

## CHAPTER IV

### RESULT AND DISCUSSION

#### Results

The refined palm oil is epoxidized by the in situ peracetic acid, the product is the epoxidized palm oil that contains epoxide ring. The suitable reaction conditions and the properties of PVC compounded with epoxidized palm oil are studied and the results are expressed as the following.

#### 1. Effect of The Variables on Epoxidation of Palm Oil

The results of the 2<sup>4</sup> factorial design experiment are in Table 4.1.

The quantities of the chemicals and the oxirane oxygen are calculated by a statistical method for a variance analysis(21) to find the significance of each variable as expressed in Table 4.2.

Table 4.1 The results of 2<sup>4</sup> factorial design experiment.

Expt. No.	The amount of chemicals				Expt.1		Expt.2	
	H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	HOAc <sup>b</sup>	H <sub>2</sub> SO <sub>4</sub> <sup>c</sup>	C <sub>6</sub> H <sub>14</sub> <sup>d</sup>	Ox O <sub>2</sub> ,%	iodine value	Ox O <sub>2</sub> ,%	iodine value
1	0.7	0.15	0.5	5	1.65	22	1.67	23
2	0.7	0.15	0.5	30	1.60	22	1.84	19
3	0.7	0.15	2	5	2.12	9	2.15	16
4	0.7	0.15	2	30	2.06	18	2.10	16
5	0.7	0.8	0.5	5	1.92	18	1.98	17
6	0.7	0.8	0.5	30	1.96	12	1.83	18
7	0.7	0.8	2	5	1.65	18	1.38	18
8	0.7	0.8	2	30	1.88	16	1.40	17
9	1.5	0.15	0.5	5	1.93	21	1.91	21
10	1.5	0.15	0.5	30	1.95	18	1.38	22
11	1.5	0.15	2	5	2.78	2	2.83	2
12	1.5	0.15	2	30	2.79	1	2.78	1
13	1.5	0.8	0.5	5	2.85	3	2.89	1
14	1.5	0.8	0.5	30	2.75	2	2.76	2
15	1.5	0.8	2	5	2.44	3	2.95	1
16	1.5	0.8	2	30	2.90	2	3.23	1

a,b The quantity of H<sub>2</sub>O<sub>2</sub> and HOAc in mole per mole of the double bond in palm oil.

c The amount of H<sub>2</sub>SO<sub>4</sub> in % by weight of palm oil.

d The amount of C<sub>6</sub>H<sub>14</sub> in % by weight of palm oil.

Table 4.2 Variance analysis of chemical variables.

Source of	Sum of Squares	DF	Mean Squares	F
Main Effects	5.626	4	1.407	25.240
H <sub>2</sub> O <sub>2</sub>	4.568	1	4.568	145.936
HOAc	0.359	1	0.359	11.473
H <sub>2</sub> SO <sub>4</sub>	0.699	1	0.699	22.339
2-way Interactions	3.047	6	0.508	16.230
H <sub>2</sub> O <sub>2</sub> HOAc	1.040	1	1.040	33.240
H <sub>2</sub> O <sub>2</sub> H <sub>2</sub> SO <sub>4</sub>	0.538	1	0.538	17.195
HOAc H <sub>2</sub> SO <sub>4</sub>	1.374	1	1.374	43.888
HOAc C <sub>6</sub> H <sub>14</sub>	0.330	1	0.330	1.061
H <sub>2</sub> SO <sub>4</sub> C <sub>6</sub> H <sub>14</sub>	0.620	1	0.620	1.984
3-way Interactions	0.960	4	0.024	0.767
H <sub>2</sub> O <sub>2</sub> HOAc H <sub>2</sub> SO <sub>4</sub>	0.009	1	0.009	0.281
H <sub>2</sub> O <sub>2</sub> HOAc C <sub>6</sub> H <sub>14</sub>	0.019	1	0.019	0.591
H <sub>2</sub> O <sub>2</sub> H <sub>2</sub> SO <sub>4</sub> C <sub>6</sub> H <sub>14</sub>	0.041	1	0.041	0.132
HOAc H <sub>2</sub> SO <sub>4</sub> C <sub>6</sub> H <sub>14</sub>	0.027	1	0.027	0.863
4-way Interactions	0.002	1	0.002	0.062
H <sub>2</sub> O <sub>2</sub> HOAc H <sub>2</sub> SO <sub>4</sub> C <sub>6</sub> H <sub>14</sub>	0.002	1	0.002	0.062
Total	8.771	15	0.585	
Corrected for means	0.501	16	0.031	
Total uncorrected	9.272	15	0.616	

### 1.1 Significance of the Variables.

The relation of the variables is considered from the F significance of each variable. The F from Table 4.2 is compared with the F from the Table of F distribution (21). Since the degree of freedom of each chemical variable is 1 and the degree of freedom of all the variables is 15. The F value from the Table of F distribution that is considered is  $F_{1,15}$  at the level of significant of ( ) 0.05 and the level of confidence of 95%, the value of  $F_{1,15}$  is 4.54. When the F of the variable is higher than 4.54, it means that variable imposes the effect on the result. In contrast, if it is lower, it does not effect to the result.

1.1.1 Main Effect. From Table 4.2, only the amounts of hydrogen peroxide, acetic acid, and sulfuric acid exert effects on the oxirane oxygen yield,

because their F values are all greater than 4.54. The amount of solvent is not the effective parameter on the yield of oxirane oxygen because the F value is lower than 4.54 and has a little value that is not significant, it is not expressed in Table 4.2. Nielderhauser and coworkers (13) explained that solvent tends to suppress the formation of by-products and reduce viscosity of the palm oil in the reaction.

1.1.2 Variable Interactions. Interaction of each effective chemical is also of important consideration as each can cross influence the other. The amount of hydrogen peroxide, acetic acid and sulfuric acid must be in a proper ratio so that an optimum yield of the oxirane oxygen can be achieved.

## 1.2 Effect of the Reaction Parameters.

Based on the statistical evaluation of parameter importance, the following observations can be obtained.

1.2.1 Effect of Hydrogen Peroxide and Acetic Acid. Theoretically, the ratio of the oxygen peroxide and acetic acid should be 1:1 as shown in eq (4.1).



Practically, acetic acid amount should be from 0.25 to 1 mole per mole of the unsaturation, and hydrogen peroxide as the source of oxygen should be slightly excess(12,14,20). The oxirane oxygen content in Table 4.1 is high when the amount of hydrogen peroxide is excess than acetic acid and the amount of acetic acid is more than 0.15 mole per mole of the unsaturation such as those in Expts. 13-16.

1.2.2 Effect of Sulfuric Acid. Sulfuric acid also is significance when the same ratio of hydrogen peroxide and acetic acid are used; when the different amount of sulfuric acid was used, the oxirane oxygen content was different. For example, Expts. 11-12 that used 2% of sulfuric acid, the oxirane oxygen was higher than Expts. 9-10 that used sulfuric acid of only 0.5% by weight of palm oil. The sulfuric acid functions as a catalyst to produce peracetic acid rapidly (12,20).

The proper amounts of the three chemicals are determined as presented in Tables 4.3 - 4.5 and in Figures 4.1 - 4.3.

Table 4.3 Effect of 50 % hydrogen peroxide on oxirane oxygen and iodine value.

H <sub>2</sub> O <sub>2</sub> <sup>a</sup>	Expt.1		Expt.2		Average of Ox O <sub>2</sub> ,%
	Ox O <sub>2</sub> ,%	Iodine value	Ox O <sub>2</sub> ,%	Iodine value	
0.8	2.41	8	2.32	10	2.37
1.0	3.05	2	2.83	4	2.94
1.3	2.97	2	2.96	2	2.97
1.5	3.10	2	3.17	1	3.14

<sup>a</sup> The quantity of H<sub>2</sub>O<sub>2</sub> is in mole per mole of the double bonds in palm oil.

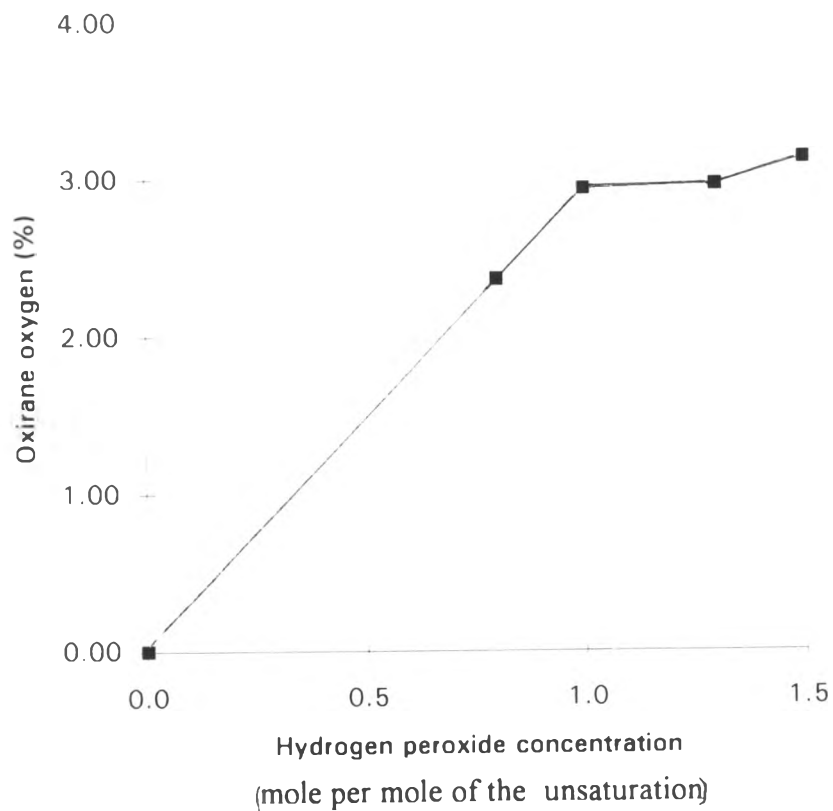


Figure 4.1 Effect of the concentration of 50% hydrogen peroxide on oxirane oxygen..

Table 4.4 Effect of the concentration of glacial acetic acid on oxirane oxygen and iodine value.

HOAc <sup>a</sup>	Expt.1		Expt.2		Average of Ox O <sub>2</sub> , %
	Ox O <sub>2</sub> ,%	Iodine value	Ox O <sub>2</sub> ,%	Iodine value	
0.3	2.86	3	2.88	4	2.87
0.5	2.88	3	2.80	1	2.84
0.6	2.87	1	2.80	1	2.84
0.8	3.10	2	3.17	1	3.14

a The quantity of HOAc in mole per mole of the double bonds in palm oil.

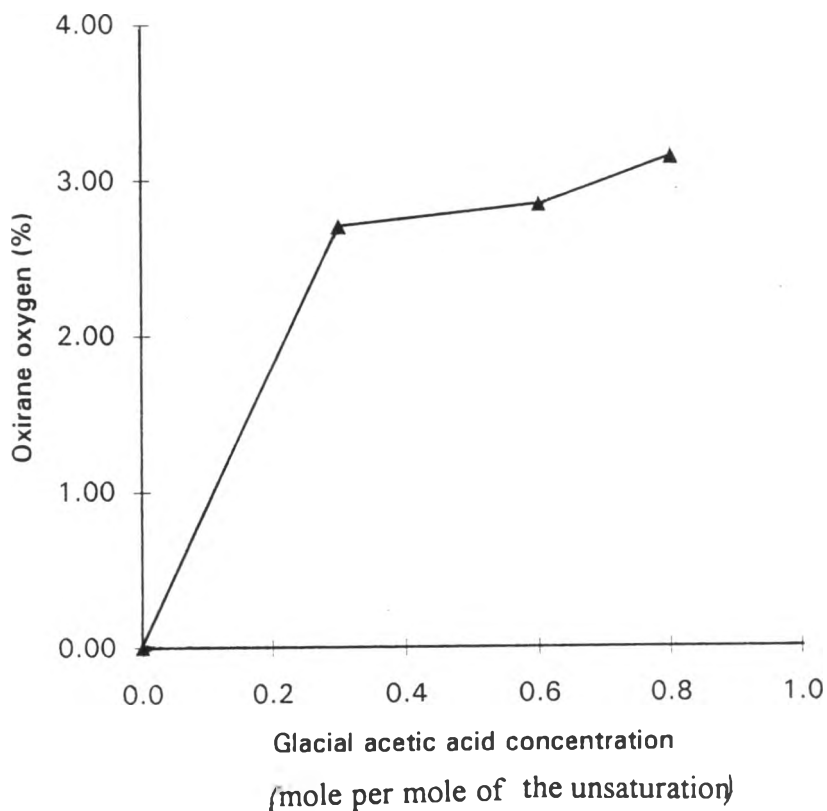


Figure 4.2 Effect of the concentration of glacial acetic acid on oxirane oxygen.

Table 4.5 Effect of the concentration of sulfuric acid on oxirane oxygen and iodine value.

H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	Expt.1		Expt.2		Average of Ox O <sub>2</sub> ,%
	Ox O <sub>2</sub> ,%	Iodine value	Ox O <sub>2</sub> ,%	Iodine value	
0.5	2.75	2	2.76	2	2.76
1.0	2.93	2	2.81	2	2.87
2.0	3.10	2	3.17	1	3.14

<sup>a</sup> The quantity of H<sub>2</sub>SO<sub>4</sub> is in % by weight of palm oil.

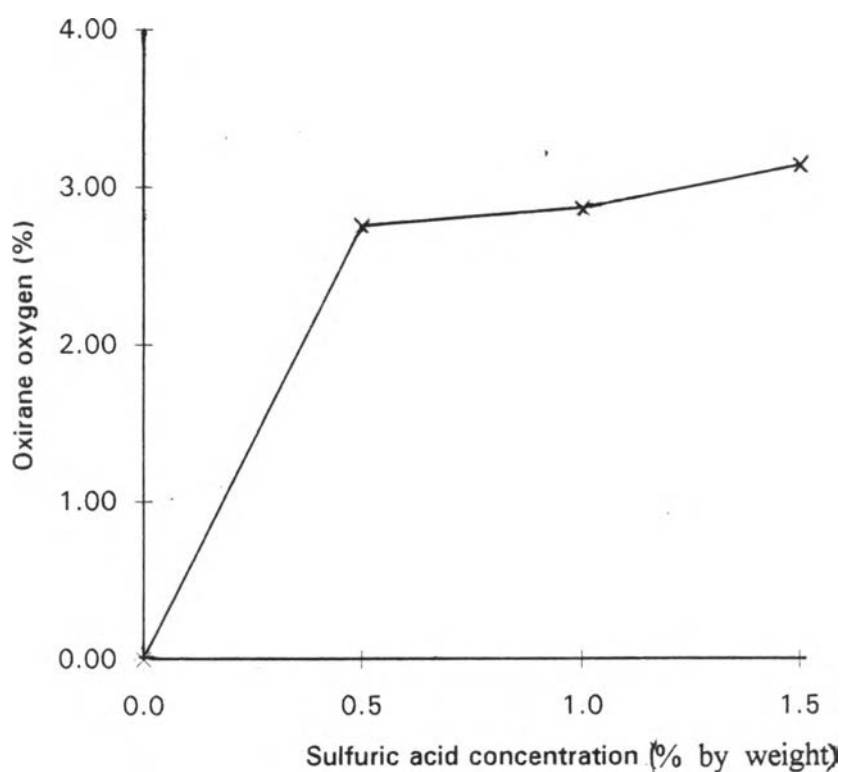


Figure 4.3 Effect of the concentration of sulfuric acid on oxirane oxygen.

The maximum oxirane oxygen is found at the hydrogen peroxide concentration of 1.5 mole per mole of the double bond and iodine value is 1. The quantities of acetic acid and sulfuric acid that give the highest yield of oxirane oxygen are 0.8 mole per mole of the double bond and 2% of sulfuric acid. Greenspan and Gall (32) had expressed that the high molar ratio of acetic acid to hydrogen peroxide caused

excessive ring opening. As shown in Table 4.1 the experiment cannot produce the product with an iodine value of 0, i.e., the reaction cannot completely proceed until all the double bonds are used up, so it is useless to increase the amount of reactants. Actually, the concentration of hydrogen peroxide is very high (50%) if it mixes with an acetic acid in a high ratio, it will probably explode (33).

1.2.3 Effect of Temperature. Table 4.6 and Figure 4.4 show the effect of the reaction temperature on oxirane oxygen and iodine value.

Table 4.6 Effect of the reaction temperature on oxirane oxygen and iodine value.

