CHAPTER IV
RESULTS AND DISCUSSION

4.1 Composition of Crumb Rubber

Table 4.1 shows the chemical composition of original crumb rubber which obtained from Thai Union Commercial Development Company Limited. This composition was analyzed by X-ray fluorescence spectrometry or XRF. From the results, calcium and zinc were found as the additives in the crumb rubber. Moreover, the sulfur used in the vulcanization process to improve the physical properties of rubber was discovered.

Table 4.1 Chemical composition of crumb rubber before the oxidation analyzed by XRF spectrometry

Composition	wt.%	Composition	wt.%
ZnO	2.13	K_2O	0.06
MgO	0.10	CaO	3.75
Al_2O_3	0.07	TiO_2	0.01
SiO_2	0.81	Fe_2O_3	0.06
P_2O_3	0.13	NiO	0.01
SO_3	3.01	Cl	0.01

4.2 The Sulfur Content

The sulfur content was obtained from bomb calorimetry and XRF. From the XRF result, the sulfur content of crumb rubber was 1.20 wt.% corresponding to 0.38 mmol/g (Appendix A). It was comparable to the sulfur content attained by bomb calorimetry which was 1.52 wt.%, corresponding to 0.38 mmol/g (Appendix A). The data from both techniques were close proximity. This research chose bomb calorimetry to analyze the sulfur content because it spends smaller amount of sample and has lower cost. Table 4.2 shows the sulfur content of crumb rubbers before and after the oxidation. The oxidation of crumb rubber with only hydrogen peroxide resulted in the sulfur loss of 14.7% while using hydrogen peroxide mixed with formic acid increase the sulfur loss to 28.8%. In case of nitric acid, the sulfur loss was the highest, 54.0 wt.%

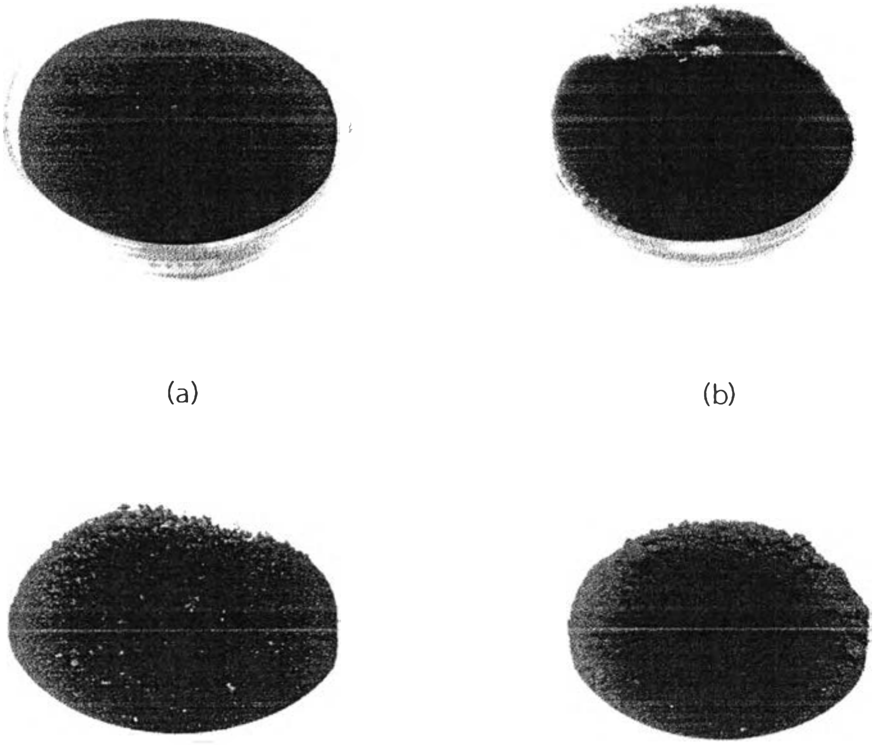
Table 4.2 The sulfur content of the oxidized crumb rubber

Sample	Sulfur content[1]		Sulfur loss
	(wt.%)	(mmol/g)	(wt.%)
Original crumb rubber	1.52	0.38	-
CR-H_2O_2 (30%NoF)	1.26	0.32	14.7
CR-H_2O_2 (30%)	1.00	0.27	28.8
CR-HNO_3 (6M)	0.63	0.17	54.0

[1] Sulfur content was analyzed by bomb calorimetry

Figure 4.1 shows photographs of the original crumb rubber and the oxidized crumb rubbers. The physical appearance of the original crumb rubber was soft and finely powdery rubber. After the oxidation using only hydrogen peroxide, the physical appearance was similar to the original crumb rubber (Figure 4.1(b)) but in the case of using nitric acid and hydrogen peroxide with formic acid the physical characteristics was changed. The crumb rubber oxidized by using hydrogen peroxide with formic acid (Figure 4.1(c)) was hard and agglomerate. In case of using nitric acid as the oxidizing agent, the oxidized crumb rubber (Figure 4.1(d)) was attenuated. Moreover, black color easily stained on the finger upon touching the oxidized rubber powder.

It is possible that hydrogen peroxide is a weak oxidizing agent. As a result, the crumb rubber oxidized by using only hydrogen peroxide had the lowest sulfur loss and retained the physical appearance of original rubber. When formic acid was co-added with hydrogen peroxide, the oxidation became severe, resulting in the appearance changed and the increase in the sulfur loss. It can presume that formic acid assisted hydrogen peroxide in breaking down the sulfidic bonds containing in the crosslinked structure of the crumb rubber. In case of nitric acid, the strong oxidizing nature promoted the sulfur loss above 50% and the physical appearance of the oxidized rubber was remarkably changed.



(a) (b)

(c) (d)

Figure 4.1 Photographs of (a) original crumb rubber (b) CR-H_2O_2 (30%NoF) (c) CR-H_2O_2 (30%) and (d) CR-HNO_3 (6M).

4.3 Functional Groups of the Oxidized Crumb Rubber

Figure 4.2 shows the FTIR spectrum of the original crumb rubber. The starting crumb rubber had the characteristic IR bands which indicated the copolymer of cis 1,4 poly isoprene, as the main chain of natural rubber, and styrene-butadiene rubber (SBR). These IR bands were the C=C stretching of the rubber backbone, =C-H stretching, -CH_3 stretching, -CH_3 bending, -CH_2 stretching and -CH_2 bending. The bands related to the rubber backbone (C=C stretching) and =C-H stretching were located at 1630 and 3010 cm^{-1}, respectively. The characteristic band at 2960 cm^{-1} corresponded to the –CH_3 stretching. The band at 1380 cm^{-1} related to the –CH_3 bending. The bands at 2915 and 2850 cm^{-1} related to the –CH_2 asymmetric stretching and –CH_2 symmetric stretching, respectively. The band owing to the $-CH_2$ bending was observed at 1440 cm^{-1}. The $-CH_3$ in-plane and $-CH_3$ out-of-plane bending were located at 1050 and 870 cm^{-1}, respectively. The bands at 710 and 1100 cm^{-1} were assigned to $-CH_2$ in-plane and $-CH_2$ out-of-plane bending. Moreover, the presence of the sulfidic bonds in the crumb rubber can be confirmed by the C-S stretching and S-S stretching. The corresponding IR bands were observed at 570 and 480 cm^{-1}, respectively. The sulfidic bonds were present as the sulfur crosslinks generated by the vulcanization. Moreover, the band at 2510 cm^{-1} was assigned to the S-H stretching of incomplete sulfur crosslinks. However, the presence of –OH group at 3420 cm^{-1} was related to stearic acid and functional group on carbon black as the rubber fillers [44, 45]. The bands derived from styrene-butadiene rubber were almost overlapped with the characteristic bands of natural rubber. The band at 1630 cm^{-1} was assigned to the C=C stretching. The bands around 1440-1380 cm^{-1} were assigned to the $-CH_2$ and $-CH_3$ bending. The C-H (aromatic) bending was observed at 1800 cm^{-1}.

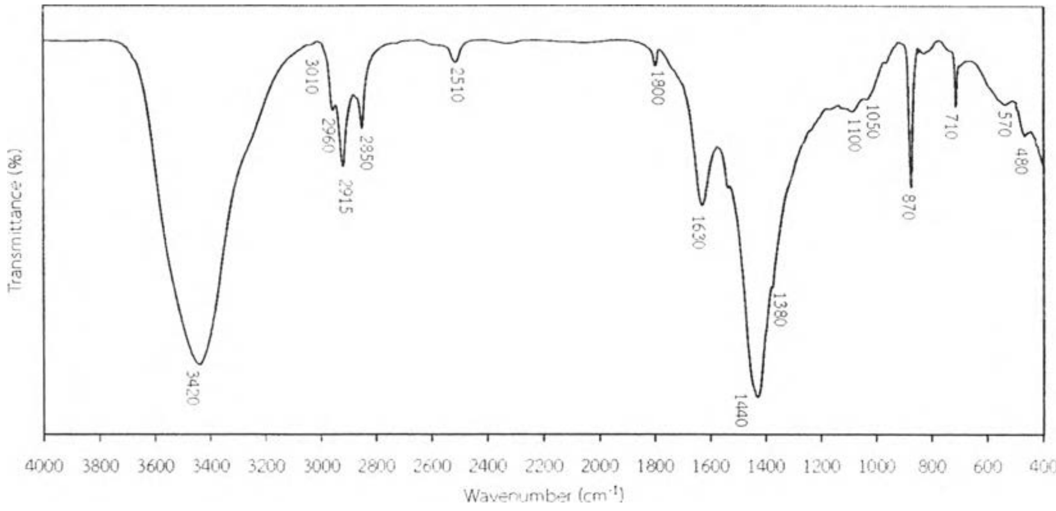


Figure 4.2 FTIR spectrum of the original crumb rubber.

Figure 4.3 shows the FTIR spectra of the crumb rubber oxidized by using only hydrogen peroxide as the oxidizing agent. The IR spectra of the oxidized rubbers in Figure 4.3(b) and Figure 4.3(c) were similar to that of the original rubber (Figure 4.3(a)). All bands related to the natural rubber and styrene-butadiene rubber structure remained intact with increasing the concentration of hydrogen peroxide. Furthermore, the IR bands found at lower than 570 cm^{1}, which were attributed to the C-S stretching and S-S stretching, decreased when the concentration of hydrogen peroxide was increased. This phenomena indicated that the sulfidic bonds in the rubber were oxidized. However, the new IR bands were not observed after the oxidation by using hydrogen peroxide in any concentrations.

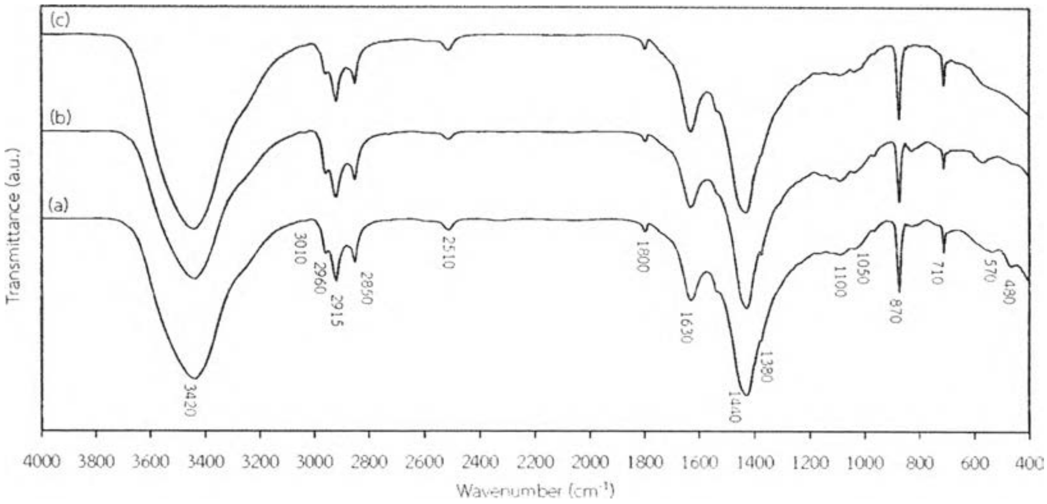


Figure 4.3 FTIR spectra of (a) crumb rubber (b) CR-H_2O_2 (20 wt.%NoF) and (c) CR-H_2O_2 (30 wt.%NoF).

