CHAPTER III

WATER-SOLUBLE CHITIN-CHITOSAN DERIVATIVES AND THEIR APPLICATIONS ON A RUBBER FLOCCULANT

3.1 Abstract

A series of water-soluble chitosan derivatives, i.e. CM-CS, CS-HOBt, CS-Acetate, and Iodo-CS, is successfully prepared. The chitosan derivatives obtained initiate the agglomeration of natural rubber particles and perform the phase separation of rubber from natural rubber latex. The optimal concentration of the water-soluble chitosan derivative required to separate the rubber coagulum is evaluated. The residual flocculant in the resulting dry rubber was determined by using thermogravimetric analysis (TG-DTA), is reported.

Keywords: Chitin-chitosan, Water-soluble chitosan, flocculants, Natural rubber (NR)

3.2 Introduction

Natural rubber (NR) latex can be obtained from the *Hevea brasiliensis* tree and is presented as a colloidal system of rubber particles in aqueous serum.[1] In freshly tapped NR latex, the rubber particles are enrobed in a continuous monolayer of negatively charged phospholipid-protein complex providing the stability for colloidal system.[2,3] The rubber latex includes polyisoprene and non-rubber components such as lutoids, Frey-Wyssling particles protein, carbohydrate, lipid, inorganic, and organic salts.[4]

In general, coagulation of natural rubber latex has been done by adding acids such as formic acid or sulfuric acid. Some salts, for example sodium silicofluoride, are also reported as precipitating agents functioning at pH 5.1-4.8.[4] The acidic coagulation

of latex is practical since it is simple and cheap. However, the consequent acid mal-order treatment is also needed in order to achieve the product without smell.[5]

As ecologically friendly materials become an ultimate goal for product development in this area, the separation of rubber from the latex is also a case that needs some improvement to avoid environmental problems. The concept of "flocculation", which emphasizes the effective interaction of polymer chains with colloidal particles, allows us to develop a functional polymer to substitute the coagulant. The interaction of the flocculant and colloidal particles might be van der Waals interaction via hydrophobicity or hydrophilicity, hydrogen bonding, ionic interaction, etc., including a synergistic interaction. Poly[2-(N,N,N-trimethylamino)-ethyl acrylate] (chloride salt) is an example of a cationic acrylamide-based copolymer flocculant used for metal ion removal in water treatment.[6]

Flocculation in synthetic rubber latex treatment has already been developed. For example, Verezhnikov et al. reported the use of poly-N,N-dimethyl-N,N-diallylammonium chloride as a cationic flocculant to separate styrene-butadiene rubber from latex.[7] Shatalov et al. reported the flocculation of synthetic rubber latex using homopolymers of N-vinylcaprolactam and water-soluble copolymers of N-vinylcaprolactam and N-vinylimidazoles.[8] Verezhnikov et al. showed the use of water-soluble polymeric ammonium salts of N,N-dimetylaminoethyl methacrylate and mineral acids in butadiene-styrene latex flocculation.[9]

The difference between coagulant and flocculant is as follow. In general, coagulants are small molecules those especially acids whereas flocculants are polymer with ionic charges. The significant difference between coagulation and flocculation is about the aggregation of rubber from NR latex. The coagulation gives a hard coagulum due to the slow coagulation whereas only small amount of flocculation initiates aggregation of microparticles via charge-charge interaction of polymer and rubber particles.

Although the concept of using ionic polymer as a flocculant is another choice to separate ionic colloidal solution, the degradability after use is another point to be

considered.[10] On this viewpoint, an environmentally friendly biodegradable flocculant is an ideal.

In the case of NR latex, the effective and efficient flocculant should meet the following requirements: (i) the biodegradability, so that the polymer, after use, will not remain in the environment; (ii) the effectiveness, which allows us to use only in small amount and the elimination from the system after use will not be the problem; (iii) the water solubility, which would enable a simple step of washing thoroughly by water to exclude the polymer from the aggregated particles; and, (iv) the availability and the cost effectiveness so that the flocculation treatment will not affect the price of the rubber.

Chitin-chitosan is the most abundant naturally occurring amino polysaccharide, found in the shells of crustaceans, insects, and in the cell walls of fungi and algae.[11] The specific properties of chitin-chitosan are biodegradability, biocompatibility, and non-toxicity[12] whereas its amino-copolysaccharide structure brings the cationic performance. As chitin-chitosan is under the inter- and intramolecular hydrogen bond network, it is difficult to dissolve in most solvents. The derivatization of chitin to chitosan with percent deacetylation more than 80 brings chitosan be soluble in acids. Modification of chitosan with carboxylate salts as seen in the case of N,O-carboxymethyl chitosan is a good way to bring water solubility to chitosan. Based on the above mentioned points, chitosan is a potential material to develop as a flocculant for NR. Recently, Chaikumpollert *et al.* proposed the use of N-(2-hydroxy)propyl-3-trimethylammonium chitosan chloride as a flocculant in collecting rubber particles remained in skim NR latex.[13]

The present work, thus, focuses on flocculation induced by water-soluble chitosan derivatives. The work covers the comparative studies on a series of derivatives to clarify the factor related to the flocculation efficiency.

3.3 Experimental

3.3.1 Materials

Chitosan with 95% deacetylation (MV = 255,000 g/mol) was provided by Sea Fresh (Lab) Company Limited, Thailand. Natural rubber (NR) latex (dry rubber content ~ 31%) was supplied by Unimac Rubber Co., Ltd, Thailand. N,N'-Carbonyldiimidazole (CDI) was obtained from TCI, Japan. 1-Hydroxybenzotriazole monohydrate (HOBt·H2O) was purchased from Wako Pure Chemical Industries Co. Ltd., Japan. N,N-dimethylformamide (DMF), methanol, ethanol, and acetone were purchased from Acros, USA. Sodium hydroxide, phthalic anhydride, 1-methyl-2-pyrrolidone and monochloroacetic acid were achieved from Fluka Chemicals, Switzerland. Iodomethane was obtained from Sigma aldrich, The Netherlands. Acetic acid and hydrochloric acid were purchased from Labscan, Ireland. All chemicals were AR grade and used without further purification.