Temperature °C	Expt.1		Expt.2		Average of Ox O <sub>2</sub> ,%
	Ox O <sub>2</sub> ,%	iodine value	Ox O <sub>2</sub> ,%	iodine value	
40-45	2.39	3	2.62	2	2.51
50-55	3.10	2	3.17	1	3.14
60-65	2.90	2	3.23	1	3.07
70-75	1.60	3	1.02	1	1.31

The oxirane oxygen yield was 2.39-2.62% at 40-45°C. At higher temperatures of 60-65°C and 70-75°C, the oxirane oxygen decreased. Although the oxirane ring could be formed at high temperatures, hydrolysis of the product took place at a high rate, to give the dihydroxy compound, as shown in the reaction number 1 of Table 2.2 and the oxirane oxygen is thus decreased. The suitable temperature for epoxidation is approximately 50-55°C.

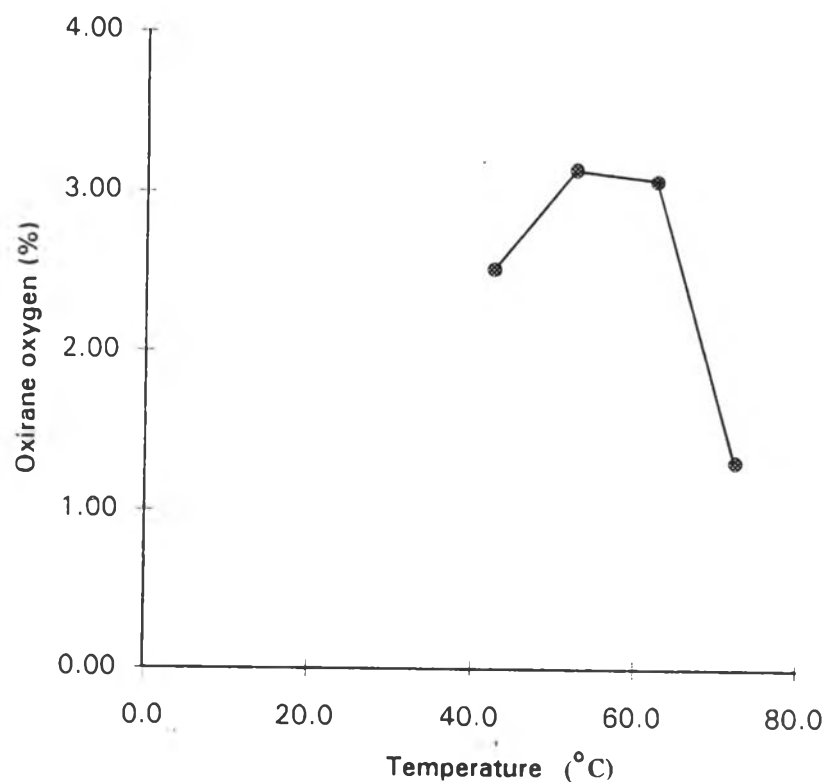


Figure 4.4 Effect of the reaction temperature on oxirane oxygen.

1.2.4 Effect of the Agitation Speed. The result shows that the suitable agitation speed for the reaction is 200 rpm as shown in Table 4.7 and in Figure 4.5. The oxirane oxygen obtained is 3.10-3.17% and iodine value 1-2.

The oxirane oxygen amount decreases when the agitation speed is higher because the higher agitation speed increases the epoxide cleavage as well as the decomposition of the  $H_2O_2$ .



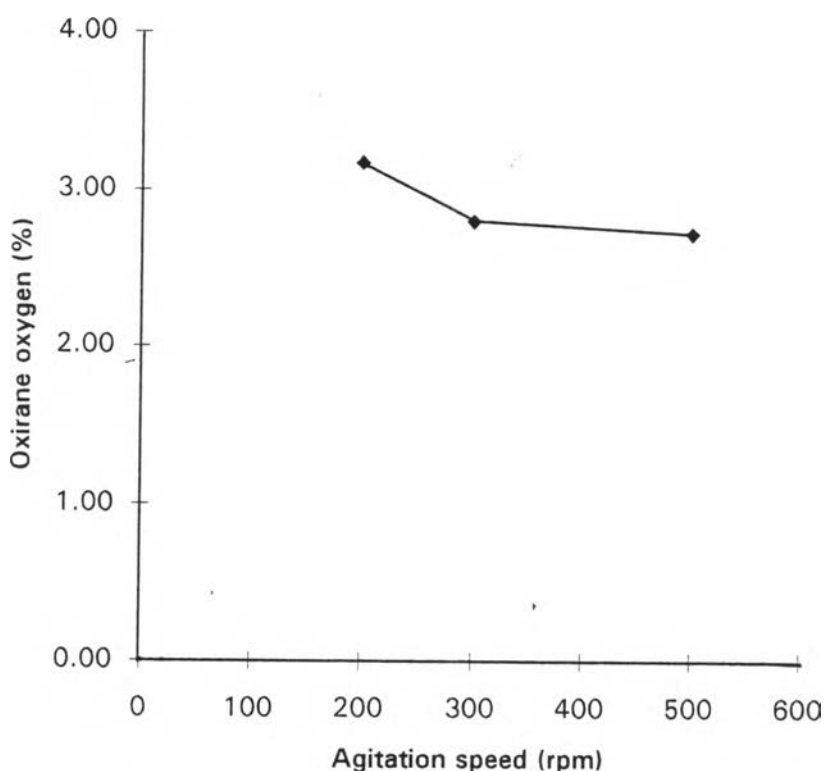


Figure 4.5 Effect of the the agitation speed on oxirane oxygen .

Table 4.7 Effect of the agitation speed on oxirane oxygen and iodine value.

Agitation speed ,rpm	Expt. 1		Expt. 2		Average of Ox O <sub>2</sub> ,%
	Ox O <sub>2</sub> ,%	iodine value	Ox O <sub>2</sub> ,%	iodine value	
200	3.10	2	3.17	1	3.14
300	2.86	1	2.74	1	2.80
500	2.77	1	2.66	1	2.72

Wohlers and coworker (34) studied the agitation control to improve the yields of epoxidized soybean oil in epoxidation reaction. He found that the mild agitation produced the highest oxirane oxygen; at a higher agitation, the epoxide cleavage increased. He explained that the cleavage was catalyzed by sulfuric acid, which remained in the aqueous phase. The cleavage was considered as a

heterogeneous reaction which occurred at the interface of oil and water. Increasing the agitation speed increases the interfacial area of the two phases. The speeds that are lower than 200 rpm are much too slow, the palm oil and the chemicals could not be mixed homogeneously. Therefore, it is no use to carry out the work at the speeds lower than 200 rpm.

1.2.5 Effect of the Reaction Time. The Table 4.8 indicates the effect of reaction time on epoxidation.

Table 4.8 Effect of the reaction time on oxirane oxygen and iodine value.

Time hr	Expt.1		Expt.2		Average of Ox O <sub>2</sub> ,%
	Ox O <sub>2</sub> ,%	iodine value	Ox O <sub>2</sub> ,%	iodine value	
0	0	52	0	52	0.00
1	-	-	1.87	15	1.87
2	2.42	9	2.50	7	2.46
3	2.57	5	2.56	7	2.57
4	2.60	4	2.69	4	2.65
5	2.65	4	-	-	2.65
6	2.75	3	2.97	3	2.86
7	2.74	3	-	-	2.74
8	2.83	2	3.06	1	2.95
9	2.70	2	2.91	1	2.81
10	2.70	2	2.88	1	2.83

The proper time is 8 hrs as shown in Figure 4.6 that oxirane oxygen content is high and iodine value is low. At a short time of reaction, the reaction could not proceed although the iodine value was high as the reaction stopped. At 9 or 10 hrs of the reaction time, the iodine value was low, and so was the oxirane oxygen.

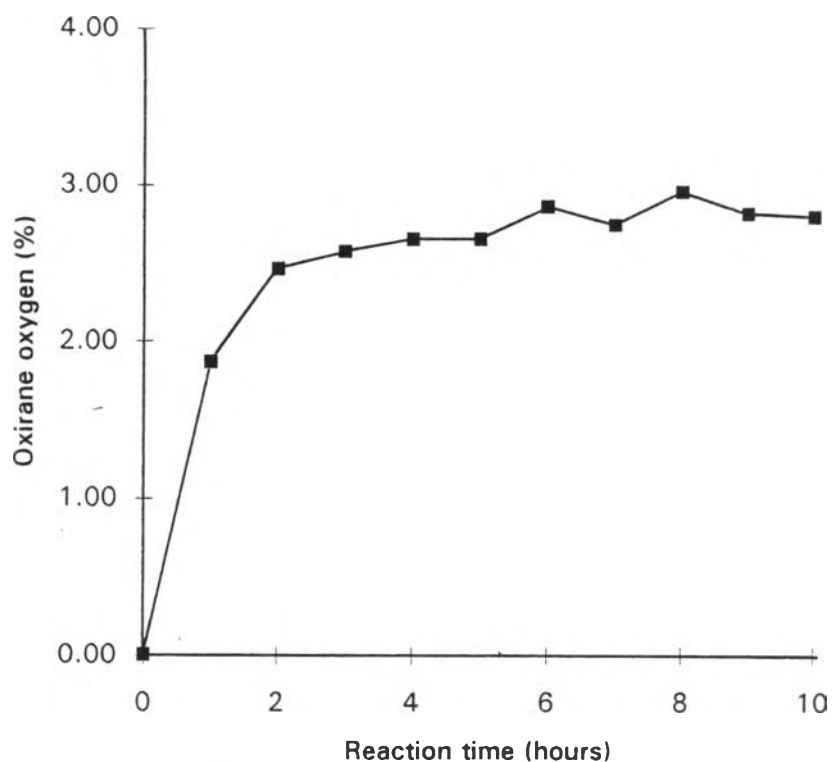


Figure 4.6 Effect of the reaction time in epoxidation of palm oil.

The reason is that the epoxide is so sensitive to any acid condition that cannot react with the active ingredients. After the reaction mixture was left for a long time, the epoxide underwent a ring opening reaction.

Based on the above experimental result, the optimum conditions for epoxidation of palm oil are concluded in Table 4.9.

This epoxidized palm oil possesses an oxirane oxygen of 3.17%, iodine value of 1. The colour is pale yellow.

Table 4.9 The optimum conditions of palm oil epoxidation.

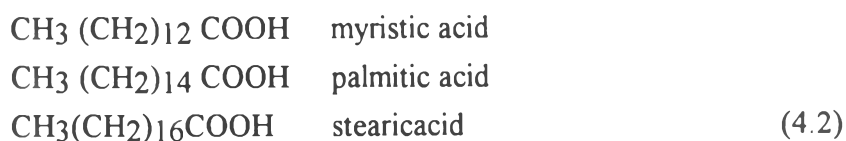
Reaction condition	Optimum value
50% Hydrogen peroxide <sup>a</sup>	1.5
Glacial acetic acid <sup>a</sup>	0.8
Sulfuric acid <sup>b</sup>	2
Temperature, °C	50-55
Agitation speed, rpm	200
Reaction time, hr	8

<sup>a</sup> mole per mole of the double bonds in palm oil.

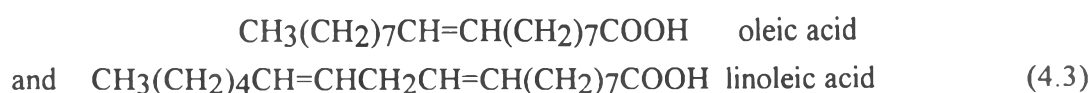
<sup>b</sup> % by weight of palm oil used.

### 1.3 Characterization of the Epoxidized Palm Oil.

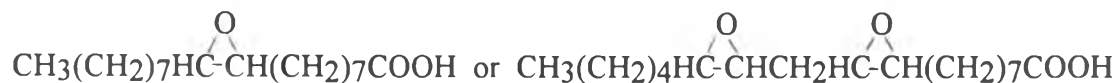
The product of the palm oil epoxidation is the epoxidized palm oil with the epoxide rings. The oxirane oxygen in the product was detected by the method as mentioned in Chapter III. The proton NMR (HNMR), <sup>13</sup>C NMR and FTIR spectrometer was provided for detecting the epoxide rings. The palm oil is composed of the saturated fatty acids and the unsaturated fatty acids (35). The saturated fatty acids are given in eq. (4.2).



The unsaturated fatty acids are shown in eq. (4.3).



The epoxidized palm oil is proposed to possess the structure as the following structure in eq. (4.4).



The saturated fatty acids remain in the original forms.

1.3.1 The FTIR Characterization. The epoxidized palm oil is analyzed by the FTIR spectrometer, the spectrum is shown in Figure 4.7. The spectrum of epoxidized palm oil is compared to the spectra of the refined palm oil (Figure 4.8) and of the epoxidized soybean oil (Figure 4.9). The characteristic bands are summarized in Table 4.10. The spectrum of epoxidized palm oil is different from that of the palm oil at wavenumbers of  $3004 \text{ cm}^{-1}$ ,  $826 \text{ cm}^{-1}$  and  $871 \text{ cm}^{-1}$ . The band at the wavenumbers of  $3004 \text{ cm}^{-1}$  is the band of  $\text{CH}_3$  that are connected to the CO group. The band of the CH stretching of unsaturated fatty acids usually is presented at the wavenumbers of  $3040\text{-}3010 \text{ cm}^{-1}$  that cannot appear because of the shielding influence of the saturated CH stretching. However, the unsaturated C-C double bond can be observed at the wavenumbers of about  $870 \text{ cm}^{-1}$  that was absent in the spectrum of the epoxidized palm oil.

Table 4.10 The FTIR characteristic bands of the epoxidized palm oil, palm oil and epoxidized soybean oil.

Wavenumbers, $\text{cm}^{-1}$	Materials			Assignments
	PO <sup>a</sup>	EPO <sup>b</sup>	ESO <sup>c</sup>	
3400	A	A	A	O-H stretching
2960-2850	A	A	A	C-H stretching of saturated
1744	A	A	A	C=O
1460, 1370	A	A	A	C-H bending of $\text{CH}_2$ and $\text{CH}_3$
1260	A	A	A	C-O-C stretching of acid
1110	A	A	A	C-O-C symmetry
1020	A	A	A	
950	A	A	A	C=C stretching
870	A	NA	NA	C=C
826	NA	A	A	C-O-C of ether
720	A	A	A	C-H rocking of $\text{CH}_2$ more than 4 groups

A = existence NA = non-existence. PO = palm oil.  
EPO = epoxidized palm oil. ESO = epoxidized soybean oil.

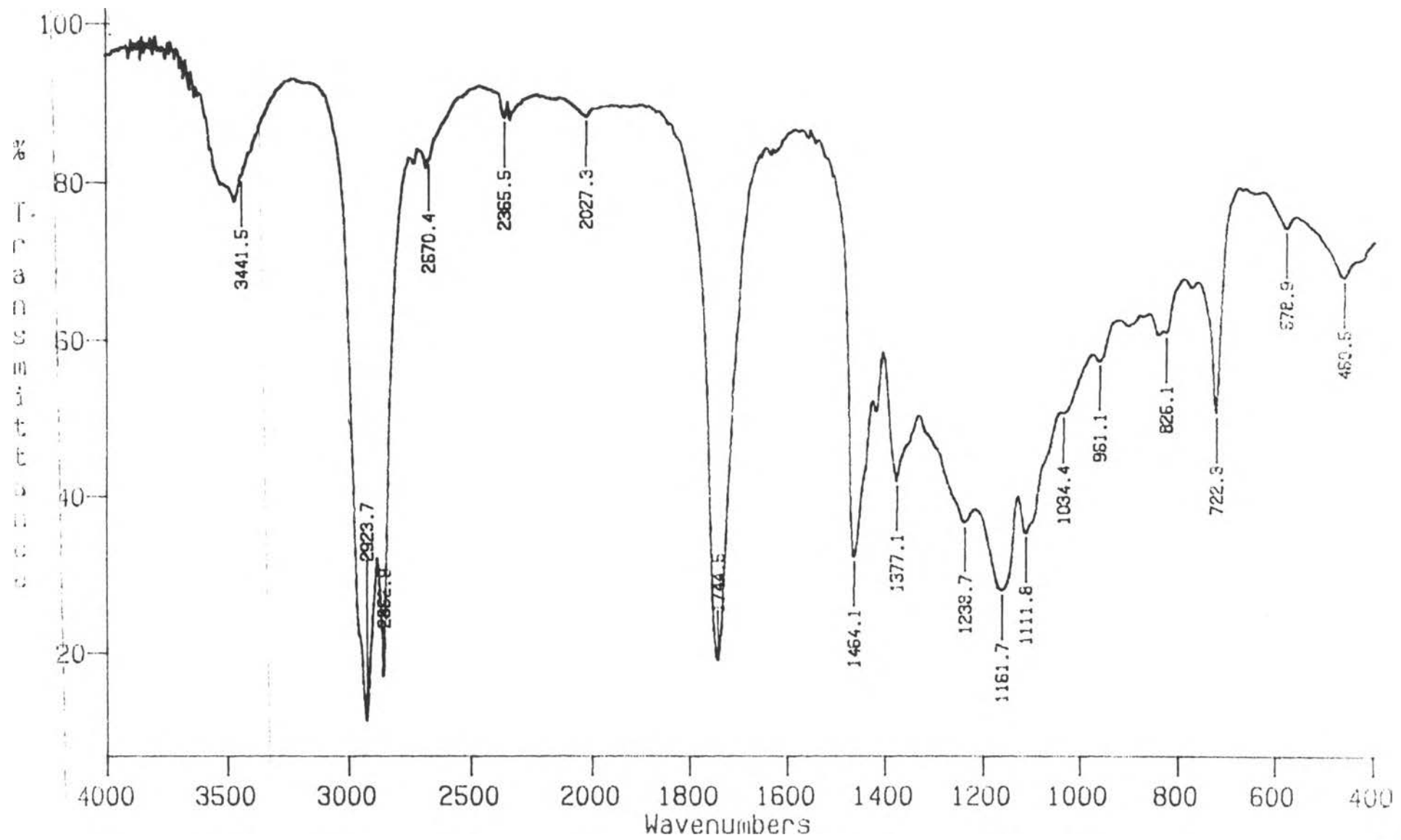


Figure 4.7 FTIR spectrum of the epoxidized palm oil.

