

CHAPTER IV

RESULTS AND DISCUSSIONS

After reprocessing non-stabilized and stabilized HDPE sample from Thai Polyethylene Co., Ltd. (TPE) and Bangkok Polyethylene Co., Ltd. (BPE) for study the effect of antioxidants on processability or processing stability as mentioned in chapter III. Quantities that use for determine processability is melt flow index value (MFI).

4.1 Properties of Commercial Grade HDPE from TPE and BPE Compare to Virgin or Non-stabilized HDPE from TPE and BPE

Table 4.1 Properties of commercial grade HDPE from TPE and BPE compare to virgin or non-stabilized HDPE from TPE and BPE.

Property	Unit	Commercial grade HDPE of BPE	Commercial grade HDPE of TPE	Reactor grade HDPE of BPE	Reactor grade HDPE of TPE
Name	-	5000S	H56905	-	-
MFI*	g/10 min	0.8g	0.9	0.62	0.83d
Density	g/cm ³	0.954	0.957	0.954	0.957

*2.16 kg/ 190°C

Table 4.1 shows a comparison between properties of virgin grade HDPE and commercial grade HDPE. The data in Table 4.1 the significantly differences in melt flow index. Thus the first suspected results after reprocessing of non-commercial grade both stabilized and non-stabilized HDPE must be different from each other. The differences in melt flow index properties between commercial grade HDPE and Reactor grade HDPE because commercial grade HDPE was already compounded with stabilizer and additive but reactor grade has none.

4.2 Processability of Virgin HDPE and Antioxidants Stabilized HDPE Observed by Melt Flow Index

Processability or processing stability is the one important factor for service properties of HDPE. Of which a plastic material can be processed in the desired part. Processability of this work was observed in MFI. The MFI (190° C/2.16 kg) of stabilized and non-stabilized HDPE from BPE and TPE were reprocessed for 7 passes as presented in Figure 4.1, Figure 4.2, Figure 4.3 and Figure 4.4. Figure 4.1 is represented as HDPE of TPE stabilized by antioxidants from Ciba specialty chemical co., ltd. Figure 4.2 is represented as HDPE of TPE stabilized by antioxidants from EONIAN. Figure 4.3 is represented as HDPE of BPE stabilized by antioxidants from Ciba specialty chemical co., ltd. Figure 4.4 is represented as HDPE of BPE stabilized by antioxidants from EONIAN.

4.2.1 Assigned Names of HDPE Samples

Because this work involves 22 samples at various ratios of primary to secondary antioxidant and each sample name quite long. So the name of each sample is assigned in Table 4.3 base on type of antioxidants in Table 4.2. In this section main commercial antioxidants are presented together with the corresponding symbols used throughout the chapter IV and V. For primary

antioxidants Irganox1010 and Reonox 10, phenols, the symbol AO- is used, for phosphite or secondary antioxidants, Irgafos 168 and Reonox 68, P-.

Table 4.2 Class, symbol, and structure of antioxidants.

Class and Symbol	Structure
Hydroxyphenylpropionates	
AO-1 = Irganox 1010 AO-2 = Reonox 10	
P-1 = Irgafos 168 P-2 = Reonox 68	

Table 4.3 Abbreviated names of HDPE samples.

Sample by	Shorten name
Overall antioxidants = 0.1%	
Virgin HDPE of TPE (0/0)	Virgin TPE
Virgin HDPE of BPE (0/0)	Virgin BPE
HDPE of TPE + Irganox 1010 (100/0)	TPE_AO-1
HDPE of BPE + Irganox 1010(100/0)	BPE_AO-1
HDPE of TPE + Irgafos 168 (0/100)	TPE_P-1
HDPE of BPE + Irgafos 168 (0/100)	BPE_P-1
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 25/75	TPE_0.025%AO-1/0.075%P-1
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 25/75	BPE_0.025%AO-1/0.075%P-1

Cont...

Table 4.3 (Continued)

Sample by Overall antioxidants = 0.1%	Shorten name
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 50/50	TPE_0.05%AO-1/0.05%P-1
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 50/50	BPE_0.05%AO-1/0.05%P-1
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 75/25	TPE_0.075%AO-1/0.025%P-1
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 75/25	BPE_0.075%AO-1/0.025%P-1
HDPE of TPE + Reonox10 (100/0)	TPE_AO-2
HDPE of BPE + Reonox 10 (100/0)	BPE_AO-2
HDPE of TPE + Reonox 68 (0/100)	TPE_P-2
HDPE of BPE + Reonox 68 (0/100)	BPE_P-2
HDPE of TPE + Reonox 10/Reonox 68 ratio = 25/75	TPE_0.025%AO-2/0.075%P-2
HDPE of BPE + Reonox 10/Reonox 68 ratio = 25/75	BPE_0.025%AO-2/0.075%P-2
HDPE of TPE + Reonox 10/Reonox 68 ratio = 50/50	TPE_0.05%AO-2/0.05%P-2
HDPE of BPE + Reonox 10/Reonox 68 ratio = 50/50	BPE_0.05%AO-2/0.05%P-2
HDPE of TPE + Reonox 10/Reonox 68 ratio = 75/25	TPE_0.075%AO-2/0.025%P-2
HDPE of BPE + Reonox 10/Reonox 68 ratio = 75/25	BPE_0.075%AO-2/0.025%P-2

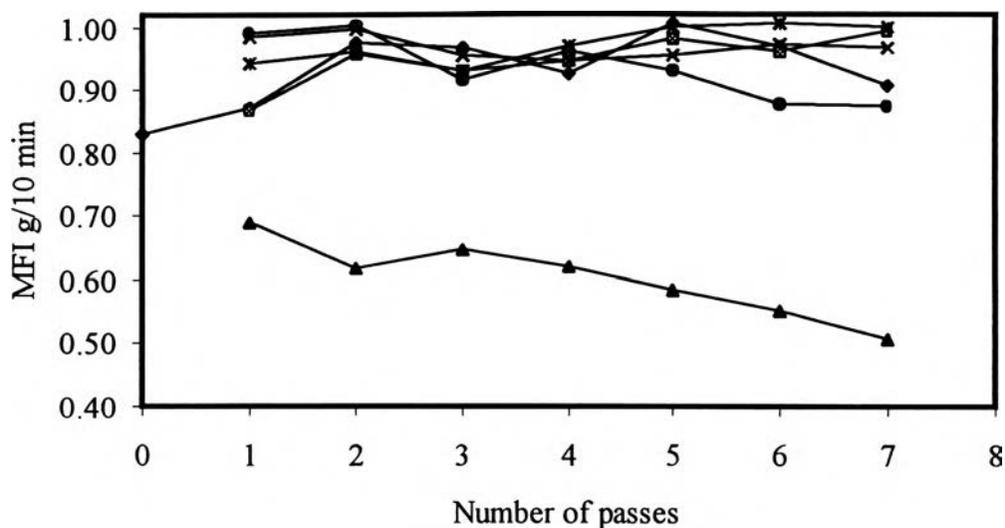


Figure 4.1 MFI of HDE of TPE samples when increase processing history: virgin HDPE of TPE represented by; ♦, HDPE of TPE stabilized by AO-1 represented by; ◻, P-1; ▲, 0.025%AO-1/0.075%P-1; ×, 0.050%AO-1/0.050%P-1; ◊, and 0.075%AO-1/0.025%P-1; ◊.

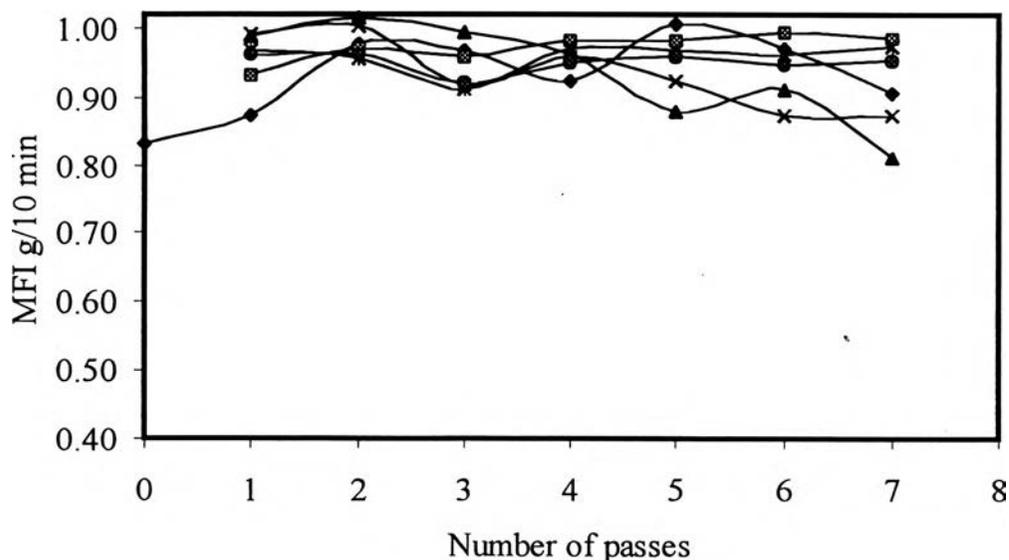


Figure 4.2 MFI of HDE of TPE samples when increase processing history: virgin HDPE of TPE represented by; ♦, HDPE of TPE stabilized by AO-2 represented by; ◻, P-2; ▲, 0.025%AO-2/0.075%P-2; ×, 0.050%AO-2/0.050%P-2; ◊, and 0.075%AO-2/0.025%P-2; ◊.

From Figure 4.1 and Figure 4.2, the results show that almost MFI of HDPE samples from TPE samples, which stabilized by antioxidants from Ciba special chemical co., ltd. (Figure 4.1) and stabilized by antioxidants from Eonian (Figure 4.2), seem to be constant all processing range. Because HDPE is low sensitive to oxidation especially in twin screw extruder poor oxygen to generate oxidation reaction. Practically, MFI of HDPE material must not change from the original MFI so much, count from 1st pass of extrusion. For this case MFI of each sample is $MFI \pm 0.2$ g/10 minutes. From objective of this thesis the best composition of antioxidants is the lower change in MFI from original MFI. However, if the data analysis consider by the original value of MFI from virgin HDPE at 1st extrusion. The acceptance for macroscopic scales of performance of antioxidant formulas are any formula both HDPE of TPE, which stabilized by Ciba's antioxidants and Eonian antioxidants but except a HDPE sample, which stabilized Irgafos 168. HDPE of TPE, which stabilized by Irgafos 168 from Figure 4.1 has difference in MFI when compare to another HDPE samples. That is Irgafos 168 made HDPE sample cross-linking or reduces MFI of HDPE sample. This result agree with the results from Figure 4.2, HDPE of TPE stabilized by Eonian antioxidants, which is all antioxidants formula and virgin HDPE of TPE except HDPE of TPE sample stabilized by Irgafos 168. Figure 4.2 MFI values of all samples, which at all processing range are stay with in 0.87 to 1. By assumption, the results of Figure 4.1 and Figure 4.2 must show the similar results or the same trend. In contrast with actual results, HDPE of TPE, which stabilized by Irgafos 168. It was show the significantly change in MFI value from conventional MFI of virgin HDPE.

Although, the formula of primary and secondary antioxidants, which used in this thesis have the same structure and the same physical properties as presented in Table 4.4 for primary antioxidants and Table 4.5 for secondary antioxidants.

Table 4.4 Physical properties of primary antioxidants used.

	Irganox 1010	Reonox 10
Melting range (°C)	110-125	110-125
Molecular weight	1178	1178
Solubility (20°C) g/100g solution	Irganox 1010	Reonox 10
Acetone	47	46
Chloroform	71	71
Ethylacetate	47	47
n-Hexane	0.3	0.3
Methanol	0.9	0.9
Water	< 0.01	< 0.01

Table 4.5 Physical properties of secondary antioxidants used.

	Irgafos 168	Reonox 68
Melting range (°C)	110-125	110-125
Molecular weight	646.9	647
Solubility (20°C) g/100g solution	Irgafos 168	Reonox 68
Acetone	1	1
Chloroform	36	36
Ethylacetate	4	4
n-Hexane	11	11
Methanol	< 0.01	< 0.01
Water	< 0.01	< 0.01
Methylene chloride	< 36	< 36

4.3 Determination of The DSC melting-Peak for Comparison of Antioxidants by Using Netzsch DSC 200

The different results between Figures 4.1 and 4.2 can be described by differential scanning calorimetric analysis (DSC). This method was based on the fact that small amounts of impurity in the sample broadens its melting range and lowers the final melting point from T_0 , the melting point of the infinitely pure material, to a lesser temperature, T_m . An example of this effect which is used to compare DSC melting peak is shown in Figure 4.3 for the DSC curves of benzoic acid of three different purities. As the impurity content increases (97.2%), the melting point decreases and the range of melting broadens. Very small impurity levels have a marked effect on the melting point and the melting range (98.6% primary standard).

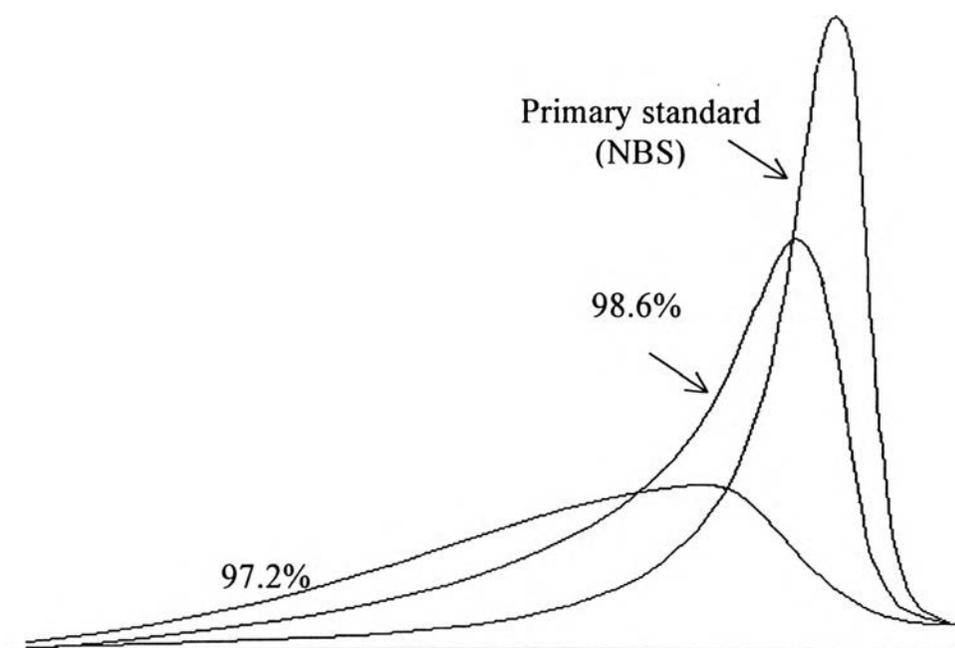


Figure 4.3 Effect of purity on the DSC melting-peak shape and melting temperature of benzoic acid.

When composition of impurity increase, peak width and peak height was changed. So this criteria was used for purity of antioxidant and DSC-melting peak behavior.

