

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Surface Characterization

4.1.1 FTIR-ATR

a) *Vulcanized Rubber Sheet*

Rubber surfaces were characterized by FTIR-ATR so as to observe whether PDMS migrated to both sides of surfaces. As shown in Figure 4.1, these spectra were for vulcanized sheet surfaces that exposed to the petridish (or inside).

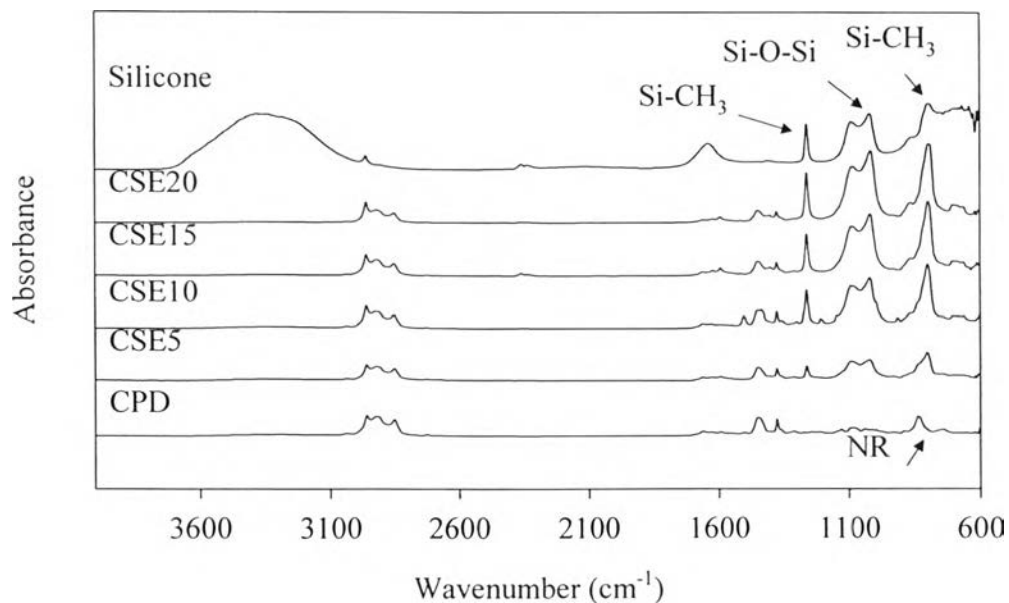


Figure 4.1 ATR-IR spectra of vulcanized rubber sheet exposed to petridish (inside).

As distinguished from the spectra of vulcanized sheet without PDMS, the spectra of vulcanized sheet with PDMS exhibited the peak height

at about $1000\text{-}1100\text{ cm}^{-1}$ and about $1200\text{-}1250\text{ cm}^{-1}$ which were ascribed to siloxane linkage (Si-O) and Si-C bond respectively.

The spectra of vulcanized sheet surfaces with and without PDMS, exposed to air (or outside), were shown in Figure 4.2. Vulcanized sheet surfaces with PDMS also showed the bands of siloxane linkage and Si-C bond.

NR was shown at the frequency about 820 cm^{-1} . When PDMS amount increased, the peak at about $820\text{-}840\text{ cm}^{-1}$ was higher. It was due to Si-CH₃ band that also showed at about 840 cm^{-1} .

