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Contributed Paper

## Applications of Oxidized Chitosan for Scale Prevention in Sugar Evaporators

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### ABSTRACT

This study explores the potential use of oxidized chitosan (O.C) as an antiscalant for calcium oxalate (CaOx) and calcium sulfate (CaSO<sub>4</sub>), which are the main components of scales during sugar processing. Chitosan was selectively oxidized by NaClO/NaBr/TEMPO at pH 10.8 and 30 °C following the procedure by Yoo *et al.* [1]. The products have oxidation degrees ranging from 31 % to 77 % (by conductivity titration). The antiscaling performance of the O.C. was observed in comparison with a commercial antiscalant, Acumer1050, at the same antiscalant concentration (10 ppm) for two types of scales: CaOx and CaSO<sub>4</sub>. For CaOx scales, the O.C with 77 % degree of oxidation (O.C-77) shows the highest inhibition (72 %), whereas Acumer1050 and O.C-31 exhibit similar percent inhibition, 46 % and 36 %, respectively. However, in the presence of 13 % sugar (w/v), O.C-77 experiences a dramatic drop in performance to 30 % inhibition, but Acumer1050 only slightly decreases to 40 %. For CaSO<sub>4</sub> scales, the results also show that the higher the oxidation degree, the better the antiscaling performance, with O.C-77 showing the highest percent inhibition (80 %) in aqueous solution, whereas Acumer1050 shows the best performance with 90 % inhibition. In 15 % sugar (w/v), the performance slightly drops to 75 % for Acumer1050 and 62 % for O.C-77.

For CaOx, sugar strongly affects antiscaling performance of the high molecular weight O.C (O.C HMW), whereas the low molecular weight O.C (O.C LMW) shows consistent performance with increasing sugar concentration. For CaSO<sub>4</sub>, O.C HMW exhibits better performance, although for both, antiscaling performance is reduced with increasing sugar concentration. The different antiscaling performance may come from the different antiscaling mechanisms involved for CaOx and CaSO<sub>4</sub>. The results from SEM and XRD suggest that O.C binds with calcium ions to form a metal ion-polymer complex to prevent CaOx scales. On the other hand, O.C prefers to adsorb onto nuclei to prevent CaSO<sub>4</sub> crystal growth. The results show that O.C can be a green alternative to the commercial antiscalant from a petroleum-based product.

**Keywords:** oxidized chitosan, TEMPO, oxidation, calcium oxalate, calcium sulfate, bio-based antiscalants, sugar processing

## 1. INTRODUCTION

In sugar processing, sugar juice moves through different stages of an evaporation system with a decreasing temperature from 115 °C to 57 °C to increase the sucrose concentration. The clarified juice starts from around 96 °C with a sucrose concentration of 12 % (w/w) and is brought into the evaporation system to achieve a sucrose concentration of about 65 % (w/w) at around 57 °C before passing to a crystallization step [2]. During the evaporation stage, water is removed, causing the ion concentrations to exceed their solubility limits [3]. As a result, scales deposit onto the surface of the heat transfer equipment causing processing problems, such as a decrease of heat transfer, corroding facilities, and growth of microorganism. Thus, it is necessary to shut down the system for cleaning and removing the scales, which increases the operation costs [4]. Rackemann *et al.* claimed that the estimated cost for cleaning scale in a typical Australian factory was about \$400,000 per season, including the cost of labor resulting from the extended season [5].

Major components of the scales consist of calcium oxalate mono and dihydrate (CaOx), calcium sulfate dihydrate (CaSO<sub>4</sub>), hydroxyapatite, amorphous silica, and organic matter [6]. In order to prevent scale formation, several methods are used. One of the most commonly used methods is to add chemical additives, known as antiscalants or scale inhibitors, because the scale inhibition is effective even at a low concentration of inhibitors [3, 7].

Most scale inhibitors adsorb on the positive-charged surface of crystals and block crystal growth. As a result, they inhibit precipitation as well as modify crystal morphology, crystal dimensions, and adhesive capability between crystals and surfaces [3, 8-10]. Commercially available antiscalants

can be classified into three major categories including phosphates, phosphonates, and polycarboxylates. These commercial polymers have their own disadvantages. Phosphorus compounds can be discharged into wastewater, resulting in environmental pollution and ecological imbalance [11-12]. At high temperature in sugar evaporators, polyphosphates with low stability hydrolyze to orthophosphates and form tricalcium phosphate precipitates [13-14]. Another main disadvantage is the toxicity of synthetic polymers that are inevitably present in the solution. In addition, when polyacrylates are used, an anti-foam agent is needed to control the foam which is produced as a consequence of the presence of protein, betaine, and saponins in the sugar solution [15]. Using bio-based polymers as antiscalants can help overcome these disadvantages.

