**OXIDATION AND CHARACTERIZATION OF MAIZE SODIUM PERBORATE/ AMINOIMINOMETHANESULFINIC ACID REDOX SYSTEM**

***Egypt. J. of Appl. Sci., 35 (1) 2020 17-36***

**Khalil , E.M. and M.M. Zahran**

Department of Chemistry, Faculty of Science, Helwan University,

Ain-Helwan, Cairo 11795, Egypt

**Key Words:** Maize starch, oxidation, potassium bromate, aminoiminomethanesulfinic acid.

**ABSTRACT**

Preparation of oxidized starch proper for sizing of cotton fabric was achieved via treatment of maize starch by sodium perborate/aminoiminomethanesulfinic acid (SPB/AIMSA) redox system. Structural changes in the starch molecules brought about by oxidation were appraised in terms of the carbonyl and carboxyl groups as well as the apparent viscosity. It was found that starch undergoes oxidative degradation using the said redox system. This was demonstrated by a significant enhancement of the carbonyl and carboxyl groups along with a significant decrease in the apparent viscosity as compared with the unoxidized starch.

**1. INTRODUCTION**

Oxidized starches are used extensively as sizing agents to improve the mechanical and film-forming properties of paper, paper board and textiles. Oxidized starches act by binding the components of paper web, including fibres, pigments and fillers **(Tolvanen, et al, 2009).** The use of oxidized starches improves the strength and printability of paper **(Parovuori, et al., 1995).**

Several oxidizing agents including, sodium hypochlorite **[Dias *et al.,* 2011 and Wei *et al.,* 2016],** sodium persulphate **[Wang *et al.,* 2012],** hydrogen peroxide **[Tolvanen *et al.2013*],** ozone [**Çatal and Ibanog lu,** **2014],** Periodate **[Veelaert et al, 1994]** have been used to oxidize starch.

This work deals with the oxidation of maize starch using sodium perborate (SPB)/aminoiminomethanesulfinic acid (AIMSA) redox system. Sodium perborate {Synonyms: dexol; sodium peroxoborate; Sodium peroxo-metaborate; Sodium oxidooxy-oxoborane; Sodium (oxoboryl) dioxidanide; perboric acid (HBO3), sodium salt}, is considered as an efficient oxidizing agent for eco-friendly bleaching of a variety of cellulosic fabrics **[Zahran, 2006 and Zahran & Ahmed, 2009].** From our point of view, SPB offers unique advantages as an oxidizing agent **[Zahran, 2006].**

The primary objective of the present work is to establish the most appropriate conditions for preparation of oxidized starch with certain properties for particular end-use.Properties examined include the carboxyl and carbonyl groups as well as the apparent viscosity at different rates of shear. Tentative mechanisms, which illustrate all events that occur during the whole course of the oxidation reaction, were also suggested.

***18 Egypt. J. of Appl. Sci., 35 (1) 2020***

**2. EXPERIMENTAL**

**2.1. Materials and Chemicals**

Maize starch was kindly supplied by Cairo Company for Starch and Glucose, Cairo, Egypt. Chemical analysis showed that this starch has a moisture content of 11.2% and a nitrogen content of 0.06%. Sodium perborate tetrahydrate (SPB), NaBO3.4H2O (Aldrich, Germany) was used as received. Aminoiminomethanesulfinic acid (AIMSA) and all other chemicals used in the titrimetry were analytical reagent grade chemicals.

**2.2. Oxidation Procedure**

 Oxidation of maize starch was carried out using sodium perborate (SPB) in acidic medium. The experimental technique adopted was as follows: A material to liquor ratio 1:2.5 was employed and the oxidation reaction was performed in a beaker placed in a thermostatic water bath. 100 g maize starch was added to 200 ml water and the pH of the reaction medium adjusted to 2.5 by using H2SO4. The reactants were kept at the desired reaction temperature under continuous stirring for a definite period of time. Known concentrations of SPBand AIMSA were added. The latter added either at beginning of the reaction or portion-wise during the oxidation duration. Finally, the product filtered on a sintered glass funnel, washed with tap water and dried at 50-55ºC for 3 hours in an oven.

**2.3. Testing and Analysis**

***2.3.1. Tensile properties of the sized cotton fabrics***

Tensile strength (TS) and elongation-at-break (EAB) of the sized cotton fabric (dimensions 25 cm of length x 5 cm of width) were measured by ISO-1934-1 tensile properties- Shimadzu-s-500.