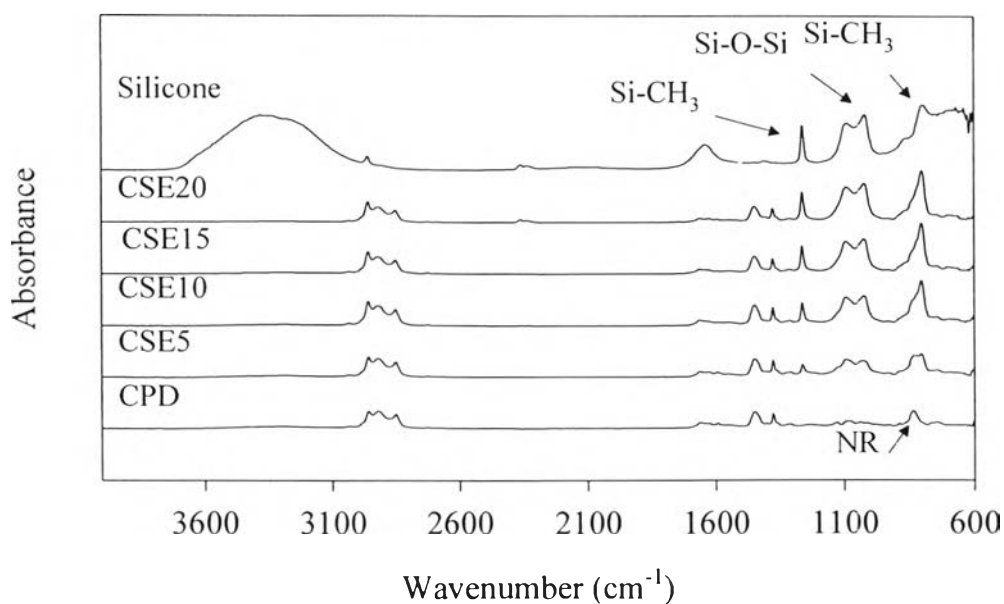


Figure 4.2 ATR-IR spectra of vulcanized rubber sheet exposed to air (outside).

The surface excess was characterized quantitatively by comparing the peak area at about $1200\text{-}1250\text{ cm}^{-1}$ to the peak area at 1370 cm^{-1} , characteristic of the C-H bending mode in the methyl group. For compounded NRL without PDMS, the peak area at 840 cm^{-1} (ascribed to trisubstituted alkene) was compared to the peak area at 1370 cm^{-1} .

Table 4.1 Relative intensity of vulcanized rubber sheet on both surfaces.

Sample	Relative intensity	
	inside	outside
CPD	2.86	3.94
CSE5	1.43	0.77
CSE10	2.98	1.31
CSE15	4.14	1.88
CSE20	6.19	2.79

The results were given in Table 4.1. The relative intensities of the Si-C peak at the surface increased with increasing PDMS content, indicating higher PDMS content at the surface. There is a measurable difference between the inside and outside. The inside had more PDMS content more than the outside.

b) Vulcanized Rubber Film

Figure 4.3 shows the spectra of vulcanized films, without PDMS and with PDMS of 5 phr, on both sides of surfaces. One side exposed to the glass tube former (or inside) and another side exposed to the air (or outside). PDMS on both sides of vulcanized film surfaces were detected at the same frequencies as for vulcanized sheet.

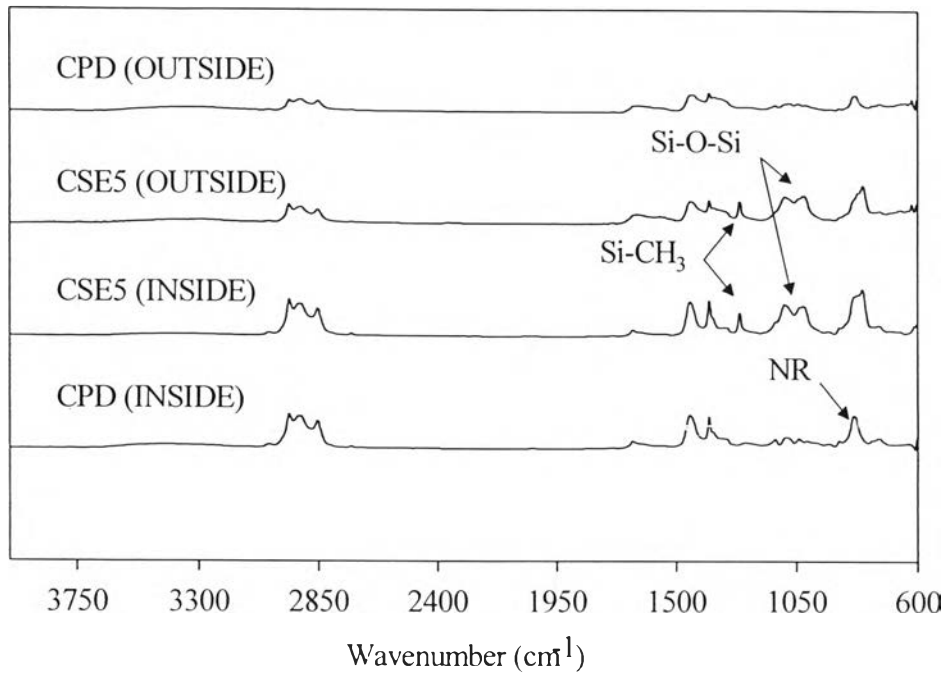


Figure 4.3 ATR-IR spectra of vulcanized rubber film exposed to former (inside) and air (outside).

From spectroscopic study, it was indicated that PDMS migrated on both sides of surfaces. In addition, PDMS can give slipperiness property that is approved by contact angle measurement. The assumption is that PDMS can reduce tack in natural rubber, which is determined by T-peel test.

