



## Photo oxidation of rice starch II. Using a water soluble photo initiator

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### ABSTRACT

A new photo oxidation system was established when rice starch was oxidized using UV irradiation and 4-(trimethyl ammoniummethyl) benzophenone chloride (BP2) as a photo initiator. BP2 is a water soluble photo initiator. The slurry prepared for photo oxidation contained rice starch, water and BP2 only. No oxidizing agents were added. Parameters affecting the photo oxidation process, i.e. temperature, concentration of BP2, material:liquor ratio and irradiation time were determined. The produced oxidized starch was evaluated by measuring the carboxyl content, carbonyl content and apparent viscosity. The produced photo oxidized rice starch showed sound increase in the carboxyl and carbonyl contents and sharp decrease in the apparent viscosity. The produced photo oxidized starch was tested for its suitability as a sizing agent for cotton yarns. Native starch and oxidized starch, used as a sizing agent by Misr Company of Spinning and Weaving in El-Mahalla El-Kubra (Egypt), were used for comparison. Sized cotton yarns were evaluated by measuring the tensile strength, elongation at break and percent of size removal. Cotton yarns sized using the prepared photo oxidized rice starch showed higher tensile strength, elongation at break and percent of size removal compared with native starch and oxidized starch used by Misr Company of Spinning and Weaving.

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### 1. Introduction

Oxidation of starch has a long history. The use of chlorine and bromine to oxidize starch goes back to 1829 and 1875 according to Wurzburg (1986, chap. 2). In addition to chlorine and bromine, oxidized starch was produced by several chemicals including chromic acid, permanganate, nitrogen dioxide, hypochlorite, air oxygen, ozone and hydrogen peroxide according to Wang and Wang (2003) and Lawala, Adebowaleb, Ogunsanwoa, Barbac, and Ilod (2005).

Photo oxidation of starch has got little interest. Harmon, Gupta, and Johnson (1971) oxidized starch using hydrogen peroxide in presence of UV. Harmon, Gupta, and Johnson (1972) also oxidized starch using hydrogen peroxide and UV in presence of ferrous sulfate and hypochlorite. Recently El-Sheikh, Ramadan, and El-Shafie (2008) photo oxidized rice starch using hydrogen peroxide as a photo initiator at neutral reaction conditions and low temperature.

Eighty to eighty-five percentage of oxidized starch is used in paper production. It is used as a surface size in paper and paper board manufacture. Since it provides sizing and adhesion characteristics it is used in making construction materials such as ceiling tiles and wallboards. In food industry, lightly oxidized starch is used in breading batters for deep fried foods. Periodate oxidized starch

is used as a substitute for formaldehyde and glutaraldehyde as hardening agents in gelatin-immobilization of yeast cells.

Oxidized starch has a long history in textile industry. It is used in printing, finishing, laundry finishing and sizing (El-Sheikh et al., 2008; Hebeish, El-Rafie, El-Sisi, Abdel Hafiz, & Abdel-Rahman, 1992). As a warp size, it provides abrasion resistance for yarns.

Among the various methods allowing the generation of radicals, e.g.,  $\gamma$  irradiation, redox chemical system, heating and photo irradiation, the later is more attractive. However, this kind of reaction requires knowledge of the photo reactivity of the initiator with respect to the chemical nature of the macro radical. Free radical generation in starch, by photosensitized excitation, has shown clearly that UV irradiation, both in photosensitized and unsensitized experiments, results in chain scission and radical generation on the glucosidic cycle according to El-Sheikh (1999).

El-Sheikh (1999) used the water soluble photosensitizer, 4-(trimethyl ammoniummethyl) benzophenone chloride, symbolized as BP2, to initiate the graft copolymerization of acrylic acid (AA) onto carboxymethyl starch (CMS) in an aqueous medium. The system produced a poly (AA–CMS) graft copolymer with an effective graft yield and high carboxylic content i.e. the system was found powerful for producing free radicals of the CMS molecule.

It was thought that the use of BP2 and UV irradiation can efficiently initiate free radical formation on the rice starch molecule. The need to produce oxidized starch with high carboxyl and carbonyl contents, low viscosity and suitable as a sizing agent for

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cotton yarns together with easy and environmentally safe processing were the motive behind this study.

In this study BP2 was used as a photo initiator for the photo oxidation of rice starch. Parameters affecting the photo oxidation process, i.e. temperature, concentration of BP2, material:liquor ratio and irradiation time were obtained. The produced oxidized rice starch was characterized by measuring the carboxyl content expressed as meq/100 g StOH (milliequivalent/100 g starch), carbonyl content expressed as meq/100 g StOH (milliequivalent/100 g starch) and apparent viscosity expressed as c.pas. (centipoises). Native rice starch and oxidized starch used as a sizing agent by Misr Company of Spinning and Weaving in Mahalla El-Kubra (Egypt) were used for comparison.

