

## EFFECTS OF OZONATION ON THERMAL, STRUCTURE AND RHEOLOGICAL PROPERTIES OF RICE STARCH IN AQUEOUS SOLUTION

Hatice Çatal\*, Şenol İbanoğlu

Department of Food Engineering, Faculty of Engineering, University of Gaziantep, Gaziantep, Turkey

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### Abstract

The effects of ozone on the thermal, structure and rheological properties of rice starch were investigated. Rice starch-water suspension was prepared in the ratio of 1:9 (dry sample to water) and treated with concentration of dissolved ozone at a 4.2 mg/L water for 1 hour. Unozonated sample was used as control. Thermal gelatinization properties of control and ozonated samples were investigated by DSC. Peak temperature of rice starch was increased, while the onset temperature of rice starch was decreased significantly by ozonation. A significant difference was not found between the values of both the conclusion temperature and the gelatinization enthalpy of control and ozonated rice starch samples. Any distinct difference was not observed between the birefringences of control and ozonated rice starch under polarized light microscopy. Changes on granule shape and surface of control and ozonated rice starch samples under SEM were not obvious due to the smaller size of granules. The shear stress versus shear rate data at 60 °C obtained by rheometer were well fitted to the power law model for control and ozonated rice starch samples. Shear-thinning behaviour was observed for both control and ozonated rice starch.

**Keywords:** Ozone, rice starch, gelatinization, structure, rheology

## OZONLAMANNIN SULU ÇÖZELTİDEKİ PİRİNÇ NİŞASTASININ TERMAL, YAPISAL VE REOLOJİK ÖZELLİKLERİ ÜZERİNE ETKİLERİ

### Özet

Ozonun pirinç nişastasının termal, yapısal ve reolojik özellikleri üzerine etkileri araştırıldı. 1:9 oranında pirinç nişastası- su süspansiyonu hazırlandı ve 4.2 mg/L suda çözünmüş ozon konsantrasyonunda 1 saat muamele edildi. Ozonlanmamış numune kontrol olarak kullanıldı. Kontrol ve ozonlanmış numunelerin termal jelatinizasyon özellikleri DSC ile incelendi. Ozonlama, pirinç nişastasının başlangıç sıcaklığını düşürürken, tepe sıcaklığını anlamlı bir şekilde arttırdı. Kontrol ve ozonlanmış pirinç nişastası örneklerinin son sıcaklıkları ve jelatinizasyon entalpileri arasında önemli bir fark bulunmadı. Polarize ışık mikroskobu altında, kontrol ve ozonlanmış pirinç nişastalarının birefrinansları arasında belirgin bir fark gözlenmedi. Kontrol ve ozonlanmış pirinç nişastası örneklerinin granül şekil ve yüzeylerindeki değişiklikler granülün küçük boyutu sebebiyle SEM altında bariz değildi. Reometre'de kontrol ve pirinç nişastası için 60 °C'de elde edilen kayma gerilimine karşı kayma hızı verileri power-law modeline tamamen uydu. Hem kontrol hem ozonlanmış pirinç nişastası için kayma incelenmesi davranışı gözlemlendi.

**Anahtar Kelimeler:** Ozon, pirinç nişastası, jelatinizasyon, yapı, reoloji

\* *Corresponding author* / Yazışmalardan sorumlu yazar;

✉ pekmez@gantep.edu.tr,

☎ (+90) 342 317 2339,

☎ (+90) 342 360 1105

## INTRODUCTION

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 (1-4). In the mid-1990s, ozone 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. 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 (5- 8).

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 (9). 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 (10). Ozone can replace traditional sanitizing agents such as chlorine and provide other benefits in the washing, sanitizing, and storage of produce (11).

Starch (an integral part of cereals) is one of the very important biopolymers widely used in the food industry (12). 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. Modification of starch was carried out to overcome shortcomings of native starches and increase the usefulness of starch for industrial applications (13).

In the food industry, the use of oxidized starch has become increasing important because it has low viscosity and good binding and film forming properties (14). Oxidized starches are used in food

products for which neutral-tasting, low viscosity starch is required, e.g. lemon curd, salad dressing, and mayonnaise (15). 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 (16). 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. In addition, a large amount of wastewater is produced during the process of oxidation (17).

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 (18) 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. (19) declared that the corona discharge method used discharges decomposed starches to low molecular fragments together with oxidation of the polysaccharides. Chan et al. (20) 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.