This study aims to apply chitosan, which is a bio-based polymer as an antiscaling agent. In order to improve its functionality, chitosan is oxidized by the TEMPO/NaOCl/NaBr oxidant, following the procedures by Yoo *et al.* [1]. The oxidized chitosan is characterized and used to examine its antiscaling performance in comparison with a commercial antiscaling agent, Acumer1050. The antiscaling performance is investigated with calcium oxalate (CaOx) and calcium sulfate (CaSO<sub>4</sub>), which are two major components of the scales in sugar processing. CaSO<sub>4</sub> forms at high temperature and has a greater affinity for the tube wall in the first effects of sugar evaporators with low sucrose concentration [5-6]. CaOx is observed to form at lower temperature and suspend in sugar solutions in the later effects with high sucrose concentration [2, 5]. Hence, in order to simulate actual conditions of scale formation in sugar evaporators, an experiment with CaOx scale formation was designed for

homogeneous conditions at low temperature (50 °C) and a high sucrose concentration of 65 % (w/w). The experiment with CaSO<sub>4</sub> formation was designed for heterogeneous conditions at high temperature with a coil heater at a low sucrose concentration of 15 % (w/w). Several values of sucrose concentrations are also chosen to observe the effects of sucrose concentration on antiscaling performance of the oxidized chitosan materials. The morphologies of the scales with and without using antiscalants are examined by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD) to observe the effects of oxidized chitosan on the morphology of CaOx and CaSO<sub>4</sub> scales.

## 2. MATERIALS AND METHODS

### 2.1 Materials

Chitosan (MW =  $2.3248 \times 10^5$  Dal, deacetylation degree average = 82.6 %), (2, 2, 6, 6-Tetramethyl-piperidin-1-yl) oxyl (TEMPO), cellulose dialysis tubing (MWCO = 14 kDal) D9652-100FT, and benzolated cellulose dialysis tubing (MWCO = 2 kDal) D2272-5FT were purchased from Sigma-Aldrich (St.Louis, MO, USA). Sodium hypochlorite (NaOCl) was purchased from Carlo Erba (Normandy, France). Commercial Acumer1050 solution (50 wt%, MW = 2000 - 3000) was supplied by Rohm and Haas (Bangkok, Thailand). Calcium chloride (CaCl<sub>2</sub>•2H<sub>2</sub>O), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), sodium oxalate (Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), and sodium bromide (NaBr) were of analytical grade.

### 2.2 Synthesis of Oxidized Chitosan

Synthesis of different oxidized chitosans followed the procedures by Yoo *et al.* [1]. A suspension of 2.5 % chitosan (by weight) in 20 g water was prepared. NaOCl (13.67 mmol/g of chitosan), NaBr (3.36 mmol/g

of chitosan), and TEMPO (0.037 mmol/g of chitosan) were mixed together to generate 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion, a form of TEMPO, that directly oxidizes the hydroxyl groups in chitosan [16]. The reaction was carried out at  $30 \pm 0.1$  °C. NaOCl was added into the solution to maintain a pH of 10.8. The reaction was stopped by adding ethanol and neutralized by HCl when the pH remained unchanged. Subsequently, the mixture was dialyzed with two types of dialysis bags to purify the materials and separate oxidized chitosan into two fractions, with the high molecular weight (HMW) fraction having a molecular weight over 14 kDal, and the low molecular weight (LMW) fraction having a range from 2 kDal to 14 kDal. Finally, the products were dried at 50 °C in a vacuum oven for 24 hours.

### 2.3 Characterization of Oxidized Chitosan

#### 2.3.1 Fourier transform infrared spectroscopy (FTIR)

The oxidized chitosan were characterized by using Fourier Transform Infrared Spectroscopy (Thermo Nicolet 6700, USA). Samples were prepared at room temperature using the KBr technique. The spectra were recorded from 680 - 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>, with 64 scans.

#### 2.3.2 Conductivity titration

A conductivity titration was conducted for both native chitosan and oxidized chitosan according to da Silva *et al.* [17] with some modification. The samples (5 mg) were suspended in an excess amount of 0.01 M HCl solution (15 mL). The suspension was titrated with 0.018 M NaOH. The carboxyl content (oxidation degree) was determined from the difference of the amount of NaOH used for titration for oxidized chitosan and native chitosan.

### 2.3.3 Molecular weight determination

After using the dialysis bags to separate oxidized chitosan products into two fractions, the high molecular weight (HMW) fraction, and the low molecular weight (LMW) fraction, the average molecular weight of oxidized chitosan was determined by Gel Permeation Chromatography (GPC). A sample (2 mg/mL) was dissolved in eluent 0.5 M sodium bicarbonate buffer (pH 11) and filtered with nylon-66 membrane (pore size 0.45  $\mu\text{m}$ ) before injection. The sample was injected into an ultrahydrogel linear column connected with a guar column, with a rate of 0.6 mL/min at 30  $^{\circ}\text{C}$ . A pullulan polysaccharide with MW 5,900 - 708,000, was used as the polymer standard.

