CHAPTER IV

RESULTS AND DISCUSSION

The major objective of this research is to characterize and to reduce mal-odor from natural rubber. Three types of rubber samples based on the process of production were used. The first is field grade raw material such as fresh latex, cup lumps and scrap. The second is ribbed smoke sheet (RSS); Smoke rubber grade 1 to 5. And the last is block rubber such as STR5L, STR5, STR10, STR20 and deproteinized natural rubber (DPNR). The collection of volatile components that may cause mal-odor from natural rubber were carried out using the headspace technique. The volatile samples were then subjected to the analysis by Gas Chromatography (GC) and Gas Chromatography / Mass Spectrometry (GC/MS).

4.1 Characterization of Mal-odor from Natural Rubber

The most suitable conditions for characterization of mal-odor by GC were first identified. The HP-5 capillary column, which is capable of separating low polarity compounds, and HP-20M, which is used for separating polar compounds, were used. The condition that was first attempted for HP-20M column was, initial temperature as 60°C (5mins) and increased to 200°C at the rate of 10°C/min for all runs. The injector and detector temperature were 200°C. Helium and nitrogen were used as the carrier gas and make-up gas, respectively at the flow rate of 2.00 mL/min. The GC

chromatogram showed two groups of peak in every sample. The conditions were varied in order to find the best way to separate the peaks in each group. The oven temperature was reduced from 60 °C to 35°C. The lowest oven temperature was 35°C. which is the optimum oven temperature in this study. The maximum column temperature was reduced from 200°C to 150°C. Using this optimum condition, the retention time of peaks in the first group was about 0-5 min. While ones of peaks in the second group was up from 6 min. An attempt to obtain an optimized condition for HP-5 column was not successful. The chromatogram obtained from HP-5 capillary column showed less number of peaks than the HP-20M capillary column implying that some peaks were not well resolved or some were not detected.

The optimum condition to separate the volatile components using HP-20M capillary column by GC was: 35°C (2 mins) to 150°C at the rate of 10°C/min for all runs. The injector and detector temperatures were 200°C. Helium and nitrogen were used as the carrier gas and make-up gas, respectively at the flow rate of 2.00 ml/min.

Figure 4.1 shows the GC chromatogram of volatile components from cup lumps which give the strongest mal-odor. It was obvious that the peaks having retention time higher than 6 min were well separated. Each peak was labeled alphabetically from *g* to *n* as the retention time increases. The peaks were later verified by GC/MS using the same optimum condition. The results from GC/MS (Figure 4.2) indicated that these components are the low molecular weight volatile fatty acids (VFA) such as acetic acid, propionic acid, butyric acid, isobutyric acid, valeric acid and isovaleric acid. The standard sample of VFA were also injected to GC and GC/MS (Figure 4.3 and 4.4) , each peak was identified as illustrated in Table 4.1.

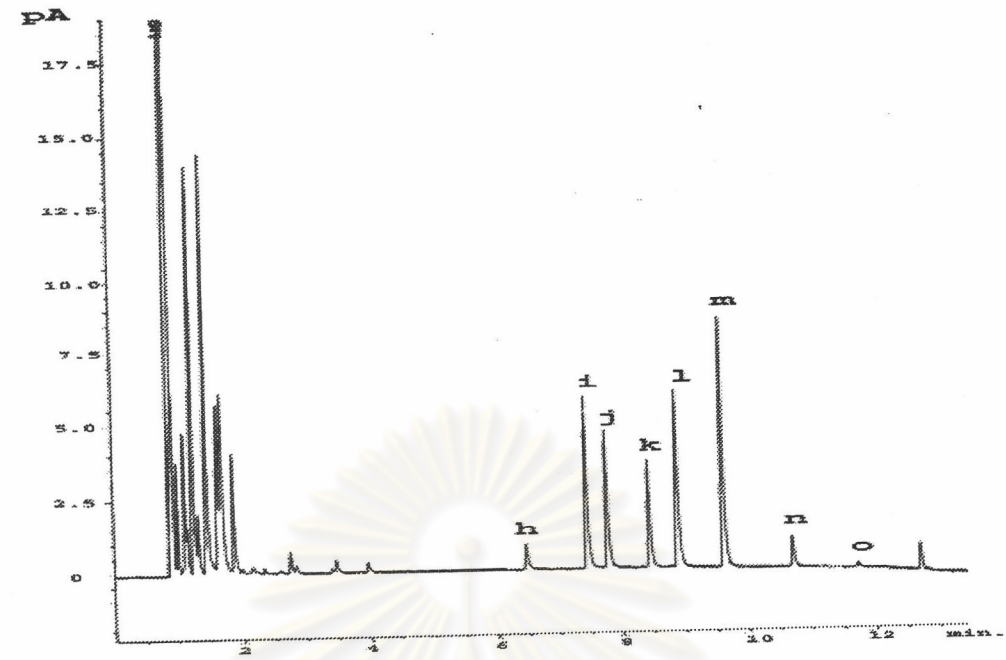

Figure 4.1 The GC chromatogram of volatile mal-odor components of cup lumps: (h) acetic acid, (i) propionic acid, (j) isobutyric acid, (k) butyric acid, (l) Isovaleric acid, (m) valeric acid, (n) hexanoic acid, (o) heptanoic acid

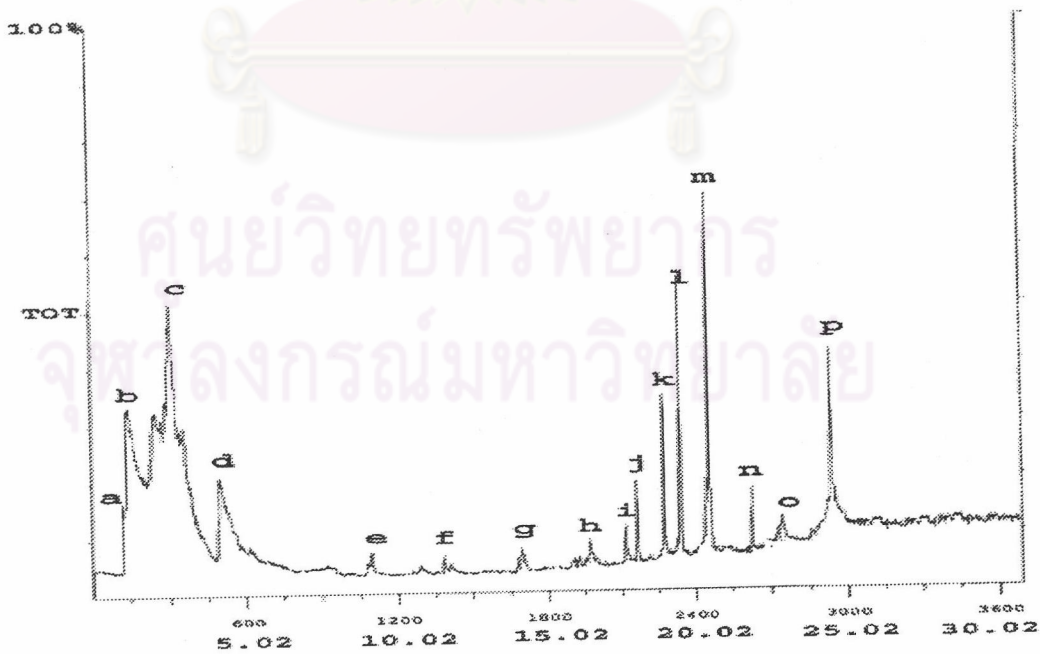

Figure 4.2 The GC/MS chromatogram of the volatile mal-odor components of cup lumps

Table 4.1 The components of mal-odor from cup lumps as identified by GC-MS (Figure 4.2)

Symbol	Retention time (mins)	MW (amu)	Compound Description
a	1.10	45	Ethylamine
b	1.13	48	Methanethiol
c	2.16	86	Pentanal
d	2.37	86	2-Pentanone
e	4.15	122	Benzylhydrazine
f	9.10	136	Camphene
g	11.30	134	1-Isopropyl-methylbenzene
h	16.27	60	Acetic acid
i	17.41	74	Propionic acid
j	18.03	88	Isobutyric acid
k	18.58	88	Butyric acid
l	19.32	102	Isovaleric acid
m	20.28	102	Valeric acid
n	21.52	116	Hexanoic acid
o	23.37	130	Heptanoic acid
p	24.33	108	p-Cresol

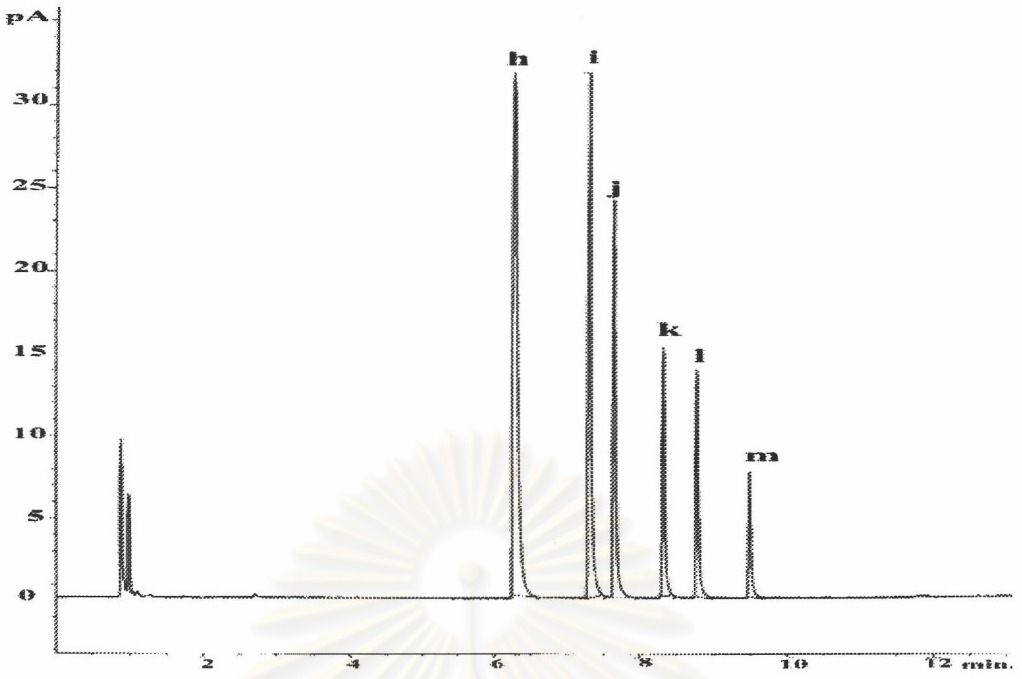

Figure 4.3 The GC chromatogram of mixed standard volatile fatty acids:(h) acetic acid, (i) propionic acid, (j) isobutyric acid, (k) butyric acid, (l) isovaleric acid, (m) valeric acid.

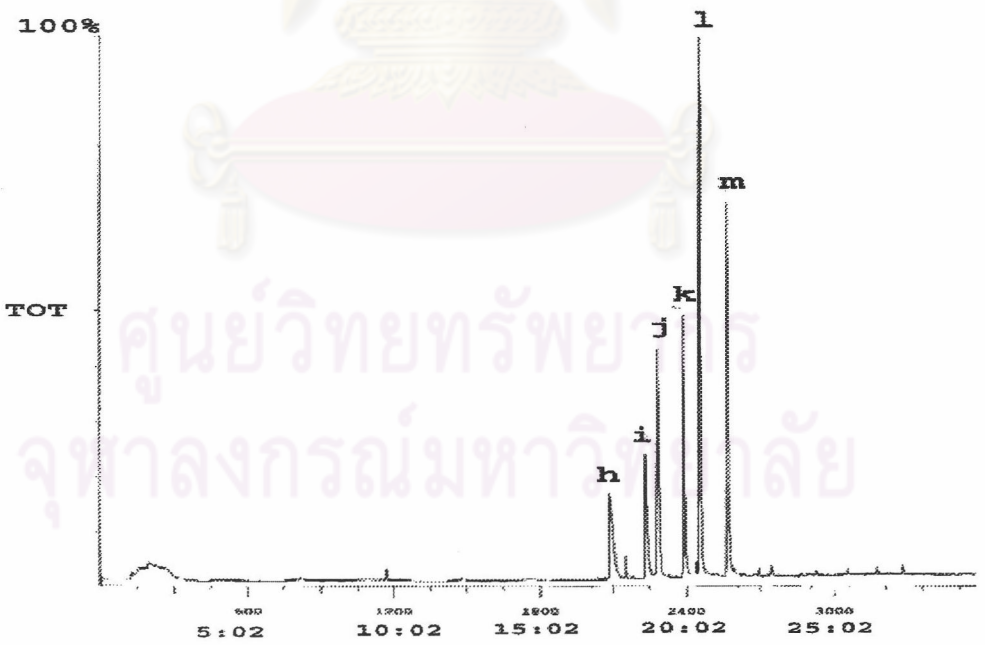

Figure 4.4 The GC/MS chromatogram of mixed standard volatile fatty acids: (h) acetic acid, (i) propionic acid, (j) isobutyric acid, (k) butyric acid, (l) isovaleric acid, (m) valeric acid.