3.3.2 Instruments and equipment

Fourier transform infrared (FTIR) spectrum was obtained from a Thermo Nicolet Nexus 670 (Madison, USA). The analysis was carried out with 32 scans at a resolution of 2 cm^{-1}, over a frequency range of 4000–400 cm^{-1}. Proton nuclear magnetic resonance spectra (^{1}H-NMR) were collected from a Bruker Avance 400 spectrometer with 512 scans by using CD_3COOD/D_2O (2% v/v) as solvent. Wide angle X-ray diffraction (WAXD) patterns were recorded over 2–35° (2θ) by a RIGAKU RINT 2000 (Tokyo, Japan) using Cu Kα as an X-ray source equipped with a Ni filter with operating conditions of 40 kV and 30 mA. Thermogravimetric analyses were carried out using a Perkin–Elmer Pyris Diamond TG-DTA (Connecticut, USA) with N_2 flow rate of 20 mL/min and a heating rate of 10 °C/min starting from 50 to 500 °C. The molecular weight of chitosan was determined by using Cannon-Ubbelohde (No.2, A149), in 0.2M

$CH_3COOH/0.1M$ CH_3COONa aqueous solution at 30 ± 0.05 °C. Particle size was observed by a Mastersizer X particle size analyzer (Malvern, UK). The zeta potential was determined at 25 °C by a Zetasizer Nano ZS (Malvern Instrument, UK). Contact angle was evaluated by a DSA10 Mk2 (KRÜSS, Germany) drop shape analysis system.

3.3.3 Synthesis of water-soluble chitosan derivatives

Chitosan-hydroxybenzotriazole, CS-HOBt (Scheme 3.1)

CS-HOBt was prepared as reported previously by Fangkangwanwong *et al.*[14] Briefly, chitosan (1g, 0.006 mol) was vigorously stirred with HOBt 0.94 g (1 mol equivalent to pyranose ring) in aqueous system at ambient temperature until the clear solution was obtained. The powder product was obtained by using a freeze dryer.

FTIR (KBr, cm^{-1}): 3500-3000 cm^{-1} (-OH), 2900-3000 cm^{-1}(-CH_3), 1561 cm^{-1} (-NH_3^+), and 1250-895 cm^{-1} (-C-O-).

^{1}H-NMR (δ, ppm): 1.9 ppm (H-Ac), 3.1 ppm (H-2 of pyranose ring), 3.5-3.9 ppm (H-3 to H-6 of pyranose ring), and 7.2-7.6 ppm (H of benzene ring).

Carboxymethyl chitosan, CM-CS (Scheme 3.1)

CM-CS was prepared as reported by Chen and Park.[15] In short, chitosan (10g, 0.061 mol) was dispersed in the solution of NaOH (13.5 g) in 80% isopropanol (100 mL) at 50 °C for 1 h. The solution of monochloroacetic acid (15g, 0.159 mol) in isopropanol (20 mL) was dropped wisely and reacted at the same temperature for 4 h. The reaction was stopped by adding 70% ethanol (200mL) to obtain Na^+-form of CM-CS which was washed by 70-90% ethanol and dried in vacuum oven at room temperature.

The Na^+-form of CM-CS (1g, 0.004 mol) was stirred in 80% ethanol 100 mL. The 37% hydrochloric acid was added and reacted at ambient temperature for 30 min to obtain H-form of CM-CS. The product was washed by 70-90% ethanol and dried in vacuum oven at room temperature.

FTIR (KBr, cm⁻¹): 3500-3000 cm⁻¹ (-OH), 2900-3000 cm⁻¹(-CH₃), 1729 cm-1 (-C=O), and 1250-895 cm⁻¹ (-C-O-).

¹H-NMR (δ, ppm): 1.9 ppm (H-Ac), 3.1 ppm (H-2 of pyranose ring), 3.2 ppm (H-b), 3.5-3.9 ppm (H-3 to H-6 of pyranose ring), and 4.1 ppm (H-a).

Chitosan-acetate, CS-Acetate (Scheme 3.1)

Chitosan (1g, 0.006 mol) was stirred in acetic acid (1 mol equivalent to pyranose ring of chitosan) in aqueous solution to obtain clear solution. CS-Acetate was freeze dried to obtain powder product.

FTIR (KBr, cm⁻¹): 3500-3000 cm⁻¹ (-OH), 2900-3000 cm⁻¹(-CH₃), 1561 cm⁻¹ (-NH₃⁺), 1644 cm⁻¹ (-COO-), and 1250-895 cm⁻¹ (-C-O-).

¹H-NMR (δ, ppm): 1.7 ppm (H-a), 1.9 ppm (H-Ac), 3.1 ppm (H-2 of pyranose ring), and 3.5-3.9 ppm (H-3 to H-6 of pyranose ring).

Iodochitosan, Iodo-CS (Scheme 3.1)

Iodo-CS was prepared following the method reported by Domard[16]. Chitosan (1 g, 0.006 mol) was dispersed in 1-methyl-2-pyrrolidone (50 mL) at ambient temperature for 12 h. 1.4 M NaOH (8.76 mL, 0.012 mmol) and iodomethane (5.77 mL, 0.092 mmol) were added and reacted at 36 °C for 6 h under N₂. The product was precipitated in ethanol and dried in vacuo.

FTIR (KBr, cm⁻¹): 3500-3000 cm⁻¹ (-OH), 2900-3000 cm⁻¹(-CH₃), and 1250-895 cm⁻¹ (-C-O-).

