

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Preparation of chlorinated rubbers

Initially, the experiments were done at high levels of chlorination refer to US patent No. 5,143,980 [10] and US patent No. 5,350,809 [11]. Nonionic surfactant and acid were added to the 30% DRC latex before chlorination. pH value of reaction was less than 1. The chlorination method used was the same as the method given in section 3.3.1. While the chlorine content was raised, the latex became concentrated and coagulated.

The following experiments were done at pH value of the latex equal 7 and varied the concentration of latex: 15-30% DRC. However, the latex still coagulated. Although the experiments were repeated by increasing the amount of surfactants in the latex, which were 1-3 phr, we were not able to obtain the high level of chlorination.

Since the primary objective was to get the latex which is capable of film forming. The latex should still maintain as fluid after chlorination. We desired to process with the latex with low content of chlorine to prevent the problem of coagulation. It was also suggested that there was no need to acidify the latex. The amount of added chlorine content, which was used for the chlorination, was 1-5 phr. However, the chlorine content of chlorinated rubber was low and showed the maximum of only 0.25 phr chlorine. The data is shown in Table 4.1.

Various attempts have been made to explain the low value and none are entirely satisfactory.

1. The ammonia present in the non-acidified latex consumed a disproportionate amount of chlorine. There was a potential to form ammonium chloride, which caused low chlorine content.

2. Previous work [12] suggested that excess amount of chlorine is necessary to achieve high content of chlorine.

Chlorinated rubbers prepared were white viscous products. They had a specific gravity similar to original rubber, since chlorine content was slightly increased.

Table 4.1: Chlorine content and specific gravity of CNR and CPVR.

Types	Added Chlorine content (%wt)	Obtained chlorine content (%wt)	Specific gravity
Chlorinated natural rubber (CNR)	1	$0.07 \pm 0.010$	0.97
	2	$0.13 \pm 0.010$	0.97
	3	$0.19 \pm 0.006$	0.97
	4	$0.21 \pm 0.006$	0.97
	5	$0.25 \pm 0.006$	0.97
Chlorinated pre-vulcanized rubber (CPVR)	1	$0.03 \pm 0.010$	0.97
	2	$0.06 \pm 0.006$	0.97
	3	$0.10 \pm 0.006$	0.97
	4	$0.14 \pm 0.010$	0.97
	5	$0.17 \pm 0.006$	0.97

Table 4.2: Chlorine content and specific gravity of CPC.

Type	Added chlorine content (%wt)	Chlorine content of PC (%wt)	Obtained Chlorine content (%wt)	Differential chlorine content (%wt)	s.g.
Chlorinated polychloroprene rubber (CPC)	1	36.34	36.38	0.04	1.06
	2	36.34	36.42	0.08	1.06
	3	36.34	36.45	0.11	1.06
	4	36.34	36.47	0.13	1.06

## 4.2 Properties of chlorinated rubbers

### 4.2.1 Film forming

In the determination of the properties of chlorinated rubbers, film forming of rubbers was necessary. The film should have the thickness at least of 2 mm for carrying out the experiment methods. In this experiment, the films prepared from chlorinated natural rubber (CNR) and chlorinated pre-vulcanized rubber (CPVR) were flat and slippery, but non-chlorinated rubbers were not. For chlorinated polychloroprene rubber (CPC) film, there was separated as same result as non-chlorinated polychloroprene rubber film. Thus, some properties studied in the experiment with chlorinated polychloroprene rubber could not be determined.



#### 4.2.2 The permanent set

The permanent set has been carried out to assess the stability of rubber before and after chlorination. The most significant result is the speed with which the chlorinated sample of NR retracted when compared to the NR. It had just 60% set after 2 minutes versus 125%. After 48 hours it had further reduced to about 2% in comparison to the NR at 35%.

Prevulcanized NR is already substantially cross-linked and retracts rapidly- even here the partially chlorinated material shows faster retraction and hence a higher cross-link density.

Table 4.3: The permanent set after elongation

Types	$L_0$ (cm)	$L_1$ (cm)	$L_2$ (cm)	$\% \left( \frac{(L_1 - L_0)100}{L_1} \right)$	$\% \left( \frac{(L_2 - L_0)100}{L_2} \right)$
Unchlorinated NR	2.00	4.50	2.70	125.0	35.0
Chlorinated NR	2.00	3.20	2.04	60.0	2.0
Unchlorinated PVR	2.00	2.30	2.04	15.0	2.0
Chlorinated PVR	2.00	2.05	2.04	2.5	2.0

Note:  $L_0$  is original length,  $L_1$  is elongation at 2 minutes,  $L_2$  is elongation at 48 hours.

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### 4.2.3 Solubility

The solubility of chlorinated rubbers in hydrocarbon solvents became higher with the higher chlorine content. When the chlorine content is higher, the product can be dissolved in hydrocarbon solvents quickly and completely. But the solubility of the chlorinated polychloroprene rubber with lower chlorine content is very poor only swelling has been observed. The solubility of chlorinated rubbers having different chlorine content is shown in Table 4.4.

Table 4.4: Solubility of chlorinated rubbers in different chlorine content.