As a result of higher sensitivity of GC/MS as compared with GC, a better resolved peaks obtained from GC/MS chromatogram were evidenced. The other 10 samples gave similar results as cup lumps. Their GC chromatograms also consist of two groups of peaks. However, the intensity of peaks in the second group which are VFA was varied in each sample depending on the intensity of odor. The GC and GC/MS chromatogram of samples having strong mal-odor: cup lumps (see Figure 4.1-4.2 and Table 4.1) and STR20 (see Figure 4.5-4.6 and Table 4.2) have high intensity of propionic acid (h) , isobutyric acid (i) , butyric acid (j), isovaleric acid (k) and valeric acid (l) than other samples. While less odorous samples such as DPNR (see Figure 4.8-4.9 and Table A-1) and STR5L (see Figure 4.10-4.11 and Table A-2) have low peak intensity of VFAs. Acetic acid and propionic acid were found in every sample. Furthermore, hexanoic acid and heptanoic acid were also found in volatile mal-odor samples such as cup lumps, STR20 and Smoke5. This result agreed well with Isa's work reported earlier that the odorous components of exhaust gases from SMR factories in Malaysia were identified as low molecular weight volatile fatty acids (C_2-C_5).[27]

The first group of peaks (retention time 0-6 min.) could not be resolved using HP-20M column in GC analysis because HP-20M column was suitable for the separation of high polarity compound, but not for the components in this group which are less polar than components in the second group. The GC conditions were also adjusted by reducing the oven temperature from 60°C to 35°C and holding the time at this temperature for 2 mins. The separation was not improved because the oven temperature could not be adjusted to lower than 35°C from the result of the warm weather in Thailand and the limitation of instrument.

All odorous rubber samples then were subjected to GC/MS analysis equipped with a ZB-Wax column which is more suitable for components having low polarity. From the comparison of the mass spectra of each peak in the first group indicated roughly that these compounds have molecular weight about 40-150 amu and consisting of nitrogen, sulfur, aliphatic compounds and aromatic compounds as illustrated in Table 4.3. However, the confirmation using GC analysis of standard compounds cannot be done since the peaks are still not well resolved.

Another experiment was conducted by analyzing the liquid that condensed inside the sample bottle after heating up the cup lumps sample. The liquid sample was injected into GC/MS equipped with ZB-Wax column using the optimum condition. Figure 4.7, the chromatogram showed that the peak intensity of the first group of peaks (retention time 0-6 min.) was close to zero. On the contrary significantly intense peaks were found for the second groups of peak. The odors from liquid sample and cup lumps samples were also compared by sniffing. The odor of liquid sample was similar to cup lumps sample (used headspace to analyze the mal-odor). This observation implied that the second group of peaks, which are polar compounds, may be the major cause of mal-odor in rubber.

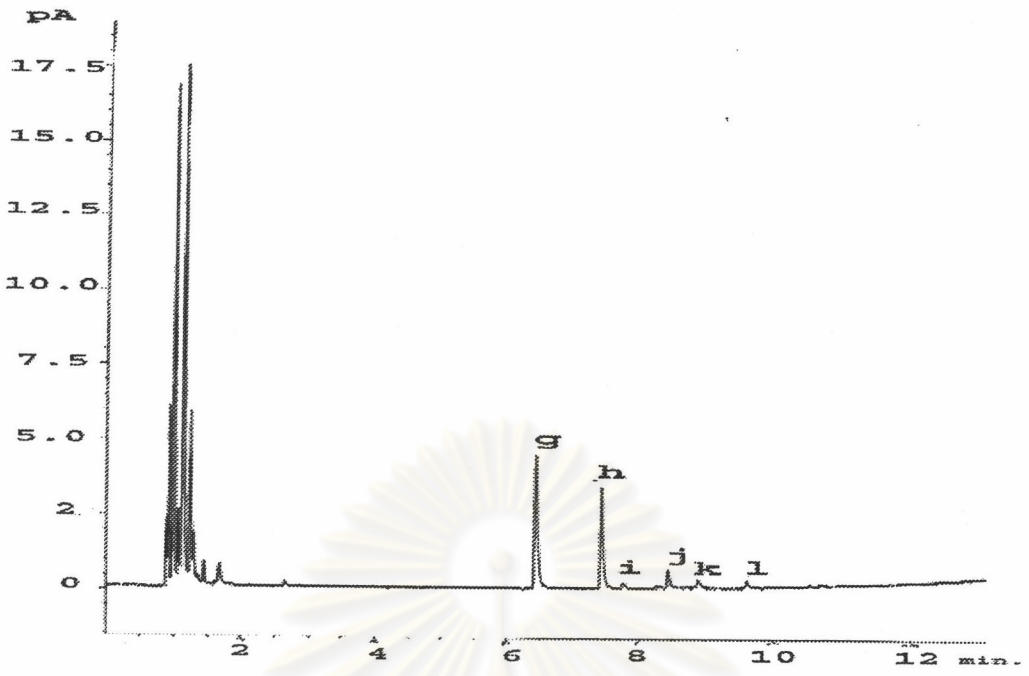

Figure 4.5 The GC chromatogram of volatile mal-odor components of STR20 (g) acetic acid, (h) propionic acid, (i) isobutyric acid, (j) butyric acid, (k) isovaleric acid, (l) valeric acid

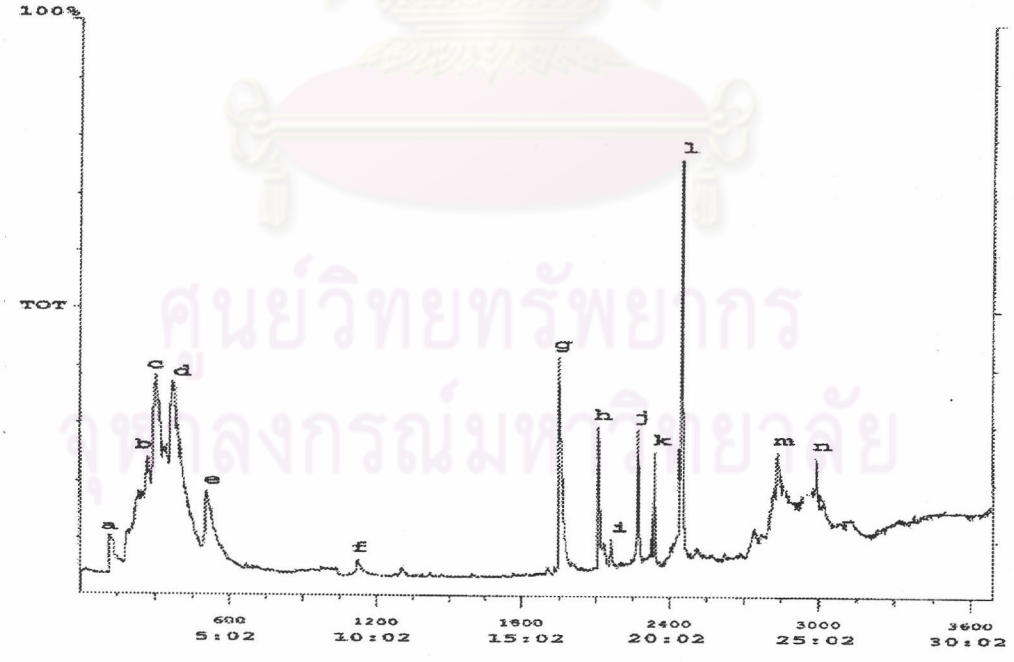

Figure 4.6 The GC/MS chromatogram of the volatile mal-odor components of STR20

Table 4.2 The components of mal-odor from STR20 as identified by GC/MS

Symbol	Retention time (mins)	MW (amu)	Compound Description
a	1.07	45	Ethylamine
b	2.16	86	Pentanal
c	2.32	59	Trimethylamine / 2-Pentanone (86)
d	3.05	100	Hexanone
e	4.16	122	Benzylhydrazine
f	9.23	114	2-Heptanone
g	16.26	74	Acetic acid
h	17.38	88	Propionic acid
i	18.04	126	Isobutyric acid
j	18.59	88	Butyric acid
k	19.32	102	Isovaleric aicd
l	20.26	102	Valeric acid
m	23.36	116	Heptanoic acid
n	24.36	84	p-Cresol

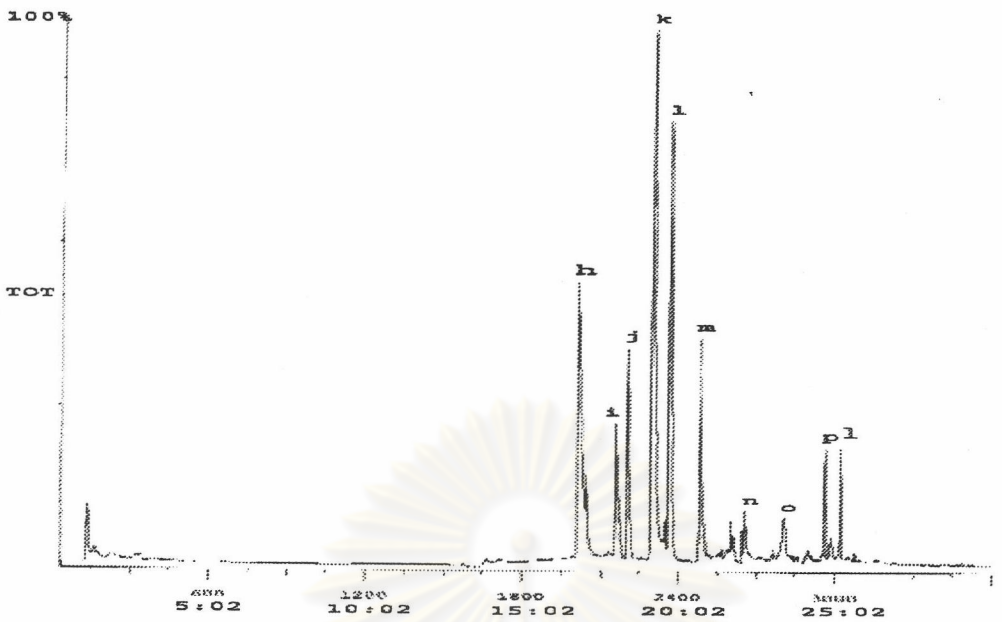

Figure 4.7 The GC/MS chromatogram of volatile mal-odor components of liquid sample from cup lumps

