

Creaming of Skim Natural Rubber Latex with Chitosan Derivatives

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ABSTRACT: To recover residual rubber from skim natural rubber (SNR) latex, a novel method was developed on the basis of the use of water-soluble chitosan derivatives. An anionic chitosan derivative, *N,O*-carboxymethyl chitosan (CMCh), and a cationic chitosan derivative, *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTACh), were prepared. It was found that the creaming process could be achieved with both chitosan derivatives. By the addition of 7.34–10.3-g/L CMCh, SNR latex was almost completely creamed, and no coagulation of SNR particles in the cream phase occurred. In the case of HTACh, the creaming process

was achieved with a lower concentration (<3.70 g/L) than in the case of CMCh, but the size of SNR particles in the cream phase was larger. Solid-state ¹³C-NMR, thermogravimetric analysis, and ζ potential measurement results provided evidence that the creaming of SNR latex with CMCh and HTACh was controlled by the depletion flocculation and adsorption mechanisms, respectively. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1022–1031, 2010

Key words: biopolymers; modification; phase separation; rubber

INTRODUCTION

Skim natural rubber (SNR) latex is residual latex obtained as a byproduct in the manufacturing of concentrated natural rubber (NR) latex. The concentration of NR latex is necessary for the preparation of latex with a suitable rubber content for the manufacturing of rubber products. SNR latex usually contains only 2.5–10% w/w of small rubber particles (with an average particle diameter of about 0.1 μ m) and a very high protein content.¹ Moreover, the surfaces of SNR particles are covered with a protective peripheral layer of proteins and phospholipids adsorbed at the rubber–water interface, which helps to maintain the colloid stability of the particles. Especially in ammonia preservation system, the stability of SNR particles is substantially increased by the formation of an anion of long-chain carboxylic acids through hydrolysis of the lipids. These characteristics of SNR latex make it difficult to recover solid SNR from SNR latex. Nevertheless, it would be

economically attractive to recover this significant fraction of lost rubber material and environmentally desirable to remove this high amount of rubber material from the effluents of processing plants. The usual method for recovering solid SNR from SNR latex is coagulation with concentrated sulfuric acid. However, in acid coagulation, the acid content of the coagulated rubber decreases its quality and shows some tendency to scorch.^{2,3} Moreover, the acid coagulation method leads to the generation of a highly acidic effluent, which necessitates additional treatment before it is discharged into the environment to prevent pollution. The coagulation of SNR latex can also be performed with proteolytic enzymes, such as trypsin, where the enzymatic deproteinization of SNR latex is achieved.⁴ However, this process is not economical because it requires a large quantity of enzyme and necessitates further steps, such as deammoniation and the addition of sodium thiosulfate and formic acid or sodium chloride. To avoid problems due to the use of acid, the biocoagulation of SNR latex has also been studied. *Acinetobacter* sp., isolated from a latex centrifugation effluent, was applied to this process. The recovered SNR was more than 80% at an optimum dilution of 1 : 10 v/v and with an inoculum concentration of 6.4 mg of dry cells/mL.⁵

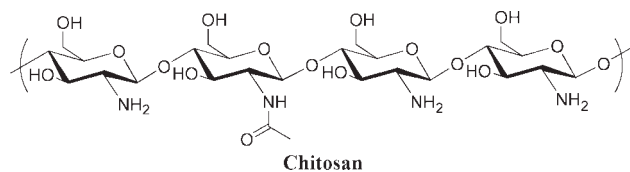
In this study, with regard to creating a method to recover SNR and reduce water pollution, we focused

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on creaming. Nowadays, creaming is mainly used in the art of food and drink manufacturing,^{6,7} although most studies have emphasized the reduction of the creaming rate of emulsions or the prevention of the creaming of the emulsion particles.^{8–10} In NR latex industry, creaming will allow the latex to separate into two layers under a gravitational force: an upper layer of concentrated residual rubber and a lower layer of serum containing a very small amount of rubber.^{1,11} The creaming process has several important advantages, such as simple requisite equipment, ease of operation, and a negligible power requirement. The creaming of SNR latex has been studied recently. Sakdapipanich et al.¹² incubated the small rubber particles in SNR latex with a proteolytic enzyme at 37°C for 2 days followed by the addition of NaCl. The decomposition of proteins, which covered the surface of the rubber particles, resulted in the aggregation of the rubber particles. The phase separation between the cream and serum phases depended on several factors, such as the reaction time, type of enzyme, and salt concentration. Tangboriboonrat et al.¹³ prepared creamed SNR latex by the addition of 15–45 part per hundred parts of rubber of sodium alginate. The data showed that the values of the separation ratio were dependent on the sodium alginate concentration and creaming time.