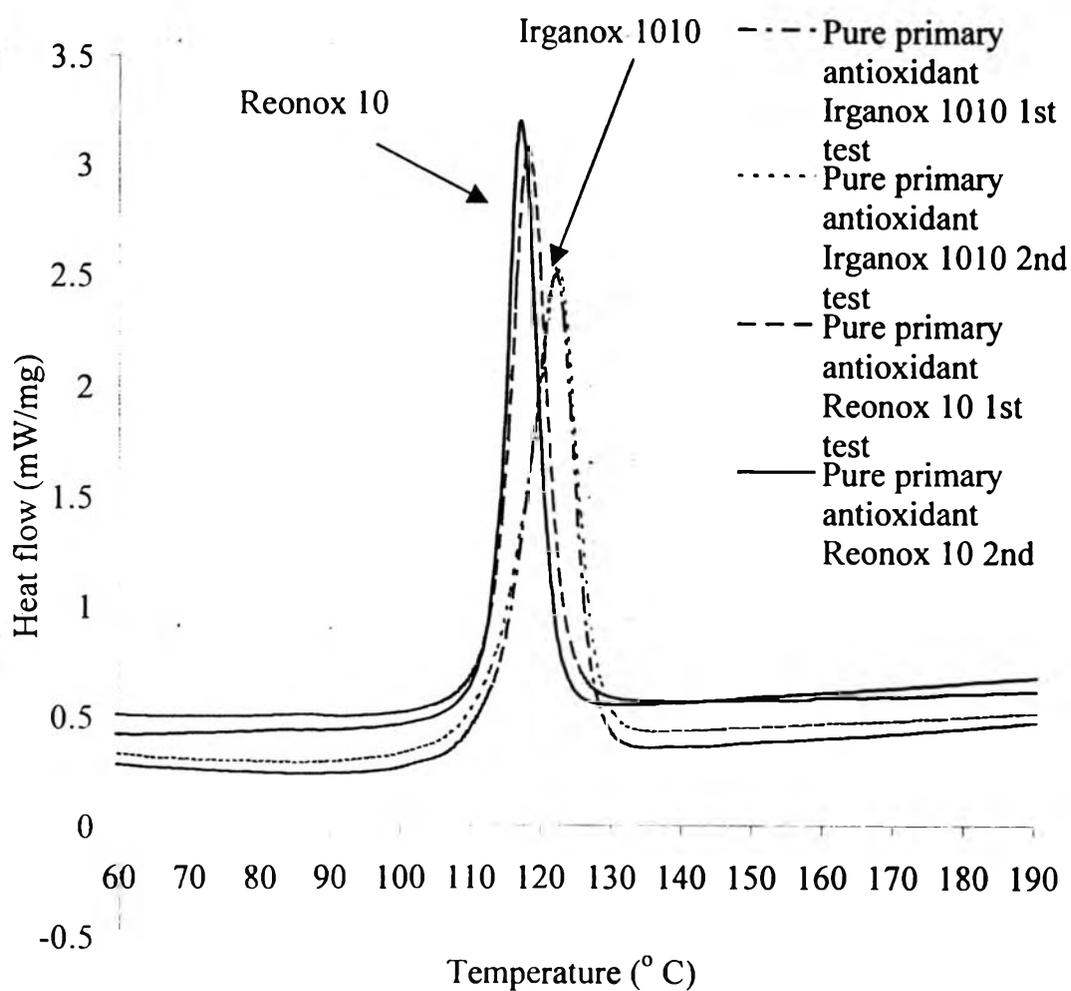


Figure 4.4 DSC melting-peak of pure primary antioxidant Irganox 1010 and Reonox 10.

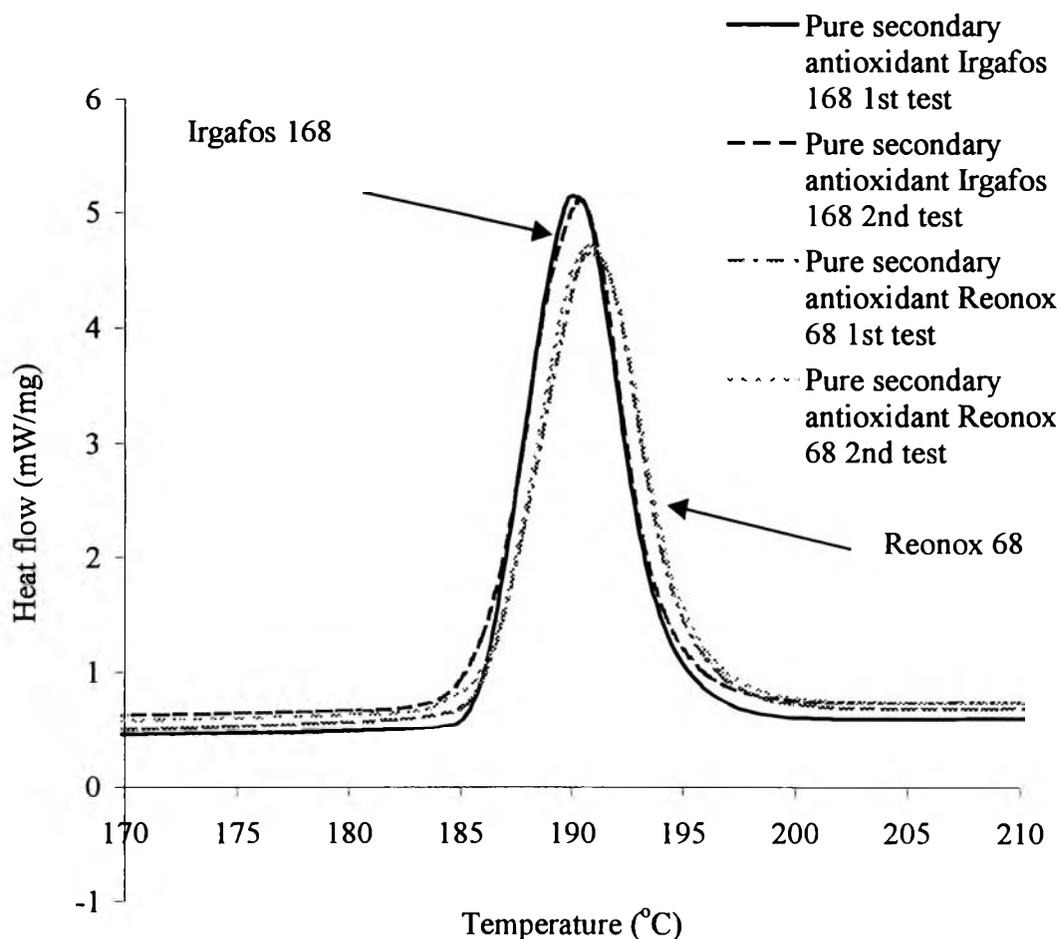


Figure 4.5 DSC melting-peak of pure secondary antioxidant Irgafos 168 and Reonox 68.

Comparisons of DSC melting-peak of each antioxidant, from figure 4.4 DSC-peak of Reonox 10 seem to be shift higher than Irganox 1010 and also shift to right hand side of the graph. The maximum endothermic temperature for Reonox 10 is 117.25 and Irganox 1010 is 122.5. However, enthalpy of melting is not different so much between Irganox 1010 and Reonox 10, equal to 2.5 mW/mg (measured from base of peak to top of peak). This technique also use for describing Figure 4.5 too. Melting range of Reonox 68 and Irgafos 168 are also the same range but differences in the enthalpy of melting for Irgafos 168 is equal

to 4.7 mW/mg and Reonox 68 is equal to 4.0 mW/mg. As comparison above, It can solve this thesis problem that why processing by use the same type of polymer but different in type of antioxidant shown the incompatible effect on MFI when increasing processing history.

In contrast with HDPE of BPE, which stabilized by Ciba specialty chemical and Eonian antioxidants. The results are shown the similar trends as presented in Figures 4.7 and 4.8. The results from Figures 4.7 and 4.8 chain scission is dominating and agree with reference book by Gächter and Müller 1990. Figure 4.6 shows the result of this book, which was studied processing stability of Zeigler-HDPE in multiple extrusion at 260°C and screw speed at 100 rpm.(base stabilization 0.05% Ca stearate + 0.013% hindered phenolic antioxidant (Figure 4.6). Ziegler-HDPE that was not stabilized by antioxidants seems to be decrease in MFI values at high decreasing rate. Hindered phenolic antioxidant stabilized Ziegler-HDPE at 0.02% w/w concentration was decreased a little bit rate of MFI changing and shift up MFI value more than non-stabilized Ziegler-HDPE. However, the best stabilizing system belong to the combinations of phosphites and phenolic antioxidants. It was shown more effective than using only primary antioxidant because it can retain MFI value for all processing range.

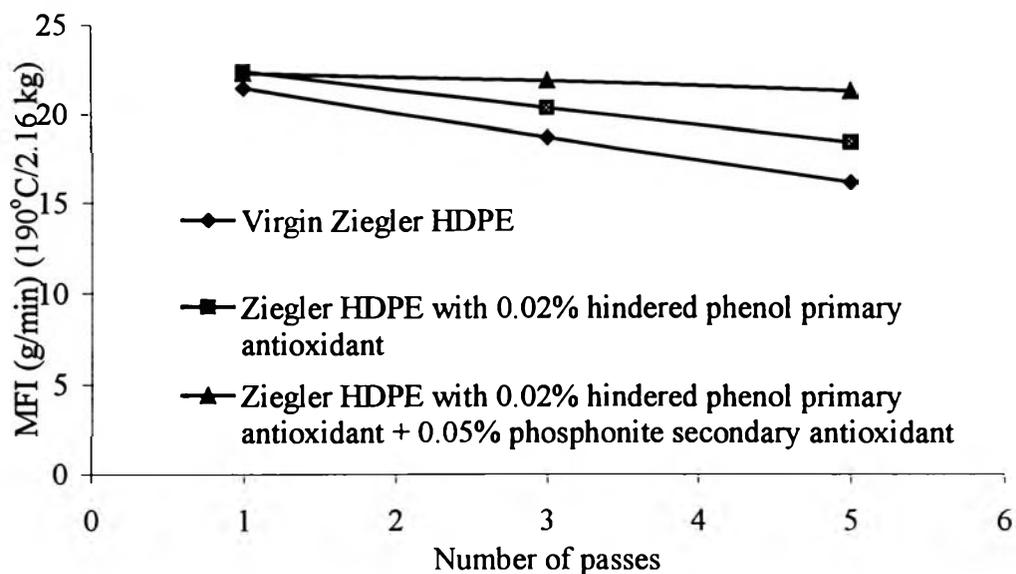


Figure 4.6 Processing stability of Ziegler HDPE ; multiple extrusion at 260°C and 100 min⁻¹ (base stabilization : 0.05% Ca stearate + 0.013% hindered phenolic antioxidant).

To determine the best performance of antioxidant ratios and types, statistic analysis was used. By using standard deviation of MFI values and delta maximum-minimum of MFI .

By definition (Appendix A)

$$\text{Standard deviation} = \sqrt{\frac{\sum nx^2 - (\sum x)^2}{n(n-1)}}$$

where n = number of data

x = data value

Delta of MFI = MFI maximum – MFI minimum of the same sample

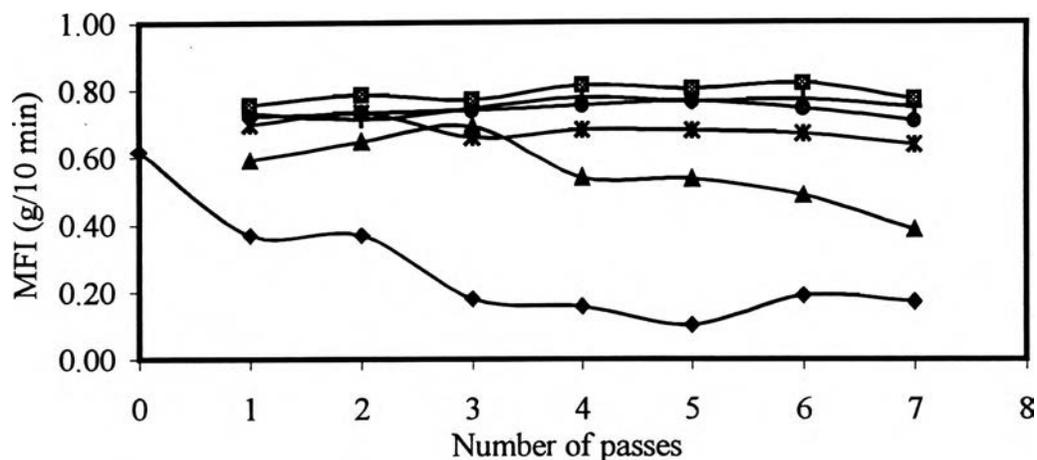


Figure 4.7 MFI of HDE of BPE samples when increase processing history: virgin HDPE of BPE represented by; ♦, HDPE of TPE stabilized with AO-1 represented by; ■, P-1; ▲, 0.025%AO-1/0.075%P-1; ×, 0.050%AO-1/0.050%P-1; *, and 0.075%AO-1/0.025%P-1; •.

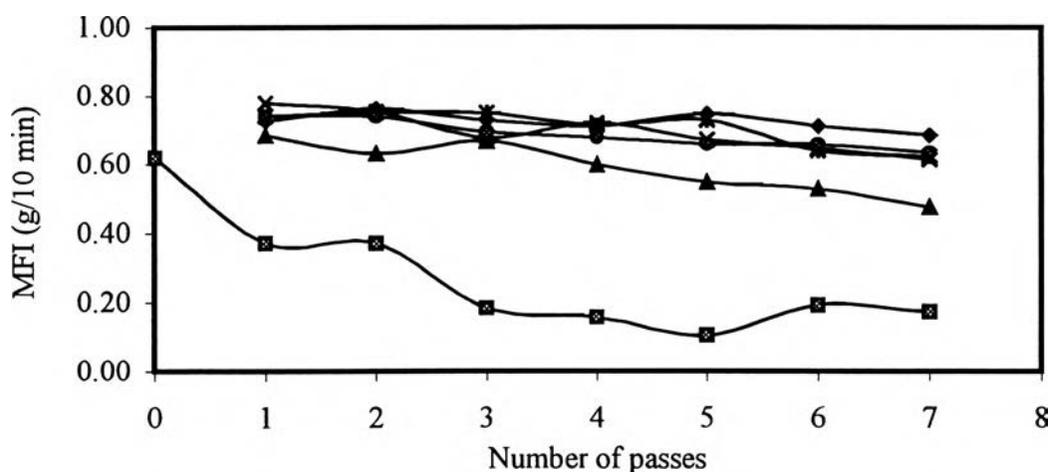


Figure 4.8 MFI of HDE of BPE samples when increase processing history: virgin HDPE of BPE represented by; ■, HDPE of TPE stabilized with AO-2 represented by; ♦, P-2; ▲, 0.025%AO-2/0.075%P-2; ×, 0.050%AO-2/0.050%P-2; *, and 0.075%AO-2/0.025%P-2; •.

The results of processing stability, which analyzed by a using statistic analysis represented in Figure 4.9, Figure 4.10, Figure 4.11, and Figure 4.12.

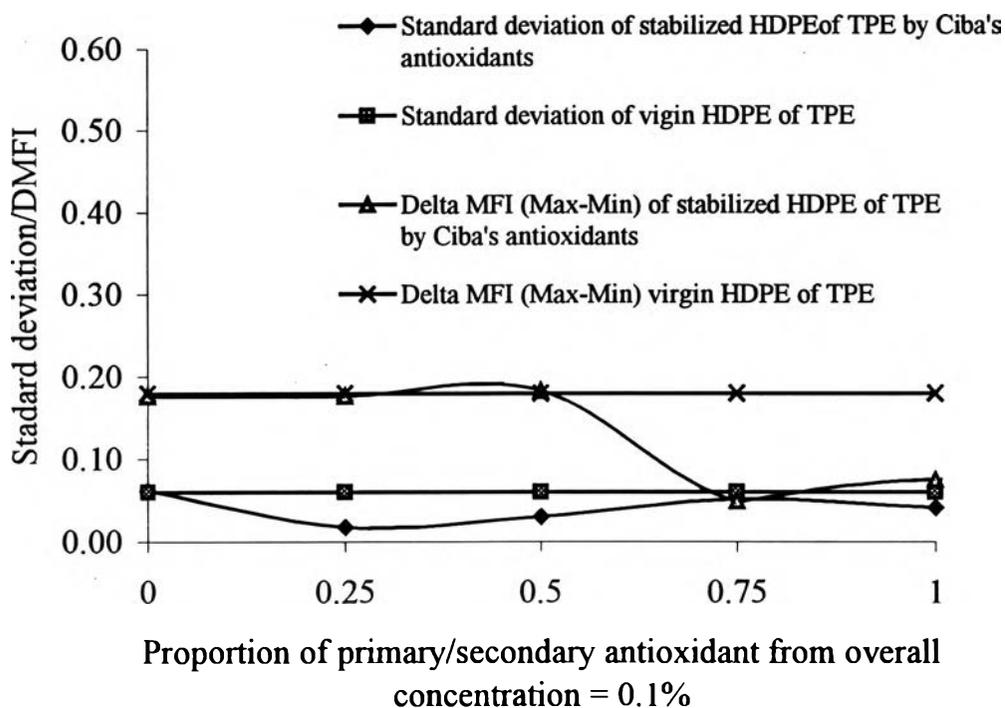


Figure 4.9 The effect of primary to secondary antioxidants from Ciba in HDPE of TPE during multiple extrusion on MFI variation.