## 2.4 Antiscalant Performance

The effectiveness of the antiscalant was evaluated by the amount of scale formed in comparison with the amount of scale in the blank sample with no additives. The antiscalant performance was reported as percent inhibition (%), which was determined from Equation (1).

$$\text{Percent Inhibition (\%)} = \frac{\text{Wt of Scale Blank Sample} - \text{Wt of Scale with Antiscalant}}{\text{Wt of Scale in Blank Sample}} \times 100 \% \quad (1)$$

### 2.4.1 Calcium oxalate (CaOx)

A series of tests with CaOx scales were designed with 10 ppm of oxidized chitosan and Acumer1050 in a supersaturated solution of 0.0061 M  $\text{Ca}^{2+}$  and 0.00149 M  $\text{C}_2\text{O}_4^{2-}$  to simulate CaOx formation based on Doherty *et al.* [18]. The mixture was equilibrated at 50  $^{\circ}\text{C}$  for one hour, after which the precipitates were collected by a Whatman No. 42 filter paper. The precipitates were dried at 50  $^{\circ}\text{C}$  in a vacuum oven overnight, and the dry samples were weighed to determine percent inhibition.

The formation of CaOx was observed in various sugar concentrations (0 %, 13 %, 30 %, and 65 %).

### 2.4.2 Calcium sulfate (CaSO<sub>4</sub>)

A supersaturated solution of 0.025 M  $\text{Ca}^{2+}$  and 0.025 M  $\text{SO}_4^{2-}$  was prepared by rapidly mixing  $\text{CaCl}_2$  and  $\text{Na}_2\text{SO}_4$  solutions (with and without 10 ppm of oxidized chitosan and Acumer1050) according to the previous study [19]. The solution was heated by a coil heater for six minutes.  $\text{CaSO}_4$  scales, both from the coil heater and the precipitates suspended in the solution, were collected by a Whatman No. 42 filter paper for further observations. The formation of  $\text{CaSO}_4$  was observed in various sugar concentrations (0 %, 15 %, and 30 %).

## 2.5 Morphology Observation

The collected precipitates of CaOx and  $\text{CaSO}_4$  were examined by Scanning Electron Microscopy (JEOL JSM-7800F), operating at an accelerating voltage of 3 kV. The samples of CaOx and  $\text{CaSO}_4$  were also analyzed by X-ray powder diffraction (XRD), D8-advanced Bruker powder diffractometer operating with  $\text{Cu K}\alpha$  radiation, working at 30 mA and 40 kV. For the CaOx samples, the  $2\theta$  ranged from 10  $^{\circ}$  to 60  $^{\circ}$  at a scan rate of 1.0 deg  $2\theta$ /min and a step size of 0.02 deg  $2\theta$ . For the  $\text{CaSO}_4$  samples, the  $2\theta$  ranged from 10  $^{\circ}$  to 50  $^{\circ}$  at a scan rate of 0.1 sec/step and a step size of 0.02 degree/step.

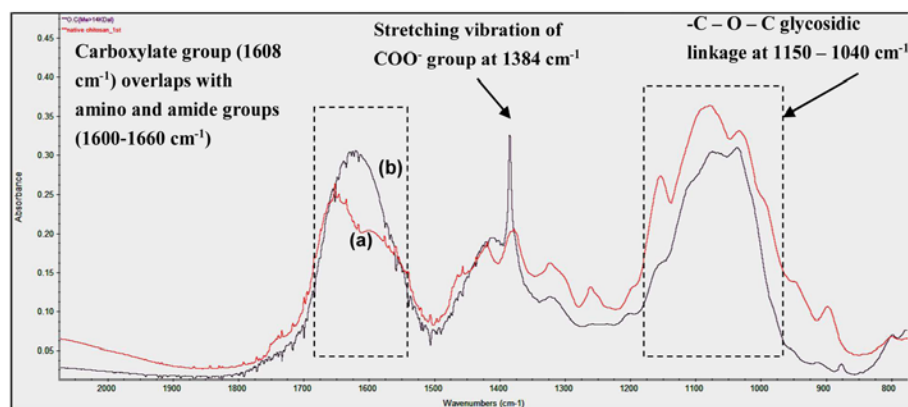
## 3. RESULTS AND DISCUSSION

### 3.1 Synthesis of Oxidized Chitosan

Figure 1 shows FTIR spectra of oxidized chitosan (O.C), including the presence of carboxylate groups at 1608  $\text{cm}^{-1}$  [17] and 1384  $\text{cm}^{-1}$  [20]. The peak at 1608  $\text{cm}^{-1}$  of carboxylate groups overlaps with the peaks of amino groups in the range of

1600 - 1660  $\text{cm}^{-1}$ . There is a reduction of the absorbance of -C-O-C in the glycosidic linkage in the range of 1150 - 1040  $\text{cm}^{-1}$  [21], compared to native chitosan. This is a sign of depolymerization that occurs during the oxidation reaction. Different oxidized chitosan products are shown in Table 1. The oxidized chitosan is reported as the high molecular weight (HMW) and the low molecular weight (LMW) fractions, based on the MWCO from the dialysis bags. The HMW fraction of oxidized chitosan was taken to measure the average molecular weight with GPC. The result shows that the

average molecular weight of the fraction was 3.6 kDal, which is not consistent with the result from MWCO of 14 kDal. The reason could be that a polysaccharide was used as a standard while the oxidized chitosan is a modified polysaccharide with -COOH functional groups. Hence, the reported molecular weight of oxidized chitosan is only based on the MWCO from the dialysis bags with the high molecular weight (HMW) fraction having a molecular weight over 14 kDal [14k, 232k], and the low molecular weight (LMW) fraction having a range from 2 kDal to 14 kDal [2k, 14k].