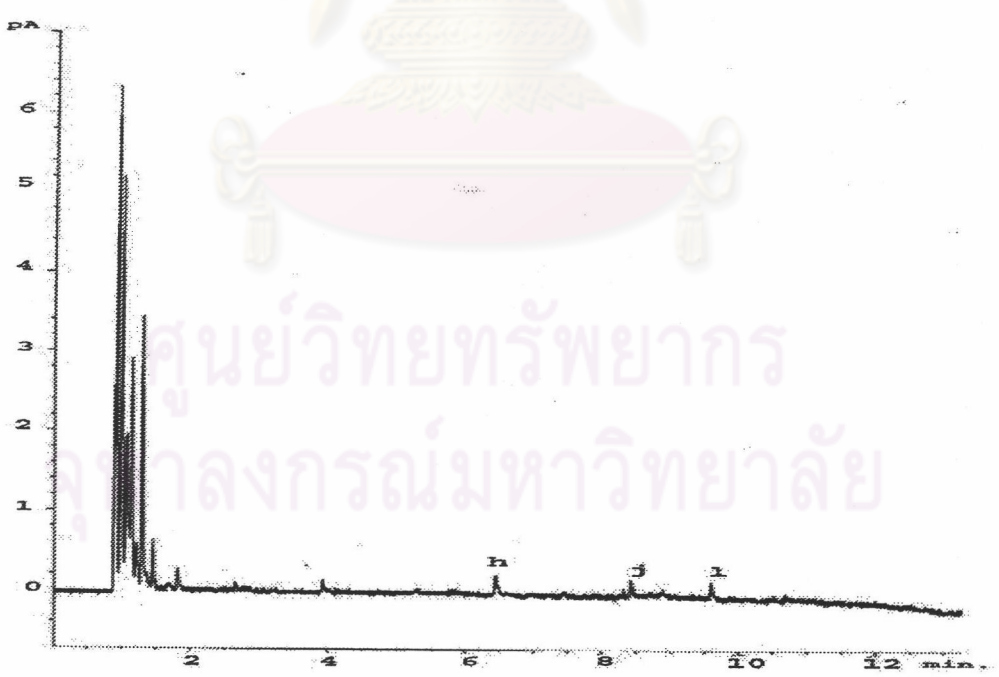

Figure 4.8 The GC chromatogram of volatile mal-odor components of DPNR

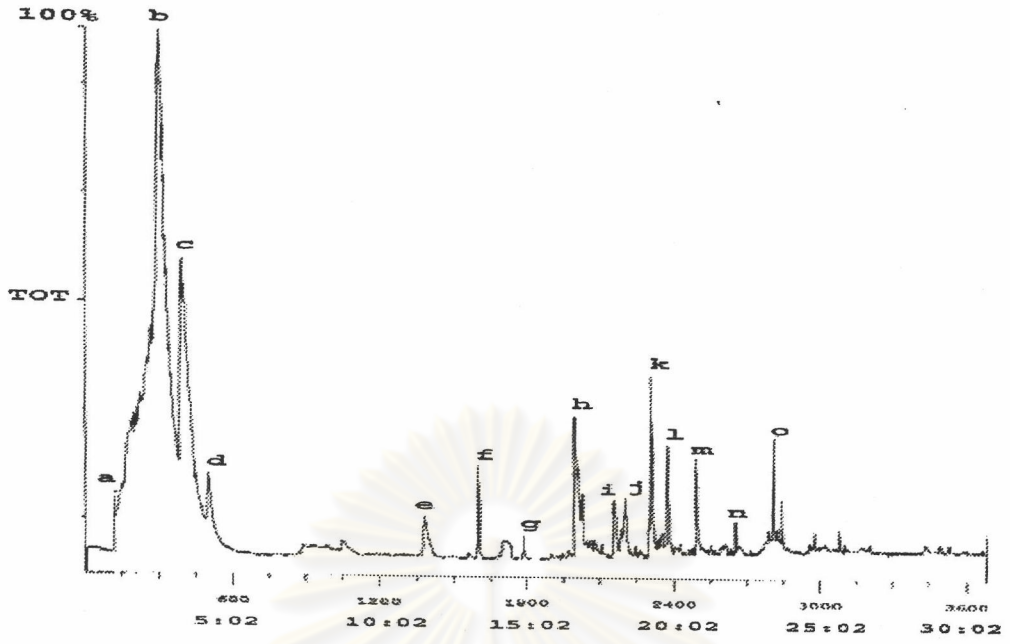

Figure 4.9 The GC/MS chromatogram of the volatile mal-odor components of DPNR (see Appendix A, Table A-1)

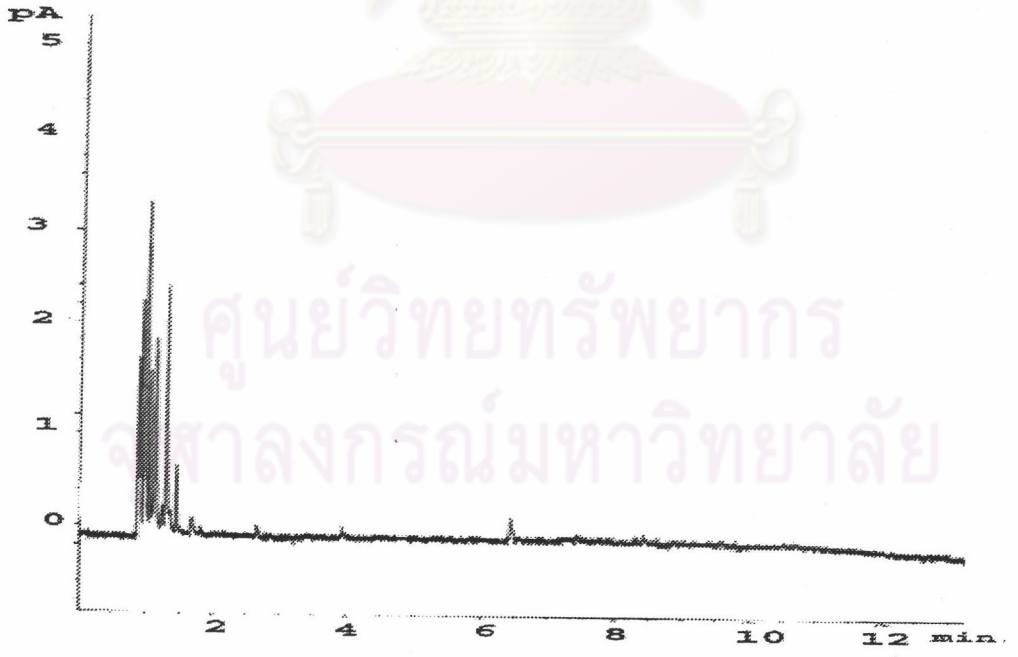

Figure 4.10 The GC chromatogram of volatile mal-odor components of STR5L

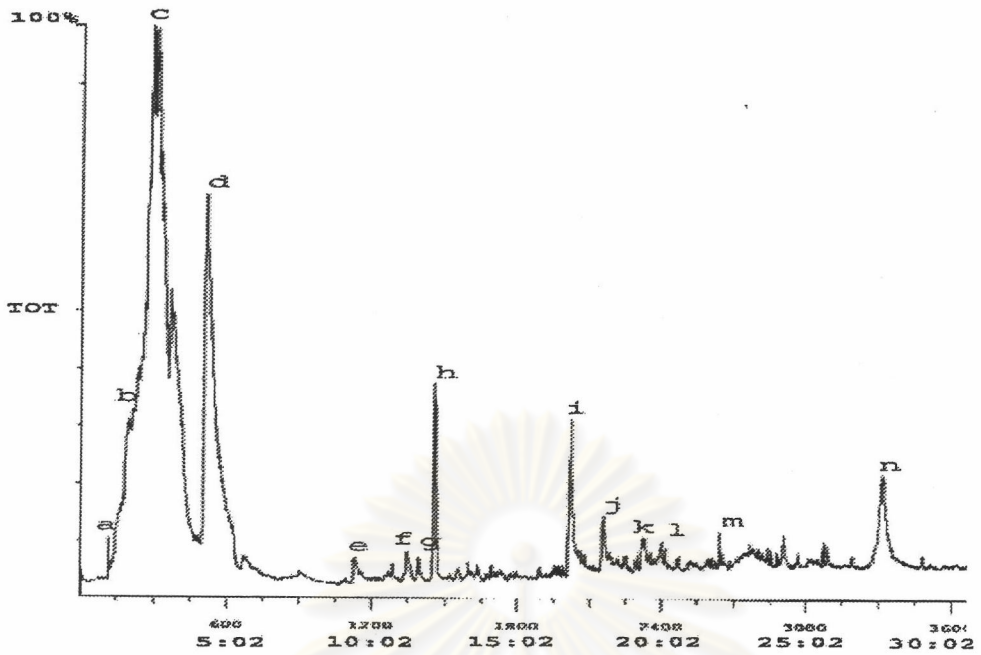

Figure 4.11 The GC/MS chromatogram of the volatile mal-odor components of STR5L(see appendix A, Table A-2)

Table 4.3 The components of the first group of peaks from natural rubber

No.	Compound	Molecular mass (m/z)	Odor descriptor
1	Dimethylamine	45.08	Colorless liquid or gas with a pungent, fishy, or ammonia-like odor.
2	Ethylamine	45.08	Colorless liquid or gas with a strong ammonia -like odor.
3	Trimethylamine	59.11	Ammonia like odor when vapor concentration are heavy. Generated in the degradation of organics in plants and animals. Hygroscopic.
4	Benzylhydrazine	122.16	
5	Butanone	72.10	Clear colorless liquid with a fragrant mint-like, moderately sharp odor.
6	2-Pentanone	86.13	Water-white liquid with a characteristic ketone odor.
7	Heptanone	114.18	
8	1-Amino-2-propanol	75.11	Colorless liquid, Hygroscopic.
9	2-Pentanol	88.14	
10	n-Valeraldehyde	86.13	Colorless liquid.
11	Hexaldehyde	100.16	Flammable liquid.
12	Propionaldehyde	58.07	Colorless liquid with a suffocating fruity odor. Air sensitive.

Table 4.3 (cont.)

No.	Compound	Molecular mass (m/z)	Odor descriptor
13	N,N-dimethylformamide	73.09	Colorless liquid with a faint, ammonia-like odor.
14	N,N-dimethylacetamide	87.12	Colorless liquid with a faint, ammonia-like odor.
15	Thiophene	84.13	Clear, colorless liquid. lachrymator; Stench.
16	Thiazole	85.12	Colorless or pale yellow liquid. Foul odor.
17	Ethylbenzene	106.16	Colorless liquid with an aromatic odor.
18	p-Xylene	106.67	Clear liquid; colorless plates or prisms at low temperature.
19	o-Xylene	106.67	Colorless liquid with aromatic odors.
20	1-Phenyl propadiene	116.00	
21	Isopropylbenzene	120.19	Colorless liquid with a sharp, penetrating, aromatic odor.
22	1,2,3-Trimethylbenzene	120.19	Liquid.
23	1,2,4-Trimethylbenzene	120.19	
24	Isobutylbenzene	134.22	
25	Isopropyl methylbenzene	134.22	
26	Trans-hexene	84.12	