Solvent	CNR		CPVR		CCR	
	Soluble	Insoluble	Soluble	Insoluble	Soluble	Insoluble
Water		✓		✓		✓
Methanol		✓		✓		✓
Ethanol		✓		✓		✓
Toluene	✓		✓			✓
Xylene	✓		✓			✓
Cyclohexene	✓		✓			✓
Carbon tetrachloride	✓		✓			✓
Methylene chloride	✓		✓			✓
Ethyl acetate	✓		✓			✓

#### 4.2.3 Ozone resistance [8]

Ozone exists in small quantities in the atmosphere but even levels of less than 1 part per hundreds million (pphm) can severely attack non-resistant rubbers if they are in the strained condition. Hence, ozone attack is often the most important effect of exposure to the atmosphere. The effect of ozone is to produce clearly visible and mechanically very damaging cracking of the rubber surface. The result of ozone test is simply expressed as either cracking or no cracking. The degree of cracking can be described and a number of arbitrary scales have been used, but they are all subjective.

The method may not give results correlating exactly with outdoor exposure test, since the correlation of accelerated ozone tests with outdoor performance is, in general, highly dependent upon the specific conditions of both the accelerated and outdoor exposure [15].

From Table 4.5, it expressed that the ozone resistance of CNR is slightly better than NR, because of the degree of cracking. For the ozone resistance of CPVR with various chlorine contents, they have the same results as pre-vulcanized rubber. Thus, the ozone resistant properties of chlorinated rubbers with low chlorine content hardly differ from original rubbers.

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Table 4.5: The result of ozone test

Types	%Chlorine content	Results
CNR	0.00	No crack
	0.07	A small number of cracking which the length was less than 1 mm
	0.13	A small number of cracking which the length was less than 1 mm
	0.19	A small number of cracking which the length was less than 1 mm
	0.20	A small number of cracking which the length was less than 1 mm
	0.25	A small number of cracking which the length was less than 1 mm
CPVR	0.00	A large amount of cracking which the length was less than 1 mm
	0.03	A large amount of cracking which the length was less than 1 mm
	0.06	A large amount of cracking which the length was less than 1 mm
	0.10	A large amount of cracking which the length was less than 1 mm
	0.14	A large amount of cracking which the length was less than 1 mm
	0.17	A large amount of cracking which the length was less than 1 mm

#### 4.2.4 Water and chemical resistance

The measurement of the water and chemical resistance depends on the deformation of dimension, weight or texture of CNR film after it is exposed to chemical reagent. The greater deformation shows the poorer in chemical resistant property.

Results of the water and chemical resistant tests of rubbers are expressed as percentage of the change in each physical property (weight) as follows;

Table 4.6: Chemical resistant property of CNR in various chemical reagents.

Chlorine content (%wt)	%Weight change				
	H <sub>2</sub> O	5%wt.NaOH	5%wt.HCl	Vegetable Oil	Lubricating oil
0.00	4.57	1.75	2.77	>100	91.44
0.07	13.88	3.52	8.66	>100	>100
0.13	11.56	2.96	4.69	90.84	>100
0.19	6.35	2.53	2.93	81.45	91.19
0.21	4.83	1.77	2.75	79.63	69.10
0.25	4.58	1.73	2.31	64.29	56.56

Table 4.7: Chemical resistant property of CPVR in various chemical reagents.

Chlorine Content (%wt)	%Weight change				
	H <sub>2</sub> O	5%wt.NaOH	5%wt.HCl	Vegetable Oil	Lubricating oil
0.00	9.89	3.93	9.66	61.34	58.06
0.03	7.34	8.77	9.35	58.31	59.49
0.06	5.51	3.84	5.81	55.23	53.77
0.10	4.75	3.19	4.90	55.12	51.68
0.14	4.69	2.50	4.08	38.38	37.50
0.17	4.64	2.05	3.28	34.70	37.05



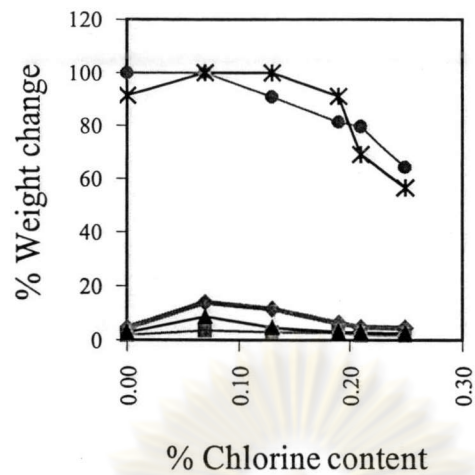


Figure 4.1 Changes in mass of CNR having different chlorine contents in various chemical reagents: ♦ H<sub>2</sub>O, ■ 5%wt. NaOH, σ 5%wt. HCl, ● vegetable oil, and \* lubricating oil.

