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Water Soluble Chitosan as an Environment-Friendly Coagulant in Removal of Rubber Particles from Skim Rubber Latex

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Abstract

Water soluble chitosan, dissolved in hot deionized water to obtain 0.8% solution, was used for the coagulation-flocculation of skim natural rubber latex. The efficiency of coagulation-flocculation of skim rubber latex without pH adjustment was much poorer than that of neutral skim rubber latex. When adding chitosan solution to the neutral skim rubber latex with a rubber content of 5.300 %wt/vol until the concentration of chitosan in the dispersion was 0.107%, the phase separation between rubber particles and yellow serum was clearly observed. At this condition, the removal efficiency of skim rubber particles was found to be the best among all trials. It was also found that dilution of skim rubber latex with deionized water did not increase the removal efficiency.

Key word : chitosan; skim rubber latex; coagulation; flocculation

Introduction

Chitosan, a deacetylated derivative of chitin, is a biodegradable and non-toxic cationic polymer. Knorr, D. 1984 discovered that chitosan was an effective agent for coagulation of suspended solids from various food processing wastes. In addition,[(6)] found that chitosan could be used as a potent coagulant in surface water treatment for source waters of medium and low turbidity. Not only has chitosan been widely used in food industry, but it has also been used for the coagulation-flocculation of mineral colloids and colloids in agricultural industry. Guibal, et al. 2007 mentioned that the physico-chemical properties, for instance, acid-base properties, solubility, cationicity, of chitosan were related to the presence of amine function leading to efficiency for binding metal cations in near neutral solution and for interacting with anionic solutes in acidic solutions.

Natural Rubber Latex (NRL) is originally defined as the stable dispersion of natural rubber particles in aqueous solutions as produced in the rubber tree *Heavea Brasilienesis*. Fresh latex tapped from the rubber tree and known as field latex is a cloudy, white liquid, similar in appearance to cow's milk. Field latex contains about 30% rubber fraction and about 5% non-rubber such as proteins and lipids. It is well known that the commercial high ammonia natural rubber latex concentrate can be produced by centrifugation of field latex,[(4)] leaving behind a by-product of this process which consists highly of non-rubber and small rubber particles or skim rubber particles in dilution. Skim latex has always been discarded and has not received much attention due to the high ratio of the aqueous phase. The usual method to recover solid rubber is by coagulation with sulfuric acid. However, in acid coagulation, the acid content of the coagulated rubber reduces its quality and the remaining acid leads to generation of highly acidic effluent. This research paper seeks to recover rubber in skim latex and at the same time reduce water pollution.

Materials and Experimental Procedures

Materials

Water soluble chitosan (degree of deacetylation = 96.4%) was derived from high molecular

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weighted chitosan from A.N. Lab Aquatic Nutrition, Thailand. Sodium nitrite and acetone were purchased from Fluka. Sodium hydroxide (NaOH) was purchased from Labscan. Hydrochloric acid (HCl) was supplied from Merck. All chemicals were of analytical grade and used without further purification. Skim (Total solid content; TSC = 7.96%, Dry rubber content; DRC = 3.84%) obtained from Thai Rubber Latex Corporation (Thailand) Public Co., Ltd., Chonburi.

Synthesis of Water Soluble Chitosan

Chito-oligosaccharide (COS) or water soluble chitosan was synthesized according to[1] Initially, 2.0 wt% of chitosan was dissolved in 4 liters of 0.22 M HCl solution. The solution was heated to 60°C. Then, sodium nitrite was added and the mixture was left reacted for 20 mins. Afterwards, the pH of the reaction mixture was adjusted to 7 by gradually adding 20 M aqueous NaOH solution at room temperature. The sediment was then filtered with filter cloth three times and the remaining solution was concentrated until the final volume was 500 ml. After that, COS was precipitated and washed with 90% acetone solution twice. Finally, the washed product was dried in a vacuum oven at room temperature. The average molecular weights, M_w, of the synthesized COS were measured with Gel Permeation Chromatography (PL-GPC 110) by using ultrahydrogel linear column and acetate buffer as a mobile phase. The molecular weight of chitosan (M_w) was evaluated 324,371 Da. The dynamic viscosity of the COS solution determined with Brookfield viscometer (programmable DV-II plus) at 20°C 200 rpm, was evaluated to be 2.25 cP. The pH of COS solution was 5.93.