¹H-NMR (δ, ppm): 1.9 ppm (H-Ac), 3.0 ppm (H-a), 3.2 ppm (H-2 of pyranose ring), and 3.6-3.9 ppm (H-3 to H-6 of pyranose ring).

Zeta potential and contact angle of all water-soluble chitosan derivatives were determined by using a Zetasizer Nano ZS and contact angle analysis.

Scheme 3.1 Preparation of (a) CS-HOBt, (b) CM-CS, (c) CS-Acetate, and (d) Iodo-CS
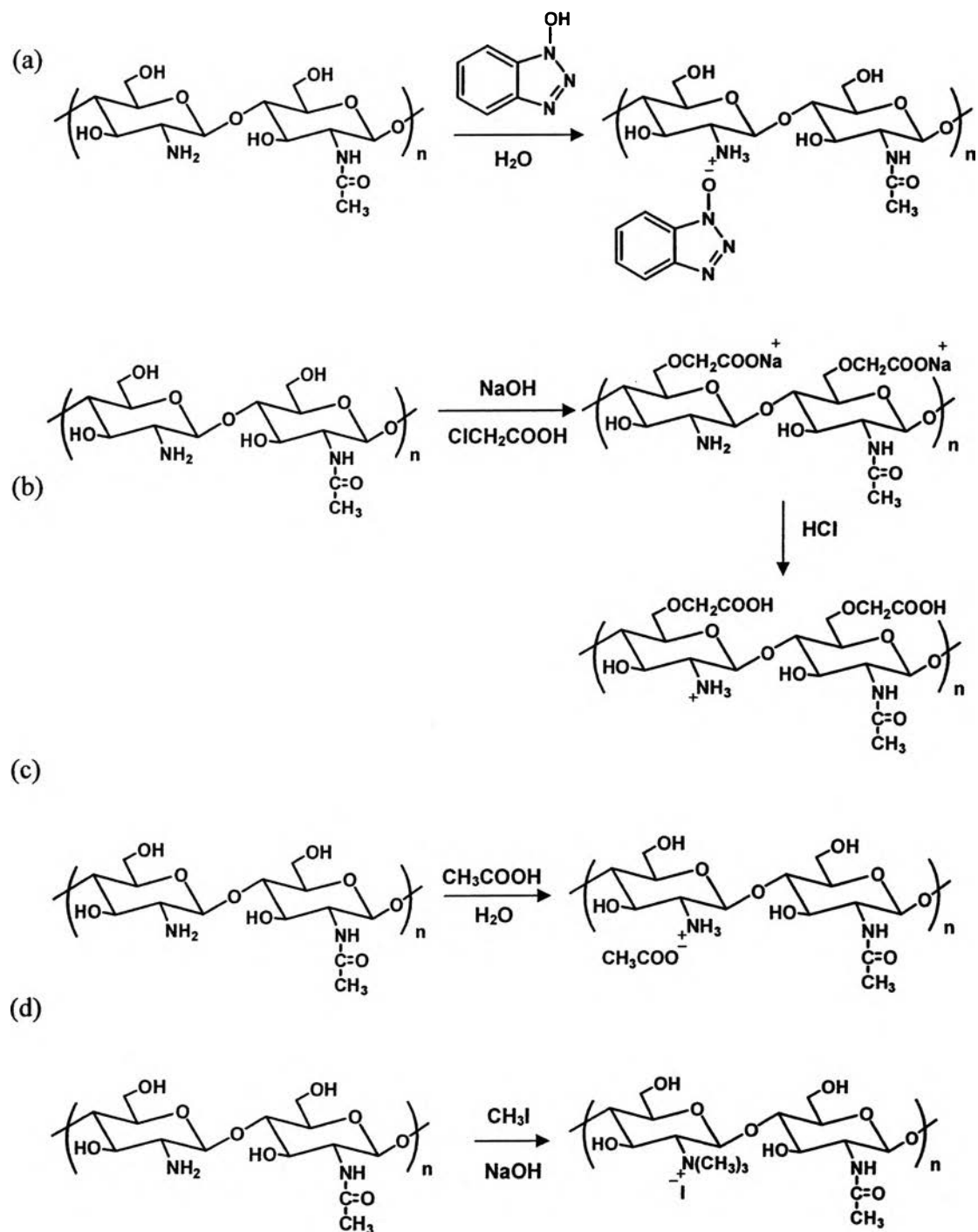
3.3.4 Natural rubber flocculation

Each aqueous solution of water-soluble chitosan derivative was prepared at the concentrations of 0.0125, 0.025, 0.0375, 0.05, 0.075, 0.1, and 0.125 M. The solution obtained (30 mL) was used to mix with NR latex (5g). After 24 h, the particle size of NR latex was determined by particle size analyzer. The rubber phase was collected by filtrating the serum using sieve with 180 μm ± 10 μm mesh size according to ISO-706:2004. Then, the rubber obtained was washed with distilled water 500 mL and dried at 60-70 °C. The recovered rubber efficiency was determined by using the following equation.

$$\text{Recovered rubber efficiency (\%)} = \left[\frac{\text{Recovered rubber (g)} \times 100}{\text{Dry rubber content (g)}} \right] - \text{\%Content}^* \quad (1)$$

*%Content is the remaining of water-soluble chitosan derivatives, water, and ash in the rubber, which were determined by using thermogravimetric-differential thermal analyzer (TG-DTA).

3.4 Results and discussion

3.4.1 Characterization of chitosan and its derivatives

FT-IR of chitosan (Figure 3.1a) shows the typical peaks at 1661, 1595 cm^{-1} (amide I and -NH$_2$ group), 1250-895 (-C-O-) and 3500-3000 cm^{-1} (-OH) and ^{1}H-NMR of chitosan gives the chemical shift at 3.5-3.9 ppm (H-3 to H-6 of pyranose ring), 3.1 ppm (H-2 of pyranose ring), and 1.9 ppm (-CH$_3$ of chitin unit).