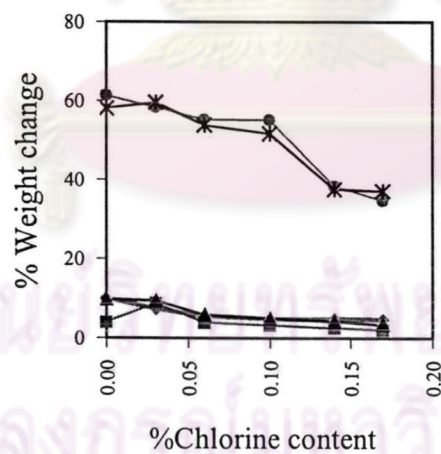


Figure 4.2 Changes in mass of CPVR having different chlorine contents in various chemical reagents: ♦ H<sub>2</sub>O, ■ 5%wt. NaOH, σ 5%wt. HCl, ● vegetable oil, and \* lubricating oil.

From Figure 4.1 and Figure 4.2, the trend of changing in mass decreases, when the chlorine content is raised. It shows that the chemical resistant properties of chlorinated rubbers have been improved increased with chlorine content. It is clearly compared with vegetable oil and lubricating oil. The slope is sharp. It means that the chemical resistance of the product is much higher than rubber, even at comparatively low levels of chlorine.

#### 4.2.5 Morphology

The films of prepared chlorinated rubbers should have the properties suitable for application. Hence, their surface and cross-section should be flat and have small amount of split or crack. The Scanning Electron Microscope technique (SEM) was used for investigating the surface and cross-section of the chlorinated rubber films.

Figure 4.3 shows scanning electron micrographs of natural rubber films (left) and CNR films (right). There are the cracks distributing on the surface of NR films, whereas there are less number of cracks on the surface of CNR films as compared to ones that evenly distributed on NR surface. Similar trend was observed from cross-section.

Figure 4.4 shows scanning electron micrographs of pre-vulcanized rubber films (left) and CPVR films (right). When surface of PVR films are considered, they can be found that there are longer cracks than CPVR films. However, cross-section of CPVR films has smoother surface than PVR films.

Scanning electron micrographs of polychloroprene rubber films (left) and CPC films (right) were shown in Figure 4.5. The surface of PC films has a lot of cracks that distribute on the surface. However, the surface of CPC film has a long white split. It can be expressed that film forming of chlorinated polychloroprene rubber and polychloroprene rubber is quite similar. At cross-section, PC films have rougher surface than CPC films.

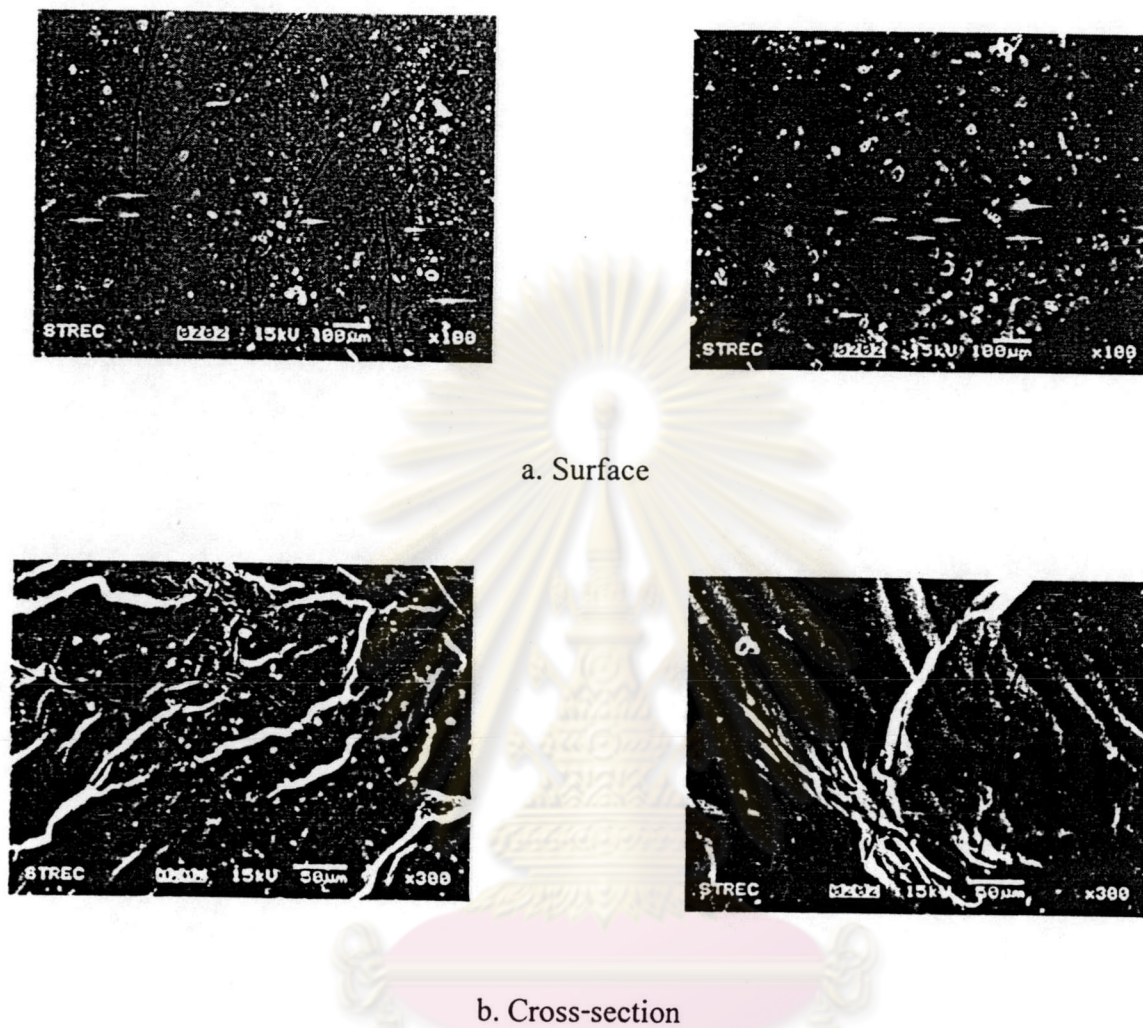
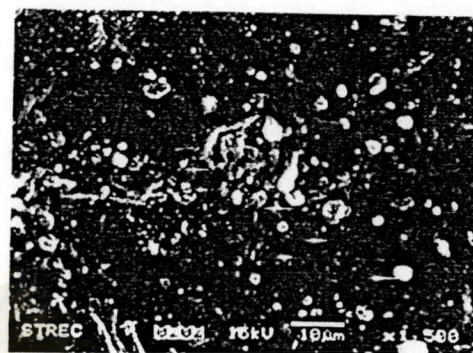