From results in Figure 4.9, at first Δ MFI at concentration of primary antioxidant Irganox 1010 lower or equal to 0.05% seem to be show a high variation, approximately the same value of non-stabilized HDPE of TPE (Δ MFI = 0.18). The best performance of this case is the composition that composed by Irganox 1010/Irgafos 168 at ratio 75/25 from 0.1% over all antioxidants concentration. For standard deviation of results quite not outstanding for this analysis because it is less than 0.1%, no significant.

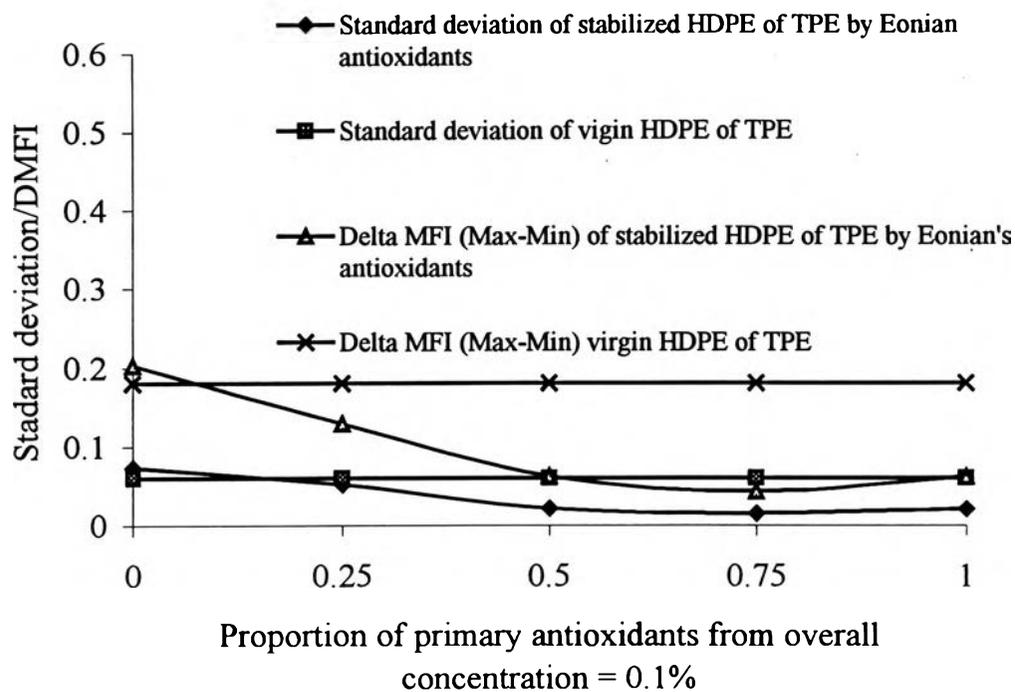


Figure 4.10 The effect of primary to secondary antioxidants from Eonian in HDPE of TPE during multiple extrusion in term of MFI variation.

Almost MFI variation results for this experimental section decrease by increasing ratio of primary antioxidant. For Figure 4.10 the best ratio of primary antioxidant to secondary antioxidant is at 0.75. Practically, useable ratios are 0.5, 0.75, and 1. Antagonism effect was found in Figure 4.10, when added only secondary antioxidants at 0.1%. Antagonism effect from HDPE (first point of Δ MFI line) that was stabilized by secondary antioxidant, it was shown delta MFI more than non-stabilized HDPE or virgin HDPE. Further more, synergism effect was occurred in Figures 4.9, 4.10, and 4.11. Synergism effect for this analysis is the point that shown better stabilized in MFI than added only primary antioxidant, normally synergism point must be the same point at the best formula of antioxidants ratio. Synergistic point and antagonistic point of each graph is shown in Table 4.6.

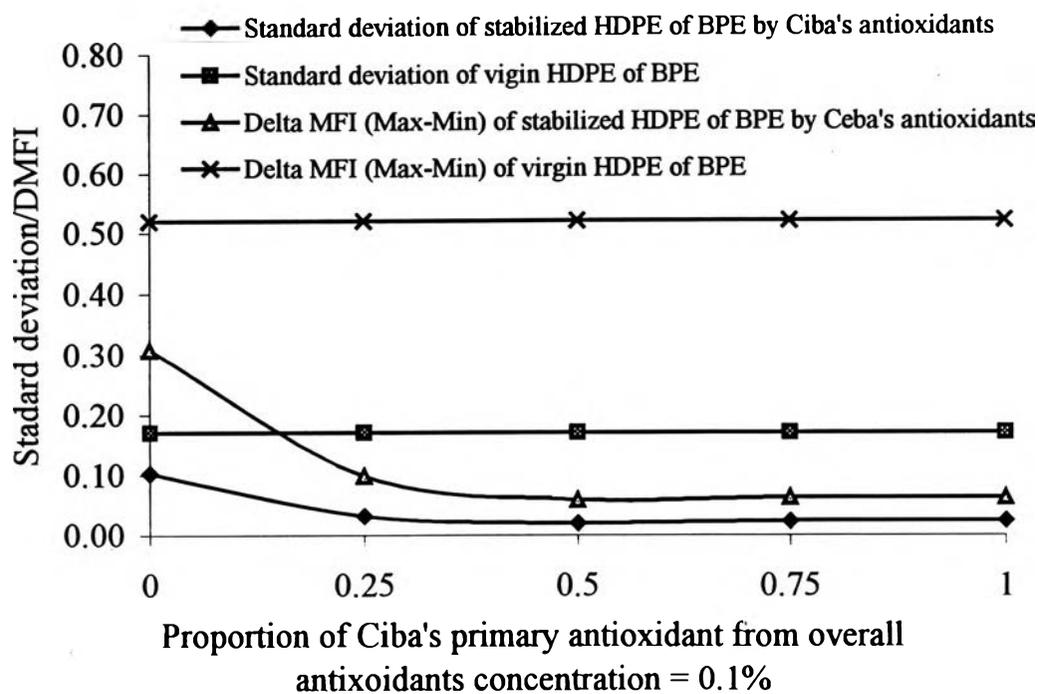


Figure 4.11 The effect of primary to secondary antioxidants from Ciba specialty chemical in HDPE of BPE during multiple extrusion on MFI variation.

Table 4.6 The synergistic point and antagonistic point of each graph.

Figure number	Antagonistic point	Synergistic point
4.8	Ratio = 0.5	Ratio = 0.75
4.9	Ratio = 0	Ratio = 0.75
4.10	-	Ratio = 0.5
4.11	-	-

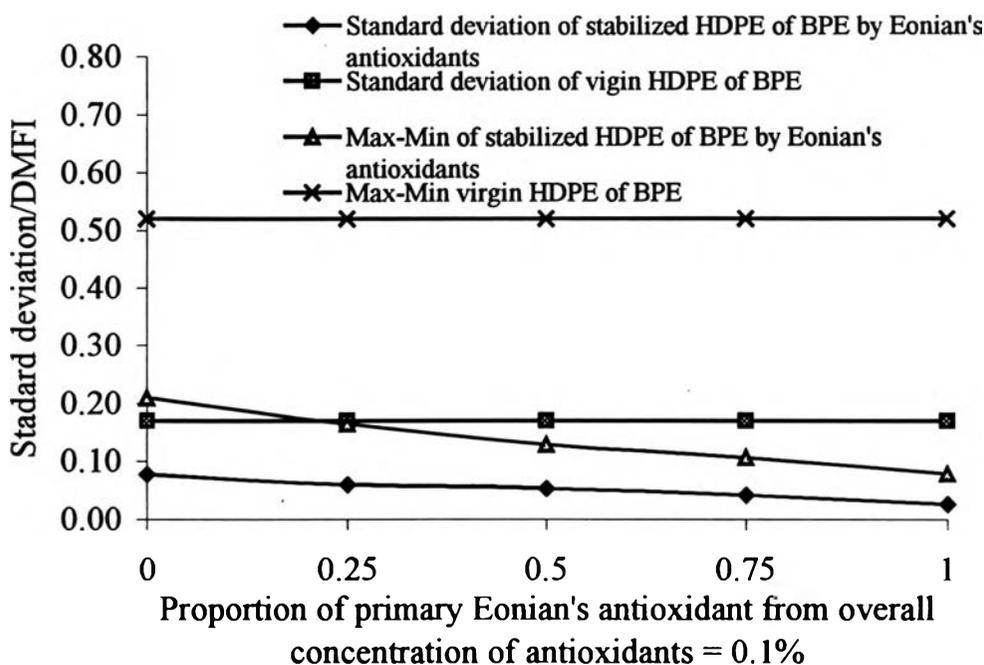


Figure 4.12 The effect of primary to secondary antioxidants from Eonian in HDPE of BPE during multiple extrusion on MFI variation.

Finally, the best performance of antioxidants formula must have lowest standard deviation and lowest in Δ MFI as presented in Figure 4.9, Figure 4.10, Figure 4.11, and Figure 4.12 sequentially.

4.4 Oxidative Induction Time of Stabilized and Non-stabilized HDPE

Oxidative induction time, is the method that use for quality control and testing of polymer in highly oxidative environment, to determine thermal oxidative stability of polymer. The oxidation exotherm obtained from a standard scanning mode DSC curve of the sample, in an oxygen atmosphere, at an elevated temperature. This technique offers the advantage of shorter analysis times for well-stabilized HDPE, where the effect of the antioxidant would be very persistent during the isothermal and purely oxygenated environment. The resulting DSC trace was characterized by a brief periods during which thermal equilibrium was

established followed by a flat, stable baseline during the isothermal interval until the oxidation chain reaction commenced to produce an exotherm.

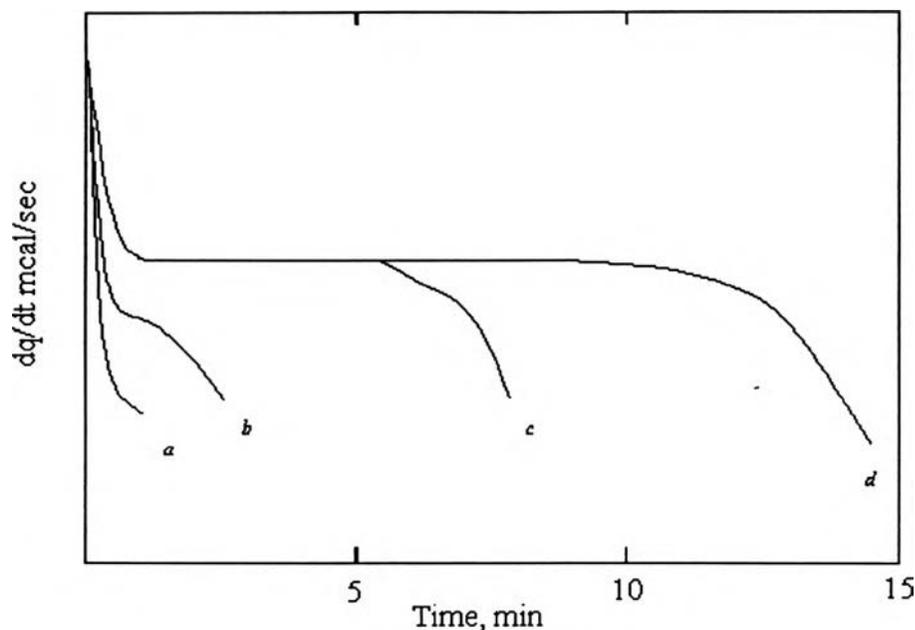


Figure 4.13 Oxidative induction time curves for polyethylene samples containing (a) no stabilizer, (b) 0.005%, (c) 0.02%, (d) 0.05% Irganox 1010.

The residence time of the resin at 200°C prior to the onset of the exotherm is referred to as the oxidative induction time. Thus, this test was interpreted as a titration of the surface antioxidant with oxygen gas using the DSC as a thermal indicator technique in Figure 4.12, sample weights were 5 ± 1 mg. From a book of “thermal analysis” that edited by Wendlandt (1986), presented that polyethylene samples containing various amounts of antioxidant additives are compared with each other using the OIT

From Figure 4.13 the non-stabilized resin failed to establish a base line and exhibited immediate exothermicity. The induction time generally increased as the antioxidant concentration increased for the stabilized samples.

The results of this part based on ASTM D3895 – 92 standard test method for oxidative induction time of polyolefins by differential scanning calorimetry, as presented in chapter III. It is applicable to polyethylene and polypropylene resins

that are in a fully stabilized/compounded form. Sometimes the oxidative induction time is an accelerated thermal ageing test and as such can be misleading. OIT results are often used to select resin formulation choices. Volatile antioxidants may generate poor OIT results even though they may be adequate at their intended use temperature, normally at atmospheric ambient.

When the sample was test in DSC, the set temperature has been reached from 35 to 200°C, discontinue programmed heating and equilibrate the sample for 5 minutes at nitrogen fully environment. Then Netzsch DSC 200 switched itself to oxygen for exceedingly 60 minutes, time since switched nitrogen to oxygen say oxidative induction time. The cycle of run from start to end experiment is presented in Figure 4.14.

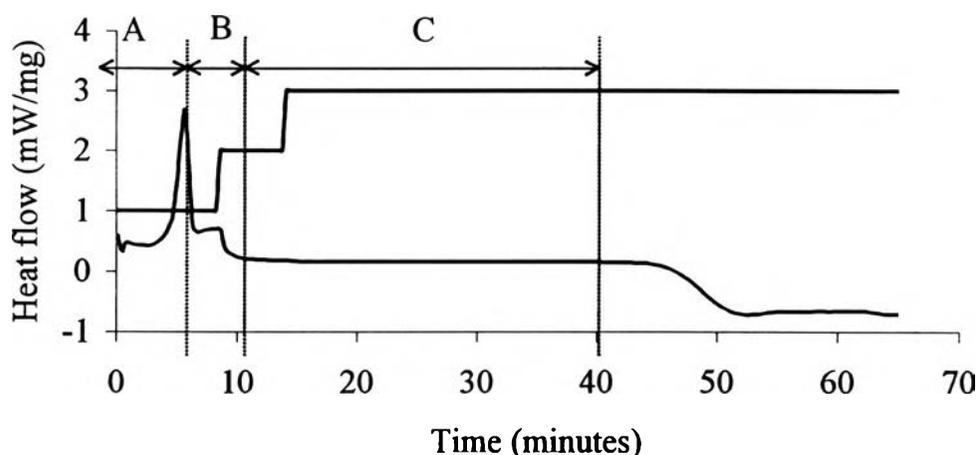


Figure 4.14 Evaluation of oxidative induction time; (A) dynamic period in nitrogenated environment, (B) isothermal period in nitrogenated environment, (C) isothermal period in oxygenated environment.

According to methods of oxidative induction time calculation or thermal analysis, the data is plotted with the heat flow signal on the y-axis, versus time on the x-axis. The x-axis should be expanded as much as possible to facilitate analysis. Extend the recorded baseline beyond the oxidative reactive exotherm.

Extrapolate the steepest linear slope of this exotherm to intercept the extended baseline (see Figure 4.15). The oxidative induction time is measured to within ± 0.1 min from zero time to the intercept point. The selection of the appropriate tangent to the exotherm sloped line may be difficult if the exothermic peak has a leading edge. Exothermic peaks with leading edges may occur if the oxidation reaction is slow. In some case, if the selection of the appropriate baseline is not obvious using the tangent method, try the offset method. Draw a second baseline parallel to the first baseline at a distance of 0.05 mW/mg above the first baseline. The intersection of this second line with the exotherm signal is defined as the onset of oxidation. The time from this intersection to zero time is not OIT.