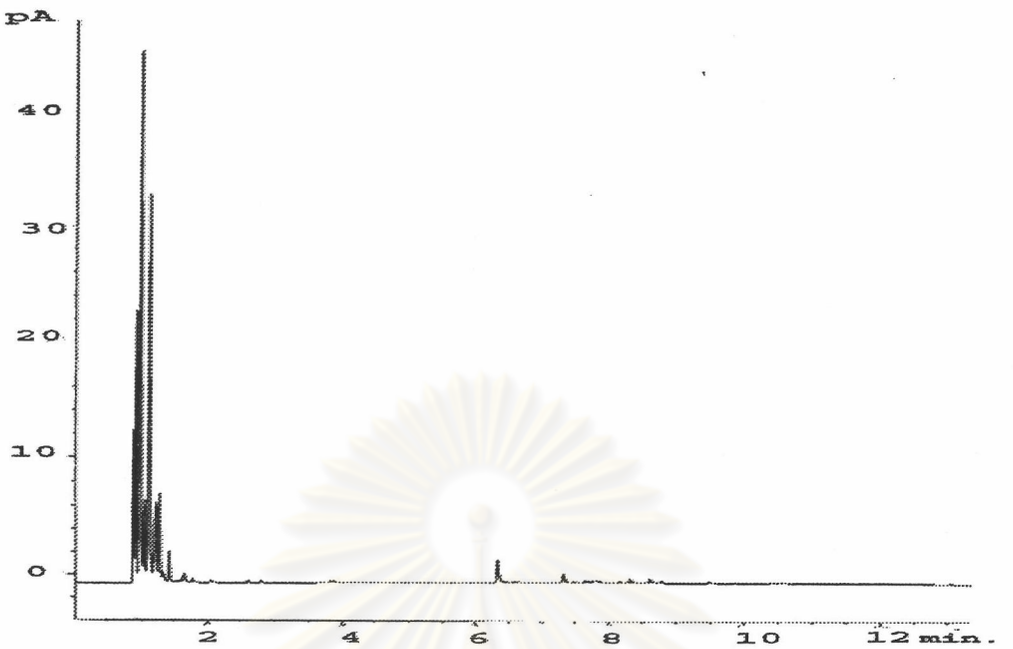

Figure 4.12 The GC chromatogram of volatile mal-odor components of STR5

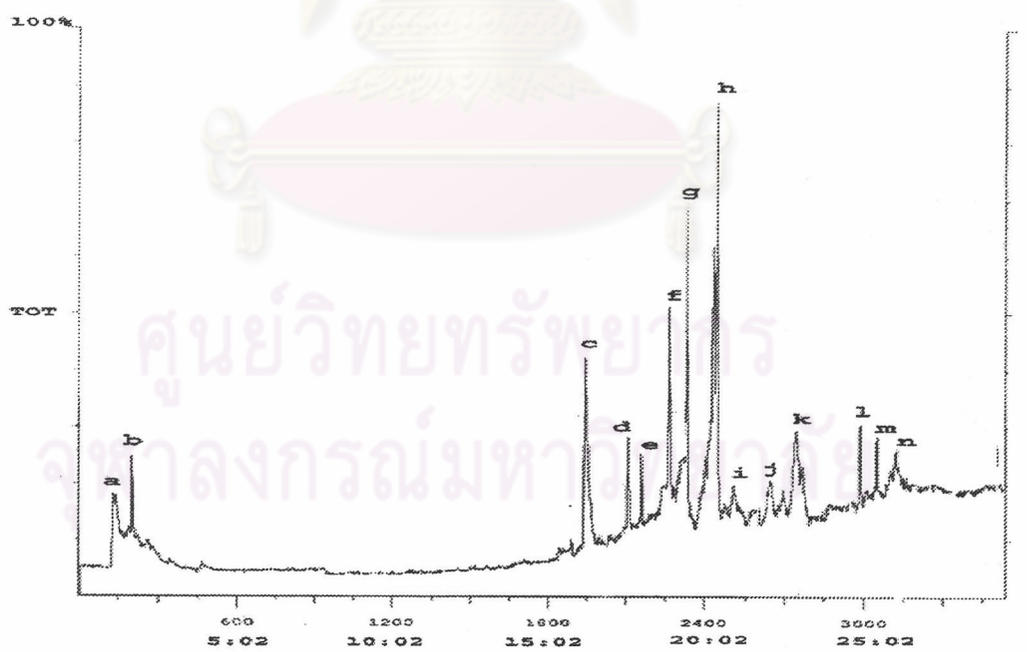

Figure 4.13 The GC/MS chromatogram of the volatile mal-odor components of STR5(See appendix A, TableA-3)

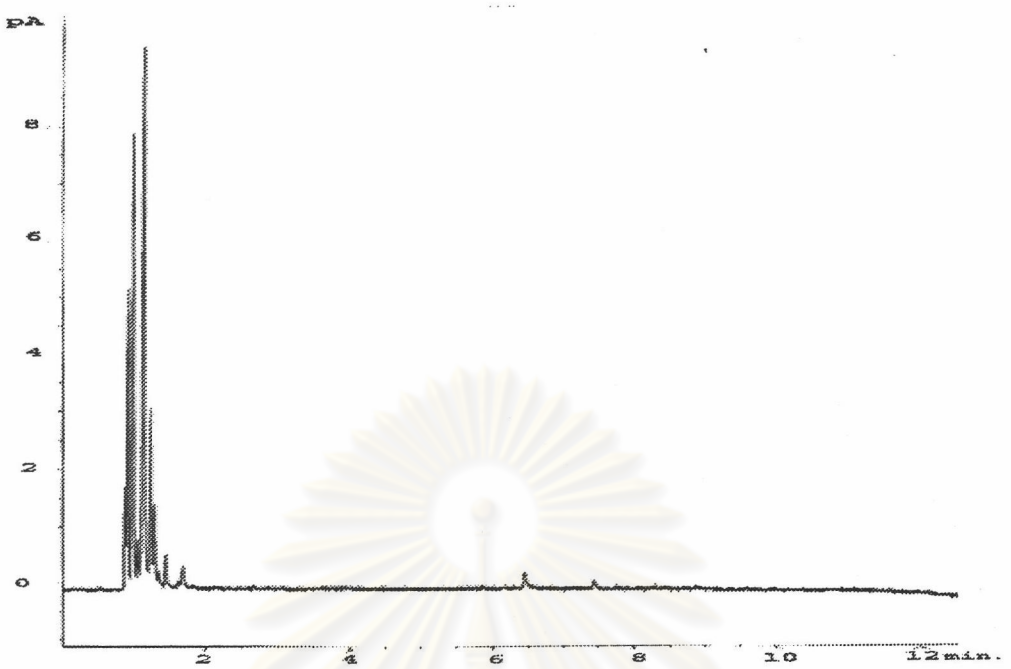

Figure 4.14 The GC chromatogram of volatile mal-odor components of STR10

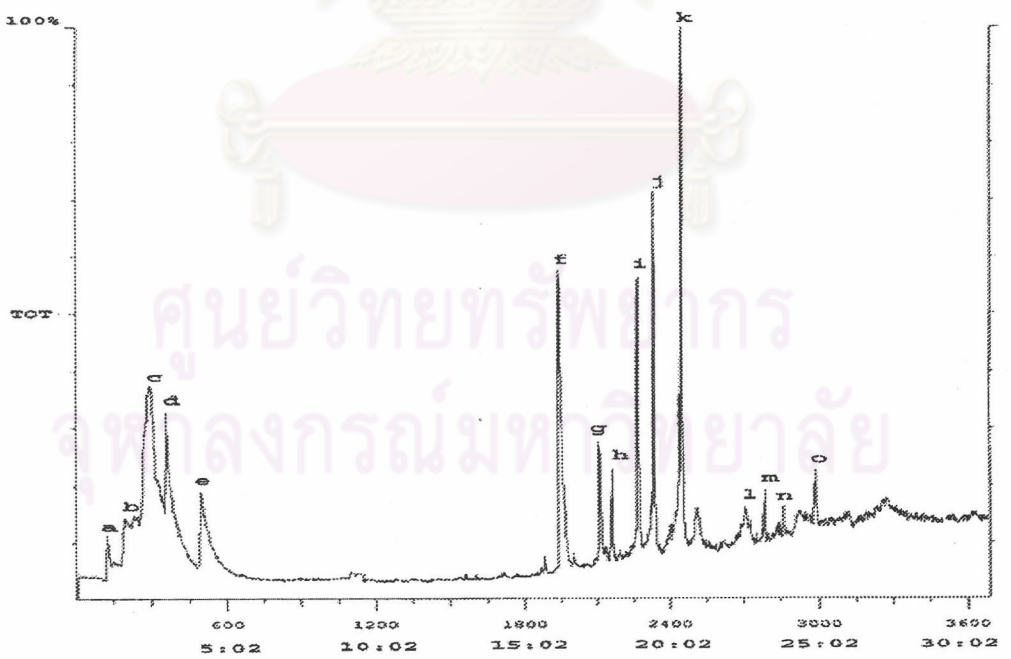

Figure 4.15 The GC/MS chromatogram of volatile mal-odor components of STR10 (see Appendix A, Table A-4)

The smoke rubber samples were analyzed using the optimum condition by both GC and GC/MS. The results were shown in Figure 4.16-4.25 and Table 4.7, the mal-odor components in the second group were VFA which appeared in other smoke samples. Aromatic compounds were found among the first group of peaks that were different from cup lumps and STR samples. They were the major components that cause mal-odor in smoke rubber, which were probably originated during smoking process.

Figure 4.16 The GC chromatogram of volatile mal-odor components of Smoke1

Table 4.4 (cont.)

Symbol	Retention time (mins)	MW. (amu)	Compound Description
n	20.00	128	Naphthalene
o	20.25	102	Valeric acid
p	22.66	94	Phenol
q	24.30	108	p-Cresol
r	24.79	137	Tryamine

Three types of rubber samples used in this experiment are cup lumps, block rubber and ribbed smoke sheet rubber. These samples were processed from natural rubber of "*Hevea brasilliensis*" tree. The different types of sample were the raw material used in processing. Ribbed smoke sheet was made by coagulation field latex with acid before the sheet was squeezed and passed into a smoke house. STR5L was made from coagulation field latex under strictly controlled conditions. The product must have light color and clean. STR5, 10 and 20 were made from field grade materials based on Unsmoke Sheet (USS), lump and scrap. These materials gave strong smell of mal-odor. From the above results, the same odorous components of mal-odor from 3 types of samples were ethylamine(C_2H_7N), benzylhydrazine ($C_7H_{10}NO$), 2-pentanone, volatile fatty acids(VFA). All components of mal-odor from rubber sample were concluded in Table 4.5. For the sample giving strong mal-odor as cup lumps and STR20, the quantity is higher than one of STR5L and RSS that were processed from the fresh field latex. This fresh field latex is cleaner and less contaminated. Hence, there is little amount of non-rubber components in the latex, which can usually be fermented in air by bacteria and produce the compounds that cause mal-odor. Cup lumps and scrap were actually the waste rubber obtained from trapping, coagulating, or cutting process. They contain larger amount of contaminants

and have been through extensive fermentation. The methods, place and storage time were also affected the mal-odor from cup lumps and scrap. The smoke rubber samples showed that the major odorous components were the aromatic compounds, which were different from cup lumps and block rubber.

Table 4.5 The components of mal-odor from natural rubber

No.	Compound	Molecular mass (m/z)	Odor descriptor
1	Dimethylamine	45.08	Colorless liquid or gas with a pungent, fishy, or ammonia-like odor.
2	Ethylamine	45.08	Colorless liquid or gas with a strong ammonia -like odor.
3	Trimethylamine	59.11	Ammonia like odor when vapor concentration are heavy. Generated in the degradation of organic in plants and animals, hygroscopic.
4	Piperidine	85.14	Clear colorless liquid, amine-like odor, strongly basic.
5	Benzylhydrazine	122.16	
6	Tyramine	137.18	
7	Butanone	72.10	Clear colorless liquid with a fragrant mint-like, moderately sharp odor.
8	2-Pentanone	86.13	Water-white liquid with a characteristic ketone odor.
9	Cyclopentanone	84.11	Liquid, agreeable odor somewhat like peppermint.
10	Piperidinone	99.13	
11	Heptanone	114.18	
12	Diethylsulfone	122.18	
13	2(3H)-Furanone,3,3,5-trimethyl	126.17	
14	Acetothiophene	126.17	Stench, white crystal.
15	1-Amino-2-propanol	75.11	Colorless liquid, hygroscopic.
16	2-Pentanol	88.14	
17	Phenol	94.11	Colorless to pink solid or thick liquid with sweet tarry odor detectable at 0.06 ppm., hygroscopic and light sensitive.
18	P-Cresol	108.13	Colorless to pink crystals, light sensitive, hygroscopic, combustible.

Table 4.5 (cont.)

No.	Compound	Molecular mass (m/z)	Odor descriptor
19	2-Methoxy phenol	124.12	Colorless to amber crystals or liquid, air sensitive and light sensitive.
20	p-Phenolsulfonic acid	174.17	
21	1-Dodecanol	186.33	Colorless white solid.
22	n-Valeraldehyde	86.13	Colorless liquid.
23	Hexaldehyde	100.16	Flammable liquid.
24	Propionaldehyde	58.07	Colorless liquid with a suffocating fruity odor and air sensitive.
25	Piperinal	150.00	
26	N,N-dimethylformamide	73.09	Colorless liquid with a faint, ammonia-like odor.
27	N,N-dimethylacetamide	87.12	Colorless liquid with a faint and ammonia-like odor.
28	Acetic acid	60.05	Colorless liquid or solid with a strong vinegar-like odor.
29	Propionic acid	74.07	Colorless liquid with a slightly sweetish odor.
30	Isobutyric acid	88.10	Stench and colorless liquid.
31	Butyric acid	88.10	Colorless liquid with a pungent, putrid odor.
32	Isovaleric acid	102.13	Stench and colorless liquid.
33	Valeric acid	102.13	Colorless liquid with unpleasant odor.
34	Caproic acid	116.15	Colorless or slightly yellow oily liquid and stench.
35	Heptanoic acid	130.18	
36	n-Decanoic acid	172.26	White and crystalline solid.
37	Thiophene	84.13	Clear, colorless liquid, lachrymator and stench.
38	Thiazole	85.12	Colorless or pale yellow liquid and foul odor.
39	Ethylbenzene	106.167	Colorless liquid with an aromatic odor.
40	p-Xylene	106.67	Clear liquid; colorless plates or prisms at low temperature.
41	o-Xylene	106.67	Colorless liquid with aromatic odors.
42	1-Phynyl propadiene	116.00	
43	Isopropylbenzene	120.19	Colorless liquid with a sharp, penetrating and aromatic odor.
44	1,2,3-Trimethylbenzene	120.19	Liquid.

Table 4.5 (cont.)