In case of using hydrogen peroxide with formic acid as oxidizing agent (Figure 4.4b)). The characteristic bands of natural rubber (1630, 3010 cm^{-1}) were decreased in the intensity concomitantly with a disappearance of the bands related to the thiol group (2510 cm^{-1}). When HNO_3 was used as the oxidant (Figure 4.4(c)), the band of sulfidic bonds (480 cm^{-1}) was not observed anymore, but it still remained in the case of CR-H_2O_2(30 wt.%). The sulfonic acid group in the oxidized crumb rubber was evidenced by the bands at 1360 cm^{-1} corresponding to the S=O asymmetric stretching, at 1160 and 1030 cm^{-1}, related to the S=O symmetric stretching, and at 3420 cm^{-1} that can be ascribed to -OH group. However, the observed S=O stretching might be related to other sulfur oxide groups, such as sulfone (-SO_2-) and sulfoxide (-SO-) all of which gave the IR bands in the similar wave numbers to sulfonic acid group [1, 43, 46] . Moreover, the oxidation resulted in the formation of carboxylic group (-COOH) since the bands owing to the O-H, C=O and C-O stretching appeared at 3400, 1716, 1270 and 1230 cm^{-1}, respectively. In the case of H_2O_2 as the oxidizing agent, the bands at 1730 and 2710 cm^{-1} were attributed respectively to the C=O and C-H stretching of aldehyde (R-CHO). The bands related to the C–H bonds (2960, 2915 and 2850 cm^{-1})

were intensified by an increase in the amount of the C–H group which was explained in Figure 4.5.

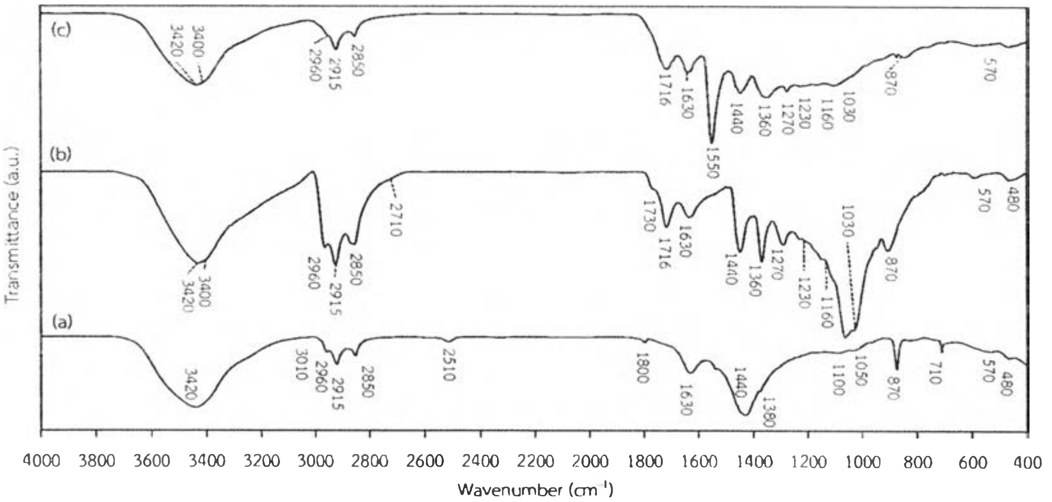


Figure 4.4 FTIR spectra of (a) crumb rubber (b) CR-H_2O_2 (30 wt.%) and (c) CR-HNO_3 (6M).

These results indicated that hydrogen peroxide is relatively mild oxidizing agent because the rubber structure was not changed after the oxidation (Figure 4.3). In contrast, the structure of rubber was changed by the presence of both hydrogen peroxide and formic acid. When formic acid assisted hydrogen peroxide in the oxidation process, the quantity of the crosslinked structure in as the C-S and S-S bonds was decreased. Moreover, new functional groups, such as sulfonic acid (-SO_3H), carboxylic acid (-COOH) and aldehyde (-CHO), were found. Figure 4.5 shows the mechanism for the oxidation of the rubber structure by using hydrogen peroxide mixed with organic acid [8]. Generally, an organic acid (RCOOH) reacts with hydrogen peroxide to form the corresponding peroxy acid (RCOOOH) which is able to act as a catalyst for epoxidation. Then, some epoxy groups were hydrolyzed, causing the ring opening to generate alpha-hydroxyl hydro-peroxide. Finally, the hydrolyzed rubber was rearranged and cleaved to shorter polymer chains that were terminated with aldehyde and ketone groups.

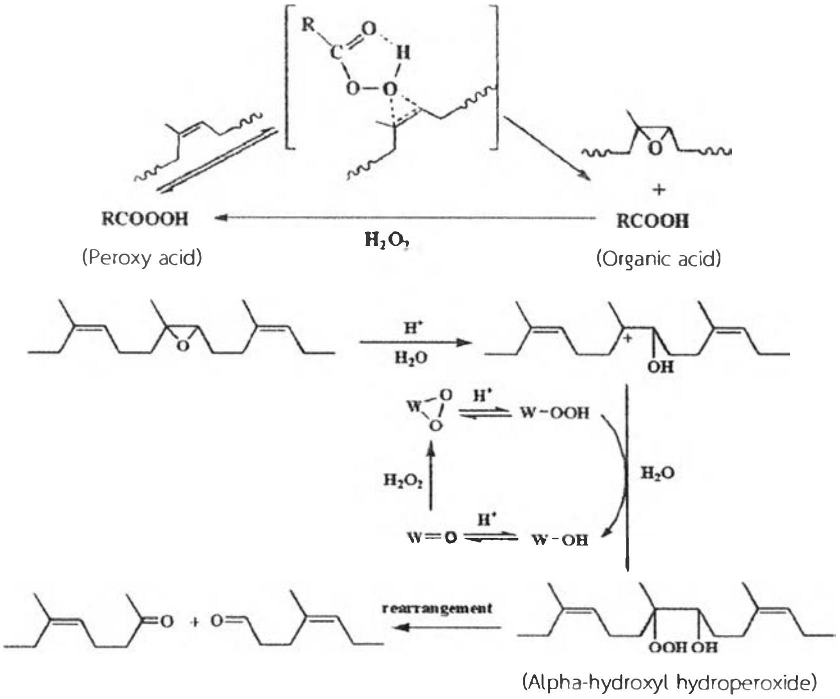


Figure 4.5 Mechanism for oxidation of natural rubber by using hydrogen peroxide with organic acid [8].

In case of using nitric acid, the physical appearance and chemical structure of the resulting rubber were remarkably changed. The IR bands of the C-S stretching and S-S stretching were considerably decreased concomitantly with the sulfur loss of 54 wt.% (Table 4.2). After the oxidation, the new IR bands appeared which were attributed to carboxylic acid (-COOH) and sulfonic group (-SO_3H). Moreover, the strong absorption band at 1550 cm^{-1} was clearly observed in CR-HNO_3 (6M) It was related to nitro group (-NO_2) formed by the nitration of aromatic rings presenting in Figure 4.6 [1]. The mechanisms for the formation of these functional groups were described below.

$$\text{Polymer-Ph} \xrightarrow{HNO_3} \text{Polymer-Ph-}NO_2$$

Figure 4.6 The nitration of aromatic ring by the oxidation of nitric acid [1].

Figures 4.7 and 4.8 show the effect of the oxidizing agent concentration on the functional groups of the oxidized crumb rubbers. Figure 4.7 shows the rubbers oxidized by using hydrogen peroxide with formic acid as oxidizing agent. When the concentration of the oxidants increased, the IR bands attributed to the sulfonic group (1030, 1160 and 1360 cm^{-1}) became intense. Likewise, the C=O stretching of carboxylic group (1716 cm^{-1}) and of carbonyl group of aldehyde (1730 cm^{-1}) were increased. Moreover, an increase in the IR bands related to the C-H stretching in aldehyde at 2710 and 2915 cm^{-1} was observed.

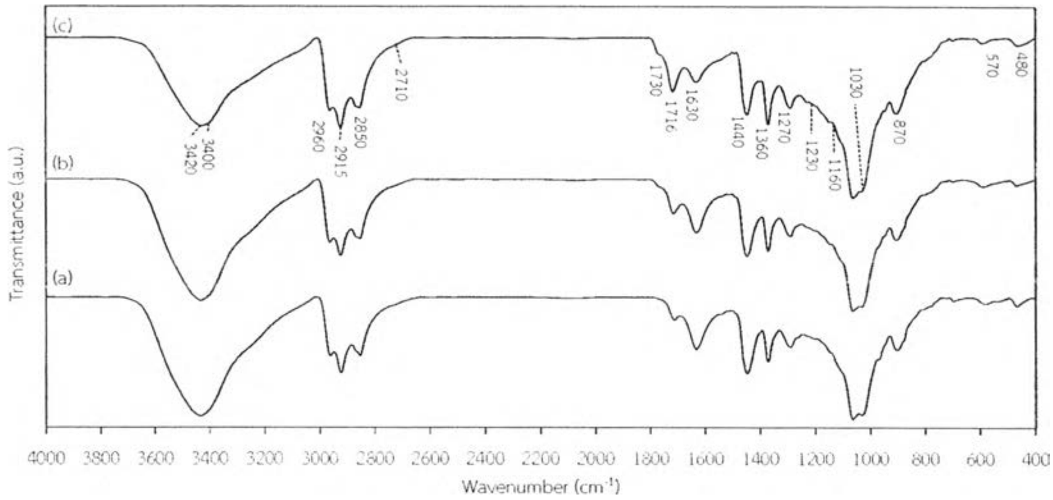


Figure 4.7 FTIR spectra of (a) CR-H_2O_2 (10 wt.%) (b) CR-H_2O_2 (20 wt.%) and (c) CR-H_2O_2 (30 wt.%).

Figure 4.8 shows the FTIR spectra of the oxidized rubbers prepared by using nitric acid with different concentrations. It can be seen that the bands related to the C-S and S-S stretching still remained in the oxidized crumb rubber oxidized with 2 M HNO_3 as the lowest concentration. These bonds disappeared when using higher concentrations. The absorption band of nitro group (-NO_2) was found at 1550 cm^{-1} of which the intensity was decreased with increasing of the concentration of HNO_3 solution (4M-6M). In contrast, the IR bands of the S=O stretching (1360, 1160, 1030 cm^{-1}) and O-H stretching (3420 cm^{-1}) originated from sulfonic acid group and the C=O stretching (1716 cm^{-1}), the C-O stretching (1270, 1230 cm^{-1}) and O-H stretching (3400 cm^{-1}) originated from carboxylic acid group were increased. Furthermore, the highest oxidant concentration promoted the formation of free –OH groups as can be seen from a large increase in the band intensity at 3670 cm^{-1} (CR-HNO_3 (8M)). Furthermore, the intensity of sulfonic acid group was increased and the nitro group was decreased when the concentration of nitric acid was increased. Possibly, nitric acid was a strong oxidizing agent that the aromatic ring in styrene-butadiene rubber might be severely oxidized to generate the highly functionalized short-chain polymers which were soluble and lost in water [47].

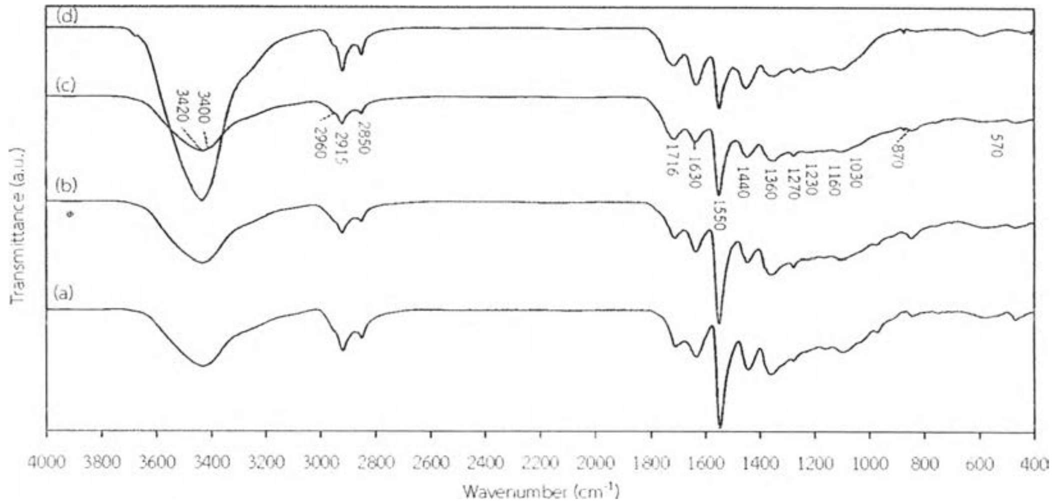


Figure 4.8 FTIR spectra of (a) CR-HNO_3 (2M) (b) CR-HNO_3 (4M) (c) CR-HNO_3 (6M) and (d) CR-HNO_3 (8M).

