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Electrocatalytic oxidation of rice starch using mixed oxidant generated via titanium/rhodium thermally activated modified electrode: Part (I)

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ABSTRACT

Oxidation of rice starch was achieved via electro-generated mixed oxidant due to the electrolysis of saline solution using the titanium/rhodium thermally activated modified electrode. The factors affecting the oxidation criteria such as the pH value of the reaction medium, current density, duration, temperature of oxidation, and the supporting electrolyte concentration were studied. The resultant oxidized starch was evaluated via determining the carbonyl and carboxyl contents as well as the apparent viscosity at different rates of shears. Results obtained indicate that, the optimum operating conditions for the electrocatalytic oxidation of rice starch “suitable sizing materials for cellulosic based textile warps” by the titanium/rhodium thermally activated modified electrode are, current density 7.5 mA/cm^2, pH 3, solution temperature 25 °C, time of electrolysis 60 min. and 7.5 g/l of sodium chloride as supporting electrolyte.

1. Introduction

Starch oxidation as a process, as well as starch oxidation products, has attracted considerable attention because of several practical and potential nutritive and non-nutritive applications. One of the most important engineering applications of starch is its use as a sizing agent in textile industry. Starch suffers from serious defects, the most outstanding of which are: (a) instability of viscous solution of starch particularly when there is fluctuation of temperature during cooking and sizing operations, (b) the very high molecular size of starch limits the penetration in the bulk of textile threads, (c) rigidity of the starch films particularly in absence of good lubricant, and (d) susceptibility of starch to rot and degradation by microorganisms. These defects detract from the properties of starch as sizing agent for textile. To eliminate or, at least, to minimize these shortcomings, chemical modification of starch has become a must. Chemical modification of starch with a view of improving its properties has been the subject of several studies (Rutenberg & Solarek, 1984). It can be effected via oxidation (Ali & Kempf, 1986; Daris Kuakpetoon & Ya-Jane Wang, 2006; Kawaljit, Maninder, Narpinder, & Seung-Taik, 2007; Li & Vasanthan, 2003; Muhrbeck, Eliasson, & Salomonsson, 1990; Salomonsson, Anderson, Torneport, & Theander, 1991; Salomonsson & Theander, 1992; Sánchez-Rivera, Garcıa-Suárez, del Valle, Gutierrez- Meraz, & Bello-Pérez, 2005), hydrolysis (Abraham, Krishnaswamy, & Ramakrishna, 1988; Pessa, Suorit, Auto, & Poutanen, 1992; Singh & Ali, 1987), esterification (Agboola, Akingbala, & Oguntimein, 1991; Jarowenko, 1987; Maroza & Tomasik, 1991; Muhrbeck, Svensoon, & Eliasson, 1991; Muhrbeck & Tellier, 1991), etherification (Forrest, 1992; Hellwlg, Bishoff, & Rubo, 1992; Nachergaele, 1989), crosslinking (Chaudhari, Kamath, Bhide, & Kale, 1989; Hahn & hood, 1980; Kulicke, Aggour, & Elsabee, 1990), dextrinization (Jones, Morgan, Robert, & Todd, 1955), and grafting (Chinnaswamy & Hanna, 1991; El-Rafie, Zahran, El- Tahlawy, & Hebeish, 1995; Fanta, Burr, & Doane, 1984; Hebeish, El-Rafie, Higazy, & Ramadan, 1992; Hebeish, Zahran, El- Rafie, & El-Tahlawy, 1996; Hong & Carr, 1992). Such reaction process cause significant changes in the physical as well as chemical structure of starch which, in turn, are reflected in solubility, viscosity performance and resistance to ageing of native starch and solution or pastes prepared thereof. Oxidation of starch is one of the most promising techniques for modification of starch to achieve suitable sizing agent for textile industry. Oxidation of starch could be achieved via chemical oxidation in several mediums such as hypochlorite, chlorates, hydrogen peroxide,. . ..etc (Qin, Rainer, Kari, & Eric, 1998; Ya-Jane & Linfeng, 2003; Zahran, Salah El-Deen, & El-Rafie, 1999) and Air oxidation (Anna & Piotr, 1999).On the industrial production of oxidized starch by chemical means acquire that the law reaction temperature (⩾50 °c) to inhibit cooking during the oxidation process .The chemical oxidation of starch has several disadvantages such as loss of catalytic activity, unstable concentration due to storage, unused residual oxidant at the end of the reaction and difficulty of handling and some of them are environmentally and healthy unsafe. Electrocatalytic oxidation is a new trend for oxidation of starch due to the ease of control of the electrochemical oxidation process, the high catalytic and chemical activity of the Electrogenerated species and

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no storage is required due to the so called Onsite generation of oxidizing species. The chief objective of the present work is to optimize formulations and establish appropriate conditions for preparation of oxidized rice starch with certain properties for particular end use using electro-generated mixed oxidants. To achieve the goal, factors affecting the oxidative degradation of rice starch were studied (1) current density (mAm/cm^2), (2) initial PH of the reaction medium, (3) duration of the oxidation process (min.), (4) effect of the supporting electrolyte concentration (gm/l) and (5) the reaction temperature (°C). The resultant oxidized starches were evaluated via determining the carboxyl content, carbonyl content and apparent viscosity of the cooked samples measured at different rates of shear.