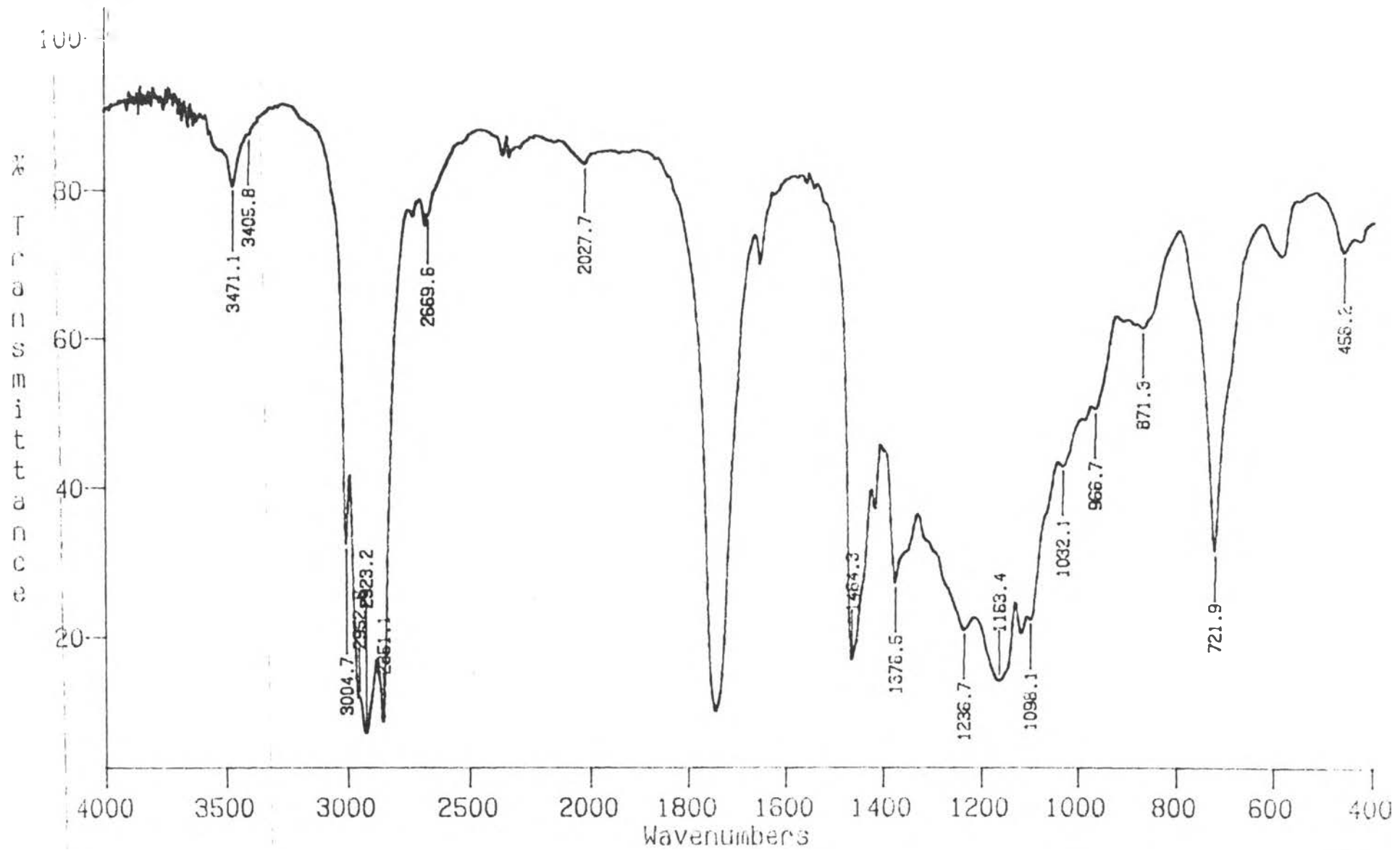


Figure 4.8 FTIR spectrum of the refined palm oil.

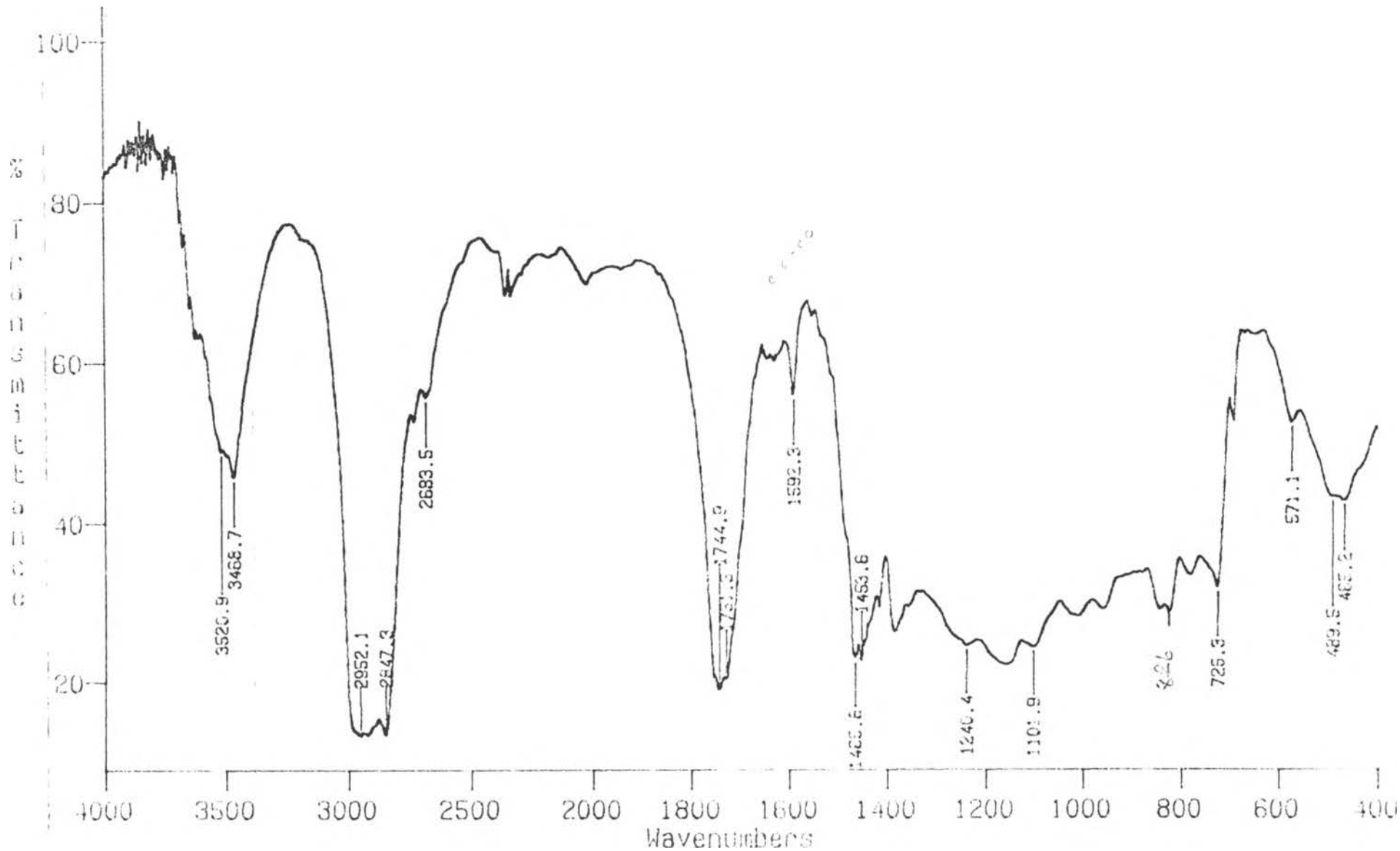


Figure 4 9 FTIR spectrum of the epoxidized soybean oil.



Shreve and coworkers (36) interpreted the spectra of oxirane derivatives of oleic acid and elaidic acid, esters and alcohols that the trans epoxy compounds showed a band near the wavenumbers of  $890\text{ cm}^{-1}$ , whereas the cis- epoxy compound showed a band at  $830\text{ cm}^{-1}$ . Paterson (37) confirmed that the two bands in the range of the wavenumbers of  $950\text{-}863\text{ cm}^{-1}$  and  $864\text{-}786\text{ cm}^{-1}$ , with the majority falling near the wavenumbers of  $910\text{ cm}^{-1}$  and  $830\text{ cm}^{-1}$  appeared in the spectra of epoxy compounds. These two bands are the asymmetric C-O-C band in the three-membered ring of epoxy compounds(38,39). The spectrum of epoxidized palm oil shows a band at the wavenumbers of  $826\text{ cm}^{-1}$  that is shifted from the wavenumbers of  $830\text{ cm}^{-1}$ . The FTIR spectrum indicates that epoxide ring synthesized is the cis-isomer because of the existence of the  $826\text{ cm}^{-1}$  peak.

1.3.2 HNMR Characterization. The epoxidized palm oil, palm oil and soybean oil are analyzed by HNMR as illustrated in Figures 4.10 - 4.12. The interpretation of these spectra is expressed in Table 4.11

Table 4.11 The interpretation of HNMR spectra of palm oil, epoxidized palm oil and soybean oil.

Chemical shift( $\delta$ ) ppm	Materials			Assignmen
	PO	EPO	ESO	
0.9	A	A	A	CH <sub>3</sub> -
1.3	A	A	A	(CH <sub>2</sub> ) <sub>n</sub>
2.0-2.35	A	A	A	CH <sub>2</sub> C=O
2.9-3.2	NA	A	A	CH CH O
4.28	A	A	A	C=C
5.38	A	A	A	CH=CH

A = existence NA = non-existence. PO = palm oil.  
EPO = epoxidized palm oil. ESO = epoxidized soybean oil.

The chemical shifts at 0.9 ppm and 1.3 ppm are the general characteristics of the proton of the CH<sub>3</sub> group and a lot of protons in the CH<sub>2</sub> group of the long chain of fatty acids (eqs. 4.3 - 4.4), the chemical shifts at 2.0-2.35 ppm are the protons attached to the carbonyl group: CH<sub>2</sub> C=O and that at 5.38 ppm is the proton of the carbon double bond in oleic acid and linoleic acid in palm oil (40). In the epoxidized palm oil spectrum, the new peak at the chemical shift of 2.9 ppm is the proton in the epoxide ring of the structure in eq.(4.5) at the labelled positions.

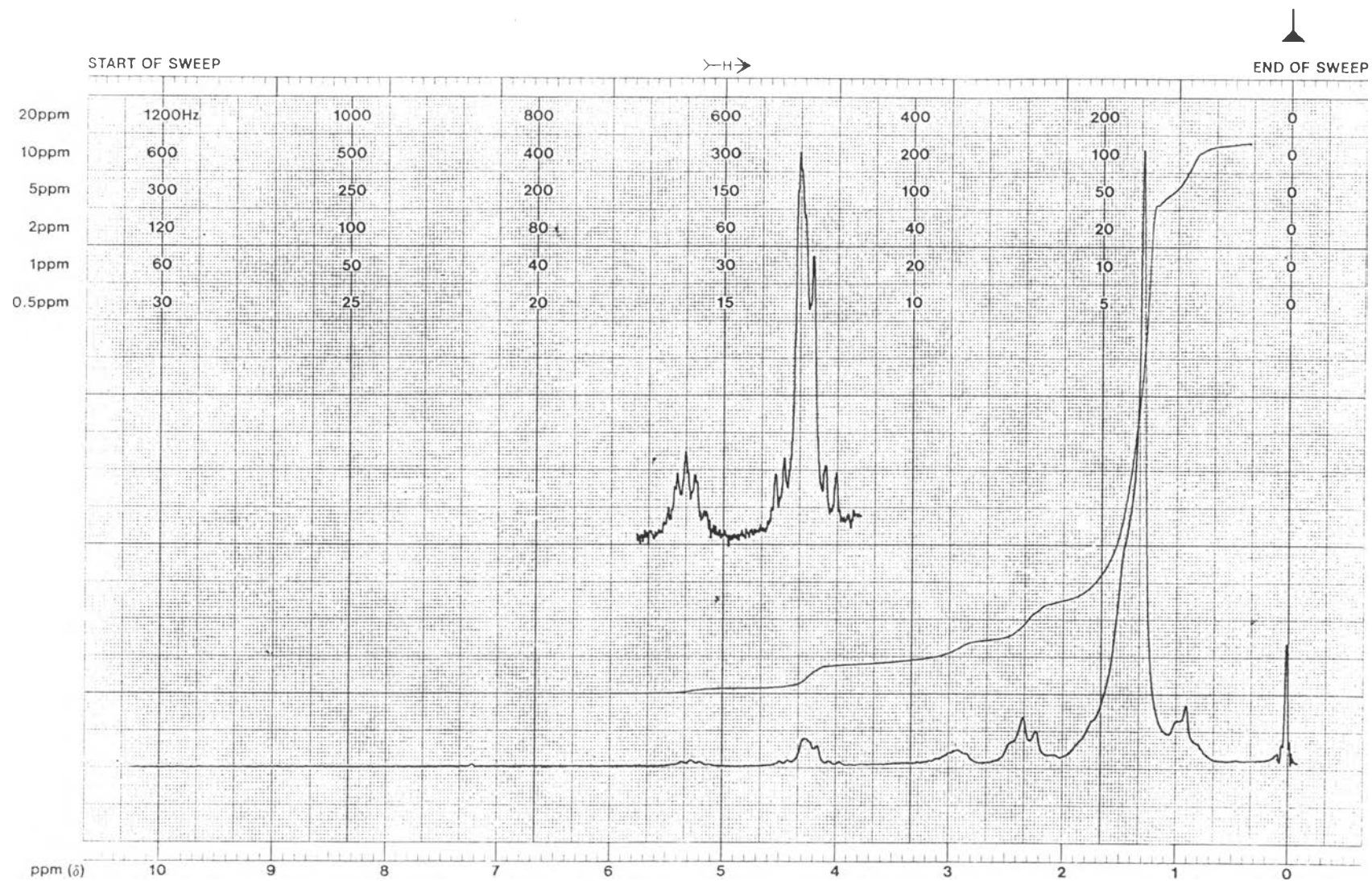


Figure 4 10 HNMR spectrum of the epoxidized palm oil.