CS-HOBt was successfully prepared in an aqueous system as confirmed by FT-IR and ^{1}H-NMR techniques. FT-IR shows the new peak at 1561 and 742 cm^{-1} implying the protonated -NH$_3^+$ of chitosan (Figure 3.1b). ^{1}H-NMR also shows the new

chemical shift at 7.2-7.6 ppm belonging to HOBt in chitosan as shown in Figure 3.2a. The results are relevant to those reported by Fangkangwanwong et al.[14]
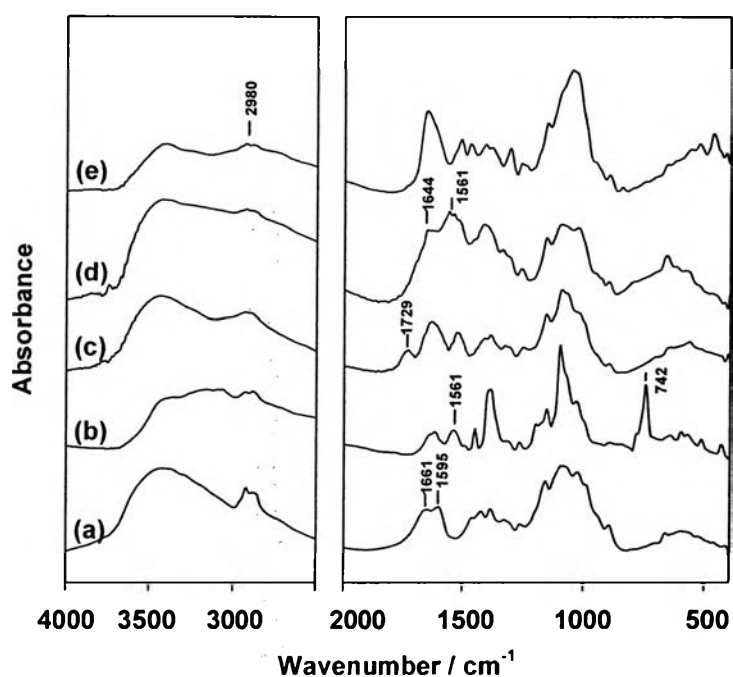
Figure 3.1 FT-IR spectra of (a) chitosan, (b) CS-HOBt, (c) CM-CS, (d) CS-Acetate, and (e) Iodo-CS.

For CM-CS, the new peak of –COOH group is at 1729 cm^{-1} (Figure 3.1c). Figure 3.2b shows ^{1}H-NMR spectrum with the new signals from H-a and H-b at 3.2 and 4.1 ppm, which are similar to those reported by Chen and Park.[15]

The degree of substitution on –OH and –NH$_2$ was calculated based on the number of proton atoms at H-a and H-b. CM-CS has carboxymethyl group on –OH and –NH$_2$ by 40 and 19%, respectively.[17,18]

By simply mixing chitosan with acetic acid, an aqueous system of CS-Acetate was obtained. CS-Acetate shows the new band of NH$_3^+$ and COO$^-$ at 1561 and 1644 cm^{-1}(Figure 3.1d) indicating that the -NH$_2$ group of chitosan was protonated by

acetate group. From ^{1}H-NMR result, the new signal at 1.8 ppm confirming the acetate group incorporated in chitosan as shown in Figure 3.2c.
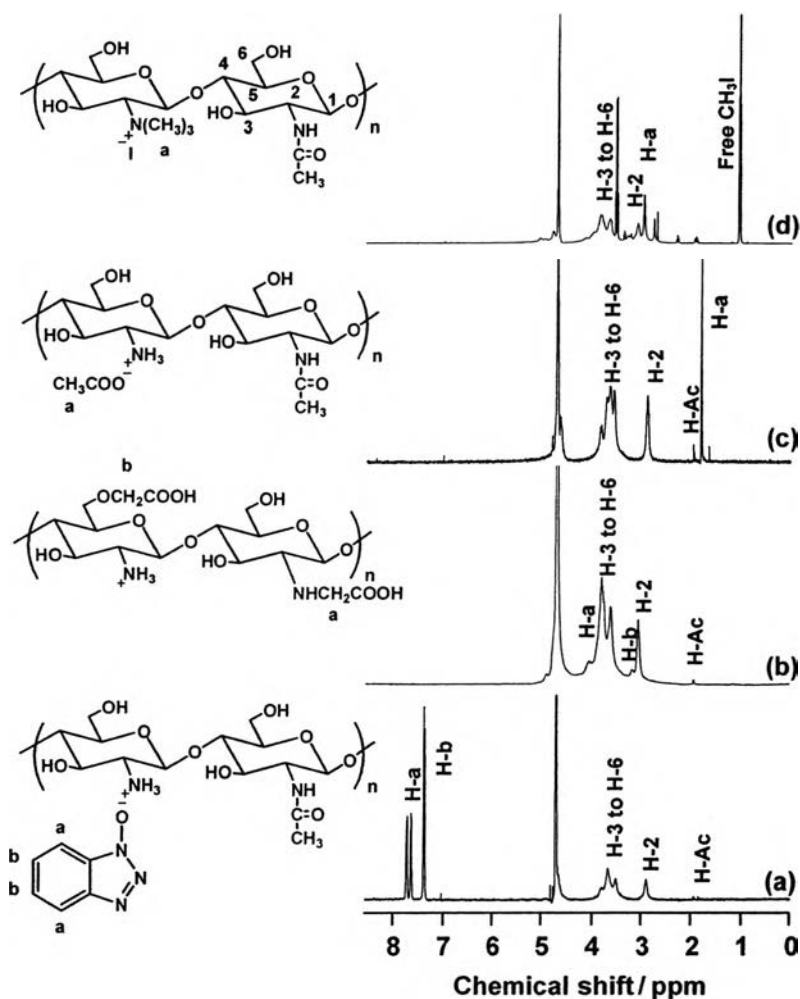
Figure 3.2 ^{1}H-NMR spectra of (a) CS-HOBt, (b) CM-CS, (c) CS-Acetate, and (d) Iodo-CS.