2. Experimental

2.1. Experimental setup

The titanium/rhodium thermally activated modified electrode was prepared via electrodeposition of rhodium metal over titanium pretreated and pre-anodized titanium substrate as described elsewhere (Baraka, Shaarawy, & Hamed, 2002), followed by chemical soaking in 3% sulfuric acid for 60 min. then thermally activated for 3hr at 350 °C in the presence of air flow with a constant rate of 5 L/s. The cell used in the electrocatalytic oxidation of rice starch was made of transparent Perspex in the form of rectangular trough. The anode (Ti/Rh) thermally activated modified electrode was supported in a vertical position midway between, and parallel to the graphite cathodes. The distance between each cathode and the anode was 3 cm, and the electrolyte in each experiment was 1 L. All experiments were carried out with stirring (the liquid inside the cell and between the electrode is agitated). The electrical circuit used in this process is shown diagrammatically in Fig. 1.

2.2. Materials

Rice starch was supplied by the Egyptian starch and glucose Manufacturing Company, Cairo, Egypt. Sodium chloride, sodium sulfate, sodium carbonate, sodium hydroxide, and hydrochloric acid were of reagent grade.

2.3. Electrolysis procedure

Unless otherwise stated, the oxidation process was carried out as follows:

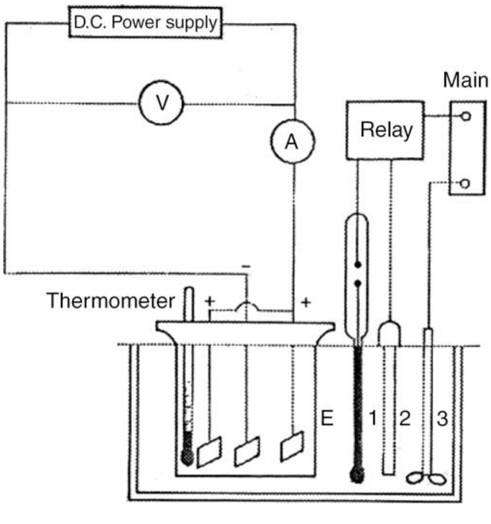

Fig. 1. Electrocatalytic oxidation circuit.

The electrocatalytic oxidation reaction was carried out in the electrolytic cell placed in a thermostatic water bath. A known concentration of supporting electrolyte was added to 1000 ml water and the desired pH was adjusted, 100gm rice starch was added to the reaction medium and the reactants were kept at the desired temperature under continuous stirring. The electric current is switched on at the desired current density. Once the desired electrolysis time is finished the current is switched off and filtration of the slurry is carried out followed by washing with 50% ethyl alcohol solution. After complete filtration oxidized starch is dried at 50–55 °C for 3 h in an oven.

2.4. Analysis

The carboxyl content of starch before and after oxidation was determined according to the reported method (Daul, Rinhardt, & Reid, 1953). The carbonyl content was determined according to the hydroxylamine hydrochloride method (Kalimova & Zabrodina, 1960). The rheological characterization was carried out using coaxial rotary viscometer (Haake RV20) at rates of shear ranging between 258 and 1290 S^{-1}. All rheological properties were evaluated at a temperature of 80 °C. Studies were carried out for the investigation of optimum operation conditions for the oxidation of the rice starch in their aqueous electrolyte solutions, by the electrocatalytic oxidation process using the titanium/rhodium thermally activated modified electrode.

3. Results and discussion

3.1. Tentative mechanisms

Since this investigation is dealing with oxidation of rice starch with mixed oxidants generated by electrocatalytic cell using titanium/rhodium thermally activated modified electrode, it is not out of space to summarize the reaction mechanism involved in this regards. It has been reported (Schmittinger, 1986) that if sodium chloride solution is electrolyzed in an individual cell, Cl_2 formed at the anode disproportionate in the presence of OH$^-$ ions generated at the cathode resulting in the formation of hypochlorite.