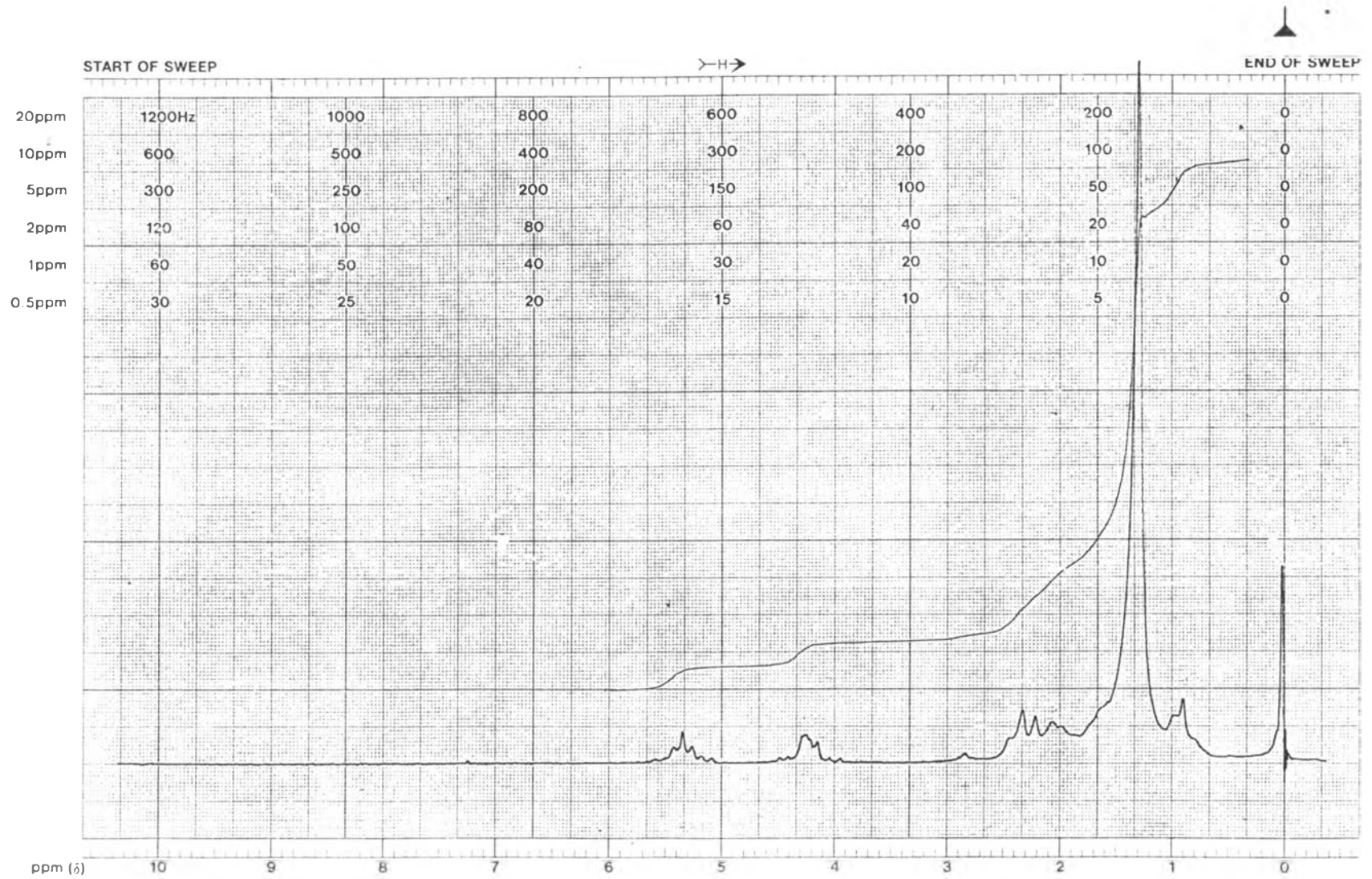


Figure 4 11 HNMR spectrum of the refined palm oil.

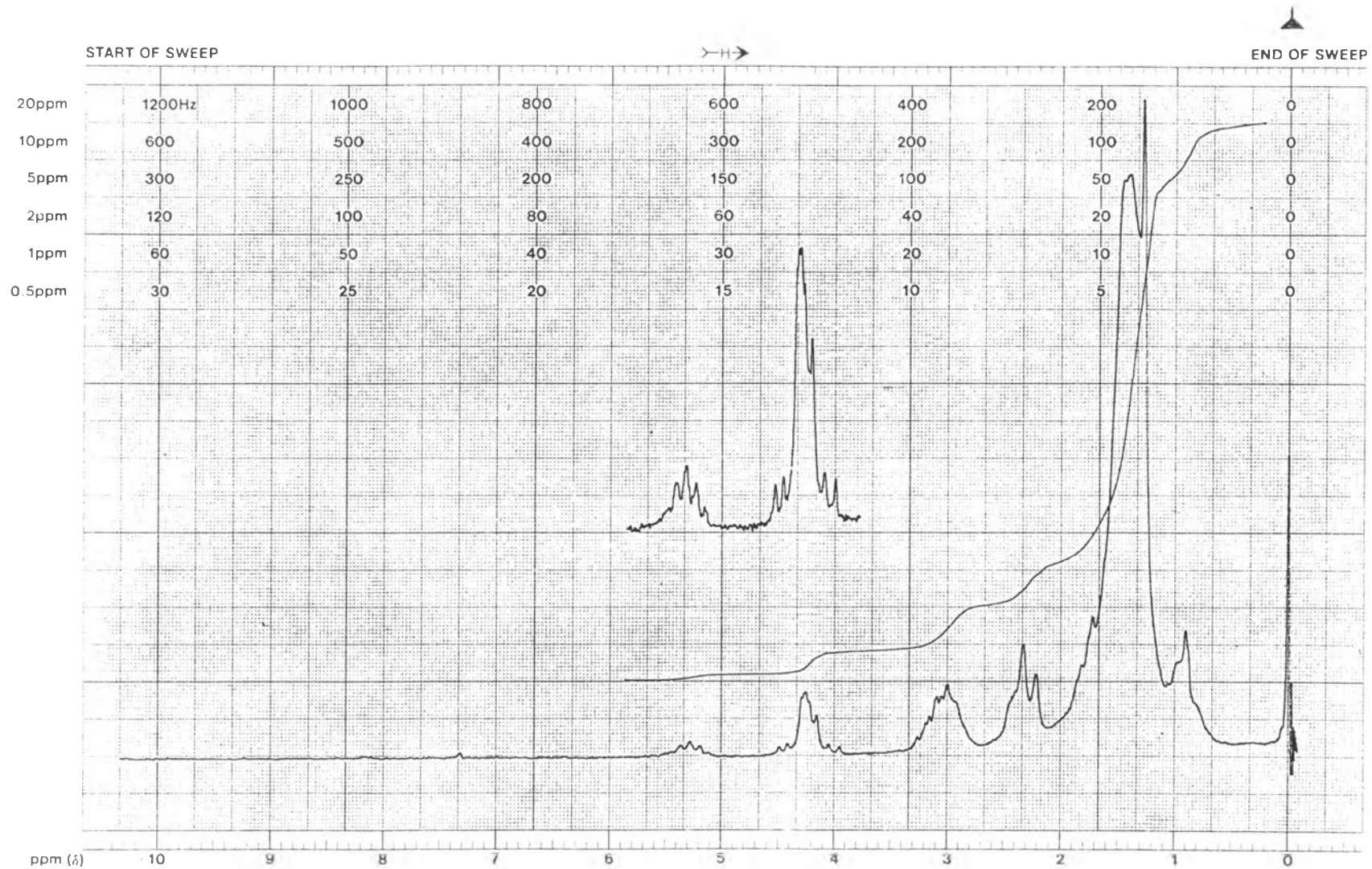


Figure 4 12 HNMR spectrum of the epoxidized soybean oil



The value of peak intensity at the chemical shift of 5.38 ppm decreases inevitably because the double bonds have been reacted to form the epoxide ring. However, the reaction cannot be completed, as the double bond still remains in the product. The chemical shift at 4.8 ppm is the protons of the double bonds that cannot be reacted so they are left in the same amount (considered by the intensity that does not decrease). Since the palm oil is composed of the abundant protons in the CH<sub>3</sub>, CH<sub>2</sub> and CH groups in many types of fatty acids that complicate the HNMR due to peak overlapping and splitting. The CNMR spectrum is perhaps a better tool worthwhile to investigate the existence of the epoxidation.

1.3.3 CNMR Characterization. The <sup>13</sup>CNMR spectra of the refined palm oil, the epoxidized palm oil and the epoxidized soybean oil are shown in Figures 4.13 - 4.15. The interpretation are in Table 4.12.

Table 4.12 The interpretation of <sup>13</sup>CNMR of the refined palm oil, epoxidized palm oil and epoxidized soybean oil.

Chemical shift(δ) ppm	Materials			Assignments
	PO	EPO	ESO	
172	A	A	A	C=O
127,129	A	NA	NA	C=C
61,64,68	A	A	A	CH <sub>2</sub>
54,56,57	NA	A	A	C- C O

A = existence NA = non-existence. PO = palm oil.

EPO = epoxidized palm oil. ESO = epoxidized soybean oil.

The chemical shift at 127 and 129 ppm are the characteristic of the carbon double bonds in fatty acids that appear in the spectrum of refined palm oil. In the spectrum of the epoxidized palm oil, the double bond is existence but the chemical shifts at 54 - 57 ppm that indicate the carbons attaching to the oxygen in the epoxide ring.

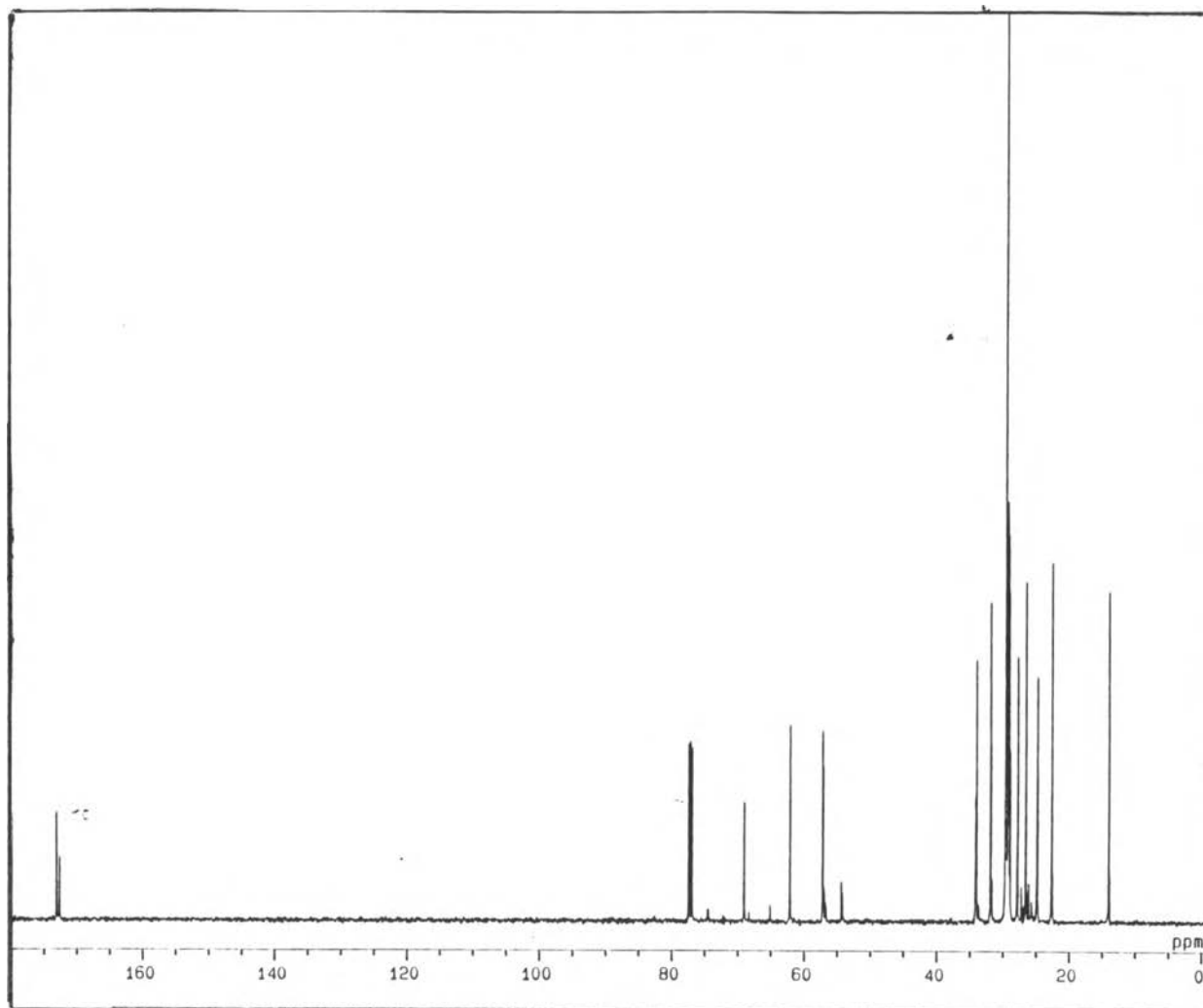


Figure 4 13 CNMR spectrum of the epoxidized palm oil.

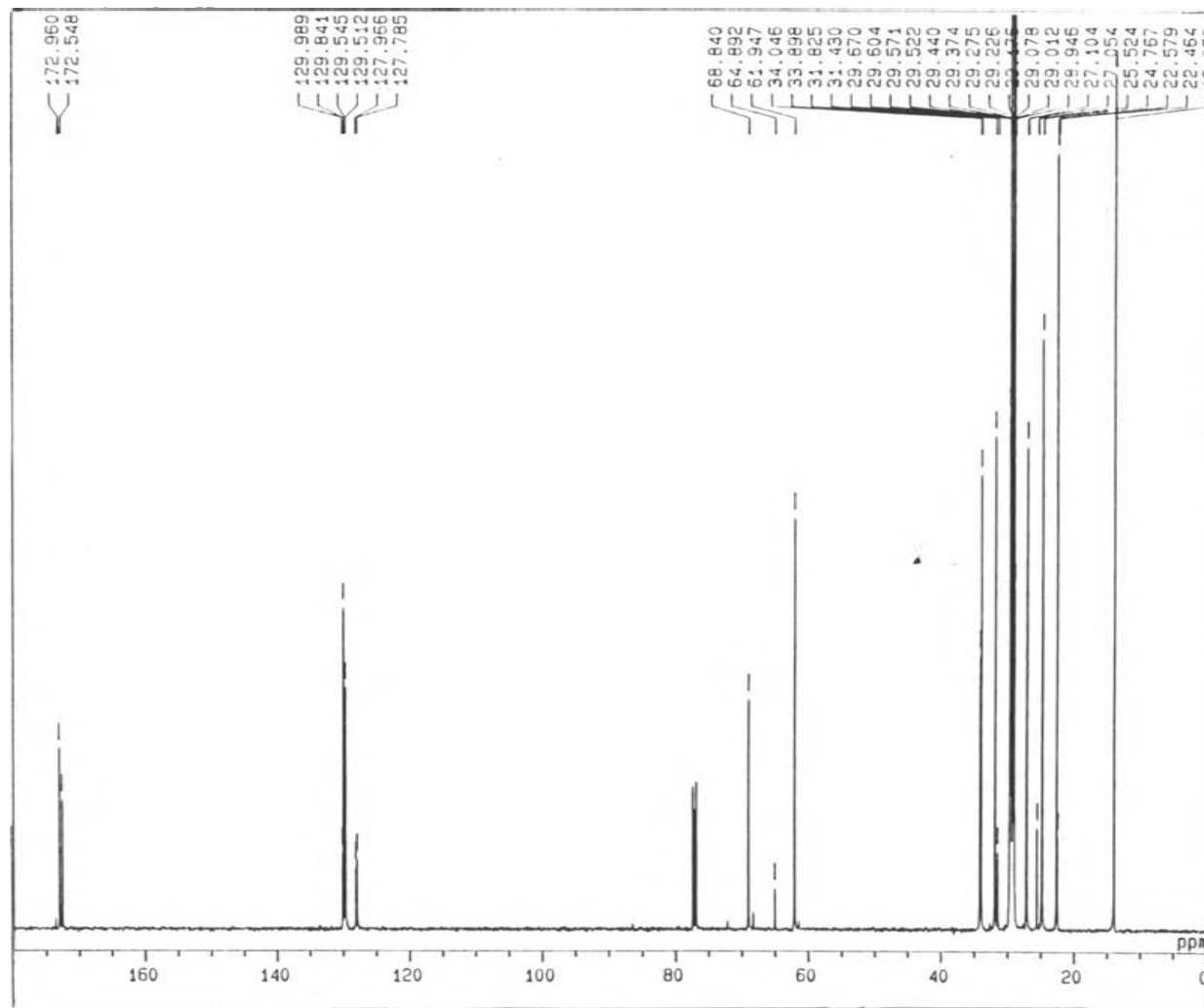


Figure 4 14 CNMR spectrum of the refined palm oil.

