tendencies of pastes and gel syneresis but also improves paste clarity and sheen, paste and gel texture, film formation and adhesion. Modification of starches has brought about an evolution of new processing technologies and market trends. These highly functional derivatives have been tailored to create competitive advantage in a new product, improve product aesthetics, simplify product proclamation, lower recipe/production costs, increase product all through, eliminate batch rejects, ensure product consistency and extend shelf-life whilst clearly making starch relevant in all stages of a food product's lifecycle. Modification of starch is an ongoing process as there are numerous possibilities. There is a huge market for the many new functional and added value properties resulting from these modifications. Over the last few decades, starch has been modified by various methods to achieve functionalities suitable for various industrial applications. Basically there are four broad based kinds of modifications; chemical, physical, enzymatical and genetical (Kaur et al., 2011).

Chemical modification of starch involves the polymer molecules of the starch granule in its native form. Modification is generally achieved through derivatization such as etherification, esterification and crosslinking, oxidation, cationization and grafting of starch. Physical modification can be safely used as a modification process in food products as it does not involve any chemical presence. Some of the new physical modifications are osmotic pressure treatment, deep freezing, dry heating, etc. Enzymatic modification has mainly used hydrolyzing enzymes in its modification and one of its products is syrup be it glucose syrup or high fructose corn syrup. The advancement of genetic engineering technologies has made the genetic modification of starch in plants possible by targeting the enzymes of the starch biosynthetic pathway. Starch modification has come a long way since it was first carried out in the 1800s. As with any modification, the possibilities are numerous with starch modification but there should be an eye on the safety and health measurements taken for consumers and the environment (Kaur et al., 2011).

### 2.2.7. Oxidation of Starch

In the food industry, the use of oxidized starch has become increasingly important because it has low viscosity and good binding and film forming properties (Kuakpetoon and Wang, 2006). Oxidized starches are used in food products for which neutral-tasting, low viscosity starch is required, e.g. lemon curd, salad dressing, and mayonnaise (Adebowale and Lawal, 2003).

Two main reactions are involved in oxidation. First, hydroxyl groups in starch molecules are oxidized to carbonyl groups, primarily at C-2, C-3, and C-6. Second, oxidation also causes depolymerization of starch molecules by cleaving  $\alpha$ -(1 $\rightarrow$ 4)-glucosidic linkages (Chan et al., 2011a).

Oxidized starch is produced by reacting starch with a specified amount of oxidizing reagent under controlled temperature and pH. Sodium hypochlorite is the most common chemical oxidizing agent used to study starch oxidation. However, in the hypochlorite oxidation process, the oxidized starch yield is low because small molecules are lost due to starch breakdown (Chan et al., 2011b). Sodium bromide, gaseous chlorine, calcium hypochlorite, hydroperoxide, potassium permanganate, ammonium persulfate, oxygen, and bromide are other chemical oxidizing agents used to oxidize starch. However, chemical agents used for oxidation of starches can create safety and environmental hazards, chemical waste problems, and leave undesirable residues in final products. Ozone can eliminate the disadvantages of traditional chemical oxidizing agents. Ozone gas which is a powerful oxidant (oxidation–reduction potential of 2.07 V), does not leave a residue, can be generated on site, requires no storage and subsequent disposal of chemical containers (Sandhu et al., 2012).

Ozone is a more powerful oxidant than oxygen, it reacts with most substances at ambient temperatures, and it creates no waste water disposal problem. Furthermore, a dry process using ozone can reduce the purification cost and produce a product with high recovery. Several patents have been filed for a method of oxidizing dry starch and polysaccharides using ozone as an oxidizing agent. In addition, some recent scientific publications have reported the use of ozone in starch modification. An and King (2009) reported that ozonated rice starch exhibited similar pasting properties to

those from oxidized starches treated with low concentrations of chemical oxidizing agents. On the other hand, Lii et al. (2003) declared that the corona discharge method used discharges decomposed starches to low molecular fragments together with oxidation of the polysaccharides. Chan et al. (2009) demonstrated that ozone gas successfully oxidized starches from a variety of different starches and postulated that if the ozone gas has more access to the interior or subsurface of the starch granule, a higher degree of oxidation would occur.

## CHAPTER III

### MATERIAL AND METHODS

#### 3.1. Materials

Commercial wheat, corn, potato and rice starches were used as test materials. All starch samples, Migros trademark, were purchased from a commercial source (Migros A.Ş., İstanbul, Turkey). The starches were used directly without any purification. Wheat starch was produced from ordinary wheat variety (i.e. *Triticum aestivum*). Corn (*Zea mays L.*) starch was produced from dent and flint types of corn. Potato (*Solanum tuberosom L.*) was produced from a mixture of amado, calla, cers, hermes and komet types. Rice (*Oryzae sative L.*) was obtained from round-grain variety. The starches used had a shelf life of two years as labelled by the manufacturer. The experiments were carried out when the freshness of the samples were around 3-4 months. The moisture contents of starch samples were determined by a moisture analyzer (Metler Toledo, MJ33 Moisture analyzer, Switzerland).

#### 3.2. Ozonation of Starches

Ozone was obtained by an ozone generator (OMS Model Ozone Generator, İzmir, Turkey) using the coronal-discharge method (Figure 3.1). The generator has a mixing part, a degasser for removing of undissolved ozone in water, a redox control (ORP) system and an integrated oxygen unit using atmospheric air. It has a maximum ozone production capacity of 60g/h. Samples were ozonated in a 500 mL glass gas washing bottle (Figure 3.2 and Figure 3.3). Gas is directed from the generator to the bottle by a connection whose end was equipped with a gas disperser to increase solubility and diffusion by creating bubbles. Dissolved ozone concentration was determined by oxidation/reduction potential (ORP). It was converted to ppm by using a calibration table (Table 3.1). Undissolved ozone gas was driven to the atmosphere by a discharging tube.

Wheat starch-water, corn starch-water, potato starch-water and rice starch-water mixtures were prepared in the ratio of 1:9 (dry sample to distilled water ratio). The prepared wheat starch-water (pH= 4.08), corn starch-water (pH= 5.48), potato starch-

water (pH= 6.60) and rice starch-water (pH=6.04) mixtures were treated with ozone at a rate of 60g/h in the bottle for 1 hour while unozonated starch samples were used as controls. Also a wheat-starch-water mixture was ozonated for 15 min and 30 min in the bottle.



Figure 3.1. Photograph of ozone generator



Figure 3.2. Photograph of gas washing bottle

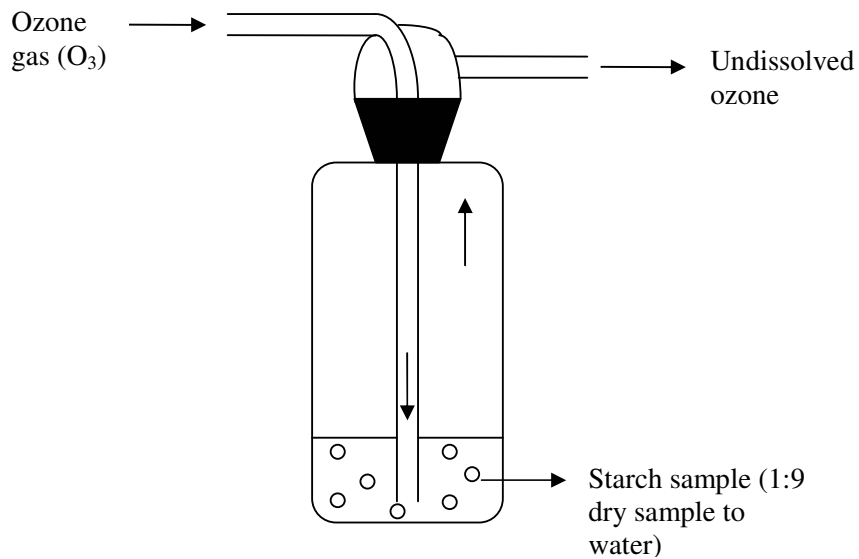


Figure 3.3. Schematic diagram of gas washing bottle for ozonation

### 3.3. Gelatinization Analysis by DSC (Differential scanning calorimetry)

Control and ozonated wheat, corn, potato and rice starch-water mixture samples were evaluated using DSC (Perkin-Elmer DSC 6 equipped with a Pyris software, Perkin-Elmer Inc., Wellesley USA). 50 $\mu$ l starch-water mixture (1:9 ratio of sample to water) was placed into a DSC pan with a micropipette and sealed. An empty pan as reference was also sealed. Samples were analyzed in triplicate. The samples were heated at a rate of 5°C/min from 5 to 150°C with nitrogen flushing (40mL/min). The starch gelatinization characteristics (onset temperature,  $T_o$ , peak temperature,  $T_p$ , conclusion temperature,  $T_c$  and enthalpy,  $\Delta H$ ) were computed.

Table 3.1. Calibration table of conversion of ozone concentration from ORP to ppm

mV-orp	ppm-mg/L
100	0
200	0.04
300	0.08
400	0.13
500	0.16
600	0.20
700	0.22
750	0.25
800	0.39
860	0.50
875	1.00
900	1.25
925	1.50
950	1.75
975	2.00
1000	2.25
1025	2.50
1050	2.75
1075	3.00
1100	3.25
1125	3.50
1150	3.75
1175	4.00
1200	4.25
1225	4.50
1250	4.75
1275	5.00
1300	5.25
1325	5.50
1350	5.75
1375	6.00
1400	6.25
1425	6.50
1450	6.75
1475	7.00
1500	7.25
1525	7.50
1550	7.75
1575	8.00
1600	8.25

### 3.4. Structure Analysis by Polarized Light Microscopy

Control and ozonated wheat, corn, potato and rice starch-water mixture samples were observed using a polarized light microscope (Model BX51, Olympus Corp., Tokyo, Japan) equipped with a 100-W halogen light source. 10 µl sample was placed on a slide covered by a cover slip to observe at a magnification of 20X. A Pixera camera (Model PVC 100C, Los Gatos, CA, USA) was used to acquire the images.



### **3.5. Structure Analysis by SEM (Scanning Electron Microscope)**

A Scanning Electron Microscope (SEM) (JEOL JSM-6390LV, Tokyo, Japan) was used to study the structure of the starch granules before and after the ozonation treatment. Both control and ozonated samples (1:9) were dried at room temperature. Then a dry sample was adhered on a SEM mount using double-sided conductive adhesive tape and sputter coated with a Au-Pd mixture in a vacuumed atmosphere (8 pascal) for 45 s (Quorum SC7620 Sputter Coater, UK). The mounted sample was then placed on the SEM stage and images were digitally captured at 20 kV with 2000–3000 magnification.

### **3.6. Pasting Properties by RVA (Rapid Visco Analyser)**

Pasting properties of control, 15 min ozonated, 30 min ozonated and 60 min ozonated wheat starch and also control and 60 min ozonated corn, potato and rice starch samples were tested by using a Rapid Visco Analyser (RVA 4, Newport Scientific, Warriewood, Australia). 4 g (14% moisture basis) of samples were dispersed in 25 ml distilled water in an aluminum sample canister. The RVA pasting curve was obtained by using a 23 min test profile: initial equilibrium at 50 °C for 1 min, heating to 95 °C over 7.5 min, holding at 95 °C for 5 min, cooling to 50 °C over 7.5 min and holding at 50 °C for 2 min. Peak temperature, peak viscosity, trough, breakdown and final viscosity values were evaluated with the data analysis software (Thermocline for Windows, Newport Scientific, Australia).

### **3.7. Rheological Measurement**

Dynamic rheological measurements for control, 15 min ozonated, 30 min ozonated and 60 min ozonated wheat starch-water and also control and 1 hr ozonated corn starch- water, potato starch-water and rice starch-water mixtures in the ratio of 1:9 (dry sample to distilled water ratio) were performed at 60°C with a CVOR Rheometer (Bohlin, Malvern, Worcestershire, United Kingdom), using parallel plate geometry (20mm diameter, 1mm gap). For each measurement, 1ml of sample was carefully deposited over the plateau of the rheometer. After the plateau came contact with the plate, the exposed surface of the sample was covered with a thin layer of low-density silicone oil to prevent evaporation during the measurement. In order to describe the variation in the rheological properties of samples under steady shear, the data were fitted to the well-known power law model (Eqn. 3.1), which is used

extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications (Choi and Yoo, 2009).

$$\sigma = K\dot{\gamma}^n \quad (3.1)$$

where,

$\sigma$  = the shear stress (Pa),

$\dot{\gamma}$  = the shear rate ( $s^{-1}$ ),

$K$  = the consistency index ( $Pa\ s^n$ ),

$n$  = the flow behaviour index (dimensionless).

### **3.8. Measurement of Gelatinized Starch by Enzymatic Method**

This method is used to quantitatively determine gelatinized starch (Chiang and Johnson, 1977). It is based on the principle that gelatinized starch is easily digested by amyloglucosidase to form glucose.

#### **Reagents**

*o*-toluidine reagent: 1.5 g of thiourea was dissolved in 940 ml of glacial acetic acid and 60 ml of *o*-toluidine was added. It was stored in an amber bottle.

Sodium acetate buffer: 4.1 g of anhydrous sodium acetate in 1 litre distilled water and pH adjusted to 4.8 with acetic acid.

Glucoamylase solution: 2 g of amyloglucosidase from *Aspergillus niger* (catalog No.10115, Fluka) was dispersed in 250 ml of acetate buffer and filtered rapidly through glass fibre paper. It was used within 2 hr. Specific activity of the amyloglucosidase was 70 unit/mg at pH 4.8 and 60°C.