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \tag{1}$$

The resultant hypochlorite can be further oxidized to chlorate:

$$2ClO^- + H_2O \rightarrow 2/3ClO_3^- + 4/3Cl^- + 2H^+ + 1/2O_2 + 2 \tag{2}$$

However, this leads to the requirement of nine Faradays per mole of chlorate, whereas only six are needed if a chemical disproportionate route is followed:

$$2ClO^- + 2H_2O \rightarrow 2HClO + 2OH^- \tag{3}$$

$$2HClO + ClO^- \rightarrow ClO_3^- + 2Cl^- + H^+ \tag{4}$$

On the basis of the above reactions, we can see that from reaction (2), the hypochlorite is favored by keeping the chloride concentration as high as possible. In addition to chlorine generated by electrolysis it was suggested that ozone and chlorine dioxide or hydrogen peroxide could be generated (Eqs. (5)–(9)), summarize the important reactions that can occur between chlorine and each subsidiary oxidant under acidic conditions (Son et al., 2004).

$$HOCl + O_3 \rightarrow ClO_2^- \tag{5}$$

$$HOCl + H_2O_2 \rightarrow H_2O + O_2 + Cl^- + H^+ \tag{6}$$

$$HOCl + 2ClO_2 + H_2O \rightarrow 2ClO_3^- + Cl^- + 3H^+ \tag{7}$$

$$HOCl + 2ClO_2^- + H^+ \rightarrow 2ClO_2 + H_2O + Cl^- \tag{8}$$

$$2HOCl + ClO_2^- \rightarrow ClO_3^- + Cl_2 + H_2O \tag{9}$$

Recently (Anodo & Tanaka, 2004; Sudoh, Kitaguchi, & Koide, 1985a; Sudoh, Kitaguchi, & Koide, 1985b) the production of hydrogen peroxide by electrolysis have been examined .Peroxide ion is produced on the cathode of the electrolysis cell by the reduction of oxygen gas (Eqs. (10)–(12)),

$$2OH^- + O_2 \rightarrow 2HOO^- \quad (10)$$

Cathode:

$$2O_2 + 4e^- + H_2O_2 \rightarrow 2HOO^- + 2OH^- \quad (11)$$

Anode:

$$4OH^- \rightarrow 2H_2O_2 + O_2 + 4e^- \quad (12)$$

Taking the above mechanisms in mind rice starch molecules may be attacked by one or more of the active spices formed in the oxidation medium leading to the formation of rice starch containing aldehydic and carboxylic groups. In order to investigate the efficiency of the electrocatalytic oxidation system, a series of experiments have been carried out by using different operating conditions. The results obtained with their appropriate discussion are given below.

3.2. Factors affecting the oxidation process

3.2.1. Effect of initial pH

Figs. 2–4 show the effect of initial PH of the reaction medium on the extent of oxidation of rice starch expressed as apparent viscosity, carbonyl, and carboxyl content. It was observed that the pH of the reaction medium increasing by increasing the duration of the electrolysis which leads to a variation in the mixed oxidants formed in the reaction medium and the mode of interaction of the formed active species with each other and thereby its effect on starch macromolecules.

It is evident from the data (Figs. 2–4) that the value of the apparent viscosity indicates that (a) decreasing the initial pH of the reaction medium is accompanied by a significant decrease in the apparent viscosity, (b) this decrement in the pH also leads to the formation of oxidized starch having higher carbonyl content value compared with those prepared in neutral or slightly alkaline medium and (c) the reverse holds true, with respect of the carboxyl content. Taking the above results in mind it could be concluded that the electrocatalytic oxidation is preferred at pH ⩽3.

3.2.2. Effect of current density

Figs. 5–7 show the effect of current density, used during the electrocatalytic oxidation of rice starch, on the apparent viscosity,

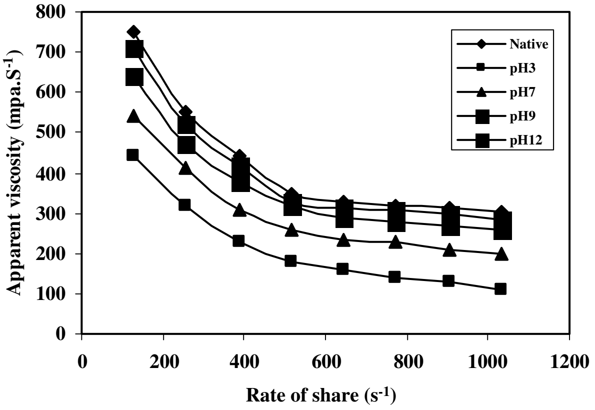

Fig. 2. Effect of pH of the reaction medium on the apparent viscosity measured at different rate of shear drying electrocatalytic oxidation of rice starch.