There is some available data about the effects of ozone gas, but not the effects of aqueous ozone use on rice starch. In present study, the effects of ozonated water on the gelatinization, inner and outer structure and rheological properties of rice starch were investigated.

## MATERIAL AND METHODS

### Materials

Commercial rice starch was used as test material. Starch sample, Migros trademark, were purchased from a commercial source (Migros A.Ş., İstanbul, Turkey). The starch was used directly without any purification. Rice (*Oryzae sativa* L.) starch 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 (Mettler Toledo, MJ33 Moisture analyzer, Switzerland).

### Ozonation of Starches

Ozone was produced by an ozone generator (OMS Model Ozone Generator, İzmir, Turkey) with coronal-discharge method. 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 1). Gas is directed from the generator to the bottle by a connection with the end 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 1). Undissolved ozone gas was driven to the atmosphere by a discharging tube.

Rice starch-water suspension was prepared in the ratio of 1:9 (dry sample to distilled water).

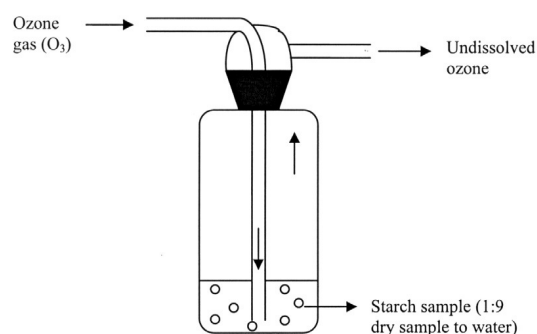


Figure 1. Schematic diagram of glass gas washing bottle for ozonation

The reason for selecting this ratio was that there should be enough water for a good bubbling effect to obtain maximum solubility of ozone in water. The prepared rice starch-water suspension was treated with a concentration of 4.2 mg dissolved ozone/L water (1200 ORP) in the bottle for 1 hour while unozonated starch samples were used as controls. Less than 1 hr ozonation was not as effective as 1 hour ozonation on oxidation of starch. After that time, pH of suspensions did not change.

### Thermal Measurement by Differential Scanning Calorimetry (DSC)

Control and ozonated starch water samples were analyzed using DSC (Perkin-Elmer DSC 6 equipped with a Pyris software, Perkin-Elmer Inc., Wellesley USA). 50µl starch-water suspension (1:9 ratio of dry sample to water) was placed into a DSC pan with a micropipette. An empty pan was used as reference. The samples were heated at a rate of 5°C/min from 5 to 150°C using 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 calculated by the software provided by the DSC system. Samples were analyzed in triplicate.

Table 1. Calibration table of conversion of ozone concentration from ORP to ppm

mV-orp	ppm-mg/L	mV-orp	ppm-mg/L	mV-orp	ppm-mg/L	mV-orp	ppm-mg/L
100	0	875	1	1125	3.5	1375	6
200	0.04	900	1.25	1150	3.75	1400	6.25
300	0.08	925	1.5	1175	4	1425	6.5
400	0.13	950	1.75	1200	4.25	1450	6.75
500	0.16	975	2	1225	4.5	1475	7
600	0.2	1000	2.25	1250	4.75	1500	7.25
700	0.22	1025	2.5	1275	5	1525	7.5
750	0.25	1050	2.75	1300	5.25	1550	7.75
800	0.39	1075	3	1325	5.5	1575	8
860	0.5	1100	3.25	1350	5.75	1600	8.25

### Structure Analysis by Polarized Light Microscopy and Scanning Electron Microscopy (SEM)

Control and ozonated starch-water suspensions (1:9; dry sample to water ratio) were examined visually using a polarized light microscope and SEM. A 10 µl sample was examined at a magnification of 20X under a polarized microscope (Model BX51, Olympus Corp., Tokyo, Japan) equipped with a 100-W halogen light source. A Pixera camera (Model PVC 100C, Los Gatos, CA, USA) was used to acquire the images.

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. A dry sample was then adhered on a SEM mount using double-sided conductive adhesive tapes and sputter coated with 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.