4.1.2 Contact Angle Measurements

Contact angle is observed to study the chemical changes in rubber surface and indicate the surface property. Generally a slippery surface shows a higher contact angle than a high-friction surface. However this generalization depends on the chosen liquid for contact angle measurement.

a) *Vulcanized Rubber Sheet*

The vulcanized rubber sheets with PDMS displayed slippery surface when compared to that without PDMS. As shown in Table 4.2, the

contact angle decreased with increasing the amount of PDMS. This indicated that amount of PDMS at surface increased with its content consistent with FTIR-ATR results. Although the contact angle decreased, it did not mean that vulcanized sheets with PDMS exhibited sticky

Table 4.2 Contact angles of ethylene glycol on various sheet samples

Compound	Contact angle (°)
CPD	63.3±2.1
CSE5	59.7±2.7
CSE10	54.8±2.0
CSE15	51.3±0.5
CSE20	50.1±2.8

surface. The decrease of contact angle was due to the adhesion between the polarity of hydroxy group of ethylene glycol and the lone pair oxygen of PDMS at the rubber surface.

b) Vulcanized Rubber Film

The contact angles for ethylene glycol on vulcanized rubber films were shown in Table 4.3. Like the vulcanized rubber sheet, the vulcanized rubber film with PDMS of 5 phr had contact angle less than that without PDMS. The same reason was described.

Table 4.3 Contact angles of ethylene glycol on dipped film samples

Compound	Contact angle (°)
CPD	61.8±1.2
CSE5	54.6±1.4

4.2 T-peel Test

a) Vulcanized rubber Sheet

The autohesive tack was determined by T-peel test. As shown in Figure 4.4, the work of separation (W_a) to separate two pieces of unaged rubber sheets apart decreased with increasing the amount of PDMS consistent with PDMS migration to the surface and reducing tack.

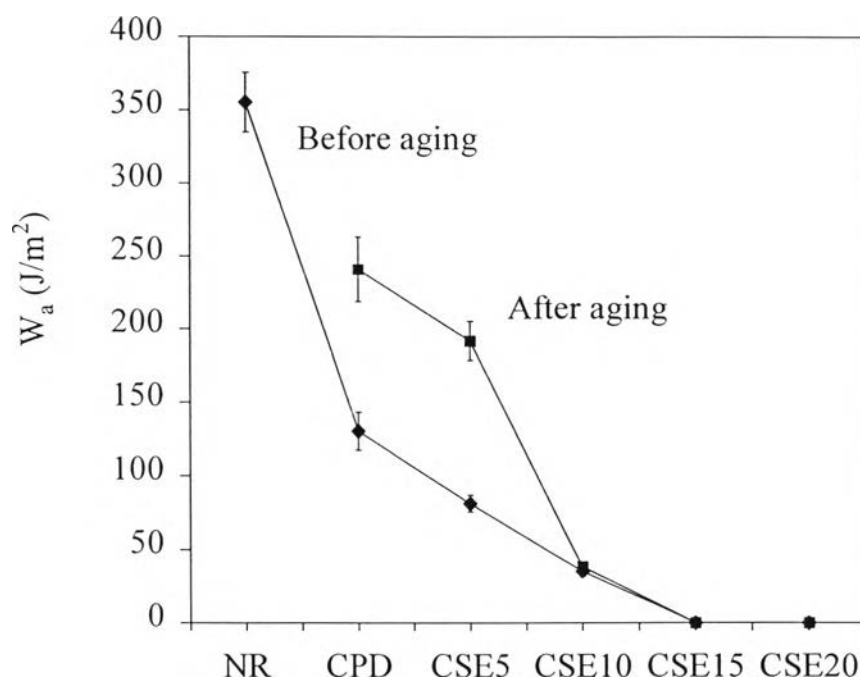


Figure 4.4 Work of separation, W_a , of vulcanized rubber sheet before and after aging.

At lower values of work of separation, lowering of the contact angle is expected, see Figure 4.5.