***2.3.2. Carboxyl content***

The carboxyl content of the oxidized samples was determined according to a method described elsewhere **[Daul *et al.,* 1952]**. The determination depends on formation of the protonated form of the carboxyl groups in starch molecules by soaking the samples in a mixture of HCl/ ethanol/water (1/80/20, w/w) for 24 h, then they were filtered off and washed several times with ethanol/water (80/20, w/w) until free from HCl, then dried at 40oC. An exact weight of the dried protonated form of oxidized starch was then soaked in an excess of aqueous NaOH (0.01 mol) for another 12 h. The excess unreacted NaOH was back titrated with 0.01 mol HCl using phenolphthalein as indicator.

***2.3.3. Carbonyl content***

***Egypt. J. of Appl. Sci., 35 (1) 2020 19***

The carbonyl content was determined according to the hydroxylamine hydrochloride method **[Kilmova, 1977].** The method depends on the oximation of the carbonyl groups with hydroxylamine hydrochloride in the presence of triethanolamine. The latter neutralizes the liberated hydrochloric acid to shift the equilibrium towards quantitative formation of the oxime. Excess triethanolamine was determined by titration with standard hydrochloric acid using bromophenol blue as indicator.

***2.3.3. Rheological properties***

 The rheological properties were measured using a co-axial rotary viscometer (Hake RV20 - Germany) at rates of shear ranging between 258-1290 s-1. All rheological properties were evaluated at a temperature of 90oC. The apparent viscosity was calculated using the following equation:

**η**$ =\frac{T}{D}(Pa.s)$

Where **η** is the apparent viscosity [in pascal-second ( Pa.s)], **T** is the shear stress and **D** is the rate of shear. Because 1 Pa.s = 1000 milliPa.s and 1 mPa.s=1 centipoise (Cp), **η = (T/D) x 1000** (Cp). Because the centipoise is frequently used in practice, it is used instead of Pascal unit throughout the present study.

**3. RESULTS AND DISCUSSION**

***Tentative Mechanisms***

Since this investigation deals with oxidation of starch using a SPB/AIMSA activated system, it is not improper to review the reaction mechanisms involved.

* **Reactive species from self-decomposition of SPB**

Sodium perborate (SBP) is a genuine inorganic peroxide containing a cyclic peroxide ring structure:

The anionic formula of this peroxo salt **[**B2(O2)2((OH)4**]**2ˉ has two peroxidic bonds (O-O) which are viewed as active and fit for oxidizing a diversity of organic and inorganic compounds

SPB can be made by the reaction between hydrogen peroxide and sodium metaborate (SMB) and in aqueous solution (**Eq.** **1**):

***20 Egypt. J. of Appl. Sci., 35 (1) 2020***

When SPB is dissolved in water, it is hydrolyzed into the starting materials from which is formed, *viz.*, H2O2 and SMB. In an aqueous system consisting of a polysaccharide, once H2O2 is liberated from SPB, it attacks the monomeric rings as well as the glycosidic linkages. SPB acts well as oxidizing agent even in the absence of an activator. However, in the presence of activator, the oxidation efficiency of the SPB is greatly ameliorated.

Sodium perborate should be represented by the formula NaBO2.H2O2.3H2O, since its properties appear to be those corresponding to an addition product of hydrogen peroxide rather than to a salt of some hypothetical peroxyboric acid**.**

When SPB coexists with the polysaccharides in the current work, *viz.* starch in aqueous medium, it releases H2O2 which, in turn, generates free radical species capable to oxidizes the starch chains. This reaction is greatly enhanced in acidic medium.

(SMB)

NaBO

3

 . 4 H

2

O NaBO

2

 + H

2

O

2

 + 3 H

2

O

(SPB)

...........

 ( 3 )

The experimental results suggest that the oxidation reaction of the polysaccharide proceeds mainly via the hydroxyl free radical species generated from the homolytic fission of H2O2 (**Eq.** **4**).

On the other hand, heterolysis of H2O2 results in the formation of perhydroxyl anion (HOO **–**) (**Eq.** **5**). The latter undergoes disproportionation reaction with another H2O2  molecule (**Eq. 6&7**) to create perhydroxyl radical (HOO•), hydroxyl radical, superoxide anion radical (hyperoxide O2**–**•), and inactive species. Oxidation reaction by the free radical species resulted from the heterolytic path, may possibly occurs to a very limited extent, or even not occur at all.