### Rheological Measurement

Dynamic rheological measurements for control and rice starch-water suspensions in the ratio of 1:9 (dry sample to distilled water) 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. 1), which is used extensively to describe the flow properties of non-Newtonian liquids in theoretical analysis as well as in practical engineering applications (21).

$$\sigma = K\dot{\gamma}^n \quad (1)$$

where,

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

$\dot{\gamma}$  = the shear rate (s<sup>-1</sup>),

K = the consistency index (Pa sn),

n = the flow behaviour index (dimensionless).

### Statistical Analysis

Statistical analysis (SPSS 13.0 software for Windows) was performed to compare the experimental results under the ozonation treatment and untreated control by using a one-factor analysis of variance (ANOVA). All experimental values are at least mean of triplicate determination. In order to determine the data that are significantly different from each other, Duncan multiple range test method was applied. Trends were considered significant when means of compared parameters differed at  $p < 0.05$  significance level.

## RESULTS AND DISCUSSION

### Effect of ozonation on rice starch gelatinization

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 to see if there is an effect of ozonation on the gelatinization characteristics of sample or not.

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 2. There is a significant difference ( $p < 0.05$ ) between both the onset temperature and peak temperature of control and 1 hr ozonated rice starch, while 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 rice starch samples. The onset temperature of rice starch was significantly reduced, while the peak temperature of rice starch was increased ( $P < 0.05$ ) after 1 hr ozonation process. 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 did not change. This means that ozonated starch sample begins to progress at lower temperature, but is gelatinized at higher temperatures and need

Table 2. The values of starch gelatinization characteristics of control and 1 hr ozonated rice starch-water suspension

Rice starch sample	T <sub>o</sub> (°C)	T <sub>p</sub> (°C)	T <sub>c</sub> (°C)	ΔH (j/g)	pH
Control rice starch	67.83±0.77b	72.98±0.33a	79.75±0.89a	2.2423±0.34a	6.04±0.07b
1 hr ozonated rice starch	67.01±0.04a	73.77±0.76b	79.47±1.31a	2.5341±1.34a	1.76±0.05a

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.

same amount energy with the control one for gelatinization. It is known that intact small starch molecules have higher gelatinization temperatures (22) owing to possible reassociation of small molecules upon heating. This may require a higher temperature for disordering the resulting structure of starch.

Chan et al. (16) 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. The increase in the gelatinization temperatures and the decrease in gelatinization enthalpy obtained in our study can be attributed to the application of ozonation in aqueous solutions rather than exposing dry starch powders to ozone gas. It has been stated that efficacy of ozone application in aqueous media is greater when compared to an application in the gaseous phase (23). Therefore, ozonation in the aqueous phase could result in more destruction of starch crystalline regions under the conditions of this study.

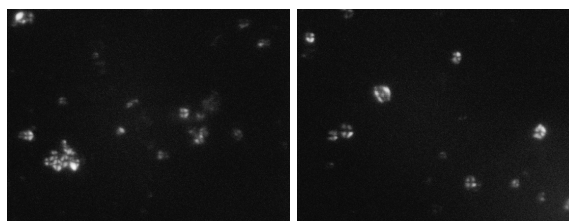
#### Effect of ozonation on rice starch structure

The conditions used in this study were chosen, so that the ozone gas could be dissolved in water with maximum efficiency at the temperature studied. One of the objectives of this study was to see whether ozonation at maximum ozone concentration had any effect on the morphological properties of rice starch granules. Because very limited scientific information is available on the morphology of ozonated starch granules, it was decided to apply one level of ozone at maximum

concentration to obtain an overall insight of ozonation on the granule morphology. In order to understand why the gelatinization properties of rice starch 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. 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 (24).

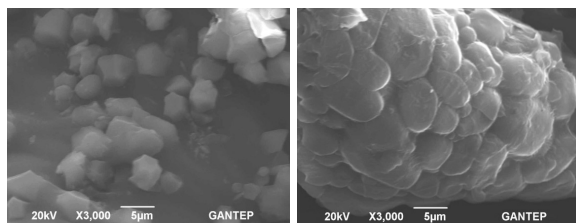
Polarized light micrographs of ozonated and control rice starch-water suspensions are given in Figure 2. Micrographs showed that the Maltese crosses were observed for both control and ozonated rice starch granules. In our present study, it was hypothesized that ozonation might change the ordered structure, and therefore might cause a change in the birefringence. However, when control and ozonated rice starch samples were viewed under polarized light, they could not be clearly differentiated visually in terms of birefringence (Figure 2). These results might be due to the fact that the birefringence of starch in polarized light could 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.