4.4 Thermal stability of the Oxidized Crumb Rubber

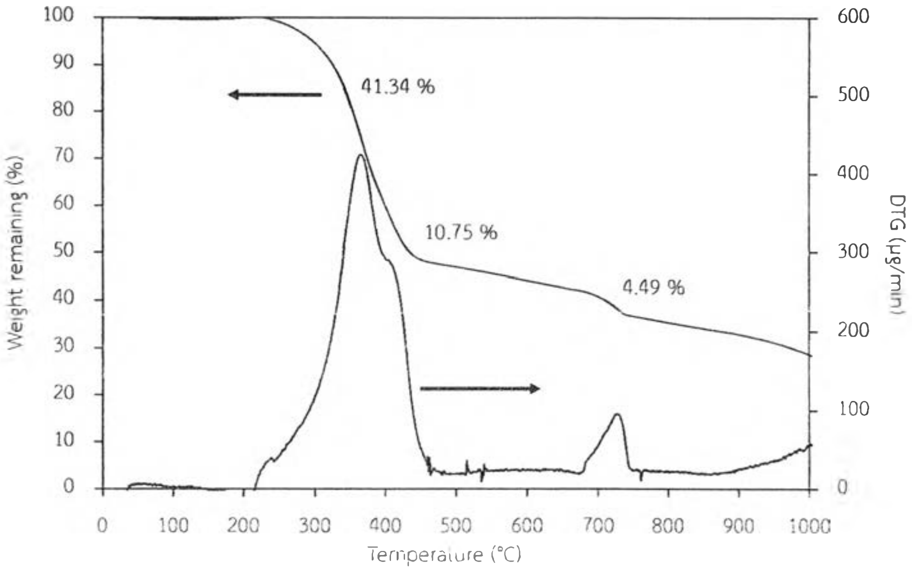


Figure 4.9 Thermal degradation behavior of the original crumb rubber.

The thermal stability was tested by thermogravimetric and differential thermal analysis or TGA. This technique can be applied to analysis of composition and structure of the original crumb rubber and the oxidized rubber products. Figure 4.9 shows the thermal degradation behavior of the original crumb rubber, which was studied under N_2 atmosphere between 50 and 1000 °C. The decomposition pattern of original crumb rubber showed three-step weight loss. The first and second steps occurred at around 250-390 °C and 390-480°C, which were assigned to the decomposition of natural rubber (41.3%) and styrene-butadiene rubber (10.8%), respectively. Then the degradation of carbon black was found in the range of 695-750 °C (4.5%) [48].

Figure 4.10 shows the thermal degradation behavior of the crumb rubber oxidized by using hydrogen peroxide without the formic acid addition. The degradation pattern of the oxidized rubbers was not much different to that of the original rubber at all concentrations of the oxidant. These results suggested that the composition and structure of crumb rubber remained intact after the oxidation process. However, the carbon black might be loss during the oxidation in which the weight loss of rubber fraction was changed.

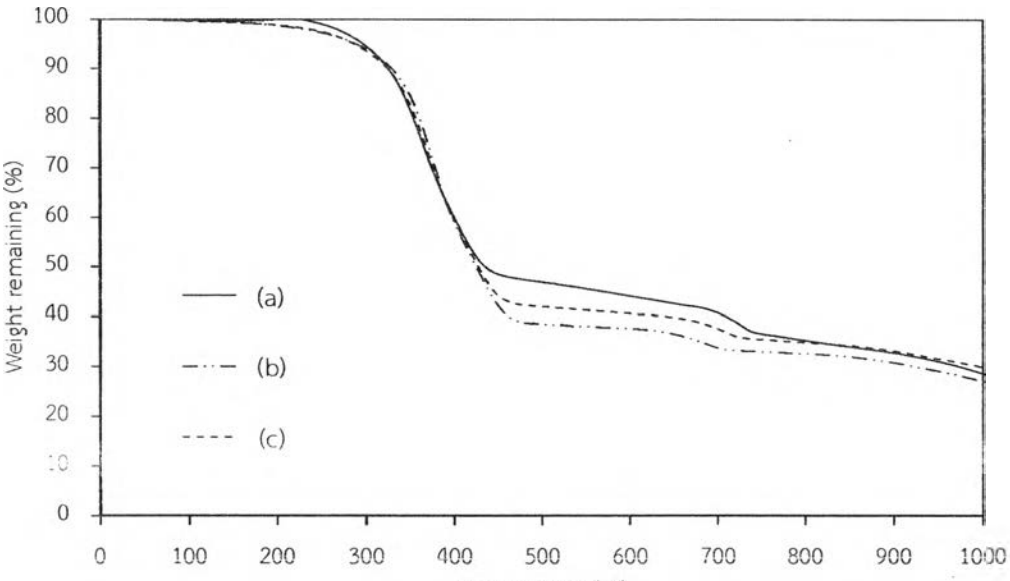


Figure 4.10 Thermal degradation behavior of (a) crumb rubber (b) CR-H_2O_2 (20%NoF) and (c) CR-H_2O_2 (30%NoF).

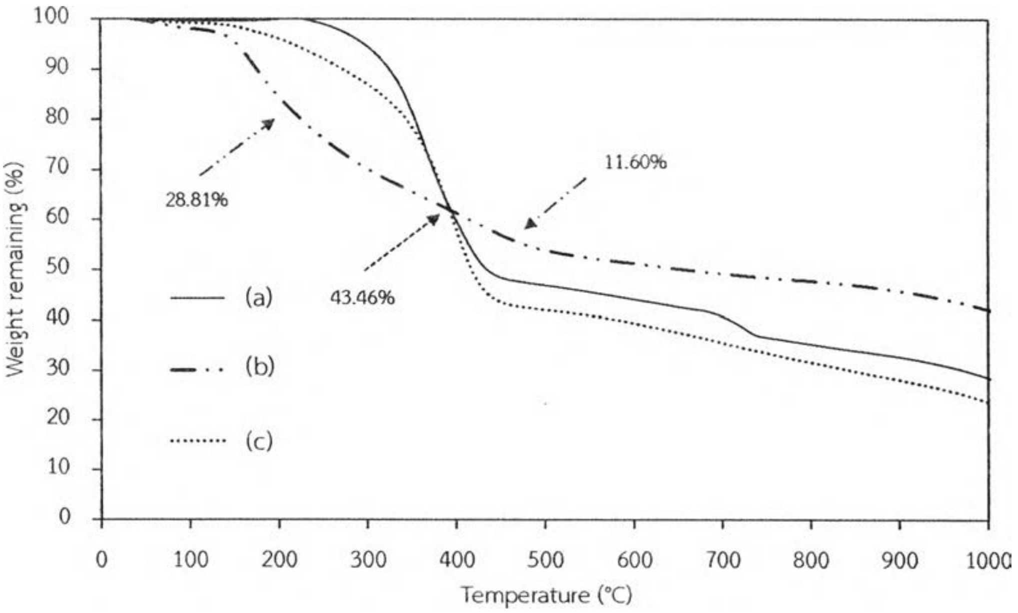


Figure 4.11 Thermal degradation behavior of (a) crumb rubber (b) CR-HNO_3 (6M) and (c) CR-H_2O_2 (30 wt.%).

Figure 4.11 shows the thermal degradation behavior of the crumb rubber oxidized by using hydrogen peroxide with formic acid (Figure 4.11b)) or nitric acid (Figure 4.11(c)) as the oxidizing agent. The oxidation with 30 wt.% H_2O_2 and 6 M HNO_3 totally changed the decomposition behavior of crumb rubber. In case of nitric acid, CR-HNO_3(6M) lost weight in two steps. The first step was in the range of 180-350 °C, which was attributed to the decomposition of functional groups, such as -COOH and -NO_2 groups [49]. The final step was related to the polymer backbone that was decomposed at 390-480 °C. This result indicated that nitric acid was a strong oxidizing agent by which both natural rubber and styrene-butadiene rubber were oxidized, giving less thermally stable product. These polymers were the highly functionalized short-chain polymer which were probably composed of polar highly oxygenated molecules. This result was supported by FTIR as shown in Figure 4.4. In the case of CR-H_2O_2 (30 wt.%), it was confirmed that the oxidation by using only hydrogen peroxide was not effective enough to devulcanize the crumb rubber structure. However, the thermal decomposition of the oxidized crumb rubber by using hydrogen peroxide with formic acid showed that the decomposition behavior of styrene-butadiene rubber remained intact. It should be due to the selectivity of the oxidation by using hydrogen peroxide with formic acid. The thermal decomposition was changed to weight loss at 200-480 °C due to the formation of new functional groups in the rubber chains. In addition, the weight loss ascribed to carbon black disappeared after the oxidation using either H_2O_2 or HNO_3. These results indicated that carbon black in the crumb rubber can be easily oxidized to produce water soluble polyaromatic compounds [47].

Figures 4.12 and 4.13 show the influence of the oxidizing agent concentration on the thermal degradation behavior of the oxidized crumb rubbers. In case of using hydrogen peroxide with the addition of formic acid (Figure 4.12), the weight loss pattern was similar at all concentrations. The presence of new species generated from the oxidation of natural rubber was observed at 150-300 °C. Moreover, the weight loss at this step tended to increase with increasing the oxidizing agent concentration. In contrast, the weight loss related to the styrene-butadiene rubber tended to decrease when the concentration of the oxidizing agent was increased. However, the remaining weight of the oxidized rubbers attained at all concentrations was similar.

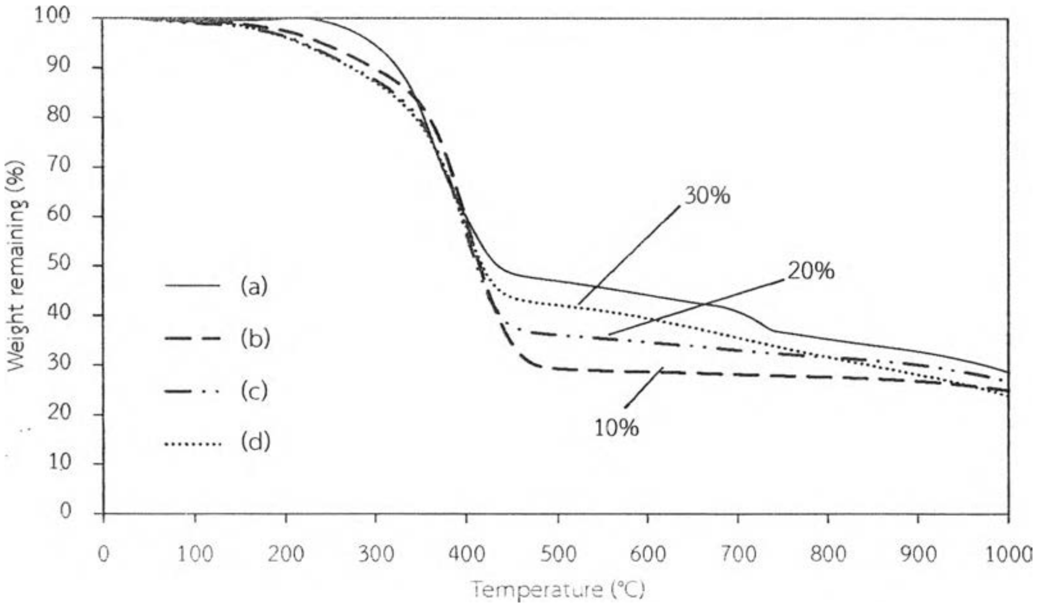


Figure 4.12 Thermal degradation behavior of (a) crumb rubber (b) CR-H_2O_2(10 wt.%) (c) CR-H_2O_2(20 wt.%) and (d) CR-H_2O_2(30 wt.%).

In case of using nitric acid as the oxidizing agent (Figure 4.13), the natural rubber and styrene-butadiene rubber decomposed at temperatures lower than the original crumb rubber due to the presence of new functional groups, especially nitro group (Figure 4.4). In addition, the crumb rubbers oxidized with nitric acid at all concentrations had the weight remaining higher than the original one. Possibly, the natural rubber and styrene-butadiene rubber might be severely oxidized to generate the highly functionalized short-chain polymer which were soluble in water. These results also suggested that the remains fraction of original natural rubber fraction were lower than that of styrene-butadiene rubber.