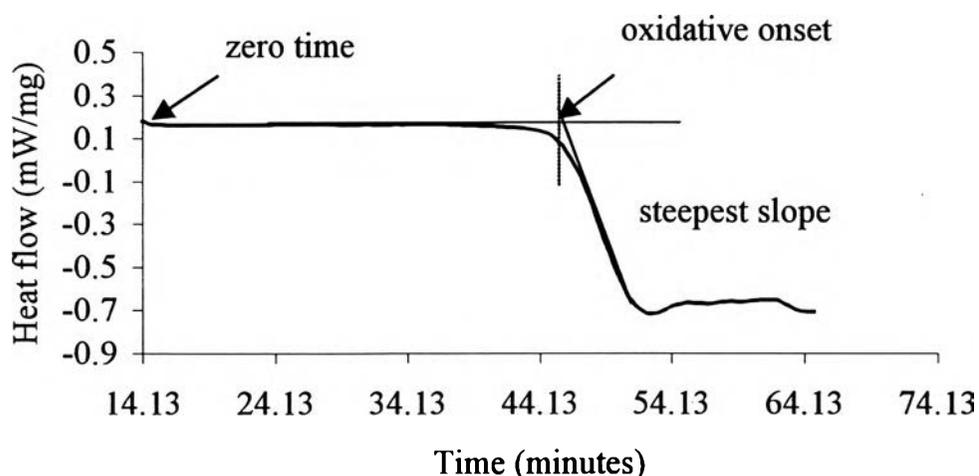


Figure 4.15 Determination of OIT from Figure 4.14 the value of OIT equals to $45.63 - 14.13 = 31$ minutes.

The results for oxidative induction time of HDPE sample were presented in Figure 4.16, Figure 4.17, Figure 4.18, and Figure 4.19.

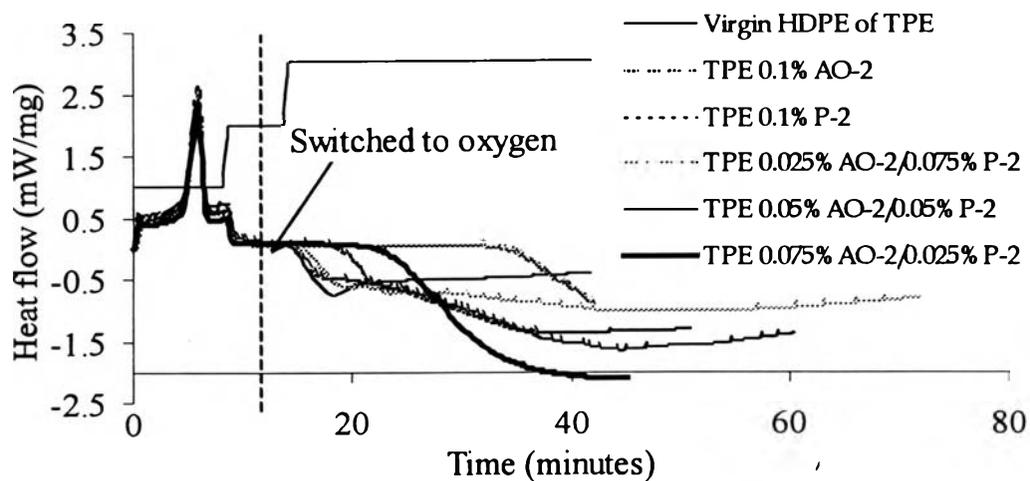


Figure 4.16 The DSC results of HDPE of TPE stabilized by Ciba antioxidants.

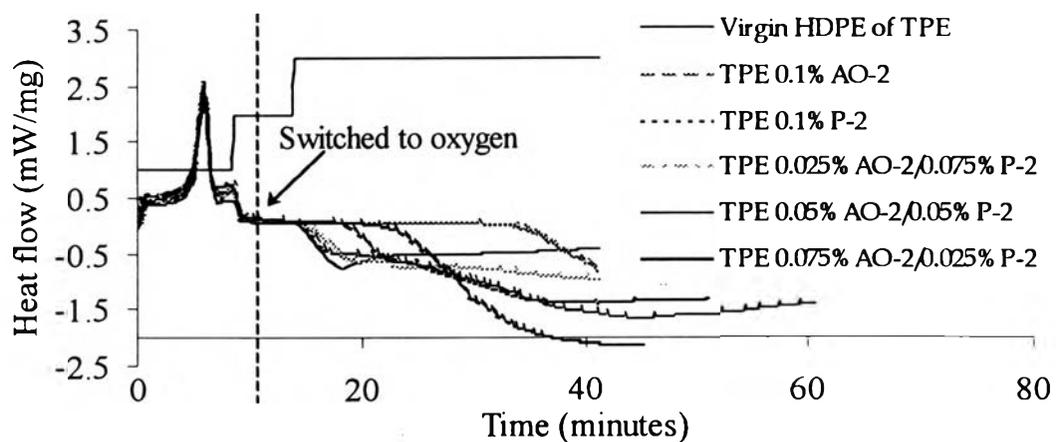


Figure 4.17 The DSC results of HDPE of TPE stabilized by Eonian antioxidants.

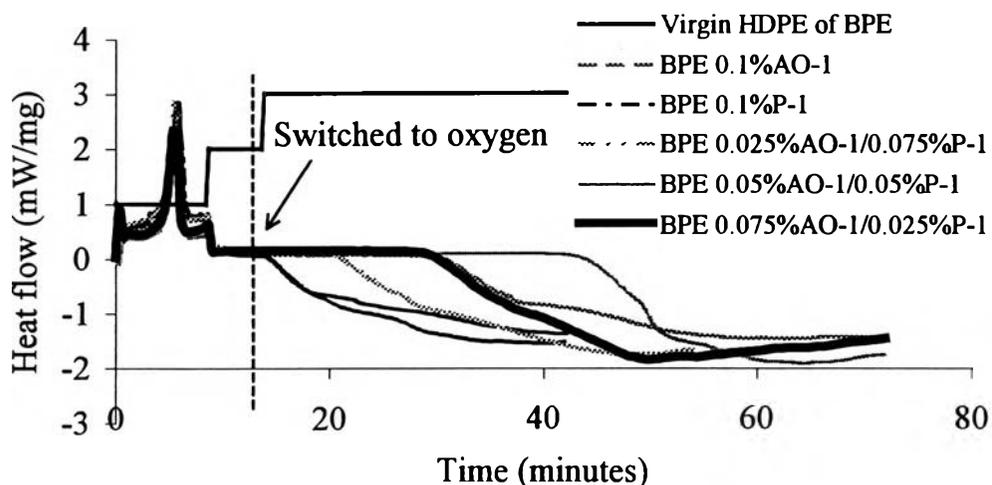


Figure 4.18 The DSC results of HDPE of BPE stabilized by Ciba antioxidants.

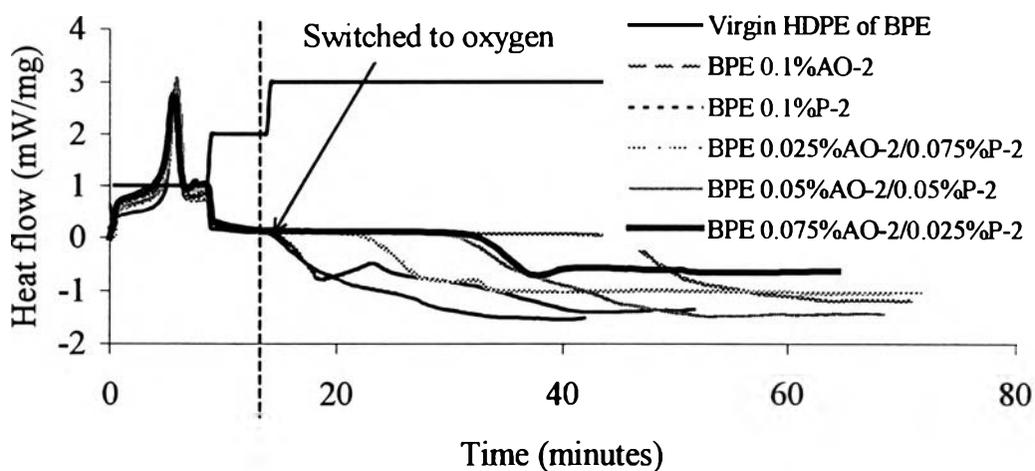


Figure 4.19 The DSC results of HDPE of BPE stabilized by Eonian antioxidants.

As the results above, each line of every graph was calculated for oxidative induction time by onset method. Table 4.7 and Table 4.8 was presented the values of oxidative induction time of each sample.

Table 4.7 Oxidative induction times of HDPE of TPE samples.

Sample	Ratios	OIT 1	OIT 2
Virgin HDPE of TPE	(0/0)	0.5	0.5
TPE 0.1%P-1	(0/100)	0.9	0.9
TPE 0.025%AO-1/0.075%P-1	(25/75)	2.6	3.2
TPE 0.05%AO-1/0.05%P-1	(50/50)	5.7	6.1
TPE 0.075%AO-1/0.025%P-1	(75/25)	9.7	14.3
HDPE with 0.1%AO-1	(100/0)	32.1	29.1
TPE 0.1%P-2	(0/100)	0.7	0.7
TPE 0.025%AO-2/0.075%P-2	(25/75)	4.4	6.1
TPE 0.05%AO-2/0.05%P-2	(50/50)	4.9	8
TPE 0.025%AO-2/0.075%P-2	(75/25)	10.4	9.1
TPE with 0.1%AO-1	(100/0)	20.6	23.6

Table 4.8 Oxidative induction times of HDPE of BPE samples.

Samples	Ratios	OIT 1	OIT 2
Virgin HDPE of BPE	(0/0)	0.5	0.5
BPE 0.1%P-1	(0/100)	0.9	0.9
BPE 0.025%AO-1/0.075%P-1	(25/75)	15.5	17.4
BPE 0.05%AO-1/0.05%P-1	(50/50)	31.7	37.2
BPE 0.075%AO-1/0.025%P-1	(75/25)	6.4	5.4
HDPE with 0.1%AO-1	(100/0)	16.6	26.7
BPE 0.1%P-2	(0/100)	1.52	1.52
BPE 0.025%AO-2/0.075%P-2	(25/75)	18.6	13.9
BPE 0.05%AO-2/0.05%P-2	(50/50)	17	13.9
BPE 0.025%AO-2/0.075%P-2	(75/25)	9	9.1
BPE with 0.1%AO-1	(100/0)	31.2	27.3

All data above are plotted in Figures 4.20 and 4.21 for compare performance of each sample.

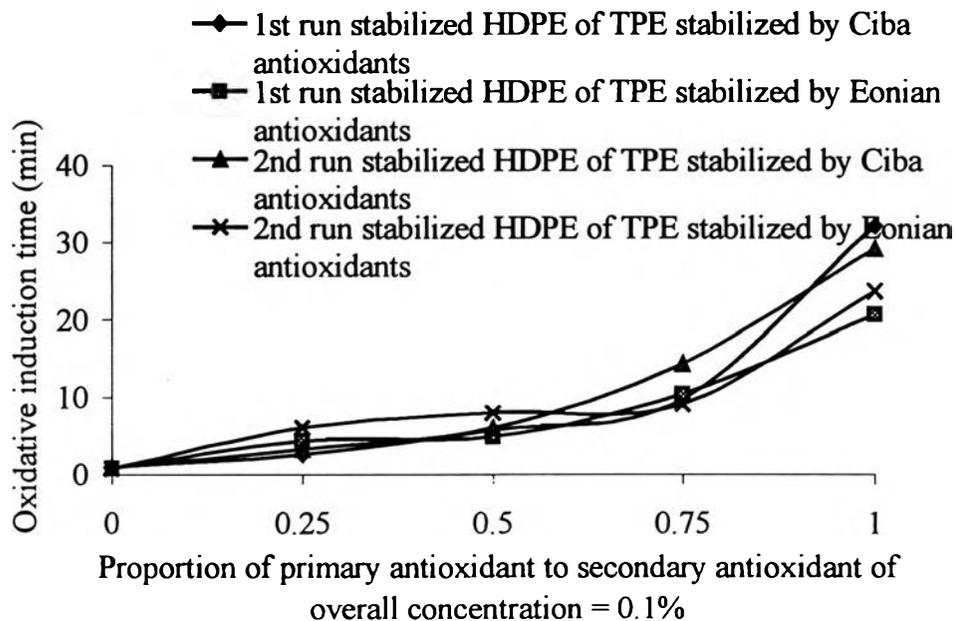


Figure 4.20 Effect of antioxidants on oxidative induction time of HDPE of TPE samples by varying ratio of primary antioxidant to secondary antioxidant.

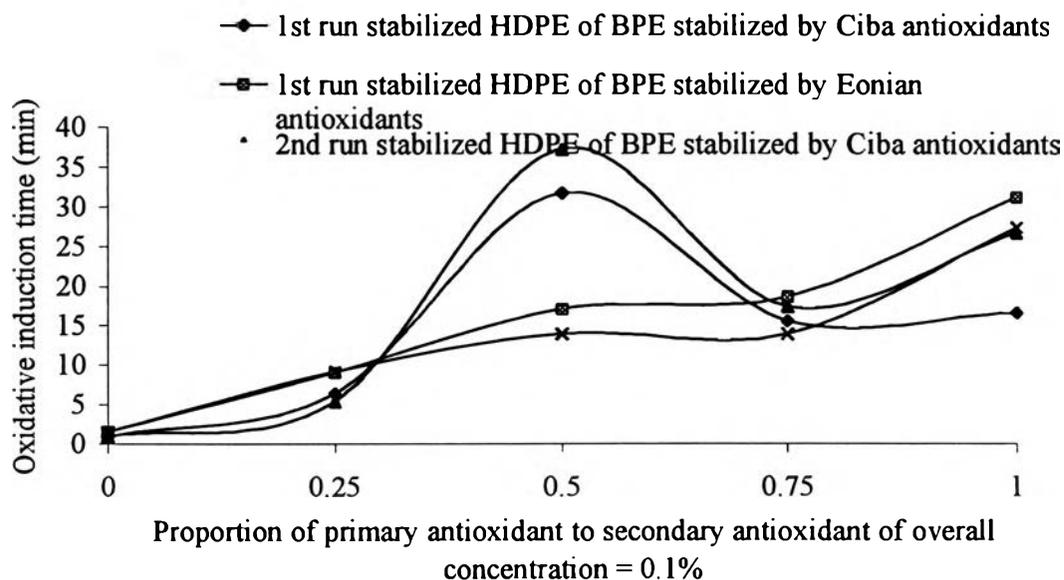


Figure 4.21 Effect of antioxidants on oxidative induction time of HDPE of BPE samples by varying ratio of primary antioxidant to secondary antioxidant.

From Figure 4.20, the results illustrated that when increasing amount of primary antioxidant, increasing in oxidative induction time. The trends of HDPE of TPE stabilized by Ciba antioxidant graphs were shown the similar trend of HDPE of TPE stabilized by Eonian antioxidant graphs. From Figure 4.21, when stabilized HDPE of BPE samples were increased amount of primary antioxidants, oxidative induction time is increase. Specifically, synergistic effect was found during this experiment. HDPE of BPE sample which was stabilized by Ciba antioxidants have showed the unexpected oxidative induction time at the composition of primary to secondary antioxidant equal to 0.5. The oxidative induction time at that composition is higher than oxidative induction time of HDPE of BPE samples that stabilized by only primary antioxidant about 15.1 to 19.8 minutes. About synergistic effect in Figure 4.21 for Ciba antioxidants stabilized HDPE of BPE, there is no single explanation of synergism valid for all combinations of phenolic antioxidants with organophosphite antioxidants. Synergism published so far regard as presented in chapter II essentially the reduction of the rates of the initiating and chain-branching steps by the hydroperoxide decomposer to be responsible for the enhanced effectiveness. Synergism also be observed with combinations of phenolic antioxidants. The reaction equations 4.1, 4.2, 4.3, and 4.4 are illustrated mechanism of secondary antioxidants which cooperative works with primary antioxidants. If AH is highly hindered phenol and A'H a less hindered phenol, hydrogen abstraction by peroxy radicals (reaction 4.1) is particularly fast with A'H. The phenoxy radical A' is rather reactive and may particulate in chain transfer reactions such as (4.2) and (4.3)



In the presence of a more hindered phenol AH, A'^{\bullet} can also enter the exchange reaction (4.4).