* **Reactive species from self-decomposition of AIMSA**

***Egypt. J. of Appl. Sci., 35 (1) 2020 21***

AIMSAis a versatile reducing agent is more efficient reducing agent than thiourea. When it is coupled with an oxidizing agent, it establishes an efficient redox system with the formation of a variety of active species capable of attacking and oxidizing the polysaccharides chains.

AIMSA is thought to adopt a zwitterionic structure in the solid state (**Scheme II.1**) **[Sullivan and Hargreaves, 1962].** Tautomerism to the neutral form was investigated. In the presence of water, AIMSA converts to the tautomer, a sulfinic acid, (H2N)HN=CS(O)(OH), **[Makarov, 2001]** (**Scheme II.2**).

 …………(12)

**Scheme 1. Tautomerization of AIMSA**



 **Thiourea dioxide Formamidine sulfinic acid**

 **(stable form) (unstable form)**



**Scheme 2. Historical description of the formamidine sulfinic acid tautomers and the proposed decomposition route to the sulfinate anion, as exists in aqueous solution [Lewis *et al.,* 2014].**

 The mechanism of decomposition of AIMSA is pH dependent **[Svarovsky *et al.,* 2000 &2001 ;** **Walter & Randau, 1969** ; **Gao *et al.,* 2006]**. At neutral and low pH, AIMSA tend to decompose to the formamidine or formamidinium salt. At high pH, AIMSA usually decomposes to furnish a powerful, sulfur-containing reducing species. The key question which has fuelled the debate was the mechanism of C-S bond dissociation *via* homolysis or heterolysis. Both mechanisms account for the formation of sulfur containing anions.



***22 Egypt. J. of Appl. Sci., 35 (1) 2020***

**Scheme 3. Homolysis and heterolysis of the C-S bond in AIMSA**

 An alternative mechanism of heterolysis has been proposed by several authors. Budanov suggested that heterolytic cleavage is most likely to occur in protic solvents whereas homolytic cleavage is favoured in aprotic solvents and in the solid-state **[Budanov, 2002].**

 The formation of the SO2•− radical anion is supported by EPR spectroscopic studies **[McGill & Lindstrom, 1977** ; **Nakagawa & Minami, 1972].** What is agreed amongst the authors in this area is that AIMSA acts as a precursor to a radical anion SO2•− and subsequently, dithionite S2O42− **[Svarovsky *et al.,* 2000 and Svarovsky *et al.,* 2001 ; McGill & Lindstrom, 1977 ; Nakagawa & Minami, 1972 ; Budanov, 2002].** Dithionite is formed *via* the dimerization **[Janzen, 1972; Lambeth & Palmer, 1973]** of the radical anion, as demonstrated by **Creutz and Sutin(1974)**, who also proposed that the radical anion not dithionite, is the kinetic reducing species **[Creutz & Sutin, 1974]**. The formation of the SO2•− radical anion has been used to explain the formation of pinacol products from the reduction of ketones **[Nakagawa & Minami, 1972]** and initiation reactions regarding polymer synthesis **[Percec *et al.,* 2005].**

 

**Scheme 3. Formation of dithionite *via* dimerization**

 The formation of the SO2•− radical anion, and consequently dithionite, are dependent on the oxygen. The sulfinate dianion SO22− was then thought to rapidly oxidize with dissolved molecular oxygen to afford the radical anion SO2•− **[Svarovsky *et al.,* 2001].**

* **Starch Oxidation**

 Different active species generated from SPB (equations 4, 6-10) and AIMSA (Sch. II. 2&3) oxidize the starch molecule by attacking the starch hydroxyls and the glycosidic linkages.



***Egypt. J. of Appl. Sci., 35 (1) 2020 23***

**Scheme 4. Simplified reaction scheme showing starch oxidation using AIMSA/H2O2 Activated system.**

 Based on the aforementioned tentative mechanisms, it seems that the oxidative action of SPB in the absence and in the presence of AIMSA is due to formation of one or more of the active species depicted in the above equations. The factors affecting the oxidative degradation of maize starch were studied. The oxidation reaction was monitored via determining the percent SPBdecomposed. The resultant oxidized starch was evaluated via determining the carboxyl content, carbonyl content and the apparent viscosity measured at different rates of shear. The sizeability and desizeability of cotton fabric were also studied. The results obtained are given below with their appropriate discussion.