In this article, we report a study to use chitosan derivatives as a novel method for the recovery of SNR. Chitosan, a copolymer of D-glucosamine and N-acetyl-D-glucosamine, is derived from chitin, which is the second most abundant polysaccharide in nature after cellulose:



Chitin can be obtained from agricultural waste, such as shrimp, squid, or crab shells. The interest in using chitosan lies in the fact that it comes from a renewable resource. Furthermore, it is biodegradable and nontoxic, and it does not pollute the environment. Chitosan has been considered for various applications, including flocculation and coagulation in food processing, heavy-metal recovery from wastewater, and the fabrication of structural matrices for food, cosmetic, biotechnological, and biomedical applications.^{14,15} However, chitosan has an important limitation for the application to latex. It is water-insoluble and is dissolved only in aqueous acidic medium below pH 6.5. Thus, for the intended application of chitosan as a recovery agent for SNR, it is necessary for one to modify chitosan, either by lowering its molecular weight or introducing more

hydrophilic groups, to increase its solubility in the aqueous SNR system. In this study, *N,O*-carboxymethyl chitosan (CMCh) and *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTACh) were used. This was not only because of their solubility in water but also because they could be easily prepared in high yields.^{16,17}

EXPERIMENTAL

Materials

Commercial chitosan from shrimp shells supplied by AN Laboratory (Samutsakorn, Thailand) was used to prepare the chitosan derivatives. Its degree of deacetylation was determined to be 97.2% by solid-state ¹³C-NMR (DPX 300, Bruker, Falländén, Switzerland). Its molecular weight determined by gel permeation chromatography (600E fraction collector II, Waters 2410 (Milford, MA), with pullulan as a standard; detector, refractive index; column, one ultrahydrogel linear column and one guard column; eluent, 0.5M acetic acid/0.5M sodium acetate; flow rate = 0.6 cm³/min; operating temperature = 25°C) is shown in Table I. SNR latex was obtained from Orient Surat Rubber Latex Co., Ltd. (Suratthani, Thailand). The total solid content and dry rubber content, determined according to ASTM D 1076, were 6.67 and 3.67%, respectively. The pH of SNR latex was tested to be 10.2 with a pH meter (IQ 240, IQ Scientific Instruments, San Diego, CA). The average original rubber particle diameter, analyzed with photon correlation spectroscopy (S4700, Malvern, Worcestershire, UK), was 152.0 nm. The chemical structure of SNR was analyzed with solid-state ¹³C-NMR (DPX 300, Bruker). Resonance peaks at 134.9 and 125.4 ppm referred to carbons at double bonds in the polymeric chain. The methyl and methylene carbons peaks showed up at 23.7–32.6 ppm. Other reagents were analytical grade and were used as received.

Depolymerization of the chitosan

To obtain low-molecular-weight chitosan (chitosan-L) for the preparation of low-molecular-weight *N,O*-carboxymethyl chitosan (CMCh-L) and low-molecular-weight *N*-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride (HTACh-L), the nitrous acid (HNO₂) depolymerization of chitosan was carried out by the addition of a freshly prepared aqueous solution of NaNO₂ to a chitosan solution containing excess HCl, similar to a method reported in the literature.¹⁸ Because 2,5-anhydro-D-mannose, formed at the new reducing end, was unstable, as reported by Tømmeraaas et al.,¹⁹ a reduction to 2,5-anhydro-D-mannitol was carried out by the use of NaBH₄. Its molecular weight determined by gel permeation chromatography is shown in Table I (chitosan-L).

TABLE I
Molecular Weights and DS Values of Chitosan and the Chitosan Derivatives

Sample	Starting chitosan	M_w (kg/mol) ^a	M_n (kg/mol) ^a	M_w/M_n ^a	DS
Chitosan	—	530	173	3.06	—
Chitosan-L	—	23.7	10.4	2.28	—
CMCh	Chitosan	609	279	2.18	1.21 ^b
CMCh-L	Chitosan-L	27.6	16.8	1.64	1.53 ^b
HTACh	Chitosan	532	284	1.87	0.98 ^c
HTACh-L	Chitosan-L	24.7	11.8	2.09	0.96 ^c

M_n = number-average molecular weight.

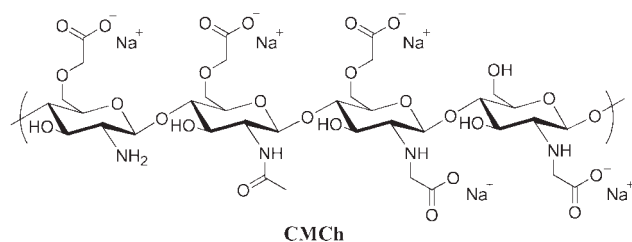
^a Determined by gel permeation chromatography with pullulan standards (eluent = 0.5M acetic acid/0.5M sodium acetate for chitosan, chitosan-L, HTACh, and HTACh-L; eluent = 0.5M NaOH for CMCh and CMCh-L).