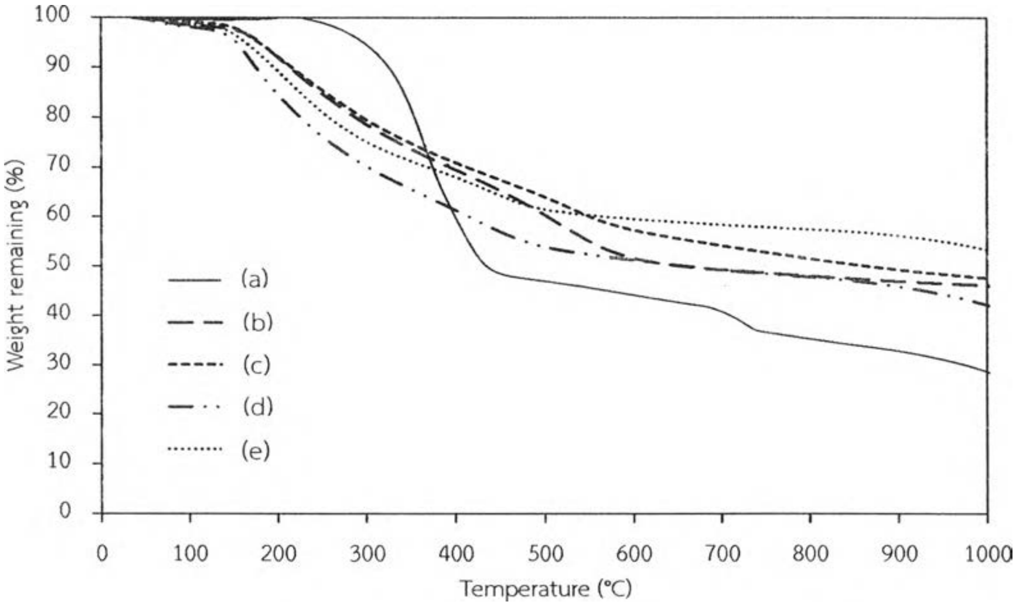


Figure 4.13 Thermal degradation behavior of (a) crumb rubber (b) CR-HNO_3 (2M) (c) CR-HNO_3 (4M) (d) CR-HNO_3 (6M) and (e) CR-HNO_3 (8M).

To elaborate the possible structure of the crumb rubber oxidized by using nitric acid, the extraction technique was used. Typically, 3 g of the oxidized crumb rubber was refluxed with 25 mL of solvent at 60 °C for 5 h. Then, the refluxed rubber was dried in a vacuum oven at 60 °C for 3 h. Table 4.3 shows the amount of CR-HNO_3 (6M) remained after the extraction. The weight loss of CR-HNO_3 (6M) extracted by using hexane was lower than that in ethanol. This result suggested that the polar fraction was higher than the non-polar fraction in CR-HNO_3 (6M). It should be due to the natural rubber (non-polar chain) was extensively oxidized and leached as the soluble fraction during the oxidation process. This result was supported by the thermal decomposition of CR-HNO_3 series as shown in Figure 4.13. Figure 4.14 shows the solution mixture form the extraction by using hexane and ethanol as solvents. The solution color from the hexane extraction was transparent yellow (Figure 4.14(a)) while the ethanol extraction gave yellow turbid solution (Figure 4.14(b)), indicating that CR-HNO_3 (6M) was more soluble in the polar solvent.

Table 4.3 The extractable content of CR-HNO_3 (6M) in the different solvents[1]

Solvent	Initial weight (g)	Final weight (g)	Recovery (%)
Hexane	3.000	2.726	90.9
Ethanol	3.000	2.306	76.9

[1]Extraction condition : CR-HNO_3(6M), 3 g; solvent, 25 mL; temperature, 60 °C; time, 5 h

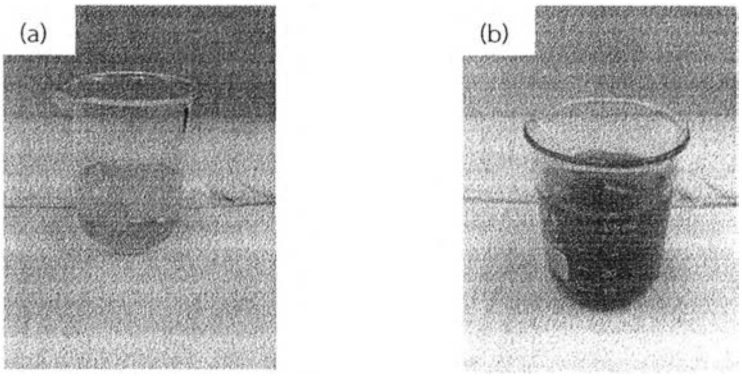


Figure 4.14 The solution mixture form the extraction by using different solvents; (a) hexane and (b) ethanol.

4.5 The Morphology of the Oxidized Crumb Rubber

The morphology of rubber samples was studied by SEM technique at three magnifications, x 200, x 1,000 and x 5,000. Figure 4.15 shows the SEM images of the original crumb rubber. It can be seen that the size of crumb rubber was bigger than 100 micron. Most of particles had rough surface, whereas the minority was smooth as surface cut during the crushing process. At the highest magnification, there were agglomerates of particles with different sizes. Figure 4.16 shows the SEM images of the crumb rubber oxidized by using only hydrogen peroxide as the oxidizing agent. The morphology of the oxidized product was similar to that of the original crumb rubber.

Figures 4.17 and 4.18 show the SEM images of the crumb rubbers oxidized by using hydrogen peroxide with formic acid as the oxidizing agent. For CR-H_2O_2 (10%) (Figure 4.17), the particle size distribution was wider than the original crumb rubber. When the surface of a large particle was magnified, there were small particles with the size of less than 10 micron agglomerated. Moreover, the interparticle voids were found. In case of CR-H_2O_2 (30%) (Figure 4.18), the rubber particles were merged to large sizes. There was no primary particles found on the surface of CR-H_2O_2 (30%). Moreover, many small interparticle voids were observed. These results indicated that the agglomerate size of the particles was increased with increasing the concentration of hydrogen peroxide.

The morphology of rubbers produced from the oxidation by using nitric acid as the oxidizing agent was shown in Figures 4.19 and 4.20. The particle size of CR-HNO_3 (2M) was smaller than that the original rubber. Moreover, the morphology was definitely changed after the oxidation. There were small particles deposited on the surface, generating the interparticle voids. When the concentration of nitric acid was increased to 6 M, the particle size of the oxidized rubber was decreased and showed more uniform distribution. Furthermore, there were many interparticle voids on the surface which looked like a sponge. Therefore, the increasing of the nitric acid concentration reduced the particle size and increased the particle porosity.

The morphology of the oxidized rubber remained intact in the case of using only hydrogen peroxide while the addition of formic acid assisted hydrogen peroxide to promote the oxidation. The morphological study was in accordance with the results of the sulfur content, FTIR and TGA. In the case of using nitric acid as the oxidizing agent, the morphology of the oxidized rubber was remarkably changed. From the thermal decomposition, there was a noticeable change in the structure of natural rubber and styrene-butadiene rubber, which directly resulted in the particle size reduction and the generation of porosity on the particle surface

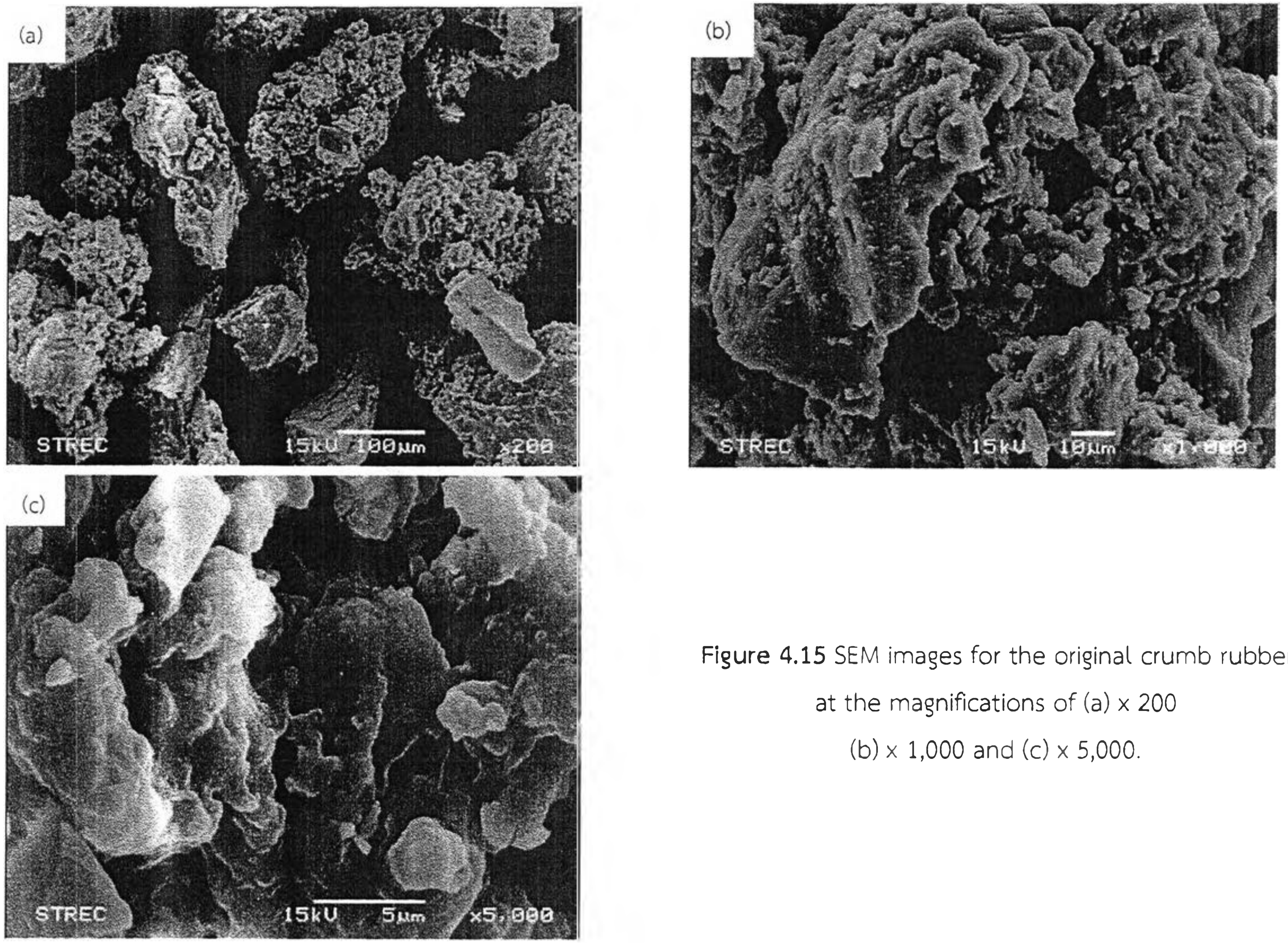


Figure 4.15 SEM images for the original crumb rubber at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

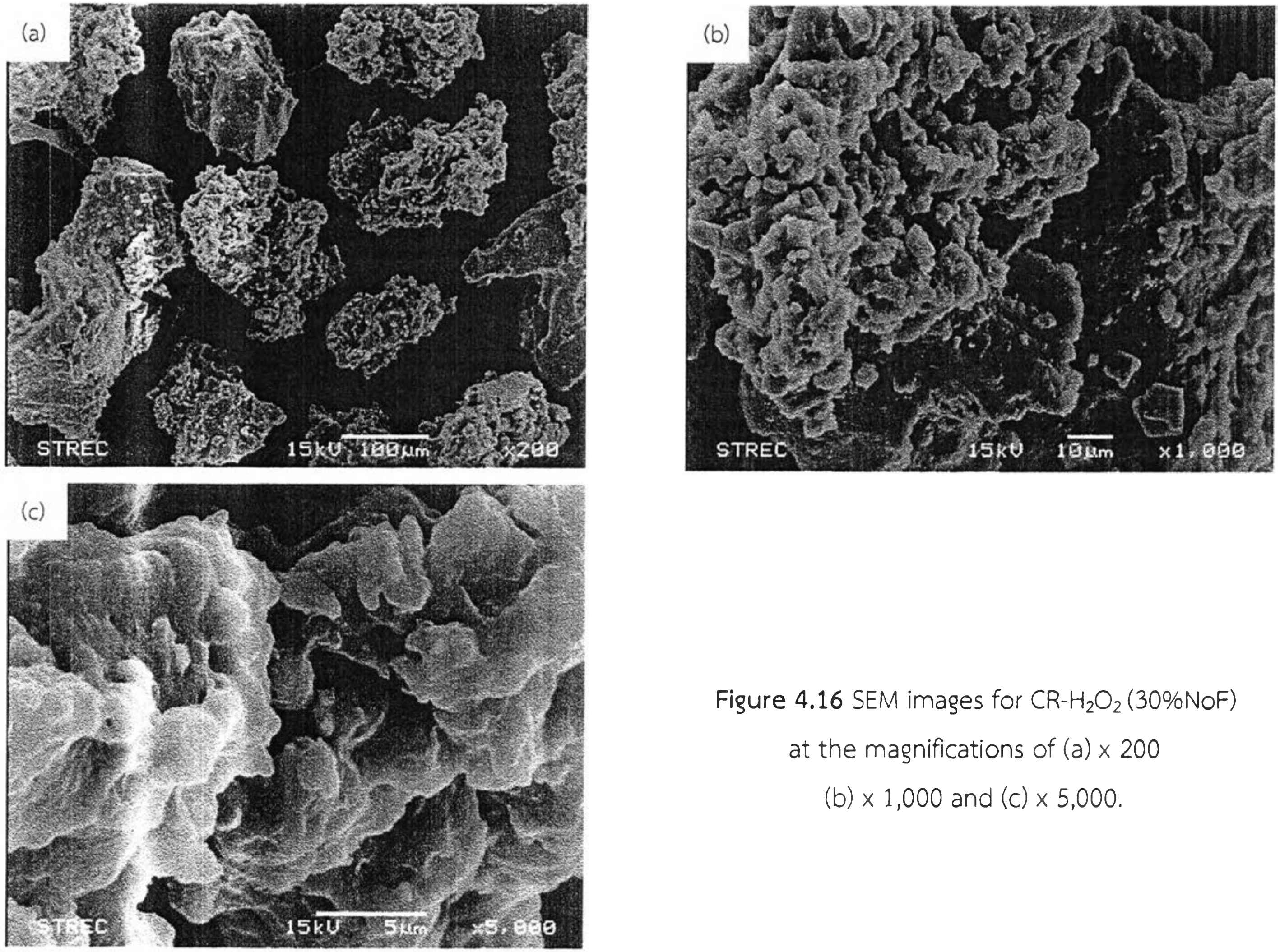


Figure 4.16 SEM images for CR-H_2O_2 (30%NoF) at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