***Effect of Redox Pair Concentration***

 **Figure 1** show the influence of various molar ratios of SPBto AIMSA on the percent decomposed perborate during oxidation of maize starch at 50ºC for 3 hours. Different amounts of SPB(2.5,5,10 and 15 mmol/l00g starch) were firstly added to the starch suspension followed by addition of different amounts of AIMSA, keeping in mind the molar ratio needed. It is clear that the percent decomposed perborate, regardless of the concentration of SPBused, increases by increasing the amounts of AIMSA. It reaches a maximum when the molar ratio corresponds to 1:1.2 was used. Besides, for a given SPB: AIMSA molar ratio, the percent decomposed perborate increases by increasing the amounts of SPB incorporated in the reaction medium. This is due to that the employment of higher concentrations of SPBor AIMSA, or both, causes these redox components to react drastically with each other and/or with starch chains

***24 Egypt. J. of Appl. Sci., 35 (1) 2020***

**Figure 1. Effect of [SPB]:[AIMSA] molar ratio on the percent decomposed perborate :** [SPB] : 2.5, 5, 10, 15 mmol/100g starch ; temperature , 50oC ; time , 3hrs. ; pH, 2.5 ; material-to-liquor ratio , 1:2.5 .

 **Figures 2&3** show the dependence of carboxyl and carbonyl contents of the oxidized maize starch on the molar ratios of SPBto AIMSA. Apparently, the carboxyl and carbonyl contents increase by increasing the concentration of AIMSA within the range studied. This is true irrespective of the concentration of SPBused. The latter, however, heightens the carboxyl and carbonyl contents up to 10 mmol/l00g starch at any given SPB: AIMSA molar ratio. The concentration of SPBcorresponds to 15 mmol/l00 g starch brings about a decrement in carboxyl and carbonyl contents.

 The increments in the carboxyl and carbonyl contents by increasing AIMSA concentration (within the range studied) and/or SPBconcentration (from 2.5 up to 10 m mole/ 100 g starch) could be associated with the formation of greater amounts of the oxidizing species created from this redox component.

 Nevertheless; the decrements in the carboxyl and carbonyl contents, when the SPB concentration higher than 10 mmol/ 100 g starch was used may be ascribed to the enhancement of the oxidative degradation rate of the starch molecules resulting in the formation of low-molecular weight fragments. The latter, are referred to as highly oxidized starch with very short chains and high carboxyl and carbonyl contents, are washed-out during the process of filtration of the resultant oxidized starch.

***Egypt. J. of Appl. Sci., 35 (1) 2020 25***

**Figure 2. Dependence of the carboxyl content of maize starch on the [SPB]:[AIMSA] molar ratios :** [SPB] : 2.5, 5, 10, 15 mmol/100g starch ; temperature , 50oC ; time , 3hrs. ; pH , 2.5 ; material-to-liquor ratio , 1:2.5 .

**Figure 3. Reliance of carbonyl content of the oxidized maize starch on the [SPB]:[AIMSA] molar ratios :** [SPB] : 2.5, 5, 10, 15 mmol/100g starch ; temperature , 50oC ; time , 3hrs. ; pH , 2.5 ; material-to-liquor ratio , 1:2.5 .

 **Figure 4** shows the dependence of the apparent viscosity of the oxidized starch on SPB: AIMSA molar ratio, at a shear rate of 12.9 s-1, when the oxidation was carried out using different perborate concentrations at 50oC.

***26 Egypt. J. of Appl. Sci., 35 (1) 2020***

 It is seen that: (i) for a given SPBconcentration, the apparent viscosity decreases as the [SPB]:[ AIMSA] ratio increases and (ii) at any [SPB]:[ AIMSA] ratio, the apparent viscosity decreases wth increasing the perborate concentration from 2.5 up to 10 mmol/l00 g starch. Increasing the perborate concentration up to 15 mmol lead to an increase in the apparent viscosity.

 It is to be expected that increasing the redox components concentration causes the reaction medium to be plenty with various oxidizing species capable to degrade the starch macromolecules, thereby, the apparent viscosity decrease. However, the increase in the apparent viscosity at the higher SPBconcentration (l5 mmol/l00g starch) is attributed to solubilization of the highly degraded starch molecules and its removal during filtration of the resultant oxidized starch.

**Figure 4. Apparent viscosity (measured at** 90oC **and a rate of shear 12.9 s-1) as a function of [SPB]:[AIMSA] molar ratio : [SPB] :** 2.5, 5, 10, 15 mmol/100g starch ; temperature , 50oC ; time , 3hrs. ; pH , 2.5 ; material-to-liquor ratio , 1:2.5 .