^b Determined by pH titration.¹¹

^c Determined by ¹H-NMR.¹²

Preparation of CMCh

CMCh was prepared from chitosan according to the method of Muzzarelli.¹⁶

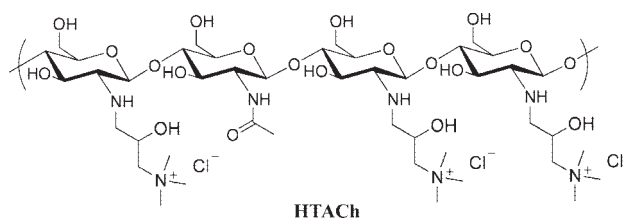


Typically, chitosan powder (50.0 g) was suspended in isopropyl alcohol (500 mL) and was left at room temperature overnight. Aqueous NaOH (40% w/v, 125 mL) was then added dropwise into the stirred slurry. The resulting mixture was stirred at room temperature for an additional 45 min, and the small portion of solid monochloroacetic acid (58.5 g, 620 mmol) was added. Then, the mixture was continuously stirred at 60°C for 3 h. Finally, the mixture was cooled to room temperature and neutralized by the slow addition of 2N HCl. The mixture was filtered, and the solid product was washed twice with CH₃OH/H₂O mixture (70% v/v, 750 mL) and CH₃OH (750 mL). The washed product was eventually filtered and dried in a vacuum oven at room temperature. The weight of the resultant CMCh was 67.7 g (69% yields). The chemical structure of CMCh was characterized with solid-state ¹³C-NMR (DPX 300, Bruker). The positions at 45–85 ppm corresponded to carbons of methyl, methylene, and methine groups. The peak at 165–185 ppm referred to carbons of carboxylated groups. Its degree of substitution (DS), the number of carboxymethyl groups per glucosamine monomer unit in CMCh, was determined by pH titration and was then confirmed by elemental analysis and infrared spectroscopy from the ratio of the absorption band of carboxylate ions near 1650–1550 cm⁻¹ and the

absorption bands of C–H stretching at 1418 and 1312 cm⁻¹. The DS and molecular weight of CMCh prepared from chitosan and CMCh-L prepared from chitosan-L are presented in Table I.

Preparation of HTACh

HTACh was prepared from chitosan according to the modified method used by Seong.¹⁷



Typically, chitosan powder (10.0 g) was dissolved in 1.0% v/v acetic acid (200 mL), and then, glycidyltrimethylammonium chloride (37.6 g, 248 mmol) was added. The mixture was stirred at 70°C for 24 h and then precipitated in acetone/ethanol (1:1) three times. The product obtained was eventually filtered and dried in a vacuum oven at room temperature. The weight of the product was 18.2 g (95% yields). The chemical structure of HTACh was analyzed with solid-state ¹³C-NMR (DPX 300, Bruker). The positions at 45–85 ppm represented the carbons of methyl, methylene, and methine groups. The resonance peak at 165–185 ppm signified the carbons of *N*-acetyl groups. Its DS was determined by ¹H-NMR. The DS and molecular weight values of HTACh prepared from chitosan and HTACh-L prepared from chitosan-L are shown in Table I.

Creaming of the SNR latex

The chitosan derivatives were dissolved in deionized water (50 mL) to prepare the chitosan derivative solution. SNR latex (200 g) was then mixed with

various concentrations of the chitosan derivatives solution, and the mixtures were constantly stirred for 1 h to ensure thorough mixing of the system. The viscosity of the SNR latex/chitosan derivative mixture was measured by a viscometer (DV-II+, Brookfield, Stoughton, MA) with spindle no. 21 at a speed of 160 rpm at 25°C. The mixture was then allowed to stand at room temperature for 3 days in separating funnel. After creaming, the percentage of phase separation was calculated according to

$$\text{Phase separation (\%)} = V_1/V_0 \times 100$$

where V_1 and V_0 are the volume of the serum phase and the total volume of the latex mixture, respectively.

Characterization of SNR

The SNR in the cream phase was recovered by the addition of a small amount of 2% v/v H_2SO_4 , concentrated H_2SO_4 , and 6% v/v HCOOH . The recovered SNR was washed with deionized water, sheeted to 2 mm in thickness, and then dried in a vacuum oven at 60°C for 24 h. The percentage of recovered SNR was calculated according to the following equation:

$$\text{Recovered SNR (\%)} = W_1/W_0 \times 100$$

where W_1 and W_0 are the weight of dried SNR in the cream phase and the weight of dried SNR in the SNR latex, respectively. The contents of CMCh and HTACh remaining in the recovered SNR were determined by solid-state ^{13}C -NMR (DPX 300, Bruker) with a sample weight of 30–50 mg and measured by a thermogravimetric analyzer (SDTA 851^E, Mettler Toledo, Columbus, OH). The samples (5–10 mg) were heated at a heating rate of 20°C/min under a nitrogen atmosphere (50–600°C) and an oxygen atmosphere (600–900°C). The thermograms were recorded as a function of temperature. The percentage of transmittance of the serum phase was measured by ultraviolet–visible spectrophotometry (V-530, Jasco, Essex, UK) at 900 nm. The size of the rubber particles in the cream phase was determined by photon correlation spectroscopy (S4700, Malvern) with a He–Ne laser source at a wavelength of 488 nm and a scattering angle of 90° (in the case of CMCh) or by laser diffraction spectroscopy (Mastersizer S, Malvern) with an Ar laser source at a wavelength of 633 nm (in the case of HTACh). The ζ potential of the rubber particles in the cream phase was characterized by a Zetasizer 4 (Malvern) with an Ar laser source at a wavelength of 633 nm.

RESULTS AND DISCUSSION

Both the anionic chitosan derivative, CMCh, and cationic chitosan derivative, HTACh used as the creaming agents in this study could be completely dissolved in deionized water. A clear solution was obtained, depending on concentration of the polymer. Their solutions could be successfully mixed with SNR latex at an alkaline pH value, and homogeneous mixtures were observed.

Creaming of the SNR latex by CMCh

The creaming of the SNR latex was studied with various concentrations of CMCh solution (1.47–11.7 g/L). When the SNR latex that contained CMCh was allowed to stand at room temperature in a separating funnel, the separation of SNR particles occurred, as shown in Figure 1. SNR formed the cream phase, which floated to the top of the latex mixture because its density (0.93 g/cm³) was lower than that of water.