Gelatinized starch percentage of control, 15 min ozonated, 30 min ozonated and 60 min ozonated wheat starch samples dried at room temperature was determined by glucoamylase and *o*-toluidine reagent. 20 mg of sample was dispersed in 5 ml of distilled water for partially gelatinized starch, while 20 mg sample was dispersed in 3 ml of distilled water and 1 ml of 1 N NaOH and five minutes later, 1ml of 1 N HCl was added. 25 ml of amyloglucosidase solution was then added and incubated at 60°C for 30 min. 2ml of 25% trichloroacetic acid (TCA) was added to inactivate the glucoamylase and centrifuged at 10,000Xg for 10 min. 4.5 ml of *o*-toluidine reagent

was added to 0.5 ml of the supernatant solution. The test tubes were placed into boiling water for 10 min and cooled with cold water. 5 ml of glacial acetic acid was then added and absorbance was measured at 630 nm. Gelatinized starch percentage (Eqn. 3.2 and Eqn. 3.3) was calculated by following equations:

$$Y = 100 (B - k) / (A - k) \quad (3.2)$$

$$k = A(C - B) / (A - 2B + C) \quad (3.3)$$

where,

A= the absorbance of total gelatinized starch

B= the absorbance of a mixture of partially gelatinized after 30 min enzymatic hydrolysis

C= the absorbance of a mixture of partially gelatinized after 60 min enzymatic hydrolysis

k= the absorbance of 1% of intact starch digested in 30 min and is a constant for each variety or specially treated starch

Y= gelatinized starch percentage

### 3.9. Color Analysis

Colors of all control and ozonated wheat, corn, potato and rice starches samples were measured with a HunterLab ColorFlex (A60-1010-615 Model Colorimeter, Hunter lab, Reston VA). A white standard plate ( $L_o=93.01$ ,  $a_o=-1.11$ ,  $b_o=1.30$ ) was used to calibrate the colorimeter. Triplicate measurements for L, a, and b were done where L is the brightness coefficient from dark (0) to bright ( $\infty$ ), a is the coefficient from green (-) to red (+) and b is the coefficient from blue (-) to yellow (+). Chroma (Eq. (3.4)), hue (Eq. (3.5)), whiteness (Eq. (3.6)) and total color difference (TCD; Eq. (3.7)) were obtained by following equations:

$$Chroma = \sqrt{(a^2 + b^2)} \quad (3.4)$$

$$Hue = \arctan \frac{b}{a} \quad (3.5)$$

$$\text{Whiteness} = 100 - \sqrt{(100 - L^2) + a^2 + b^2} \quad (3.6)$$

$$\text{TCD} = \sqrt{(L_o - L)^2 + (a_o - a)^2 + (b_o - b)^2} \quad (3.7)$$

### 3.10. pH Measurement

The pH values of all control and ozonated starch-water mixtures were determined by a pH-meter (Hanna instruments, pH 211, Microprocessor pH-meter, Portugal). All pH analyses were carried out in triplicate.

### 3.11. Microbial Analysis (Total bacteria and Mold/yeast Counts)

Serial dilutions from  $10^{-1}$  to  $10^{-4}$  levels were made from control and ozonated wheat, corn, potato and rice starch samples. The aerobic spread-plate technique was carried out for both total bacterial count and mold/yeast count.

Aerobic plate count agar (PCA; Merck, Darmstadt, Germany) was used for the total bacteria analysis. The inoculated samples (0.2 mL) were incubated at 37°C for 24-48hr. Potato dextrose agar (PDA; Merck, Darmstadt, Germany) was used for the mold and yeast count analysis. The inoculated samples (0.2 mL) were incubated at 25°C for 2-5 days. The plates were counted as colony forming units (cfu) and expressed as log cfu/g. All analyses were carried out in triplicate for each dilution.

### 3.12. Statistical Analysis

Statistical analysis (SPSS; Statistical package for social sciences, Statics 16.0, version 2.0, 2006) was performed to compare the experimental results under the ozonation treatment including untreated control by using one-factor analysis of variance (ANOVA). In order to determine the data that are significantly different from each other, Duncan multiple range test method was applied. All experimental values are at least mean of duplicate determination. Trends were considered significant when means of compared parameters differed at  $P < 0.05$  significance level.

These parameters are;

- Effects of ozone treatment on gelatinization characteristics (onset temperature,  $T_o$ , peak temperature,  $T_p$ , conclusion temperature,  $T_c$  and enthalpy,  $\Delta H$ ) of wheat, corn, potato and rice starches.
- Effects of ozone treatment on pasting properties (peak temperature, peak viscosity, trough, breakdown and final viscosity) of wheat, corn, potato and rice starches.
- Effects of ozonation time on pasting properties (peak temperature, peak viscosity, trough, breakdown and final viscosity) of wheat starch.
- Effects of ozone treatment on rheological properties of wheat, corn, potato and rice starches under steady shear.
- Effects of ozonation time on rheological properties of wheat starch under steady shear.
- Effects of ozonation time on quantitatively gelatinized starch of wheat starch.
- Effects of ozone treatment on color of wheat, corn, potato and rice starches.
- Effects of ozone treatment on pH of wheat, corn, potato and rice starches.
- Effects of ozone treatment on total bacteria and mold/yeast counts of wheat, corn, potato and rice starches.

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

There are many applications of ozone in water treatment throughout the world. Unfortunately, a limited number of researches have been conducted on ozone use on food materials, especially on types of starch which is an important macromolecule used in the food industry. In the past studies, ozone was generally used to inactivate microorganisms. To date, there are a lack of studies of the effects of ozonation on thermal properties, internal and outer structure properties, pasting properties, rheological properties, physico-chemical properties, microbiological properties and gelatinization degree of types of starch (wheat, corn, potato and rice starches). In the current study, the reasons why these properties of starch were chosen and the results obtained by the experiments are discussed.

#### **4.1. Differential Scanning Calorimetry (DSC) Measurements**

The gelatinization of starch granules is dependent on moisture content and temperature. In an ample water environment, starch is easy to gelatinize, while in a limited water environment, starch is hard to gelatinize even at 100 °C. When starchy foods such as rice grains, spaghetti, etc. are boiled, starch granules at or near the surface may be easy to gelatinize, on the other hand, starch granules near the center in the food body are hard to gelatinize due to a lack of water (Fukuoka et al., 2002).

DSC thermograms possibly give transition enthalpies occurring during melting of the starch. Therefore, DSC was used to analyse the gelatinization of starch in control and ozonated samples in the presence of excess water (90%, w/w) to see if there is an effect of ozonation on the gelatinization characteristics of samples or not.

The values (average values of triple analysed samples) of starch gelatinization characteristics including onset temperature (temperature at which the gelatinization begins to progress), peak temperature (temperature at maximum rate of gelatinization), conclusion temperature (temperature at which the gelatinization is

completed) and enthalpy (the energy that has to be supplied to obtain complete starch gelatinization) of control and ozonated samples are listed in Table 4.1. The gelatinization properties of control and 1 hr ozonated samples are also shown in Figure 4.1, Figure 4.2 and Figure 4.3. It was observed that starch gelatinization characteristics of 1 hr ozonated corn and potato starch samples are significantly different ( $p<0.05$ ) from their control samples (Table A.1, Table A.2., Table A.3. and Table A.4). Although, there is a significant difference ( $p<0.05$ ) between both the onset temperature and peak temperature of control and 1 hr ozonated wheat starch (Table A.1 and Table A.2), a significant difference was not found ( $p>0.05$ ) between the values of both the conclusion temperature and the gelatinization enthalpy of control and 1 hr ozonated wheat starch samples (Table A.3 and Table A.4). Ozone has similar effects for gelatinization properties of rice starch samples except onset temperature characteristic. The onset temperature of 1 hr ozonated rice starch is significantly reduced ( $p<0.05$ ) from control rice starch (Table A.1).

Table 4.1. The values of starch gelatinization characteristics of control and 1 hr ozonated starch-water mixtures

Starch sample	$T_o$ (°C)	$T_p$ (°C)	$T_c$ (°C)	$\Delta H$ (j/g)
Control wheat starch	59.93±0.30a	65.36±0.17a	73.13±0.29a	8.9846±0.05b
Ozonated wheat starch	61.92±0.23b	67.09±0.01b	73.82±0.63a	10.2333±0.58b
Control corn starch	70.11±0.36g	74.82±0.18g	80.54±0.71d	13.6356±1.89c
Ozonated corn starch	72.62±0.16h	76.58±0.08h	82.64±0.35e	9.1905±0.85b
Control potato starch	64.10±0.36c	68.64±0.50c	75.91±1.11b	15.5702±12.9c
Ozonated potato starch	65.35±0.27d	70.30±0.13d	77.41±0.35c	9.7188±4.36b
Control rice starch	67.83±0.77f	72.98±0.33e	79.75±0.89d	2.2423±0.34a
Ozonated rice starch	67.01±0.04e	73.77±0.76f	79.47±1.31d	2.5341±1.34a

Values followed by the different letter in the same column are significantly different ( $p<0.05$ ). Means ( $\pm$  standard deviation) are based on triplicate analyses.

The gelatinization temperatures of wheat, corn and potato starches were increased by 1.73-2.51 °C and the corresponding gelatinization enthalpies were reduced except the wheat starch after the ozonation process (Table 4.1). However, there is no significant difference ( $p>0.05$ ) between the gelatinization enthalpy of control wheat starch and 1 hr ozonated wheat starch samples (Table A.4). Most probably, the starch granules were unfolded and degraded during the ozonation process. The peak temperature of gelatinization ( $T_p$ ) increased, while the amount of heat ( $\Delta H$ ) required for gelatinization decreased. This means that ozonated starch samples are gelatinized at higher temperatures, but need less energy for gelatinization. Our results indicated that ozonation behaves like an oxidation modification process.

Typical DSC thermograms for non-treated wheat starch were shown in the study of Fukuoka et al., (2002). According to their study, the first peak was observed at 55–75 °C for all samples. In addition, transition temperatures and enthalpy of endothermic peaks of flours (wheat, corn, rice, potato, etc.) heated in the presence of excess water (70%, w/w) were presented by the study of Liu et al., (2006). In our present study, these ranges were also confirmed for unozonated starch-water mixtures. However, there is very little knowledge about the effects of ozone on the thermal properties of starch.

Chan et al. (2011a) investigated the effects of oxidation by ozone gas on the thermal properties of starch (corn, sago and tapioca). Starch, in dry powder form, was exposed to ozone gas for 1, 3, 5 and 10 min ozone generation times. However, no differences were noted in gelatinization temperatures and gelatinization enthalpies of all ozone oxidized starches compared to unmodified starch unlike the results presented in this study. Their results suggest that the process of gelatinization, that involves destruction of starch crystallite and loss of helical conformation, was not affected by the oxidation conditions used. This may be due to inadequate ozonation time and/or ozonation without the use of water. Because water holds more ozone than air and ozone needs to remain in the water long enough to disperse fully (Tiwari et al., 2010), this greatly increases the ozone penetration into the starch granule.

Karaoğlu et al. (2006) prepared pregelatinized modified starch solution by incubation at 63 °C for 5 min and dextrinized modified starch by mixing with 0.1 M HCl . They



found that in pregelatinized and dextrinized starches, initial, peak and completion temperatures increased while transition enthalpy decreased (except dextrinized wheat starch sample) when compared to the nonmodified starch. While transition enthalpy decreased in dextrinized corn starch, it was increased in dextrinized wheat starch samples. These results are very similar to those in our study. It has been reported that the gelatinization temperature increase was probably caused by sugars coming from the degradation of starch.

In the study of Gunaratne and Corke (2007), a 40% (db) starch (wheat, potato and maize starches) slurry was acid-modified with slight modifications using 0.1 M, 0.5 M and 1M hydrochloric acid at 50 °C for 1.5 h. Increases were found for gelatinization temperature and enthalpy of all the starches after acid modification. The effect was more pronounced as the acid concentration was increased. In the similar study of Sandhu et al. (2007), the starches isolated from normal and waxy corn varieties were hydrolyzed with hydrochloric acid (0.14 mol equivalent/L). Native normal corn starches showed lower onset temperature ( $T_o$ ) and peak temperature ( $T_p$ ) as compared to their counterpart acid thinned starches, whereas the reverse was observed for waxy corn starch. Enthalpy of gelatinization ( $\Delta H_{gel}$ ) was lower in acid thinned normal and waxy starches when compared to their native starches. In our present study, ozonated starch samples gave higher gelatinization temperatures, but lower gelatinization enthalpy. Ozone treatment most probably attacks the amorphous regions in the granules causing decoupling of the crystallites and therefore melting at higher temperatures by using less energy to complete the gelatinization.