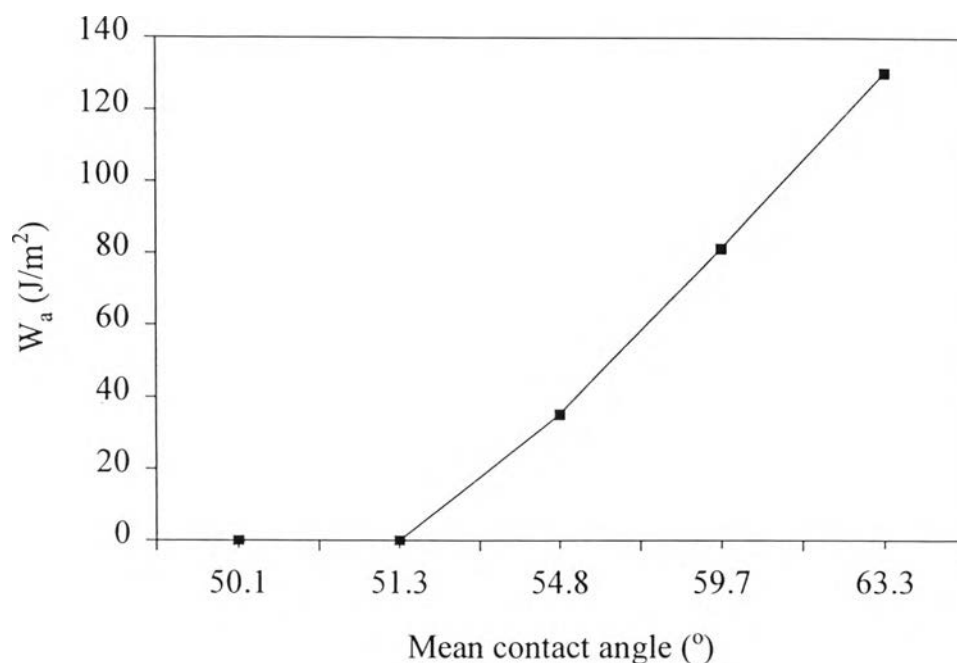


Figure 4.5 Work of separation (W_a) versus contact angle of ethylene glycol on vulcanized rubber sheet surface.

After aging, the vulcanized rubber sheets with PDMS of 15 and 20 phr had the same work of separation as the said sheets before aging. In contrast, the work of separation for CPD, CSE5, and CSE10 after aging arose when compared to that before aging. The increment of work of separation was due to two effects; the distribution of PDMS in bulk rubber, and oxidation during aging.

One possibility to explain these results is that NR is oxidized under these conditions, and oxidation tends to form functional groups that increase tack so that more work of separation is required. Another possibility is that aging cause more PDMS to diffuse into the bulk, reducing the concentration of PDMS at the surface, which would increase tack. At high enough PDMS contents, this reduction in concentration was not enough to significantly change the tack.

Experiments were therefore carried out to test these hypotheses. Aged rubber sheet samples of CPD and CSE5 were examined with FTIR-ATR to test whether the sample was oxidized.

FTIR spectra for aged and unaged CPD was shown in Figure 4.6 and that for aged and unaged CSE5 were shown in Figure 4.7 and Figure 4.8. Aging did not cause any noticeable changes in the spectra of either system, indicating that oxidation was not the cause of the increase in work

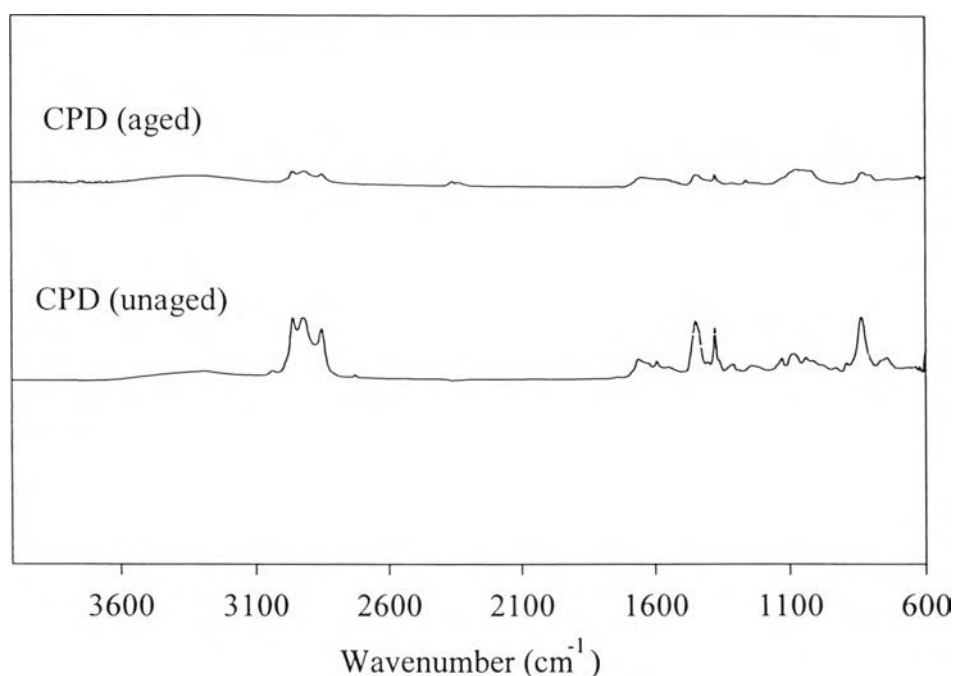


Figure 4.6 ATR-IR spectra of vulcanized rubber sheet without PDMS (CPD) before and after aging.

of separation with aging. Changes in peak broadness were almost certainly due to poorer sample/ATR cell contact of the aged samples. Unfortunately, it could not approve the latter possibility since the peak areas could not be reliably measured because of aforementioned increase in broadness.