The creaming of SNR latex by CMCh was found to depend on the CMCh concentration, as presented in Figure 2. When CMCh below 4.40 g/L was used, almost 100% of the rubber phase was separated within 1 day. However, when greater amounts of CMCh were used, the percentage of phase separation decreased continuously with increasing concentration of CMCh. Further phase separation of SNR occurred on the second and third days, as shown by the observed rises in the percentage of phase separation of the SNR latex creamed for 2 and 3 days. The observed creaming behavior of the SNR latex at various concentrations of CMCh could be explained in relation to the viscosity of the mixture. As shown in Figure 2, the viscosity of the mixture increased rapidly with increasing concentration of CMCh. According to Stokes' law²

$$V = (2gR^2)(D_1 - D_2)/9\eta$$

where V is the particle velocity, g is the acceleration of gravity, R is the particle diameter, D_1 is the density of the particles, D_2 is the density of the medium, and η is the viscosity of the medium. The rate of movement of a suspended spherical particle under gravity is inversely proportional to the viscosity of the dispersion medium. Thus, the rapid creaming of rubber particles will be favored by a low-viscosity medium. For this reason, the separation of rubber particles was slower at a higher concentration of CMCh.

In addition to the quantitative separation of rubber from the SNR latex that was of interest, it was interesting to study the ability of CMCh to separate the rubber according to the particle size. Thus, the

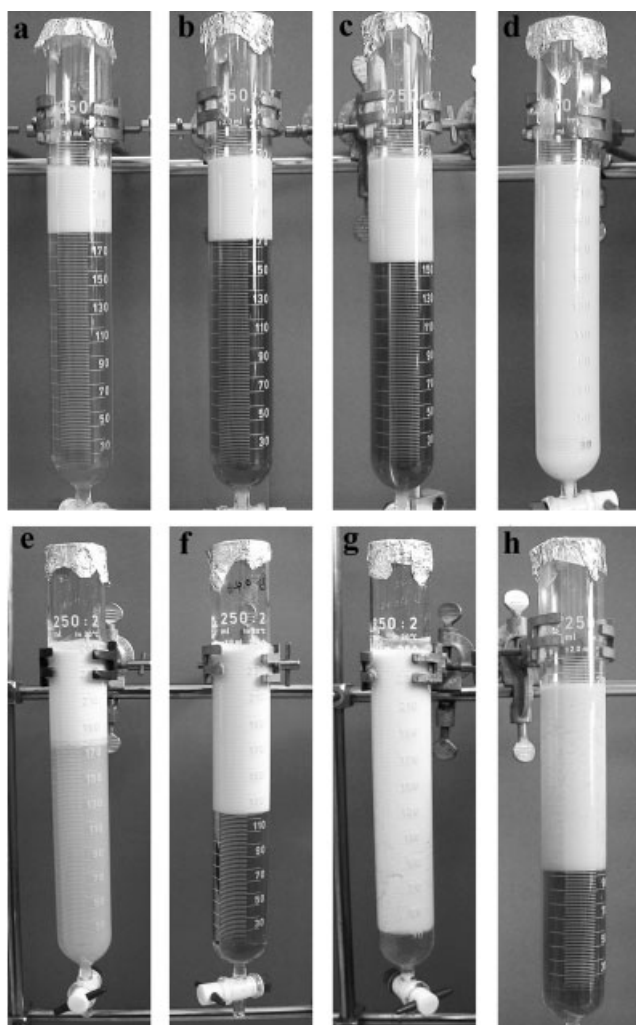


Figure 1 Photographs of the phase separation of the SNR latex with (a) 5.87 g/L CMCh, (b) 7.34 g/L CMCh, (c) 8.81 g/L CMCh, (d) 7.34 g/L CMCh-L, (e) 0.37 g/L HTACh, (f) 1.85 g/L HTACh, (g) 3.70 g/L HTACh, and (h) 1.85 g/L HTACh-L as creaming agents for a creaming time of 3 days.

average particle sizes of the rubber in the cream phase when the CMCh concentration was altered were measured. The results are shown in Table II. The average particle size of the rubber in the cream phase decreased with increasing CMCh concentration and reached a constant value of about 160 nm at CMCh concentrations of 5.87 g/L and above. This value was very close to that of the original SNR latex (152 nm). The results obtained thus confirmed that no coagulation of the rubber particles occurred by the application of CMCh as a recovering agent for the SNR latex.

Furthermore, the average particle size of the rubber remaining in the serum phase after creaming was also measured. The results are given in Table II. Again, as shown in Table II, the average particle size significantly decreased with increasing CMCh

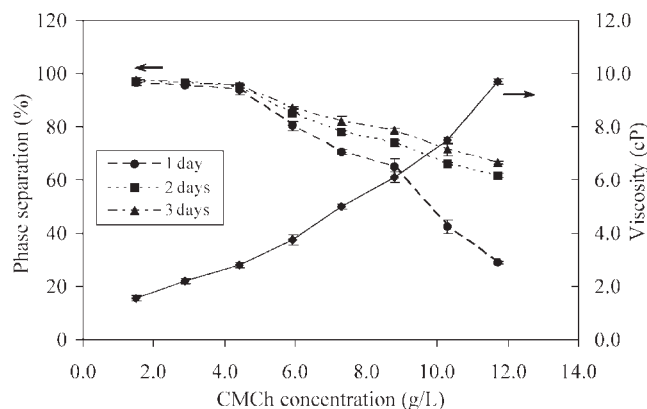


Figure 2 Percentage of phase separation and the viscosity of the mixture as functions of the CMCh concentration and creaming time.

concentration and was approximately constant at about 60 nm at CMCh concentrations of 8.81 g/L and higher. The residual particles might have been rubber and nonrubber particles. The results obtained thus showed that large rubber particles were the first to transfer to the cream phase, followed by smaller particles in respective order. This could be explained based on the speed at which the rubber particles moved up the serum phase to form the cream phase. The velocity of a particle moving through dispersion medium was directly proportional to the square of the particle diameter, according to Stokes' law, as previously cited.