## 2. Experimental

### 2.1. Materials

Native rice starch was kindly supplied by the Starch and Yeast Company, Alexandria (Egypt), BP2 was prepared and supplied by The associated Octel Ltd., Widnes, Great Britain, and used without further purification.

### 2.2. Equipment

The irradiation reaction vessel consists of a water-cooled 125 W medium-pressure Hg lamp assembly (wavelength distribution, 190 nm to the visible region with some IR energy output as well) as a UV irradiation source immersed in a beaker contains a slurry of rice starch, water and BP2. The total dose of the UV irradiation was controlled by controlling the time of exposure, i.e. the reaction time. The reaction temperature was controlled using a thermostatic water bath.

### 2.3. Method

#### 2.3.1. Photo oxidation of rice starch

A known weight of the native rice starch was mixed with a known volume of distilled water in a beaker using a mechanical stirrer. After making the starch–water slurry, a known weight of BP2 was added to the obtained slurry under continuous stirring until complete mixing of the whole contents. Doing so, the beaker was transferred to a thermostatic water bath with a magnetic stirrer. The UV lamp is now immersed in the slurry to just above the bottom of the beaker in order to allow the magnet to move and to the whole slurry to be exposed to the UV irradiation. The temperature was then allowed to rise gradually until the required temperature is reached. The UV lamp is now switched on and the whole contents were kept at the oxidation temperature for a known period of time under continuous stirring in the presence of air. After oxidation, the oxidized rice starch is precipitated with acetone then filtered and dried at 50 °C.

#### 2.3.2. Cooking

A solution containing 10 g of NS or oxidized starch in 100 cm<sup>3</sup> of water was kept under stirring in a thermostatic water bath. The temperature of the water bath was raised gradually until it reached to 90 °C and left, at this temperature, for 20 min.

#### 2.3.3. Sizing of cotton yarns

An aqueous slurry (10%) of rice or oxidized rice starch was cooked at 90 °C for 20 min. Cotton yarn samples were treated with the cooked solution via impregnation followed by squeezing to a wet pick up ca. 100% then dried at 100 °C for 5 min after being conditioned (65% RH at 25 °C for 48 h). The sized samples were monitored for tensile strength (kg), elongation at break (%) and percent size removed by washing.

## 2.4. Analyses

The carboxyl content was determined according to a reported method (Daul, Reinhardt, & Reid, 1953).

The carbonyl content was determined according to a reported method (Klimova & Zabrodina, 1960).

The apparent viscosity was measured using viscosity equipment at Misr Company of Spinning and Weaving in Mahalla El-Kubra.

The percent size removal was calculated after washing the sample with hot water (95 °C for 10 min.) as follows:

$$\% \text{ size removal} = [(W_1 - W_2)/(W_1 - W_0)] \times 100$$

where  $W_0$ : weight of sample before sizing,  $W_1$ : weight of sample before washing,  $W_2$ : weight of sample after washing.

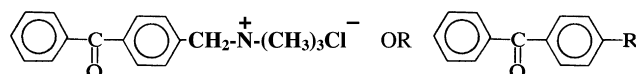
The decomposition of BP2 during the photo oxidation reaction was determined by measuring the concentration of the filtrate of BP2 in the slurry before, during and after the photo oxidation reaction using UV–VIS spectrophotometer, Shimadzu Scientific Instrument. The BP2 was found to absorb UV light at 256 nm ( $\lambda_{\text{max}}$ ).

The tensile strength and elongation at break of the sized cotton yarns were measured according to ASTM method.

## 3. Results and discussion

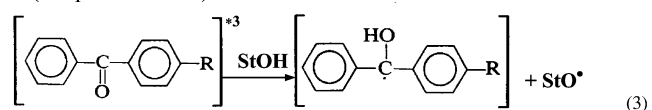
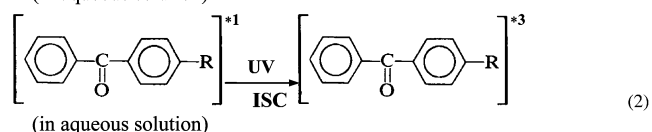
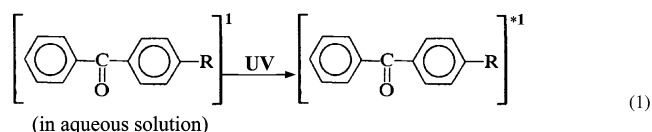
### 3.1. Photo oxidation mechanism

BP2 is a benzophenone derivative, 4-(trimethyl ammoniummethyl) benzophenone chloride.