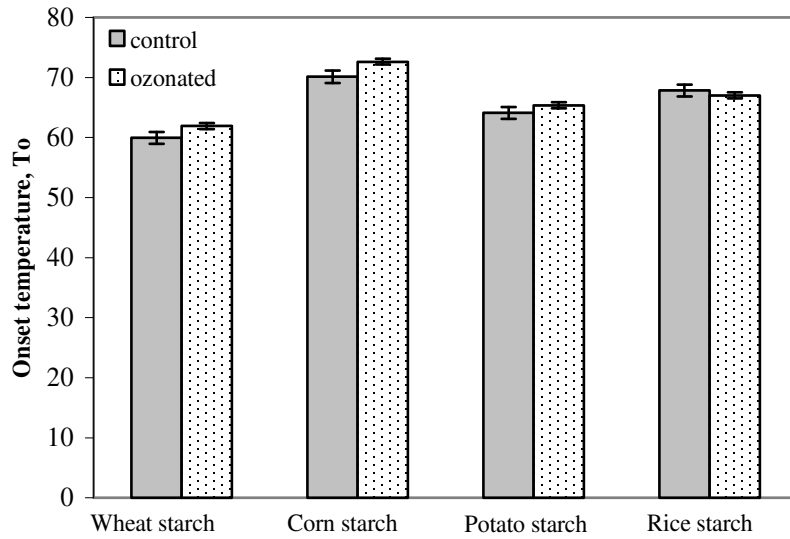


Figure 4.1. Effect of ozonation on the gelatinization onset temperatures of wheat, corn, potato and rice starches

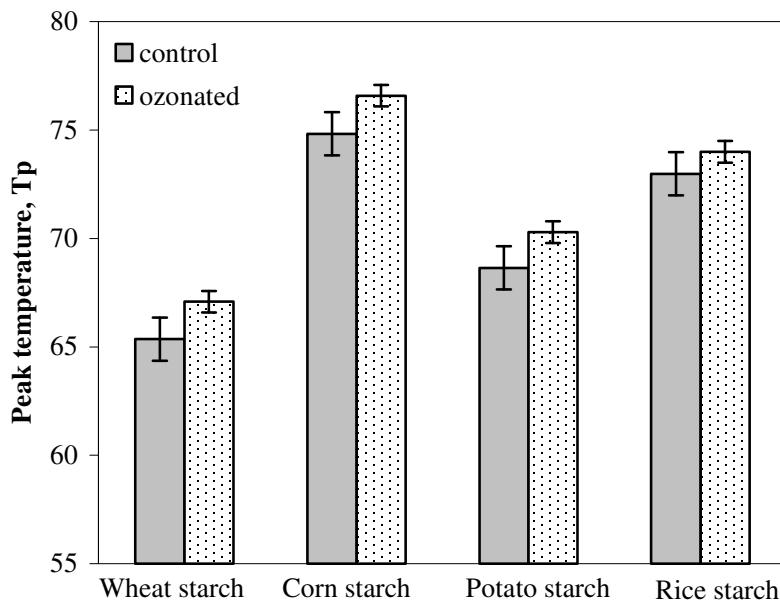


Figure 4.2. Effect of ozonation on the gelatinization peak temperatures of wheat, corn, potato and rice starches

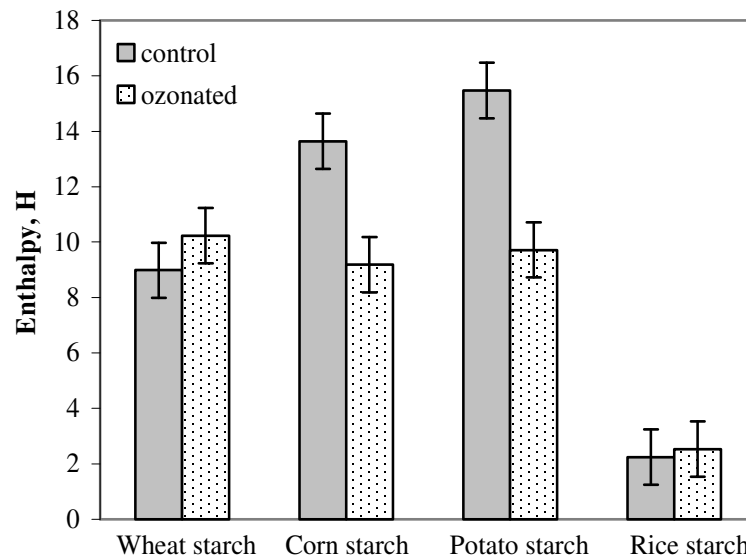


Figure 4.3. Effect of ozonation on the gelatinization enthalpies of wheat, corn, potato and rice starches

#### 4.2. Birefringence

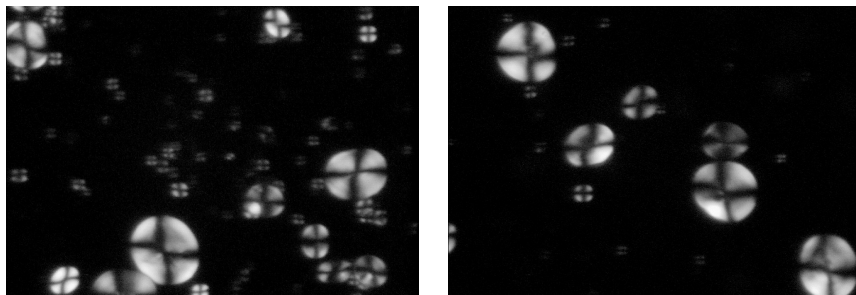
In order to understand why the gelatinization properties of various starches (wheat, corn, potato and rice starches) were altered by ozonation, their birefringence under polarized light were studied.

Polarized light microscopy (optical technique) is used to differentiate between crystals and amorphous material and investigate the physical state of starch granules. When starch granules are viewed under the microscope using polarized light, they exhibit birefringence. Birefringence measures the difference in the speed of light for two perpendicularly plane polarized beams. The refraction of polarized light by the intact crystalline regions in starch gives a maltese cross effect. Loss of birefringence is an indication of the irreversible swelling of starch granules that occurs above the gelatinization temperature (Zimeri and Kokini, 2003).

It can be stated that there was a little change in the birefringence for ozonated starch samples (Figure 4.4, Figure 4.5, Figure 4.6 and Figure 4.7). There is a more distinct difference between the birefringence of control and ozonated corn starch (Figure 4.5) and also between the birefringence of control and ozonated potato starch (Figure 4.6)

samples under polarized light microscopy. However, there is almost no difference between the birefringence of control and ozonated wheat starch (Figure 4.4) and between the birefringence of control and ozonated rice starch (Figure 4.7). These results might be due to the fact that the birefringence of starch in polarized light may not be sensitive enough to reflect the internal structure change of starch granules caused by the ozonation, or there was not much change in the internal structure of starch granules during the ozonation treatment.

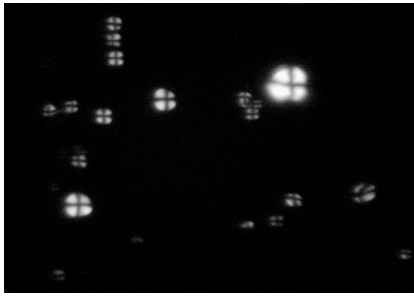
In the study of Liu et al. (2008), wheat, corn and potato starches (native) were viewed in polarized light. The results are similar to the results presented in this study for unozonated starch samples. In our present study, it was hypothesized that ozonation might change the ordered structure, and therefore might cause a change in the birefringence. However, when control and ozonated wheat and rice starch samples were viewed in polarized light, they could not be clearly differentiated visually in terms of birefringence (Figure 4.4 and Figure 4.7). However, the internal structure change of starch granules caused by 1 hr ozonation are more pronounced for corn and potato starch samples (Figure 4.5 and Figure 4.6) than wheat and rice starch samples (Figure 4.4 and Figure 4.7). This state can be explained by easier penetration of ozone into large granules of corn and potato starches compared with the small size granules of wheat and rice starches.



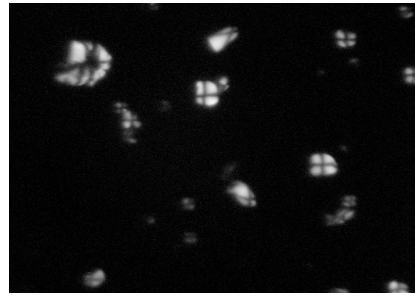
Control wheat starch

1 hr ozonated wheat starch

Figure 4.4. Polarized light micrographs of wheat starch-water samples (1:9; sample to water ratio)

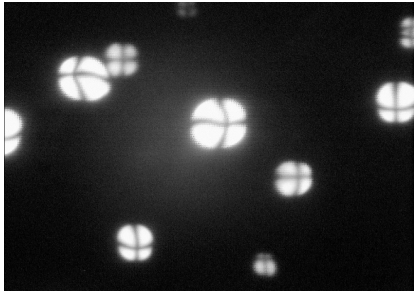


Control corn starch

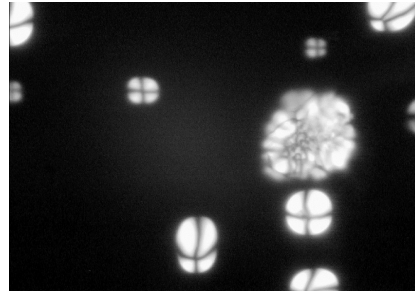


1hr ozonated corn starch

Figure 4.5. Polarized light micrographs of corn starch-water samples (1:9; sample to water ratio)

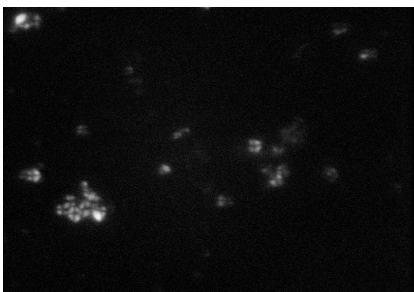


Control potato starch

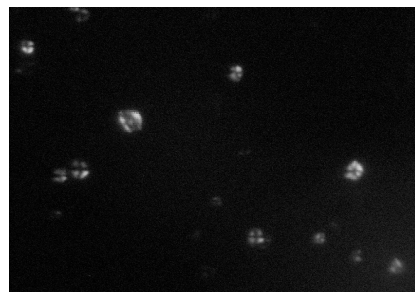


1hr ozonated potato starch

Figure 4.6. Polarized light micrographs of potato starch-water samples (1:9; sample to water ratio)



Control rice starch



1 hr ozonated rice starch

Figure 4.7. Polarized light micrographs of rice starch-water samples (1:9; sample to water ratio)

### **4.3. Morphological Properties**

Starch granules (after drying at room temperature) were examined under scanning electron microscopy (SEM) to investigate the outer structure changes after ozonation. The granule morphologies (starch granule shape and surface smoothness/roughness) of wheat, corn, potato and rice starches were viewed under SEM in order to underlay the changes in gelatinization properties and birefringences of starch types after 1 hr ozone treatment.

The shapes of starch granules were changed and the original smooth surfaces became rough and fibrous after 1 hr ozonation (Figure 4.8, Figure 4.9, Figure 4.10 and Figure 4.11). Control starch samples showed that the granules are round to polygonal in shape similar to shapes reported in the literature. The granule surface is relatively smooth and free from pores, cracks or fissures (Liu et al., 2008; Khattoon et al., 2009).

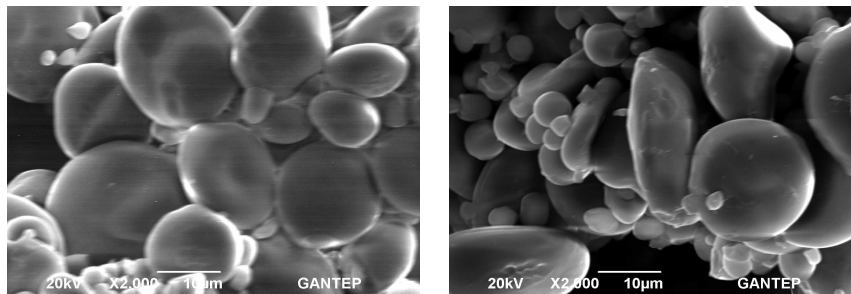
Wheat starch granules are roughly spherical or polygonal in shape, while potato starch granules are oval and irregular or cuboidal in shape. The starch granules are angular-shaped for corn, and pentagonal and angular-shaped for rice (Singh et al., 2003). In our present study, shape and surface of unozonated wheat, corn, potato and rice starch granules under SEM were observed identically to that study.

Due to the irregular shapes of rice starch granules, changes in the granule shape and surface caused by ozonation were not obvious (Figure 4.11). Similarly, any noticeable change was not observed for ozonated wheat starch sample (Figure 4.8). However, changes in the granule shape and surface induced by the ozonation were visually distinct for corn and potato starch granules (Figure 4.9 and Figure 4.10). Similar observations were obtained by Liu et al. (2008) for the study of high pressure treatments of wheat and potato starches and by Hui et al. (2009) of modified potato starch.

The average granule size ranges from 1 to 20  $\mu\text{m}$  for small and 20 to 110  $\mu\text{m}$  for large potato starch granules. The average size of individual corn starch granules ranges from 1 to 7  $\mu\text{m}$  for small and 15 to 20  $\mu\text{m}$  for large granules. The rice starch granules range from 3 to 5  $\mu\text{m}$  in size. At maturity, wheat endosperm contains two

types of starch granules: large A- and small B-type. A-type granules have diameters ranging from 10 to 35  $\mu\text{m}$ . On the other hand, B-type starch granules range from 1 to 10  $\mu\text{m}$  in diameter (Singh et al., 2003). Granule sizes of potato and corn starches are greater than wheat and rice starches.