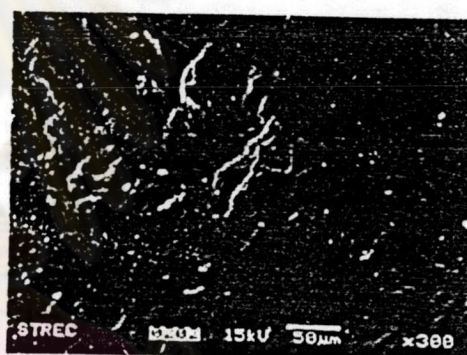
Figure 4.3 Scanning electron micrographs of natural rubber films (left) and CNR films (right): (a) Surface ( $\times 100$ ) and (b) Cross-section ( $\times 300$ ).

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a. Surface



b. Cross-section

Figure 4.4 Scanning electron micrographs of pre-vulcanized rubber films (left) and CPVR films (right): (a) Surface ( $\times 1,500$ ) and (b) Cross-section ( $\times 300$ ).



a. Surface



b. Cross-section

Figure 4.5 Scanning electron micrographs of polychloroprene rubber films (left) and CPC films (right): (a) Surface ( $\times 150$ ) and (b) Cross-section ( $\times 300$ ).



#### 4.2.6 Thermal stability

It is known the thermal stability of chlorinated rubbers has an important effect on their preparation, storage, processing, and applying properties. Then, the thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) methods were adopted to study the stability of chlorinated rubbers prepared. Jie-Ping Zhong and others studied the stability of CNR with high chlorine content under nitrogen atmosphere. Only at 291 °C did a peak appear on the DTG curve, which indicated that thermal degradation of CNR is a one-step reaction.

In this study, the TG and DTG curves of degradation of NR under nitrogen atmosphere are shown in Figure 4.6. Only at 381.96 °C does a peak appear on the DTG curve, which indicates that the thermal degradation of NR is a one step reaction. It can be seen from TG curve that the thermal degradation of NR tends to stabilize at 386 °C. Figure 4.7 shows the TG and DTG curves of degradation of CNR in nitrogen. Peak appears on the DTG curve at 382.12 °C, which is similar to the DTG curve of NR. The thermal degradation of CNR tends to stabilize at the same points as NR. From above, the thermal stability of CNR with high chlorine content has lower level than CNR with low chlorine content. Figures 4.8 and 4.9 show the TG and DTG curves of degradation of PVR and CPVR in nitrogen. From the DTG curves, peaks appear at the same point, that is 380.90 °C. The thermal degradation of PVR and CPVR stabilize at 380 °C.

The TG and DTG curves of degradation of PC in nitrogen are shown in Figure 4.10. Peaks of DTG curves of PC and CPC almost appear at the same point, that is 372.59 and 368.08 °C. From these results, chlorinated rubbers have the same thermal resistant property as non-chlorinated rubbers, because of the similar major structure of rubbers and low chlorine content.



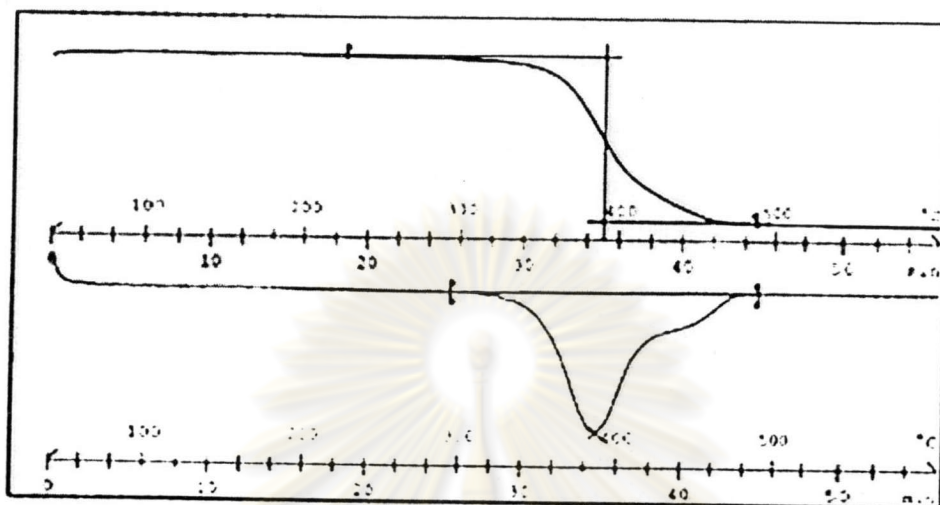


Figure 4.6 The TG and DTG curves of the thermal stability of NR.