For Iodo-CS, FT-IR spectrum shows the significant –CH– stretching peak at 2980 cm^{-1} and whereas the disappearance of the peak at 1590 cm^{-1} (-NH$_2$ group) indicating the structure of –N(CH$_3$)$_3$ (Figure 3.1e). ^{1}H-NMR shows the new chemical shift of –N(CH$_3$)$_3$ at 3.0 ppm and free CH$_3$I at 1.0-1.1 ppm (Figure 3.2d). The number of proton atoms at –N(CH$_3$)$_3$ was determined the degree of substitution of iodomethane to be 15%.[19]

Packing Structure and Thermal stability

The thermal stability of chitosan and its derivatives was studied by using TG-DTA under N_2 atmosphere to identify the degradation temperature (T_d) of chitosan and its derivatives as shown in Table 3.1. Figure 3.3 shows the WAXD pattern of each derivative. In general, chitosan shows the peaks at 9-10° (2θ) and 19-20° (2θ) reflecting the hydrogen bond network in the structure. For the derivatives, the peaks are observed. CS-HOBt shows the peak shift from 10° to 5° (2θ) (Figure 3.3b). It should be noted that CS-Acetate retains the peaks as similar to chitosan. The thermal stabilities of all derivatives were summarized in Table 3.1. Chitosan shows the T_d at 300 °C whereas CS-HOBt, CM-CS, and Iodo-CS show the T_d at 234-240 °C. For CS-Acetate, the degradation temperature is close to that of chitosan. Taking WAXD pattern and T_d of CS-Acetate into the consideration, CS-Acetate might maintain the H-bond network similar to that of chitosan.

Table 3.1 Degradation temperature (T_d) of chitosan and its derivatives

Compound	T_d / °C
Chitosan	300
CS-HOBt	237
CM-CS	238
CS-Acetate	291
Iodo-CS	234
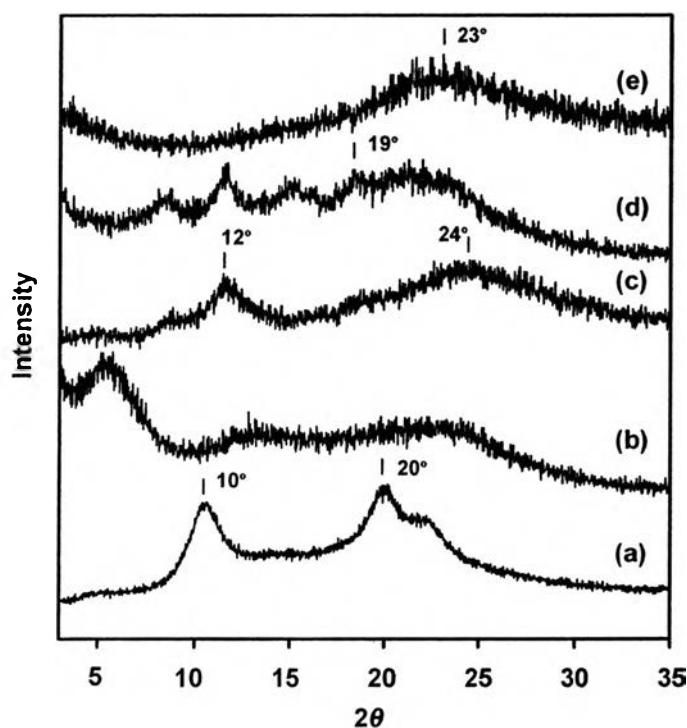
Figure 3.3 WAXD patterns of (a) chitosan, (b) CS-HOBt, (c) CM-CS, (d) CS-Acetate, and (e) Iodo-CS.

Zeta potential and contact angle characteristics

The zeta potential of NR latex and water-soluble chitosan derivatives was observed to clarify the charge on the surface. The rubber particles in NR latex exhibit the negative charge of 48.4 ± 5.4 mV, whereas the water-soluble chitosan derivatives demonstrate the positive charge as shown in Table 3.2. For example, Iodo-CS shows the highest zeta potential value as compared to other water-soluble chitosan derivatives. In other words, Iodo-CS has the highest positive charge among all derivatives in the experiment. As the high positive charge is a key factor in neutralizing and forming bridge on rubber particles[6,12], Iodo-CS can be expected to show a significant flocculation ability.

The contact angle was observed to identify hydrophobicity and hydrophilicity of the derivatives. Table 3.2 summarizes the contact angle of each derivative. CS-Acetate shows the significant hydrophilicity whereas other derivatives are rather hydrophobic. The hydrophobicity is also another key factor to evaluate the interaction between rubber particles and flocculant. Iodo-CS shows the highest contact angle value, which is $81.5°$, indicating that Iodo-CS has high hydrophobicity as compared to the other water-soluble chitosan derivatives.