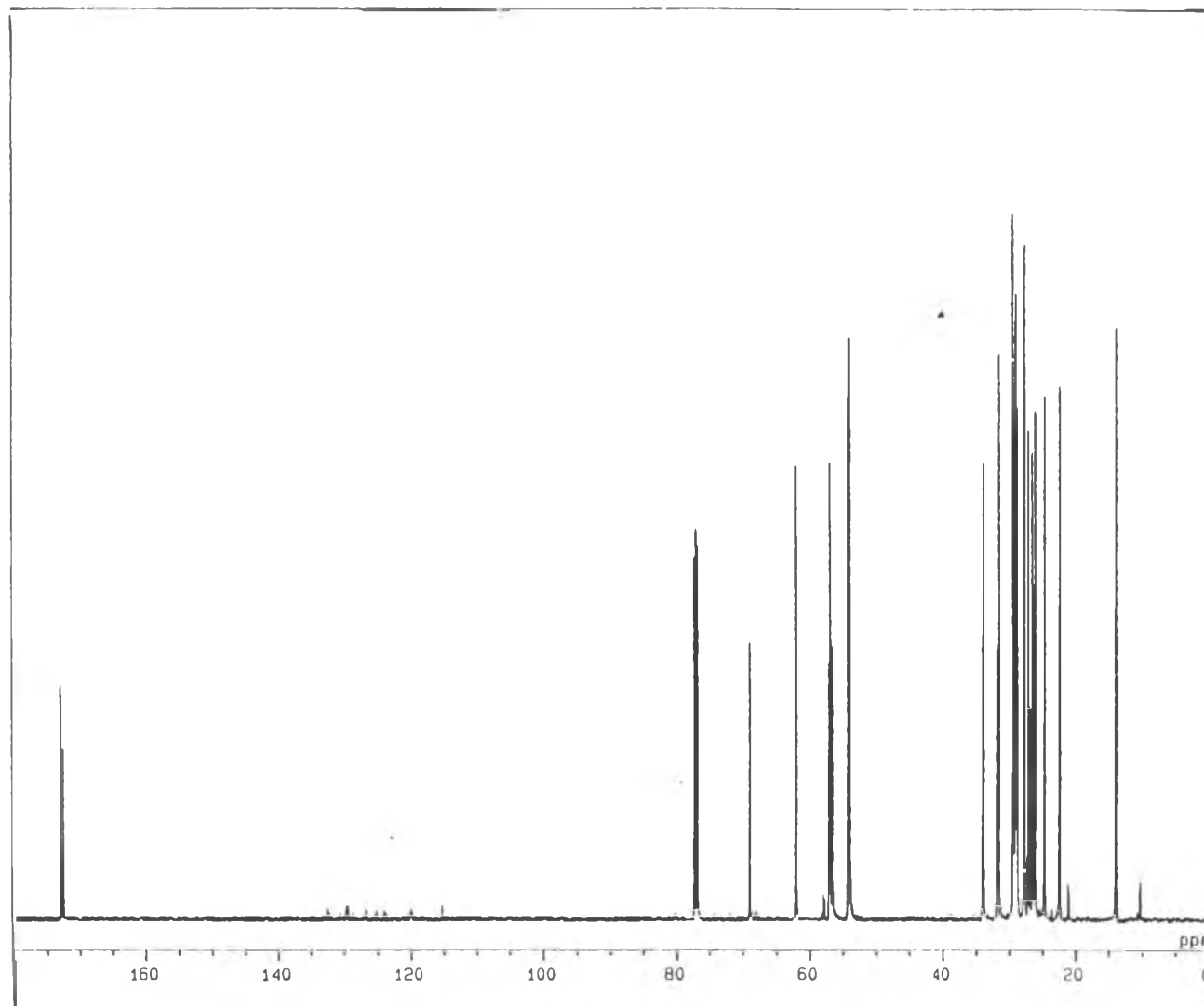


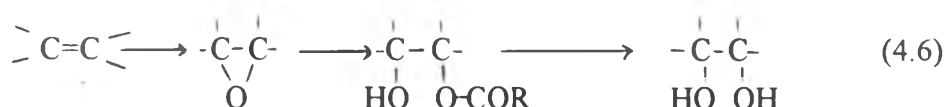
Figure 4.15 <sup>13</sup>C NMR spectrum of the epoxidized soybean oil.



From FTIR, HNMR and  $^{13}\text{C}$ NMR show that the epoxidized palm oil consists of the epoxide rings.

## 2. Effect of Epoxidized Palm Oil on PVC sheet.

In general, an unsaturated compound having a high iodine value is regarded as a poor plasticizer because of low compatibility. The compatibility of long chain compounds with PVC can be increased by the introduction of the three membered oxirane ring into the molecule (41,42). However, the epoxidation reaction is generally accompanied by some ring opening reaction such as hydroxylation; the product thus consists of the small amount of the hydroxy-acetoxy compound along with the desired epoxy derivative as in eq. (4.6).



The carboxyl and hydroxyl groups formed in the ring opening or the hydroxylation reaction cause the incompatibility of the epoxy plasticizer to a PVC resin (33). By this reason, the epoxidized palm oil is used as a secondary plasticizer for PVC compounding (3-5). The DOP has to be used as a primary plasticizer. The compounded PVC is a clear flexible sheet.

### 2.1 Mechanical Properties of the PVC Sheets.

The mechanical properties of the PVC sheet compounded by the formulation of Table 3.6 were measured and shown in Table 4.12. The mechanical properties that are worthwhile to measure for this particular application as sheet are the tensile properties: tensile strength property: tensile strength and elongation at yield and at breaking points, a flexural strength property, an izod impact strength property and a hardness property.

Table 4.13 Mechanical properties of the PVC sheets compounded by the general formulation.

Expt. No.	Materials, phr.			Mechanical properties		
	DOP	EPO	Ba-Cd-Zn stearate	Tensile strength (MPa)	Elongation (%)	Hardness Shore A
1	30	2	2	20.0±0.85	213±12.5	90±3.0
2	30	2	2.5	22.2±1.33	260±33.8	87±2.1
3	30	3	2	23.5±1.25	251±21.2	86±2.1
4	30	3	2.5	24.4±2.45	252±13.7	88±2.1
5	60	2	2	17.8±1.78	256±11.9	75±2.1
6	60	2	2.5	14.0±0.68	339± 7.8	74±2.5
7	60	3	2	14.8±0.78	334± 9.4	77±2.3
8	60	3	2.5	16.2±2.31	295±13.2	78±2.6

2.1.1 Tensile Strength and Elongation. The stress strain curve of PVC sheet is as illustrated in Figure. 4.13. There is no actual yield point, tensile strength and elongation at yield cannot be measured directly from the machine. This PVC sheets behave like a pseudo - plastic material. At the higher shear rates, this curve becomes approximately linear where an extrapolation of the curve to the stress axis, the value of shear stress as an apparent yield value can be obtained.

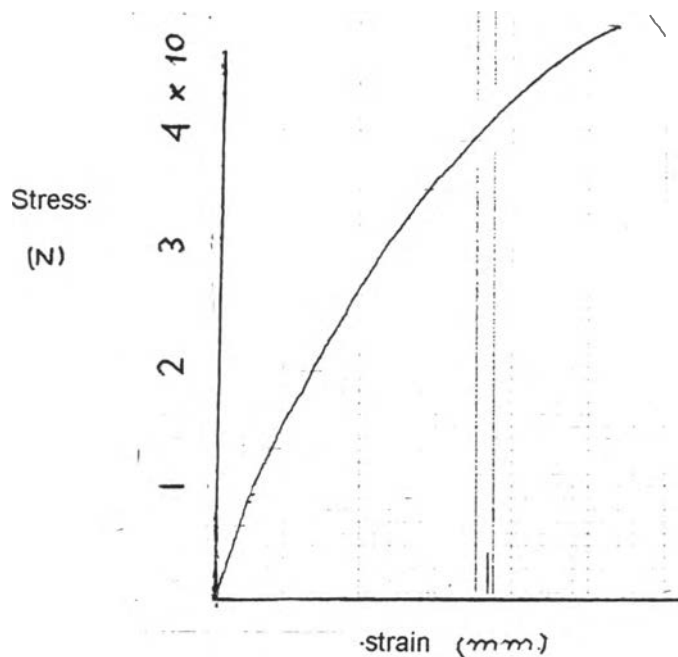


Figure 4.16 Stress-strain curve of the PVC sheets.

The tensile strength and elongation of PVC compound with EPO is different when DOP concentration is different. In the case of 60 phr DOP, the tensile strength at break is lower than that contains the 30 phr of DOP. This is in accordance with the reports of Sear and Darby (4). They discovered that the amount of plasticizer adding to PVC makes the PVC to be softer, more flexible, reduces the modulus and tensile and gives greater elongation as the amount of plasticizer is over 20 phr. The effect of DOP plasticizer properties is illustrated in Fig.4.17.

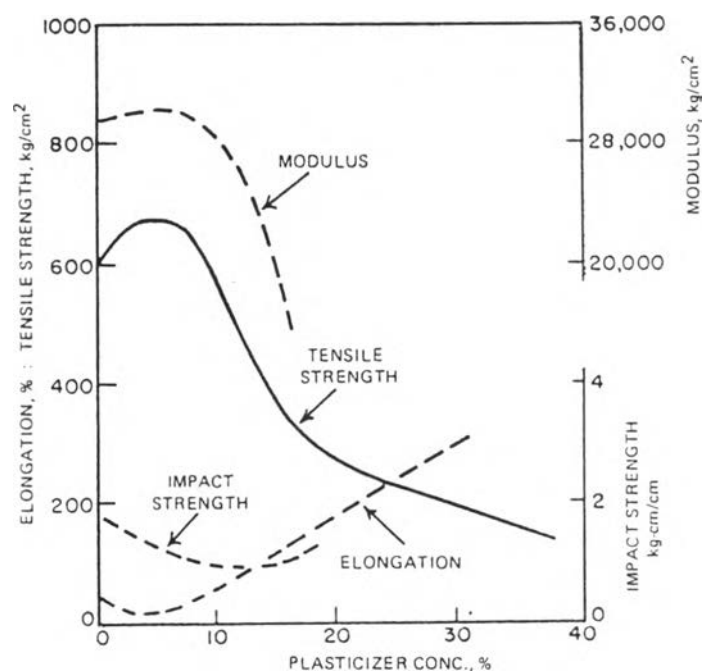


Figure 4.17 The effect of DOP plasticizer on the tensile property of PVC (2).

2.1.2 Hardness. The hardness of the PVC sheets are nearly the same with those that contain the same amount of epoxidized palm oil. However, the experiments that contain 60 parts of the DOP tend to have the lower hardness than those that have 30 parts of DOP. The reason is expressed in Section 2.1.1

The mechanical properties of the plasticized PVC depend on 2 variables: types and concentrations of the plasticizer used. DOP is the primary plasticizer that is normally used in a great amount, which is a major controlling factor of the mechanical properties (4).

2.1.3 The Izod Impact Strength. The specimen was not broken after hit with the hammer of the Impact tester. Because the PVC sheets are soft and flexible. The impact strength of all the PVC compounded by the general formula cannot be measured.

2.1.4 The Flexural Strength. When the tested load was applied, the specimen of PVC sheets bended but did not break. The flexural strength cannot be evaluated. However, the low temperature bend test of coated fabrics (according to ASTM D 2136) is introduced (43). The method is to bend the PVC sheets to a specific angle at a certain temperature, below room temperature. The crack or fracture in specimen was examined. This is the simple flexibility test. For transparent PVC sheets, the recommended temperature for bend test is about minus 20 °C. Witnauer and coworkers (42) found that the epoxy monoester (ester of oleic acid) had better low temperature flexibility than DOP. The epoxy triester of higher molecular weights (epoxidized soybean oil) had better low temperature flexibility than DOP and epoxy monoesters. The PVC compounded with the EPO should have the low temperature flexibility better than DOP because the epoxidized palm oil consists mainly of oleic acid. This property may probably be of inferior flexibility than the PVC compounded with the ESO.

## 2.2 Mechanical Properties of the Conventional PVC Compound.

The conventional formulation of PVC compound mentioned in Table 3.7 was chosen for comparing their mechanical properties with those compounded

with the epoxidized ybean oil (Epoxy D 81) and without the epoxidized oil. The mechanical properties are presented in Table 4.14

Table 4.14 Mechanical properties of the PVC sheets compounded by the conventional formulation.

Types of Plasticizer	Tensile strength at break, MPa	Elongation at break %	Hardness shore A
EPO	16.8±1.04	330±13.2	85±0.7
ESO	16.0±1.26	308±15.5	78±1.6
NO EO	17.8±1.31	291±10.1	85±5.1

2.2.1 Tensile Strength and Elongation. Both of the PVC sheets compounded with the epoxidized palm oil and soybean oil possess almost equal tensile strength that are lower than the PVC sheet compounded without a secondary plasticizer. The elongation of the sheet of PVC compounded with the epoxidized palm oil is somewhat greater than those compounded with the epoxidized soybean oil and those without any secondary plasticizer. The ESO has a higher content of oxirane oxygen (more than 6%). The roles of the plasticizer in plastic matrix especially the hard and rigid PVC are attributed by either the gel theory or the free volume theory, which have been described in Section 2.2 and 2.3 in Chapter II. The increase in elongation of the epoxidized oil plasticized PVC is probably due to the interaction of the polymer/plasticizer interface through adsorption, absorption, fusion and toughening.

2.2.2 Hardness. The hardness of the PVC sheets compounded with the epoxidized palm oil is equal to the PVC sheet without a secondary plasticizer and higher than the PVC compounded with the epoxidized soybean oil. It may suggest that the function of the EPO plasticizer be less effective than the ESO resulting from the higher oxirane contents in ESO.

The results of impact strength and flexural strength are the same as Section 2.1.3 - 2.1.4 of this chapter.

### 2.3 Thermal Properties of the Compounded PVC Sheets.

The other properties of the PVC sheets measured are the following.

2.3.1 The Glass Transition Temperature. The transition temperature ( $T_g$ ) of PVC is shown in Figure 4.18 to 4.20. The  $T_g$ s of the PVC compounded sheets are expressed in Table 4.15.

Table 4.15 The  $T_g$  of PVC compounded sheets.

Types of Plasticizer	$T_g$ °C
NO EO	-39
EPO	-32
ESO	32

In plasticized polymer, the free volume between the polymer and the plasticizer molecules increases at the increasing temperatures. The available large free volume permits the higher freedom of movements. The incorporation of any plasticizer to the polymer like PVC is to lower the  $T_g$  of the system because it increases the free volume and the movement of the PVC chains (4). At low temperatures, the epoxidized oil crystallizes, therefore, the free volume of the PVC chains is decreased. The  $T_g$  of the epoxidized oil plasticized plastics is higher than the PVC without the epoxidized oil as shown in Table. 4.15

2.3.2 Thermal Stability. There are many methods to determine the thermal stability. In this research, the thermogravimetric analysis is used. The thermogravimetric analysis of the PVC compounded sheets are illustrated in Figure 4.21- 4.23.

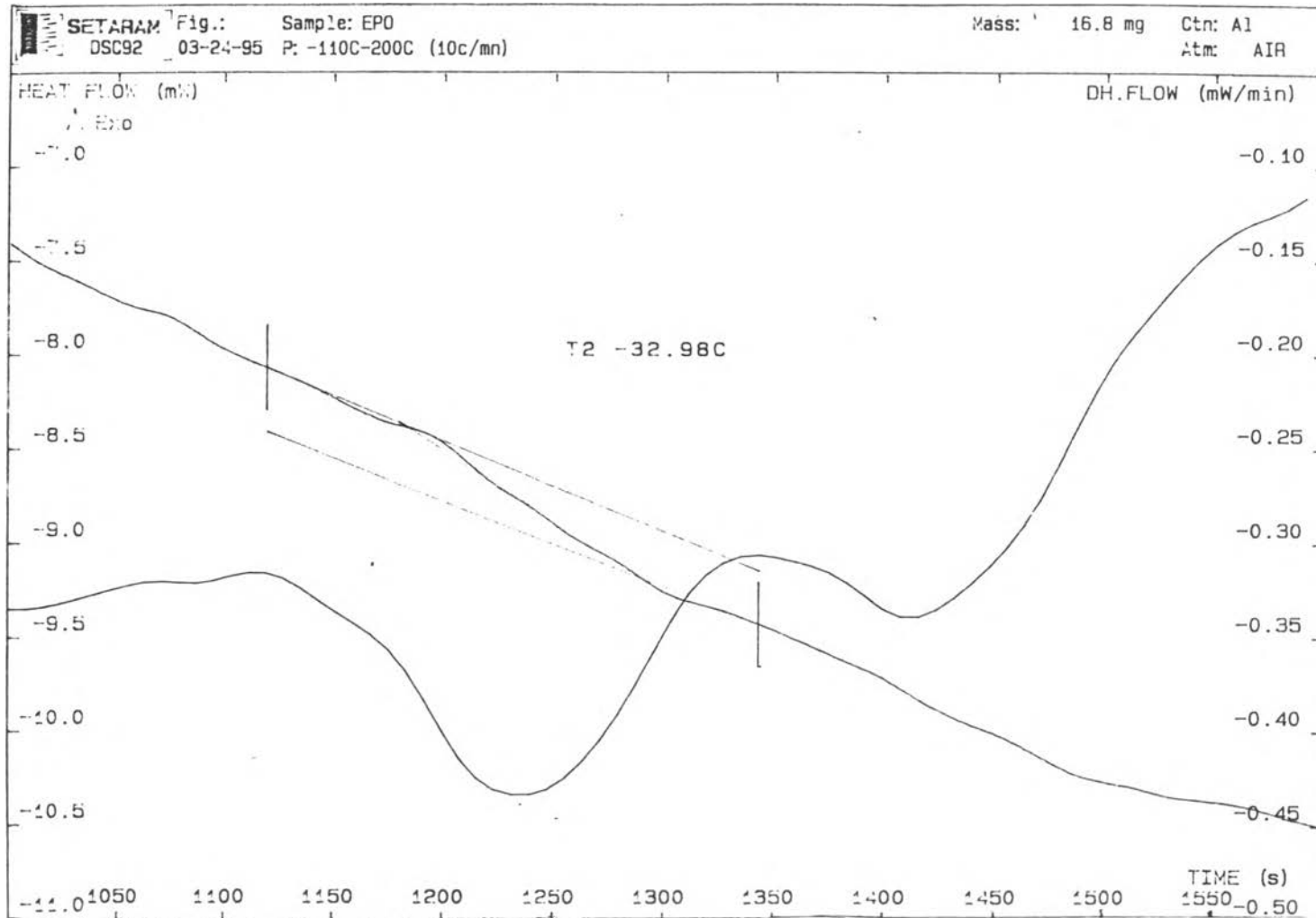


Figure 4.18 The DSC analysis of the PVC compounded with the epoxidized palm oil.