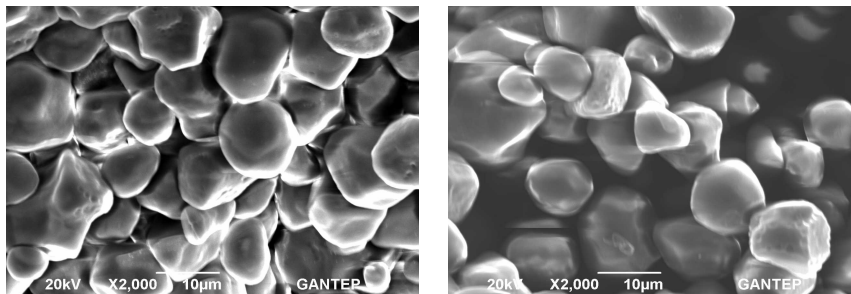
Ozone treatment resulted in swollen starch granules for corn and potato starch samples (Figure 4.9 and Figure 4.10). This swollen condition could result from the large granule sizes of corn and potato starches. Because of this, ozone could diffuse and penetrate into starch granules easily. SEM performance for starch samples showed that ozonation is more effective on starch granules with greater size. In other words, the outer structures of corn and potato starch samples were affected by 1 hr ozone treatment but not the outer structures of wheat and rice starch samples.



Control wheat starch

1 hr ozonated wheat starch

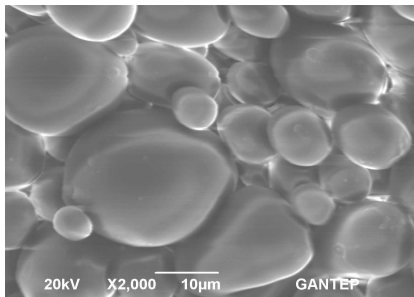
Figure 4.8. Changes of the outer structure of wheat starch granules after ozone treatment under SEM.



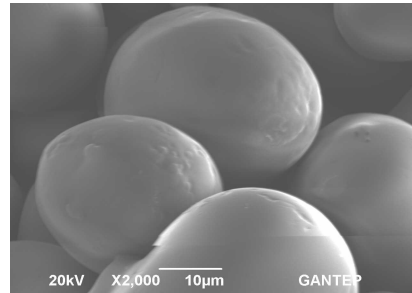
Control corn starch

1 hr ozonated corn starch

Figure 4.9. Changes of the outer structure of corn starch granules after ozone treatment under SEM.

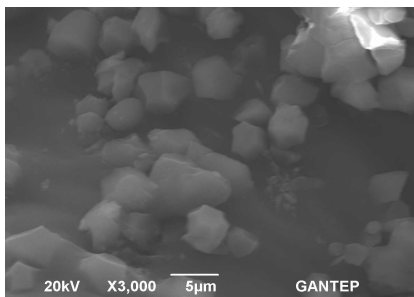


Control potato starch

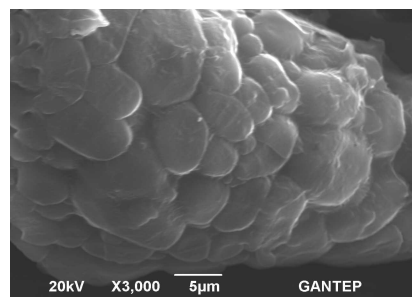


1 hr ozonated potato starch

Figure 4.10. Changes of the outer structure of potato starch granules after ozone treatment under SEM.



Control rice starch



1 hr ozonated rice starch

Figure 4.11. Changes of the outer structure of rice starch granules after ozone treatment under SEM.

#### 4.4. Pasting Properties

The pasting properties of wheat, corn, potato and rice starch samples were investigated in order to confirm the changes in gelatinization properties, birefringences and granule morphologies of starches after 1 hr ozone treatment.

The crystalline order in starch granules is often the basic underlying factor influencing functional properties. Collapse of crystalline order within the starch granules manifests itself as irreversible changes in properties, such as granule swelling, pasting, loss of optical birefringence, loss of crystalline order, uncoiling and dissociation of the double helices, and starch solubility. The order-disorder transitions that occur on heating an aqueous suspension of starch granules have been



extensively investigated using DSC (Singh et al., 2003), while RVA (Rapid Visco Analyser) viscosity curves reflect the pasting characteristics of starch during processing and use. The pasting temperature is the temperature at which the viscosity starts to rise. Usually pasting temperature is higher than the gelatinization temperature, meaning the starch granules are gelatinized before the viscosity begins to rise and be detected by RVA. Lower pasting temperature means faster swelling. Peak viscosity reflects the extent of granule swelling. The drop in viscosity from a maximum value (peak viscosity) to a minimum value (trough viscosity) is the breakdown value. Breakdown value reflects the stability of the paste during cooking, whereas the final viscosity at 50°C indicates the stability of the cooked paste (Liang and King, 2003). In other words, the peak viscosity is the maximum hot paste viscosity, trough viscosity is the lowest viscosity immediately following the peak viscosity, breakdown viscosity is the difference between peak and trough viscosity and final viscosity is the viscosity at the end of the run after cooling and holding at 50°C (Gray et al., 2010).

RVA pasting properties of control and ozonated wheat, corn and potato starch samples are presented in Table 4.2. RVA pasting curves of control and ozonated wheat, corn and potato starches are shown in Figure 4.12, Figure 4.13 and Figure 4.14. Similar pasting curves were obtained for all starch samples. Unfortunately, any available pasting data were not obtained for rice starch sample due to instrumental error. As all of the control starch samples were gelatinized after heating, high peak viscosities were observed, but ozonation changed their pasting characteristics. Ozonation treatment resulted in a significant decrease ( $p < 0.05$ ) in pasting temperature of wheat starch, while a significant increase ( $p < 0.05$ ) was observed for both ozonated corn and ozonated potato starch samples (Table A.5). No peak formation was observed for ozonated wheat, corn and potato starches. 1 hr ozone treatment caused a significant reduction ( $p < 0.05$ ) in peak, trough, breakdown and final viscosities of all starch samples (Table A.6, Table A.7, Table A.8 and Table A.9). This state shows that although the effect of ozonation on the structure change of starch granules was not clear, the inner parts of the surface of starch granules could become hollow by 1 hr ozone process. These results are supported by the findings of Karaoğlu et al. (2006) reporting that dextrinized modified starch had very low viscosity due to a high dissociation value.

The pasting properties of control, 15 min ozonated, 30 min ozonated and 60 min ozonated wheat starch samples measured using rapid visco analyzer (RVA) are summarized in Table 4.3 and the pasting profiles are presented in Figure 4.15. Various parameters observed were peak, trough, breakdown, final viscosity and pasting temperature. A significant reduction ( $p < 0.05$ ) in values of pasting parameters was observed with increase in ozonation time (Table A.10, Table 11, Table 12, Table 13 and Table A.14). The reduction was more pronounced in the case of the 60 min ozonation process of wheat starch. Sandhu et al. (2007) reported similar observations in their study on acid thinned corn starch. A significant reduction in peak, trough, breakdown, final and setback viscosity was observed by acid thinning and explained that the viscosity change can be caused by the increased degree of amylose recrystallization by acid thinning. According to them, the amylose double helices were not melted in the cooking procedure, and the starch particles might be more resistant to swelling.

In the study of Chan et al. (2009), starch (corn, sago and tapioca starches), in dry powder form, was exposed to ozone for 1, 3, 5 and 10 min ozone generation times. They observed that carboxyl and carbonyl contents increased markedly in all starches with increasing ozonation time. Oxidation significantly increased swelling power of oxidized corn starch. There was an insignificant change in the solubility of oxidized corn starch. Intrinsic viscosity of all oxidized starches decreased significantly. Similarly, in the study of Chan et al. (2011a), all ozone oxidized starches showed a significant decrease in viscosity compared to unmodified starch parallel to the results obtained in our present study (Table 4.2 and Table 4.3). In their study, tapioca starch exhibited a pronounced decrease in viscosity upon oxidation by ozone. According to them, the reduction in the viscosity of oxidized corn, and sago starches could be attributed to partial depolymerization of the starch molecules. The decrease in the molecular weight of oxidized starch molecules could be due to partial cleavage of the glycosidic linkages after treatment with gaseous ozone; a partially degraded network would not be resistant to shear and could not maintain the integrity of the starch granule, thereby reducing the viscosity of the starch solutions. On the other hand, they explained the significant reduction in viscosity of oxidized tapioca starch could not be attributed to depolymerization of starch, rather it might be due to a higher content of carbonyl groups.

Table 4.2. RVA pasting properties of control and 1 hr ozonated starch samples

Starch sample	Pasting temperature (°C)	Peak viscosity (cP)	Trough (cP)	Breakdown (cP)	Final viscosity (cP)
Control wheat starch	69.05±0.6c	4549±51b	1632±50b	2917±0.7d	3639±146b
Ozonated wheat starch	56.35±0.1a	77±4.2a	0±4.2a	79±2.1b	49±3.5a
Control corn starch	73.5±0.7d	5308±26c	2712±15d	2612±11c	5998±12d
Ozonated corn starch	94.5±0.7f	30±2.1a	0±4.2a	33±4.9a	7±1.4a
Control potato starch	64.0±1.4b	15099±126d	1820±7.7c	13384±29e	4972±4.9c
Ozonated potato starch	81.2±0.3e	15±4.2a	0±11.3a	29±2.1a	0±1.4a

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on duplicate analyses.

Similarly, Gunaratne and Corke (2007) reported that acid-thinning greatly decreased peak viscosity of wheat, maize and potato starches and stated that increased total amylose content and degree of amylose leaching reflect the creation of more linear segments during acid modification probably due to the cleavage of amylopectin branch points. Such cleavage, including amylose chains, facilitates more realignment and self-association of macromolecules within the starch granules affecting gelatinization, pasting, and retrogradation properties. In addition, Sandhu et al. (2008) stated that oxidized normal corn starches showed decreases in pasting viscosity as compared to their native counterpart starches. Karaoğlu et al. (2006) declared that dextrinized modified starch had very low viscosity due to a high dissociation value and Koxsel et al., (2008) reported that the loosened granule structure resulted in a decrease in pasting temperature.

Spectral studies of enzyme modified starches suggested the formation of an amorphous structure with concomitant decrease in the ordered structure of starches. A marked decrease in solid content and overall resistance to flow of the sample were observed in the hydrolyzed starches. Therefore, these modified starches may be suitable to formulate products that can easily flow and spread (Khatoun et al., 2009).

Singh et al., (2007) expressed that acid, enzyme hydrolysis and oxidation modification techniques reduce molecular weight polymers, exhibit reduced viscosity, increase retrogradation and setback, show high clarity and low temperature stability. These modified starches are used in confectionery as binders, in batters, in breading for coating various food stuffs, as film formers, in dairy as texturizers. Ozonation can be an alternative modification technique in this area with an advantage of no reagent use.