No.	Compound	Molecular mass (m/z)	Odor descriptor
45	1,2,4-Trimethylbenzene	120.19	
46	Naphthalene	128.17	Colorless to brown solid with an odor of mothballs.
47	Isobutylbenzene	134.22	
48	Isopropyl methylbenzene	134.22	
49	Trans-hexene	84.12	
50	Camphene	136.23	Colorless crystals.
51	1-Dodecyne	166.30	

4.2 Reduction of Mal-odor

Rubber samples were mixed with several odor-reducing substances, which were expected to reduce mal-odor. The methods of reducing mal-odor from the material is in fact to change mal-odor to more pleasant character by masking and / or reducing the odor intensity to more acceptable level by counteraction.

Benzalkonium chloride, carbon black(CB), chitosan, cyclodextrin, zeolite13X and sodium dodecyl sulphate(SDS) were chosen as odor-reducing substances. They were mixed with the 4 rubber samples; STR5L, Smoke5, STR20 and cup lumps by two-roll mill with the ratio of 100 g of rubber samples: 1.5 phr. of odor-reducing substance. The mixed samples were analyzed by GC using headspace technique to determine the efficiency of mal-odor reduction. The results indicated that the odor-reducing substances that have tendency to reduce mal-odor were SDS, CB, zeolite13X and chitosan. The ratio of odor-reducing substance was also increased from 1.5 to 5.0 phr, except SDS of which only 3.0 phr was used since the rubber that

was mixed with 5.0 phr appeared to have lost some mechanical properties after mixing.

To analyze the reduction of mal-odor, each sample after mixing was injected for once a week during 5 week period, (one bottle / week). This was done in order to study the intensity of mal-odor as a function of time. Each sample has been divided into three bottles in order to obtain statistically reliable data (see Appendix B).

Figure 4.26 – 4.29 show the results of odor quantity of STR5 and Smoke3 by considering fourteen components of mal-odor as references. It was found that the volatile volume continuously increased as a function of time when the sample was taken from the same bottle. This implies that the vapor pressure of volatile components inside sample bottles were built up as the sample was kept in the closed system. To assess odor reduction quantitatively, comparative studies with controlled sample (no odor-reducing substances added) must be performed at the same time.

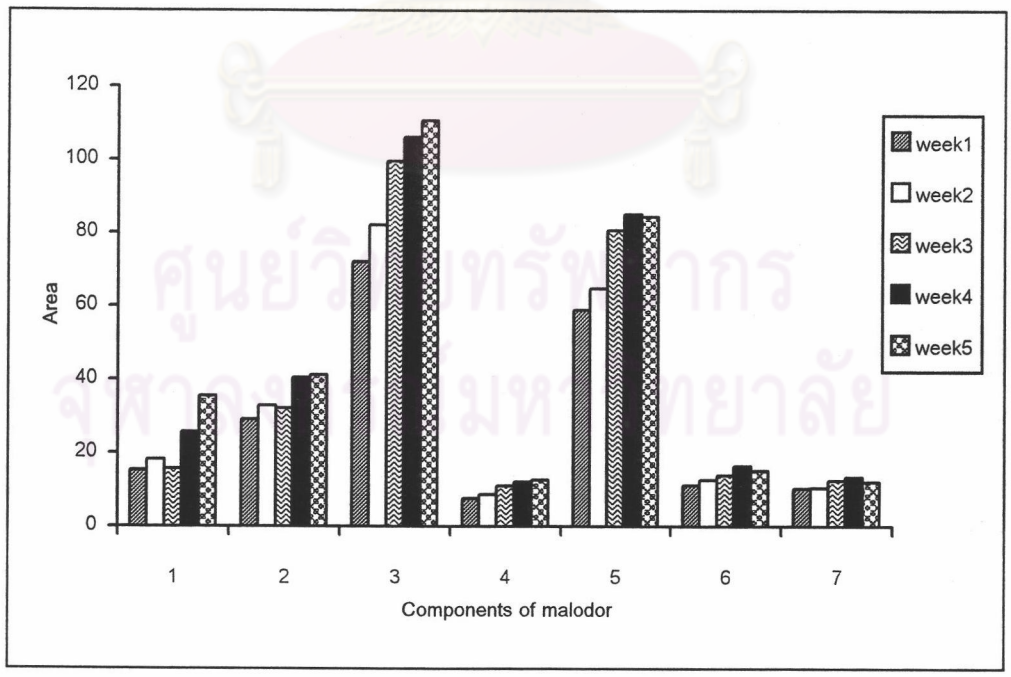

Figure 4.26 The quantity of odor components no.1-7 from STR5 as characterized by GC [b]

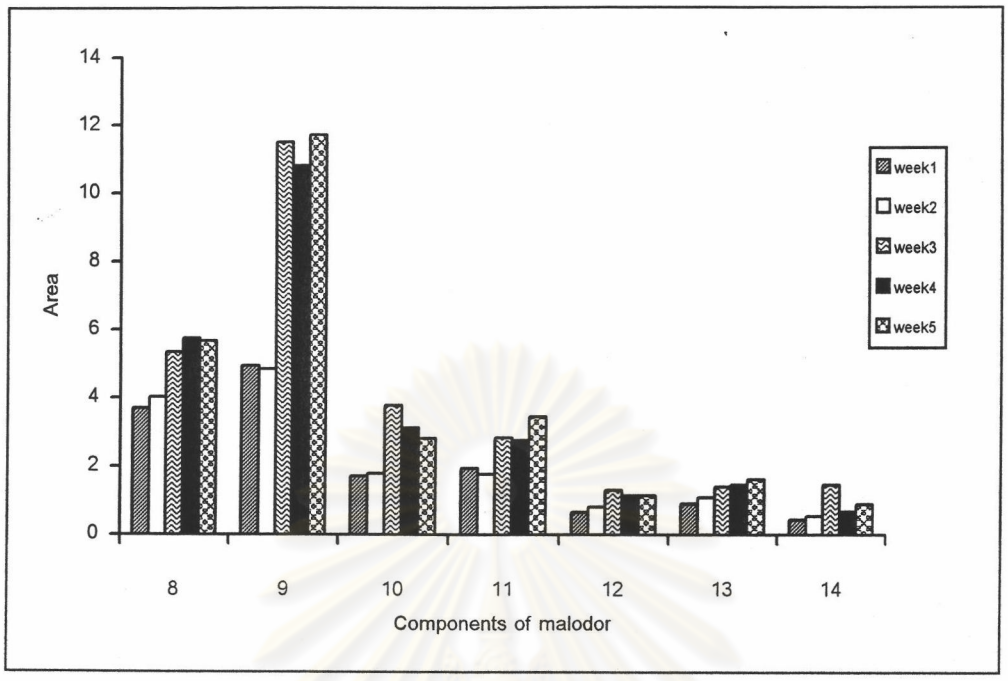

Figure 4.27 The quantity of odor components no.8-14 from STR5 as characterized by GC [b]

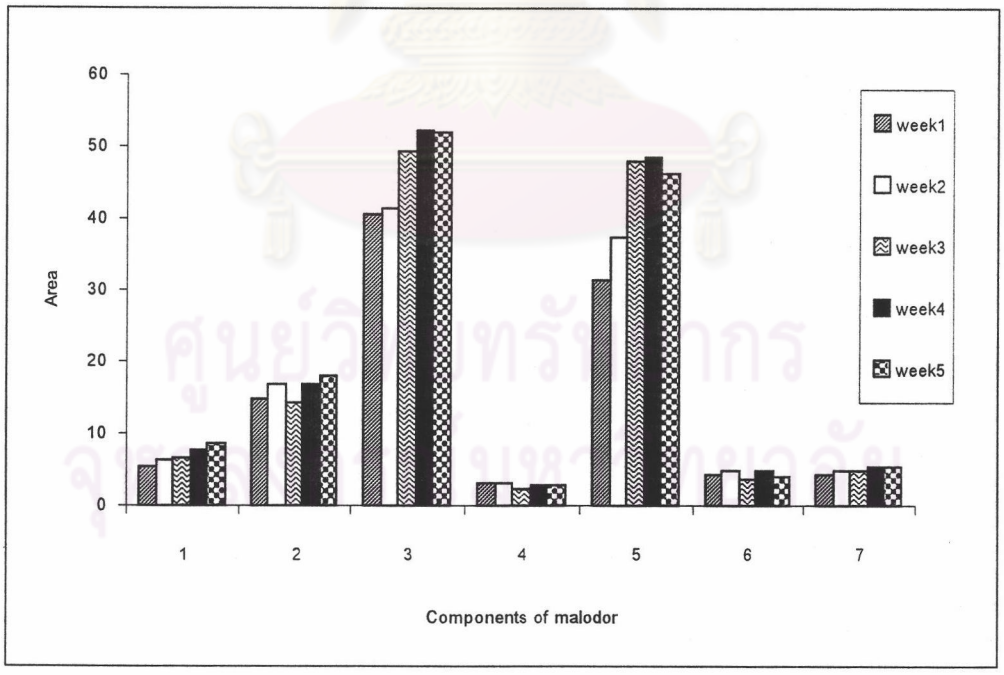

Figure 4.28 The quantity of odor components no.1-7 from Smoke3 as characterized by GC [b]

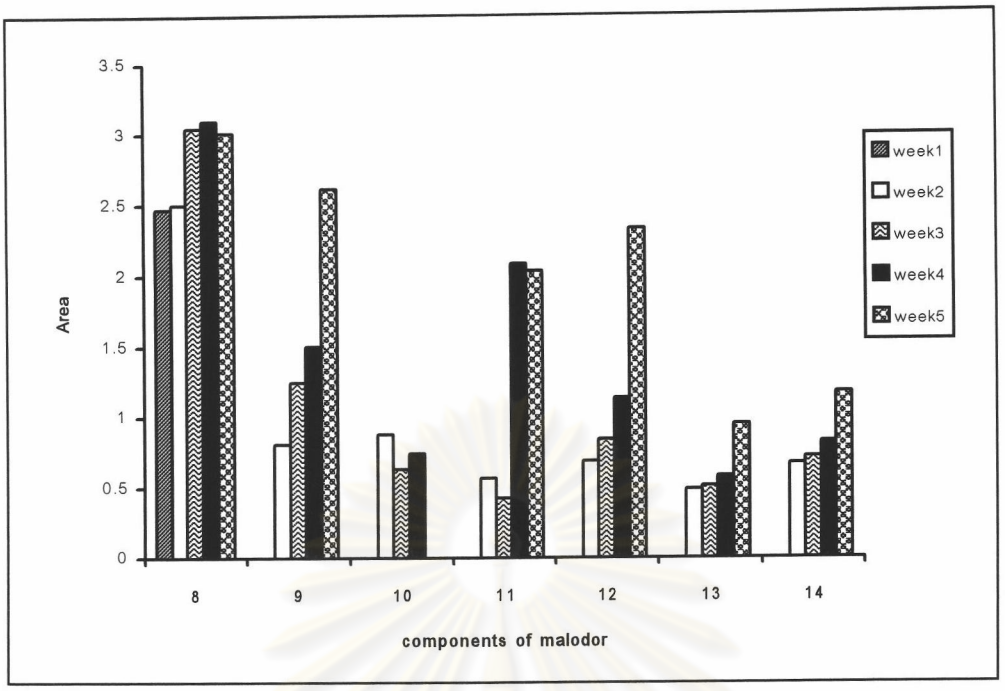

Figure 4.29 The quantity of odor components no.8-14 from Smoke3 as characterized by GC [b]

**b = all GC chromatogram were demonstrated in Appendix B

Methyl valerate was added into rubber samples, STR20 and Smoke5 as an internal standard. Each peak area value was averaged from 5 samples. It was found that, as shown in Table 4.6-4.7, incubation at 60°C for 2 hours provide consistent results (low S.D. value). This implied that the 2 hours incubation time resulted in an equilibrium amount of volatile substances in the sampling bottles. It was found that the amounts of volatile mal-odor and standard were the same range in all injection.