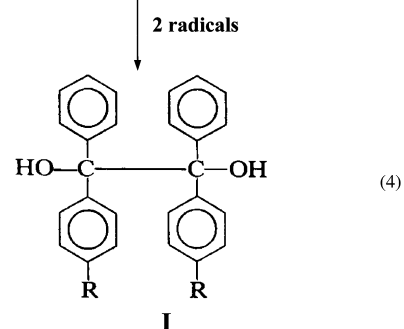


Where  $R = \text{CH}_2\text{-N}^+(\text{CH}_3)_3\text{Cl}^-$

Under UV light excitation, BP2 (in an aqueous medium) is first promoted to its excited singlet state (1) then, via fast intersystem crossing (ISC), it converts into triplet state (2). In presence of NS, which acts as a H-donor, the triplet transient state can undergo hydrogen abstraction with NS to yield reactive radical species (3). Inactive species formation could take place by combination of two



Where StOH = native starch



radicals of BP2 (4) forming the pinnacol derivative (I). The greater the extent formation of compound I, the more pronounced is the inactivation of the photo oxidation process.

### 3.2. Decomposition of BP2

Fig. 1 shows the decomposition of BP2 over five hours of photo oxidation of rice starch when photo oxidation took place using 4% BP2 based on weight of starch (ows) and a material:liquor ratio (M:L ratio) of 1:8 at 60 °C. It is clear (Fig. 1) that the concentration of BP2 decreases as the irradiation time increases. This is due to the formation of the BP2 radical and/or the pinnacol derivative (Eqs. (3) and (4)). Results in Fig. 1 could be an evidence of the success of the BP2-UV system of forming starch macro radicals.

### 3.3. Effect of temperature on the extent of oxidation

Table 1 shows the effect of increasing the oxidation temperature from 30 to 70 °C on the extent of the photo oxidation reaction expressed as the carboxyl and carbonyl contents and also the apparent viscosity of the produced oxidized starch. Oxidation was carried out using BP2-UV system for one hour of UV irradiation, BP2 concentration was 5% (ows) and M:L ratio 1:10.

As is clear from the table, both the carboxyl and carbonyl contents increase by increasing the temperature from 30 to 60 °C above which both carboxyl content and carbonyl content slightly decreased. Increasing the temperature favors formation of carboxyl and carbonyl groups. Further increase in the reaction temperature (70 °C) favors the formation of the pinnacol derivative (I) according to reaction 4. Consequently, the inactivation of the photo oxidation process is more pronounced. In addition, during the oxidation of starch three reactions take place: (a) oxidation which is accompanied by the creation of carboxyl and carbonyl groups, (b) further oxidation of the carbonyl to carboxyl groups and (c) decarboxylation. The magnitude of these reactions seems to be governed by the temperature of the reaction. It is also likely that during the la-

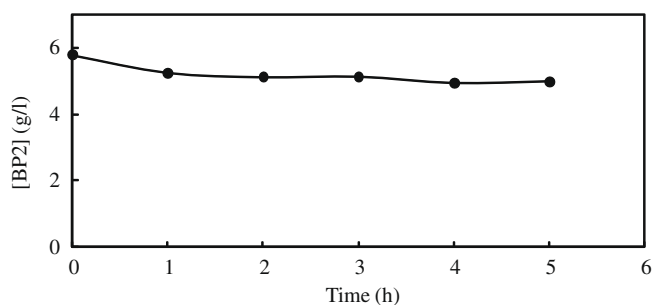


Fig. 1. Decomposition of BP2 during the photo oxidation of rice starch. Conditions used: StOH, 75 g; Temperature, 60 °C; Irradiation time, 0–5 h; [BP2], 4% (ows); M:L ratio, 1:8.

Table 1

Effect of oxidation temperature on the carboxyl and carbonyl contents and the apparent viscosity of the oxidized starch.

Temperature (°C)	Carboxyl content (meq/100 g StOH)	Carbonyl content (meq/100 g StOH)	Apparent viscosity (c.pas.)
30	20	10.56	2500
40	20.2	11.75	1700
50	26.7	12	1500
60	32.7	12.8	600
70	30.8	11.5	590

StOH, 75 g; Temperature, 30–70 °C; Irradiation time, 1 h; [BP2], 5% (ows); M:L ratio, 1:10.

ter stages of the reaction, some of the oxidized starch becomes highly degraded and, therefore, soluble in water, and is washed out along with its high content of carbonyl and/or carboxyl groups (El-Sheikh et al., 2008).