Table 3.2 Zeta potential and contact angle value of water-soluble chitosan derivatives

Water-soluble chitosan derivatives	Zeta potential /mV	Contact angle /°
CS-HOBt	45.09 ± 2.41	57.4 ± 6.2
CM-CS	42.17 ± 2.79	60.8 ± 4.7
CS-Acetate	61.38 ± 1.99	14.8 ± 1.8
Iodo-CS	75.06 ± 7.54	81.5 ± 3

3.4.2 Rubber flocculation

Acids, such as acetic and formic acid, are good coagulants to coagulate NR particles to form coagulum at pH~4.[6] Here, the water-soluble chitosan derivatives were applied as cationic flocculants for rubber flocculation.
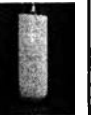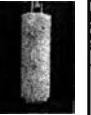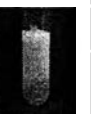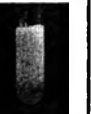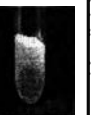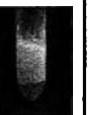
Table 3.3 tabulates the appearances of rubber flocculation and pH values after adding water-soluble chitosan derivatives at various concentrations. In the case of CM-CS, the pH value of mixture decreases from pH 10 (NR latex) to pH 6 with increasing the concentration of CM-CS. The phase separation of rubber phase gradually proceeded. As an index of the phase separation, a rough guideline of flocculation efficiency can be estimated. Here, CS-Acetate, CS-HOBt, and Iodo-CS show clearly phase separation at the concentration of 0.075 M mixed in the NR latex.

In order to carry out qualitative and quantitative evaluation for the flocculation, the particle size of the latex obtained from each step were statistically analyzed. Figure 3.4(A) shows the concentration dependency of particle sizes of the aggregated rubber belonging to CM-CS system. It is clear that the peak due to initial particle size of 0.2-1.5 μm significantly decreases and the peak including the particle size of 1.6-26.7 μm and 26.8-148.7 μm gradually increases in amount. Figure 3.4(B) shows the statistic of the rubber particle at each CM-CS concentration in NR latex system. It should be noted the rubber particle exists in NR latex with the size of 0.2-1.5 μm (Figure 3.4 (B)). Here, the disappearance of 0.2-1.5 μm rubber particles is determined at the initial phase separation concentration. It is clear that the initial phase separation concentration for CM-CS is 0.075 M.

Figure 3.5 shows the initial concentration for other derivatives. For CS-HOBt and CS-Acetate, the initial concentration is at 0.025 M whereas for Iodo-CS, the concentration is 0.0125 M. It should be noted that the rubber particles obtained from flocculant are in small size (~100 μm) and suspended in latex until a certain amount of the derivatives was added to enhance the solidification. As rubber particles form suspension during flocculation, this offers an in-site rubber purification which further investigation is in progress.