Table 4.6 Peak areas and their percentages of the volatile component from STR20. Methyl valerate was added as an internal standard.(see Appendix B, Table B-3)

Retention time	Peak area	S. D.	Area %	S. D.
0.932	4.82	0.09	3.18	0.05
0.994	7.22	0.11	4.76	0.09
1.060	0.74	0.02	0.49	0.01
1.132	0.83	0.02	0.55	0.02
1.225	1.38	0.01	0.91	0.00
1.277	0.71	0.04	0.47	0.03
1.331	0.24	0.02	0.16	0.01
1.423	0.59	0.02	0.39	0.01
1.650	0.40	0.02	0.27	0.01
1.819**	131.78	1.13	86.91	0.12
6.350	1.08	0.04	0.71	0.02
7.335	0.52	0.02	0.35	0.01
8.312	0.52	0.04	0.34	0.03
9.497	0.79	0.01	0.52	0.01

** retention time of methyl valerate

Table 4.7 Peak areas and their percentages of the volatile component from Smoke5. Methyl valerate was added as an internal standard (see Appendix B, Table B-4).

Retention time	Peak area	S. D.	Area %	S. D.
0.919	4.14	0.11	2.63	0.07
0.997	11.81	0.19	7.51	0.09
1.084	1.94	0.07	1.23	0.04
1.134	58.58	0.50	37.23	0.22
1.228	48.66	0.58	30.92	0.13
1.815**	20.07	0.07	12.76	0.17
2.292	4.53	0.19	2.88	0.10
6.350	1.00	0.05	0.63	0.03
7.327	0.48	0.03	0.31	0.02
8.312	0.31	0.01	0.20	0.01
8.776	0.40	0.03	0.25	0.01
9.495	5.13	0.47	3.25	0.27
11.897	0.28	0.03	0.17	0.02

** retention time of methyl valerate

STR20 and Smoke5 were selected as other representative samples. A similar trend of odor quantity as a function of time was observed. After mixing, the samples were analyzed under the same condition to characterize mal-odor components by GC. For STR20, by comparing odorous compound having retention time of 0.994 (components in the first group) (see Figure 4.30 and Table 4.8) and one having retention time of 6.426 (components in the second group: acetic acid) (see Figure 4.31

and Table 4.9) were determined in 5 weeks period. This component was selected since its high quantity in all samples. Zeolite 13X and chitosan showed the best result in reducing volatile mal-odor by comparing both peaks (retention time = 0.994, 6.426). While carbon black, cyclodextrin and SDS had good tendency to reduce mal-odor. Benzalkonium chloride was not efficient odor-reducing substance despite the cationic nature, which is believed to counteractant with major odorous components such as VFA.

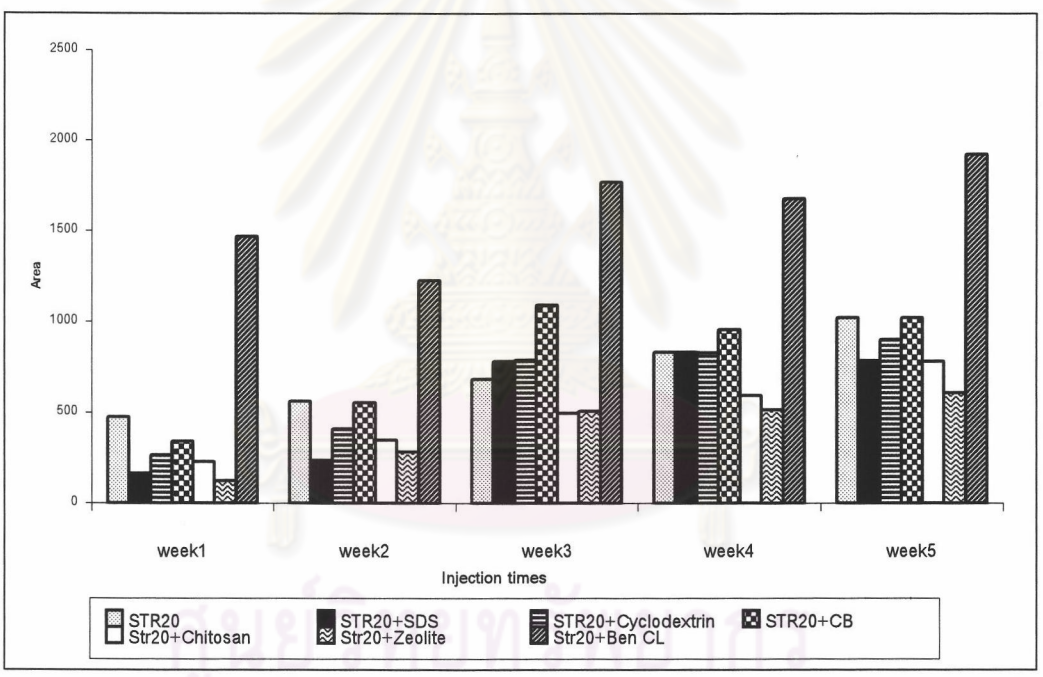

Figure 4.30 The quantity of mal-odor from STR20 mixed with odor-reducing substances as characterized by GC by comparing retention time of 0.994

Table 4.8 The peak area of volatile mal-odor component from STR20 mixed with odor-reducing substances (retention time of 0.994)

Mixing Rubber	Peak area of the volatile mal-odor component [c]				
	Week1	Week2	Week3	Week4	Week5
STR20	474.24	560.05	684.14	834.23	1021.85
STR20+SDS	163.14	235.02	781.98	834.60	786.84
STR20+Chitosan	229.92	347.60	495.29	594.15	782.59
STR20+Cyclodextrin	262.82	409.95	788.08	831.22	901.59
STR20+Benzalkonium Chloride	1468.00	1225.04	1769.42	1677.64	1923.14
STR20+Zeolite13X	122.17	283.60	505.67	515.73	609.59
STR20+Carbon black	339.04	553.17	1088.70	956.07	1022.34

c = all GC chromatogram were demonstrated in Appendix C

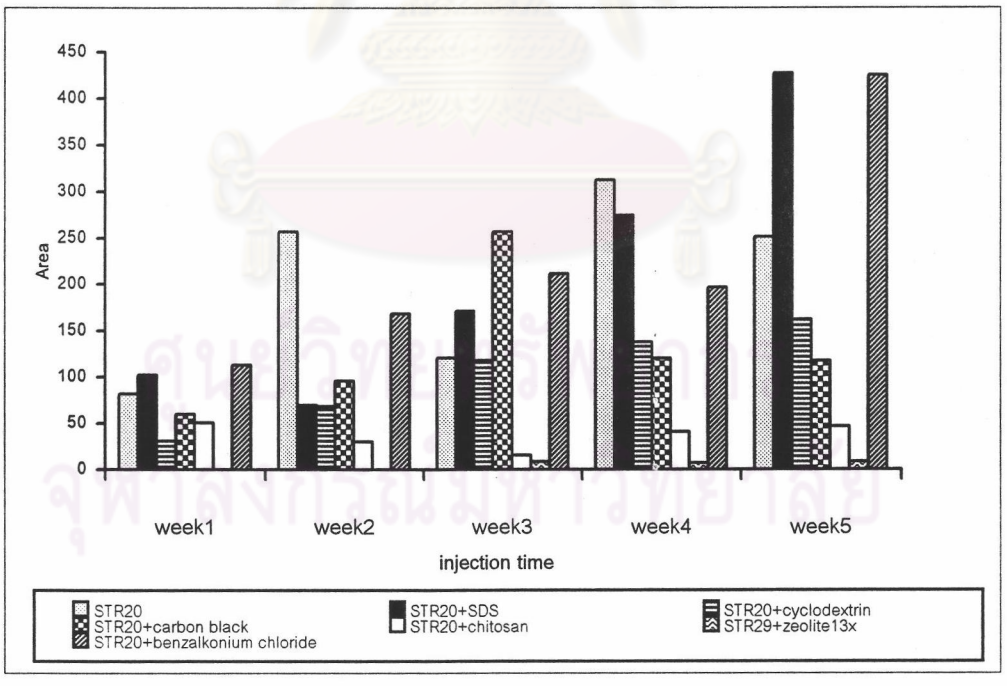

Figure 4.31 The quantity of mal-odor from STR20 mixed with odor-reducing substances as characterized by GC by comparing retention time of 6.426

Table 4.9 The peak area of volatile mal-odor component from STR20 mixed with odor-reducing substances (retention time of 6.426).

Mixing Rubber	Peak area of the volatile mal-odor component [c]				
	Week1	Week2	Week3	Week4	Week5
STR20	82.04	256.57	120.32	312.54	250.96
STR20+SDS	102.29	69.96	171.60	274.21	427.48
STR20+Chitosan	50.64	30.07	15.45	40.88	46.63
STR20+Cyclodextrin	31.30	68.38	117.96	137.36	161.96
STR20+Benzalkonium Chloride	112.71	168.92	211.61	196.91	425.58
STR20+Zeolite13X	0.00	0.00	8.16	7.13	8.14
STR20+Carbon black	59.85	95.96	256.73	120.17	117.18

c = all GC chromatogram were demonstrated in Appendix C

For Smoke5 (Figure 4.32 and Table 4.10, Figure 4.33 and Table 4.11), chitosan, zeolite13X as well as carbon black appeared to be good odor-reducing substances. This may be explained as the effect of high surface area of non-polar carbon black that assists adsorption of some odorous components. Unlike benzalkonium chloride, chitosan whose chemical composition consists of some amino groups turns out to help reducing the mal-odor. In the case of cyclodextrin and zeolite13X, the odor-reducing properties may be regarded as the appropriate pore size of both substances that can fit some odorous components.

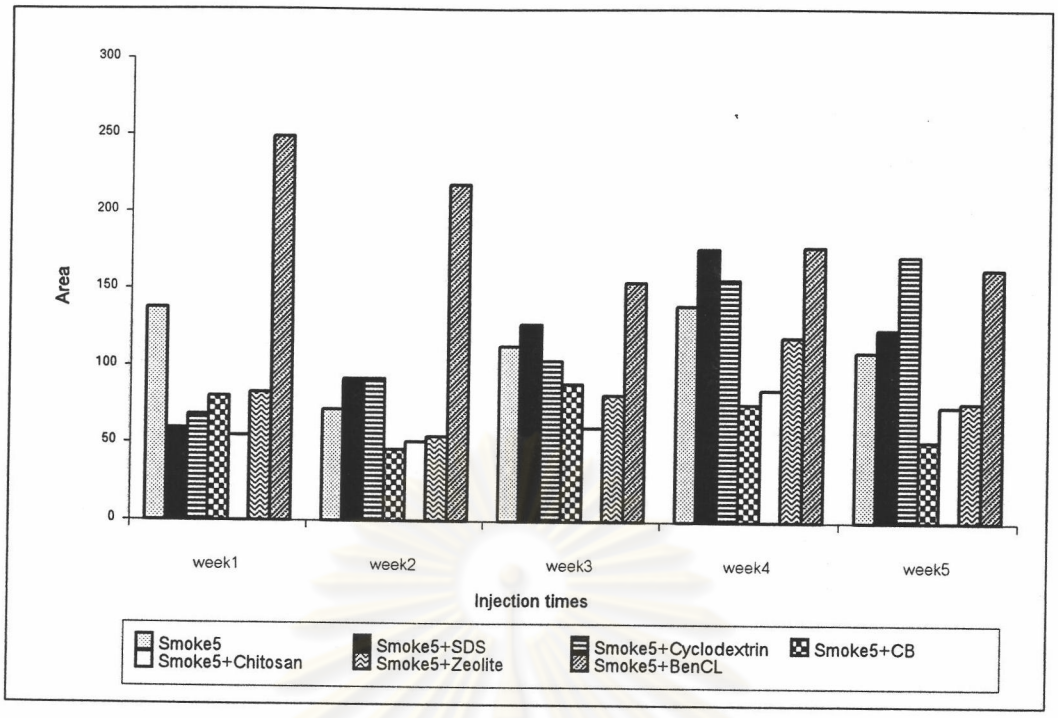

Figure 4.32 The quantity of mal-odor from Smoke5 mixed with odor-reducing substances as characterized by GC by comparing retention time of 0.928

Table 4.10 The peak area of volatile mal-odor component from Smoke5 mixed with odor-reducing substances (retention time of 0.928)