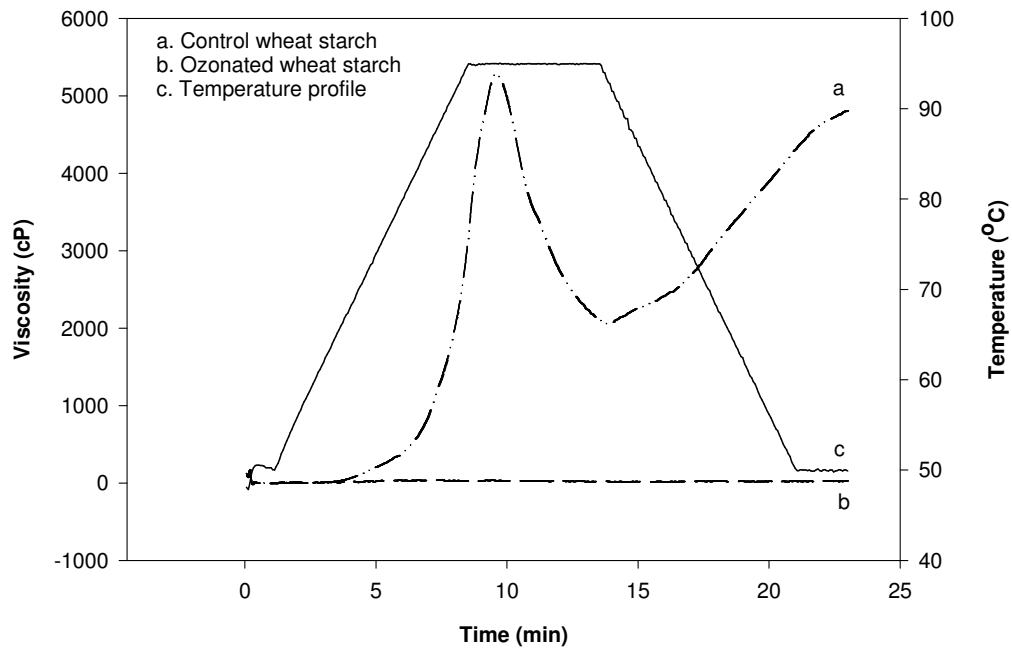


Figure 4.12. RVA pasting curves of control and 1 hr ozonated wheat starch

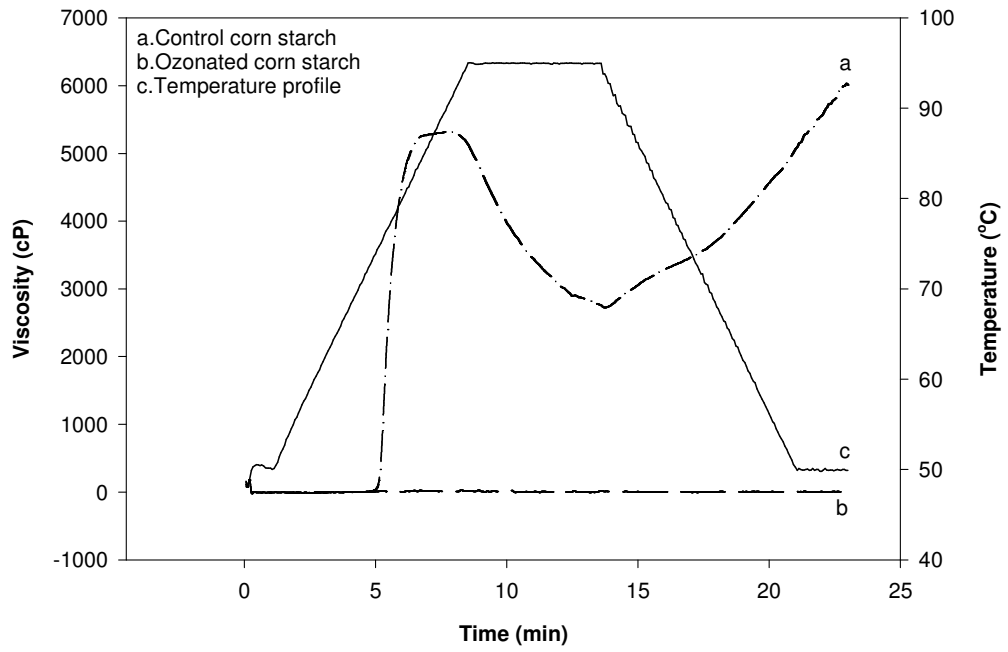


Figure 4.13. RVA pasting curves of control and 1 hr ozonated corn starch

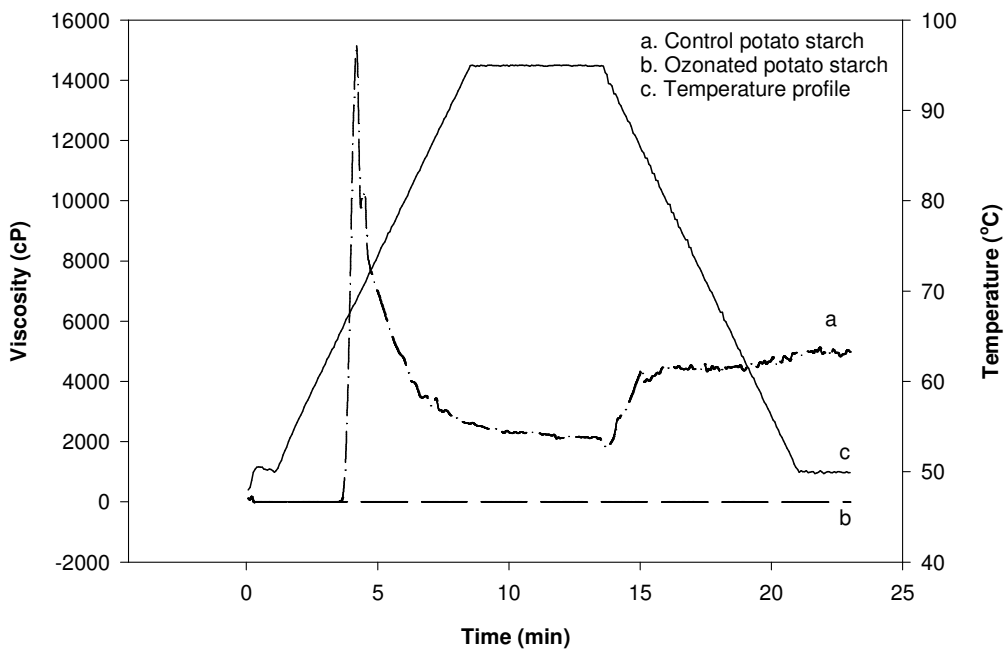


Figure 4.14. RVA pasting curves of control and 1 hr ozonated potato starch

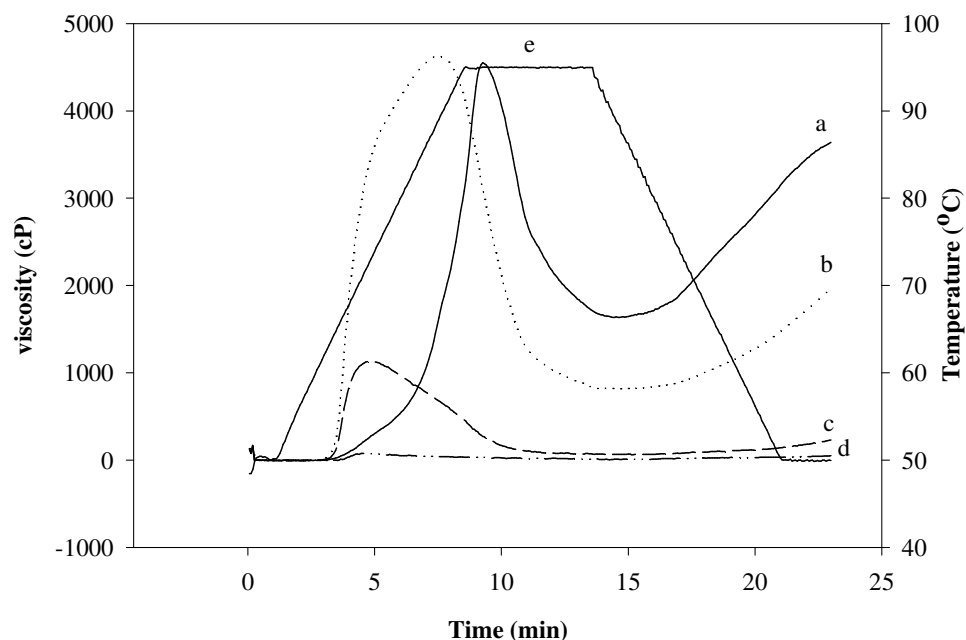


Figure 4.15. RVA pasting curves of control wheat starch (a), 15 min ozonated wheat starch (b), 30 min ozonated wheat starch (c) and 60 min ozonated wheat starch (d) with temperature profile (e)

Table 4.3. RVA pasting properties of control and ozonated wheat starch samples

Starch sample	Pasting				
	temperature (°C)	Peak viscosity (cP)	Trough (cP)	Breakdown (cP)	Final viscosity (cP)
Control wheat starch	69.05±0.6c	4549.5±51c	1632.0±50c	2917.5±0.7c	3639.5±146c
15 min ozonated wheat starch	62.95±0.3b	4628.0±18c	810.5±16b	3817.5±2.1d	1958.0±49b
30 min ozonated wheat starch	63.55±0.1b	1133.5±31b	59.0±2.8a	1074.5±26b	231.0±2.8a
60 min ozonated wheat starch	56.30±0.1a	77.0±4.2a	0±4.2a	78.0±2.1a	49.5±3.5a

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on duplicate analyses.

#### 4.5. Rheological Properties

Rheological properties of a material provide us a view about its structure. During gelatinization, starch granules swell to several times their initial volume. Swelling is accompanied by leaching of granule constituents, predominantly amylose, and the formation of a three dimensional network. These changes are responsible for the rheological characteristics exhibited by starch suspensions during heating and shearing. Rheological behaviour of starch is governed by amylose content, granule size distribution, granule volume fraction, granule shape, granule-granule interaction and continuous phase viscosity. Starch exhibits unique viscosity behaviour with change of temperature, concentration and shear rate. This can be measured in terms of rheological curves obtained with a rheometer. Relationship of shear stress/shear rate in liquids is demonstrated in Figure 4.16. Information obtained from rheology curves is vital when considering a starch as a possible component of a food product (Singh et al., 2007). Gelatinized starch dispersions have a non-Newtonian, time-independent and viscoelastic behaviour (Lagarrigue and Alvarez, 2001).

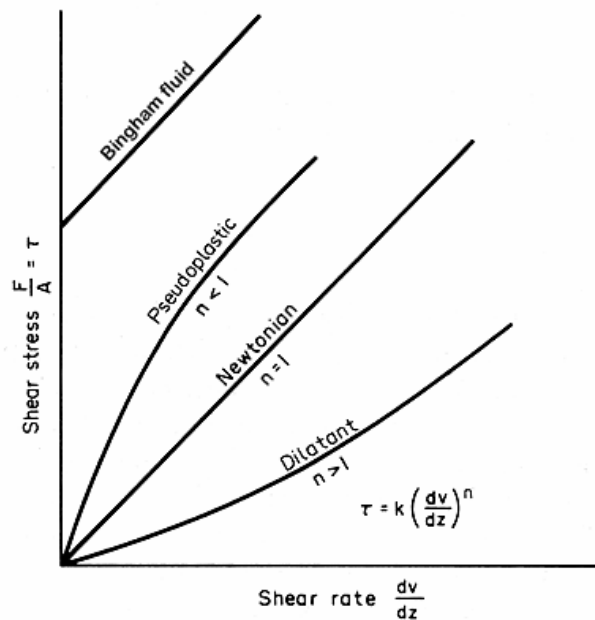


Figure 4.16. Shear stress/shear rate relationships in liquids (Singh et al., 2007)

Rheological behaviour of ozonated starch samples were investigated in this section. Typical flow curves, shear stress as function of shear rate, of control and ozonated wheat starch, corn starch, potato and rice starch pastes at 60°C are shown in Figure 4.17, Figure 4.18, Figure 4.19 and Figure 4.20. Parallel behaviours were exhibited by wheat and maize starch pastes and reported in the literature for control wheat and corn starch samples (Thebaudin et al., 1998). However, there is a deviation for flow curves of control and ozonated potato starch pastes measured at 60°C (Figure 4.19) due to a possible exposure of the large granule size surface of potato starch molecules. Also Chen and Ramasvamy (1999) showed the flow curves for tapioca, potato and maize starch solutions were similar to those in our present study.

The shear stress ( $\sigma$ ) versus shear rate ( $\dot{\gamma}$ ) data at 60°C for control, 15 min ozonated, 30 min ozonated and 60 min ozonated wheat starch samples fitted well to the simple power law model with high determination coefficients ( $r^2=0.99$ ), as shown in Table 4.4. Control and all ozonated wheat starch samples exhibited a shear-thinning behaviour (if  $n < 1.0$ , the material is shear thinning) with values of flow behaviour indices ( $n$ ) between 0.57-0.76. The viscosities of control and ozonated wheat starch samples were characterized at near values. There is no significant difference ( $p > 0.05$ ) between control and ozonated wheat starch samples at the shear stress points of 10.83, 20.82, 30.84 Pa (Table A.15, Table A.16 and Table A.17). These starch dispersions have similar sensitivity to shearing for both control and ozonated samples. However, the data in Table 4.4 shows that that ozonated wheat starch samples exhibited more pronounced shear-thinning behaviour than did the control wheat starch. This result does not agree with that of Chan et al. (2011a), who observed that 1, 3, 5 and 10 min ozonated starch samples (corn, sago and tapioca) showed an increase in  $n$  values compared to their unozone forms. In their study, the Herschel–Bulkley model was used to fit a flow curve to the data obtained at 25°C instead of the power law model used in our study. Also in that study, all starches exhibited non-Newtonian behaviour (i.e., the viscosity decreased when shear rate was increased) exactly the same results as presented in our study. The consistency coefficients ( $K$ ) for corn starch also increased after treatment with ozone gas in that study. They explained that an increase in  $K$  values upon oxidation illustrates that oxidation enhanced the viscous properties of starch. Possibly, the shorter degraded



polymers tend to come close to each other to form networks that contribute to the viscous property of oxidized corn starch.

Xie et al. (2009) reported that the decrease in the power law index ( $n$ ) with increasing amylose content was generally attributed to an increase in entanglements between amylose chains, since the highly branched amylopectin was not expected to form effective entanglements. The power law consistency value ( $K$ ) has a direct relationship with viscosity and therefore it can be used to represent the viscosity characteristics of a material under certain conditions. They also showed that higher amylose content resulted in a higher  $K$  value. It has been noticed that the higher the amylose content, the higher the viscosity (Xie et al., 2009).

Sopade and Kiaka (2001) reported that the viscosity was generally time-independent and irrespective of the temperature; shear stress increased with the rate of shear for sago starch (pseudoplastic). Samples with low pH were generally of a low consistency index irrespective of the temperature. The power-law model was suitable in describing the shear stress-rate relationship of sago starch samples.

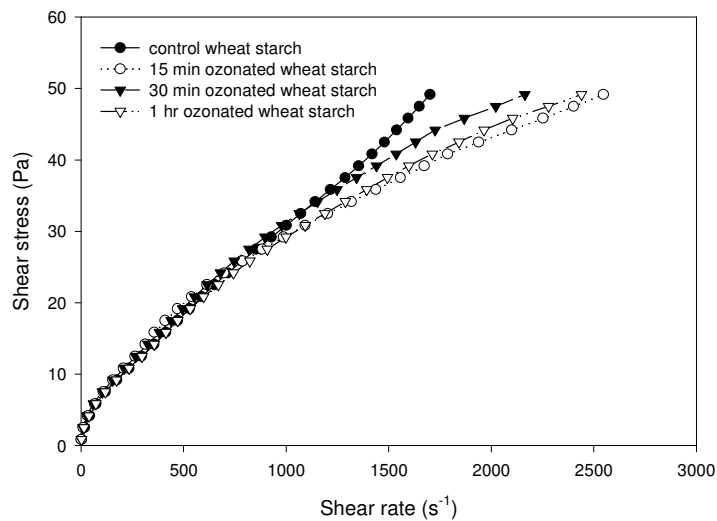


Figure 4.17. Flow curves of control and ozonated wheat starch pastes measured at 60°C

Table 4.4. Flow rheological properties of control and ozonated wheat starch samples at 60°C

Starch sample	n	K (Pa s <sup>n</sup> )	r <sup>2</sup>
Control wheat starch	0.76± 0.01	0.15± 0.01	0.99
15 min ozonated wheat starch	0.57± 0.01	0.55± 0.02	0.99
30 min ozonated wheat starch	0.63± 0.01	0.37± 0.01	0.99
60 min ozonated wheat starch	0.62± 0.01	0.37± 0.01	0.99

Means (± standard deviation) are based on duplicate analyses.