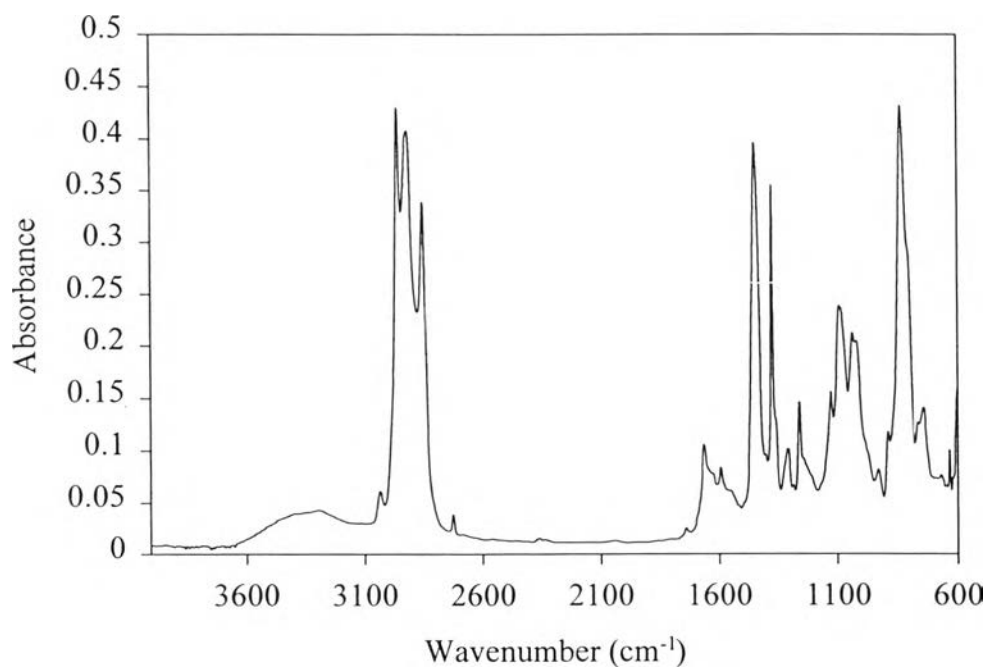


Figure 4.7 ATR-IR spectra of vulcanized rubber sheet with PDMS of 5 phr (CSE5) before aging.

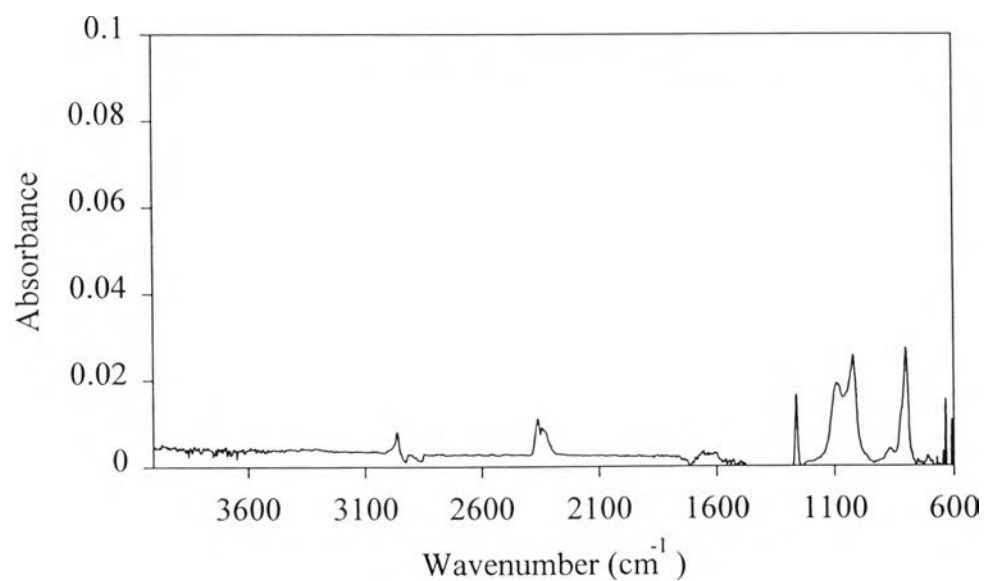


Figure 4.8 ATR-IR of vulcanized rubber sheet with PDMS of 5 phr (CSE5) after aging.