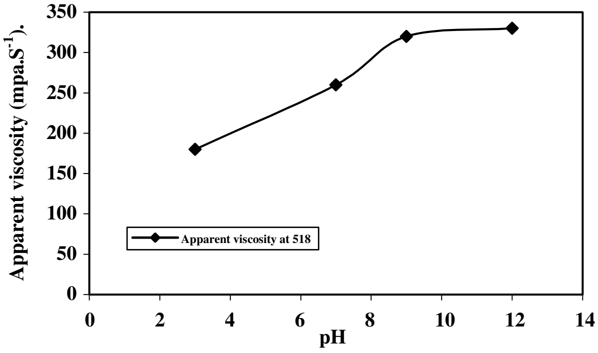

Fig. 3. Effect of pH of the reaction medium on the apparent viscosity measured rate of shear 518 (S^{-1}).

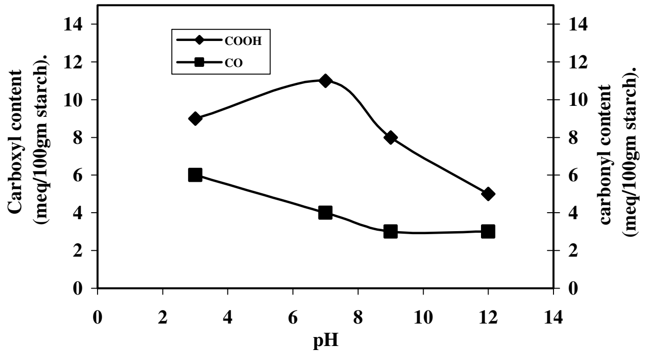

Fig. 4. Effect of pH of the reaction medium on the carboxyl and carbonyl content.

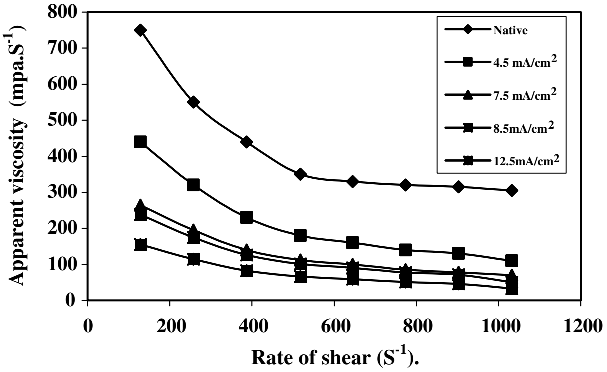

Fig. 5. Effect of applied current density on the apparent viscosity at different rate of shear.

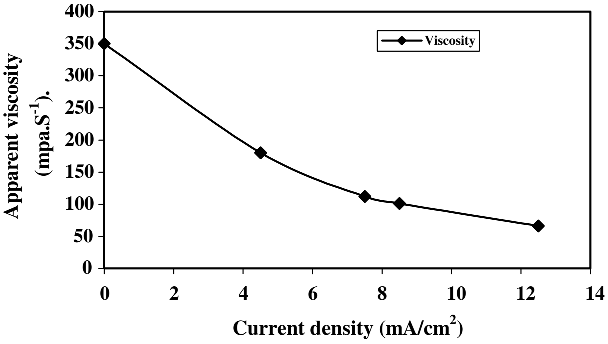

Fig. 6. Effect of applied current density on the apparent viscosity at rate of shear 518 (S^{-1}).

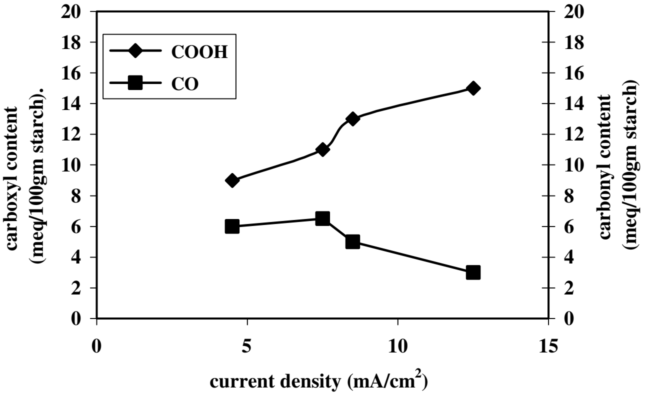

Fig. 7. Effect of applied current density on the carboxyl content and carbonyl content.

carbonyl and carbonyl content of resultant oxidized starch. The data from Figs. 5–7 reflected the effect of current density on the amount and the type of the active species liberated in the reaction medium. These mixed oxidant formed in the reaction medium oxidize starch molecules to form reducing aldehydic and/or ketonic groups (carbonyl group), further oxidation leads to formation of carboxyl groups. These oxidation reactions may be accompanied by chain scission of starch molecules.