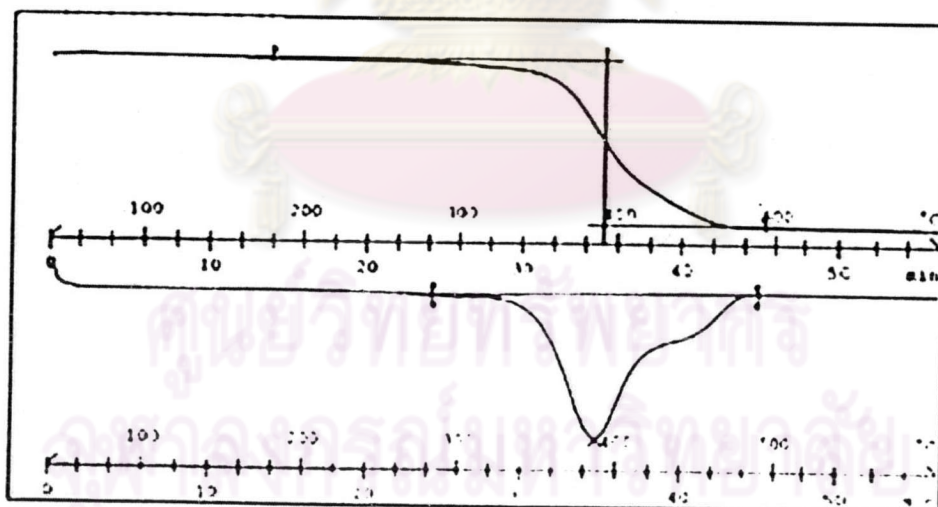


Figure 4.7 The TG and DTG curves of the thermal stability of CNR.

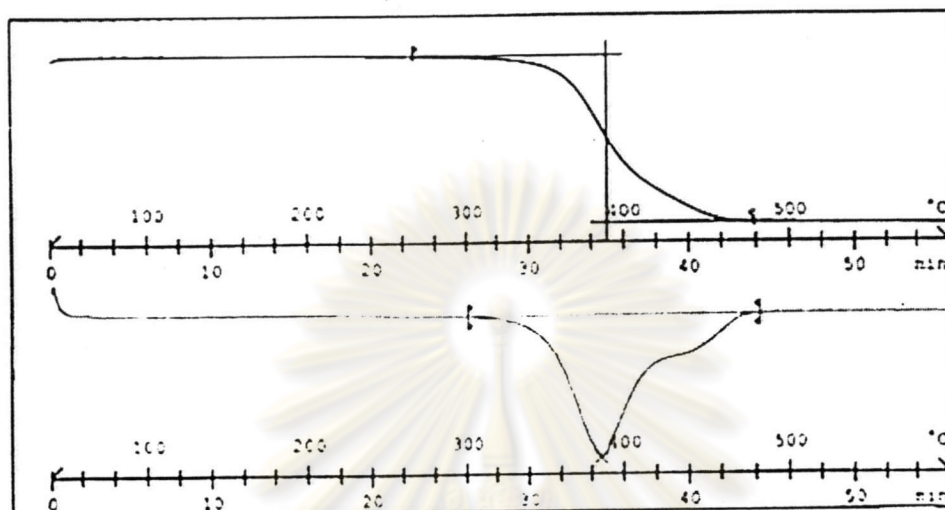


Figure 4.8 The TG and DTG curves of the thermal stability of PVR.

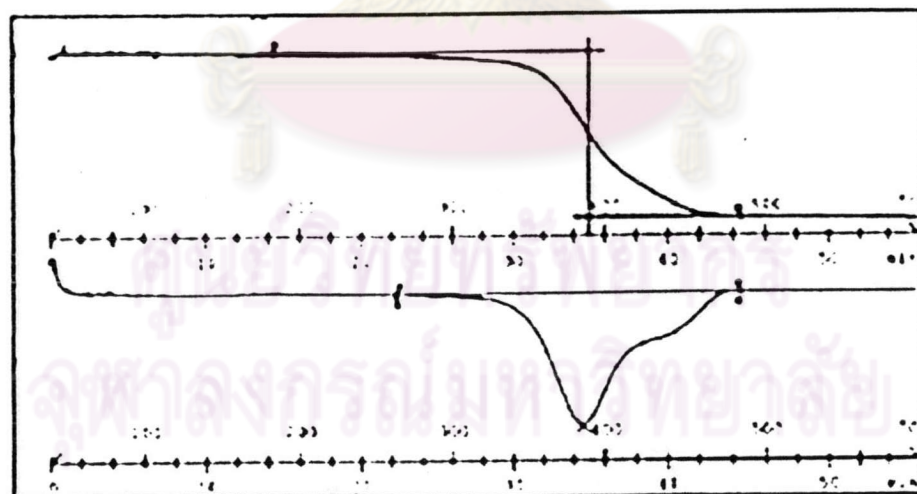


Figure 4.9 The TG and DTG curves of the thermal stability of CPVR.