Table 3.3 Flocculation capability of water-soluble chitosan derivatives

Concentration (M) Chitosan Derivatives	0.0125	0.025	0.0375	0.05	0.075	0.1	0.125
CM-CS (pH~5)	pH~9	pH~9	pH~8	pH~8	pH~7	pH~7	pH~6
CS-Acetate (pH~5)	pH~9	pH~9	pH~8	pH~7	pH~7	pH~7	pH~6
CS-HOBt (pH~5)	pH~9	pH~8	pH~8	pH~7	pH~6	pH~6	pH~6
Iodo-CS (pH~5)	pH~9	pH~8	pH~7	pH~6	pH~6	pH~6	pH~6
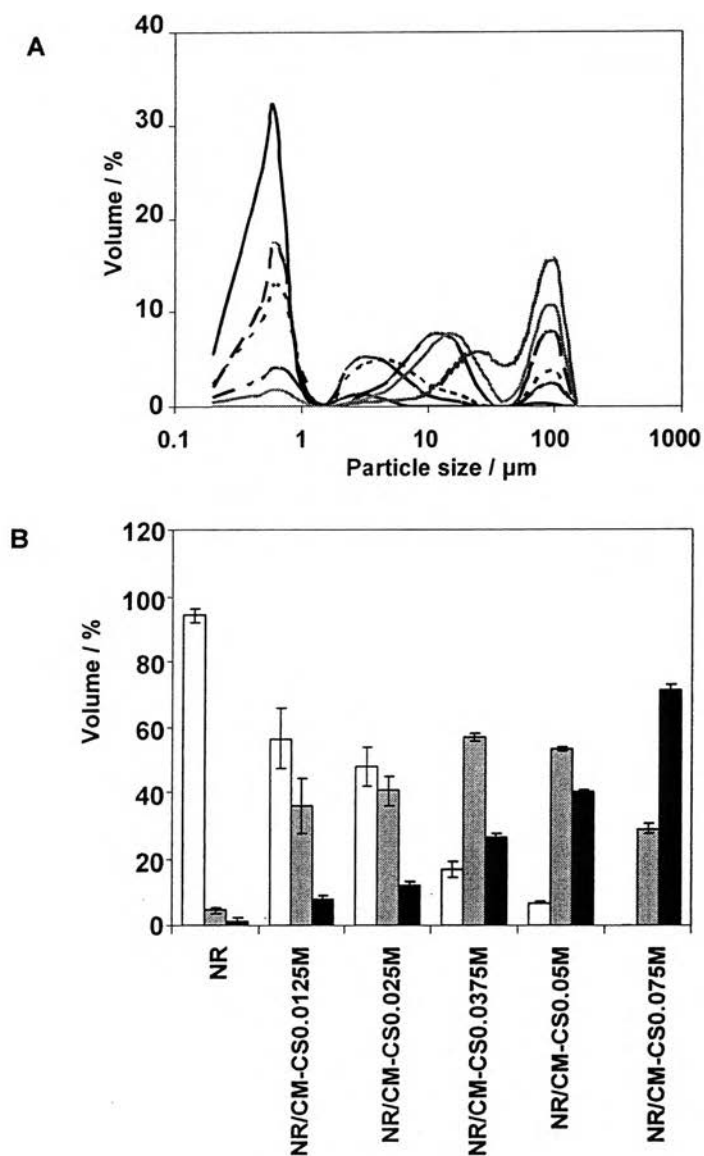
Figure 3.4 (A) Particle size of NR (——) and that of NR mixing with CM-CS at various concentrations of 0.0125M (— -), 0.025M (- - -), 0.0375 (—··), 0.05 (—) and 0.075M (—) and (B) Particle size of NR and that of NR mixing with CM-CS at various concentrations in the range of 0.2-1.5 (□), 1.6-26.7 (■), and 26.8-148.7 μm (■).
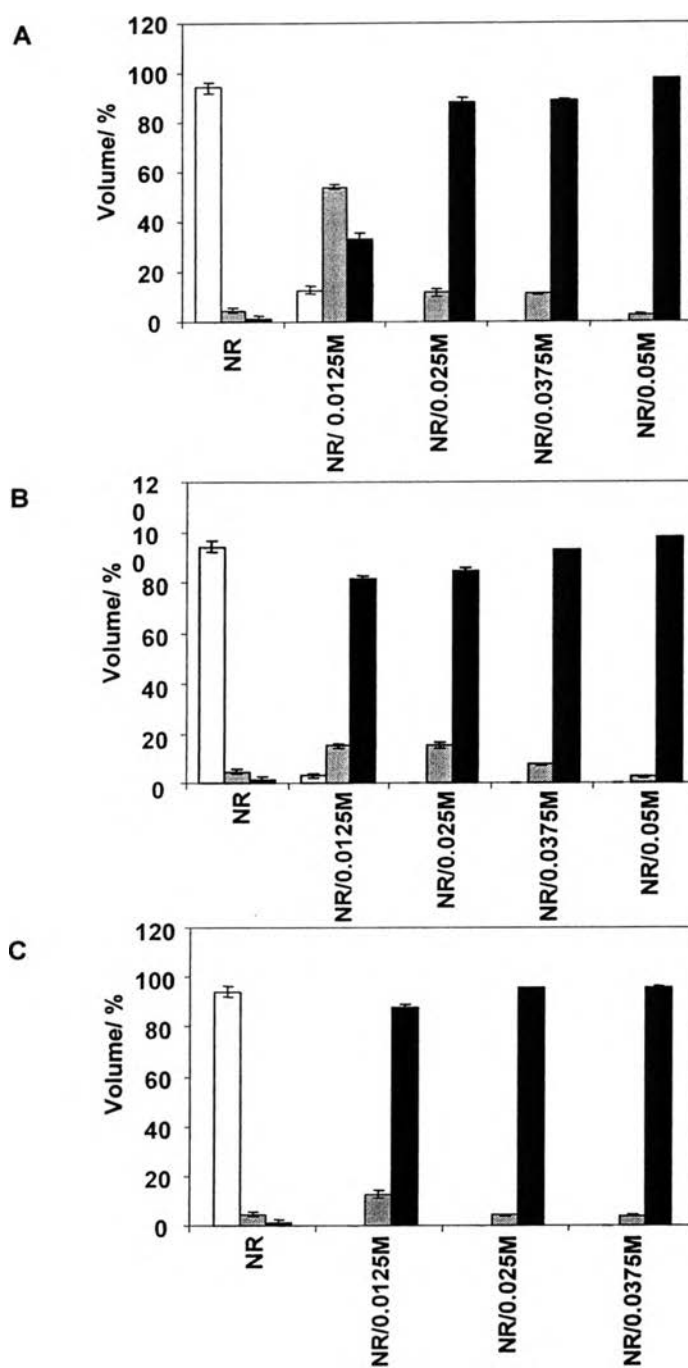
Figure 3.5 Particle size of NR and that of NR mixing with (A) CS-HOBt, (B) CS-Acetate, and (C) Iodo-CS at various concentrations in the range of 0.2-1.5 (□), 1.6-26.7 (■), and 26.8-148.7 μm (■).

3.4.3 Efficiency of rubber recovery

After 24 h, the recovered rubber phase was collected and dried to obtain the dry rubber. In order to observe the purity of rubber phase obtained, the remaining of flocculant in rubber phase was evaluated by using TG-DTA in N_2 atmosphere. Table 3.4 shows the content of water, ash, and flocculant remaining in rubber. Both the ash content and remaining of water in pure NR, obtained by using acetic acid as a coagulant, are around 4%.

Table 3.4 % Content in rubber obtained from flocculation by TG-DTA

| Rubber / Flocculant	Content / %		
	Water	Flocculant	Ash[*]
CS-HOBt (0.0375M)	2	12	4
CM-CS (0.075M)	4	6	6
CS-Acetate (0.0375M)	3	12	4
Iodo-CS (0.0375M)	3	17	6

* Ash of rubber ~ 4%.

The water-soluble chitosan derivatives are found to be remained in the rubber. For example, the remaining of CS-HOBt in the rubber was about 12% (Table 3.4). In other cases, the remaining of chitosan was about 6, 12, and 17%, respectively. This implied that chitosan flocculant forms interaction with NR particles or washing of the coagulum with water was insufficient.

The efficiency of rubber recovery, i.e., the recovered efficiency of rubber by chitosan derivatives was evaluated by using equation (1). In order to study rubber flocculation by using water-soluble chitosan derivatives as cationic flocculant, acetic acid was varied in the same concentrations for comparison. In the case of acetic acid, it

started to recover rubber from latex at 0.075M and recovered rubber almost 100% when acetic acid concentration is 0.1 M (Figure 3.6).