To further test the effect of oxidation, thermogravimetry (TG) was applied to investigate the decomposition of aged and unaged samples. As illustrated in Figure 4.9, aged and unaged CPD and CSE5 showed the same

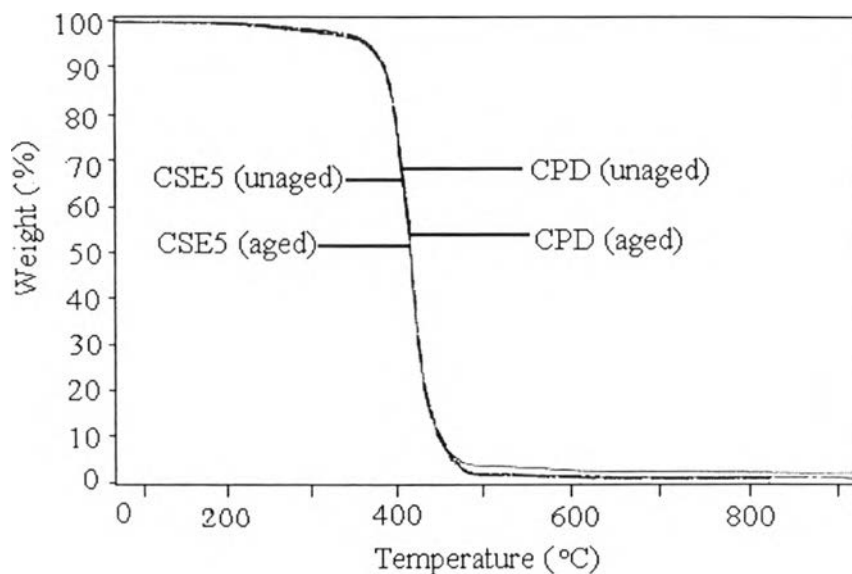


Figure 4.9 TG thermogram of vulcanized rubber sheets; CPD and CSE5 before and after aging.

thermogram and there was no oxidation at 70°C. This experiment support the conclusion that oxidation is not the reason for the increase in the work of separation.

To confirm that the change in tack was due to the diffusion of PDMS into the bulk, the elemental analysis was carried out by SEM. As illustrated in Table 4.4 and Table 4.5, percent of atomic of element, essentially oxygen, at the surface of unaged and aged rubber sheet was slightly different indicating that oxidation did not substantially occur. Percent of atomic of silicon of unaged CSE5 was lower than that of aged CSE5. It means that aged CSE5 has more PDMS content at the surface than unaged CSE5 although the content of PDMS is relatively small, contrasting the T-peel test results. If polarity due to oxygen content is then considered,

the increment of oxygen content after aging is larger than oxygen content corresponding to silicon in PDMS repeating unit (Si:O = 1:1) indicating that there are some polar species present at the surface and they do not come from oxidation. The increase in tack after aging should be due to some small molecule in NR having high polarity and no longer compatible with hydrophobicity of the bulk diffusing to the surface and rendering more adhesion.

Table 4.4 Element content of unaged and aged rubber sheets.

Element	Unaged CPD		Aged CPD	
	Element (%)	Atomic (%)	Element (%)	Atomic (%)
C	58.96	66.42	63.76	70.54
O	37.51	31.73	33.92	28.17
Na	2.08	1.22	1.99	1.15
S	0.21	0.09	0.05	0.02

Table 4.4 Element content of unaged and aged CSE5.

Element	Unaged CSE5		Aged CSE5	
	Element (%)	Atomic (%)	Element (%)	Atomic (%)
C	70.04	75.76	65.09	71.52
O	29.66	24.09	33.89	27.96
Si	0.19	0.09	0.29	0.13
Na	0.10	0.06	0.57	0.32
S	0	0	0.11	0.04

b) Vulcanized Rubber Film

Like vulcanized rubber sheets, the vulcanized rubber film with PDMS of 5 phr (CSE5) before and after aging displayed about the same work of separation, shown in Figure 4.10. Due to the thin thickness of film or small content of NR, the aging effect on W_a is not significant. In other