Mixing Rubber	Peak area of the volatile mal-odor component [c]				
	Week1	Week2	Week3	Week4	Week5
Smoke5	137.69	72.00	113.34	139.75	110.41
Smoke5+SDS	59.42	91.83	127.42	176.44	124.71
Smoke5+chitosan	54.57	50.76	60.24	85.62	74.84
Smoke5+ cyclodextrin	68.23	92.05	103.88	156.39	171.92
Smoke5+Benzakonium Chloride	248.84	217.74	154.54	177.92	163.81
Smoke5+ Zeolite 13X	82.84	54.18	81.80	119.60	77.39
Smoke5+Carbon black	80.34	45.87	89.01	80.34	52.13

c = all GC chromatogram were demonstrated in Appendix C

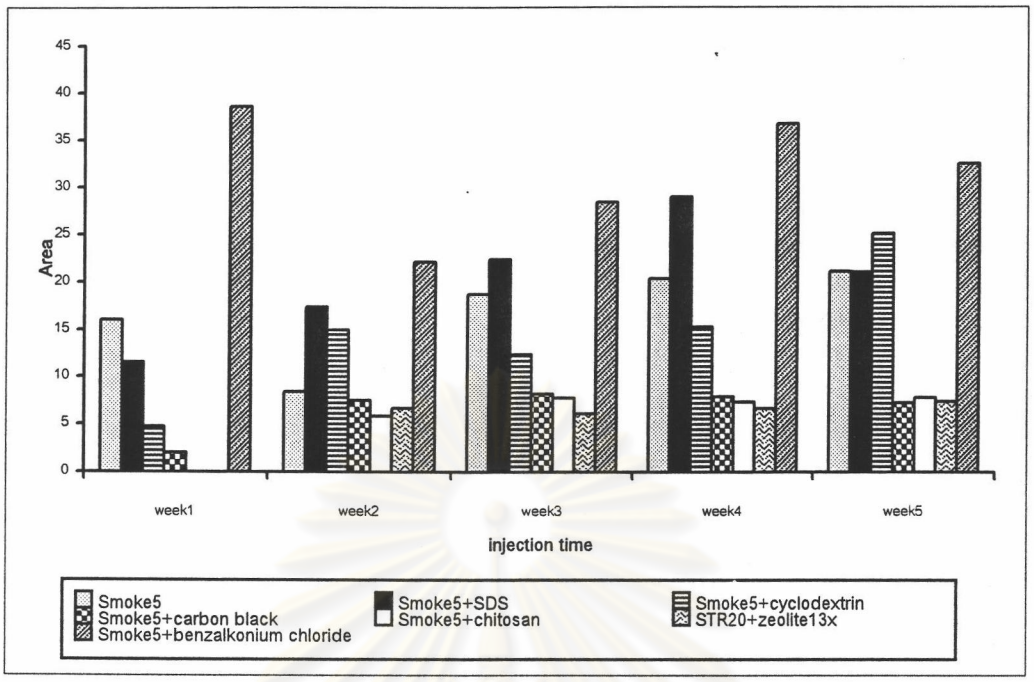

Figure 4.33 The quantity of mal-odor from Smoke5 mixed with odor-reducing substances as characterized by GC by retention time of 6.426

Table 4.11 The peak area of volatile mal-odor component from Smoke5 mixed with odor-reducing substances (retention time of 6.426)

Mixing Rubber	Peak area of the volatile mal-odor component [c]				
	Week1	Week2	Week3	Week4	Week5
Smoke5	16.05	8.43	18.75	20.39	21.19
Smoke5+SDS	11.56	17.45	22.41	29.02	21.11
Smoke5+chitosan	0.00	5.83	7.81	7.35	7.84
Smoke5+ cyclodextrin	4.75	14.98	12.38	15.36	25.15
Smoke5+Benzakonium Chloride	38.64	22.16	28.47	36.75	32.52
Smoke5+ Zeolite 13X	0.00	6.64	6.09	6.69	7.41
Smoke5+Carbon black	2.02	7.53	8.17	7.93	7.31

c = all GC chromatogram were demonstrated in Appendix C

Furthermore, we also attempted to test the efficiency of mal-odor reduction using olfactometry. 20 peoples (10 male, 10 female; age 20-35) were convened to test the samples that were mixed with odor-reducing substances. The result of olfactometry test was shown in Table 4.12- 4.13.

Table 4.12 Olfactometry test of STR20 mixed with odor-reducing substances:

STR20 + Odor-Reducing substances	**Percentage of olfactometry test**				
	Ref.Bottle1 (1 g of rubber)	**Ref.Bottle2 (5 g of rubber)**	**Ref.Bottle3 (10 g of rubber)**	**Ref.Bottle4 (15 g of rubber)**	**Ref.Bottle5 (20 g of rubber)**
STR20 + SDS	60	20	10	10	0
STR20 + Chitosan	40	40	20	0	0
STR20 + Carbon black	60	40	0	0	0
STR20 + Cyclodextrin	20	20	20	20	20
STR20 + Benzalkonium chloride	10	40	10	10	30
STR20 + Zeolite13X	20	50	30	10	0

Table 4.13 Olfactometry test of Smoke5 mixed with odor-reducing substances.

Smoke5 + Odor-Reducing substances	**Percentage of olfactometry test**				
	Ref.Bottle1 (1 g of rubber)	**Ref.Bottle2 (5 g of rubber)**	**Ref.Bottle3 (10 g of rubber)**	**Ref.Bottle4 (15 g of rubber)**	**Ref.Bottle5 (20 g of rubber)**
Smoke5 + SDS	40	20	20	20	0
Smoke5 + Chitosan	40	40	20	0	0
Ssmoke5 + Carbon black	40	40	20	0	0
Smoke5 + Cyclodextrin	40	30	30	0	0
Smoke5 + Benzalkonium chloride	20	10	10	30	20
SMOKE5 + Zeolite13X	20	50	20	10	0

From the tables, the percentage of mixed samples that had the odor intensity less than the reference were reported. Carbon black and chitosan showed the best results in reducing mal-odor in all rubber samples. Zeolites13X, cyclodextrin and SDS could reduce some mal-odor. Benzalkonium chloride was found to be the least efficient odor-reducing substance. The results obtained by olfactometry test were in fact similar to GC analysis.

4.3 Mechanical Property Testing

After the efficient mal-odor-reducing substances were found, the rubber samples were compounded using the standard formula according to the following ratio.

Table 4.14 The standard formulas of compounded rubber

Ingredient	Quantity of mix (phr)
Natural rubber sample	100
Sulfur	3.5
Zinc oxide	6.0
Steric acid	0.5
TMTD	0.5
Reduction substances:	
Carbon black	5.0
Chitosan	5.0
Zeolite 13X	5.0
SDS	3.0

These studies were performed in order to test whether it is feasible to add the mal-odor-reducing substances while mechanical properties of natural rubber are still maintained. Benzalkonium chloride was not used because it was previously observed that mechanical properties of mixed rubber were deteriorated as compared to original samples. The vulcanized rubber compounds were compressed in compression molding at 150°C for 4 min. The vulcanized compounded rubbers were tested for the tensile stress-strain, stress at 300% modulus, specific gravity and hardness. The result was shown in Figure 4.34- 4.38 and Table 4.15 for STR20 vulcanized rubber and the Figure 4.39- 4.43 and Table 4.16 for Smoke5 vulcanized rubber.

Table 4.15 The mechanical properties of compounded rubber: STR20

Sample	Stress at Max.load (MPa)	%Strain at Max.load (%)	Specific Gravity	Hardness	Stress at 300% Modulus
STR20	22.49±1.01	730.00±44.80	0.9777	40.0	1.98±0.12
STR20+SDS	12.40±1.47	991.40±32.37	0.9876	37.9	1.61±0.11
STR20+Chitosan	21.06±1.24	656.60±21.22	0.9939	46.1	2.74±0.15
STR20+Carbon black	21.47±0.71	737.63±50.45	0.9939	41.7	2.33±0.18
STR20+Zeolite13X	22.11±0.58	736.93±52.81	1.0231	43.7	2.41±0.15