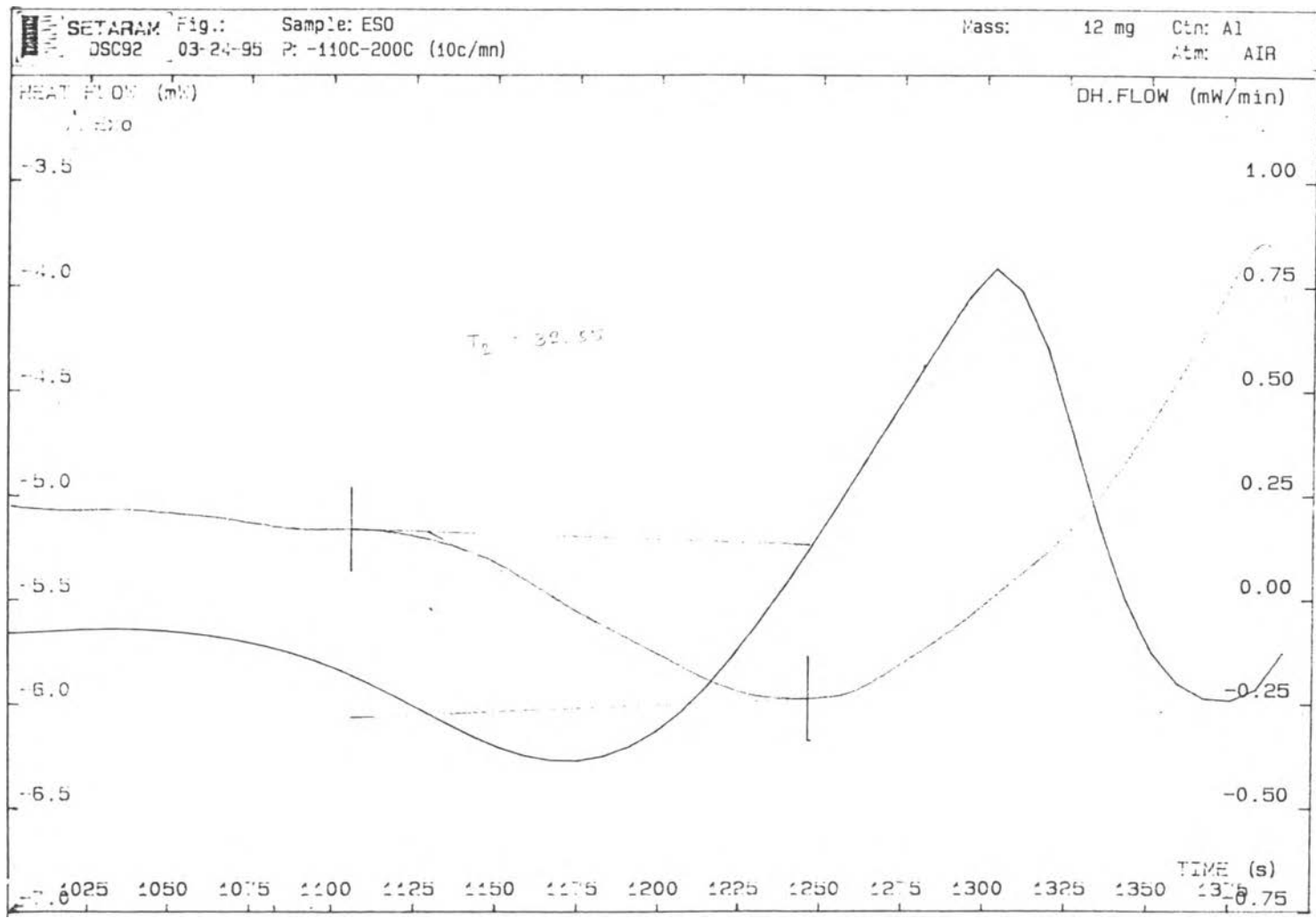


Figure 4.19 The DSC analysis of the PVC compounded with the epoxidized soybean oil.



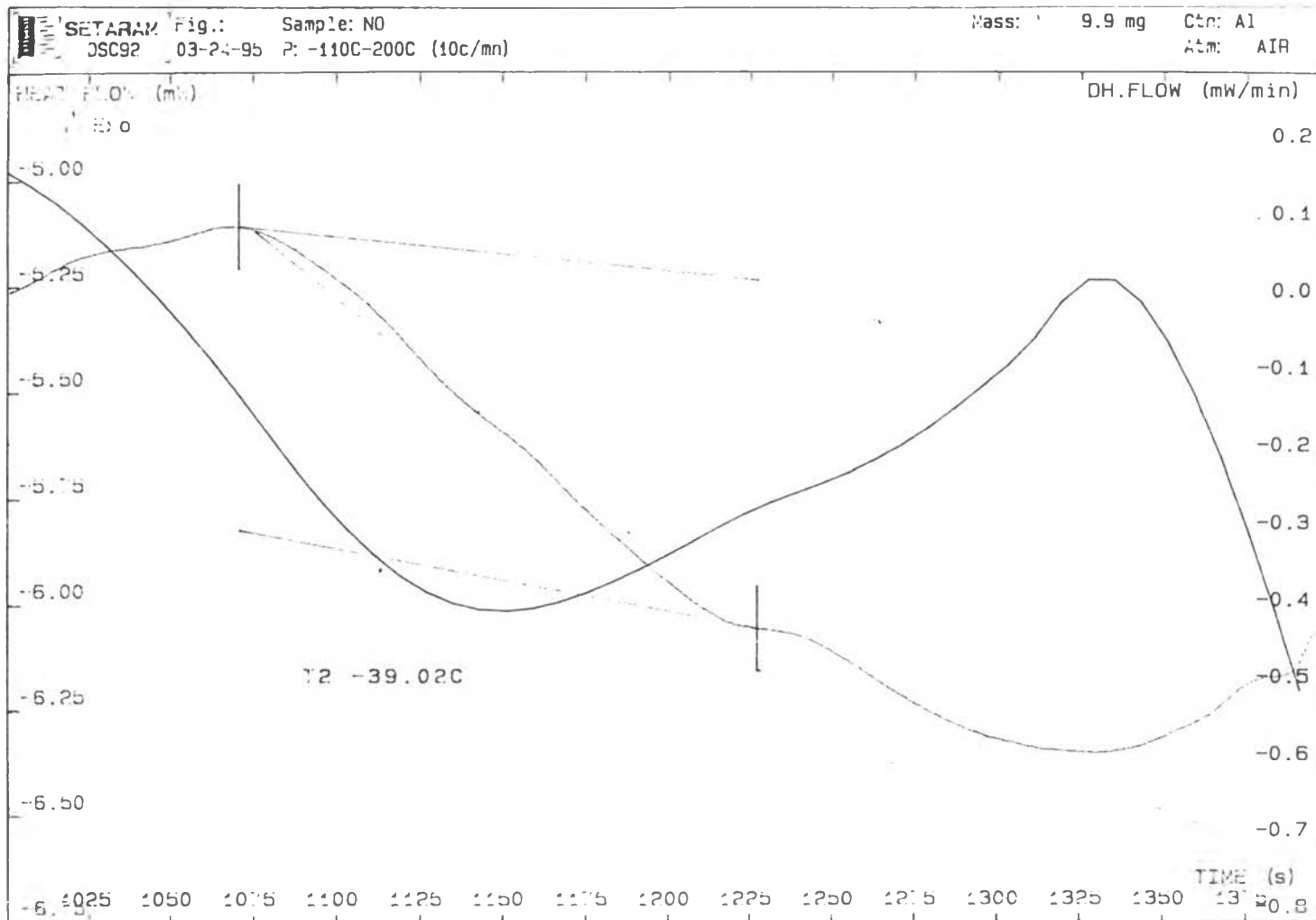


Figure 4.20 The DSC analysis of the PVC compounded without the epoxidized oil.

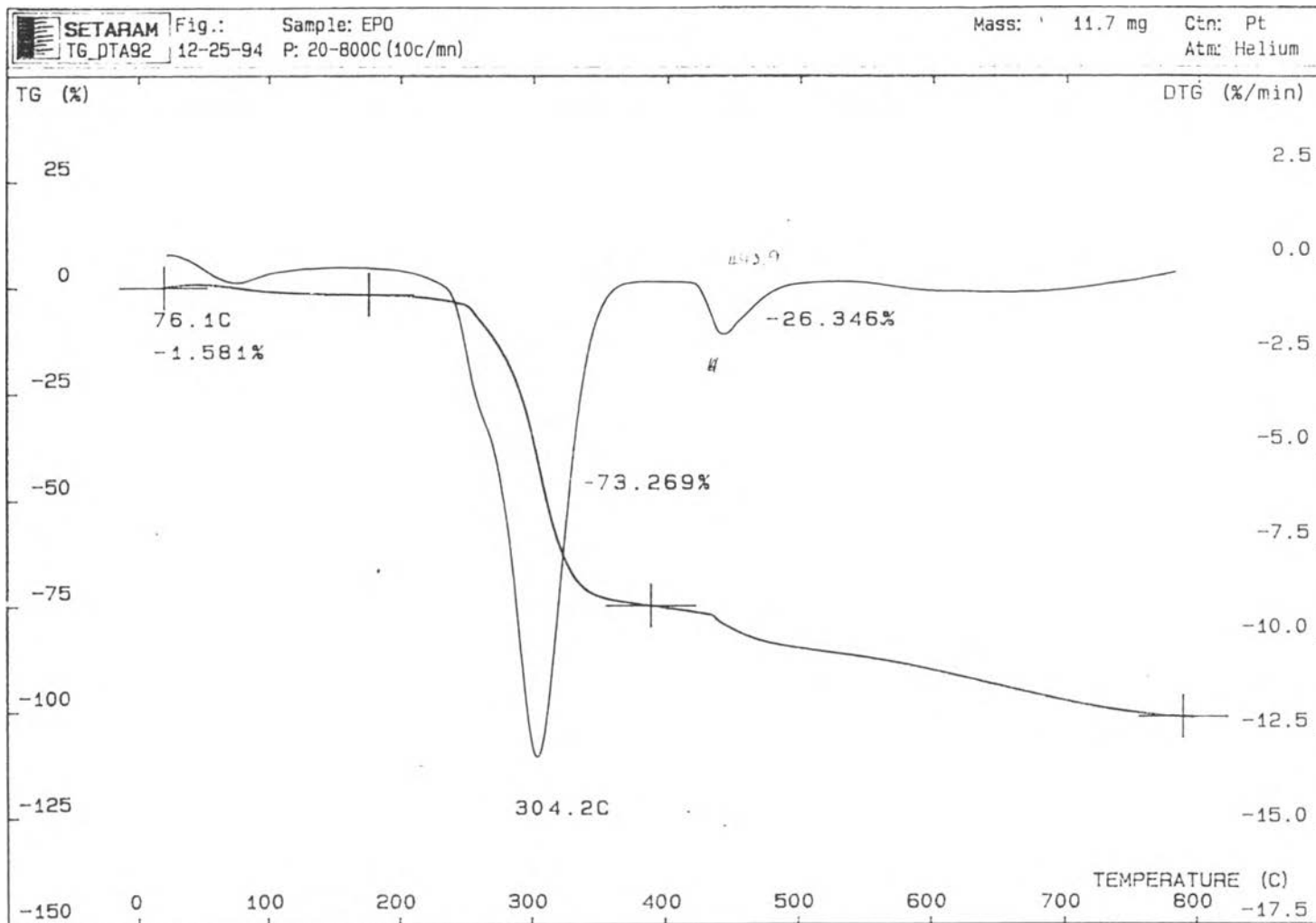


Figure 4.21 The TGA analysis of the PVC compounded with the epoxidized palm oil.

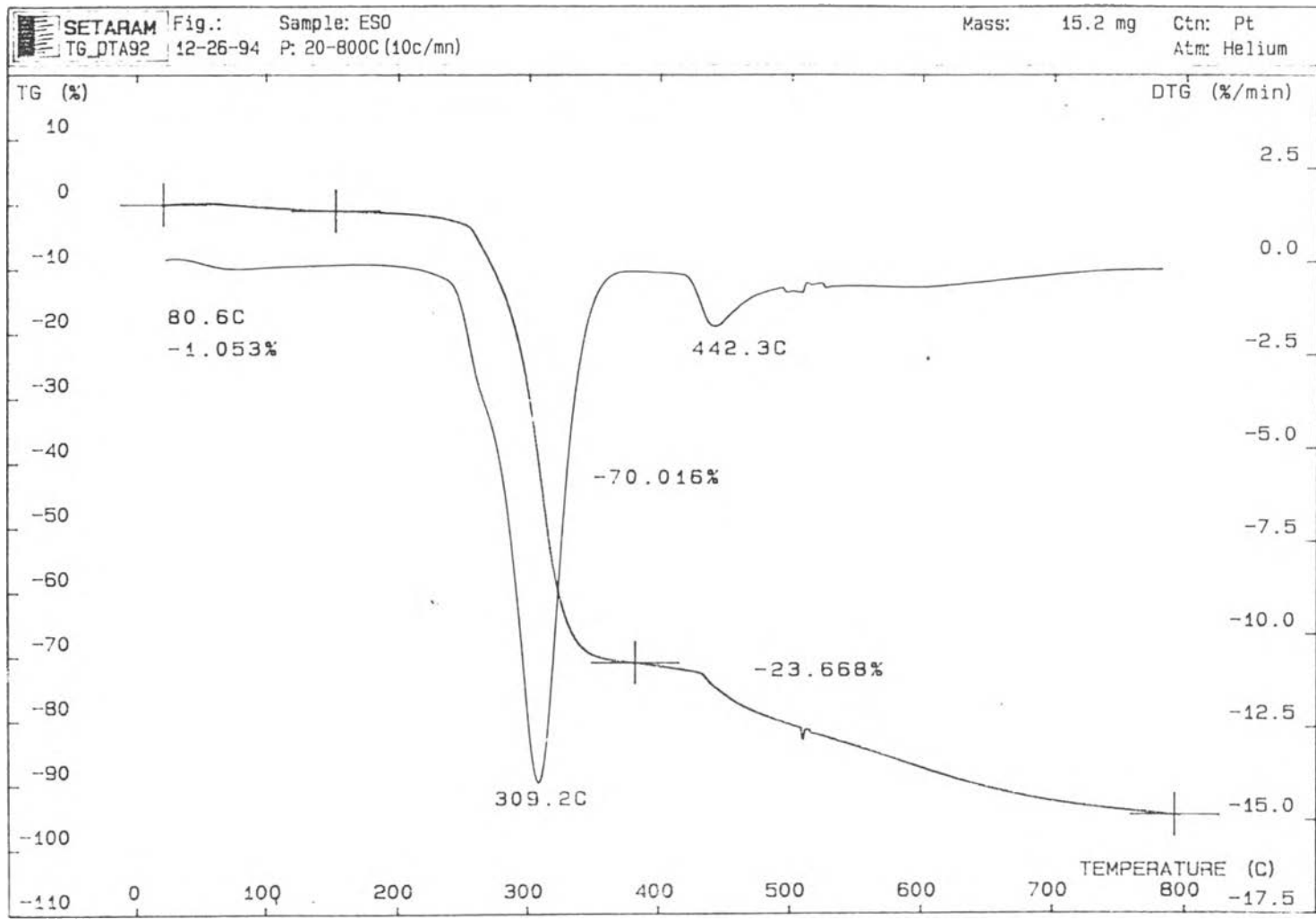


Figure 4.22 The TGA analysis of the PVC compounded with the epoxidized soybean oil.