**Figure 1.** FTIR spectrum of (a) native chitosan and (b) oxidized chitosan.

**Table 1.** Summary information of different oxidized chitosans.

Abbreviation	Molecular weight range (Dal)	Oxidation degree (OD) by conductivity titration (%)
O.C-31 (HMW)	[14k, 232k]	31
O.C-77 (HMW)	[14k, 232k]	77
O.C-58 (HMW)	[14k, 232k]	58
O.C-29 (LMW)	[2k, 14k]	29

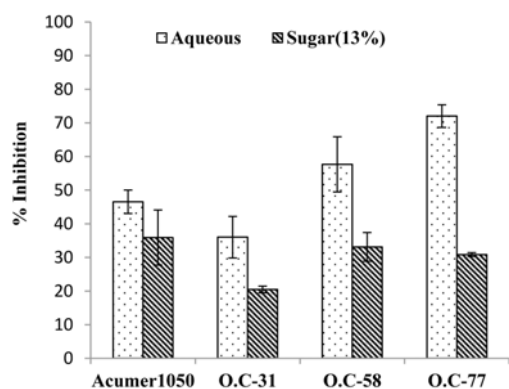
### 3.2 Antiscaling Performance of Oxidized Chitosan

#### 3.2.1 Calcium oxalate (CaOx)

Figure 2 shows that O.C-77 has the highest inhibition percentage (above 70 %), and it performs better than Acumer1050 at the same concentration. It also shows that the higher the oxidation degree of oxidized chitosan, the better the antiscaling

performance because the ability of the carboxylate residue to bind with calcium ions or to adsorb onto nuclei strongly depends on the charge density on the polymer chains [3, 8-10]. In the presence of 13 % sugar (w/w), O.C-77 and O.C-58 experience a dramatic decrease in antiscaling performance while Acumer1050 performance only slightly decreases.



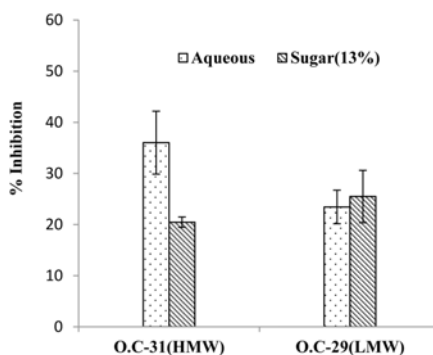


**Figure 2.** Antiscaling performance of oxidized chitosan compared to Acumer1050 with CaOx scales, in aqueous solution and in sugar solution.

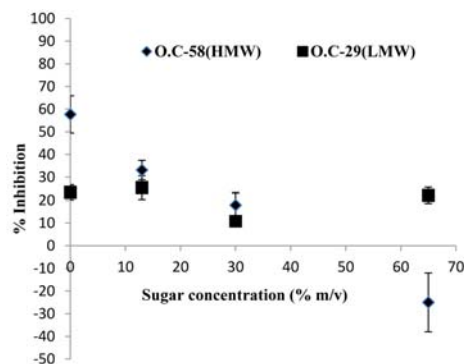
Figure 3 compares the performance of oxidized chitosan of high molecular weight (O.C-31 HMW) and low molecular weight (O.C-29 LMW). In aqueous solution, the result shows that O.C-31 HMW has significantly higher percent inhibition than O.C-29 LMW, even though they have a similar degree of oxidation. However, the performance of O.C-29 LMW is more consistent in the solution with and without sugar. It is suggested that in aqueous solution, the oxidation degree plays a key role in improving the performance of chitosan, but in the presence of sugar, LMW oxidized chitosan seems to perform consistently across different sugar concentrations.

Figure 4 shows that the performance of O.C-58 HMW dramatically decreases with increasing sugar concentration, whereas the percent inhibition of O.C-29 LMW chitosan remains consistent, about 25%. The reason for the decline in antiscalant performance in the sugar solution is due to an increase in viscosity, resulting in reduced mobility of O.C in sugar solutions [22]. In addition, it has been reported that calcium oxalate dihydrate (COD) occurs at a high sugar concentration, and at 40 % sugar concentration, COD become the

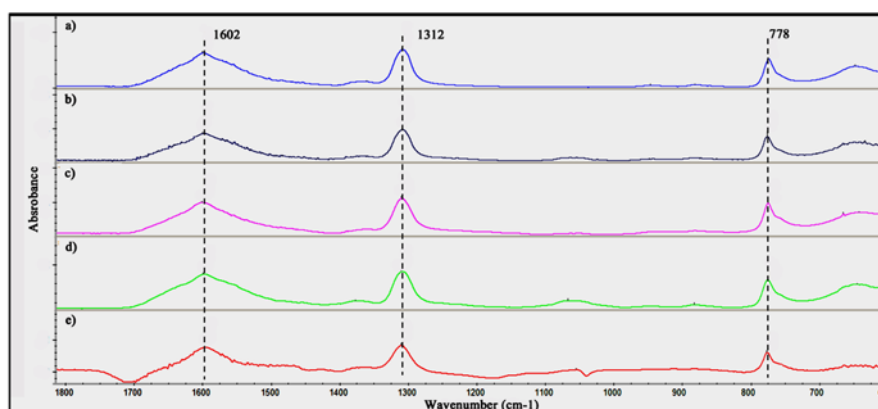
main component [23]. Previous work also shows that a polyelectrolyte does not absorb onto COD as well as onto calcium oxalate monohydrate (COM). Thus, the less the adsorption of O.C onto COD, the lower the percent inhibition [24]. In a high concentration of sugar, HMW oxidized chitosan may act as a coagulant to induce aggregation, resulting in a negative percentage of inhibition [18]. The FTIR results in Figure 5 show that the components of CaOx scale include both COM and COD, as the presence of a strong peak of antisymmetric carbonyl stretching at  $1619\text{ cm}^{-1}$ , a symmetric carbonyl stretching band at  $1317\text{ cm}^{-1}$ , and an absorption band at  $777\text{ cm}^{-1}$  [25, 26].