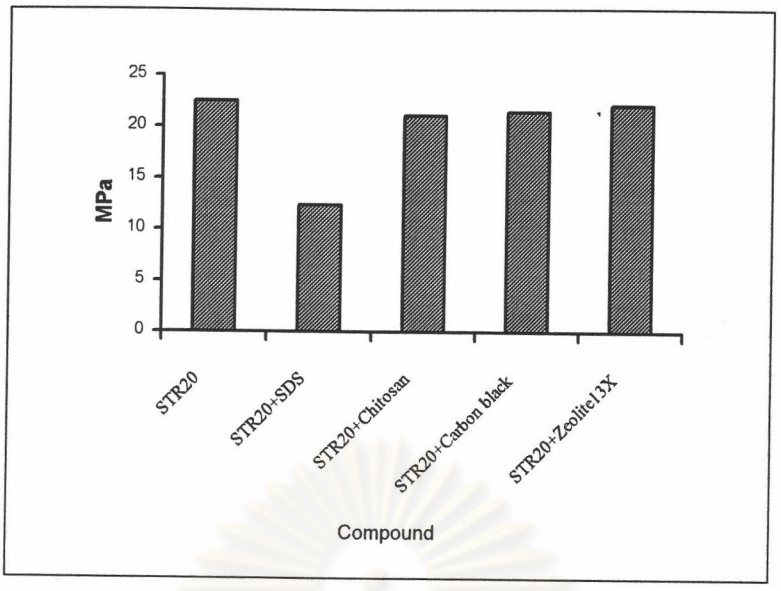

Figure 4.34 The tensile stress of compounded rubber: STR20

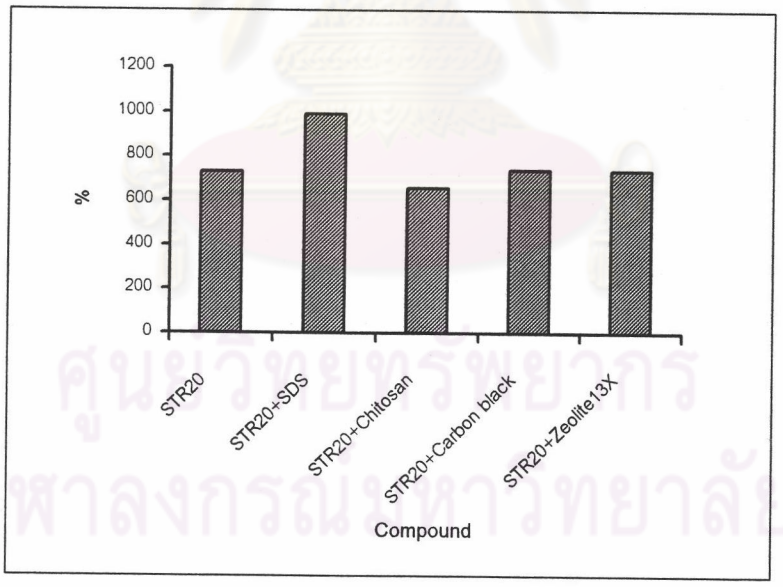

Figure 4.35 The strain at max load of the compounded rubber: STR20

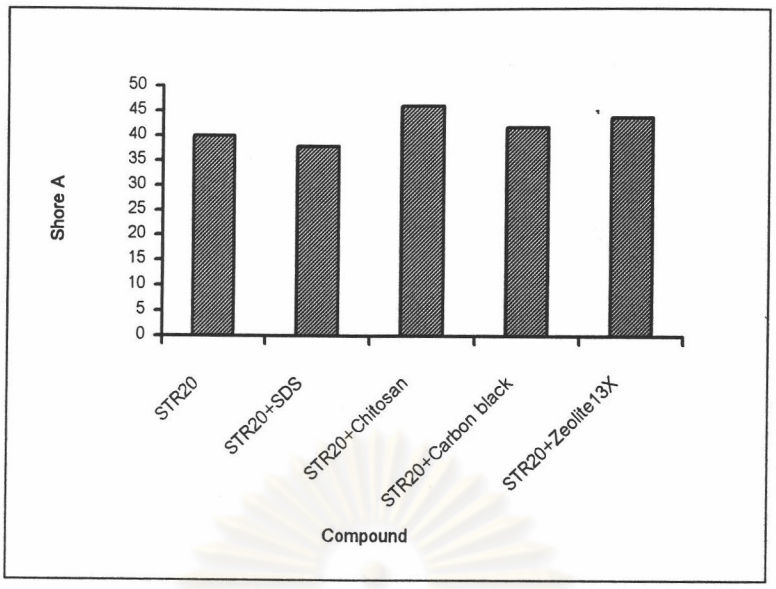

Figure 4.36 The hardness of compounded rubber: STR20

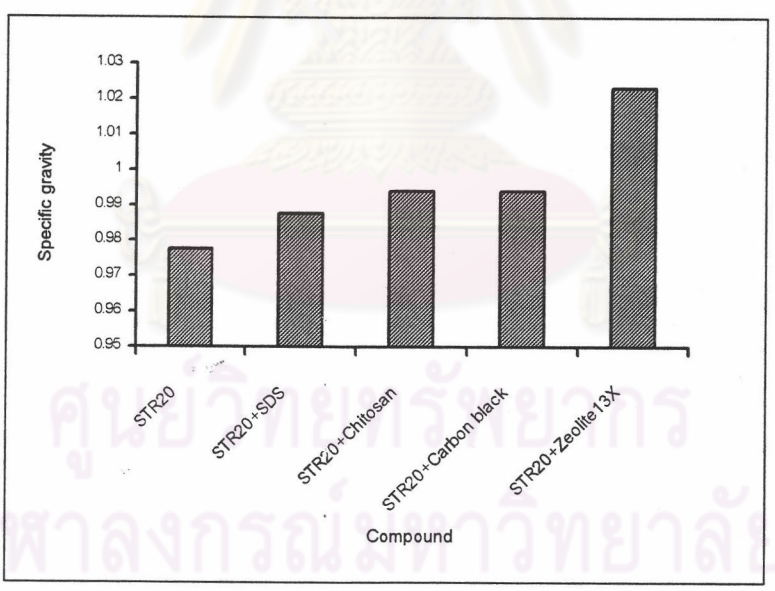

Figure 4.37 The specific gravity of compounded rubber: STR20

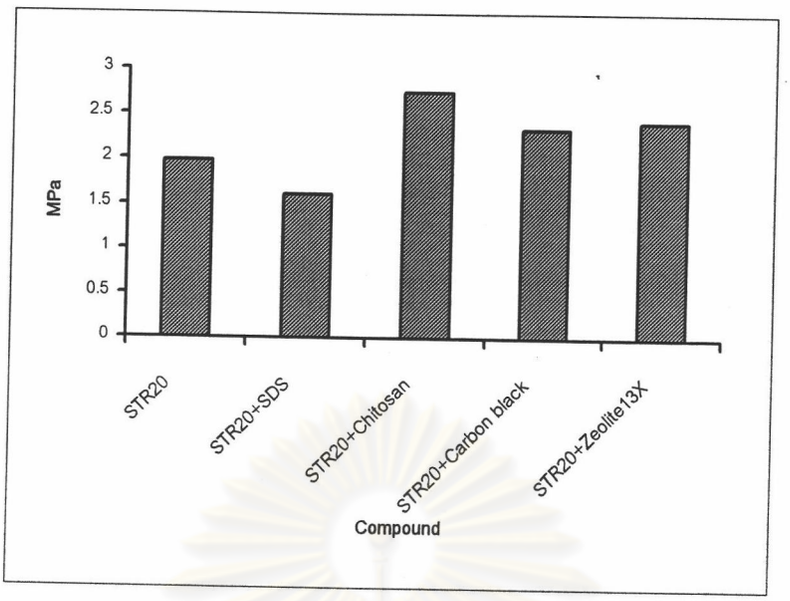

Figure 4.38 The stress at 300% modulus of compounded rubber: STR20

The information above demonstrated that all compounded STR20 rubber samples containing odor-reducing substances except the rubber mixed with SDS have stress value close to the original STR20 sample. The sample mixed with SDS have the lowest stress, stress at 300% modulus and hardness. The ductility increased as the strain increased. While the sample mixed with chitosan showed the highest stress at 300% modulus and hardness indicating that the rubber became stronger with lower toughness. Carbon black and zeolite13X also caused the strain, stress at 300% modulus and hardness to increase from the controlled rubber. This data suggested that chitosan, carbon black and zeolite13x behave like reinforced fillers. As expected, the specific gravity of all rubber were higher than the original rubber.

Table 4.16 The mechanical properties of compounded rubber: Smoke5

Sample	Stress at Max.load (MPa)	%Strain at Max.load (%)	Specific Gravity	Hardness	Stress at 300% modulus
Smoke5	23.33±1.81	713.90±55.80	0.9700	40.2	2.33±0.29
Smoke5+SDS	11.34±2.04	774.40±82.99	0.9700	34.9	1.46±0.30
Smoke5+Chitosan	21.74±0.49	712.90±13.23	0.9900	44.4	2.41±0.16
Smoke5+Carbon black	22.03±0.99	715.45±6.87	0.9900	40.8	2.57±0.08
Smoke5+Zeolite13x	23.65±1.55	764.37±56.17	1.0100	40.2	2.02±0.24

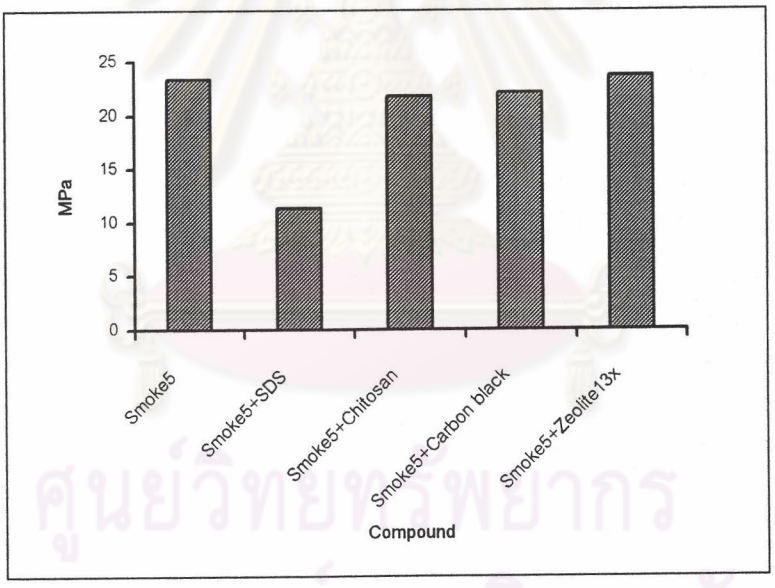

Figure 4.39 The tensile stress of compounded rubber: Smoke5

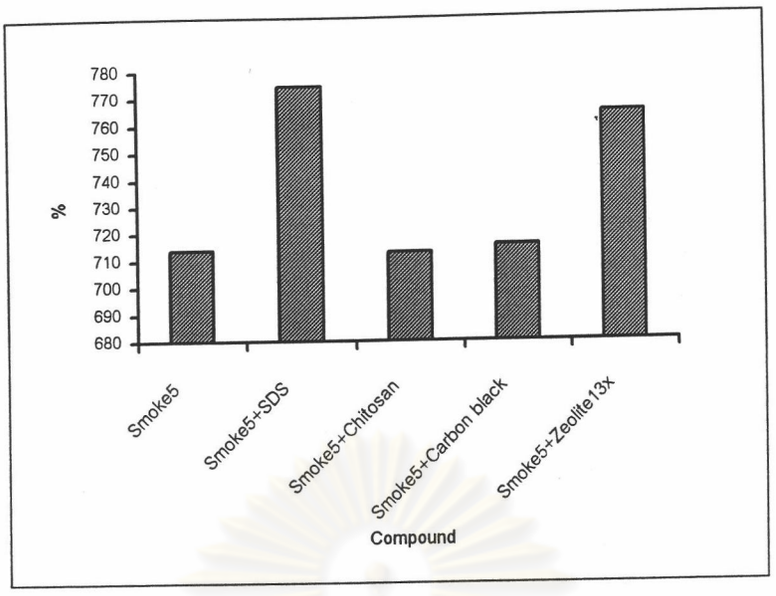

Figure 4.40 The strain at max load of compounded rubber: Smoke5

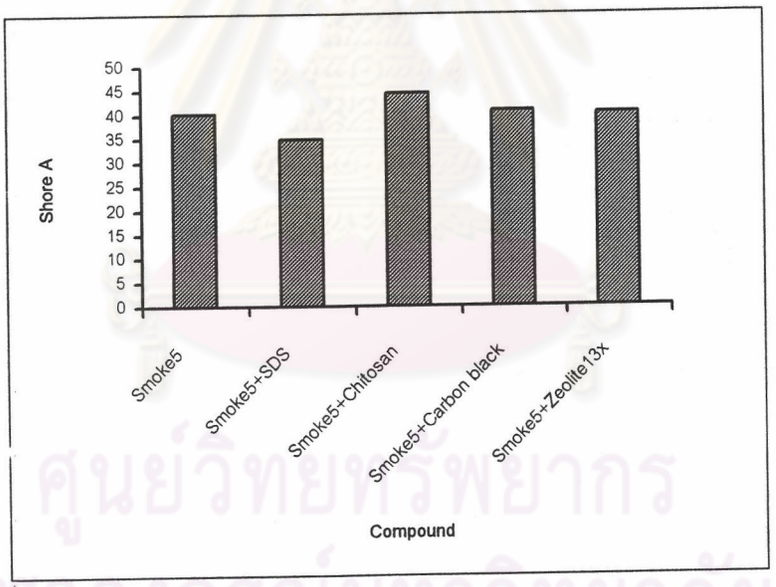

Figure 4.41 The hardness of compounded rubber: Smoke5

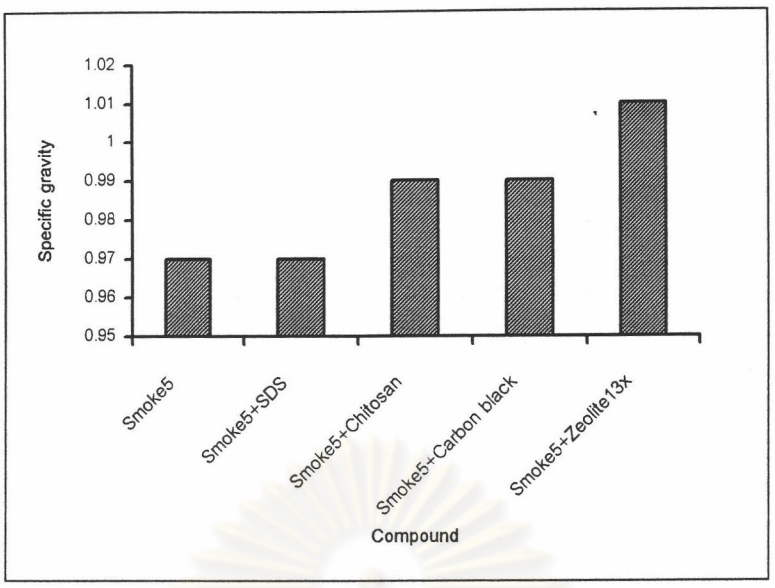

Figure 4.42 The specific gravity of compounded rubber: Smoke5

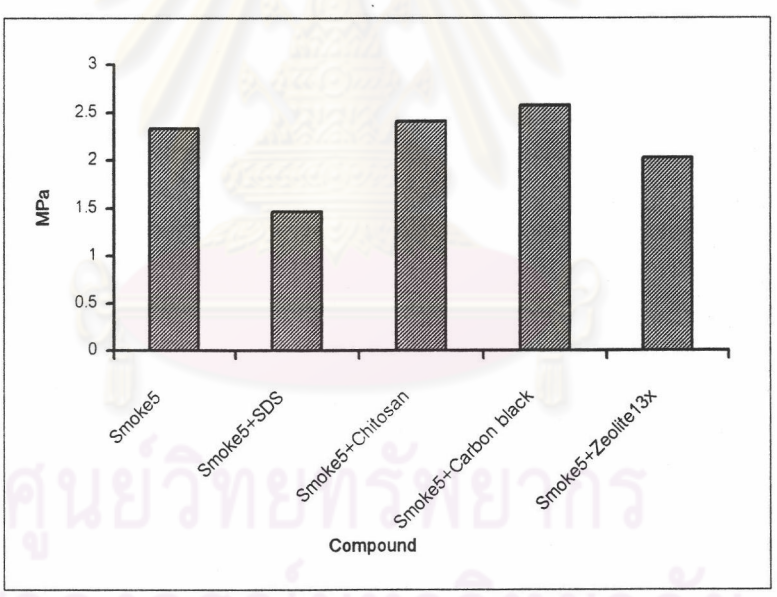

Figure 4.43 The stress at 300% modulus of compounded rubber: Smoke5

In the case of the compounded Smoke5 rubber, the sample mixed with SDS showed similar results as ones of STR20. It was found that the mechanical properties of compounded natural rubber mixed with odor-reducing substances, were varied depending on the type of substance. Some can increase elasticity, while others can

improve the toughness. The selection of which substance should be used really depends on the applications.