For flocculant, the factors, involved with efficiency of recovered rubber from latex, might be (i) hydrophobicity of chitosan chain to form interaction efficiency by van der Waals force[6], (ii) high positive charge to neutralize the negative charge on NR particle, and (iii) the high dissociation of counter ion to provide high efficient of positive charge.
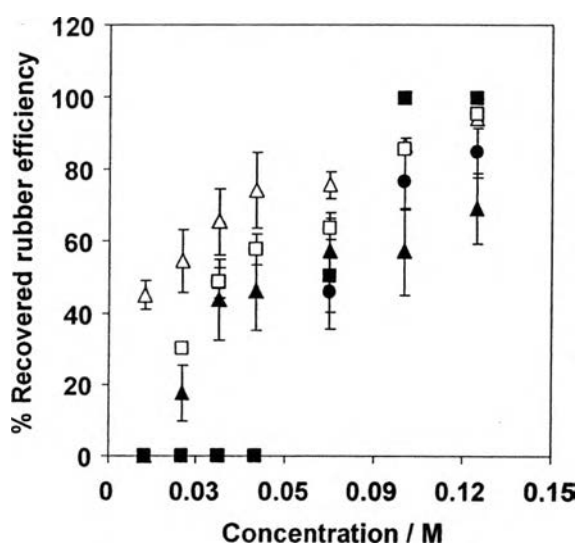
Figure 3.6 % Recovered rubber efficiency of acetic acid (■), CS-HOBt (▲),CM-CS (●), CS-Acetate(□), and Iodo-CS(△) with various concentrations.

Figure 3.6 shows the case of Iodo-CS, which recovers rubber from latex at 0.0125M. This is the lowest concentration as compared to others water-soluble derivatives. In other words, Iodo-CS gives the highest rubber recovery efficiency. As the result is relevant to the high zeta potential and contact angle, it is suspected that Iodo-CS has the good interaction with rubber particles to enhance the effect of cationic charge. Figure 3.6 shows that CS-Acetate gives higher efficiency to recover rubber form latex than CS-HOBt. It is noteworthy that CS-Acetate has the higher zeta potential, while much lower contact angle than CS-HOBt. This finding brings the estimation that the

ionic charge might play much more important role than the hydrophobicity in flocculating the rubber particles.

It should be noted that in the case of CM-CS at a certain level of concentration, the dissociated anionic polymer chain might repulse the anionic rubber particles and as a result the recovery becomes less significant at the concentration above 0.1 M as shown in Figure 3.6.

3.5 Conclusion

A series of water-soluble chitosans were developed and applied as flocculants for NR latex. All derivatives showed good rubber aggregation implying the chitosan chains forming the bridge with rubber particles and the polymer-rubber of charge-charge interaction as evaluated by the particle size of the rubber aggregated in the solution. As compared to CM-CS, CS-HOBt, and CS-Acetate, Iodo-CS with the highest zeta potential and the highest contact angle showed the most efficiency in flocculating the rubber. At present, the detailed conditions to remove chitosan out of the rubber phase are under investigation.

3.6 Acknowledgments

3.7 References

1. Dupont, J.; Moreau, F.; Lance, C.; Jacob, J-L. Photochem 1976; 15: 1215.

2. Márcia, R. M.; Lay-Theng, L.; Carlos, L. A. P.; Fernando, G. J. Colloid Interf Sci 2003; 268: 330.

3. Rippel, M. M.; Lee, L-T.; Leite, C. A. P.; Costa, C. A. R.; Galembeck, F., Acta Microscopica 2003; 12:115.

4. Greve, H-H. Ullmann's Encyclopedia of Industrial Chemistry 6th Edition, New York, John Wiley & Sons; 2003: 447.

5. Hoven, V. P.; Rattanakaran, K.; Tanaka, Y. Rubber Chem Technol 2003 ; 76 : 1128.

6. Burkert, H.; Hartmann, J. Ullmann's Encyclopedia of Industrial Chemistry, 6th Editions, New York, John Wiley & Sons, 2003; 201.

7. Verezhnikov, V. N.; Nikulin, S. S.; Poyarkova, T. N.; Misin, V. M. Russ J Appl Chem 2001; 74(7): 1225.

8. Shatalov, G. V.; Verezhnikov, V. N.; Churilina, E. V.; Kuznetsov, V.A.; Poyarkova, T. N. Russ J Appl Chem 2003; 76(11): 1839.

9. Verezhnikov, V. N.; Minkova, T. V.; Poyarkova, T. N. Russ J Appl Chem 2004; 77: 830.

10. Wang, J-P.; Chen, Y-Z.; Zhang, S-J.; Yu, H-Q. Bioresource Technol 2008; 99: 3397.

11. Pariser E. R.; Lombardi D. P. Chitin Source Book, Wiley, Chichester, 1989.

12. Mattioli-Belmonte, M.; Muzzarelli, B.; Muzzarelli, R. A. A. Carbohy Eur 1997; 19: 30.

13. Chaikumpollert, O.; Rakdee, C.; Loykulnant, S.; Suchiva, K. Proceeding.

14. Fangkangwanwong, J.; Akashi, M.; Kida, T.; Chirachanchai, S. Macromol Rapid Comm 2006; 27: 1039.

15. Chen, X-G., Park, H-J. Carbohy polym 2003; 53: 355.

16. Domard, A.; Rinaudo, M.; Terrassin, C. Int J Biol Macromol 1986; 8: 105.

17. Degree of substitution on $-OH$ (%) $= \{(I_{H-a}/2)/(I_{H\ of\ pyranose\ ring}/6)\} \times 100 = \{(41.5/2)/(309.6/6)\} \times 100 = 40.21\%$.

18. Degree of substitution on $-NH_2$ (%) = $\{(I_{H-b}/2)/(I_{H\ of\ pyranose\ ring}/6)\} \times 100$ = $\{(19.4/2)/(309.6/6)\} \times 100 = 18.80\%$.

19. Degree of substitution (%) = $\{(I_{H-a}/9)/(I_{H-2})\} \times 100 = \{(13/9)/(9.4)\} \times 100 = 15.37\%$.