***Effect of Oxidation Temperature***

 To investigate the effect of temperature, the oxidation reaction was conducted at 30o, 40o and 50oC for different lengths of time. Concentrations of SPB and AIMSA were set at 10 mmol and 12 mmol/100 g starch respectively. Results are shown in **Figures 5-8**.

 The effect of oxidation temperature on the decomposition rate of SPBis shown in **Figure II.5**. A perusal of the results indicates that the rate of SPBdecomposition accelerates by raising the oxidation temperature from 30 to 50 and reaches a maximum in the latter. This is valid during the first 120 minutes. However, at the later stages of oxidation, the rate of SPB decomposition is levelled off, irrespective of the temperature applied.

 The acceleration of the oxidation rate upon raising the temperature suggests that the latter performs the following functions: (i) intensifying reaction of the redox components, giving rise to more active species; (ii) enhancing the kinetic energy and diffusibility of SPB and AIMSA molecules; (iii) enlarging the number of collisions between the reacting molecules; and (iv) accentuating the swelling properties of starch.

***Egypt. J. of Appl. Sci., 35 (1) 2020 27***

**Figure 5. Effect of duration and temperature of oxidation reaction on the percent decomposed perborate :** [SPB] , 10 mmol/100g starch ; [AIMSA] , 12 mmol/ 100g starch ; pH , 2.5 ; oxidation temperature , 30oC, 40oC, 50oC ; material-to-liquor ratio , 1:2.5 .

 **Figures 6&7** demonstrate the influence of the oxidation temperature on the carboxyl and carbonyl contents of the oxidized maize starch, respectively. From data of these figures; it is evident that: (a) the carboxyl content increases by raising the oxidation temperature; it follows the order: 50º>40º>30ºC. The opposite holds true for the carbonyl content; and (b) regardless of the temperature applied, the carboxyl content increases by increasing duration of the oxidation reaction up to 90 min.; beyond this, it mains unaltered. In other words, the carbonyl content increase as the duration increases up to 120 min., then levels off.

 The above findings could be explained in terms of the two-competitive reactions: (i) oxidation of the starch hydroxyls to aldehydic groups, and (ii) oxidation of the newly introduced aldehydic groups to carboxylic groups. The magnitude of these reactions is expected to rely on the temperature of the reaction. Current data indicate that reaction (i) prevails over reaction (ii) at the elevated temperature.

***28 Egypt. J. of Appl. Sci., 35 (1) 2020***

**Figure 6. Influence of duration and temperature of oxidation on carboxyl content of the oxidized maize starch:** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature, 30oC, 40oC, 50oC; material-to-liquor ratio, 1:2.5

**Figure 7. Effect of duration and temperature of oxidation on the carbonyl content of maize starch:** [SPB], 10 mmol/ 100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature, 30oC, 40oC, 50oC ; material-to-liquor ratio , 1:2.5.

**Figure II.8** shows the relation between the apparent paste viscosity of the cooked untreated and oxidized maize starches, and the rate of shear during oxidation of maize starch using 10 mmole SPBalong with 12 mmole AIMSA /l00 g starch at 30º, 40º and 50ºC for 90 min. The data reveal that; (a) the apparent viscosity of the untreated starch is much higher than that of the oxidized starches; (b) the apparent viscosity decreases as the rate of shear increases; and (c) for a given rate of shear the apparent viscosity decreases as the temperature increases.

***Egypt. J. of Appl. Sci., 35 (1) 2020 29***

The decrement in the apparent viscosity by increasing the temperature reflects the enhancement in the oxidative degradation reaction at high temperature as explained above.

The higher carboxyl content in the oxidized starch is more soluble than the cooked samples. If this is the case, and bearing in mind the increase in the carboxyl content by raising the reaction temperature, one would interpret the lower apparent viscosity of the oxidized starch at higher temperatures in terms of the starch paste to flow (express as apparent viscosity) is essentially due to swelling of the starch granules. Resistance to flow decreases as the solubility increases.

**Figure 8. Apparent viscosity *versus* rate of shear of starch before and after oxidation at different temperatures and times:** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; material-to-liquor ratio, 1:2.5.