In reaction (4.3), the equilibrium is displaced to the right-hand side, because the highly hindered phenoxy radical A^{\bullet} is less reactive than the less hindered phenoxy radical A'^{\bullet} . So combination between primary and secondary antioxidant is more effective than add only primary antioxidant in HDPE.

The basic mechanisms outlined above have been supplemented recently to explain the special phenomena in Figure 4.21. In fact, for some polyphenols such as Irganox 1010 or Reonox 10, the main stabilization reactions seem to be donation of hydrogen atoms to peroxy radicals. As a consequence, the chain termination reaction involves disproportionation of two phenoxy radicals located on the same antioxidant molecule to yield quinone methide and regenerated hindered phenol.

4.5 Thermogravimetric Analysis

4.5.1 Thermal Decomposition of HDPE Samples

The thermal analysis technique in this section is one in which the change in sample mass (mass loss or gain) is determined as a function of temperature and time. Three modes of thermogravimetry are commonly used, as illustrated in Figure 4.22: (a) isothermal thermogravimetry, in which the sample mass is recorded as a function of time at constant temperature; (b) quasi-isothermal thermogravimetry, in which the sample is heated to constant mass at each of a series of increasing temperatures; and for this thesis work (c) dynamic thermogravimetry, in which the sample is heated at a linear rate.

The TG curve of all HDPE samples were generated the curve in form (c) (multi stage reactions), but occurred in single stage nonisothermal reaction. Testing the thermal stability of HDPE is based mainly on the major

degradation process of HDPE, i.e. elimination of ethylene gas, which leads to weight loss, typical for HDPE. The Figures 4.23, 4.24, 4.26, and 4.26 are TG curve of HDPE samples.

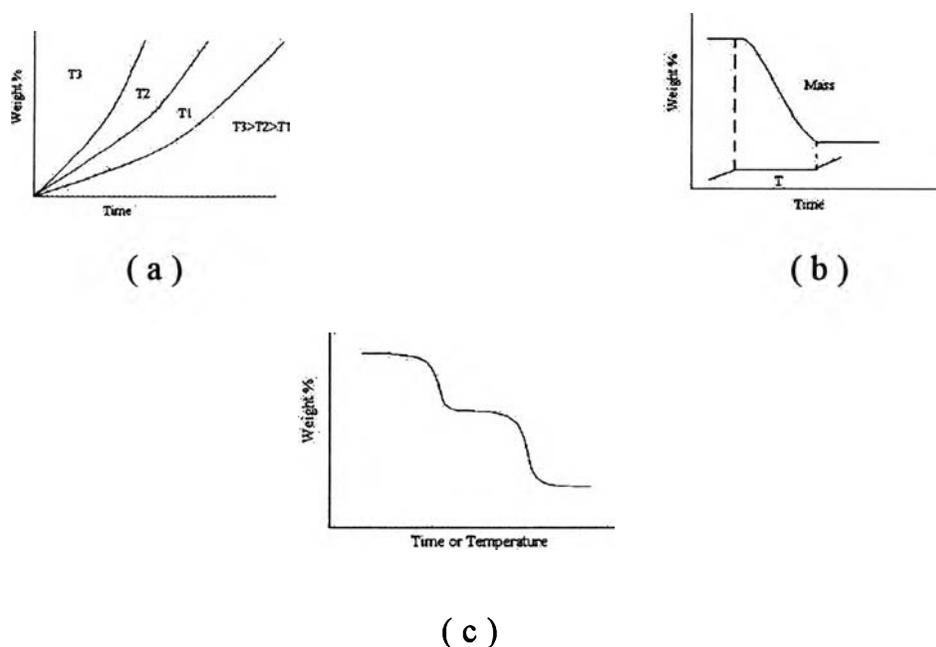


Figure 4.22 The general forms of TG curves (a) isothermal, (b) quasi-isothermal, and (c) dynamic.

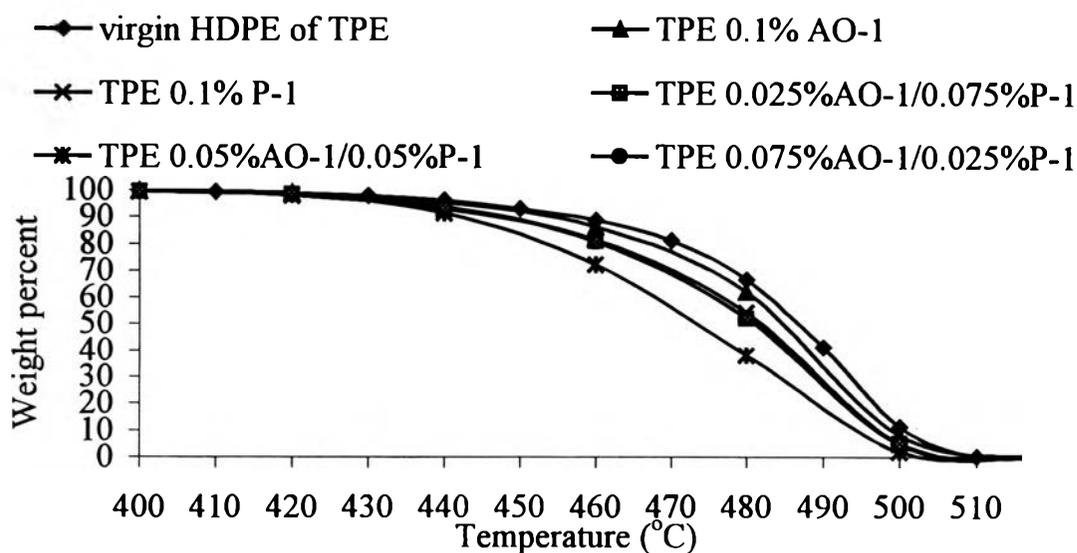


Figure 4.23 TG curve of HDPE of TPE stabilized by Ciba antioxidants.

The effects of antioxidants on HDPE that is, it can reduced rate decomposition temperature and reduce rate of decomposition. Table 4.9 is present the maximum rate of decomposition of HDPE sample that affected by ratios of primary to secondary antioxidant.

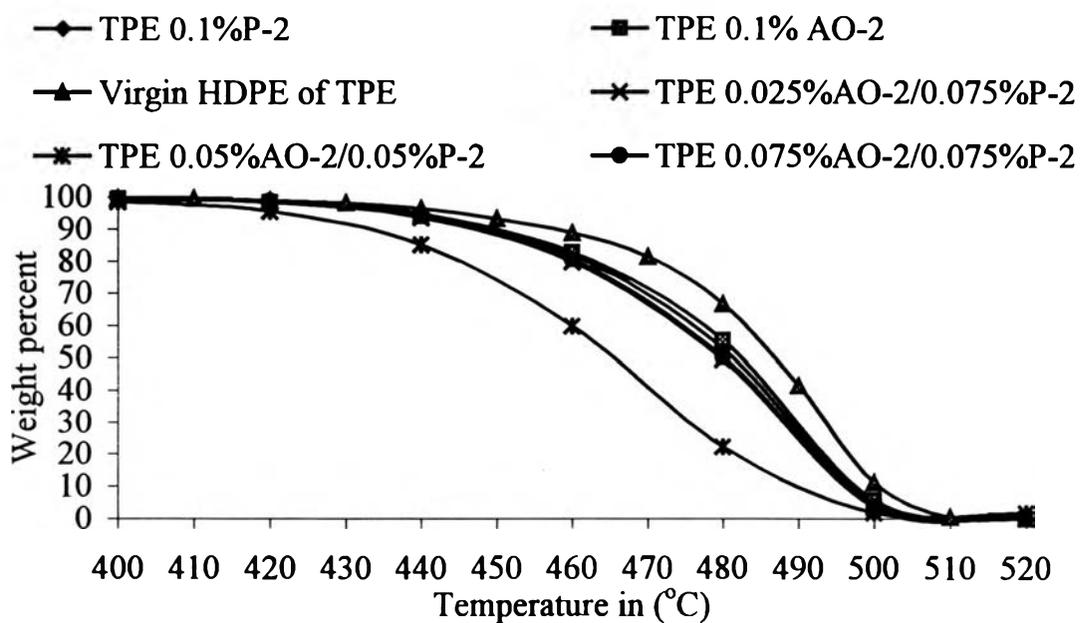


Figure 4.24 TG curve of HDPE of TPE stabilized by Eonian antioxidants.

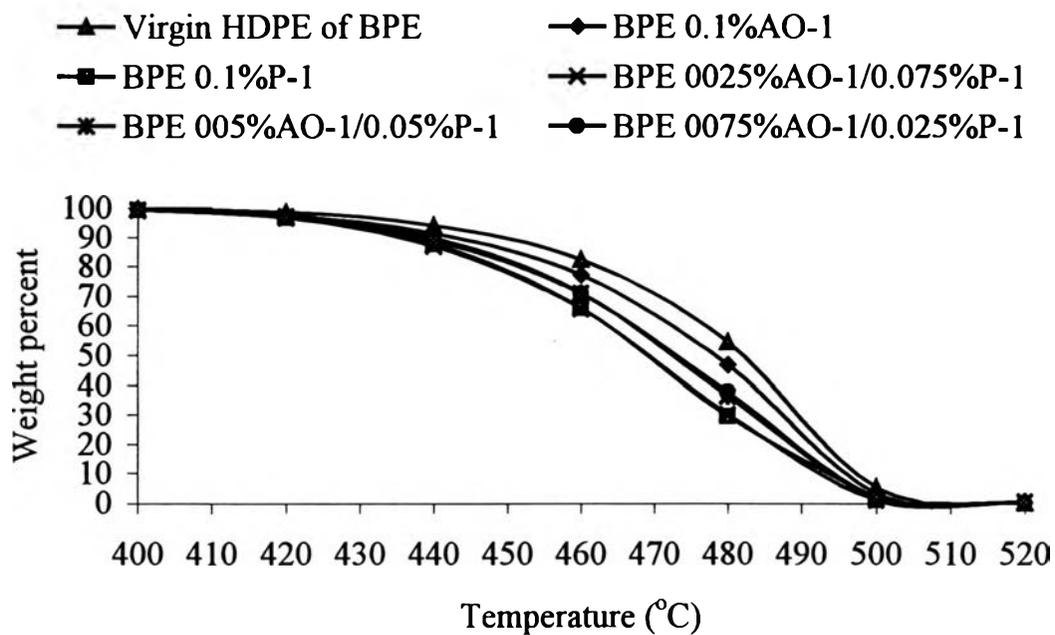


Figure 4.25 TG curve of HDPE of BPE stabilized by Ciba antioxidants.

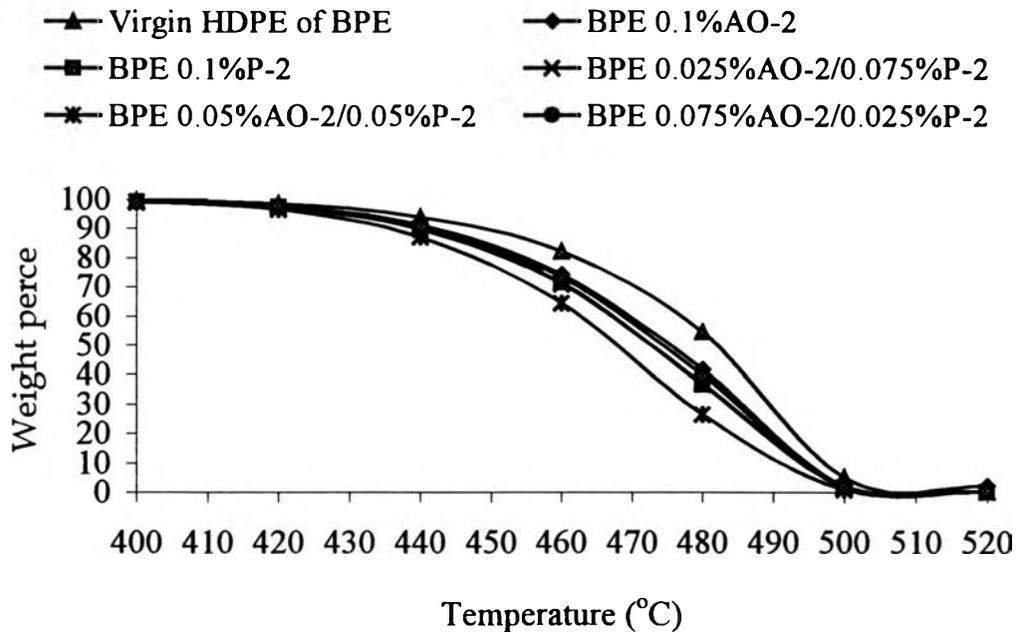


Figure 4.26 TG curve of HDPE of BPE stabilized by Eonian antioxidants.

TG curve from Figures 4.23 to 4.26 was analyzed the values of rate of decomposition by tangent method $\Delta y/\Delta x$ of each point on the TG curve of each HDPE sample.

Table 4.9 Maximum decomposition rates of HDPE samples.

Samples	Maximum rate of decomposition (Weight%/minute)
Virgin HDPE of TPE	63.81
TPE 0.1%AO-1	62.38
TPE 0.1%P-1	50.29
TPE 0.025%AO-1/0.075%P-1	55.05
TPE 0.05%AO-1/0.05%P-1	45.9
TPE 0.075%AO-1/0.025%P-1	54.67
TPE 0.1%AO-2	57.71
TPE 0.1%P-2	55.43
TPE 0.025%AO-2/0.075%P-2	55.05
TPE 0.05%AO-2/0.05%P-2	39.52
TPE 0.075%AO-2/0.025%P-2	54.29
Virgin HDPE of BPE	56.86
BPE 0.1%AO-1	51.62
BPE 0.1%P-1	42.1
BPE 0.025%AO-1/0.075%P-1	42.1
BPE 0.05%AO-1/0.05%P-1	45.9
BPE 0.075%AO-1/0.025%P-1	45.9
BPE 0.1%AO-2	49.33
BPE 0.1%P-2	45.9
BPE 0.025%AO-2/0.075%P-2	46.31

Cont...

Table 4.9 (Continued)

Sample	Maximum rate of decomposition (Weight%/minute)
BPE 0.05%AO-2/0.05%P-2	41.71
BPE 0.075%AO-2/0.025%P-2	47.05

From Table 4.9, the lowest rate of decomposition of each set of sample is the best ratio of antioxidant formula. For HDPE of TPE stabilized by Ciba antioxidants is a ratio that having composition of primary to secondary antioxidant equal to 0.05%/0.05%. HDPE of TPE stabilized by Eonian antioxidants is 0.05% primary antioxidant to 0.05% secondary antioxidant. Incredible results for HDPE of BPE stabilized by only primary antioxidant and at ratio of primary to secondary antioxidant equal to 0.025%/0.075%, that it can minimized rate of decomposition. As a consequent, the ratio of primary to secondary antioxidant at 0.05%/0.05% of HDPE of BPE stabilized by Eonian antioxidant is show the best reduced rate of decomposition of HDPE samples for Figure 4.26.

4.6 Oven Ageing

4.6.1 Tensile Test for Dumbbell Ageing Specimens

Oven ageing, is the important one for testing performance of antioxidants. Instead of holding a polymeric material in storage conditions or used conditions for a long time for determine the deterioration of polymer by time. Oven ageing was used to accelerated time of polymer that was observed for degradation behavior. The results of oven ageing for this part divided in to two parts, the first part is oven ageing at 105°C and the second part is oven ageing at

115 °C. The tested properties for oven ageing of HDPE samples at 105°C are stress at zero slope point yields and melt flow index.