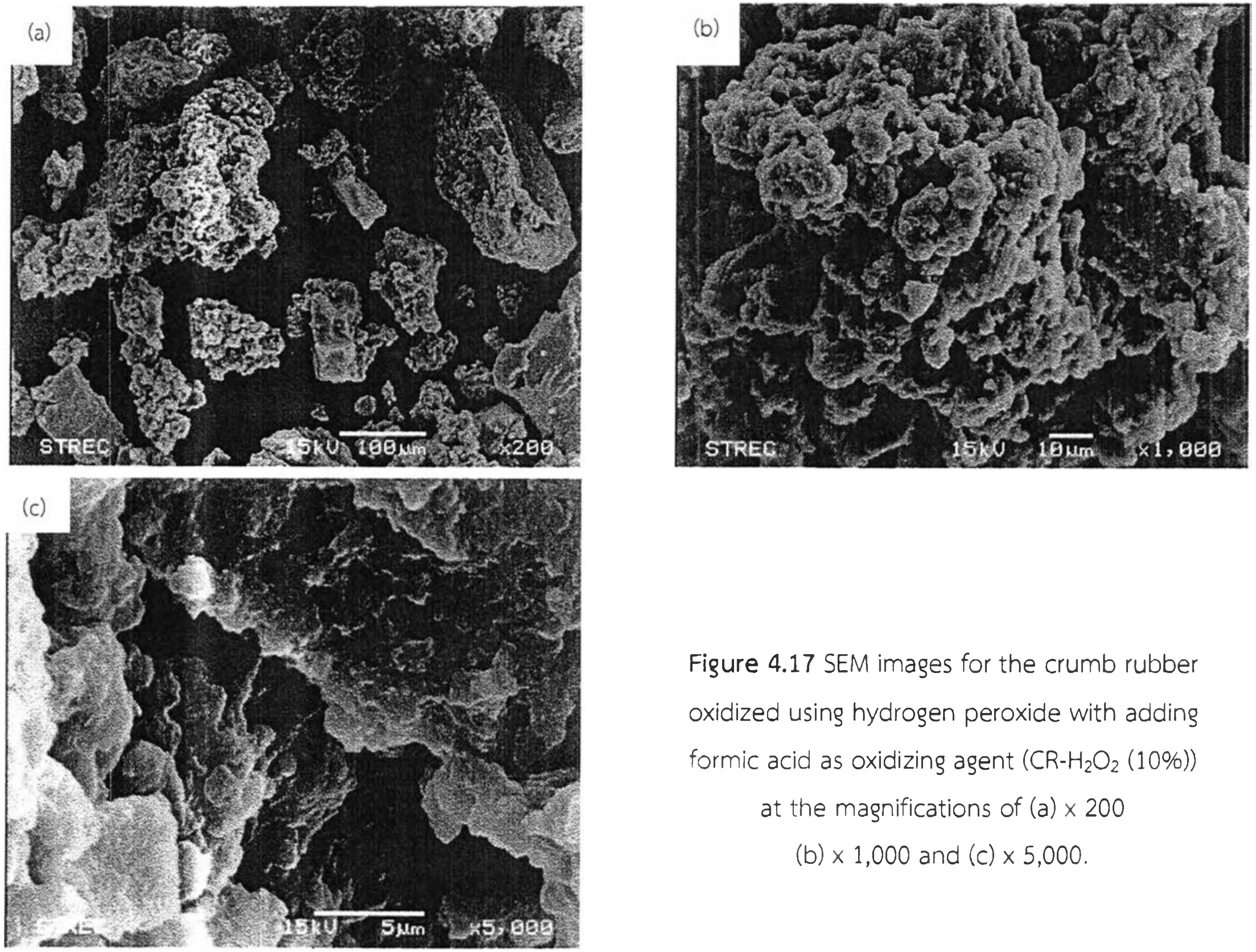


Figure 4.17 SEM images for the crumb rubber oxidized using hydrogen peroxide with adding formic acid as oxidizing agent (CR-H_2O_2 (10%)) at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

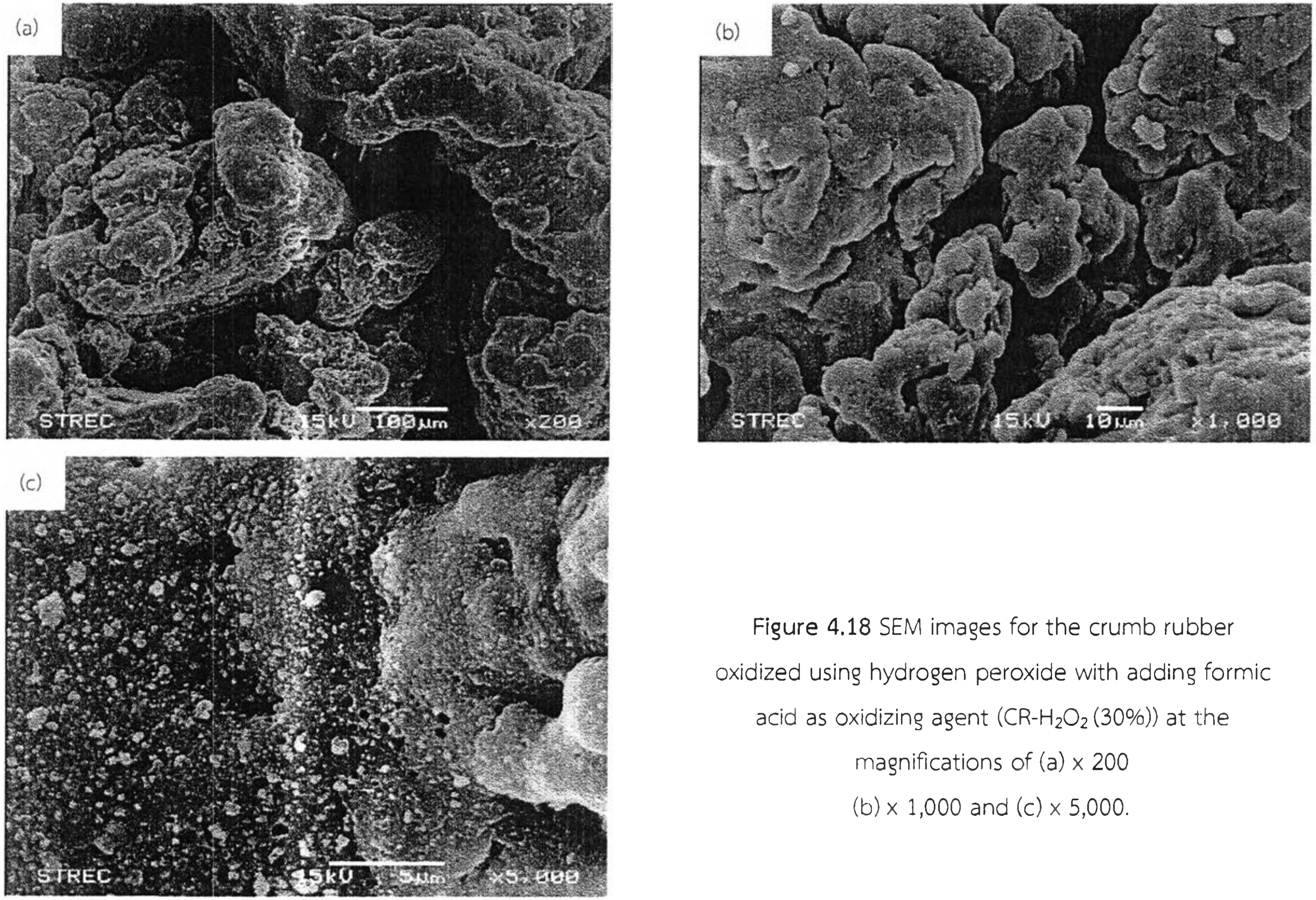


Figure 4.18 SEM images for the crumb rubber oxidized using hydrogen peroxide with adding formic acid as oxidizing agent (CR-H_2O_2 (30%)) at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

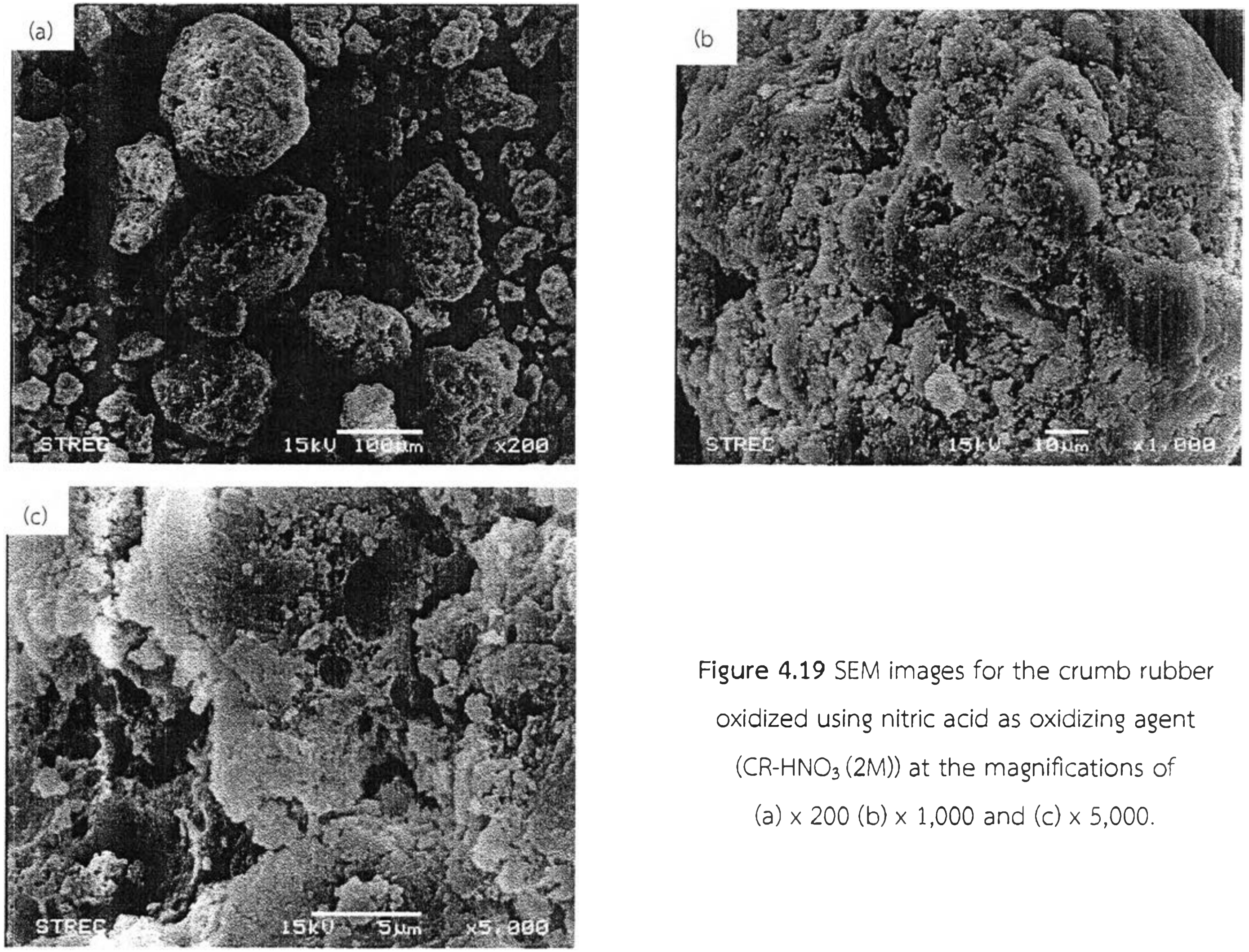


Figure 4.19 SEM images for the crumb rubber oxidized using nitric acid as oxidizing agent (CR-HNO_3 (2M)) at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