***Effect of Sequence of AIMSA Addition***

 **Figures 9-13** show the effect of the modality of the AIMSA addition on the oxidation of maize starch. The latter was performed using aqueous starch suspension containing SPB (10 mmol/100 g starch) and AIMSA (12 mmol/100 g starch) keeping the material to liquor ratio of 1:2.5, at 50°C and pH2.5. The desired amount of AIMSA, i.e., 12 mmol/100 g starch, was added to the reaction mixture either in one-dose at the beginning of the reaction or divided inequality into six-doses which were sequentially added throughout the oxidation reaction at zero, 30 , 60 , 90 , 120 and 150 min.

 It is evident (**Figs. 9-11**) that, the addition of AIMSA in one-dose causes:

***30 Egypt. J. of Appl. Sci., 35 (1) 2020***

1. complete decomposition of SPBwithin the first 90 minutes; beyond this, it levels off ; and
2. heightening the carboxyl content by increasing the duration of the reaction up to 90 min. and then leveled off (**Fig. 10** ). The same holds true for the carbonyl content.

 Generation of greater amounts of AIMSA radicals and bromine ions within the first 90 minutes of the reaction interprets the enlargement of the percent decomposed and the carboxyl and carbonyl contents of the oxidized starch. Levelling off of these oxidation criteria may be due to depletion of the above-mentioned active species beyond 90 min.

 It is also clear (**Figs. 9-11**) that, sequential addition of AIMSA in six-doses brings about:

1. decomposition of SPBat a slower rate than that of one-dose addition (**Fig.9**); full decomposition was attained in 180 minutes; and
2. gradual enhancement in the carboxyl and carbonyl contents during the whole duration. At later stages of oxidation; the carboxyl and carbonyl contents are higher than those obtained in the one-dose addition.

**Figure 9. Effect of duration and sequence of AIMSA addition on the percent decomposed perborate:** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature 50oC; material-to-liquor ratio, 1:2.5.

***Egypt. J. of Appl. Sci., 35 (1) 2020 31***

**Figure 10. Reliance of carboxyl content of the oxidized maize starch on duration and sequence of AIMSA addition:** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature 50oC; material-to-liquor ratio, 1:2.5.

**Figure 11. Influence of duration and sequence of AIMSA addition on carboxyl content of the oxidized maize starch:** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature 50oC; material-to-liquor ratio, 1:2.5.

 Sequential addition of AIMSA in six-doses seems to regulate the extent of SPB decomposition during the whole duration. That is, the active species released in the reaction medium tend to attack and oxidize the starch chains, rather than they react with each other. Formation of oxidized starches having higher carboxyl and carbonyl contents proves this. On the other hand, in one-dose addition of AIMSA; the reaction medium is repleted by the oxidizing species, therefore, they tend to attack the starch molecules besides to their tendency to react with each other.

**Figures 12&13**) show the dependence of the apparent viscosity of oxidized maize starch when AIMSA was added in one-dose and in six-doses, respectively. The results disclose that: (i) the apparent viscosity decreases as the rate of shear increases; (ii) the apparent viscosity of the highly oxidized starches is not seriously affected by increasing the rate of shear; (iii) for a given rate of shear, in case of one-dose addition, the apparent viscosity decreases by prolonging the reaction duration up to 60 min. and increases thereafter (**Fig.12**). On the other hand, in the case of six-doses addition, the apparent viscosity decreases by prolonging the reaction duration up to 120 min. then increases (**Fig.13**); and (iv) the apparent viscosity values in case of one-dose addition of AIMSA are lower as compared with those of six-doses addition of the same amount of AIMSA, however, at the end of gradual addition of AIMSA, the reverse holds true.

***32 Egypt. J. of Appl. Sci., 35 (1) 2020***

 The decrements in the apparent viscosity as the oxidation proceeds is a logical consequence of the degradation of the starch chains. However, it is surprising that the apparent viscosity begins to increase after 60 min. (for one-dose AIMSA addition) or 120 min. (for six-doses) of the reaction duration. Combination of oxidized starch short chains and/or the starch macroradicals seems to be responsible for the enhancement of the apparent viscosity.

**Figure 12. Influence of duration and rates of shear on the apparent viscosity of maize starch oxidized with SPB along with AIMSA ( in one-dose ) :** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature 50oC; material-to-liquor ratio, 1:2.5.

***Egypt. J. of Appl. Sci., 35 (1) 2020 33***

**Figure 12. Effect of duration and rates of shear on the apparent viscosity of maize starch oxidized with SPB along with AIMSA ( in six-doses ) :** [SPB], 10 mmol/100g starch; [AIMSA], 12 mmol/100g starch; pH, 2.5; oxidation temperature 50oC; material-to-liquor ratio, 1:2.5.

