Control of Foam Formation by Antifoam during Demineralization of Crustacean Shell in Preparation of Chitin

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The effects of antifoam on the control of foam formation during the demineralization of crab shell in the preparation of chitin were evaluated. Foam formation was markedly controlled by addition of antifoam and decreased with increasing antifoam concentrations. At 1.00 mL of antifoam/L of 1 N HCl, the performance of antifoam was more efficient during demineralization with smaller shell particle size (<0.425 mm) and under a slightly faster stirring speed (300 rpm). Deproteinization followed by demineralization was found to be a more desirable process on the basis of the performance of the antifoam at a lower concentration. Antifoam effectively controlled foam formation during demineralization with deproteinized shell even at a low concentration of 0.33 mL of antifoam/L of 1 N HCl. Results for ash analysis of the shell demineralized without and with antifoam (1.00 mL/L) showed no noticeable difference.

Keywords: *Foaming control; antifoam; demineralization; chitin preparation*

INTRODUCTION

Crustacean shell waste consists mainly of 30−40% protein, 30−50% calcium carbonate, and 20−30% chitin on a dry basis (Johnson and Peniston, 1982). Isolation of chitin from crustacean shell waste consists of two basic steps: (1) protein separation−deproteinization and (2) calcium carbonate (and calcium phosphate) separation−demineralization. These two steps also can be conducted in a reverse order, that is, demineralization followed by deproteinization.

Demineralization is conventionally accomplished by extraction with dilute hydrochloric acid at room temperature to dissolve the calcium carbonate present as calcium chloride (No and Meyers, 1995). During this process, excessive undesirable foams are formed by CO_2 generation. Such excessive foaming poses various problems, for example, reduction of tank capacity by increasing the need for headspace, loss of product, and reduced rates of processing.

Silicone antifoams have found application in a wide range of industries, including food, packaging, chemical, textile, cosmetic, and pharmaceutical. In the food industry, silicone antifoam liquids (fluids and emulsions) have been used to control formation of unwanted foam in nonstandardized food processing applications (Pszczola, 1991). However, there is no available information on the use of antifoam for control of foam formation during demineralization of crustacean shell in the commercial preparation of chitin.

The objective of the present research was to investigate the effect of antifoam on the control of foam formation during demineralization of crustacean shell in the preparation of chitin and chitosan.

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EXPERIMENTAL PROCEDURES

Materials. Dried crab (*Chionoecetes opilio*) shell waste was obtained from commercial crab processors (Youngduk, Korea). The shell was ground through a Wiley mill (model 4, Thomas Scientific) with a 2 mm mesh screen, sifted with 20 (0.841 mm) and 40 mesh (0.425 mm) sieves, placed in opaque plastic bottles, and stored at ambient temperature. Ground shell of 0.841−0.425 mm particle size was used throughout this research, except for the study on the effect of different particle sizes, to obtain reproducible and consistent results.

Antifoam used was Antifoam A emulsion [a 30% aqueous emulsion of Antifoam A concentrate (100% active silicone polymer; no emulsifiers present), Sigma Chemical Co., St. Louis, MO]. This was diluted to 10% with deionized water before use.

Studies on Control of Foam Formation. To evaluate the effect of antifoam on the control of foam formation during demineralization of crab shell, demineralization was achieved by stirring 2 g of shell and 30 mL of 1 N HCl (containing appropriate concentrations of antifoam) in a 100 mL beaker using a magnetic stirrer (300 rpm) at room temperature. After 30 and 60 s of reaction, stirring was stopped and heights of foam and liquid phase of the reactant in the 100 mL beaker were measured. All experiments were carried out in duplicate, and average values are reported.

For evaluation of the effect of stirring speed, two different speeds (300 and 200 rpm) were selected. In studies of the effect of particle size, two different size ranges (0.841−0.425 and <0.425 mm) of shell were used. To evaluate the effect of antifoam on deproteinized shell, the shell was deproteinized with 5% NaOH with a solids-to-solvent ratio of 1:15 for 1 h at 65 °C (No and Lee, 1995).

Ash Content. Ash content was determined (AOAC, 1990) to compare extraction efficiency after demineralization of the shell, without and with antifoam (1.00 mL/L of 1 N HCl), for 30 min following procedures developed by No and Lee (1995).