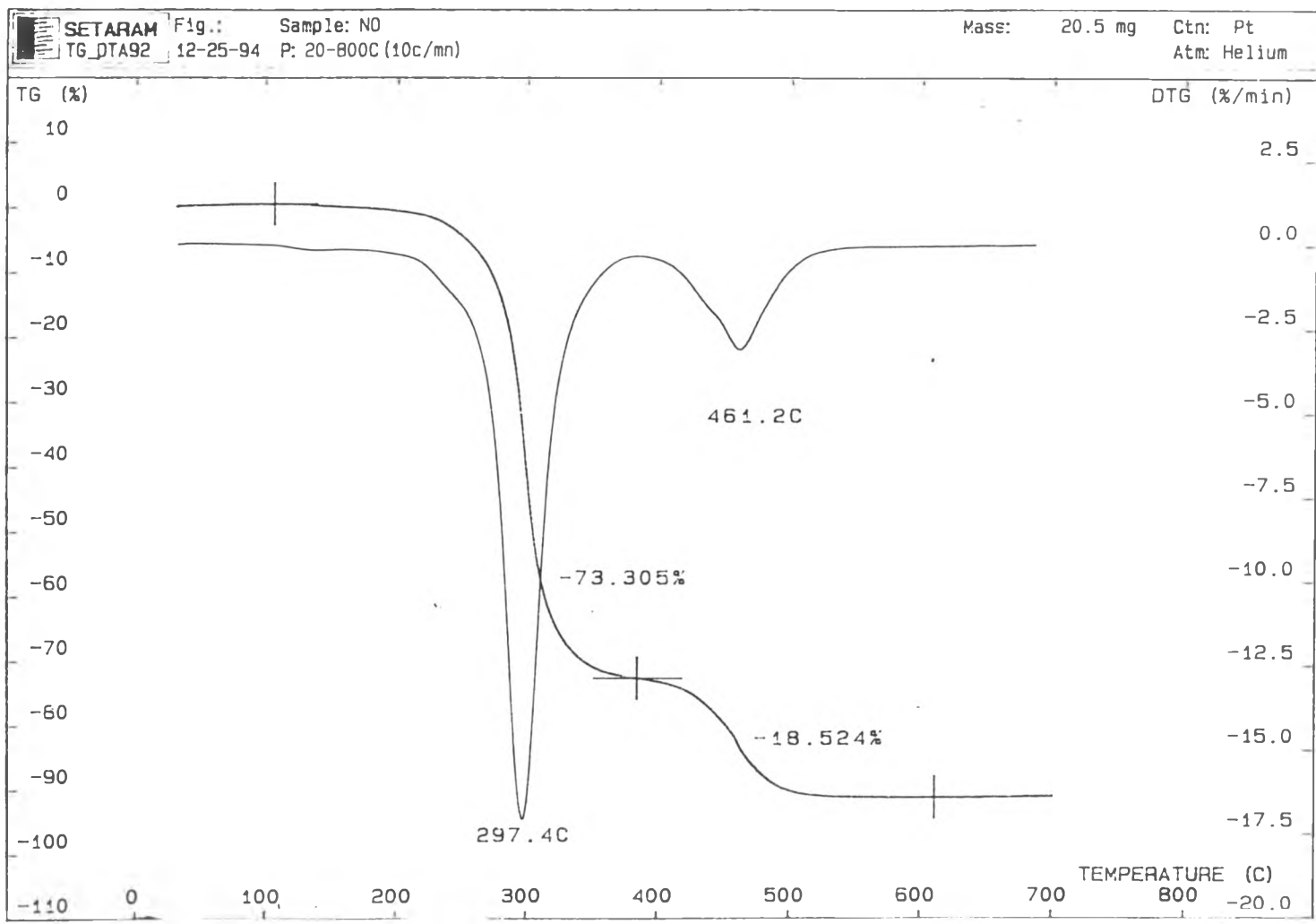


Figure 4.23 The TGA analysis of the PVC compounded without the epoxidized oil.

Table 4.16 The results of the TGA analysis of PVC sheets.

Types of Plasticizer	Thermal stability	
	T, °C	% wt. loss
EPO	76	1.58
	304	73.27
	443	26.35
ESO	80	1.05
	309	70.02
	442	23.67
NO EO	297	73.31
	461	18.52

The results of the TGA analysis are summarized in Table 4.16. At the temperature of 76°C, the epoxidized palm oil was expelled from the PVC sheet by 1.58%, while the epoxidized soybean oil lost about 1.05% at the higher temperature of 80°C. Since the boiling points of the two oils are less than 80°C, so they can evaporate from the PVC sheet at these temperatures. The PVC sheet without the epoxidized oil does not lose so severely at this temperature. The severe weight loss of PVC sheets also occurs at the temperature of about 300°C and about 440°C in all of the three PVC sheets. At the temperature of 300°C, the loss of organic compounds is significant that is suspected to be the PVC and DOP. The change found at 440°C may be due to the Ba - Cd - Zn stearate as it can withstand higher temperatures no greater than 440°C, which is anticipated as the decomposition temperature. The other method of testing for the thermal stability is based on the ASTM D 4202, the result is expressed in Table 4.17

Table 4.17 Heat stability of PVC compound by ASTM D 4202.

Types of Plasticizer	Time, min
EPO	15
ESO	40
NO EO	5

This method is to measure the HCl liberated from the degradation of the PVC sheets. The PVC compounded with the epoxidized palm oil decomposed after being heated for 15 min at 180°C while that plasticized with the epoxidized soybean oil decomposed at 40 min after heating; the PVC without the epoxidized oil decomposed rapidly after 5 min of heating. The reason will be later explained in Section 2.3.4 and 2.4 as follows:

2.3.3 Weathering Stability. The weathering stability of a material imposes a direct effect on mechanical properties of the material concerned. The weathering study can be obtained by a direct exposure of the materials of interest in the accelerated weathering cabin for a specific interval. The result of this experiment is shown in Table 4.18.

Table 4.18 Mechanical properties of the PVC sheets after exposure to accelerated weathering tester for different times.

Time week	NO EO PVC			ESO PVC			EPO PVC		
	Tensile strength Mpa	Elongation %	Hardness Shore A	Tensile strength Mpa	Elongation %	Hardness Shore A	Tensile strength Mpa	Elongation %	Hardness Shore A
0	17.8	291	85	16.0	308	78	16.8	330	85
	±1.31	±10.0	±5.1	±1.26	±15.5	±3.1	±1.04	±13.2	±0.7
1	14.6	198	91	12.7	203	90	13.3	208	89
	±0.92	± 8.2	±1.4	±0.82	±29.6	±1.6	±0.34	± 6.8	±1.9
2	14.0	156	86	12.5	173	84	12.0	167	84
	±0.48	± 8.2	±2.8	±0.30	±16.0	±1.3	±0.75	±22.4	±1.9
3	13.6	171	84	12.4	157	82	12.4	169	82
	±0.21	±11.9	±2.9	±1.31	±26.8	±2.2	±1.15	±15.9	±2.2
4	13.6	150	89	13.6	136	88	11.1	154	85
	±0.78	±13.8	±2.1	±2.36	±26.0	±2.3	±0.67	±9.6	±1.8

NO EO PVC = PVC sheets compounded without the epoxidized oil.

ESO PVC = PVC sheets compounded with the epoxidized soybean oil.

EPO PVC = PVC sheets compounded with the epoxidized palm oil.

The tensile strength of PVC sheets compounded with the epoxidized palm oil and the epoxidized soybean oil are decreased severely after one week's exposure as shown in Figure 4.24. At a longer period of exposure time, such as 2 to 3 weeks, the tensile strength of all the PVC sheets is slightly decreased; it is nearly constant. The colour of the PVC sheets changed from clear to yellow and finally dark brown. As mentioned, in Chapter II, the light and heat induce the degradation of the PVC sheets. The heat of 70°C causes the plasticizer volatilization to occur and the water in a condensation form (vapor) also extracts the plasticizer from the plasticized PVC sheets. The migrated plasticizer is, of course, the secondary plasticizer (ESO,EPO) that has the lower boiling point than the primary plasticizer(DOP).

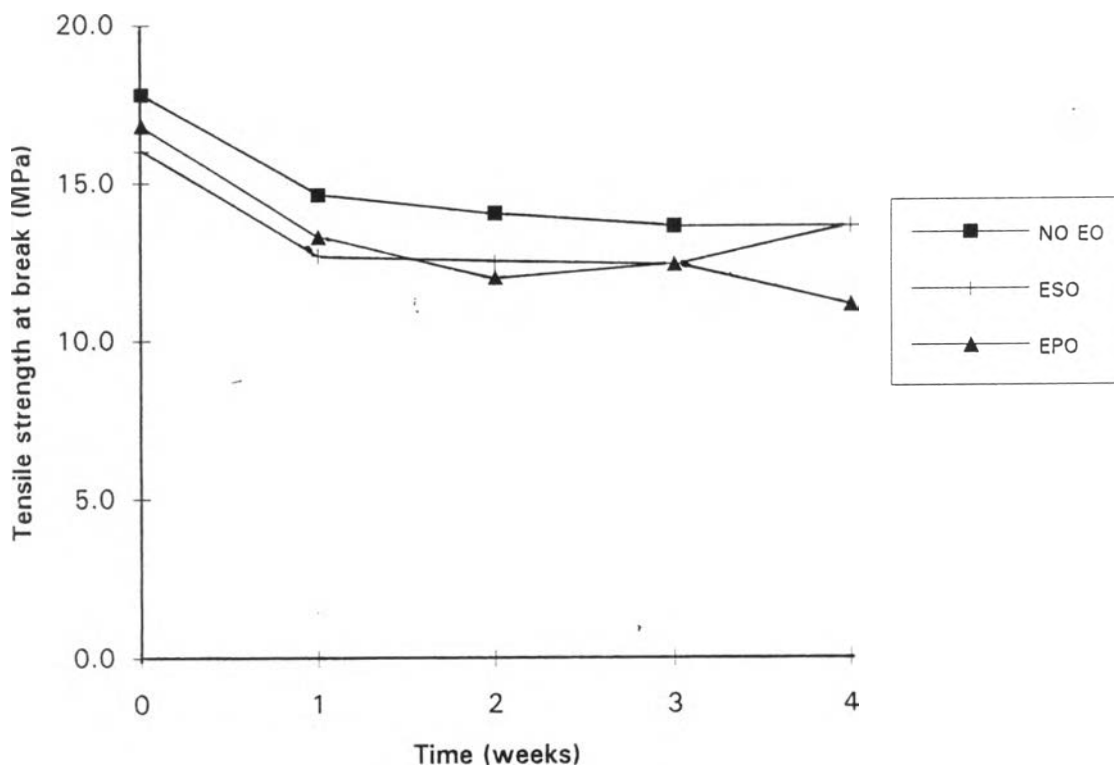


Figure 4.24 Tensile strength of the PVC sheets after the exposure to the accelerated weathering tester.

During the course of weathering test, the polyene sequence is formed during the first week of exposure that could be detected from the colour of the PVC sheet changed to yellow. After that, the degradation proceeded the colour of the PVC sheets, which was change to yellow. After that, the degradation continued until the colour of the PVC sheets was turn to light brown and dark brown. The occurrence of the dark brown colour in the PVC was possibly developed by the formation of conjugations similar to a quinonoid structure from the decomposed unsaturated fatty acids of the palm oil.



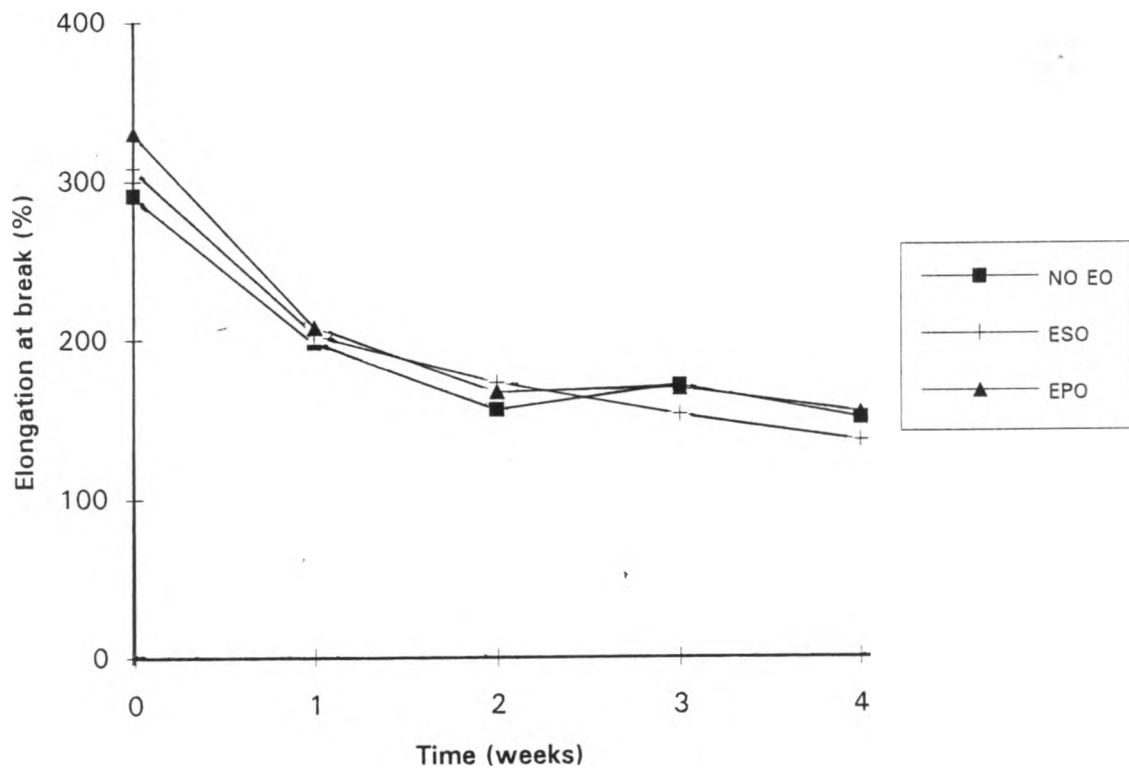


Figure 4.25 Elongation of the PVC sheets after the exposure to the accelerated weathering tester.

The hardness of the PVC sheet increased during one week's exposure because of the loss of the secondary plasticizer. After a week's exposure, the hardness decrease gradually as illustrated in Figure 4.26 because the plasticizer was lost from the PVC sheets by the water extraction and the volatilization due to the accelerated heat.

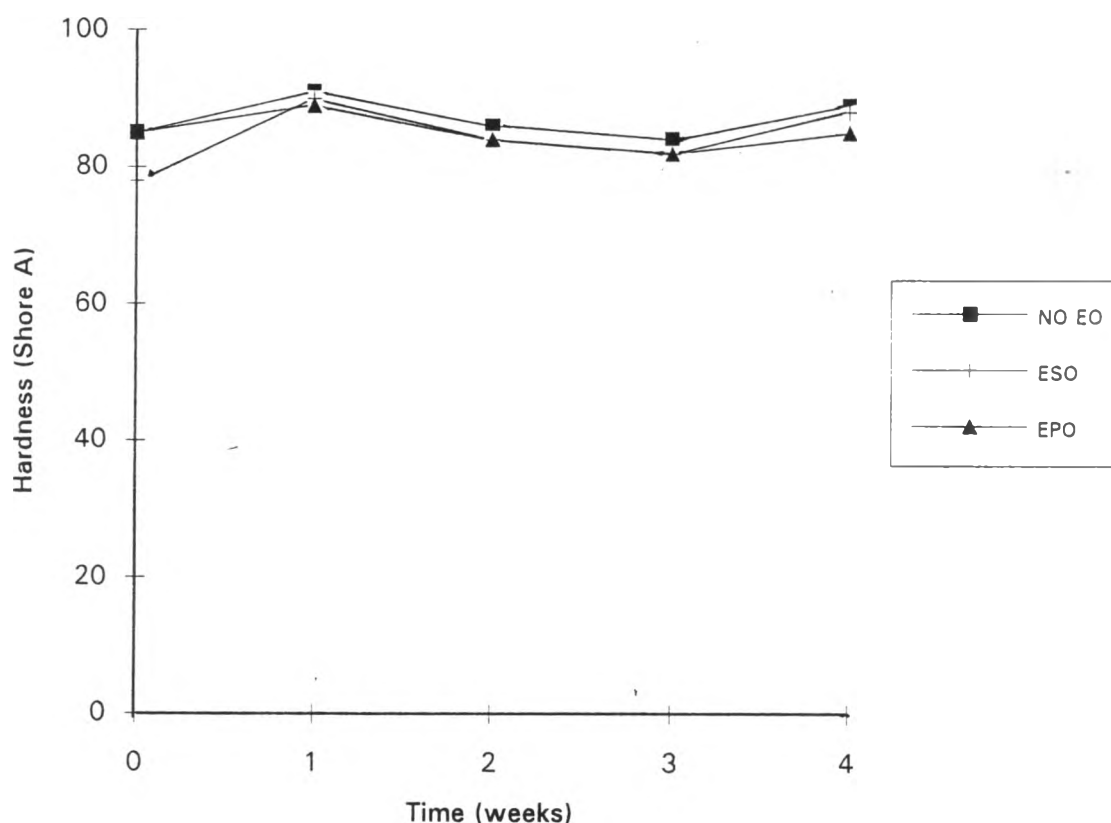


Figure 4.26 Hardness of the PVC sheets after the exposure after the exposure to the accelerated weathering tester.