It is clear from the data (Figs. 5 and 6) that (a) regardless the current density used the apparent viscosity decreases by increasing the rate of shear then levels off, (b) increasing the current density is accompanied by a significant decrease in the apparent viscosity and (c) increasing the extent of oxidation leads to stability in the apparent viscosity by varying the rate of shear. Fig. 7 show the reliability of the carboxyl and carbonyl content of the resultant oxidized starch on the current density used during the electrocatalytic oxidation process. It is clear from the data (Fig. 7) that the carbonyl content increase by increasing the current density up to 6mAm/cm^2, further increase above this limit is accompanied by a significant decrease in the carbonyl content, this behavior supports the assumption that starch oxidation occurs in two steps. The first leads to formation of reducing aldehydic and or ketonic groups (carbonyl group) while the second leads to further formation of carboxyl groups. This is clear from the data (Fig. 7) that the carboxyl content increases by increasing the current density. The enhancement in the values of carboxyl and carbonyl contents by increasing the current density is indicative of the increase in the mixed oxidants formed in the reaction medium.

3.2.3. Effect of reaction temperature

To investigate the effect of reaction temperature, the electrocatalytic oxidation reaction was conducted at 20, 30, and 45 °C at the listed operating conditions. Figs. 8–10 show the rheological and chemical properties of the resultant oxidized starch prepared at different temperatures. The data indicates that the oxidation reaction is favored at low temperature. Raising the reaction temperature is accompanied by variation in carboxyl content in the order 30 °C > 45 °C > 20 °C, on the other hand, with respect of the carbonyl content different situation is encountered where the order is 45 °C > 20 °C > 30 °C. It was found that the value of the apparent viscosity, carboxyl and carbonyl content of the oxidized starch prepared at 30 °C represents the proper values for starch used as sizing agent.

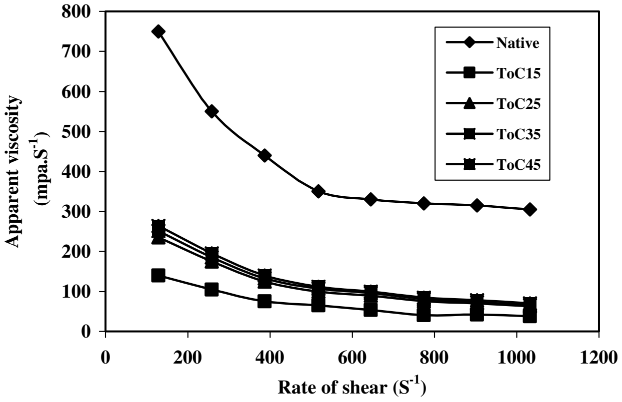

Fig. 8. Effect of reaction temperature on the apparent viscosity at different rate of shear.

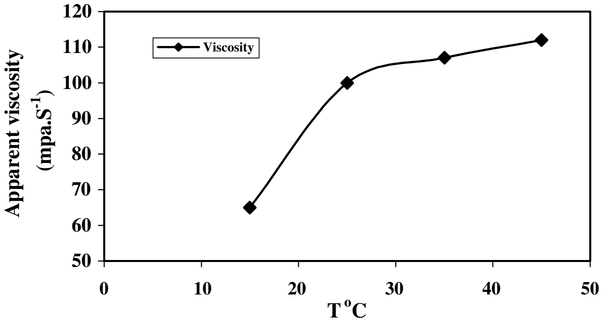

Fig. 9. Effect of the reaction temperature on the apparent viscosity at rate of shear 518 (S^{-1}).

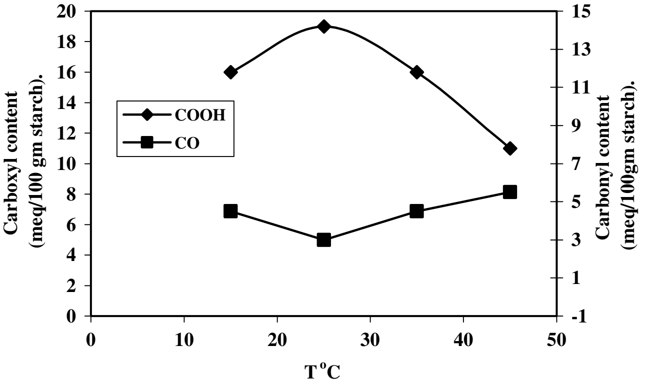

Fig. 10. Effect of reaction temperature on carboxyl content and carbonyl content.