Determination of Solid Content in Skim Rubber Latex

The solid content in skim rubber latex could be expressed by both total solid content (TSC) and dry rubber content (DRC). In order to determine the total solid content, the latex with known weight around 10 g was poured on a Petri dish and left to dry at 70-80°C until the skim latex became a yellow film. The dried film was then weighed. The experiments were done in triplicate. The TCS was obtained according to Eq. (1) and it was the average of three samples.

$$TSC = \frac{dried\ \ film\ weight}{actual\ \ skim\ weight} \times 100 \qquad (1)$$

To determine the dry rubber content (DRC), 2% H2SO4 was dropped gradually onto the skim rubber latex with known weight around 20 g until the pH of the skim rubber latex reached 4.5. The rubber particles were coagulated upon adding the acid solution. The solid was filtered using the filter paper no.1. The solid was then dried at 70-80°C and it was weighed. The experiments were done in triplicate. The DRC was obtained according to Eq. (2) and it was the average of three samples.

$$DRC = \frac{dried\ \ weight}{actual\ \ skim\ weight} \times 100 \qquad (2)$$

Preparation of the Coagulant

As a coagulant, the 0.8% wt/vol chitosan solution was prepared by adding chitosan to hot deionized water and mixing until completely dissolved. Usually, ammonia is added in skim rubber latex as a preservative against bacterial attack for long-term stability. The pH of skim rubber dispersion is about 9.5-9.7. Hereafter, skim rubber dispersions with and without pH adjustment are called neutral skim rubber dispersion and normal skim rubber dispersion, respectively. HCl solution (10% wt) was used to adjust the pH of the dispersion. To study the effect of chitosan amount, 100 ml dispersion was put in each beaker and various amounts of chitosan solution (5, 10, 20, 25, 30, 35, 40, 45 and 50 ml) were added. The dispersion was mixed at 200 rpm paddle speed. After that, all samples were filled with water until the total volume was 150 ml. The dispersion was then rapidly mixed for another 5 mins, followed by slow mixing at 50 rpm for 20 mins. Later, it was left unstirred for 1 hour. Subsequently, the aggregate was filtered with the filter cloth. To study the effect of dilution, the concentration of rubber was varied by adding various amounts of water to the original skim rubber. The ratios of the volume of water added to the volume of skim rubber suspension were 3:1, 2:2, 1:3, and 0:4. In each experiment, 100 ml original and diluted skim rubber dispersions were used and the amount of chitosan solution was fixed at 20 ml. The mixing was done similarly.

After that, the cream phase removed by filtration was dried at 75°C and weighed.

Results and Discussion

The total solid content of neutral skim rubber latex was very close to that of normal skim rubber latex, i.e. the total solid content (TSC) is 7.95% and the dry rubber content (DRC) is 3.83%. Therefore, the degree of coagulation resulted from pH adjustment is, in this case, negligible.

The effect of the Amount of Added Chitosan

The amount of chitosan added was varied by adding various volumes which are equivalent to various concentrations of chitosan in the dispersion prepared as shown in Table 1.

Table 1. The volume of chitosan solution and the concentration of COS in rubber latex suspension.

VOL of COS Solution (ml)	Concentration of COS in dispersion (w/v %)
5	0.027
10	0.053
20	0.107
25	0.133
30	0.160
35	0.187
40	0.213
45	0.240
50	0.267

The efficiency of coagulation-flocculation of skim natural rubber latex was represented by percentage of dry-removed solid weight in the original total solid weight, including the weights of suspended solids and dissolved solids. The solid removal percentage is convenient to determine although the efficiency should refer to how efficient chitosan removes rubber content in the suspension exclusively. To obtain such value is difficult since it involves the separation of suspended solids and dissolved solids which in this experiment are salt, original dissolved solids in skim rubber latex, and the remaining unreacted chitosan. Figure 1 displays the solid removal percentage for neutral and normal skim rubber latex when varying amount of coagulating solution. The efficiency of coagulation-flocculation of normal skim rubber latex was only 0.8-1.42%, much poorer than that of coagulation-flocculation of neutral skim rubber latex, which was 0.45-70.53%. It is possible that the coagulation resulted from coulombic interactions among anionic proteins coating rubber particle surfaces and cationic chitosan or protonated chitosan. Generally, it is known that the chitosan chain is protonated in an acidic condition. However, according to[5], the degree of protonation ranges from non-protonation to complete protonation when the pH of the solution ranges from 9.12 to 3.86 for a chitosan with %DD of 94.6%, implying that dissolving chitosan in pure water (pH 7) should result in some degree of protonation.

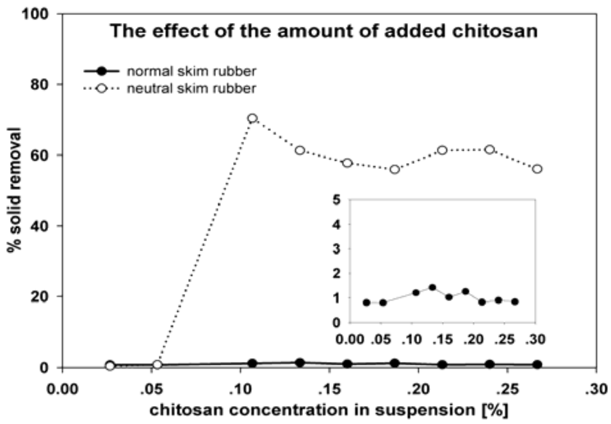

Figure 1. Solid removal by coagulation-flocculation when varying the concentration of COS solutions in normal skim rubber and neutral skim rubber.