The stiffness of the PVC sheets increased leading to the increasing of the hardness. Theoretically, it should be constant at the constant temperature(4). As described above, the PVC sheets were degraded by heat and light after being exposed by the weathering test condition for a long time. When the secondary plasticizer was destroyed by heat, HCl was evolved while the PVC sheets was undoubtedly increased due to the stiffness of the PVC chains.

The PVC sheets that were exposed to the accelerated weathering tester for one week's was analyzed by TGA. The results are illustrated in Figure 4.27 - 4.29. The weight loss of the PVC sheets during the procedure is shown in Table 4.19.

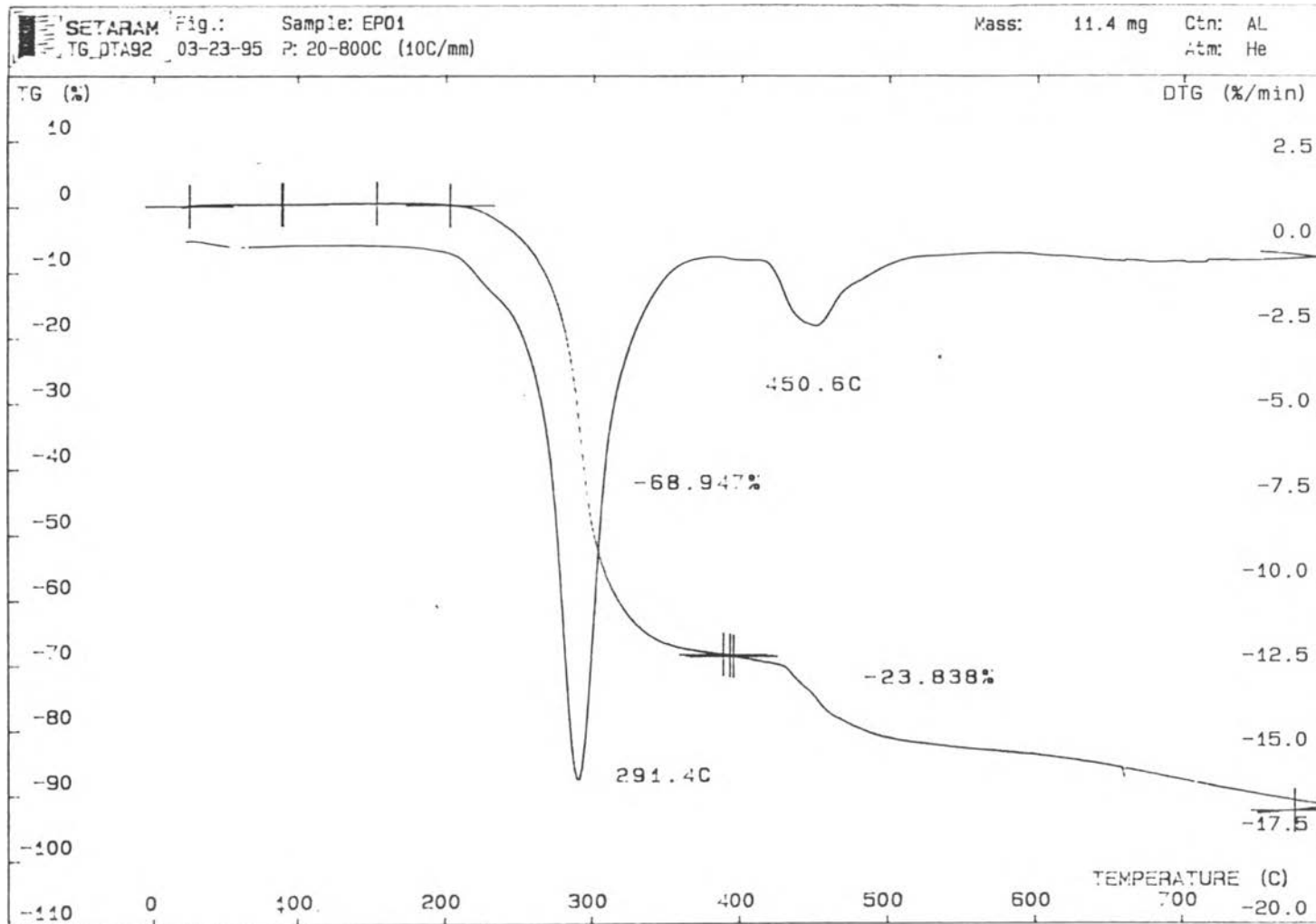


Figure 4.27 The thermogram of the PVC sheet compounded with the epoxidized palm oil.

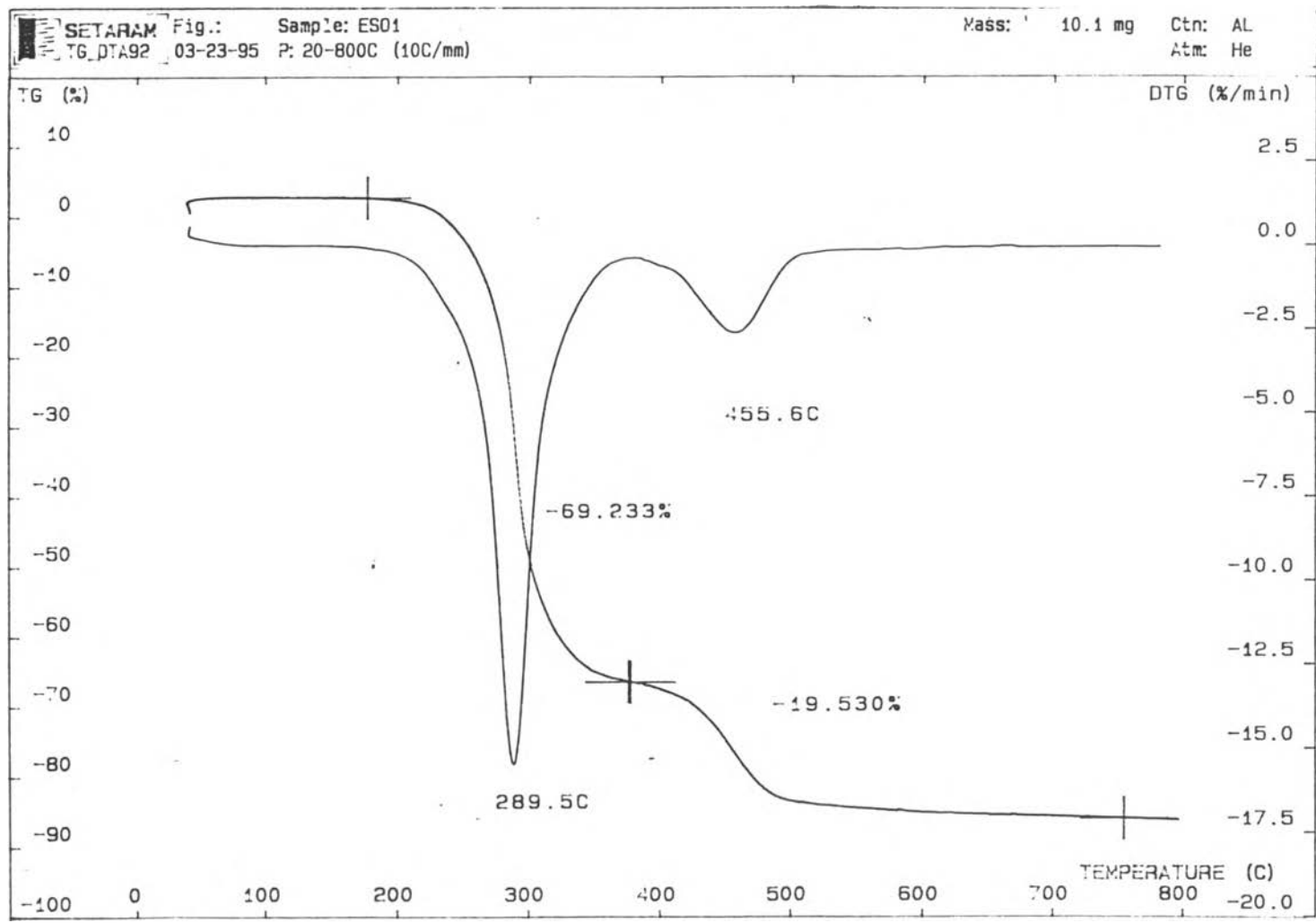


Figure 4.28 The thermogram of the PVC sheet compounded with the epoxidized soybean oil

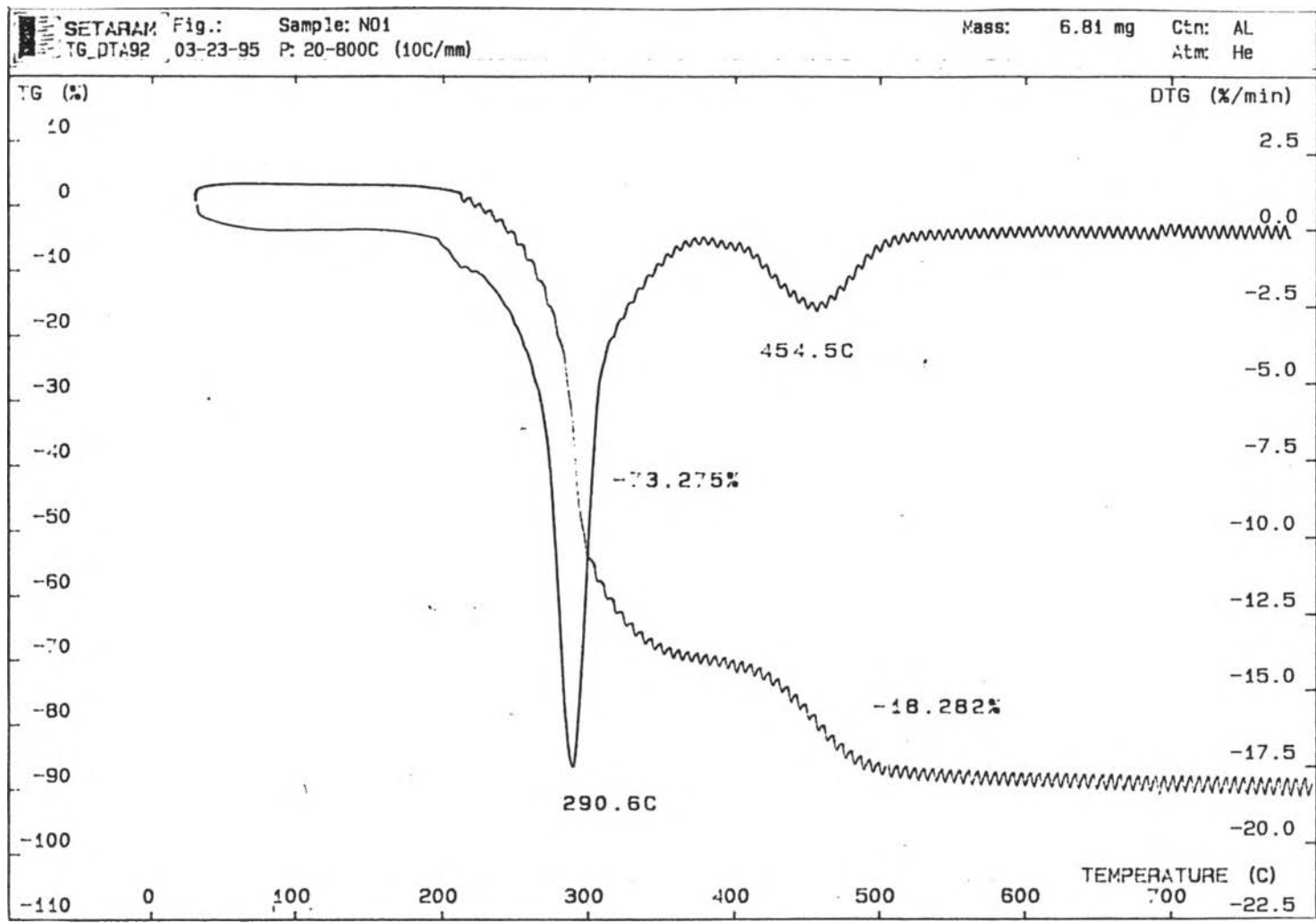


Figure 4.29 The thermogram of the PVC sheet compounded without the epoxidized oil.

Table 4.19 The weight loss of the PVC sheets after one week's of the weathering test.

Types of Plasticizer	Thermal stability	
	T, °C	% wt. loss
EPO	291	68.95
	450	23.84
ESO	289	69.23
	455	19.53
NO EO	290	73.27
	454	18.28

The pattern of the TGA thermogram of the three PVC sheets is perfectly alike. At 290°C, the weight loss of PVC and DOP was about 70%. At 450°C, the heat stabilizer was changed. The PVC sheets without the epoxidized oil have the same weight loss pattern as the PVC before the exposure (Figure 4.23). After the exposure, the PVC sheets compounded with the epoxidized palm oil and the epoxidized soybean oil, respectively, cannot lose their weight any more at 80°C because the epoxidized oils already have migrated from the PVC sheets before this temperature. Since the degradation of the PVC chains is to shorten the chains from which the consequently degradative temperatures are reduced to about 290°C compared to the unexposed one.

#### 2.4 The Migration of Plasticizer.

The important property of a good plasticizer is the permanence to the resin. The permanence of the plasticizer is expressed as the extent of the migration of plasticizer from the PVC compound by either the extraction method or the volatilization (3,4). In this research, the is presented by both techniques. The result of extraction of the PVC sheets by non polar solvent such as hexane, and the volailization at 80°C are shown in Table 4.20. The weight loss of the PVC

plasticized with the epoxidized palm oil is 5.98% that is far greater than that of the PVC compounded with the epoxidized soybean oil by a factor of five folds. The migration of the secondary plasticizer by volatility of the PVC plasticized either by the EPO or ESO is constant, 0.2 - 0.25 %.

Table 4.20 Plasticizer migration by the volatilization and the extraction methods.

Types of Plasticizer	weight loss, %	
	volatilisation	extraction
EPO	0.25	5.98
ESO	0.21	1.57

Witnauer and coworkers(42) described that an increase in the molecular weight or chain length of the epoxy plasticizer sufficiently reduced the volatility loss. However, in this research, the volatility losses of both epoxidized oils cannot be differentiate because they are alike in structures and physical properties. The amazing figures of plasticizer extraction weight loss of the epoxidized palm oil (6%) and the epoxidized soybean oil (1.5%) containing plastics may lead to the solubility parameter concept of the solvent, hexane ( $14 \text{ MPa}^{1/2}$ ) and the two plasticizers. Due to the different compositions of fatty acids of the palm oil and soybean oil as well as the extent and yield of the epoxidized palm oil, hexane, a nonpolar, dispersive solvent can solubilized differently. The epoxidized palm oil component in the plasticized PVC was far better dissolved and removed by hexane to give a high result of extracted plasticizer. In addition, the epoxidized palm oil plasticizer can therefore migrates faster and easily. The stiff and hard appearance of the extracted EPO - PVC sheets imply the loss of the plasticizer. Colour change was also observed in the extracted

samples that resulted from the degradation of PVC chains from losing the plasticizer and stabilizer.

From the observation, the PVC sheets that were extracted with hexane are more stiffness than the PVC sheets before the extraction because the loss of the plasticizers. The colour is not changed. The PVC sheets that were tested of the volatility are not as stiff as the PVC sheets after tested of the extraction but the colour of these PVC sheets turn to be brown after the test. These because the degradation by the thermal condition.

Moreover, on storage for one month the surface of the PVC sheet compounded with the epoxidized palm oil is tacky. The PVC sheet compounded with the epoxidized soybean oil is tacky on two months of the storage. These appearances occur because the exudation of the secondary plasticizers that have the low molecular weights.