To directly determine the efficiency of the recovery of SNR by this method, SNR was recovered from the cream phase by coagulation with a small amount of 2% v/v H_2SO_4 , concentrated H_2SO_4 , and 6% v/v $HCOOH$. The results are presented in Figure 3. In contrast to the difficulty in recovering SNR as a lump of rubber by the traditional procedure with concentrated H_2SO_4 , the recovery of the SNR as a lump of rubber was proven to be more efficient with the addition of the creaming step. Interestingly, the recovered SNR (in Fig. 3) was almost

TABLE II
Dependence of the Average Particle Size of Rubber in the Cream Phase and Serum Phase on the Concentration of CMCh for a Creaming Time of 3 Days

CMCh concentration (g/L)	Average particle size (nm)	
	Cream phase	Serum phase
1.47	398.2	146.3
2.94	232.0	135.6
4.40	183.7	109.6
5.87	168.1	89.9
7.34	166.3	75.6
8.81	160.1	64.1
10.3	163.9	59.5
11.7	164.2	59.2

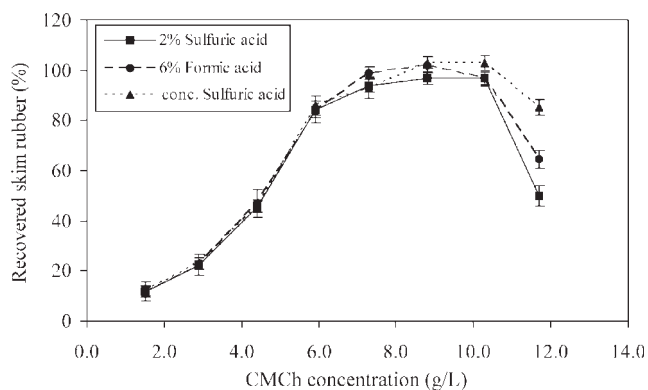


Figure 3 Recovered SNR as a function of the CMCh concentration for a creaming time of 3 days.

independent of the type and concentration of acid used. The SNR was successfully recovered even with 2% v/v H_2SO_4 or 6% v/v HCOOH . Moreover, the color of the skim rubber obtained in this study was lighter than that of SNR obtained from the traditional technique. As shown by these results, there is the possibility of reducing water-treatment costs, and the skim rubber obtained by this method might be sold at a higher price than current skim rubber. As shown in Figure 3, the quantity of SNR recovered from the SNR latex increased with increasing concentration of CMCh. SNR could be recovered from the SNR latex at more than 90% when CMCh concentrations between 7.34 and 10.3 g/L were used. It is possible that a greater number of rubber particles were transferred from the serum phase to the cream phase when the CMCh concentration was increased. This was supported by the determination of the percentage transmittance of the serum phase after 3 days of creaming. The results are shown in Figure 4. The percentage of transmittance showed maximum transmittance when the concentration of CMCh was more than 7.34 g/L. A

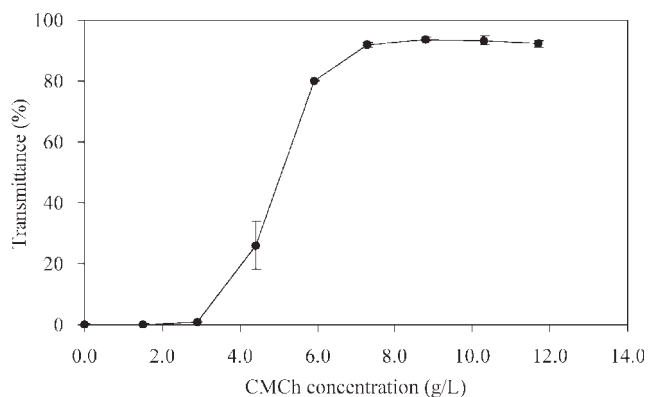


Figure 4 Transmittance at 900 nm of the serum phase as a function of the CMCh concentration for a creaming time of 3 days.

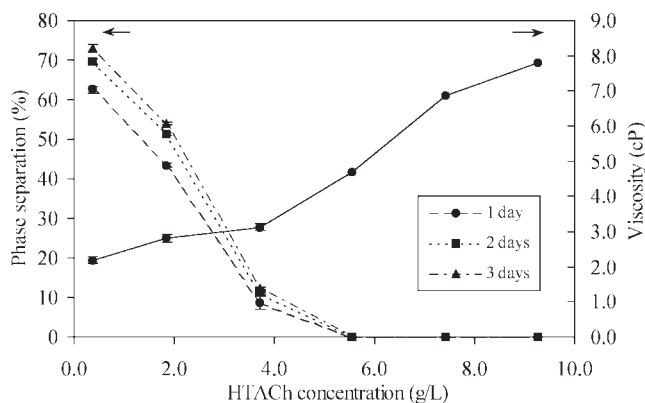


Figure 5 Percentage of phase separation and the viscosity of the mixture as a function of the HTACH concentration and creaming time.

decrease in the percentage of recovered SNR occurred when too high a concentration of CMCh (>10.3 g/L) was used. This might have been due to the low percentage of phase separation (see Fig. 2). The SNR concentration in the cream phase was too low to recover the rubber efficiently. A concentration of 7.34–10.3 g/L of CMCh provided recovered SNR more than 90%.