Table 1 shows also that apparent viscosity of the oxidized rice starch decreases significantly as the oxidation temperature rises from 30 to 70 °C. This behavior could be due to the higher extent of oxidation which leads to the formation of shorter chains of rice starch. The major decrease in the apparent viscosity at higher temperatures could be due to the high degradation of starch at the later stage of oxidation (El-Sheikh et al., 2008).

### 3.4. Effect of BP2 concentration on the extent of oxidation

Different concentrations of BP2 (from 0% to 8% ows) were used to study the effect of increasing the concentration of BP2 on the extent of photo oxidation reaction. Thus, oxidation was carried out using BP2-UV system for one hour of UV irradiation at 60 °C and M:L ratio 1:10. The dependence of carboxyl and carbonyl contents and the apparent viscosity on the concentration of BP2 is shown in Table 2.

The results obtained from Table 2 showed that at zero concentration of BP2, considerable amounts of carboxyl and carbonyl groups were obtained. This could be attributed to the formation of StO<sub>2</sub> radical as a result of the glucosidic bond scission of the StOH molecule under the effect of UV irradiation. By increasing the concentration of BP2 up to 6% (ows), both the carboxyl and the carbonyl contents dramatically increased. Incorporation of BP2 to the system enhances the formation of StO<sub>2</sub> radical (Reactions 1, 2 and 3). Consequently, initiation of the photo oxidation reaction takes place. Further increase in the BP2 concentration (8%) was accompanied by decrease in the carboxyl content and nearly leveling off in the carbonyl content. This again could be due to the formation of the pinnacol derivative (I) which, in its turn, leads to the inactivation of the photo oxidation process.

Table 2 shows also that the apparent viscosity sharply decreases with increasing the concentration of BP2. This is undoubtedly due to the glucosidic bond scission of the StOH molecule under the effect of UV irradiation in the presence of BP2. The more the concentration of BP2, the more the formation of StO<sub>2</sub> radicals (Reactions 1, 2 and 3). It is also possible that oxidative degradation might have taken place due to carrying out the oxidation in presence of air. Thus the molar mass of the starch has been decreased.

### 3.5. Effect of material:liquor ratio on the extent of oxidation

Table 3 shows the dependence of the carboxyl and the carbonyl contents and the apparent viscosity of the prepared oxidized starch on increasing the volume of the liquor containing the oxidizing system, BP2-UV irradiation, when the oxidation reaction was carried out using [BP2]; 4%(ows) at 60 °C for one hour of irradiation.

Table 2

Effect of photo initiator concentration on variation of critical properties of the oxidized starch.

[BP2] % (ows)	Carboxyl content (meq/100 g StOH)	Carbonyl content (meq/100 g StOH)	Apparent viscosity (c.pas.)
0	19.8	10.6	5000
2	22.4	10.9	1200
4	29.4	12.3	900
6	29.6	13.8	600
8	28.5	13.9	400

StOH, 75 g; Temperature, 60 °C; Irradiation time, 1h; [BP2], 0–8% (ows); M:L ratio, 1:10.

**Table 3**

Effect of material:liquor ratio on some properties of the oxidized starch.

M:L ratio	Carboxyl content (meq/ 100 g StOH)	Carbonyl content (meq/ 100 g StOH)	Apparent viscosity (c.pas.)
1:2	18	10.9	3500
1:4	22.1	10.58	2600
1:6	25.6	11.5	2500
1:8	27.0	12.0	1800
1:10	29.4	12.3	900

StOH, 75 g; Temperature, 60 °C; Irradiation time, 1h; [BP2], 4% (ows); M:L ratio, 1:2–1:10.

The results (Table 3) indicate that regardless of the material:liquor ratio used both the carboxyl and carbonyl contents increase as the volume of the liquor increases. By increasing the material:liquor ratio, the mobility of BP2 increases and causes an increase in the BP2. radicals and StO. radicals, in its turn. Consequently an increase in the carboxyl and carbonyl contents takes place.

It is seen (Table 3) that the apparent viscosity decreases by increasing M:L ratio. The decrease in the apparent viscosity of the rice starch as a result of increasing the M:L ratio reveals the efficiency of performing glucosidic bond scission of the StOH molecule under the effect of UV irradiation in the presence of BP2. In other words a decrease in the molar mass of the starch molecule and formation of shorter molecular chains of rice starch at higher liquor M:L ratio.