**Figure 3.** Performance of oxidized chitosan against CaOx scales, in aqueous solution and in sugar solution, high molecular weight (HMW) vs. low molecular weight (LMW), with comparable degrees of oxidation.



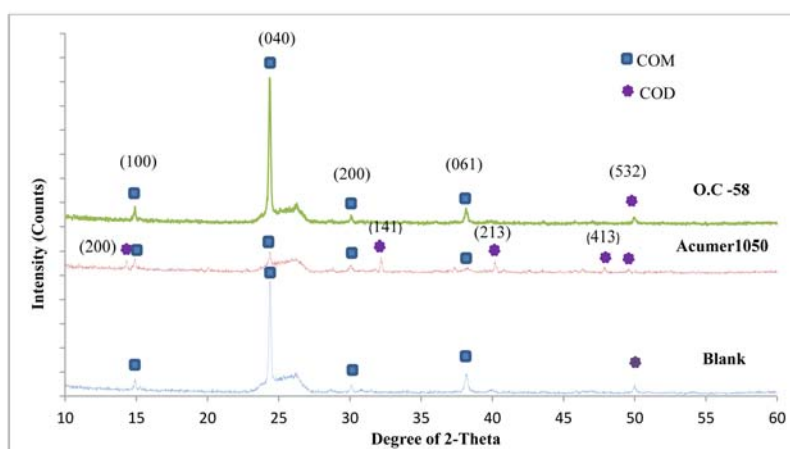
**Figure 4.** Effect of sugar concentration on antiscaling performance of oxidized chitosan with CaOx scale.



**Figure 5.** FTIR of CaOx scales collected from 13% sugar solution (w/w) (a) blank sample, (b) O.C-58 (HMW), (c) O.C-31 (HMW), (d) O.C-29 (LMW), (e) Acumer1050.

XRD powder patterns of blank samples and in the presence of O.C-58 are not different, with principal diffraction peaks of COM appearing at  $2\theta$  of 14.85, 24.25, 29.99, and 38 of COD at  $2\theta$  of 49.63

(Figure 6). An XRD pattern of CaOx in the presence of Acumer1050 displays more peaks for COD at a  $2\theta$  of 14.23, 32.11, 40.13, and 47.79 as a result of a morphology change in the presence of Acumer1050.



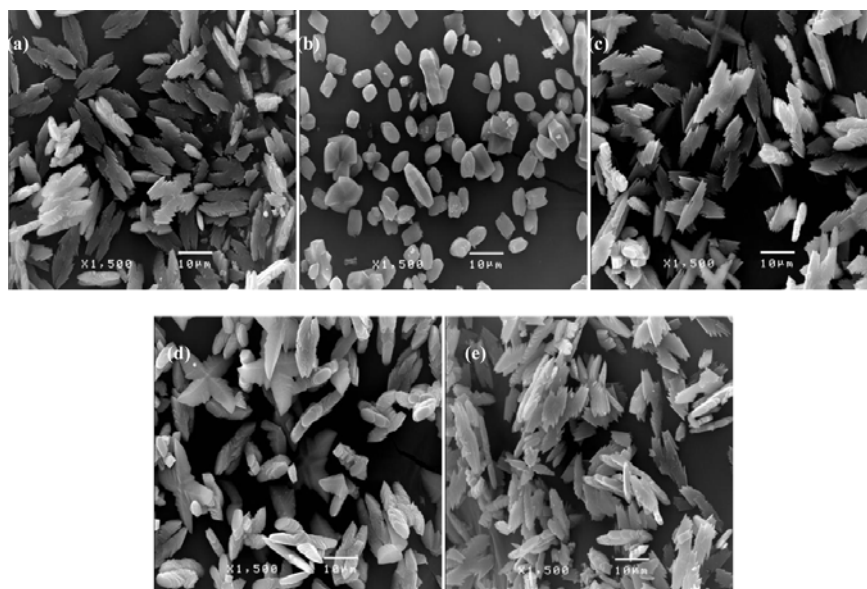
**Figure 6.** XRD patterns of CaOx scales collected from 13% sugar solution (w/w) in the blank sample, with O.C-58 (HMW), and with Acumer1050.