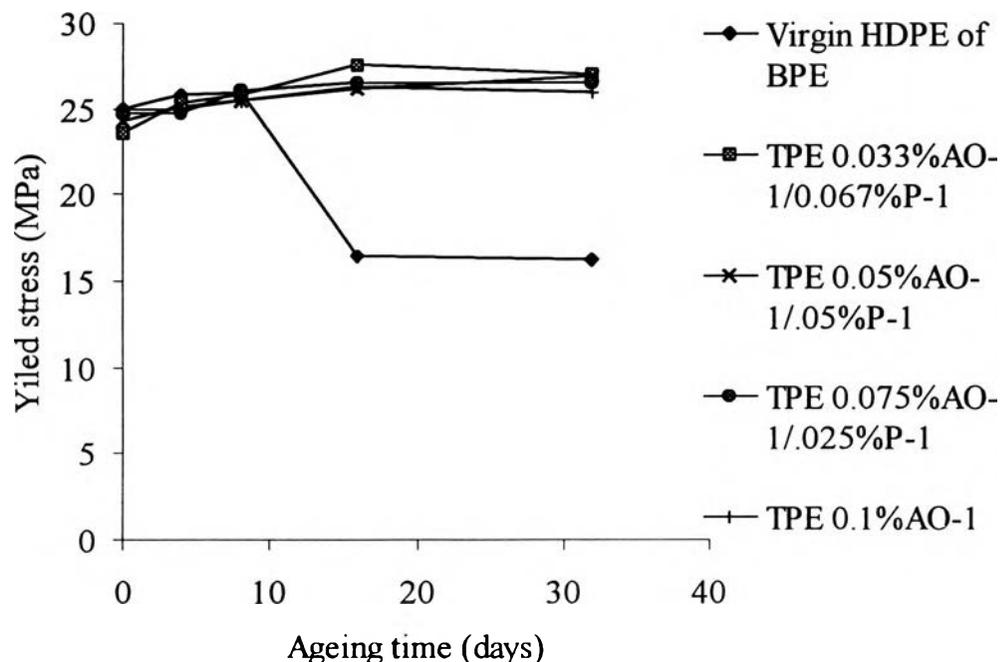


Figure 4.27 Yield stress at various ageing times of HDPE of TPE stabilized by Ciba antioxidants.

For oven-ageing at 115°C the tested properties were stress at zero slope point yields, melt flow index, and functional groups determination.

For first part only stabilized and non-stabilized HDPE of TPE was used, but not for HDPE of BPE. The results of tensile at zero slope point yield properties are reported on Figures 4.27 and 4.28.

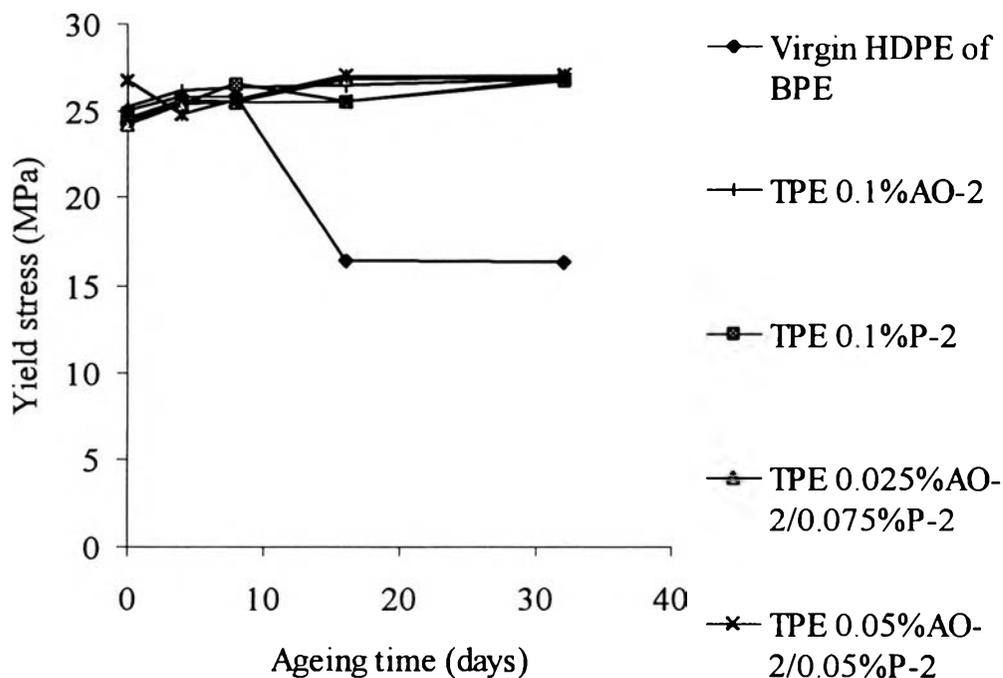


Figure 4.28 Yield stress at various ageing times of HDPE of TPE stabilized by Eonian antioxidants.

From Figure 4.27 and Figure 4.28, both HDPE samples, which stabilized by Ciba antioxidants and HDPE samples, which stabilized by Eonian antioxidants were shown a good at in stabilized all ageing periods. The stress at zero-slope point yield was determined by calculated the values of slope of each sample, which plotted between stress versus strain or elongation. The zero-slope point yield was calculated for 5 time and find average value. Example of calculation was shown in Appendix.

By definition:

Stress = Applied force/Cross sectional area of HDPE specimen

= F/A (Force unit/Area e.g. N/m^2 , or MPa)

Elongation = Increase in length of specimen/Original length of specimen

= $\Delta L/L_0$ (Length unit/Length unit e.g. mm/mm, or cm/cm)

A big failure for non-stabilized HDPE of TPE occurred after 16 days of ageing. The failures are brittleness, no-elongation (elongation at break occurred) and HDPE matter become to yellowish. In contrast with stabilized HDPE of TPE, It still retain good mechanical properties, no-elongation at break, stress at zero-slope point yield quite unchanged and no or less yellowish matter in material.

An extraordinary phenomenon was occurred in Figures 4.27 and 4.28. It is cross-linking of HDPE material by heat treatment or ageing. From 2nd point of each sample or 4 days of ageing of material, tensile strength is increase when compare to first point of each sample. Yield stress of ageing specimens was increase approximately 1 MPa from non-ageing yield stress value. This phenomena agree with Döner and Lang (1998) work, that yield stress increase about 15% of original or non-age specimens.

The results of 115°C of oven ageing is presented in Figures 4.29, 4.30, 4.31, and 4.32.

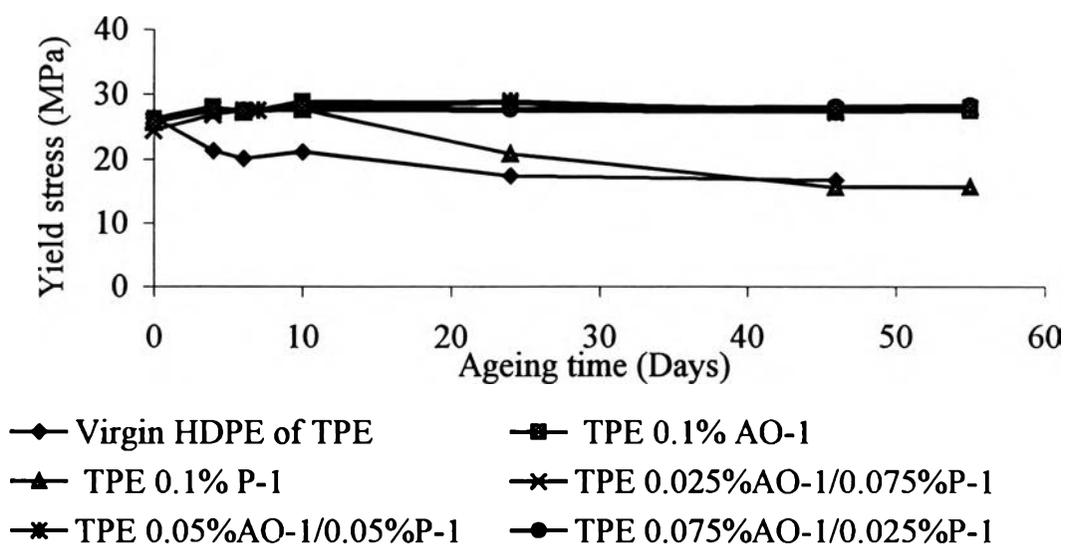


Figure 4.29 Yield stress of HDPE of TPE samples stabilized by Ciba antioxidants.

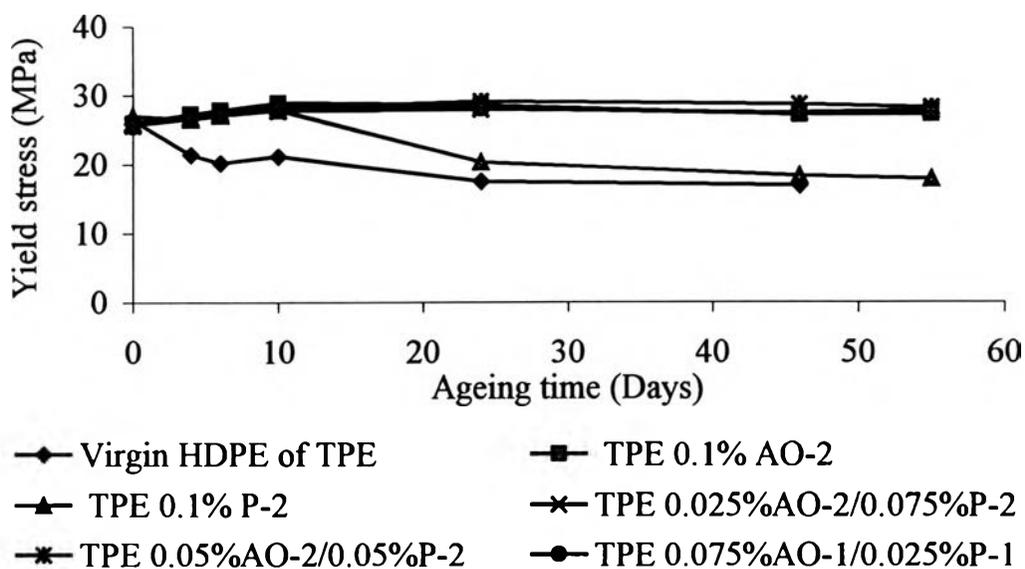


Figure 4.30 Yield stress of HDPE of TPE samples stabilized by Eonian antioxidants.

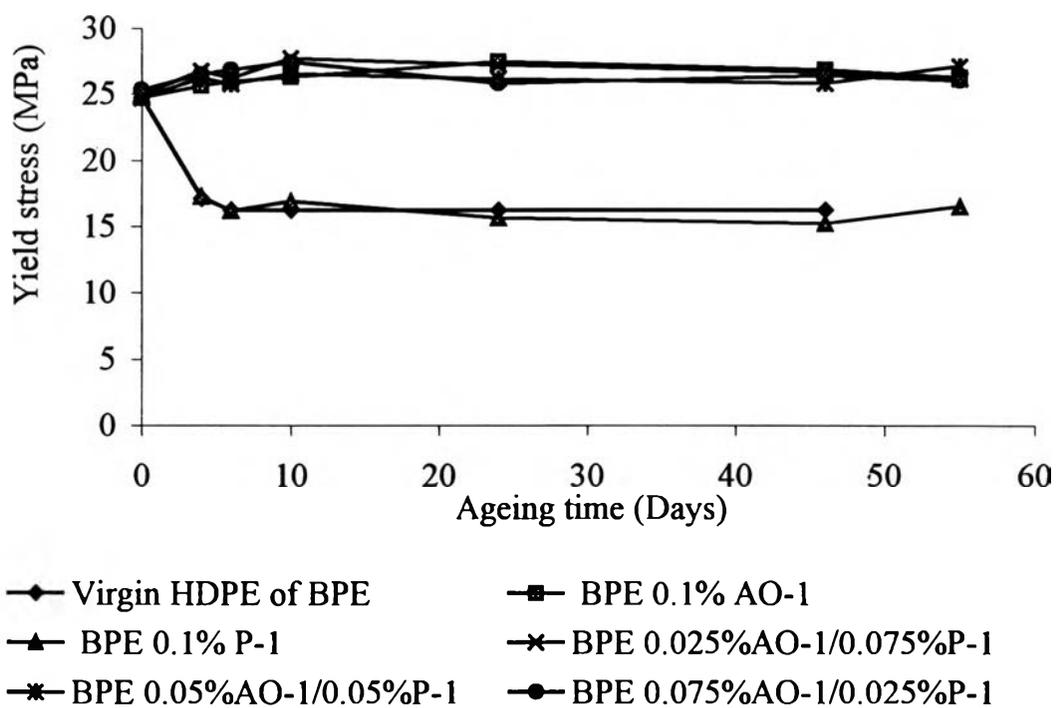


Figure 4.31 Yield stress of HDPE of BPE samples stabilized by Ciba antioxidants.

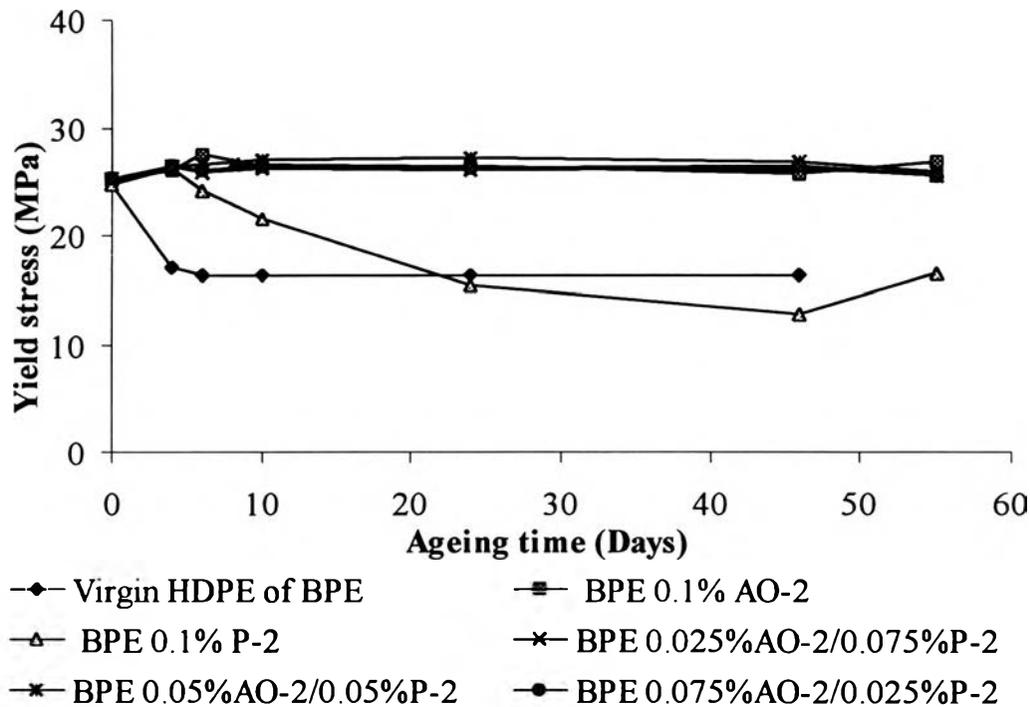


Figure 4.32 Yield stress of HDPE of BPE samples stabilized by Eonian antioxidants.

The effect of increasing oven temperature from 105°C to 115°C is to make the HDPE samples degrade faster degradation than the former one. The second point upward of each graph seems to be having more yields stress than the first point of each graph. The reason for describing this phenomenon is the same reason as results for oven ageing at 105°C, cross-linking by heat treatment. Effect of heat treatment made polymeric material be stiffer and increase in strength. Different results of oven ageing at 115°C to oven ageing at 105°C is, at 115°C all HDPE samples that is stabilized by secondary antioxidant and non-stabilized become failure in mechanical properties. The failure of HDPE of TPE stabilized by secondary antioxidant failure in mechanical properties after 10 days of ageing. Refer to Figure 4.29 and Figure 4.30, yield stress and ageing time of each Figure show a similar trend of failure, when compare sample to sample, e.g. compare

HDPE of TPE which stabilized by primary antioxidant to secondary antioxidant of each company at specific ratio. It means that HDPE of TPE which, stabilized by Ciba antioxidants comparable to HDPE of TPE, which stabilized by Eonian antioxidants.