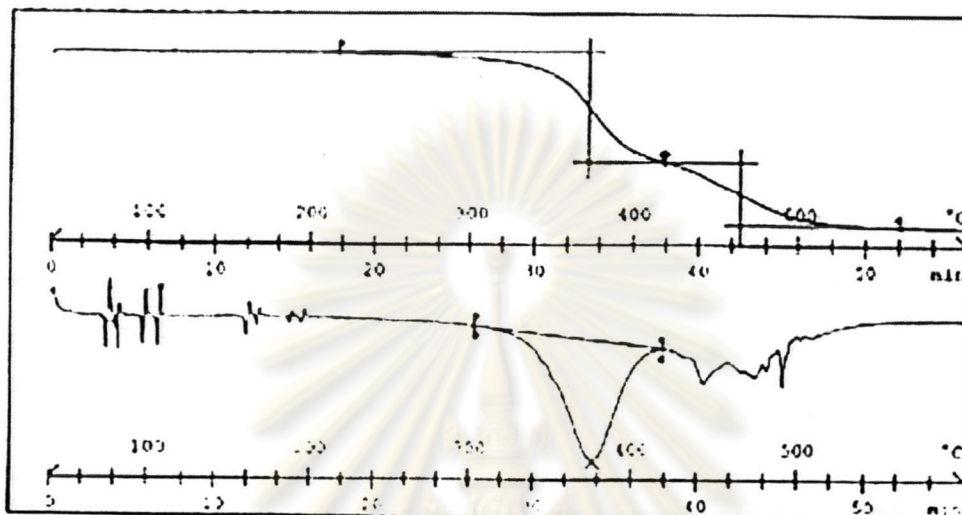


Figure 4.10 The TG and DTG curves of the thermal stability of PC.

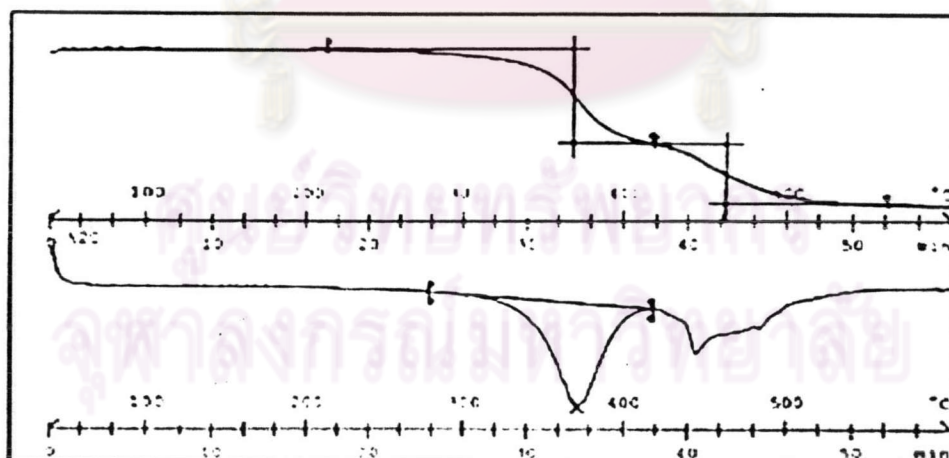


Figure 4.11 The TG and DTG curves of the thermal stability of CPC.



#### 4.2.7 Glass transition temperature

The glass transition temperature ( $T_g$ ) of unchlorinated rubbers and chlorinated rubbers are shown in Figures 4.12-4.17. They suggested that chlorinated rubbers have the same glass transition temperature value as unchlorinated rubbers ( $-63.8^\circ\text{C}$ ), because of the similar major structure of rubbers and low chlorine content.