RESULTS AND DISCUSSION

Effect of Antifoam Concentration. The effects of antifoam concentrations on control of foam formation during demineralization of the crab shell were evaluated at reaction times of 30 and 60 s (Table 1).

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Table 1. Effect of Antifoam Concentrations on Control of Foam Formation during Demineralization[a] of Crab Shell with 1 N HCl at Reaction Times of 30 and 60 s

antifoam concn (mL/L of 1 N HCl)	height[b] (mm) after 30 s			height[b] (mm) after 60 s		
	liquid	foam	total	liqiud	foam	total
0	10	37	47	15	25	40
0.33	11	14	25	13	4	17
0.67	13	9	22	14	4	18
1.00	10	8	18	13	3	16
1.67	13	6	19	14	2	16
3.33	18	0	18	17	0	17

[a] Demineralization was achieved by stirring 2 g of shell (0.841−0.425 mm) and 30 mL of 1 N HCl (containing appropriate concentrations of antifoam) in a 100 mL beaker using a magnetic stirrer (300 rpm) at room temperature. [b] Height in 100 mL beaker.

Table 2. Effect of Stirring Speeds on Control of Foam Formation by Antifoam during Demineralization[a] of Crab Shell with 1 N HCl at Reaction Times of 30 and 60 s

stirring speed (rpm)	height[b] (mm) after 30 s			height[b] (mm) after 60 s		
	liquid	foam	total	liqiud	foam	total
300	10	8	18	13	3	16
200	13	9	22	14	5	19

[a] Demineralization was achieved by stirring 2 g of shell (0.841−0.425 mm) and 30 mL of 1 N HCl (containing 1.00 mL of antifoam/L of 1 N HCl) in a 100 mL beaker using a magnetic stirrer at room temperature. [b] Height in 100 mL beaker.

Formation of foam was markedly controlled by addition of antifoam and decreased with increasing concentrations. At a reaction time of 30 s, the control reactant (without antifoam) revealed a total 47 mm height in a 100 mL beaker. In contrast, the reactant with 1.00 mL of antifoam/L of 1 N HCl showed a total 18 mm height (2.6 times reduction in height). Antifoam concentrations >1.00 mL/L did not result in corresponding decreases in total height. At 3.33 mL of antifoam/L, no foaming occurred at all. The reactant with 0.33 and 0.67 mL of antifoam/L showed total 25 and 22 mm height, respectively. The decrease in total height of the reactant with increasing antifoam concentrations can be attributed to control of foam formation (Table 1).

The total heights of the reactant were all decreased at a reaction time of 60 s due to collapse of foams formed. This indicates that foam formation increased sharply, reaching a maximum during the reaction time of 30 s. After that, the existing foam bubbles gradually collapsed, resulting in a decrease in foam height.

Pszczola (1991) reported that organic antifoams are commonly used in concentrations of ≥1000 ppm. In the present study, 1.00 mL of 10% antifoam/L of 1 N HCl (= 100 ppm) was considered to be optimum for effective foam formation control during demineralization. Subsequent experiments were carried out with 1.00 mL of antifoam/L.

Effect of Stirring Speed. The effects of stirring speed on control of foam formation by antifoam during demineralization of crab shell are shown in Table 2. A stirring speed of 300 rpm was more effective in controlling the formation of foam than a stirring speed of 200 rpm. The reactant at a stirring speed of 300 and 200 rpm showed total 18 and 22 mm height, respectively, at a reaction time of 30 s. A decrease in foam formation with increasing stirring speed probably can be attributed to accelerated breakage of the films between the bubbles (Prins, 1988).

Table 3. Effect of Particle Size Ranges on Control of Foam Formation by Antifoam during Demineralization[a] of Crab Shell with 1 N HCl at Reaction Times of 30 and 60 s

particle size (mm)	antifoam concn (mL/L of 1 N HCl)	height[b] (mm) after 30 s			height[b] (mm) after 60 s		
		liquid	foam	total	liquid	foam	total
0.841−0.425	0	10	37	47	15	25	40
	1.00	10	8	18	13	3	16
<0.425	0	11	42	53	14	18	32
	1.00	17	0	17	17	0	17

[a] Demineralization was achieved by stirring 2 g of shell and 30 mL of 1 N HCl (containing 0 or 1.00 mL of antifoam/L of 1 N HCl) in a 100 mL beaker using a magnetic stirrer (300 rpm) at room temperature. [b] Height in 100 mL beaker.