Control rice starch 1 hr ozonated rice starch

Figure 2. Polarized light micrographs of control and 1 hr ozonated rice starch

Starch granules were also examined under scanning electron microscopy (SEM) to observe surface morphology of rice starch granules after ozonation. The rice starch granules are pentagonal and angular-shaped and range from 3 to 5  $\mu\text{m}$  in size (25). In our present study, shape and surface of unozonated rice starch granules under SEM were observed identically to that study. However, as a result of the irregular shape and small size of rice starch granules, changes in the granule shape and surface caused by ozonation were hard to differentiate (Figure 3) or ozonation conditions used in present study could not be effective enough to change the surface characteristics of the samples.



Control rice starch 1 hr ozonated rice starch

Figure 3. Changes of the outer structure of control and 1 hr ozonated rice starch granules under SEM.

### Rheological Properties

Rheological properties of a material provide us a view about its structure. 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. Information obtained from rheology curves is vital when considering a starch as a possible component of a food product (26). Gelatinized starch dispersions have a non-Newtonian, time-independent and viscoelastic behaviour (27).

Rheological behaviour of ozonated rice starch

sample was investigated in the present study. Typical flow curves, shear stress as function of shear rate, of control and ozonated rice starch pastes at 60 °C are shown in Figure 4. The shear stress ( $\sigma$ ) versus shear rate ( $\dot{\gamma}$ ) data at 60 °C for control and ozonated rice starch samples fitted well to the simple power law model with high determination coefficients ( $r^2=0.99$ ), as shown in Table 3. Both control and ozonated rice starch samples exhibited a shear-thinning behaviour (if  $n < 1.0$ , the material is shear thinning). However, an increase in flow behaviour indice ( $n$ ) and a decrease in consistency coefficient ( $K$ ) were observed for ozonated rice starch sample. This result agrees with the study of Chan et al. (16), 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 unozonated 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 this 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 this study. This suggests that the flow behaviour of ozonated rice starch approaches to Newtonian fluid. This might be due to partial depolymerization of amorphous and crystalline lamella during ozone oxidation.

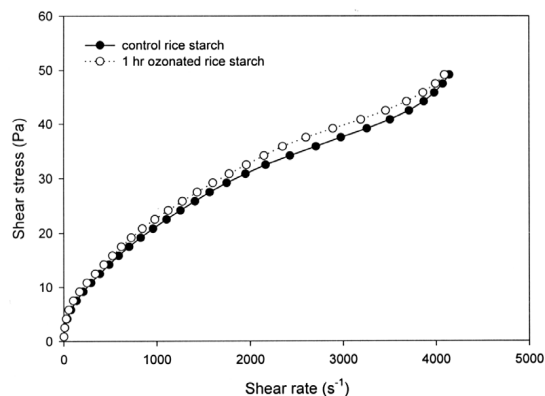


Figure 4. Flow curves of control and 1 hr ozonated rice starch pastes measured at 60 °C

Table 3. Flow rheological properties of control and ozonated rice starch samples at 60 °C

Rice starch sample	$n$	$K$ (Pa s <sup><math>n</math></sup> )	$r^2$
Control rice starch	0.48 ± 0.03	0.55 ± 0.01	0.99
1 hr ozonated rice starch	0.61 ± 0.02	0.52 ± 0.01	0.99

Means ( $\pm$  standard deviation) are based on duplicate analyses.



According to Kuakpetoon and Wang (14), oxidation occurred mostly at the amorphous lamellae and more amylose depolymerisation, from oxidation, occurred at the periphery of common corn starch.

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 lower the amylose content, the lower the viscosity (28). Sopade and Kiaka (29) reported samples with low pH were generally of a low consistency index irrespective of the temperature.

## CONCLUSIONS

Morphological properties of rice starch in aqueous solution, as determined by polarized light microscopy and SEM, did not change considerably after 1 hr ozonation. Peak temperature of rice starch sample increased as a result of ozone treatment. However, a decrease in onset temperature for gelatinization was observed for ozonated starch samples. 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 ozonated rice starch samples. There is an increase in flow behaviour index (n) and a decrease in consistency coefficient (K) for ozonated rice starch sample. This was attributed to the partial cleavage of the glycosidic linkages in starch granules during ozonation, resulting in the collapse of the granules upon shearing and heating during rheometer.

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