In normal skim rubber latex, some of chitosan chains or acetic acid molecules might react with hydroxide ions, leading to a smaller number of active amino groups to react with rubber particles. Hence, adjusting pH increased the efficiency of coagulation-flocculation of skim natural rubber latex. The efficiency was increased with the amount of chitosan up to the highest point, and then decreased. A greater amount of chitosan resulted in a higher number of amino groups. However, too many chains of chitosan may lead to entanglements between polymer chains themselves which come from the interaction among amino and hydroxyl-methyl groups on chitosan chains, thereby reducing the number of active amino groups for coagulation with rubber particles.

The suspension may, in some degree, be restabilized. The highest efficiency for normal skim rubber latex was 1.42% at the optimal condition of using 0.133% chitosan solution and the highest efficiency for neutral skim rubber latex was 70.53% when using 0.107% chitosan solution, even less than the optimal point for skim rubber latex. In addition, it was observed that the serum phase was clear and yellowish for neutral skim rubber dispersion, when adding a higher amount of chitosan than for the optimal point. This implies that beyond the optimal point, the remaining chitosan may be left unreacted in the solution.

The Effect of the Skim Rubber Dilution

The skim rubber was diluted by adding various amounts of water, thereby decreasing the concentration of the rubber latex as shown in Table 2.

Table 2. Relation between added volume of water and final concentration of rubber in dispersion.

Ratio of water added and skim rubber dispersion (ml:ml)	Concentration of skim rubber in normal dispersion (w/v %)	Concentration of skim rubber in neutral dispersion (w/v %)
3:1	1.658	1.656
2:2	3.317	3.313
1:3	4.975	4.969
0:4	6.633	6.625

As shown in Table 2, the concentration of latex in neutral skim rubber is a little less than the concentration of latex in normal skim rubber since a small amount of rubber particles was coagulated by HCl and then removed before adding chitosan. The solid removal percentage by coagulation-flocculation is shown in Figure 2. The solid removal percentage by coagulation-flocculation of normal skim rubber latex was 0.7-1.57% and by coagulation-flocculation of neutral skim rubber latex, it was 42.29-76.97%. For neutral skim rubber latex, the solid removal percentage seems to decrease linearly with degree of dilution. This implies that the amount of chitosan used contains enough amino groups to interact with the rubber particles. The higher the amount of rubber in the dispersion, the higher the amount of rubber removed. For normal skim rubber, with increasing the concentration of skim rubber, the removal percentage decreased to the minimum and then increased. When the skim was diluted a little, a smaller amount of rubber was removed. When further diluted, the removal of rubber was better, probably due to less hydroxide groups. For the best condition here, the chitosan concentration was 0.133% and the concentration of neutral skim rubber was 6.625%. The serum after cream separation was clear and yellowish.

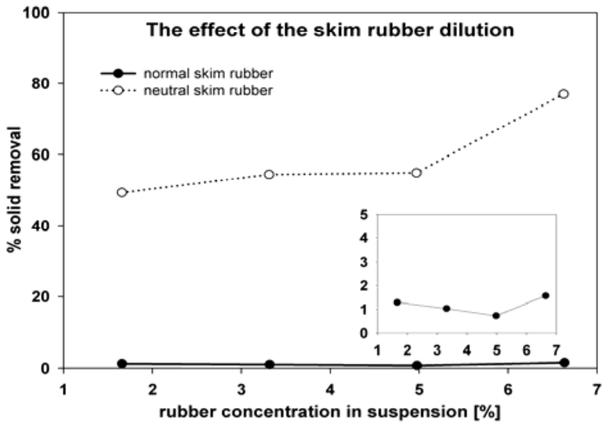

Figure 2. The effect of dilution of normal skim rubber on solid removal percentage.

Conclusions

Water soluble chitosan was used as a coagulant in coagulation-flocculation of rubber particles in skim rubber latex. It was found that the adjustment of pH to neutral seemed to be the key factor to increase the performance of the coagulation-flocculation process. This constitutes the optimal condition for adding chitosan to coagulate the rubber particles in skim rubber dispersion. For neutral skim rubber latex, the coagulation was best for dispersion without dilution (i.e. 5.3 %wt/vol rubber in dispersion). The best condition for coagulation is that using 0.107% wt/vol chitosan solution or, in other words, about 8.02 phr, where phr stands for parts per hundred parts of rubber. The serum after separation of rubber was yellowish and clear.

Acknowledgements

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