3.2.4. Effect of duration of the reaction

Figs. 11–13 show the effect of the time of the electrolysis at the listed operating conditions on the extent of the oxidation. The apparent viscosity of the oxidized starch before and after oxidation under various reaction durations 1–2 h (Figs. 11 and 12) indicate that the electrocatalytic oxidation is very efficient that reasonable viscosity is obtained after 1 h. Further increase in the reaction duration is accompanied by a marginal decrease in the apparent viscosity. On the other hand, the chemical properties of the resultant oxidized starch, expressed as carbonyl and carboxyl content, significantly increase by increasing the duration of the reaction within the range studied.

3.2.5. Effect of supporting electrolyte concentration

Figs. 14–16 show the effect of supporting electrolyte concentration on the extent of the oxidation of rice starch. The results reveals that (a) the apparent viscosity of the resultant oxidized starch significantly decreases by increasing the concentrations of supporting

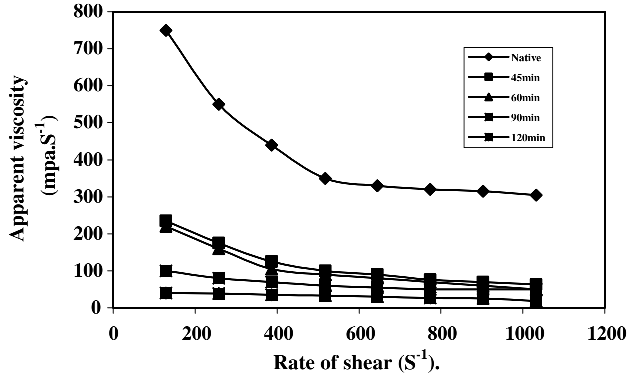

Fig. 11. Effect of electrolysis time on the apparent viscosity at different rate of shear.

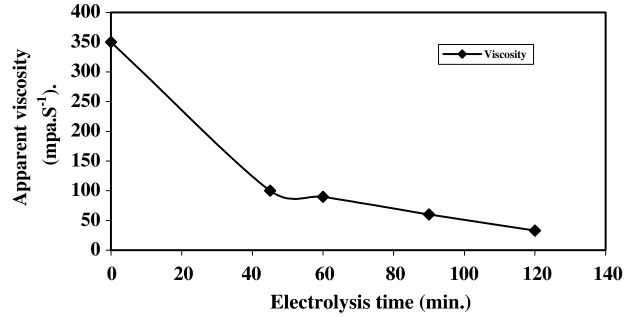

Fig. 12. Effect of electrolysis time on apparent viscosity at rate of shear 518 (S^{-1}).

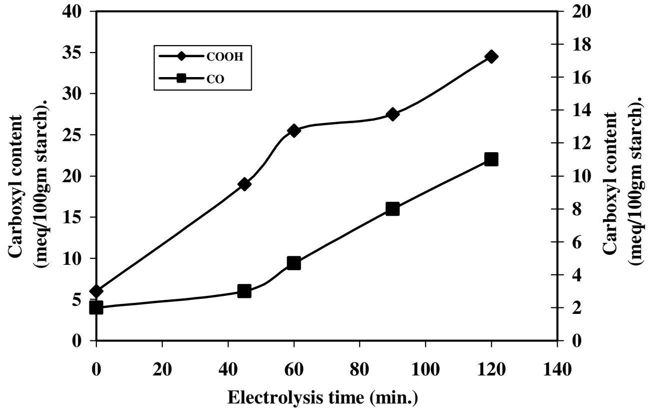

Fig. 13. Effect of electrolysis time on both carboxyl and carbonyl content.

electrolyte, (b) the carbonyl content increase by increasing the concentration of supporting electrolyte within the rang study. On the other hand, the carboxyl content increase by increasing the concentration of supporting electrolyte up to 7.5 g/l, further increase above this limit this accompanied by significant decrease in carboxyl content. The decrement in the carboxyl content at higher supporting electrolyte concentration could be ascribed to formation of highly oxidized starches with short chains, which are lost during filtration of the resultant oxidized starch.

4. Conclusion

Rice starch was successfully oxidized via Electrogenerated mixed oxidant resulted by the electrolysis of saline solution using the titanium/rhodium thermally activated modified electrode. The obtained oxidized starch was evaluated via determining the carbonyl and carboxyl contents as well as the apparent viscosity at different rates of shears. Results obtained indicate that the oxidized starch suitable to be used as a sizing agent for textile fibers could be obtained at optimum operating conditions of applied current density 7.5 mA/cm^2, pH 3, solution temperature 25 °C, time of electrolysis 60 min. and 7.5 g/l of sodium chloride as supporting electrolyte.