**CONCLUSIONS**

1. For a given SPB/AIMSA molar ratio, the percent decomposed perborate increases by increasing the amounts of either SPBor AIMSA incorporated in the reaction medium.

 The carboxyl and carbonyl contents increase by increasing the concentration of AIMSA within the range studied. This holds true with increasing the SPBconcentration up to 10 mmol/100 starch. Beyond this concentration, both carboxyl and carbonyl contents decrease. The apparent viscosity decreases as the [SPB] : [AIMSA] ratio increases.

1. The rate of SPBdecomposition accelerates by raising the oxidation temperature from 30 to 50 and reaches a maximum at the latter. This is valid during the first 120 minutes. However, at the later stages of oxidation, the rate of SPB decomposition is levelled off, irrespective of the temperature applied. The carboxyl content increases by raising the oxidation temperature; it follows the order: 50o> 40o>30oC. The opposite holds true for the carbonyl content. For a given rate of shear the apparent viscosity decreases as the temperature increases.
2. Sequential addition of AIMSA in six-doses seems to regulate the extent of SPB decomposition during the whole duration. Therefore, it superiors the addition in one-dose. The apparent viscosity values in the case of one-dose addition of AIMSA are lower as compared with those of six-dose addition of the same amount of AIMSA, however, at the end of gradual addition of AIMSA, the reverse holds true.

**REFERENCES**

***34 Egypt. J. of Appl. Sci., 35 (1) 2020***

**Budanov, V. V. (2002)** “Reactivity and Use of Sulfur–Oxygen Reducing Agents with C–S Bonds”, *Russian Journal of Coordination Chemistry*, 28: 294-300.

**Çatal, H. and S. Ibanog˘lu (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*, 47: 1958–1963.

**Creutz, C. and N. Sutin (1974).** “Kinetics of the reactions of sodium dithionite with dioxygen and hydrogen peroxide”, *Inorganic Chemistry*, 13: 2041-2043.

# Daul, G.; R. Reinhardt and J. Reid (1952) “Studies on the partial carboxymethylation of cotton“ *Textile Research Journal*., 1: 787-792.

**Dias, A.R.G. ; E.R. Zavareze ; M.C. Elias ; E. Helbig ;D.O. Silva and C.F. Ciacco (2011)** “Pasting, expansion and textural properties of fermented cassava starch oxidised with sodium hypochlorite”, *Carbohydrate Polymers*, 84: 268–275.

### Gao, B. ; X. Liu ; L. Li and J. Wang (2007) “Oxidation and decomposition kinetics of thiourea oxides” *The Journal of Physical Chemistry A*, 111: 872-877.

# Janzen, E.G. (1972) “ESR studies of thermal decomposition mechanisms. II. Electron spin resonance study of the SO2- formation in the thermal decomposition of sodium dithionite, sodium and potassium metabisulfite, and sodium hydrogen sulfite”, *The Journal of Physical Chemistry*, 76: 157-162.

**Kilmova, V.(1977)** “Basic Methods for Organic Microanalysis”, 1st ed., Mir Publisher, Moscow.

**Lambeth, D. O. and G. Palmer (1973)** “The kinetics and mechanism of reduction of electron transfer proteins and other compounds of biological interest by dithionite*”, Journal of Biological Chemistry*, 248: 6095-6103.

# Lewis, D. ; J.Mama and J. Hawkes (2014) “An investigation into the structure and chemical properties of formamidine sulfinic acid”, *Applied spectroscopy*, 68 (12): 1327-1332.

***Egypt. J. of Appl. Sci., 35 (1) 2020 35***

# Makarov, S. V. (2001) “Recent trends in the chemistry of sulfur-containing reducing agents”, *Russian Chemical Reviews*, 70, 885–895.

# McGill, J. E. and F. Lindstrom (1977) “Mechanism of reduction of cadmium by aminoiminomethanesulfinic acid in alkaline media”, *Analytical Chemistry*, 49, 26-29.

**Nakagawa, K. and K. Minami (1972)** “Reduction of organic compounds with thiourea dioxide. I. reduction of ketones to secondary alcohols”*, Tetrahedron Letters*, 13, 343-346.

**Parovuori, P. ; A. Hamunen ; P. Forssell ; K. Autio and K. Poutanen (1995)** “Oxidation of potato starch by hydrogen peroxide”, *Starch/Stärke*, 43: 19–23.