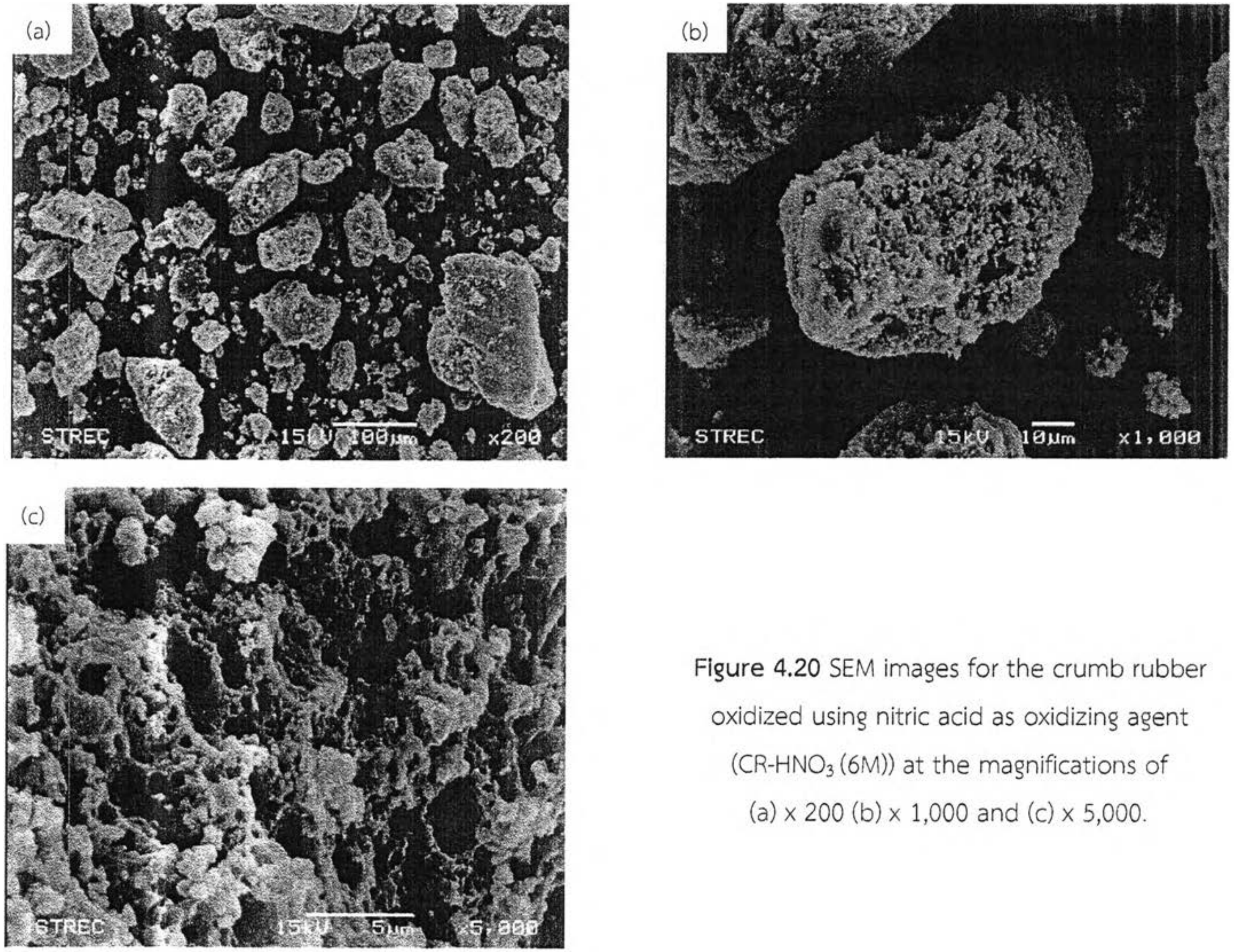


Figure 4.20 SEM images for the crumb rubber oxidized using nitric acid as oxidizing agent (CR-HNO_3 (6M)) at the magnifications of (a) x 200 (b) x 1,000 and (c) x 5,000.

4.6 The Sol/Gel and Swelling Ratio

The sol/gel ratio was applied to study the stability of the oxidized rubbers in the polar and non-polar solvents. The sol (%) is referred to as the rubber fraction that can be dissolved in the solvent while the gel fraction (%) was the undissolved part of the rubber sample after the test. The solvents applied to study were toluene, tetrahydrofuran (THF), and ethanol. THF and ethanol are polar solvents with the dielectric constant (ε) of 7.58 and 24.3, respectively. The dielectric constant of toluene is 2.38. Table 4.4 shows the sol/gel ratio of the original crumb rubber in the solvents. In the polar solvents, the sol fraction of the initial crumb rubber was around 20-23%, whereas it was 15.2% in toluene. The results showed that the crumb rubber was more stable in the non-polar solvent, although natural rubber and styrene-butadiene rubber are the non-polar polymers. It should be due to the presence of the sulfur crosslinks in the rubber. The group of polar solvents, the sol fraction in ethanol was slightly higher than that in THF. It should be due to a dissolution/leaching of the polar additives containing in rubber.

Table 4.4 The sol/gel ratio of the original crumb rubber in different solvents

Property	Solvent		
	Toluene	Tetrahydrofuran (THF)	Ethanol
Dielectric constant (ε)	2.38	7.58	24.30
Sol content (%)	15.3	20.8	22.5
Gel content (%)	84.7	79.2	77.5

Table 4.5 shows the sol/gel ratio of the oxidized crumb rubbers in three different solvents. In case of using only hydrogen peroxide as the oxidizing agent (CR-H_2O_2 (NoF) series), the sol content in toluene was slightly increased, and not significantly affected by the concentration of oxidizing agent. When formic acid was added with hydrogen peroxide in the oxidation (CR-H_2O_2 series), the sol content of the oxidized rubbers was increased, and noticeably affected by the concentration of the oxidant. In the case of using nitric acid, the oxidized rubbers (CR-HNO_3 series) had the sol fraction in the range of 17.6-22.2%, which was higher than the initial rubber for 1.15-1.45 fold, respectively. The concentration of nitric acid unclearly influenced the sol content. For the polar solvents, both of CR-H_2O_2(30%) and CR-HNO_3(6M) exhibited

an increase in the sol fraction. More precisely, CR-HNO_3 (6M) had the sol content in THF higher than CR-H_2O_2 (30%), whereas the sol content of CR-HNO_3 (6M) in ethanol was lower than that of CR-H_2O_2 (30%). These results suggested that the functional groups containing in CR-H_2O_2 (30%) had higher polarity than those in CR-HNO_3 (6M) since the polarity of ethanol is higher than that of THF. This hypothesis was suggested by the FTIR results (Figure 4.4) that CR-H_2O_2 (30%) had more variety of functional groups and sulfur oxide groups than CR-HNO_3 (6M).

Table 4.5 The sol ratio (%) of the oxidized crumb rubbers in different solvents

Sample	Ratio (%)	Solvent		
		Toluene	Tetrahydrofuran	Ethanol
CR-H_2O_2 (20%NoF)	Sol content	19.3	-	-
	Gel content	80.7	-	-
CR-H_2O_2 (30%NoF)	Sol content	20.4	-	-
	Gel content	79.6	-	-
CR-H_2O_2 (10%)	Sol content	15.8	20.7	19.1
	Gel content	84.2	79.3	80.9
CR-H_2O_2(20%)	Sol content	29.8	25.5	21.7
	Gel content	70.2	74.5	78.3
CR-H_2O_2 (30%)	Sol content	40.9	27.5	39.3
	Gel content	59.1	72.5	60.7
CR-HNO_3 (2M)	Sol content	20.8	28.2	16.7
	Gel content	79.2	71.8	84.3
CR-HNO_3 (4M)	Sol content	20.4	29.1	28.4
	Gel content	79.6	71.9	71.6
CR-HNO_3 (6M)	Sol content	17.6	36.2	29.8
	Gel content	82.4	63.8	70.2
CR-HNO_3 (8M)	Sol content	22.2	30.6	24.3
	Gel content	77.8	69.4	75.7

In case of using toluene as the solvent, the sol content of CR-H_2O_2 series was increased when the concentration of the oxidant increased. It should be due to the increase in the low molecular rubber and the non-polar fraction (styrene-butadiene rubber). The sol content of CR-HNO_3 series was slightly higher than that of the initial rubber. It might be due to the highly functionalized short-chain polymers which were generated from the severe oxidation of nitric acid. For the polar solvent, the sol content in ethanol of CR-H_2O_2 (30%) was higher than that of CR-HNO_3 (6M). In contrast, the sol content in tetrahydrofuran of CR-HNO_3 (6M) was higher than that of CR-H_2O_2 (30%). These results suggested that the polarity of CR-H_2O_2 (30%) was higher than CR-HNO_3 (6M). It corresponded to the higher amount of polar functional groups as confirmed by FTIR (Figure 4.4). Moreover, the presence of the low polar functional group (nitro group) in the CR-HNO_3 (6M) series resulted in higher sol content in relatively low polar solvent (THF).

Generally, natural rubber and styrene-butadiene rubber are the main components of the original crumb rubber. They are non-polar materials which have high affinity for the non-polar solvent absorption. Table 4.6 shows the swelling ratio of the original crumb rubber in polar and non-polar solvent. The solvents included toluene and ethanol. Ethanol was applied to the swelling study as the representative reactants in the esterification reaction in order to investigate the effect of reagent polarity on the structure of rubber catalysts. From the results, toluene was the best solvent for swelling the original crumb rubber whereas the swelling ratio of the crumb rubber in ethanol was extremely lower.

Table 4.6 The swelling ratio of the original crumb rubber in different solvents

Solvent	Dielectric constant (ε)	swelling ratio
Toluene	2.38	4.69
Ethanol	24.30	1.09

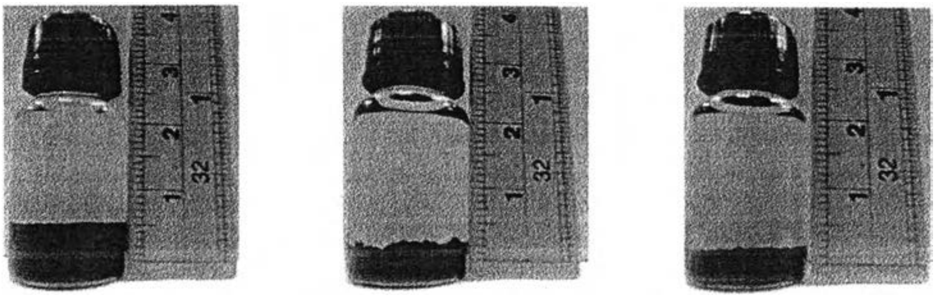
Table 4.7 shows the swelling ratio of the oxidized crumb rubbers in two different solvents. The results indicated that the swelling ratio of the oxidized crumb rubbers was significantly lower than that of the initial crumb rubber when using toluene as solvent. It should be suggested that the polar functional groups has low affinity for the non-polar solvent absorption. Moreover, the concentration of oxidizing agents also affected the swelling ratio. When the concentration of the oxidants increased, the

swelling ratio in toluene was decreased. This result was related to the shorter-chain polymer which depended on the increase in the concentration of the oxidizing agent. Moreover, the rubber products from the oxidation by using hydrogen peroxide with formic acid (CR-H_2O_2 series) were swollen easier than those oxidized with nitric acid (CR-HNO_3 series). It can be supported that the nitric acid was a severe oxidizing agent. The natural rubber and styrene-butadiene rubber were oxidized to generate the highly functionalized short-chain polymer. These results suggested more similarity of the CR-H_2O_2 series to the original crumb rubber. In case of the polar solvent, all of the oxidized rubbers were swollen easier than the initial rubber in ethanol. The swelling ratio of the CR-HNO_3 series was increased at smaller extent than the CR-H_2O_2 series. It should be due to the presence of the polar functional groups in the CR-H_2O_2 series. These functional groups had high affinity for ethanol absorption. This result suggested that the affinity for the polar solvent absorption of the CR-HNO_3 series were lower than that of the CR-H_2O_2 series.