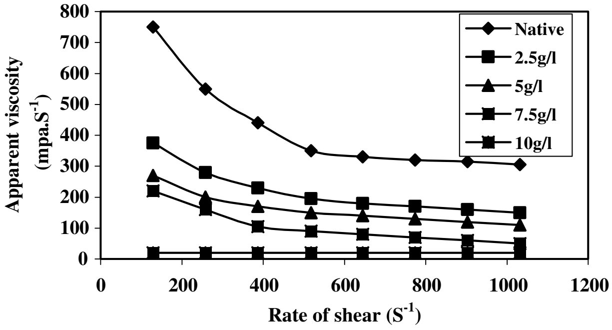

Fig. 14. Effect of supporting electrolyte concentration on the apparent viscosity at different rate of shear.

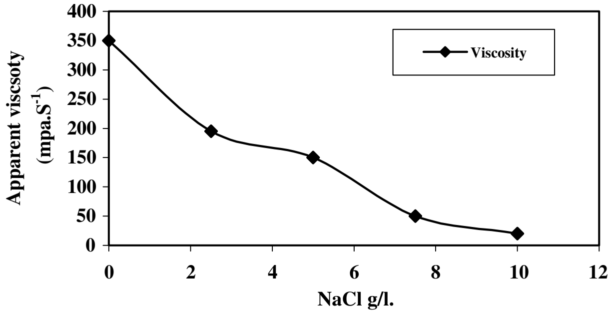

Fig. 15. Effect of supporting electrolyte concentration on the apparent viscosity at rate of shear 518^{-1}.

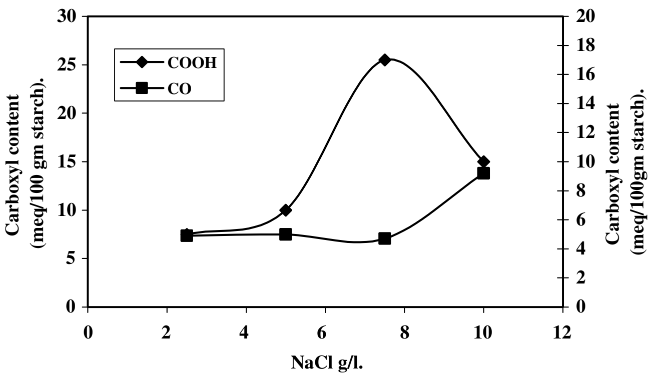

Fig. 16. Effect of supporting electrolyte concentration on both carboxyl and carbonyl content.

References

Abraham, T. E., Krishnaswamy, C., & Ramakrishna, S. V. (1988). *Starch/Starke, 40*, 387–392.

Agboola, S. O., Akingbala, J. O., & Oguntimein, G. B. (1991). *Starch/Starke, 43*, 13–15.

Ali, S. Z., & Kempf, W. (1986). *Starch/Starke, 38*, 83–86.

Anna, Bala-Piasek, & Piotr, Tomasik (1999). *Carbohydrate polymers, 38*, 41–45.

Anodo, Y., & Tanaka, T. (2004). Enhanced disinfection of mechanically mixed oxidants with free chlorine. *International Journal of Hydrogen Energy, 29*, 1349–1354.

Baraka, A. M., Shaarawy, H. H., & Hamed, H. A. (2002). Electrodeposition of rhodium metal on titanium substrates. *Anti-Corrosion methods and materials, 49*(4).

Chaudhari, M. R., Kamath, N. D., Bhide, S. V., & Kale, N. R. (1989). *Starch/Starke, 41*, 415–416.

Chinnaswamy, R., & Hanna, M. A. (1991). *Starch/Starke, 43*, 396–402.

Daris Kuakpetoon & Ya-Jane Wang (2006). Structural characteristics and physicochemical properties of oxidized corn starches varying in amylose content. *Carbohydrate Research, 341*, 1896–1915.

Daul, G. R., Rinhardt & Reid, J. D. (1953). *Textile Research Journal, 23*, 719.

El-Rafie, M. H., Zahran, M. K., El- Tahlawy, Kh. F., & Hebeish, A. (1995). *Polymer & Polymer Stability, 47*, 73–85.

Fanta, G. F., Burr, R. C., & Doane, W. M. (1984). *Journal of Applied Polymer Science, 29*, 4449–4453.

Forrest, B. (1992). *Starch/Starke, 44*, 179–183.

Hahn, D. E., & hood, L. F. (1980). *Journal of Food Science, 45*, 518–522.