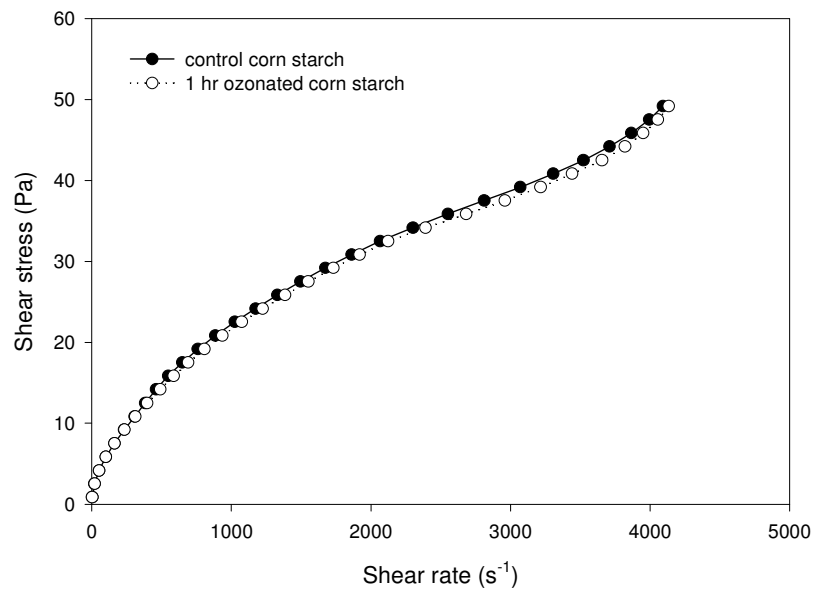


Figure 4.18. Flow curves of control and 1 hr ozonated corn starch pastes measured at 60°C

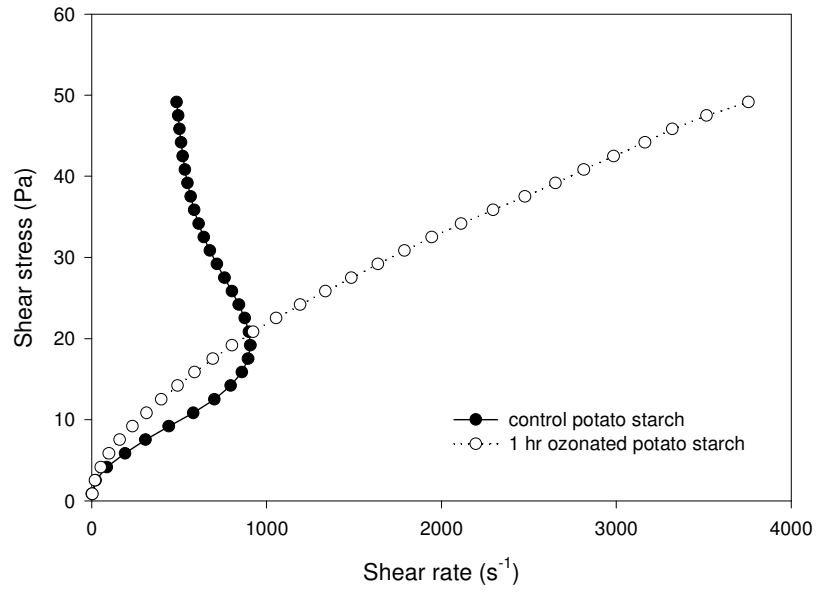


Figure 4.19. Flow curves of control and 1 hr ozonated potato starch pastes measured at 60°C

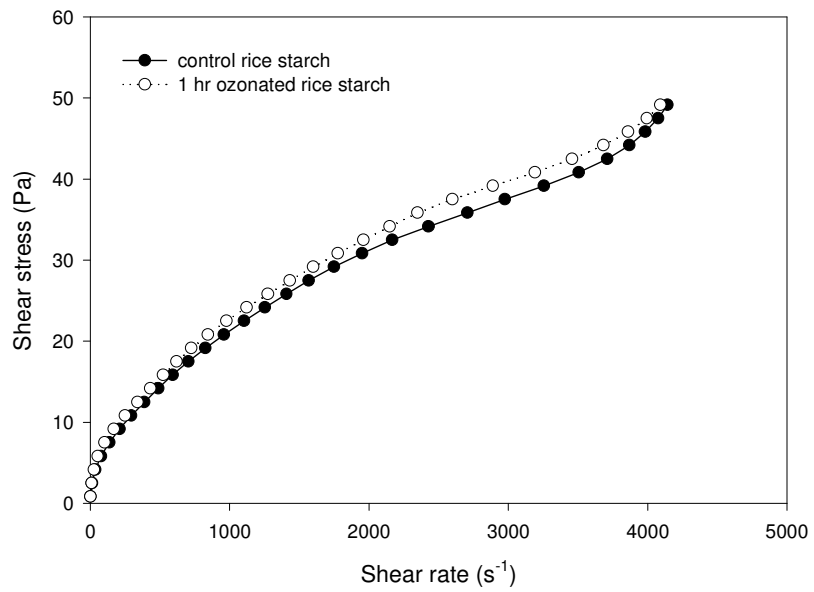


Figure 4.20. Flow curves of control and 1 hr ozonated rice starch pastes measured at 60°C

#### 4.6. Gelatinized Starch Percentage

Gelatinization changes physical properties of starches and affects their use. There are many methods to measure starch gelatinization but the most sensitive ones are enzymatic methods. In this study, gelatinized starch percentage was measured by using glucoamylase and *o*-toluidine reagent (Chiang and Johnson, 1977). The estimated degree of gelatinization of control and ozonated starch are summarized in Table 4.5. Gelatinized percentages for all ozonated wheat starch samples are higher than control starch sample. Starch samples exposed to ozone were determined as more gelatinized. It was significantly different ( $p < 0.05$ ) that the longer the ozonation time, the more gelatinized the starch molecules (Table A.18).

All enzymatic methods of measuring starch gelatinization are based on the number of carbohydrate molecules released during digestion. Glucoamylase converts gelatinized starch to many more molecules (D-glucose) than  $\alpha$ - or  $\beta$ - amylase (predominantly maltose and limit dextrin), so gelatinization is measured by differences between larger numbers when glucoamylase is used. (Shetty et al., 1974).

It is more difficult for amylases to act on raw starch granules than on gelatinized starch (Uthumporn et al., 2010). According to Leloup et al. (1990) there are several steps involved in the enzymatic reaction which are: (1) the diffusion to the solid surface, (2) the adsorption of the enzyme and finally (3) the occurrence of the catalysis. Holm and Eliasson (1988) explained that with increasing degree of starch gelatinization there was an increased susceptibility to glucoamylase as well as a gradual loss of birefringence, indicating that the highly ordered structure within the granules was destroyed to different extents in their study. The soluble starch fraction was only slightly increased for the partly gelatinized samples and for the completely gelatinized sample heated at 65 °C (just above the gelatinization temperature range). During gelatinization inter- and intramolecular hydrogen bonds are broken. This results in a loosening up of the compact granular structure and allows different degrees of swelling and absorption of water, fully hydrated starch molecules leach from the granule. Consequently, the availability of the starch granules to digestive enzymes increases to different levels with increasing degree of gelatinization. Singh et al. (2003) have stated that gelatinization starts at the hilum of the granule and swells rapidly to the periphery. Gelatinization occurs initially in the amorphous

regions of the granule, because hydrogen bonding is weakened in these areas. It is probable that ozonation caused the swelling of wheat starch granules by weakening the hydrogen bonding and glycosidic linkages between the starch molecules.

Raw starch is only slowly digested by enzymes *in vitro* whereas cooking increases the susceptibility considerably because of the rupture and disintegration of the compact crystalline granular structure. Furthermore, the glucose and insulin responses *in vivo* are significantly greater after ingestion of cooked compared with raw starches. Consequently, the degree of starch gelatinization is an extremely important factor in the rate of starch hydrolysis and metabolic response. The plasma glucose and insulin responses were positively correlated with the rate of hydrolysis with  $\alpha$ -amylase *in vitro*. Also both the plasma glucose and insulin responses, as well as the rate of hydrolysis with  $\alpha$ -amylase were positively correlated with the gelatinization degree (Holm and Eliasson, 1988). In the present study, the gelatinization degree was more pronounced for the 60 min ozonation process of wheat starch. In other words, glucoamylase showed the most susceptibility on 60 min ozonated wheat starch, while showing the least susceptibility on the control wheat starch sample. Higher degree of ozonated starch gelatinization is extremely important for starch hydrolysis and metabolic response.

Table 4.5. Gelatinized starch with percentages measured by enzymatic method

Sample	Percentage gelatinized (%)
Control wheat starch	3.13±0.02a
15 min ozonated wheat starch	6.63±0.05b
30 min ozonated wheat starch	9.76±0.02c
60 min ozonated wheat starch	11.05±0.02d

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on duplicate analyses.

#### 4.7. pH and Color

Color is an important quality parameter of starch due to the presence of phenolic compounds, ascorbic acid and caratone. There must not be any pigmentation reducing the quality and acceptability of starch (Galvez and Resurreccion, 1993).

The colors of the sample were evaluated by the 3-dimensional scales; L, a and b. The L, a, b type of scales simulate this as: L (lightness) axis-0 is black, 100 is white; a (red-green) axis-positive values are red, negative values are green and 0 is neutral; b (yellow-blue) axis-positive values are yellow, negative values are blue and 0 is neutral. The measured color parameters of control and ozonated wheat, corn, potato and rice starch samples are shown in Table 4.6. According to these data, there are significant differences ( $p < 0.05$ ) between the L values of control and ozonated wheat, corn and potato starch samples (Table A.19). 1 hr ozonation caused significant increase in the brightness (L value) of wheat, corn and potato starches, while the brightness (L value) of control rice starch was not affected ( $p > 0.05$ ) by ozonation significantly (Table A.19). Beside this, the a and b values of all control starch samples are significantly different from ozonated starch samples ( $p < 0.05$ ) by the way of decreases in the values except the b value of ozonated rice starch (Table A.20 and Table A.21). Yellowness of 1 hr ozonated rice starch were increased significantly as an unexpected result ( $p < 0.05$ ).

The calculated color parameters (chroma, hue, whiteness and total color difference; TCD) of control and ozonated wheat, corn, potato and rice starch samples are listed in Table 4.7. Chroma values of wheat, corn and potato starches were reduced ( $p < 0.05$ ) by 1 hr ozonation, while chroma value of rice starch increased ( $p < 0.05$ ) significantly (Table A.22). Calculated hue angles of ozonated starch samples are also different significantly ( $p < 0.05$ ) from the control ones (Table A.23). Whiteness values of all 1 hr ozonated starch samples are significantly higher ( $p < 0.05$ ) than control starch samples except ozonated rice starch (Table A.24). Total color difference (TCD) for ozonated starch samples are less than the control starches. However, TCD for ozonated rice starch is significantly higher ( $p < 0.05$ ) than the control (Table A.25).

A low value for chroma and a high value for lightness for starch are widely accepted by the consumer (Gani et al., 2010; Ikegwu et al., 2010; Thao and Noomhorm, 2011). Concerning the color of flours, ozone in gas or aqueous form has the ability to decolorize some food components by oxidizing the pigments (İbanoğlu, 2002). In the present study, the color of ozonated wheat, corn and potato starch samples could meet the consumer preference due to the higher lightness, whiteness and lower

chroma value caused by ozone oxidation modification. In contrast, the color parameters (high chroma, high yellowness and low whiteness) of ozonated rice starch would be unacceptable by the consumer. This could be caused by difficult diffusion of ozone into smaller size rice starch granules than the other starch types.

pH value is one of the physico-chemical properties of starch (Ikegwu et al., 2010). Beside this, the acidity or alkalinity of an environment has an effect on the activity and stability of macromolecules such as enzymes and influence both growth and metabolism of microorganisms. Every microorganisms has an optimum pH for its growth range. The pH effects enzyme function and transport of nutrients into cells. The internal pH of cells is near neutrality. When the ionic character of a medium is changed, ionizable groups are affected on either side of the cell (Erkmen and Bozoğlu, 2008a).