Creaming of the SNR latex by HTACH

The creaming of the SNR latex by the cationic HTACH was studied with various concentrations of HTACH solution (0.37–9.26 g/L). When the SNR latex that contained HTACH was allowed to stand at room temperature in a separating funnel, the separation of SNR particles also occurred, as shown in Figure 1. The creaming of the SNR latex by HTACH was found to be dependent on the HTACH concentration and creaming time, as shown in Figure 5. The creaming of the SNR latex was achieved with a very small amount of HTACH compared to CMCh. The percentage of phase separation showed a continuous decrease with increasing HTACH concentration, which could be explained in relation to the viscosity of the mixture, as described in a previous section. The percentage of phase separation that could be affected by HTACH was much lower than that affected by CMCh. The other feature of the creaming of the SNR latex by HTACH that was different from that by CMCh was that the percentage of phase separation decreased much more rapidly with increasing concentration of HTACH. In fact, no phase separation was observed when more than 3.70 g/L HTACH was used.

The creaming efficiency of HTACH was elucidated by the determination of the percentage transmittance of the serum phase after creaming for 3 days (Fig. 6). As shown by our results, the percentage

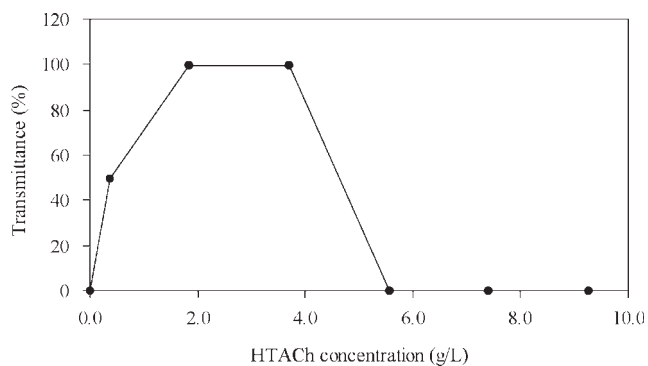


Figure 6 Transmittance at 900 nm of the serum phase as a function of the HTACh concentration for a creaming time of 3 days.

transmittance increased with increasing HTACh concentration and reached almost 100% transmittance when the concentration of HTACh was in the range 1.85–3.70 g/L. This means that rubber particles could be completely transferred from the serum phase to the cream phase. However, the percentage transmittance abruptly declined after 3.70 g/L HTACh, which corresponded to the absence of phase separation observed previously. An attempt to recover solid SNR in the cream phase by coagulation with dilute acid was met with failure. This might have been because of the adsorption of positively charged HTACh on the surface of the rubber particles. To collect the skim rubber from the cream phase, an evaporation method could be used instead of an acid coagulation technique. This was in contrast to the recovery of SNR by CMCh, where a coagulum could easily be obtained by the addition of small quantity of dilute acid.

Mechanism of creaming

Creaming with CMCh

To elucidate the mechanism of creaming, the SNR recovered from the cream phase was analyzed with solid-state ^{13}C -NMR and thermogravimetric analysis (TGA). The purpose was to determine the CMCh content in the recovered SNR. The results are presented in Figures 7 and 8, respectively. As shown in the solid-state ^{13}C -NMR results in Figure 7, small, broad peaks assigned to CMCh appeared at 45–85 and 165–185 ppm in the recovered SNR [Fig. 7(a)]. These peaks, however, disappeared after the recovered SNR was washed several times with water [Fig. 7(b)]. Furthermore, the TGA results displayed in Figure 8(c) also reveal the absence of CMCh in the recovered SNR. The results obtained, thus, indicate that residual CMCh present in the recovered SNR only weakly interacted with the rubber.

The mechanism that is usually used to explain the flocculation of dispersed solid particles is the

bridging mechanism. Here, the agglomeration of the particles is assisted by the entanglement of macromolecules that are adsorbed on the particles. In the case of CMCh, the adsorption of CMCh molecules on the SNR particles should not have been possible because CMCh molecules carry negative charges (see the structure of CMCh), similar to the charges on the surface of SNR particles. This was supported