Hebeish, A., El-Rafie, M. H., Higazy, A., & Ramadan, M. A. (1992). *Starch/Starke, 44*, 101–107.

Hebeish, A. M. H., Zahran, M. K., El- Rafie, M. H., & El-Tahlawy, Kh. F. (1996). *Polymer & Polymer Composites, 4*, 129–141.

Hellwlg, G., Bishoff, D., & Rubo, A. (1992). *Starch/Starke, 44*, 69–74.

Hong, D. H., & Carr, M. E. (1992). *Starch/Starke, 44*, 268–271.

Jarowenko, W. (1987). In O. B. Wurzburg (Ed.), *Modified starches: Properties and uses* (pp. 55–77). Fla: CRC Boca Raton.

Jones, E. I., Morgan, L. B., Robert, J. F. L., & Todd (1955). *Chemical Abstracts, 49*, 2748.

Kalimova, V. A., & Zabrodina, K. S. (1960). *Zhakh, 15*, 726.

Kawaljit, Singh Sandhu, Maninder, Kaur, Narpinder, Singh, & Seung-Taik, Lim (2007). A comparison of native and oxidized normal and waxy corn starches: Physicochemical, thermal, morphological and pasting properties. *Food Science and Technology*. doi:10.1016/j.lwt.2007.07.012.

Kulicke, W. M., Aggour, Y. A., & Elsabee, M. Z. (1990). *Starch/Starke, 42*, 134–141.

Li, J. H., & Vasanthan, T. (2003). Hypochlorite oxidation of field pea starch and its suitability for noodle making using an extrusion cooker. *Food Research International, 36*, 381–386.

Maroza, K., & Tomasik, P. (1991). *Starch/Starke, 43*, 66–69.

Muhrbeck, P., Eliasson, A.-C., & Salomonsson, B. A. C. (1990). *Starch/Starke, 42*, 418–420.

Muhrbeck, P., Svensoon, E., & Eliasson, A. C. (1991). *Starch/Starke, 43*, 466–468.

Muhrbeck, P., & Tellier, C. (1991). *Starch/Starke, 43*, 25.

Nachergaele, W. (1989). *Starch/Starke, 41*, 27–31.

Pessa, E., Suorit, T., Auto, K., & Poutanen, K. (1992). *Starch/Starke, 44*, 64–69.

Qin, Zhu, Rainer, Sjohilm, Kari, Nurmi, & Eric, Bertoft (1998). *Carbohydrate Research, 309*, 213–218.

Rutenberg, M. W., & Solarek, D. (1984). Starch derivatives: Production and uses. In R. L. Whistler, J. N. BeMiller, & E. F. Paschall (Eds.), *Starch, chemistry and technology* (pp. 311–388). London: Academic Press, inc..

Salomonsson, B. A. C., Anderson, R., Torneport, I. J., & Theander, O. (1991). *Carbohydrate Research, 217*, 221–225.

Salomonsson, B. A. C., & Theander, O. (1992). *Starch/Strake, 44*, 260–263.

Sánchez-Rivera, M. M., García-Suárez, F. J. L., del Valle, Velázquez M., Gutierrez-Meraz, F., & Bello-Pérez, L. A. (2005). Partial characterization of banana starches oxidized by different levels of sodium hypochlorite. *Carbohydrate Polymers, 62*, 50–56.

Schmittinger, P. (1986). Chlorine. *Ullmanns Encyclopedia* (Vol. 6A, pp. 399). Weinheim: VCH.

Singh, V., & Ali, S. Z. (1987). *Starch/Starke, 39*, 402–405.

Son, H., Cho, M., Kim, J., Oh, B., Chung, H., & Yoon, J. (2004). Enhanced disinfection of mechanically mixed oxidants with free chlorine. *International Journal of Hydrogen Energy, 29*, 1349–1354.

Sudoh, M., Kitaguchi, H., & Koide, K. (1985a). Polarization characteristics of packed bed electrode reactor for electroreduction of oxygen to hydrogen peroxide. *Journal of Chemical Engineering of Japan, 18*(4), 364–371.

Sudoh, M., Kitaguchi, H., & Koide, K. (1985b). Electrochemical production of hydrogen peroxide by reduction of oxygen. *Journal of Chemical Engineering of Japan, 18*(5), 409–414.

Ya-Jane, Wang, & Linfeng, Wang (2003). *Carbohydrate polymers, 52*, 207–217.

Zahran, K., Salah El-Deen, B. A., & El-Rafie, M. H. (1999). *Journal of the Textile Association*, 237–245. chem. Abstr. 49, 2748 (1955).