Table 4.6. Color parameter and pH values of control and 1 hr ozonated starch-water mixtures

Starch sample	L	a	b	pH
Control wheat starch	87.73±0.08c	0.02±0.01f	4.13±0.49e	3.56±0.01d
Ozonated wheat starch	90.55±0.01de	-0.47±0.05c	2.26±0.18d	1.46±0.03a
Control corn starch	89.57±0.17d	-1.36±0.02b	6.68±0.02g	5.48±0.07e
Ozonated corn starch	91.70±0.13e	-0.46±0.02c	0.26±0.05a	2.17±0.03c
Control potato starch	77.57±2.11a	-0.06±0.02e	1.57±0.06c	6.60±0.05g
Ozonated potato starch	82.04±0.58b	-0.15±0.01d	0.86±0.01b	1.41±0.06a
Control rice starch	86.93±0.32c	-0.48±0.02c	5.79±0.07f	6.04±0.07f
Ozonated rice starch	87.27±0.35c	-2.01±0.03a	9.55±0.15h	1.76±0.05b

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on triplicate analyses. L= lightness (black/white), a=chroma (green/red) and b=hue (blue/yellow)

The pH values were determined for all control and 1hr ozonated starch-water mixtures (Table 4.6). It was observed that the pH of control samples were found to be very near neutrality. However, the 1 hr ozonation process caused the pH's of wheat, corn, potato and rice starch samples to decrease very sharply ( $p < 0.05$ ) in the presence of water (Table A.26). Ozonated starch-water mixtures became acidic. Low pH values of ozonated starch samples could be advantageous in order to prevention of growth of many microorganisms and could provide longer shelf-life for starch products.

Table 4.7. Calculated chroma, hue, whiteness and TCD values

Starch sample	Chroma	Hue	Whiteness	TCD
Control wheat starch	4.13±0.49d	-89.68±0.15d	87.04±0.23de	6.10±0.30b
Ozonated wheat starch	2.30±0.19c	-78.16±0.55b	90.27±0.06f	2.71±0.07a
Control corn starch	6.81±0.02f	-78.51±0.16b	87.54±0.14e	6.38±0.92bc
Ozonated corn starch	0.53±0.01a	-28.93±0.673c	91.68±0.13g	1.79±0.12a
Control potato starch	1.57±0.06b	-87.91±0.85a	77.51±2.11a	15.47±2.10e
Ozonated potato starch	0.87±0.01a	-80.06±0.82b	82.02±0.58b	11.01±0.58d
Control rice starch	5.80±0.07e	-85.28±0.23a	85.69±0.27d	7.58±0.22c
Ozonated rice starch	9.76±0.14g	-78.11±0.22b	83.95±0.26c	10.09±0.19d

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on triplicate analyses. TCD= Total colour difference

#### 4.8. Microbiological Properties

The microbial population of starch is important for the overall quality and shelf-life of the product. Starch with a high number of micro-organisms can reduce the storage life due to undesired appearance, flavour and odour. Total bacterial count and mold/yeast count are generally used for the calculation of microbial load of starch by an aerobic spread-plate technique described by Jay (1986).

Microbiological analysis showed that 1 hr ozonation reduced the total bacteria and mold/yeast counts significantly ( $p < 0.05$ ) for all wheat, corn, potato and rice starch



samples (Table A.27 and Table A.28). The average values for triple studied samples are demonstrated in Table 4.8. These results are most probably because of partial dissociation of weak organic acids in starch molecules during the ozonation process due to reduced pH.

Most cereal starches contain weak organic acids, such as phosphoric acid. Partial dissociation of these weak acids plays an important role in the inhibition of microbial growth. Undissociated organic acid passes through the cytoplasmic membrane from an environment with low pH and high undissociated molecules to an environment with high pH and low undissociated molecules. The weak acids dissociate into proton ( $H^+$ ) and conjugate base in the cell, causing an equilibrium shift, and tend to acidify the cytoplasm. If the cytoplasmic pH is sufficiently reduced, growth no longer is possible and the cell eventually dies (Erkmen and Bozoğlu, 2008a).

Cereals can be contaminated by different pathogenic and spoilage microorganisms during growth, harvest and storage. Most microbial deterioration problems of cereals are caused by molds, while yeasts cause few spoilage problems. Mold spores in cereals and flour are chiefly *Aspergillus*, *Penicillium*, *Alternaria*, *Mucor*, *Cladosporium*, *Fusarium* and *Rhizopus*. The most commonly associating bacteria in cereals and cereal flours are *Bacillus* spores, coliform, *Achromobacter*, *Flavobacterium*, *Sarcina*, *Micrococcus*, *Alcaligenes* and *Serratia* (Erkmen and Bozoğlu, 2008b). Naito and Takahara (2006) reported that ozonation can reduce levels of the natural microflora and contaminating microorganisms. The microbial load of wheat kernels before milling is important for final microbial quality of the resulting flours. A high number of microorganisms reduces the storage life of the flours and causes a reduction in the overall quality of the flours. İbanoğlu (2001; 2002) suggested that ozonated water can be successfully used for wheat washing and tempering to reduce microbial populations. Considering that ozone is approximately 30,000 times more effective on *Escherichia coli* than chlorine, ozone can be an alternative for disinfectants used in processing in water. Also, Tiwari et al. (2010) demonstrated that ozone is an effective greener alternative against a range of pests, micro-organisms and mycotoxins.

Ozone is a powerful antimicrobial agent that is suitable for application in food in the gaseous and aqueous states. Molecular ozone or its decomposition products (for example, hydroxyl radical) inactivate microorganisms rapidly by reacting with intracellular enzymes, nucleic material and components of their cell envelope, spore coats, or viral capsids (Khadre et al., 2001). The antimicrobial efficacy of ozonation can be enhanced considerably when it is combined with other chemicals (e.g. H<sub>2</sub>O<sub>2</sub>) or physical (e.g. UV-C radiation) treatments (Sun, 2005).

A low microbial population is important for the quality of starch. The ozonation process can eliminate contamination by bacteria and fungi during starch production and can provide safer starch products by reducing pH. The longer the shelf-life means the more preferable the starch and the more marketing for the starch industry.

Table 4.8. Total bacteria and mold/yeast counts of control and 1 hr ozonated starch-water mixtures (log cfu/g)

Starch sample	Total bacteria	Mold/yeast
Control wheat starch	5.24±0.13c	5.09±0.04c
Ozonated wheat starch	3.10±0.17b	0.66±1.15a
Control corn starch	5.41±0.13c	5.35±0.04c
Ozonated corn starch	3.01±0.27b	1.95±0.24b
Control potato starch	5.56±0.02c	5.37±0.06c
Ozonated potato starch	2.23±0.20a	0±0.00a
Control rice starch	6.63±0.28d	5.76±0.03c
Ozonated rice starch	2.86±0.14b	0±0.00a

Values followed by the different letter in the same column are significantly different ( $p < 0.05$ ). Means ( $\pm$  standard deviation) are based on triplicate analyses.

## CONCLUSIONS

### Gelatinization Properties

The gelatinization temperatures of wheat, corn and potato starches were increased while the corresponding gelatinization enthalpies were reduced except the wheat starch after the ozonation process. There is no significant difference between the gelatinization enthalpy of control and ozonated wheat starch samples. Gelatinization properties of rice starch samples were affected by ozone in a similar way to wheat starch except the onset temperature characteristic. Ozonation reduced the onset temperature of rice starch significantly.

### Birefringence

Ozone has a distinct effect on the birefringence of corn starch and potato starch samples under polarized light microscopy. However, there is almost no difference between the birefringence of control and ozonated wheat starch and between the birefringence of control and ozonated rice starch.

### Morphological Properties

Changes in the granule shape and surface of wheat starch and rice starch were not obvious. However, changes in the granule shape and surface induced by the ozonation were visually distinct for corn and potato starches.

### Pasting Properties

Ozonation changed the pasting characteristics causing a significant reduction in peak, trough, breakdown and final viscosities of all starch samples. Ozonation resulted in a significant decrease in pasting temperature of wheat starch, while a significant increase was observed for both ozonated corn and ozonated potato starch samples.

A significant reduction in values of pasting parameters (peak, trough, breakdown and final viscosities) was observed with increase in ozonation time. The reduction was more pronounced in the case of 60 min ozonation of wheat starch.

#### Rheological Properties

The shear stress versus shear rate data at 60°C were well fitted to the simple power law. Shear-thinning behaviour was observed for the control and all ozonated wheat starch samples with values of flow behaviour indices between 0.57-0.76. There is no significant difference between the control and ozonated wheat starch samples at the shear stress points of 10.83, 20.82, 30.84 Pa.

#### Gelatinized Starch Percentage

The longer the ozonation time conducted the more gelatinized the starch molecules.

#### pH and Color

Significant increases in brightness and whiteness were observed for ozonated wheat, corn and potato starch samples. However, ozone did not change the brightness of rice starch. Chroma values of all control starch samples are significantly different from ozonated samples in terms of decreases in the values.

#### Microbiological Properties

Ozone treatment reduced not only total bacteria, but also mold/yeast counts significantly for all wheat, corn, potato and rice starch samples.

#### Contribution of the thesis to knowledge

The results obtained in this thesis have contributed to the knowledge in the field of food science/technology particularly the starch industry. There is limited scientific information on the ozonation of starch in general, and to the best of our knowledge to date, there is no published research investigating the functional properties of potato starch after ozonation in aqueous solution. Thus, the results of this thesis have contributed to the research and literature on the field of starch ozonation.

The results of this thesis suggest that ozonated starch samples have similar properties to oxidized starches. Therefore, it is likely that the ozonation process applied in this research can be an alternative to conventional oxidizing processes using chemicals such as hypochlorite, sodium bromite, hydroperoxide etc. The oxidation of starch using these chemicals gives a low yield due to the breakdown of starch with large amounts of wastewater produced. These issues are reported as the drawbacks of conventional oxidizing of starch. In this context, ozone can be regarded as an alternative to chemical oxidation due to the fact that it is able to react with starch even at ambient temperature without any problem of wastewater disposal. In addition, low purification costs and high recovery rates can be regarded as other advantages of oxidation of starch by ozone.

As a potential application of the results of this thesis to the starch industry, ozonated water can be used in the wet milling of cereals to produce oxidized starch. Ozonated starches then can be used for their low viscosity, high clarity and low temperature stability properties (i.e. in batters and breading for coating of foods) , as binders and film forming properties (i.e. in confectionery) and as texturizers (i.e. in dairy products, salad dressings, mayonnaise).

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## **APPENDICES**

Table A.1. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on onset temperature of different starch samples.

**ANOVA**

Onset Temperature, To

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	367.916	7	52.559	376.253	.000
Within Groups	2.235	16	.140		
Total	370.151	23			

**Onset Temperature, To**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05							
		1	2	3	4	5	6	7	8
Control wheat starch	3	59.9300							
Ozonated wheat starch	3		61.9167						
Control potato starch	3			64.0967					
Ozonated potato starch	3				65.3533				
Ozonated rice starch	3					67.0133			
Control rice starch	3						67.8333		
Control corn starch	3							70.1133	
Ozonated corn starch	3								72.6233
Sig.		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.2. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on peak temperature of different starch samples.

**ANOVA**

Peak Temperature, T<sub>p</sub>

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	331.033	7	47.290	361.986	.000
Within Groups	2.090	16	.131		
Total	333.123	23			

**Peak Temperature, T<sub>p</sub>**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05							
		1	2	3	4	5	6	7	8
Control wheat starch	3	65.3567							
Ozonated wheat starch	3		67.0867						
Control potato starch	3			68.6367					
Ozonated potato starch	3				70.2967				
Control rice starch	3					72.9833			
Ozonated rice starch	3						73.7700		
Control corn starch	3							74.8233	
Ozonated corn starch	3								76.5833
Sig.		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.



Table A.3. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on conclusion temperature of different starch samples.

**ANOVA**

Conclusion Temperature, Tc

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	236.435	7	33.776	53.781	.000
Within Groups	10.049	16	.628		
Total	246.484	23			

**Conclusion Temperature, Tc**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05				
		1	2	3	4	5
Control wheat starch	3	73.1333				
Ozonated wheat starch	3	73.8233				
Control potato starch	3		75.9100			
Ozonated potato starch	3		75.9100	77.4100		
Ozonated rice starch	3				79.4700	
Control rice starch	3				79.7533	
Control corn starch	3				80.5400	
Ozonated corn starch	3					82.6367
Sig.		.302	1.000	1.000	.136	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.4. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on gelatinization enthalpy of different starch samples.

**ANOVA**

Gelatinization Enthalpy,  $\Delta H$

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	458.702	7	65.529	2.721	.046
Within Groups	385.340	16	24.084		
Total	844.041	23			

**Gelatinization Enthalpy,  $\Delta H$**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05	
		1	2
Control rice starch	3	2.2423	
Ozonated rice starch	3	2.5341	
Control wheat starch	3	8.9846	8.9846
Ozonated corn starch	3	9.1905	9.1905
Ozonated potato starch	3	9.7188	9.7188
Ozonated wheat starch	3	10.2333	10.2333
Control corn starch	3		13.6356
Control potato starch	3		15.4702
Sig.		.093	.167

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.5. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on pasting temperature of different starch samples.

**ANOVA**

Pasting Temperature

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1808.634	5	361.727	613.964	.000
Within Groups	3.535	6	.589		
Total	1812.169	11			

**Pasting Temperature**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05					
		1	2	3	4	5	6
Ozonated wheat starch	2	56.3500					
Control potato starch	2		64.0000				
Control wheat starch	2			69.0500			
Control corn starch	2				73.5000		
Ozonated potato starch	2					81.2500	
Ozonated corn starch	2						94.5000
Sig.		1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.6. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on peak viscosity of different starch samples.

**ANOVA**

Peak Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	344091414.000	5	68818282.800	21273.040	.000
Within Groups	19410.000	6	3235.000		
Total	344110824.000	11			

**Peak Viscosity**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05			
		1	2	3	4
Ozonated potato starch	2	15.0000			
Ozonated corn starch	2	30.5000			
Ozonated wheat starch	2	77.0000			
Control wheat starch	2		4549.5000		
Control corn starch	2			5308.5000	
Control potato starch	2				15099.5000
Sig.		.332	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.7. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on trough viscosity of different starch samples.