From Figures 4.31 and 4.32, HDPE of BPE which have primary antioxidant in its matter (0.025-0.1% by weight), it have showed a good at in thermal degradation resistant and show a similar trend of mechanical properties. Normally, HDPE sample that stabilized with contain primary antioxidant in its matter can pay resistant on stress at approximately 25-28 MPa. This experimental part quite not success to determine the end point of stabilized HDPE samples. It is no as easily detectable. But in FTIR experimental on next part can be solved the end point of deterioration of stabilized HDPE sample. Furthermore, the different of Figure 4.31 and Figure 4.32 is HDPE of BPE sample which is stabilized by Eonian primary antioxidant or Reonox 68 seems to be more resist on thermal degradation than HDPE of BPE sample which stabilized by Irgafos 168.

By observed by eyes, at 55 days of ageing, partial surface of dumbbell specimens of stabilized HDPE at ratios of primary to secondary antioxidants equal to 25/75 was become yellowing. For this data, we can suspect that, the next failure HDPE samples should be the samples that have ratio of primary to secondary antioxidant equal to 25/75. Unpredictable, Figure 4.32 is representing the oven ageing data obtained with phenolic antioxidants for Ziegler-type HDPE. In Figure 4.32, it can be seen that, with two exceptions, there is a pronounced increase of oven lifetime or ambient lifetime with primary antioxidant concentration.

4.6.2 MFI of Oven Aged HDPE sample

Melt flow indexes, which determine in this part, is different from the topic melt flow indexes effected by processing. The differences of MFI due to oven ageing and MFI due to processing are shown in Table 4.10.

Table 4.10 The differences of MFI due to processing and oven ageing.

Observed quantities	Oven ageing	Processing
Amount of oxygen	Fully feed by ambient	Only in the initial of processing (feeding zone)
Shear	-	All time during processing
Temperature	115°C and 105°C	165-205°C
Retention time	1 month and 2 months	An hour/batch

HDPE pellets was sampling out when time of ageing reach to 4, 8, 16, and 32 days of ageing for ageing at 105°C. For ageing at 115°C HDPE samples were carried out to test MFI when ageing time reach to 4, 6, 10, 24, 46, and 55 days of ageing. The results of changing of MFI due to oven ageing are reported on Figures 4.33 and 4.34 oven ageing at 105°C. The other are reported on 4.35, 4.36, 4.57, and 4.38 for oven ageing at 115°C.

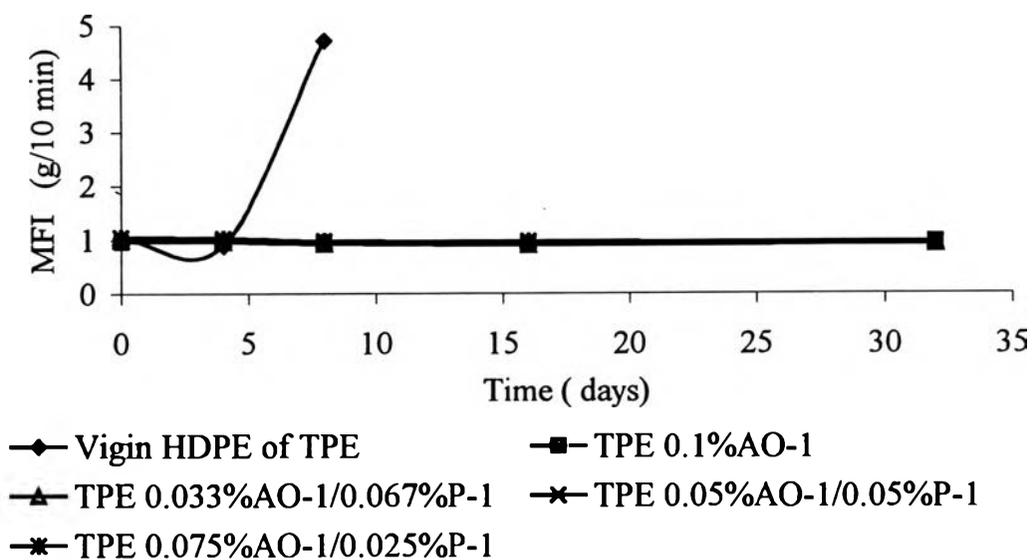


Figure 4.33 MFI variation of HDPE of TPE stabilized by Ciba antioxidant at 105°C of oven temperature.

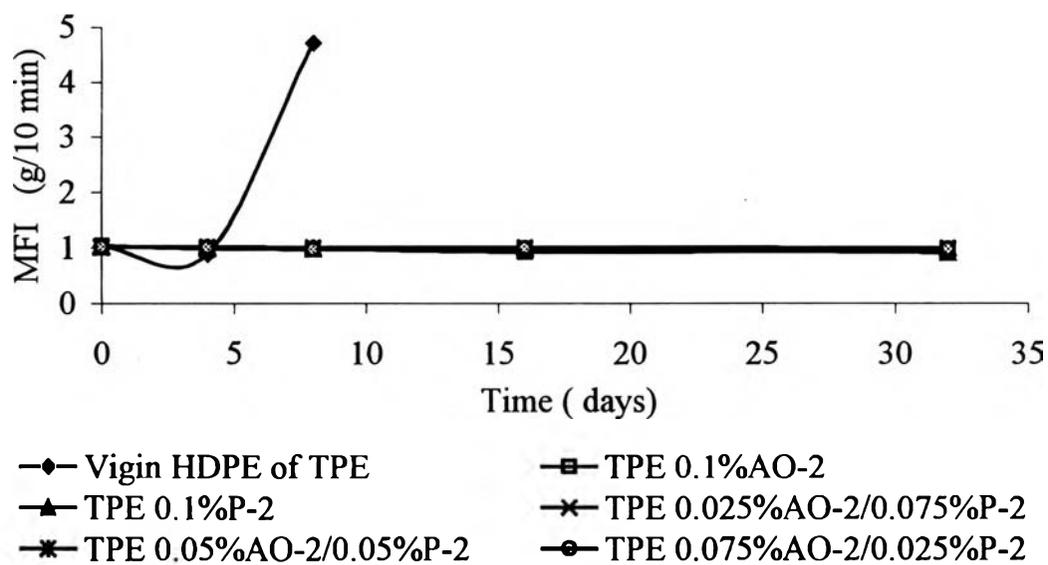


Figure 4.34 MFI variation of HDPE of TPE stabilized by Eonian antioxidant at 105°C of oven temperature.

From Figure 4.33 and Figure 4.34, the results of variation of MFI indifferent from tensile results in section 4.6.1. Both HDPE of TPE, which stabilized by Ciba antioxidants and HDPE of TPE, which stabilized by Eonian antioxidants, are shown similar trend in MFI variation. At 8 days of ageing, MFI of non-stabilized HDPE seem to be dominant, C-H bond was breaking and reacted with oxygen in air, free radical occurred. After that virgin HDPE of TPE MFI can not determined, because highly cross-linking occurred in polymer chain or very low MFI, radicals from such reactions may combine together to give cross-links or branching. In this cases (Figure 4.33 and 4.34) it seem to be consistent to results of tensile test. However, the results from Figure 4.33 and Figure 4.34 are not enough information for select formulas of antioxidant.

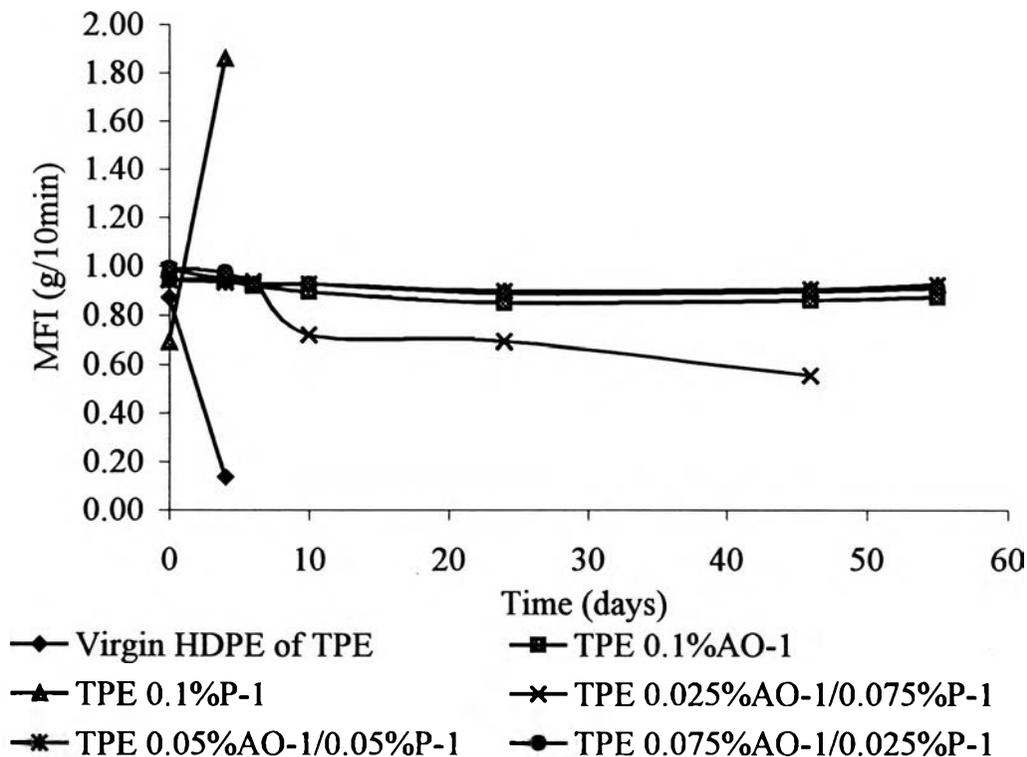


Figure 4.35 MFI variation of HDPE of TPE stabilized by Ciba antioxidants at 115°C of oven temperature.

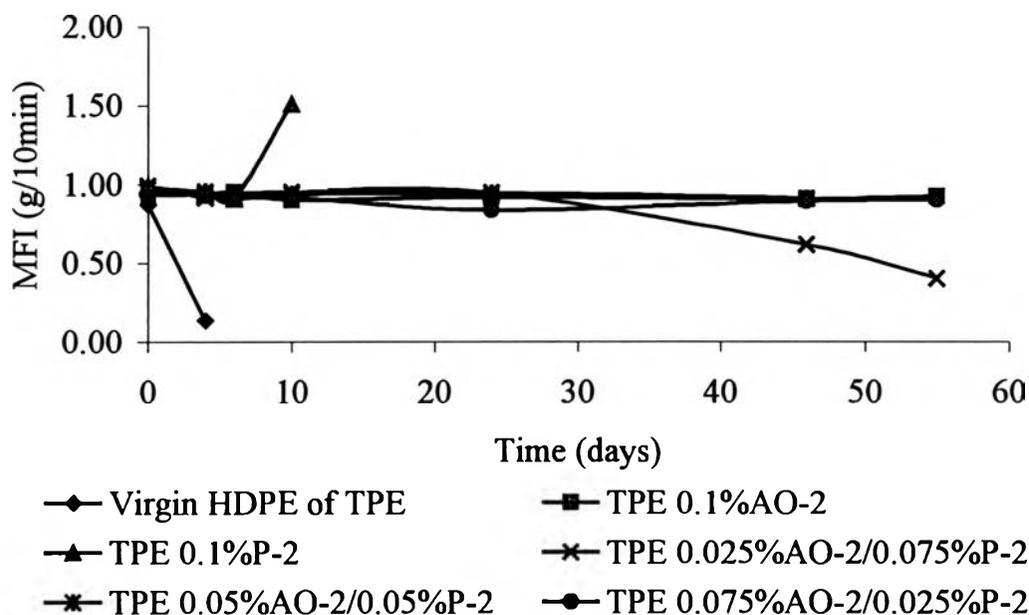


Figure 4.36 MFI variation of HDPE of TPE stabilized by Eonian antioxidants at 115°C of oven temperature.

However, data from Figure 4.35 and Figure 4.36 can assist to select the appropriate ratios of primary to secondary antioxidant. Figure 4.34 illustrated that virgin HDPE of TPE and HDPE of TPE, which stabilized by Irgafos 168 were lost in rheological properties. It was sharply degradation since starting of oven ageing experiment. It was unable to hold original properties of HDPE. Change in colour such as milky colour become to yellow colour. It was become to thermoset plastic, because during determination MFI for 4 days of oven ageing, it was not melt in Zwick MFI tester at 190°C and 2.16 kg of loading weight. At that conditions, when it was push out from barrel of MFI tester, its look like spongy. If spongy like material is cooling down, It will become agglomerate like material but easily to separate pellet form out (non-stick). Although virgin HDPE of TPE and secondary stabilized HDPE of TPE unable to hold original properties of polymer, virgin HDPE of TPE mainly reacted by cross-linking and secondary stabilized

HDPE of TPE major reaction is scission. The differences of Figure 4.35 and Figure 4.36 are explained following under this paragraph.

1. Secondary antioxidant from Eonian stabilized better than secondary Ciba antioxidant, that are secondary antioxidant from Ciba stabilized HDPE of TPE lost its properties as well as virgin HDPE of TPE but secondary antioxidant from Eonian stabilized HDPE of TPE lost its properties after 6 days of ageing.
2. For compound ratio of primary to secondary antioxidant equal to 0.025% primary antioxidant and 0.075% secondary antioxidant, Eonian compound seems to be more resist on oxidation than Ciba compound. Ciba antioxidant compound lost its properties at 10 days and decrease slowly until the end of experiment but Eonian antioxidant compound after 24 days of ageing and sharply change in melt flow index until the end of experiment.
3. For ratio of primary to secondary antioxidant that from 0.05-0.1% of primary antioxidant Ciba antioxidant compounds comparable to Eonian antioxidants compounds. Because of both of compounds can stabilize MFI approximately 0.9-1 for all range of oven ageing time.

More additional experimental data available on Figure 4.37 and Figure 4.38. All conditions, antioxidants compound comparable to Figure 4.35 and Figure 4.36 but different by type of polymer.

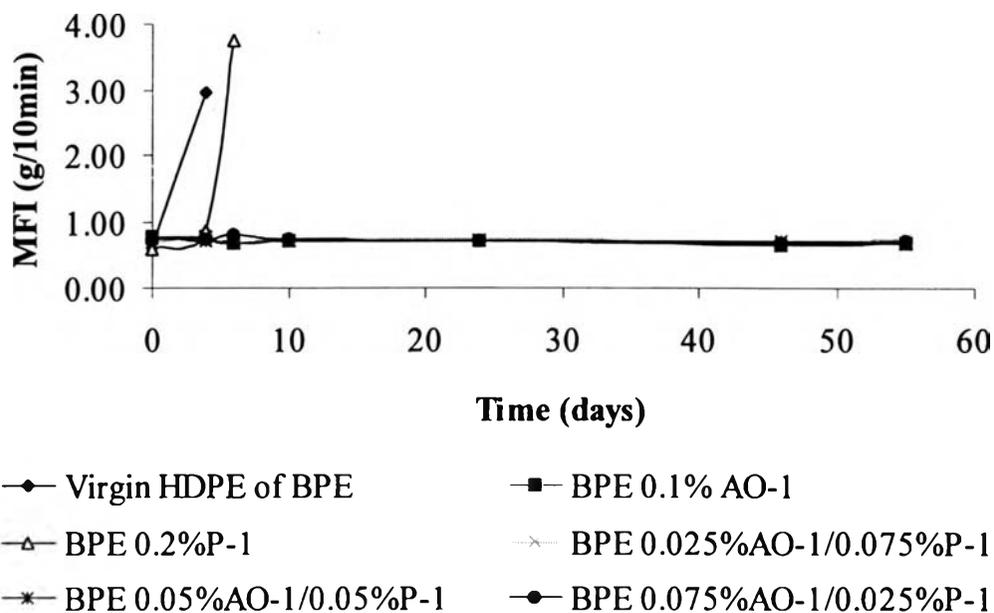


Figure 4.37 MFI variation of HDPE of BPE stabilized by Ciba antioxidants at 115°C of oven temperature.