Figures 7a-e show scanning electron micrographs of CaOx scales, collected from the antiscaling experiments. In moderate sugar concentration, CaOx crystals in the presence of oxidized chitosan are not much different from the blank sample, with a typical morphology of monoclinic twinning COM crystals seen in other studies [25, 27]. So O.C is more likely to combine with  $\text{Ca}^{2+}$  in solution

to form a metal ion–polymer complex than to adsorb onto the nuclei surface and alter the morphology of CaOx. On the other hand, in the presence of Acumer1050, CaOx crystals are significantly smaller, and a high percentage of COD bipyramids appears. This is an indication that Acumer1050 alters the morphology of CaOx by adsorbing onto scale-forming nuclei rather than binding onto

$\text{Ca}^{2+}$ , as seen in oxidized chitosan. Because it has a very low molecular weight compared to oxidized chitosan, the network of Acumer1050 chains binding to calcium

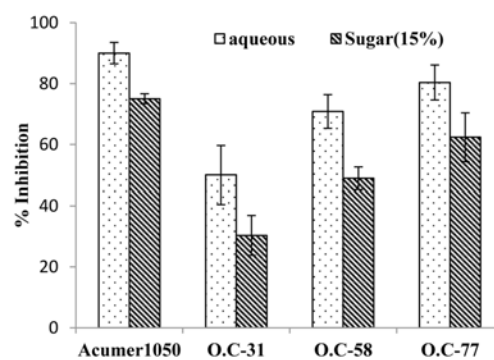
ions is not as stable as the binding of a long chain oxidized chitosan with high negative charge density [18, 22, 24, 28].



**Figure 7.** SEM images of  $\text{CaOx}$  scales collected from 13% sugar solution (w/w) (a) blank sample, (b) Acumer1050, (c) O.C-58 (HMW), (d) O.C-31 (HMW), (e) O.C-29 (LMW).

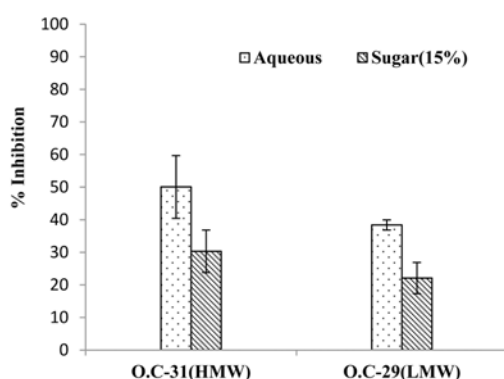
### 3.1.2 Calcium sulfate ( $\text{CaSO}_4$ )

The effect of oxidation degree on the O.C antiscaling performance with  $\text{CaSO}_4$  is similar to that of  $\text{CaOx}$  (Figure 8). The oxidized chitosan with a higher oxidation degree exhibits better performance. However, for both with and without 13 % sugar (w/w), Acumer1050 shows the best performance in preventing  $\text{CaSO}_4$  scales. Figure 9 shows that O.C-31 HMW exhibits better performance than O.C-29 LMW in both aqueous and sugar solutions. Figure 10 shows that the percent inhibition of both kinds of O.C decreases as the sugar concentration increases.

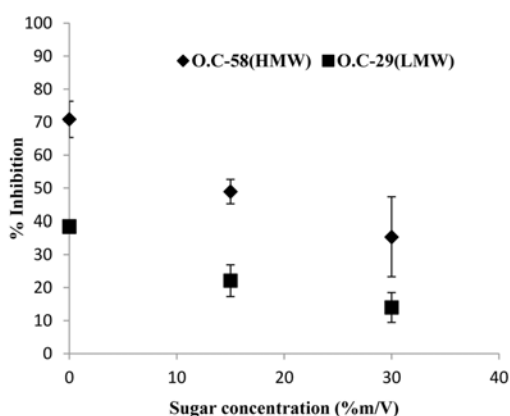


**Figure 8.** Antiscaling performance of oxidized chitosan compared to Acumer1050, with  $\text{CaSO}_4$  scales, in aqueous solution and in sugar solution.



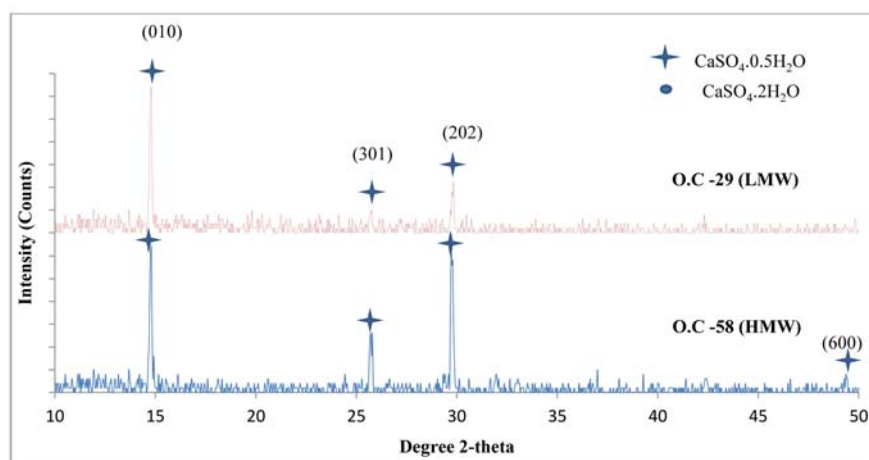


**Figure 9.** Performance of oxidized chitosan against CaSO<sub>4</sub> scales, in aqueous solution and in sugar solution, high molecular weight (HMW) vs. low molecular weight (LMW), with comparable degrees of oxidation.