Table 4. Effect of Antifoam on Control of Foam Formation during Demineralization[a] of Crab Shell before and after Deproteinization with 1 N HCl at Reaction Times of 30 and 60 s

shell condition	height[b] (mm) after 30 s			height[b] (mm) after 60 s		
	liquid	foam	total	liquid	foam	total
before deproteinization	10	8	18	13	3	16
after deproteinization	17	0	17	17	0	17

[a] Demineralization was achieved by stirring 2 g of shell (0.841−0.425 mm) before and after deproteinization and 30 mL of 1 N HCl (containing 1.00 mL of antifoam/L of 1 N HCl) in a 100 mL beaker using a magnetic stirrer (300 rpm) at room temperature. [b] Height in 100 mL beaker.

Effect of Particle Size. Two different particle size ranges (0.841−0.425 and <0.425 mm) of shell were investigated to compare performance efficiency of the antifoam (1.00 mL/L) (Table 3).

In the control reactant (0 mL of antifoam/L), foam formation increased with decreasing particle sizes at a reaction time of 30 s. This is because foaming may occur more readily with the smaller particle sizes due to increased surface areas. However, collapse of foam occurred more rapidly with smaller particle sizes. The reactant with 1.00 mL of antifoam/L showed comparable total heights for both particle size ranges of 0.841−0.425 and <0.425 mm. However, antifoam performed more effectively at the smaller particle sizes.

Effect of Deproteinization. Isolation of chitin can be conducted in an order of deproteinization followed by demineralization. Therefore, the effects of antifoam (1.00 mL/L) on the control of foam formation during demineralization with shell before and after deproteinization were compared.

As seen in Table 4, the total heights of the reactant were comparable for both shells before and after deproteinization (designated shell and deproteinized shell, respectively). However, foam formation was not observed during demineralization with the deproteinized shell, even at a reaction time of 30 s. The slight amount of protein present in the deproteinized shell compared with the shell may be responsible for the better control of foam formation by antifoam because proteins are known to have foaming properties (Huang et al., 1997). According to Huang et al. (1997), protein generally has two functions in the formation of foams: it acts as a surfactant to reduce the tension at the air/liquid interface; it also forms a continuous cohesive film at the interface which stabilizes the foam bubbles.

Further studies were conducted to investigate whether lower concentrations of antifoam can be used without reducing its performance. Antifoam effectively con-

Table 5. Effect of Antifoam Concentrations on Control of Foam Formation during Demineralization[a] of Deproteinized Crab Shell with 1 N HCl at Reaction Times of 30 and 60 s

antifoam concn (mL/L of 1 N HCl)	height[b] (mm) after 30 s			height[b] (mm) after 60 s		
	liquid	foam	total	liquid	foam	total
0	11	22	33	14	10	24
0.33	19	0	19	18	0	18
0.67	19	0	19	18	0	18
1.00	17	0	17	17	0	17

[a] Demineralization was achieved by stirring 2 g of deproteinized shell (0.841−0.425 mm) and 30 mL of 1 N HCl (containing appropriate concentrations of antifoam) in a 100 mL beaker using a magnetic stirrer (300 rpm) at room temperature. [b] Height in 100 mL beaker.

trolled the formation of foam during the demineralization of deproteinized shell even at a concentration of 0.33 mL/L (Table 5). The control reactant showed total 33 mm height at a reaction time of 30 s. This height is much lower than that (47 mm) of the control reactant during demineralization with shell (Table 1). These data clearly demonstrate that deproteinization followed by demineralization is a more desirable process in view of the performance of antifoam at a lower concentration.

Ash Content. Results for ash analysis of the shell demineralized without and with antifoam (1.00 mL/L) showed no noticeable difference, with both <1%. Therefore, addition of antifoam effectively controls the formation of foam during demineralization without affecting the efficiency of removal of calcium carbonate.

Conclusion. This investigation has demonstrated that the formation of foam during demineralization of crustacean shell in the preparation of chitin can be effectively controlled by use of an antifoam agent. Deproteinization followed by demineralization was found to be a more desirable process in view of the beneficial effect of antifoam. Its use in a demineralization process could increase the capacity of the reaction tanks by decreasing the need for headspace ~2.6 times. Without antifoam, some particles are retained in the foam and adhere to the surface of the tank after the foam was broken. Nonuniform product quality of chitin and chitosan certainly will influence their physicochemical characteristics and functional properties.

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