Table 4.7 The swelling ratio of the oxidized crumb rubbers in different solvents

Sample	Solvent	
	Toluene	Ethanol
CR-H_2O_2 (10%)	3.52	2.76
CR-H_2O_2 (20%)	3.84	2.27
CR-H_2O_2 (30%)	2.20	0.98
CR-HNO_3 (2M)	2.33	1.66
CR-HNO_3 (6M)	1.55	1.44
CR-HNO_3 (8M)	1.70	1.59

The swollen rubbers containing in toluene are representatively shown in Figure 4.21. The change of toluene color during the swelling test is an indicative for the solubility of the oxidized rubbers in the non-polar solvent. The swollen crumb rubber gave pale yellow solution (Figure 4.21(a)), while the toluene containing crumb rubber oxidized with hydrogen peroxide was more colorless (Figure 4.21(b)). In the presence of CR-HNO_3 (6M), the toluene color became dark yellow. The shorter polymer chains cleaved from the rubber backbone should result in the higher toluene solubility of the crumb rubber oxidized with nitric acid. For the ethanol, the trend of color change was similar to the case of using toluene.



(a) (b) (c)

Figure 4.21 Swollen rubbers in toluene after standing for 24 h: (a) original crumb rubber (b) CR-H_2O_2 (30 wt.%) and (c) CR-HNO_3 (6M).

4.7 The Acid Content of the Oxidized Crumb Rubber

The acid content of the oxidized crumb rubbers was represented as the content of proton (H^+) in unit of mmol per gram of the oxidized crumb rubber. This was related to the catalytic performance of the oxidized crumb rubbers when they were used as the catalysts in the esterification. The acid content was analyzed by two titration techniques, the direct titration and the back titration. The solvents in direct titration was pure deionized water (DI water) and a mixed solution of DI water and THF (10/10 V/V). The back titration was performed by immersing the sample in a solution of sodium chloride under stirring for ion-exchanging H^+ in the catalyst for the sodium ion. After 18 h of the process, the solution was titrated with a sodium hydroxide (NaOH) solution and phenopthalene was used as indicator. The acid content was calculated according to the equation A6 (Appendix A). Table 4.8 shows the acid content of the oxidized crumb rubbers attained by the different titration methods. In the case of using only hydrogen peroxide as the oxidizing agent, the acid content was low (0.05-0.10 mmol/g). The acid content was increased when the oxidation was performed in hydrogen peroxide with formic acid. The type of solvents significantly affected the acid content value. Using the solution of DI water and THF gave the highest acid content due to the presence of the swelling effect that promotes the acid-base titration. Moreover, the acid content was increased with increasing the concentration of the oxidizing agents. CR-HNO_3 (8M) had the highest acid content of 1.40 mmol/g. However, all the oxidized rubbers possessed the acid content lower than the commercial ion-exchange resin, Amberlyst-15.

It can be seen that the crumb rubber oxidized by using nitric acid had the acid content higher than the rubbers oxidized with hydrogen peroxide containing formic acid. This result was in contrast with the FTIR results that showed strong band of the S=O stretching observed for the crumb rubber oxidized by using hydrogen peroxide with formic acid. Possibly, the observed S=O stretching might be related to other sulfur oxide groups, such as sulfone ($-SO_2-$) and sulfoxide ($-SO-$) all of which gave the IR bands in the similar wave numbers to sulfonic acid group. Since these sulfur oxides are non-acidic, their presence did not enhance the acidity of the oxidized rubbers. However, the increasing of the concentration of hydrogen peroxide increased the acid content of the oxidized crumb rubber since the extent of oxidation was enhanced.

Table 4.8 The acid content of the oxidized crumb rubbers attained by different titration methods

Sample	The acid content in each method (mmol/g sample)		
	DI water[1] (20 mL)	DI water+THF[1] (10/10 V/V)	Back titration with 1M NaCl[2] (25 mL)
CR-H_2O_2 (20%NoF)	0.05	0.10	0.05
CR-H_2O_2 (30%NoF)	0.05	0.10	0.05
CR-H_2O_2 (10%)	0.05	0.20	0.15
CR-H_2O_2 (20%)	0.05	0.20	0.15
CR-H_2O_2 (30%)	0.05	0.30	0.15
CR-HNO_3 (2M)	0.15	0.65	0.20
CR-HNO_3 (4M)	0.25	0.65	0.15
CR-HNO_3 (6M)	0.40	0.85	0.20
CR-HNO_3 (8M)	0.75	1.40	1.10
Amberlyst-15	0.20	3.80	-

[1] titrate with 0.05 M NaOH

[2] titrate 0.10 M NaOH

4.8 The Catalytic Experiment in the Esterification

The oxidized crumb rubbers were applied as the catalysts in the esterification of acetic acid with ethanol. CR-H_2O_2 (30%) and CR-HNO_3 (6M) were chosen as the representatives due to the physicochemical properties. It was found that the solution mixture obtained after the esterification was remarkably changed when compared to the reactants. In the case of using CR-H_2O_2 (30%) as the catalyst, the reaction product was black turbid solution containing suspended black particles. Moreover, the particles remained in the solution even after filtering with the filter paper No.42. In the case of using CR-HNO_3 (6M) as the catalyst, the color of solution was changed from the transparent solution to dark yellow solution. It was resulted from the dissolution of catalyst into the reaction mixture since there was no significant amount of the catalyst remaining on the filter paper. These results should be explained by the high polarity of ethanol and acetic acid as mentioned already in the swelling and the sol/gel ratio. The reactants with lower polarity were applied instead to solve the solubility problem of the rubber catalysts. Octanol and 2-ethyl-1-hexanol as long-chain alcohols were used whereas the carboxylic acid was octanoic acid.

For the esterification of octanoic acid with octanol, the catalyst loss from the reaction is shown in Table 4.9. The recovery of CR-H_2O_2 (30%) and CR-HNO_3 (6M) was 15.2% and 29.6%, respectively. They were lower than Amberlyst-15. Figure 4.22 shows the pictures of the reaction mixture from the esterification of octanoic acid with octanol catalyzed by the oxidized crumb rubbers. The colorless solution of the initial reaction mixture was changed to black turbid solution in the case of using CR-H_2O_2 (30%) as the catalyst, and to transparent yellow in the case of using CR-HNO_3 (6M). These were from the reaction catalyzed by Amberlyst-15 in which the solution was still the same. After that, the reaction mixture was filtered again by using a syringe filter having the pore size of 0.2 micron in order to separate the catalysts suspended. It was found that the reaction mixture using CR-H_2O_2 (30%) was changed from the black turbid solution to transparent solution again (Figure 4.22(b)). In the case of CR-HNO_3 (6M), the resulting solution was not significantly different to the solution before the syringe filtration. The reaction without the catalyst addition gave the octanoic acid conversion of 45.6%. With CR-H_2O_2 (30%) as the catalyst, the octanoic acid conversion was decreased to 32.7%. The octanoic acid conversion was increased to 50.4% over CR-HNO_3 (6M). The highest conversion of octanoic acid (95.8%) was attained by using Amberlyst-15 as the catalyst.

Table 4.9 The catalyst recovery and the octanoic acid conversion in the esterification of octanoic acid with octanol[1]

Catalyst	Weight of catalyst (g)		Catalyst recovery (%)	Octanoic acid conversion (%)
	Before reaction	After reaction		
Blank	-	-	-	45.6
CR-H_2O_2 (30%)	0.074	0.011	15.2	32.7
CR-HNO_3 (6M)	0.076	0.023	29.6	50.4
Amberlyst-15	0.079	0.072	91.7	95.8

[1] Reaction conditions: total batch size, 20 g; molar ratio of alcohol : carboxylic acid, 2:1; catalyst amount, 1 wt.% of carboxylic acid; temperature, 120 °C; time, 8 h.

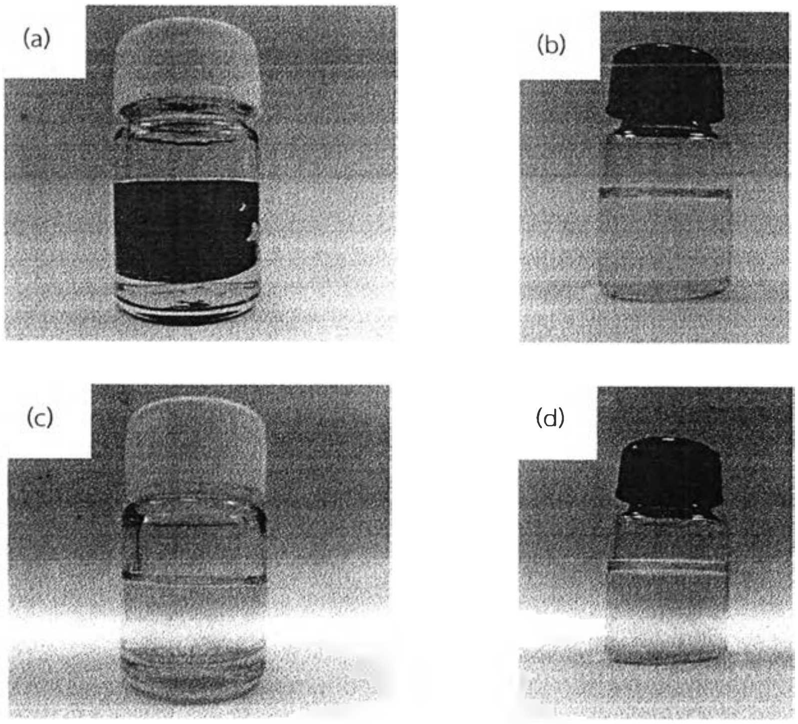


Figure 4.22 The reaction mixture from the esterification of octanoic acid with octanol by using the oxidzed crumb rubbers as the catalysts :
(a) CR-H_2O_2 (30%), before syringe filtration (b) CR-H_2O_2 (30%), after syringe filtration
(c) CR-HNO_3 (6M), before syringe filtration (d) CR-HNO_3 (6M), after syringe filtration.

For the esterification of octanoic acid with 2-ethyl-1-hexanol, the catalyst loss from the reaction is shown in Table 4.10. The recovery of CR-H_2O_2 (30%) and CR-HNO_3 (6M) was 15.6% and 31.8%, respectively. They were lower than Amberlyst-15. Figure 4.23 shows the pictures of the reaction mixture from the esterification of octanoic acid with 2-ethyl-1-hexanol catalyzed by the oxidized crumb rubbers. The colorless solution of the initial reaction mixture was changed to black turbid solution in the case of using CR-H_2O_2 (30%) as the catalyst, and to transparent yellow in the case of using CR-HNO_3 (6M). These were from the reaction catalyzed by Amberlyst-15 in which the solution was still the same. After that, the reaction mixture was filtered again by using a syringe filter having the pore size of 0.2 micron in order to separate the catalysts suspended. It was found that the reaction mixture using CR-H_2O_2 (30%) was changed from the black turbid solution to transparent solution again (Figure 4.23(b)). In the case of CR-HNO_3 (6M), the resulting solution was not significantly different to the solution before the syringe filtration. The reaction without the catalyst addition gave the octanoic acid conversion of 59.4%. With CR-H_2O_2 (30%) as the catalyst, the octanoic acid conversion was decreased to 52.4%. The octanoic acid conversion was increased to 75.3% over CR-HNO_3 (6M). The highest conversion of octanoic acid (92.6%) was attained by using Amberlyst-15 as the catalyst.

Table 4.10 The catalyst recovery and the octanoic acid conversion in the esterification of octanoic acid with 2-ethyl-1-hexanol[1]

Catalyst	Weight of catalyst (g)		Catalyst recovery (%)	Octanoic acid conversion (%)
	Before reaction	After reaction		
Blank	-	-	-	59.4
CR-H_2O_2 (30%)	0.077	0.012	15.6	52.4
CR-HNO_3 (6M)	0.078	0.025	31.8	75.3
Amberlyst-15	0.077	0.073	94.8	92.6

[1] Reaction conditions: total batch size, 20 g, molar ratio of alcohol : carboxylic acid ,2:1; catalyst amount, 1 wt % of carboxylic acid; temperature, 120 °C; time, 8 h

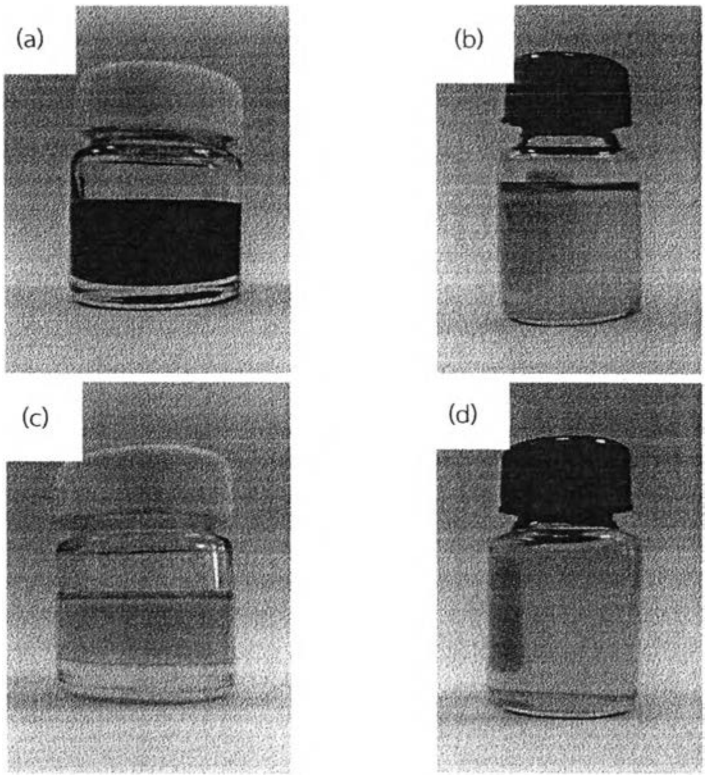


Figure 4.23 The reaction mixture from the esterification of octanoic acid with 2-ethyl-1-hexanol by using the oxidzed crumb rubbers as the catalysts : (a) CR-H_2O_2 (30%), before syringe filtration (b) CR-H_2O_2 (30%), after syringe filtration (c) CR-HNO_3 (6M), before syringe filtration (d) CR-HNO_3 (6M), after syringe filtration.