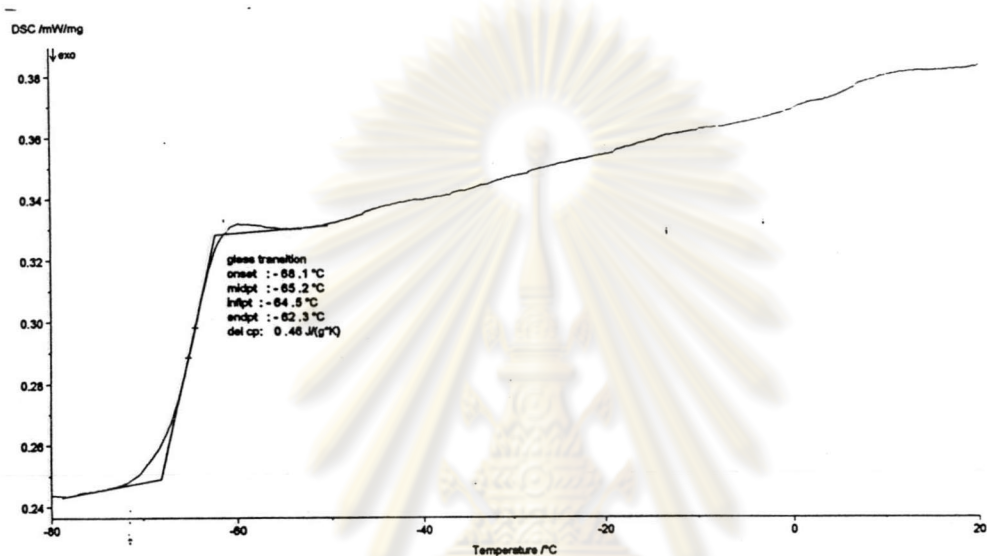


Figure 4.12 DSC thermogram of unchlorinated natural rubber.

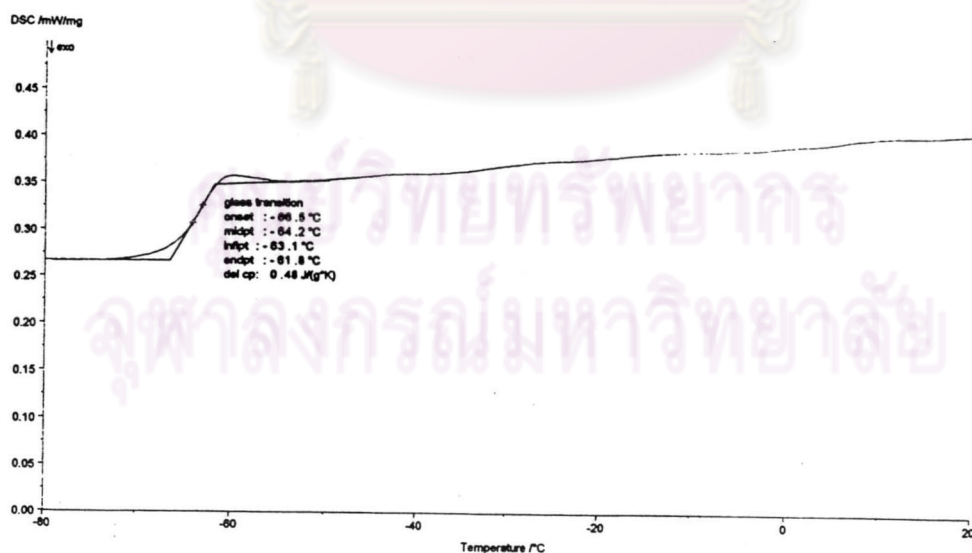


Figure 4.13 DSC thermogram of the highest chlorinated natural rubber.

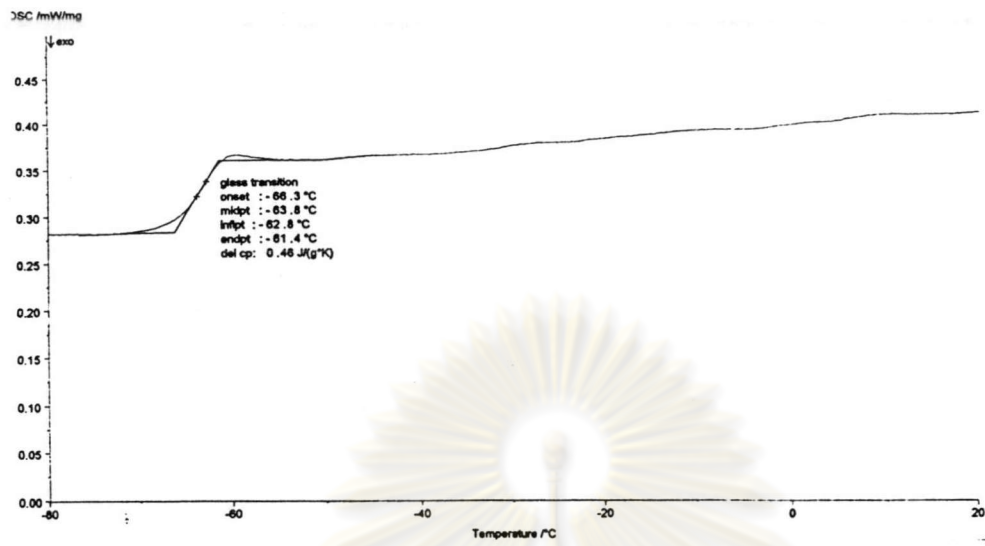


Figure 4.14 DSC thermogram of unchlorinated pre-vulcanized rubber.