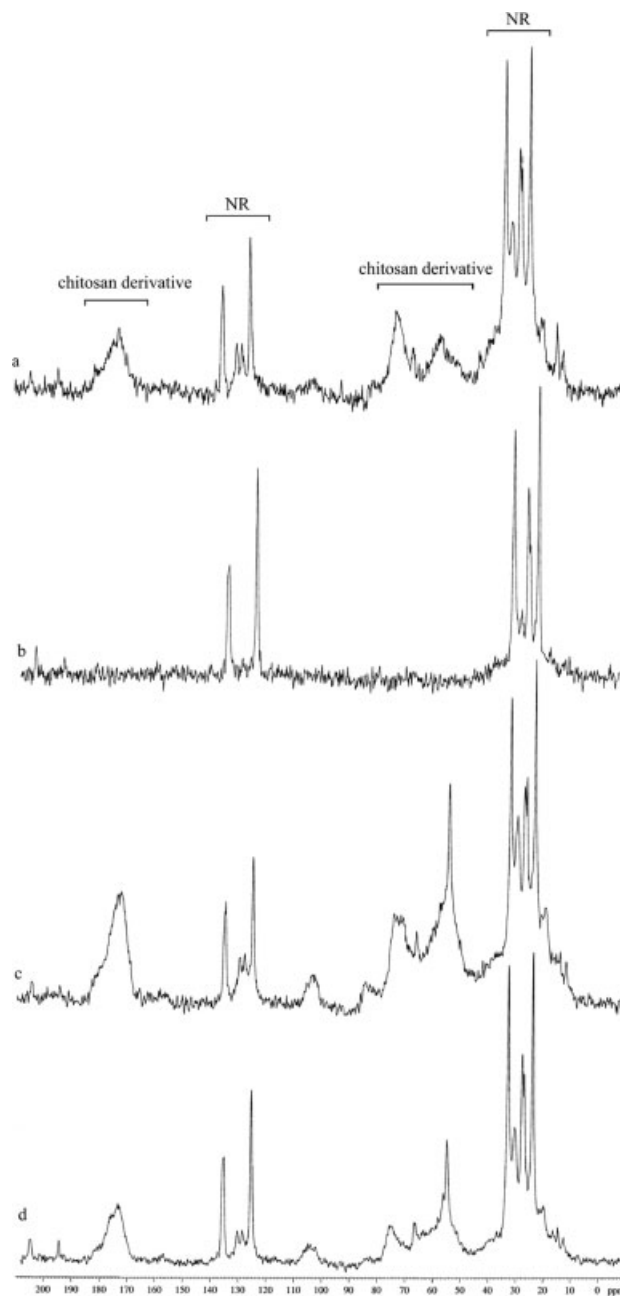


Figure 7 Solid-state ^{13}C -NMR spectra of recovered SNR obtained with (a) 6.00 g/L CMCh as a creaming agent before washing with water, (b) 6.00 g/L CMCh as a creaming agent after washing with water, (c) 4.00 g/L HTACh as a creaming agent before washing with water, and (d) 4.00 g/L HTACh as a creaming agent after washing with water.

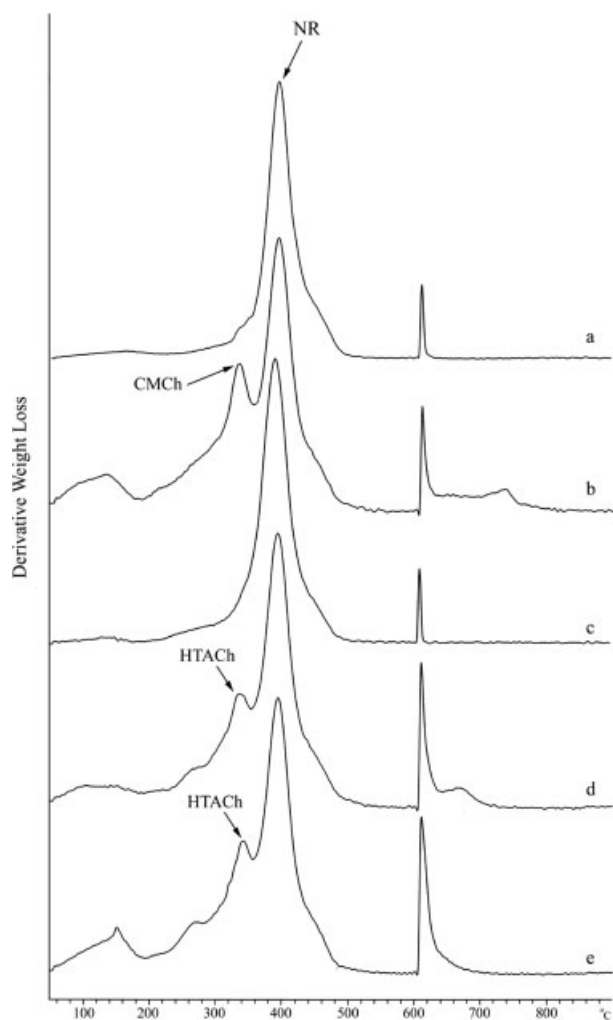


Figure 8 TGA derivative thermograms of (a) NR, (b) SNR mixed with 6.00 g/L CMCh, (c) recovered SNR obtained with 6.00 g/L CMCh as a creaming agent, (d) SNR mixed with 4.00 g/L HTACh, and (e) recovered SNR obtained with 4.00 g/L HTACh as a creaming agent.

by the observation that very little CMCh was present in the recovered SNR and that it was also easily removed by washing with water [Figs. 7(b) and 8(c)]. Furthermore, it was previously noted that CMCh did not cause coagulation of the rubber particles (Table II). Therefore, the bridging mechanism was not the operating mechanism for the flocculation of SNR particles by CMCh.