# Percec, V. ; A.V. Popov and E. Ramirez-Castillo (2005) “Single Electron Transfer-Degenerative chain Transfer mediated Living Radical Polymerization (SET-DTLRP) of vinyl chloride initiated with methylene iodide and catalyzed by sodium dithionite”, *Journal of Polymer Science Part A Polymer Chemistry*, 43: 287-295.

**Sullivan, R.A.L. and A. Hargreaves (1962)** “The crystal and molecular structure of thiourea dioxide”, *Acta Crystallographica*, 15: 675-682.

**Svarovsky, S.A.; R.H. Simoyi and S.V. Makarov (2000)** “Reactive oxygen species in aerobic decomposition of thiourea dioxides”, *Journal of the Chemical Society, Dalton Transactions*, 511-514.

**Svarovsky, S.A.; R.H. Simoyi and S.V. Makarov (2001)** “A possible mechanism for thiourea-based toxicities:  Kinetics and mechanism of decomposition of thiourea dioxides in alkaline solutions” *The Journal of Physical Chemistry B,* 105:12634-12643.

**Tolvanen, P. ; P. Maki-Arvela ; A.B. Sorokin ; T. Salmi and D. Y. Murzin (2009)** “Kinetics of starch oxidation using hydrogen peroxide as an environmentally friendly oxidant and an iron complex as a catalyst”, *Chemical Engineering Journal*, 154: 52–59.

**Tolvanen, P.; A. Sorokin ; P. Mäki-Arvela ; D.Y. Murzin and T. Salmi (2013)** “Oxidation of starch by H2O2 in the presence of iron tetrasulfophthalocyanine catalyst: The effect of catalyst concentration, pH, solid–liquid ratio, and origin of starch”, Industrial & Engineering Chemistry Research., 52 (27): 9351-9358.

**Veelaert, S. ; M. Polling and D. Wit (1995)** “Structural and physicochemical changes of potato starch along periodate oxidation”, Starch/Starke, 47: 263–268.

***36 Egypt. J. of Appl. Sci., 35 (1) 2020***

**Walter, W. and G. Randau (1969)**“Über die oxydationsprodukte von Thiocarbonsäureamiden, XX1) Thioharnstoff‐S‐dioxide”, *Justus Liebigs Annalen der Chemie*, 722: 80-97.

**Wang, H.J. ; X. Jin ; W.Y. Wang ; C.F. Xiao and L.Tong (2012)** “Preparation and electrospinning of acidified-oxidized potato starch”, *Advanced Materials Research*, 535–537: 2340–2344.

**Wei, B. ; B. Zhang ; B. Sun ; Z. Jin ; X. Xu and Y. Tian (2016)** “Aqueous re-dispersibility of starch nanocrystal powder improved by sodium hypochlorite oxidation”, *Hydrocolloids*, 52: 29–37.

**Zahran, M.K. (2006)** “One-step process for desizing, scouring and bleaching of cotton fabric using a novel eco-friendly bleaching agent”, Journal *of the Textile Association*, 67(4):153-159.

**Zahran, M.K. and B.A. Ahmed (2010)** “A greener approach for full flax bleaching”, *The Journal of The Textile Institute*, 101(7): 674-678.

**أكسدة وتوصيف نشا الذرة بإستخدام نظام الأكسدة والإختزال لبيربورات الصديوم مع أمينوإيمينوإيثان حمض سلفونيك**

**عيد متولى خليل ، محمد مجدى زهران**

قسم الكيمياء ، كلية العلوم ، جامعة حلوان ، مصر

تم تحضير نشا مؤكسد ملائم لتبويش الأقمشة القطنية عن طريق معالجة نشا الذرة بإستخدام نظام الأكسدة والإختزال لبيربورات الصديوم مع حمض أمينوإيمينوإيثان سلفونيك . (SPB /AIMSA) تم تقييم التغيرات التركيبية في جزيئات النشا والناتجة عن الأكسدة من خلال مجموعات الكربونيل والكربوكسيل وكذلك اللزوجة الظاهرية للنشا المؤكسد. وقد وجد أن النشا يخضع لتكسير تأكسدى باستخدام نظام الأكسدة المذكور. وقد تم إثبات ذلك من خلال التحسن الكبير لمجموعتي الكربونيل والكربوكسيل مع انخفاض كبير في اللزوجة الظاهرية مقارنة بالنشا غير المؤكسد.