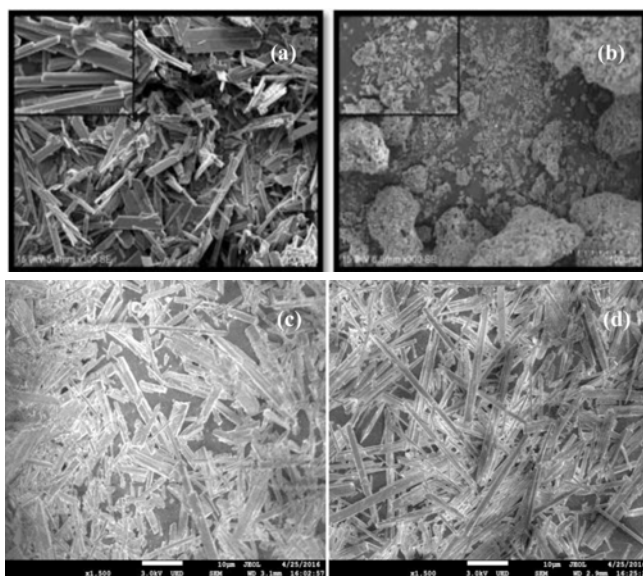


**Figure 10.** Effect of sugar concentration on antiscaling performance of two kinds of oxidized chitosan for CaSO<sub>4</sub>.

Based on the XRD patterns, Figure 11 shows that calcium sulfate hemihydrates (CaSO<sub>4</sub>•0.5H<sub>2</sub>O) is observed in the presence of O.C-58 HMW, O.C-29 LMW, and Acumer1050, whereas calcium sulfate dihydrate (CaSO<sub>4</sub>•2H<sub>2</sub>O) is formed in the blank sample. The SEM images in Figure 12 a-b shows long needles and a smooth surface of CaSO<sub>4</sub>•2H<sub>2</sub>O found in the blank sample, whereas small plates of amorphous CaSO<sub>4</sub>•0.5H<sub>2</sub>O appear in the sample with Acumer1050 [29]. The CaSO<sub>4</sub> crystals in the presence of oxidized chitosan (Figures 12 c-d) appear shortened and tend to form loose bundles, which were also observed when carboxymethylcellulose (CMC) was tested as an antiscalant [29]. Oxidized chitosan has a similar structure to CMC with a polysaccharide backbone and carboxylate side chains. The change in morphology in the presence of O.C-58 HMW and O.C-29 LMW could come from the effects of different molecular weight or different degree of oxidation. However, at a low sucrose concentration (15 wt%), two kinds of oxidized chitosan (O.C-31 HMW and O.C-29 LMW) show similar inhibition percentages for CaSO<sub>4</sub> scale (Figure 9). Hence, the different crystal morphologies in Figure 12 c and d may be attributed to different adsorption affinity due to a different number of carboxylate groups on the polymer chains.



**Figure 11.** XRD graphs of  $\text{CaSO}_4$  scales collected, from 15% sugar solution (w/w) in the presence of two kinds of oxidized chitosan materials, O.C-58 (HMW) and O.C-29 (LMW).



**Figure 12.** SEM graphs of  $\text{CaSO}_4$  scales collected from 15% sugar solution (w/w) (a) Blank sample, (b) with Acumer1050 [29] (c) O.C-58 (HMW), (d) O.C-29 (LMW).

#### 4. CONCLUSIONS

Oxidized chitosan exhibits good antiscaling performance for both  $\text{CaOx}$  and  $\text{CaSO}_4$  scales. Oxidized chitosan with a higher degree of oxidation shows better antiscaling performance for both  $\text{CaOx}$  and  $\text{CaSO}_4$ . LMW oxidized chitosan would be a suitable antiscalant for  $\text{CaOx}$ , which is mostly formed in the later effects at a high sucrose

concentration, because LMW oxidized chitosan shows consistent performance, even with a very high sugar concentration (65 wt%). On the other hand, HMW oxidized chitosan exhibits better performance for  $\text{CaSO}_4$ , which mainly appears in the first effects with a low concentration of sucrose. As a result, oxidized chitosan with high degrees of oxidation with different molecular

weights should be applied in different stages of sugar evaporation. The HMW oxidized chitosan should be added into the earlier stages of the sugar evaporation and the LMW oxidized chitosan should be added into the later stages. Our study reveals oxidized chitosan could be a promising replacement for petroleum-based commercial antiscalants for the sugar industry.