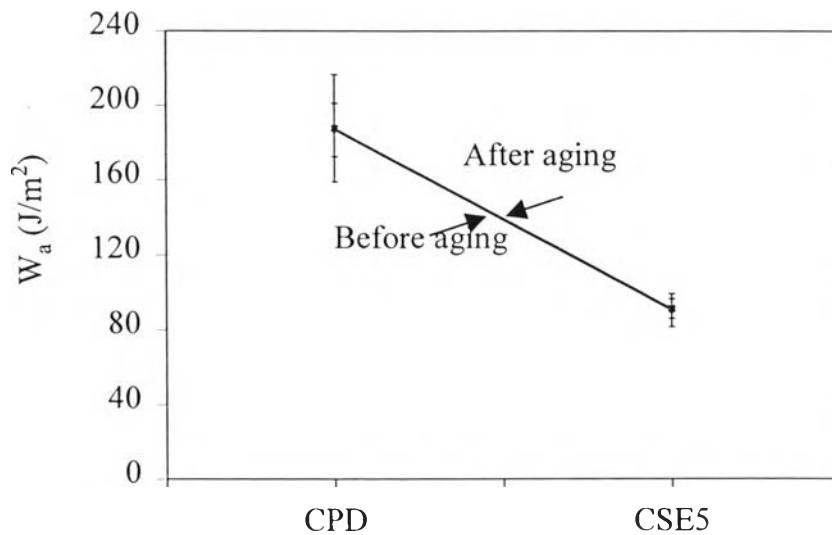


Figure 4.10 Work of separation, W_a , of vulcanized rubber film before and after aging.

word, small content of NR limited amount of small polar molecules in NR and since the film was very thin, they already dispersed well to the surface.

4.3 Tensile Test

4.3.1 Tensile Strength

a) Vulcanized Rubber Sheet

The strength of compounded NRL with PDMS was determined. The results were demonstrated in Figure 4.11. PDMS decreased the tensile strength for aged and unaged vulcanized rubber sheets which

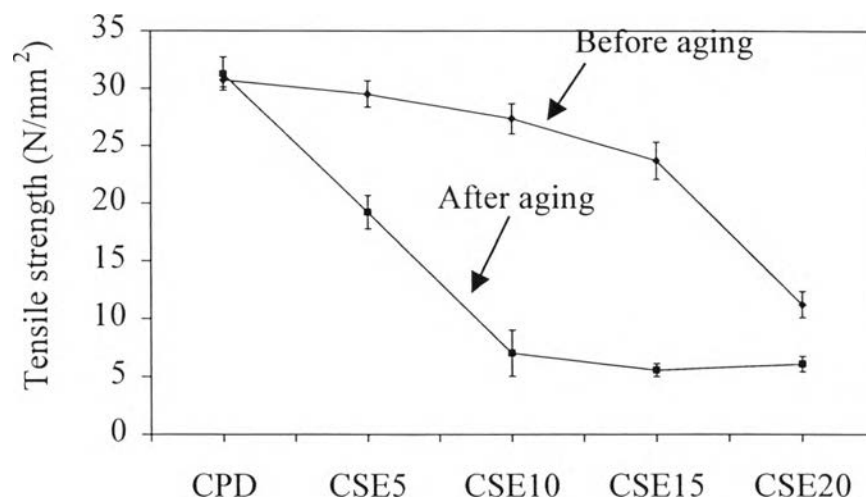


Figure 4.11 Tensile strength of vulcanized rubber sheet of varying amount of PDMS before and after aging.

were suggestive of a plasticizing effect. The tensile strength of aged sheets with PDMS decreased considerably versus the unaged sheets. Clearly aging forced more PDMS into the bulk rubber phase, therefore softening and weakening the rubber, in according with increasing autohesive tack.

b) Vulcanized Rubber Film

PDMS did not affect the tensile strength of aged and unaged rubber films, as shown in Figure 4.12. The time before solidification of the vulcnized rubber films was substantially shorter than that for the sheets,

hence on this basic one would expect more mixing of the PDMS with the rubber. However, vulcanized rubber films (0.18-0.20 mm) were substantially thinner than sheets (0.88-1.00 mm) so that PDMS was able to migrate to the surface and hence there was a depletion of PDMS in the bulk rubber.

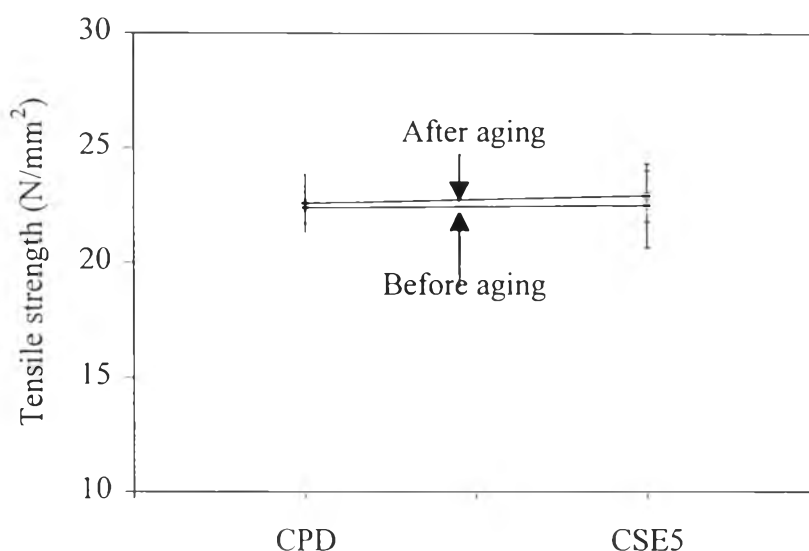


Figure 4.12 Tensile strength of vulcanized rubber film with and without PDMS before and after aging.