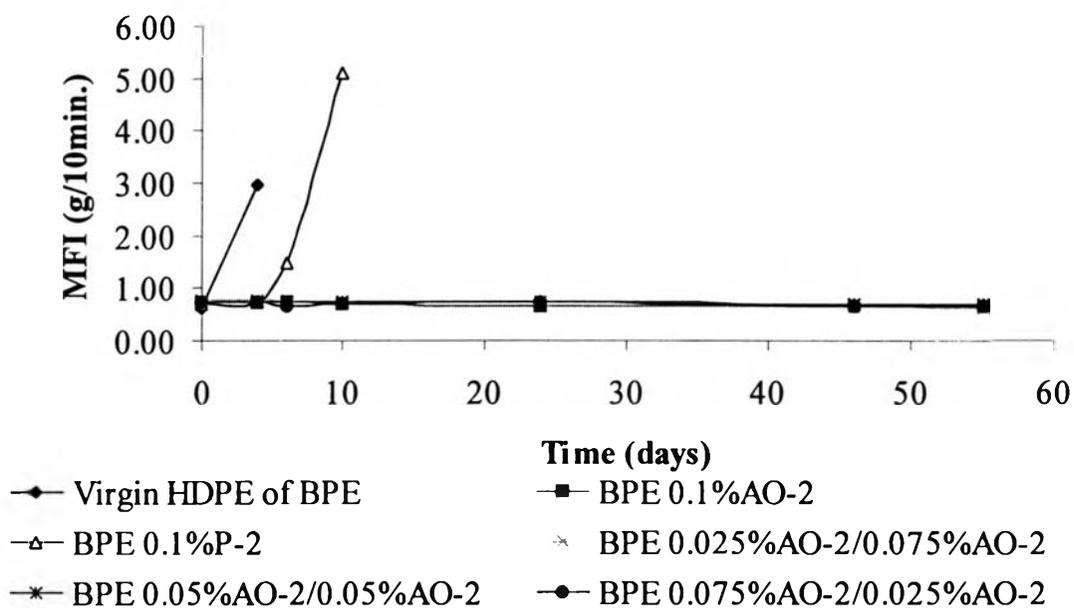


Figure 4.38 MFI variation of HDPE of BPE stabilized by Eonian antioxidants at 115°C of oven temperature.

Thai Polyethylene Co., Ltd., uses the British Petroleum process to produce HDPE. HDPE of TPE was polymerized in a fluidized bed reactor. In contrast with HDPE of Bangkok Polyethylene Co., Ltd., is use polymerization process in solution licensed by Mitsui Corporation Japan. So when comparing the results from virgin HDPE of TPE to results from virgin HDPE of BPE must different from each other, because purity of polymer. Figure 4.37 and Figure 4.38 for virgin HDPE of BPE are shown that most degradation reaction reach forward by polymer chain scission. HDPE of BPE, which have stabilized by only secondary antioxidant can pay a little bit more resistant on thermal degradation and oxidation reaction than non-stabilized HDPE of BPE. Amazingly, HDPE of BPE which have content of primary antioxidant more than 0.025% can stay original MFI (0.9 g/10min), in contrast with results from Figure 4.35 and 4.36, it can not hold rheological properties for along time. For along time, next suspect degradation sample should be a HDPE sample, which contain 0.025% concentration of primary antioxidant as occurred in HDPE of TPE samples.

4.6.3 Functional Groups Analysis During Degradation Period by Fourier Transform Infrared Spectroscopy Technique

For this section FTIR analysis was used for analyze functional groups of HDPE during oven ageing period. All analysis methods is qualitative analysis by examining the group frequency region. The degradation of HDPE is decided by occurring of aldehydes, ketones, carboxylic acids, and ester (C=O) at wave number 1690-1760 cm^{-1} and occurring of alcohol, ethers, carboxylic acids and esters (C-O) at wave number 1050-1300 cm^{-1} .

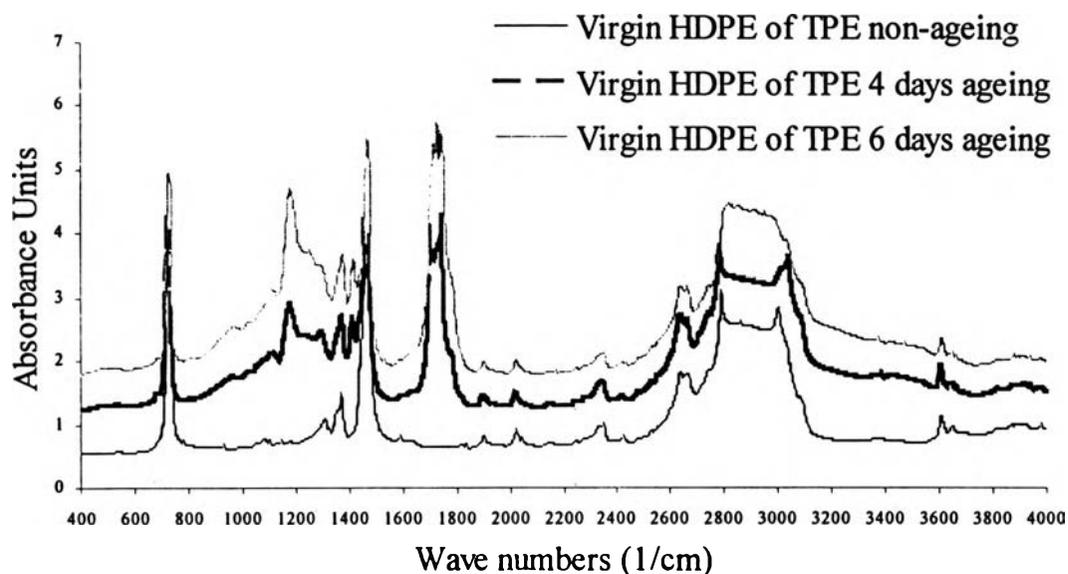


Figure 4.39 Results for FTIR peak of virgin HDPE of TPE.

Due to 250 peak of FTIR were determine from both HDPE of TPE sample films and HDPE of BPE sample films. So Figure 4.39, 4.40, 4.41, and 4.42 are some part of FTIR example peak from results of this work. Figure 4.39 belong to results of oven ageing of non-stabilized HDPE film of TPE. It was degrade at since 4 days of ageing. In Figure 4.39, FTIR peak of non-ageing HDPE of TPE is completely different from ageing HDPE film by carbonyl groups peak at wave number 1690-1760 cm⁻¹ was occurred but not for non-ageing HDPE film and also wave number 1050-1300 cm⁻¹.

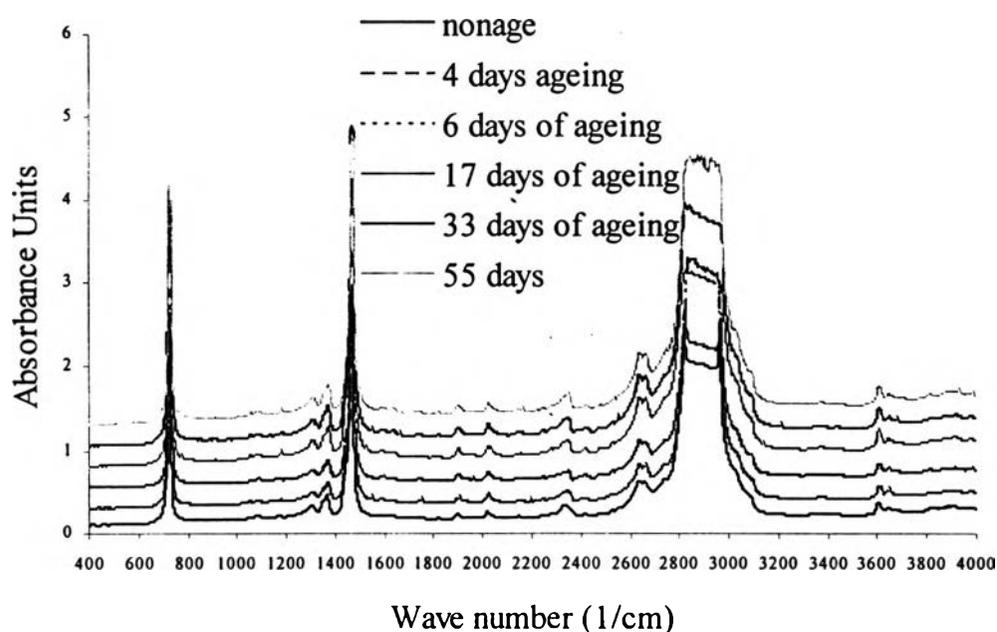


Figure 4.40 FTIR peak of HDPE of TPE stabilized by 0.1% AO-1 from bottom to top are peak at various time 0, 4, 6, 17, 33, and 55 days of ageing orderly.

Figure 4.40 illustrated that for concentration of absolutely 0.1% primary antioxidant can protect HDPE film on thermal degradation and oxidation. Because it has no observed peak at specific wave number as specify above occurred.

If only secondary antioxidants were used, Figure 4.41 can confirm that why secondary antioxidant is not helped HDPE to stabilized itself for along time.

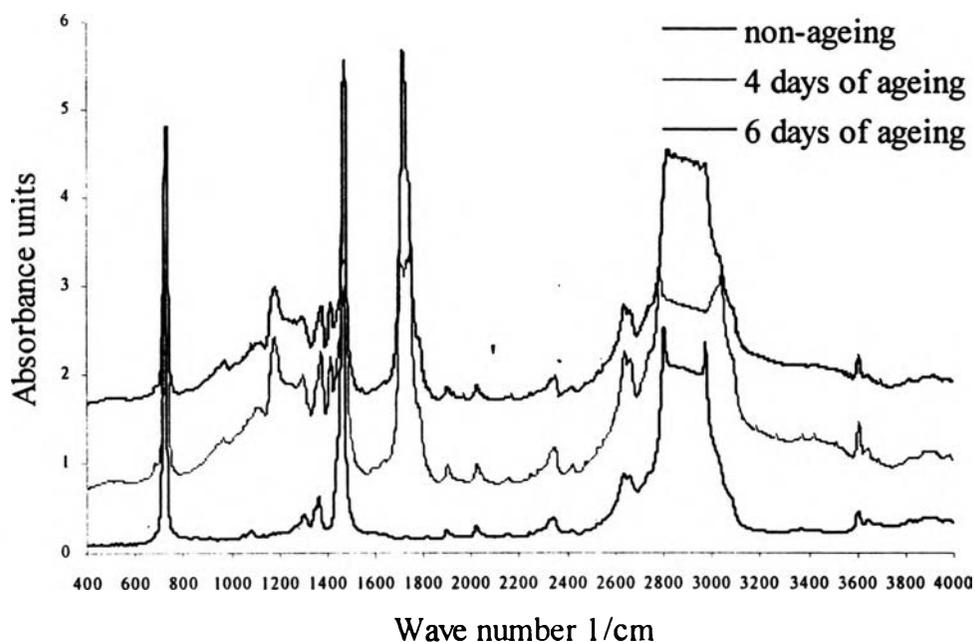


Figure 4.41 FTIR peak of HDPE of TPE stabilized by 0.1% P-1 from bottom to top are peak at various time 0, 4, and 6 days of ageing orderly.

Some set of antioxidant formula can stabilize HDPE films such a period of time as present in Figure 4.42. In this case it was shown that at degree of degradation increase with ageing time increase. Degradation of HDPE samples occurred when lack of primary antioxidant or it was consumed out. For all information about degradation of HDPE sample films both TPE and BPE is presented on Table 4.11. Table 4.11 is present about days of first observed FTIR peak occurred ($1690\text{-}1760\text{ cm}^{-1}$ and $1050\text{-}1300\text{ cm}^{-1}$). In this table it assist us to select the right, antioxidant formula, comparison between different antioxidant producer, and avoidance criterion.

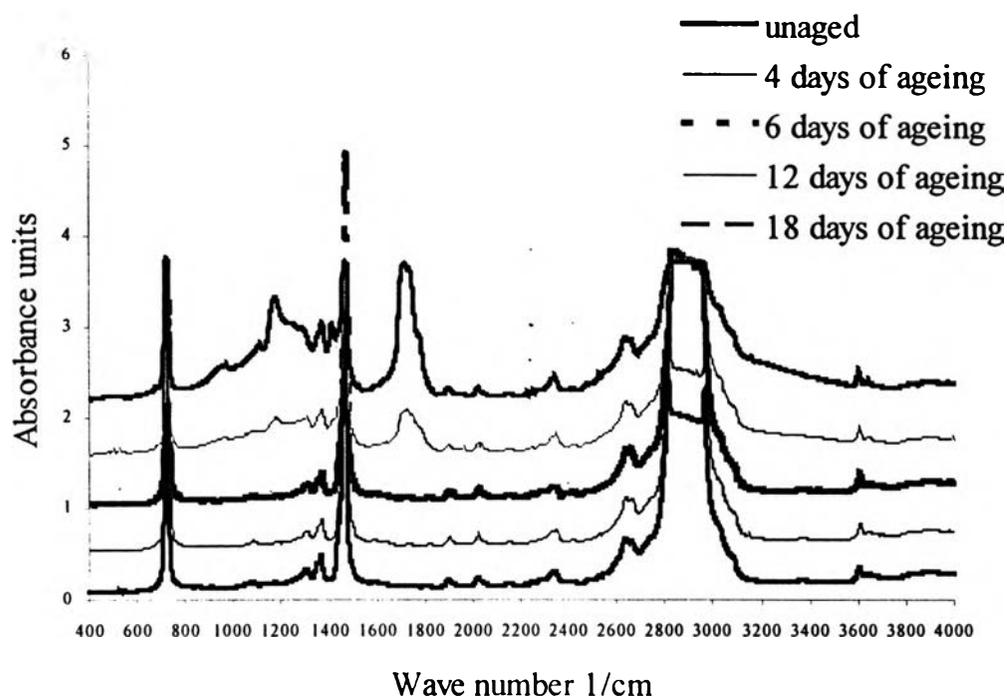


Figure 4.42 FTIR peak of HDPE of TPE stabilized by 0.025%AO-1/0.075%P-1 from bottom to top are peak at various time 0, 4, 6, 12 and 18 days of ageing orderly.

From Table 4.11 illustrated that, the optimum composition of primary to secondary antioxidant are the formulas that have concentration of primary antioxidant more than 0.05%. Antioxidants from Eonian Co., Ltd., are comparable to antioxidants from Ciba specialty chemical Co., Ltd. In some case, Eonian antioxidant systems are shown a better in stabilization than Ciba antioxidant systems. For example at ratio of primary to secondary antioxidant is equal to 50/50. HDPE of TPE which stabilized by Ciba antioxidants at that ratio can stand at severe conditions for 12 days, but not for HDPE of TPE which stabilized by Eonian antioxidants its can resist on thermal degradation more than 55 days.

Table 4.11 Time at first observed FTIR peak (1690-1760 cm^{-1} and 1050-1300 cm^{-1}) is occurred.

Sample (overall antioxidants = 0.1%)	Time (days)
Virgin HDPE of TPE	4
Virgin HDPE of BPE	4
HDPE of TPE + Irganox 1010	>55
HDPE of BPE + Irganox 1010	>55
HDPE of TPE + Irgafos 168	4
HDPE of BPE + Irgafos 168	4
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 25/75	8
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 25/75	12
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 50/50	12
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 50/50	14
HDPE of TPE + Irganox 1010/Irgafos 168 ratio = 75/25	>55
HDPE of BPE + Irganox 1010/Irgafos 168 ratio = 75/25	>55
HDPE of TPE + Reonox 10	>55
HDPE of BPE + Reonox 10	>55
HDPE of TPE + Reonox 68	6
HDPE of BPE + Reonox 68	6
HDPE of TPE + Reonox 10/Reonox 68 ratio = 25/75	20

Table 4.11 (Continued)

Sample (overall antioxidants = 0.1%)	Time (days)
HDPE of BPE + Reonox 10/Reonox 68 ratio = 25/75	39
HDPE of TPE + Reonox 10/Reonox 68 ratio = 50/50	24
HDPE of BPE + Reonox 10/Reonox 68 (50/50)	>55
HDPE of TPE + Reonox 10/Reonox 68 (75/25)	>55
HDPE of BPE + Reonox 10/Reonox 68 (75/25)	>55