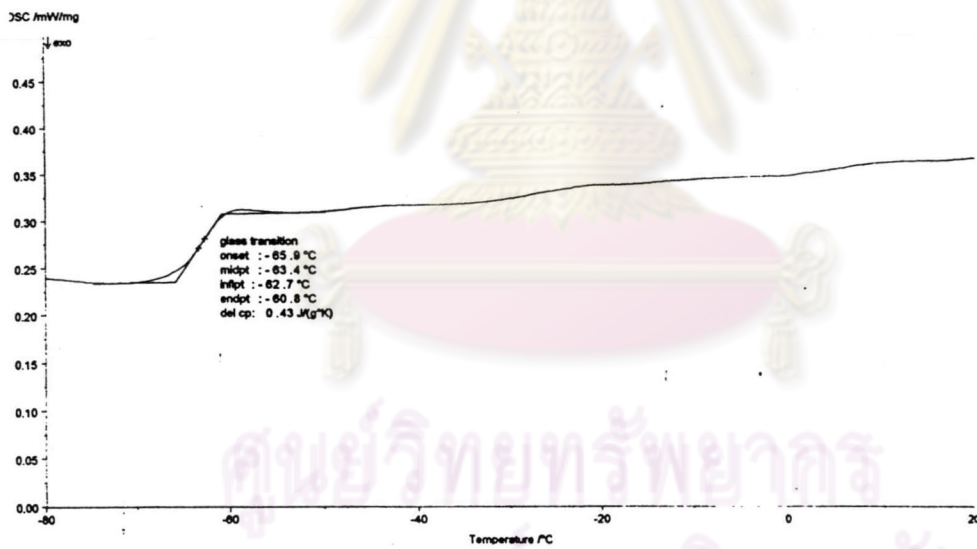


Figure 4.15 DSC thermogram of the highest chlorinated pre-vulcanized rubber.

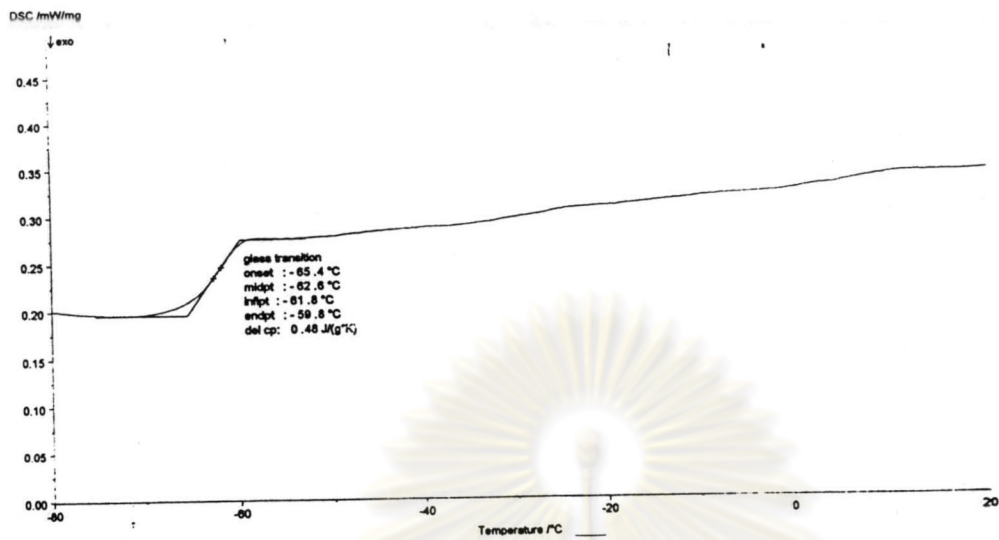


Figure 4.16 DSC thermogram of unchlorinated polychloroprene rubber.

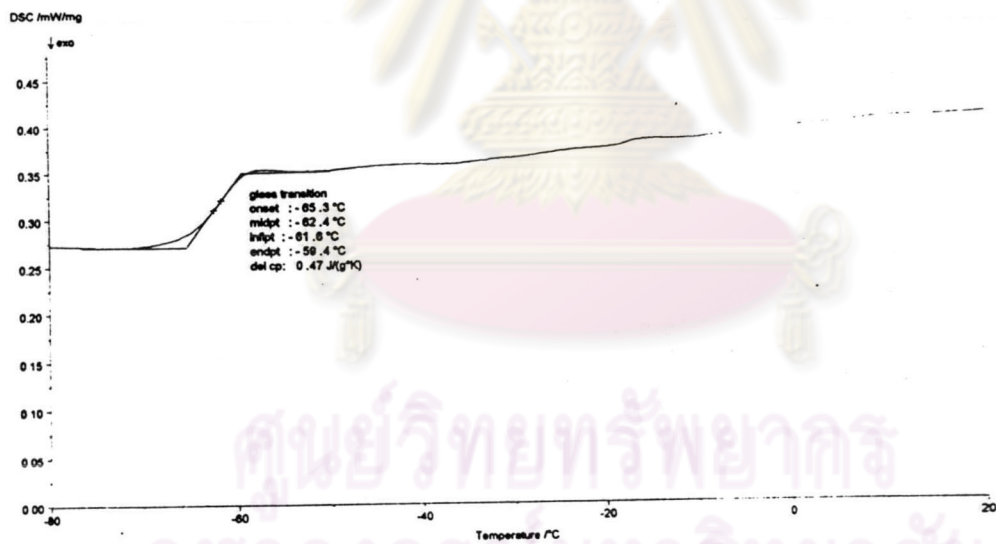


Figure 4.17 DSC thermogram of the highest chlorinated polychloroprene rubber.