### 3.6. Effect of irradiation time on the extent of oxidation

Table 4 shows the effect of irradiation time on the extent of oxidation reaction expressed as carboxyl and carbonyl contents and apparent viscosity, when the photo oxidation reaction was carried out at 60 °C, using BP2 concentration (4% ows), M:L ratio 1:8 and irradiation time (1–5 h).

The results (Table 4) reveal that, within the range studied (1–5 h), the carboxyl content increases by increasing irradiation time. On the other hand, the carbonyl content increases by increasing irradiation time from 1 to 4 h. Further increase in the reaction time is accompanied by marginal increase in carbonyl content of produced oxidized rice starch. The favorable effect of increasing the irradiation time, on the carboxyl and carbonyl contents of the produced oxidized starch is due to the formation of BP2. radicals which, in turn, produce the StO. radicals by H-abstraction from NS. Increasing the irradiation time increased the formation of BP2. radicals and, consequently, the StO. radicals.

It is as well to note that the apparent viscosity decreases by increasing the irradiation time up to 4 h. It decreases significantly by increasing the extent of oxidation of starch. Further increase in the irradiation time up to 5 h, increases the apparent viscosity. This agrees with increasing of the solubility of the oxidized starch.

**Table 4**

Effect of oxidation time on the carboxyl and carbonyl contents and the apparent viscosity of the oxidized starch.

Time (h)	Carboxyl content (meq/ 100 g StOH)	Carbonyl content (meq/ 100 g StOH)	Apparent viscosity (c.pas.)
1	27	12.0	1800
2	34	12.5	750
3	36	13.1	700
4	39	14.7	600
5	43	14.85	650

StOH, 75 g; Temperature, 60 °C; Irradiation time, 1–5 h; [BP2], 4% (ows); M:L ratio, 1:8.

**Table 5**

Effect of kind of sizing material on the properties of the sized cotton yarns.

Samples	Tensile strength (kg)	Elongation at break (%)	Size removal (%)
A	425	4.6	25
B	456	4.7	55
C	474	4.7	88

Oxidation conditions: StOH, 75 g; Temperature, 60 °C; Irradiation time, 5 h; [BP2], 4% (ows); M:L ratio, 1:8.

A: Native rice starch, B: oxidized starch used by Misr Company and C: Photo oxidized rice starch.

### 3.7. Sizability

Natural polymeric products such as maize and rice starches are used in the textile industry, particularly in cotton warp sizing. However, starch suffers from serious defects, the most outstanding of which are as follows: (a) the viscous solution of starch is unstable, particularly when there is fluctuation of temperature during cooking and sizing operations; (b) the very high molecular size of starch limits penetration into the bulk of the textile threads; (c) the starch films are rigid, particularly in the absence of a good lubricant; (d) starch is susceptible to rot and degradation by micro-organisms. To eliminate or at least to minimize these shortcomings, chemical modification of starch has become essential. When this was done by oxidation, the properties of the starch were changed significantly (Hebeish, El-Rafei, El-Sisi, Abdel Hafiz, & Abdel-Rahman, 1994). To examine the changes made by photo oxidation of rice starch using BP2-UV system on its utilization as a sizing agent, the following investigation was carried out.

Rice starch before and after photo oxidation along with native starch and commercial oxidized starch used by Misr Company for Spinning and Weaving were applied to samples of cotton yarns as described in the experimental section. These sized samples were then monitored for tensile strength, elongation at break and percent size removal after washing with hot water for 10 min. The results obtained are set out in Table 5.

It is seen (Table 5) that the tensile strength and elongation at break of sample sized with the photo oxidized rice starch are higher than those of the native starch and the commercial oxidized starch. It also seen that the percent size removal from sample sized with the photo oxidized rice starch is significantly higher than the samples sized with the native starch and commercial oxidized starch. This, indeed, reflects the comparative advantages of the photo oxidized rice starch vis-à-vis the native starch and commercial oxidized starch.

### 3.8. Conclusions

Oxidation of rice starch was done using a new photo oxidation system (BP2-UV). Best results were obtained when rice starch was photo oxidized at 60 °C for five hours of UV irradiation at a material:liquor ratio of 1:8 and BP2 concentration of 4% (ows). High carboxyl and carbonyl contents were obtained at this end. The produced photo oxidized rice starch was found suitable as a sizing agent of cotton yarns where higher tensile strength, elongation at break and% of size removal were obtained compared with those of native rice starch and oxidized starch used by Misr Company of Spinning and Weaving in El-Mahalla El-Kubra (Egypt).

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