4.3.2 Elongation

a) *Vulcanized Rubber Sheet*

Percent elongation of vulcanized rubber sheet was shown in Figure 4.13. Elongation at break of vulcanized rubber sheet with PDMS was about the same as that without PDMS except at high content of PDMS. The elongation slightly decreased at high content PDMS indicating that poor compatibility. It can be concluded that PDMS with low content had good compatibility with NR such that it did not affect percent elongation so much. However after aging the elongation of CPD almost unchanged while those of CSE5-20 reduced as a result of PDMS redistribution into bulk

rubber. The excessive content of PDMS in the bulk after aging lead to slightly poor compatibility.

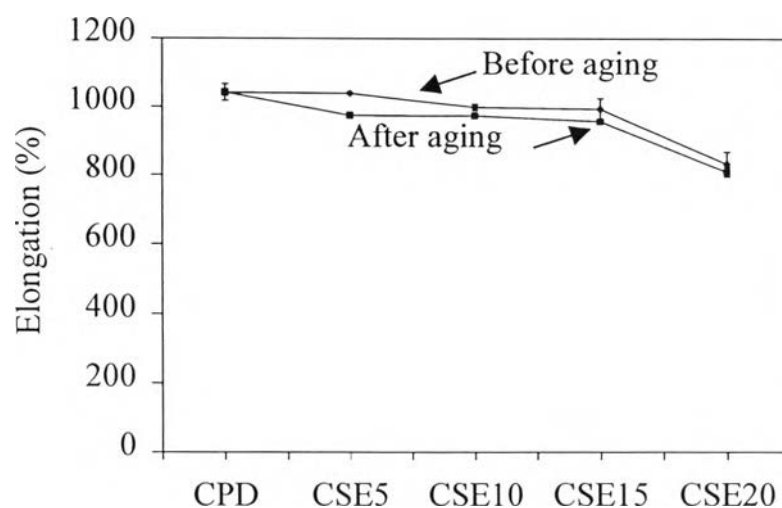


Figure 4.13 Elongation of vulcanized rubber sheet of varying amount of PDMS before and after aging.

b) Vulcanized Rubber Film

Elongation of aged and unaged rubber films with PDMS of 5 phr, shown in Figure 4.14, was slightly lower than that without PDMS. However, due to value of percent of elongation in the range of error bar, it can be concluded that due to the good compatibility at low PDMS compatibility, elongation of vulcanized rubber film was not affected by PDMS and aging.

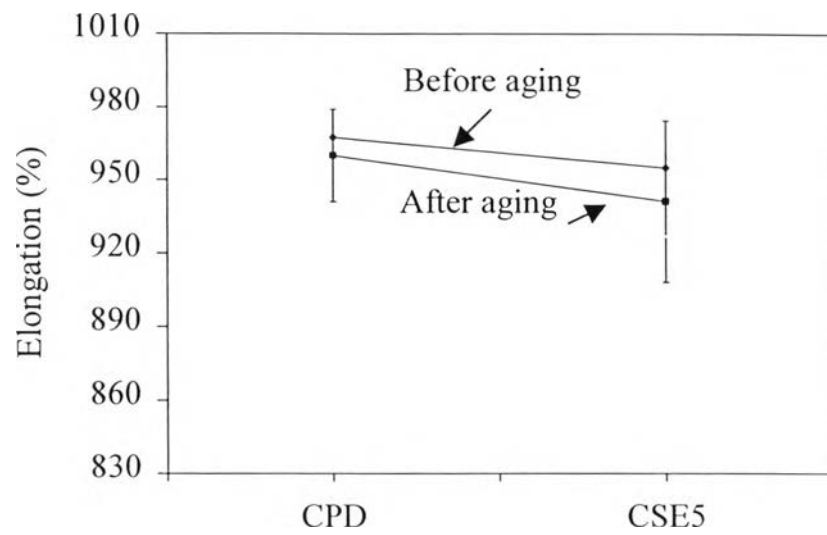


Figure 4.14 Elongation of vulcanized rubber film with and without PDMS before and after aging.