The esterification of octanoic acid with octanol or 2-ethyl-1-hexanol at 120 °C can occur without any addition of catalyst due to the self-catalysis of carboxylic acid as the reactant. When using CR-H_2O_2 (30%) as the catalyst the octanoic acid conversion was lower than the case of the blank reaction. It should be due to the presence of polar non-acidic functional groups in CR-H_2O_2 (30%), which induced the reactants absorbed into the rubber structure. As a result, the molar ratio of alcohol/carboxylic acid in the reaction mixture was changed. Generally, the higher the reactants ratio is used, the higher the degree of carboxylic acid conversion is attained [50]. CR-HNO_3 (6M) catalyzed the reaction to higher octanoic acid conversion level. This result should be ascribed to the acid functional groups as sulfonic acid and carboxylic acid groups presenting in CR-HNO_3 (6M). For the comparative octanoic acid conversion with the different alcohols, the octanoic acid conversion in case of 2-ethyl-1-hexanol was higher than octanol. It should be due to the presence of strong nucleophile (oxygen atom) in 2-ethyl-1-hexanol which was able to gain electrons from 2 carbon atoms. However, the catalytic performance of the oxidized rubbers in both the esterification cases was considerably lower than that of Amberlyst-15, which had the highest octanoic acid coversion of >90%.

CR-HNO_3 (6M) was chosen for studying the effect of catalyst loading on the conversion of octanoic acid in the esterification of octanoic acid with octanol. The esterification was performed by using the total batch size of 20 g in which the molar ratio of alcohol to carboxylic acid was 2:1. The reaction was carried out at 120 °C for 8 h. The results are shown in Table 4.11. It was observed that with increasing the catalyst loading from 1 wt.% to 8 wt.%. The octanoic acid conversion was slightly increased. It should be attributed to an increase in the amount of acid site with increasing the catalyst loading. The highest conversion of the octanoic acid (74.9%) was attained at the highest CR-HNO_3 (6M) loading (8 wt.% of the octanoic acid). Moreover, the catalyst recovery was slightly increased when the catalyst loading increased. It was possible that the solution of the catalyst reached the saturated state which remained the surplus catalyst after the reaction. Figure 4.24 shows the color of products after the esterification by using different catalyst amounts. The solution color became dark yellow when the catalyst loading was increased. It should be due to an increase in the amount of dissolution catalyst with increasing in the catalyst loading. This presumption was supported by the slight increase in the catalyst recovery.

Table 4.11 The effect of catalyst loading on the ocatanoic acid conversion and the catalyst recovery from the esterification of octanoic acid with octanol

Catalyst	Weight of catalyst (g)		Catalyst recovery (%)	Octanoic acid conversion (%)
	Before reaction	After reaction		
Blank	-	-	-	45.6
CR-HNO_3 (6M) 1%	0.076	0.023	29.6	50.4
CR-HNO_3 (6M) 2%	0.146	0.060	41.3	54.2
CR-HNO_3 (6M) 3%	0.212	0.091	42.7	63.8
CR-HNO_3 (6M) 5%	0.342	0.156	45.8	67.1
CR-HNO_3 (6M) 8%	0.570	0.279	48.8	74.9

[1] Reaction conditions: total batch size, 20 g; molar ratio of alcohol : carboxylic acid, 2:1; temperature, 120 °C; time, 8 h.

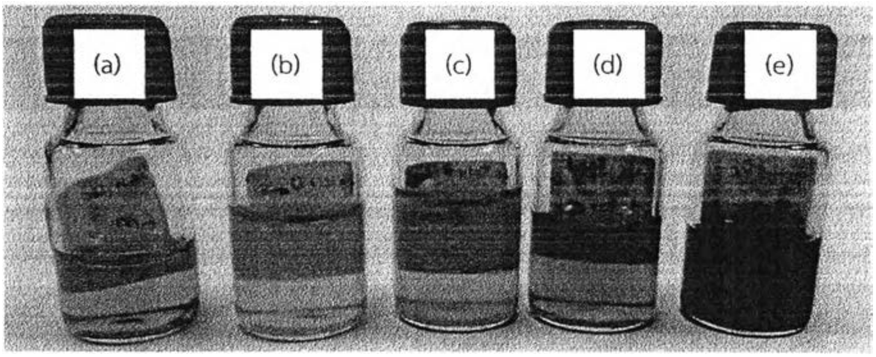


Figure 4.24 The reaction mixture from the esterification of octanoic acid with octanol over CR-HNO_3 (6M) at different loading : (a) 1 wt.%, (b) 2 wt.%, (c) 3 wt.%, (d) 5 wt.% and (e) 8 wt.%.

Figure 4.25 shows the conversion of octanoic acid attained in the absence (blank) and presence of CR-HNO_3 (6M) 5 wt.% as the function of times. Although there were the comparable conversion at the initial stage of the reaction, the reaction over CR-HNO_3 (6M) obviously gave higher octanoic acid conversion than the blank reaction after 1 h. This result indicated that the acidic function of CR-HNO_3 (6M) promoted the esterification of octanoic acid. It should be noted that at 5 h the blank reaction reached equilibrium but the conversion was gained in the presence of the oxidized rubber. However, the color of the reaction mixture from the esterification as the function of times was shown in Figure 4.26. The solution color became dark yellow when the time of reaction increased. It was the darkest at the end of reaction course (8 h).

In order to investigate the presence of the oxidized rubber catalyst dissolved in the reaction mixture, the reaction product with dark yellow color was analyzed by FTIR. Figure 4.27 shows FTIR spectrum of the reaction product with dark yellow color. The carboxylic acid remaining was evidenced by the IR bands at 1716, 1230 and 1270 cm^{-1}. The bands at 1170 and 1200 cm^{-1} related to the C-O stretching and 1735 cm^{-1}, corresponding to the C=O stretching confirmed the ester product formed by the esterification. This result was in accordance with the GC chromatogram that showed the ester product as the last peak (Appendix C). The S=O stretching of sulfonic acid group observed at 1030, 1160 and 1360 cm^{-1}. Moreover, the nitro group was confirmed by the band at 1550 cm^{-1}. These results suggested that there was the rubber catalyst dissolved the reaction mixture. This result can explain the loss of catalyst after the reaction.

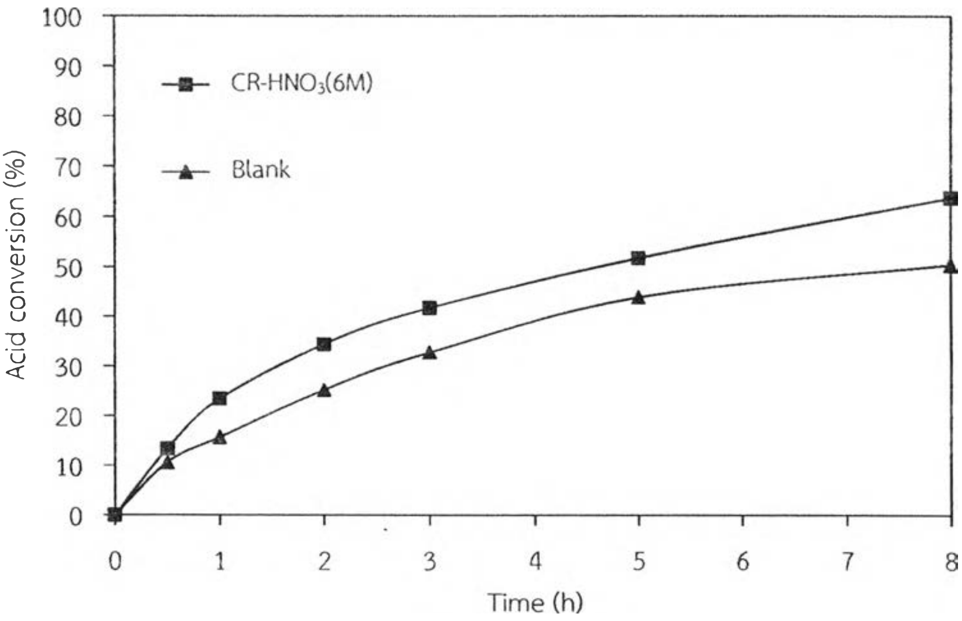


Figure 4.25 The octanoic acid conversion vs reaction time from the esterification of octanoic acid with octanol in the absence (blank) and presence of CR-HNO_3 (6M) (5 wt.%).

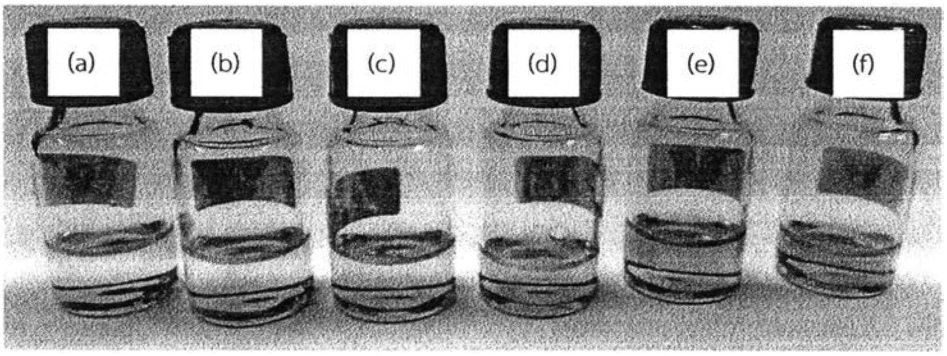


Figure 4.26 The reaction mixture from the esterification of octanoic acid with octanol over CR-HNO_3 (6M) (5 wt.%) at different reaction times : (a) 30 min, (b) 1 h, (c) 2 h, (d) 3 h, (e) 5 h and (f) 8 h.

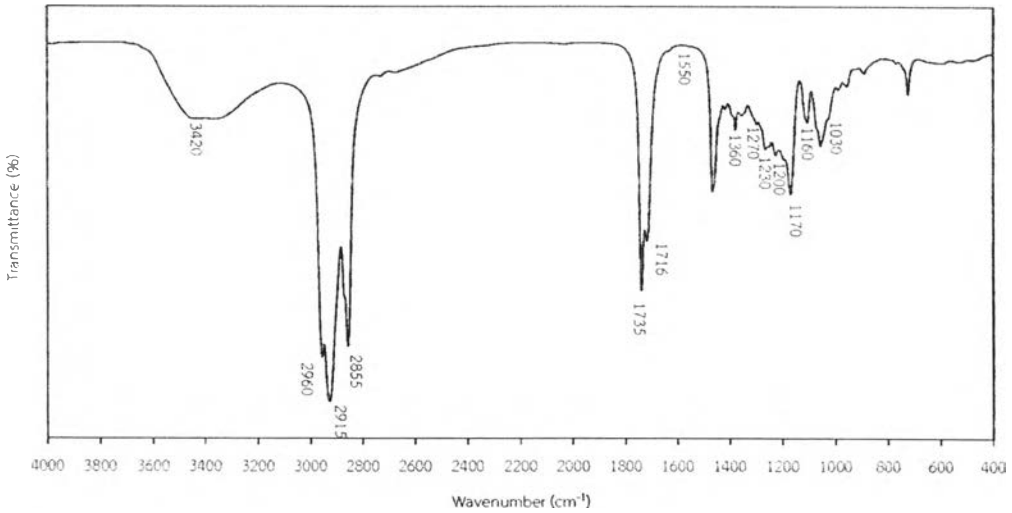


Figure 4.27 FTIR spectrum of the ester reaction product with dark yellow color.