**ANOVA**

Trough Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	14055794.417	5	2811158.883	5514.780	.000
Within Groups	3058.500	6	509.750		
Total	14058852.917	11			

**Trough Viscosity**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05			
		1	2	3	4
Ozonated potato starch	2	-8.0000			
Ozonated wheat starch	2	-4.0000			
Ozonated corn starch	2	-2.0000			
Control wheat starch	2		1632.0000		
Control potato starch	2			1820.5000	
Control corn starch	2				2712.0000
Sig.		.805	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.8. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on breakdown viscosity of different starch samples.

**ANOVA**

Breakdown Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	267904526.000	5	53580905.200	307936.237	.000
Within Groups	1044.000	6	174.000		
Total	267905570.000	11			

**Breakdown Viscosity**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05				
		1	2	3	4	5
Ozonated potato starch	2	29.5000				
Ozonated corn starch	2	33.5000				
Ozonated wheat starch	2		79.5000			
Control corn starch	2			2612.0000		
Control wheat starch	2				2917.5000	
Control potato starch	2					13384.0000
Sig.		.772	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.9. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on final viscosity of different starch samples.

**ANOVA**

Final Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	76303419.667	5	15260683.933	4237.117	.000
Within Groups	21610.000	6	3601.667		
Total	76325029.667	11			

**Final Viscosity**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05			
		1	2	3	4
Ozonated potato starch	2	-10.0000			
Ozonated corn starch	2	7.0000			
Ozonated wheat starch	2	49.5000			
Control wheat starch	2		3639.5000		
Control potato starch	2			4972.5000	
Control corn starch	2				5998.5000
Sig.		.374	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.10. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on pasting temperature of wheat starch samples.

**ANOVA**

Pasting Temperature

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	162.255	3	54.085	437.051	.000
Within Groups	.495	4	.124		
Total	162.750	7			

**Pasting Temperature**

Duncan<sup>a</sup>

Ozonation time (min)	N	Subset for alpha = .05		
		1	2	3
60.00	2	56.3500		
15.00	2		62.9500	
30.00	2		63.5500	
.00	2			69.0500
Sig.		1.000	.163	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.



Table A.11. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on peak viscosity of wheat starch samples.

**ANOVA**

Peak Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	32858899.000	3	10952966.333	10863.344	.000
Within Groups	4033.000	4	1008.250		
Total	32862932.000	7			

**Peak Viscosity**

Duncan<sup>a</sup>

Ozonation time (min)	N	Subset for alpha = .05		
		1	2	3
60.00	2	77.0000		
30.00	2		1133.5000	
.00	2			4549.5000
15.00	2			4628.0000
Sig.		1.000	1.000	.069

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.12. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on trough viscosity of wheat starch samples.

**ANOVA**

Through Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	3533438.375	3	1177812.792	1634.432	.000
Within Groups	2882.500	4	720.625		
Total	3536320.875	7			

**Through Viscosity**

Duncan<sup>a</sup>

Ozonation time (min)	N	Subset for alpha = .05		
		1	2	3
60.00	2	-4.0000		
30.00	2	57.0000		
15.00	2		810.5000	
.00	2			1632.0000
Sig.		.086	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.13. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on breakdown viscosity of wheat starch samples.

**ANOVA**

Breakdown Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	17373805.500	3	5791268.500	33379.069	.000
Within Groups	694.000	4	173.500		
Total	17374499.500	7			

**Breakdown Viscosity**

Duncan<sup>a</sup>

Ozonation time (min)	N	Subset for alpha = .05			
		1	2	3	4
60.00	2	79.5000			
30.00	2		1074.5000		
.00	2			2917.5000	
15.00	2				3817.5000
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.14. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on final viscosity of wheat starch samples.

**ANOVA**

Final Viscosity

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	16995629.000	3	5665209.667	948.351	.000
Within Groups	23895.000	4	5973.750		
Total	17019524.000	7			

**Final Viscosity**

Duncan<sup>a</sup>

Ozonation Time (min)	N	Subset for alpha = .05		
		1	2	3
60.00	2	49.5000		
30.00	2	231.0000		
15.00	2		1958.0000	
.00	2			3639.5000
Sig.		.079	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.

Table A.15. ANOVA for the effect of ozonation time on shear rate of wheat starch samples at the shear stress points of 10.83 Pa and at 60°C.

**ANOVA**

Shear Rate

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	1230.790	3	410.263	.390	.767
Within Groups	4206.510	4	1051.628		
Total	5437.300	7			

Table A.16. ANOVA for the effect of ozonation time on shear rate of wheat starch samples at the shear stress points of 20.82 Pa and at 60°C.

**ANOVA**

Shear Rate

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	4729.544	3	1576.515	.162	.917
Within Groups	38905.885	4	9726.471		
Total	43635.429	7			

Table A.17. ANOVA for the effect of ozonation time on shear rate of wheat starch samples at the shear stress points of 30.84 Pa and at 60°C.

**ANOVA**

Shear Rate

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	21828.854	3	7276.285	.119	.944
Within Groups	244126.605	4	61031.651		
Total	265955.459	7			

Table A.18. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of ozonation time on percentage of gelatinized wheat starch samples.

**ANOVA**

Gelatinized Starch Percentage

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	74.965	3	24.988	17848.893	.000
Within Groups	.006	4	.001		
Total	74.971	7			

**Gelatinized Stach Percentage**

Duncan<sup>a</sup>

Ozonation time (min)	N	Subset for alpha = .05			
		1	2	3	4
.00	2	3.1300			
15.00	2		6.6300		
30.00	2			9.7600	
60.00	2				11.0500
Sig.		1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 2.000.



Table A.19. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on lightness (L value) of different starch samples.

**ANOVA**

L value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	463.504	7	66.215	104.060	.000
Within Groups	10.181	16	.636		
Total	473.685	23			

**L value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05				
		1	2	3	4	5
Control potato starch	3	77.5733				
Ozonated rice starch	3		82.0433			
Control rice starch	3			86.9300		
Ozonated rice starch	3			87.2667		
Control wheat starch	3			87.7300		
Control corn starch	3				89.5700	
Control wheat starch	3				90.5500	90.5500
Control corn starch	3					91.7033
Sig.		1.000	1.000	.261	.152	.096

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.20. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on a value of different starch samples.

**ANOVA**

a value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	10.480	7	1.497	1963.559	.000
Within Groups	.012	16	.001		
Total	10.493	23			

**a value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05					
		1	2	3	4	5	6
Ozonated rice starch	3	-2.0100					
Control corn starch	3		-1.3567				
Control rice starch	3			-.4767			
Ozonated wheat starch	3			-.4733			
Ozonated corn starch	3			-.4633			
Ozonated potato starch	3				-.1500		
Control potato starch	3					-.0567	
Control wheat starch	3						.0233
Sig.		1.000	1.000	.584	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.21. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on b value of different starch samples.

**ANOVA**

b value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	221.797	7	31.685	803.005	.000
Within Groups	.631	16	.039		
Total	222.428	23			

**b value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05							
		1	2	3	4	5	6	7	8
Ozonated corn starch	3	.2567							
Ozonated potato starch	3		.8567						
Control potato starch	3			1.5733					
Ozonated wheat starch	3				2.2567				
Control wheat starch	3					4.1333			
Control rice starch	3						5.7867		
Control corn starch	3							6.6767	
Ozonated rice starch	3								9.5533
Sig.		1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.22. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on chroma value of different starch samples.

**ANOVA**

Chroma value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	224.922	7	32.132	818.351	.000
Within Groups	.628	16	.039		
Total	225.551	23			

**Chroma value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05						
		1	2	3	4	5	6	7
Ozonated corn starch	3	.5321						
Ozonated potato starch	3	.8698						
Control potato starch	3		1.5745					
Ozonated wheat starch	3			2.3058				
Control wheat starch	3				4.1334			
Control rice starch	3					5.8063		
Control corn starch	3						6.8131	
Ozonated rice starch	3							9.7625
Sig.		.053	1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.23. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on hue value of different starch samples.

**ANOVA**

Hue value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	77533.656	7	11076.237	1878.236	.000
Within Groups	94.354	16	5.897		
Total	77628.011	23			

**Hue value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05			
		1	2	3	4
Control potato starch	3	-87.9157			
Control rice starch	3	-85.2898			
Ozonated potato starch	3		-80.0600		
Control corn starch	3		-78.5144		
Ozonated wheat starch	3		-78.1637		
Ozonated rice starch	3		-78.1173		
Ozonated corn starch	3			-28.9371	
Control wheat starch	3				89.6809
Sig.		.204	.381	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.24. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on whiteness of different starch samples.

**ANOVA**

Whiteness

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	436.384	7	62.341	98.842	.000
Within Groups	10.091	16	.631		
Total	446.475	23			

**Whiteness**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05						
		1	2	3	4	5	6	7
Control potato starch	3	77.5180						
Ozonated potato starch	3		82.0223					
Ozonated rice starch	3			83.9533				
Control rice starch	3				85.6975			
Control wheat starch	3				87.0475	87.0475		
Control corn starch	3					87.5417		
Ozonated wheat starch	3						90.2716	
Ozonated corn starch	3							91.6863
Sig.		1.000	1.000	1.000	.054	.457	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.25. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on TCD (total color difference) of different starch samples.

**ANOVA**

TCD

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	423.464	7	60.495	96.792	.000
Within Groups	10.000	16	.625		
Total	433.464	23			

**TCD**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05				
		1	2	3	4	5
Ozonated corn starch	3	1.7940				
Ozonated wheat starch	3	2.7192				
Control wheat starch	3		6.1071			
Control corn starch	3		6.3889	6.3889		
Control rice starch	3			7.5854		
Ozonated rice starch	3				10.0988	
Ozonated potato starch	3				11.0176	
Control potato starch	3					15.4754
Sig.		.171	.668	.082	.174	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.26. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on pH value of different starch samples.

**ANOVA**

pH value

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	99.926	7	14.275	5136.464	.000
Within Groups	.044	16	.003		
Total	99.970	23			

**pH value**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05						
		1	2	3	4	5	6	7
Ozonated potato starch	3	1.4133						
Ozonated wheat starch	3	1.4567						
Ozonated rice starch	3		1.7600					
Ozonated cornstarch	3			2.1667				
Control wheat starch	3				3.5633			
Control corn starch	3					5.4833		
Control rice starch	3						6.0367	
Control potato starch	3							6.6033
Sig.		.329	1.000	1.000	1.000	1.000	1.000	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.



Table A.27. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on total bacteria counts of different starch samples.

**ANOVA**

Total bacteria (log cfu/g)

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	55.818	7	7.974	220.481	.000
Within Groups	.579	16	.036		
Total	56.396	23			

**Total bacteria (log cfu/g)**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05			
		1	2	3	4
Ozonated potato starch	3	2.2330			
Ozonated rice starch	3		2.8610		
Ozonated corn starch	3		3.0171		
Ozonated wheat starch	3		3.1003		
Control wheat starch	3			5.2484	
Control corn starch	3			5.4116	
Control potato starch	3			5.5629	
Control rice starch	3				6.6369
Sig.		1.000	.163	.072	1.000

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

Table A.28. ANOVA and Multiple Comparison Test (Duncan Test) table for the effect of 1 hr ozone treatment on mold/yeast counts of different starch samples.

**ANOVA**

Mold/yeast (log cfu/g)

	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	143.160	7	20.451	116.785	.000
Within Groups	2.802	16	.175		
Total	145.962	23			

**Mold/yeast (log cfu/g)**

Duncan<sup>a</sup>

Starch sample	N	Subset for alpha = .05		
		1	2	3
Ozonated potato starch	3	.0000		
Ozonated rice starch	3	.0000		
Ozonated wheat starch	3	.6667		
Ozonated corn starch	3		1.9584	
Control wheat starch	3			5.0918
Control corn starch	3			5.3544
Control potato starch	3			5.3723
Control rice starch	3			5.7658
Sig.		.082	1.000	.087

Means for groups in homogeneous subsets are displayed.

a Uses Harmonic Mean Sample Size = 3.000.

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2001- Present	University of Gaziantep- Food Engineering Department	Research Assistant

### **FOREIGN LANGUAGES**

English

## PUBLICATIONS

1. **Çatal, H.** & İbanoğlu, Ş. (2012). Ozonation of corn and potato starch in aqueous solution: effects on the thermal, pasting and structural properties. **International Journal of Food Science and Technology (in press)**. DOI: **10.1111/j.1365-2621.2012.03056**.
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5. **Çatal, H.** & İbanoğlu, Ş. (2010). Gıdaların Ozonlanması. **Gıda Teknolojileri Elektronik Dergisi, 5(3), 47-55**.

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6. **Pekmez, H. & Dalgıç, A.C.** Nananın Su Soğurma İzotermlerinin Modellenmesi, **Türkiye 9. Gıda Kongresi; 24-26 Mayıs, Bolu, Türkiye, 2006.**

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1. Erçelebi, E., Özkanlı, Ö., Kara, Ş. & **Çatal, H.** (2010). Kırmızı Renkli Meyvelerden Elde Edilecek Meyve Suyu Konsantrelerinin ve Bu Konsantrelerle Hazırlanacak Sosların Fizikokimyasal, Duyusal ve Reolojik Özellikleri. **Gaziantep Üniversitesi BAP Projesi.** Researcher.