#### ACKNOWLEDGEMENTS

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#### REFERENCES

- [1] Yoo S.H., Lee J.S., Park S.Y., Kim Y.S., Chang P.S. and Lee H.G., *Int. J. Biol. Macromol.*, 2005; **35(1-2)**: 27-31. DOI 10.1016/j.ijbiomac.2004.11.004.
- [2] Doherty W. and Wright P., *Proceedings of 2004 Conference of the Australian Society of Sugar Cane Technologists* Brisbane, Queensland, Australia, 4-7 May 2004; (CD-ROM).
- [3] Persinski L.J., Hotchkiss P., Ralston and Jr. R.C.G., *United States Pat. No.* 928196 (1975).
- [4] Doherty W.O.S., Crees O.L. and Senogles E., *Cryst. Res. Technol.*, 1995; **30(6)**: 791-800. DOI 10.1002/crat.2170300614.
- [5] Rackemann D.W., Doherty W.O.S. and East C.P., *Proceedings of the 27<sup>th</sup> International Society of Sugar Cane Technologists Congress*, Veracruz, Mexico, 7-11 March 2010; 199-212.
- [6] East C.P., Doherty W.O.S., Fellows C.M. and Yu H., *Surf. Interf. Anal.*, 2011; **43(9)**: 1231-1239. DOI 10.1002/sia.3704.
- [7] Amjad Z. and Masler W.F., *Proceedings of the International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials*, Boston, Massachusetts, 25-29 March 1985; 357/351-357/358.
- [8] Antony A., Low J.H., Gray S., Childress A.E., Le-Clech P. and Leslie G., *J. Membrane Sci.*, 2011; **383(1-2)**: 1-16. DOI 10.1016/j.memsci.2011.08.054.
- [9] Wang C., Li S. and Li T., *Desalination*, 2009; **249(1)**: 1-4. DOI 10.1016/j.desal.2009.06.006.
- [10] Zeppenfeld K., *Desalination*, 2010; **252(1-3)**: 60-65. DOI 10.1016/j.desal.2009.10.025.
- [11] Zhou X., Sun Y. and Wang Y., *J. Environ. Sci.*, 2011; **23(Supplement)**: 159-161. DOI 10.1016/S1001-0742(11)61102-9.
- [12] Kumar T., Vishwanatham S. and Kundu S.S., *J. Petrol. Sci. Eng.*, 2010; **71(1-2)**: 1-7. DOI 10.1016/j.petrol.2009.11.014.
- [13] Casey J.A., *United States Pat. No.* 3, 483, 033 (1969).
- [14] Keller R., *United State Pat. No.* 4, 389, 324 (1983).
- [15] Berends R. and Kuzee H.C., *United States Pat. No.* US 6, 506, 258 B1 (2003).
- [16] Bragd P.L., Besemer A.C. and van Bekkum H., *Carbohydr. Res.*, 2000; **328(3)**: 355-363. DOI 10.1016/S0008-6215(00)00109-9.
- [17] da Silva Perez D., Montanari S. and Vignon M.R., *Biomacromolecules*, 2003; **4(5)**: 1417-1425. DOI 10.1021/bm034144s.
- [18] Doherty W.O.S., Fellows C.M., Gorjian S., Senogles E. and Cheung W.H., *J. Appl. Polym. Sci.*, 2004; **91(3)**: 2035-2041. DOI 10.1002/app.13349.
- [19] Paramet J.W.S. and Cattaleeya P., *Proceedings of the 3<sup>rd</sup> International Symposium on Engineering, Energy and Environments*, Pullman King Power Hotel, Bangkok, 17-20 November 2013; 126-131.

- [20] Ismi I., Rifi E., Lebkitri A. and Oudda H., *J. Mater. Environ. Sci.*, 2015; **6(2)**: 343-348.
- [21] Pawlak A. and Mucha M., *Thermochim. Acta*, 2003; **396(1)**: 153-166. DOI 10.1016/S0040-6031(02)00523-3.
- [22] Doherty W.O.S., Crees O.L. and Senogles E., *Cryst. Res. Technol.*, 1996; **31(3)**: 281-286. DOI 10.1002/crat.2170310304.
- [23] Yu H., Sheikholeslami R. and Doherty W.O.S., *Powder Technol.*, 2005; **160(1)**: 2-6. DOI 10.1016/j.powtec.2005.04.043.
- [24] Manne J.S., Biala N., Smith A.D. and Gryte C.C., *J. Cryst. Growth*, 1990; **100(3)**: 627-634. DOI 10.1016/0022-0248(90)90261-I.
- [25] Akin B., Öner M., Bayram Y. and Demadis K.D., *Cryst. Growth Des.*, 2008; **8(6)**: 1997-2005. DOI 10.1021/cg800092q.
- [26] Sayan P., Sargut S.T. and Kiran B., *Cryst. Res. Technol.*, 2009; **44(8)**: 807-817. DOI 10.1002/crat.200900236.
- [27] Doherty W.O.S., *Ind. Eng. Chem. Res.*, 2006; **45(2)**: 642-647. DOI 10.1021/ie0509037.
- [28] Wallace A.D., Al-Hamzah A., East C.P., Doherty W.O.S. and Fellows C.M., *J. Appl. Polym. Sci.*, 2010; **116(2)**: 1165-1171. DOI 10.1002/app.31657.
- [29] Wichanrot S., *The Effectiveness of Carboxymethyl Cellulose (CMC) as a Co-antiscalant in the Sugar Cane Evaporators*, MSc Thesis, Thammasat University, Thailand, 2015.