An alternative flocculation mechanism that has been known for quite some time is the depletion mechanism.^{21–24} According to this mechanism, when pairs of rubber particles approach within a distance of less than the mean diameter of free CMCh molecules in the latex, the CMCh molecules will be depleted from between the rubber particles. The osmotic pressure between the particles is, therefore, lower than the pressure around them, and the water will flow out from the particles. Thus, the rubber

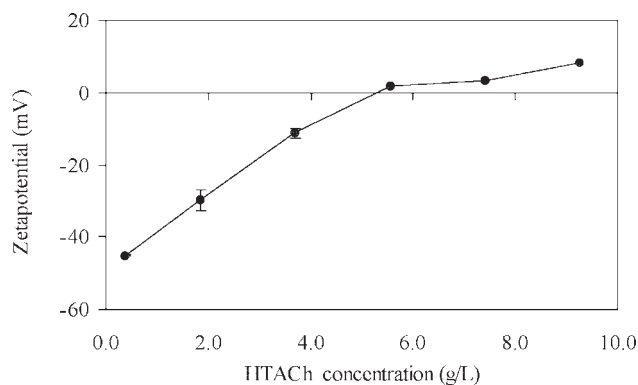


Figure 9 ζ potential of the rubber particles in the cream phase as a function of the HTACh concentration for a creaming time of 3 days.

particles will be pushed closer together. As successive particles form clusters, their buoyancy is sufficient to cause them to move upward through the aqueous phase. Thus, phase separation between the cream and serum phases occurs. Additional evidence in support of the depletion flocculation mechanism is that when the size of CMCh molecules was decreased to a weight-average molecular weight (M_w) value of 27,600 g/mol from the previously used M_w of 690,000 g/mol, no creaming was observed under the exact same conditions [Fig. 1(d)]. This may be explained by the fact that small CMCh molecules, by virtue of their size, might have been more difficult to deplete from between the rubber particles. Therefore, a sufficiently close approach of the rubber particles was not possible for flocculation to take place. This supported a simple mathematical model developed to predict the stability of multilayer systems.^{25,26} The effective radius of the creaming agent molecules in solution is a major factor influencing the concentration of the creaming agent needed for the depletion flocculation. In practice, the effective radius will increase as the molecular weight increases.²⁷ A higher concentration of CMCh would be required in the case of small CMCh molecules.

TABLE III
Dependence of the Average Particle Size of Rubber in the Cream Phase on the Concentration of HTACh for a Creaming Time of 3 Days

HTACh concentration (g/L)	Average particle size (μm)
0.37	17.4
1.85	139.1
3.70	188.8
5.56	56.8
7.41	43.8
9.26	42.0

Creaming with HTACH

Experimental evidence that supported the proposal of the mechanism of creaming of the SNR latex by HTACH was obtained from solid-state ^{13}C -NMR, TGA, and measurements of the ζ potential and particle sizes of the rubber particles in the cream phase. These are presented in Figures 7–9 and Table III. Figure 8 shows the TGA results of the SNR recovered with 4.00-g/L HTACH and also the mixture of SNR and HTACH. It was obvious that a substantial amount of HTACH was present in the recovered SNR. The solid-state ^{13}C -NMR results given in Figure 7 also show the presence of HTACH in the recovered SNR, as indicated by peaks at 45–85 and 165–185 ppm [Fig. 7(c,d)]. Furthermore, after the recovered SNR was washed with water, the solid-state ^{13}C -NMR results also signify the existence of a significant quantity of HTACH in the recovered SNR. Because HTACH is a polymer containing positive charge, we envisaged that HTACH became adsorbed to the negatively charged rubber particles. This was confirmed by the measurement of the ζ potential of the SNR particle in the cream phase. As shown in Figure 9, the ζ potential of the SNR particles in the cream phase became increasingly less negative as the concentration of HTACH used increased. At a concentration of 5.56-g/L HTACH, the charges on the rubber particles changed from negative to positive charges, which indicated an excess adsorption of HTACH on the SNR particles. The adsorption of the positively charged HTACH on the negatively charged SNR particles was expected to cause a decrease in the stability of the SNR particles as the charges on the SNR particles, which colloiddally stabilized them, were reduced. This was indeed the case because measurement of the average size of the SNR particles as a function of increasing HTACH concentration, as presented in Table III, showed an increase in the rubber particle sizes as the concentration of HTACH was increased. However, beyond an HTACH concentration of 3.70 g/L, the tendency of the SNR particles to become aggregated began to decrease and reached a constant value of 40 μm at an HTACH concentration between 7.41 and 9.26 g/L. This may have been explained by the fact that above an HTACH concentration of about 5.56 g/L, the charge on the surface of the SNR particles completely reverted from a negative charge to a positive charge; thus, the SNR particles were effectively stabilized again. The data presented provide other evidence that the adsorption of HTACH on the SNR particles did occur. We concluded, therefore, that the flocculation of the SNR particles by HTACH took place by the bridging mechanism.

Also, when HTACH-L (24,700 g/mol) was used, the flocculation and creaming of the SNR latex also occurred [Fig. 1(h)].

CONCLUSIONS

The creaming of the SNR latex could be achieved with both an anionic chitosan derivative (CMCh) and a cationic chitosan derivative (HTACH) as creaming agents. Phase separation between the cream and serum phases depended on the chitosan derivative concentration and the creaming time. With CMCh as the creaming agent, no coagulation of the rubber particles in the cream phase occurred. Solid skim rubber could be recovered from the cream phase by the addition of a small amount of 2% v/v H_2SO_4 , concentrated H_2SO_4 , or 6% v/v HCOOH . CMCh (7.34–10.3 g/L) provided recovered skim rubber at more than 90%. The creaming mechanism was proposed to be a depletion flocculation mechanism. For HTACH, the creaming of the SNR latex was affected at a lower concentration of HTACH (<3.70 g/L) than in the case of CMCh, but particle aggregation of the rubber particles were observed. An adsorption mechanism was proposed to play a role here.

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