

## **CHAPTER IV**

### **RESULTS AND DISCUSSION**

#### **4.1 Film sample preparation**

Both HDPE/MLLDPE film and HDPE/Z-NLLDPE film were prepared using the same condition of the blown film machine as producing HDPE film. At higher content of LLDPE (MLLDPE or Z-NLLDPE), a little air cooling adjustment was needed.

#### **4.2 Mechanical properties**

##### **4.2.1 Tensile strength**

Figure 4.1 and 4.2 shows the comparison of the tensile strength of HDPE/MLLDPE film and HDPE/Z-NLLDPE film in both machine and transverse directions, respectively. It can be seen that the increase of LLDPE content in both blends decreases the tensile strength of the films in either direction. In a separate study by A.K. Gupta and et al[17], they reported the similar result of HDPE/LLDPE blend, but they used only Z-NLLDPE. However, they observed the decrease in tensile strength as LLDPE content increased but with more than 25% of LLDPE content in the blend tensile strength increased until 80% of LLDPE the tensile strength dropped again. Normally HDPE has high tensile strength in both machine direction and transverse direction due to its molecular structure which has few side chains comparing to LDPE and LLDPE. In film processing, the molecule will be oriented in both machine direction and transverse direction according to the

drawing and blowing up of the film. When LLDPE content increases, its side chain branching which have several more will disturb the orientation of the molecules in the blend. It is believed that such occurrence is during processing. Consequently, the tensile strength of the films decreases.

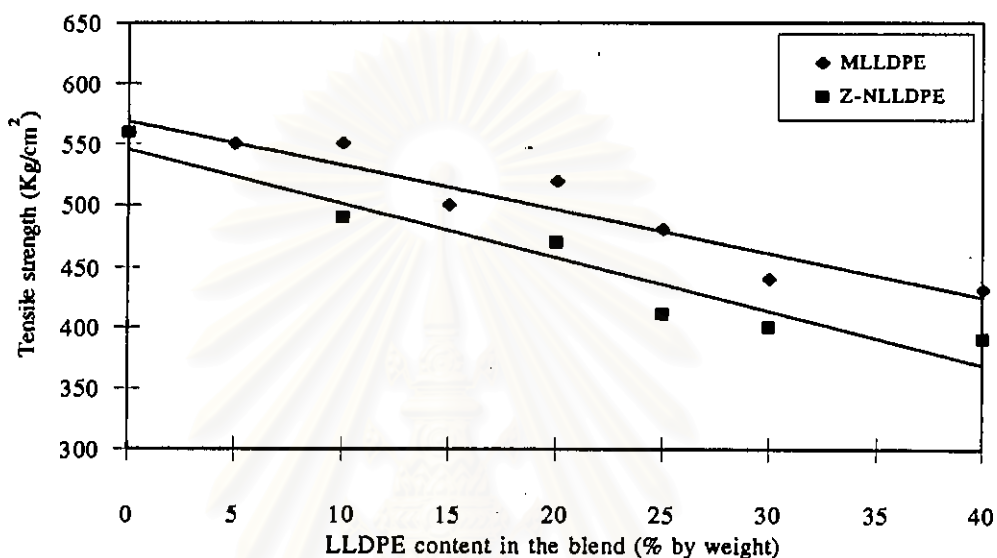


Figure 4.1 : Tensile strength in machine direction of HDPE/LLDPE film

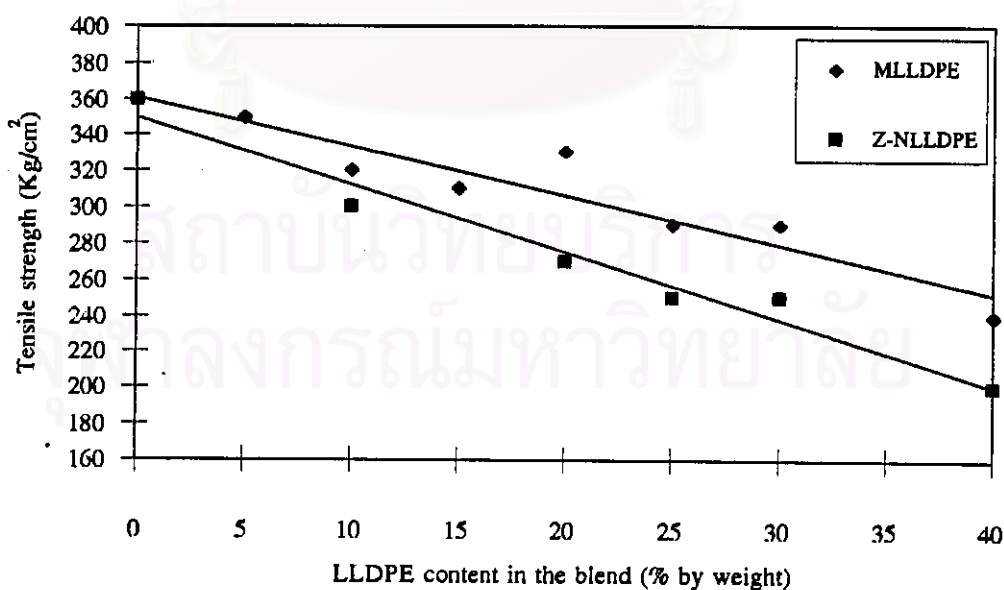


Figure 4.2 : Tensile strength in transverse direction of HDPE/LLDPE film

The tensile strength in the machine direction are higher than that in the transverse direction for both film types. The explanation for this observation is that the lower stress from the blown pressure, in transverse direction, causes less orientation of the molecules than that in machine direction.

The organization of lamella stacks seems to play a critical role on the mechanical properties of the blown HDPE film[20]. The large lamella are not perfectly aligned or there may not be optimum overlap of one lamella over another when molecules orient during the stress blowing. As a result, poor alignment or stacked lamella can reduce the strength of the film due to the weakness in the region between the lamella stacks. Since MLLDPE has two to three times smaller size of lamella than Z-NLLDPE[12], the easier alignment of lamella will be and less lamella will be stacked, the coherent orientation of lamella stacks leads to significant anisotropy of tensile properties[20]. Consequently, HDPE/MLLDPE film has higher tensile strength than HDPE/Z-NLLDPE film.

Tensile strength of HDPE/Z-NLLDPE film meet the requirement of industrial film, then HDPE/MLLDPE has superior tensile strength for the industrial film.

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#### 4.2.2 Elongation

On contrary to tensile strength, elongation at break of both types of films slightly increase linearly as more LLDPE content is in the blend as shown in Figure 4.3 and 4.4. The elongation depends on the amorphous part of the molecule, which contains the segment of freely mobile chains[15]. Due to more amorphous phase of LLDPE than HDPE, higher LLDPE content in the blend will increase in amorphous phase which will lead to higher free volume. The free volume could allow the chain to move easier when the stress is applied. Consequently, the blending film has higher elongation than HDPE film. The result in this present study is different from the work by A.K. Gupta. He found that elongation at break decreased, with respect to its value for HDPE, with increasing LLDPE content of the blend up to 50% LLDPE content and then remained almost unchanged on further addition of LLDPE up to 70% LLDPE content[17]. The cause of the different result should come from the different way of sample preparation, by injection mold and blown film. He suggested that the break occurred before the LLDPE component contributed to the elongation of the sample beyond the limit of maximum elongation of HDPE[17]. For the blown film process, the molecule is slightly oriented. Therefore, when the force is applied during the elongation testing, the LLDPE component can be contributed to the elongation.

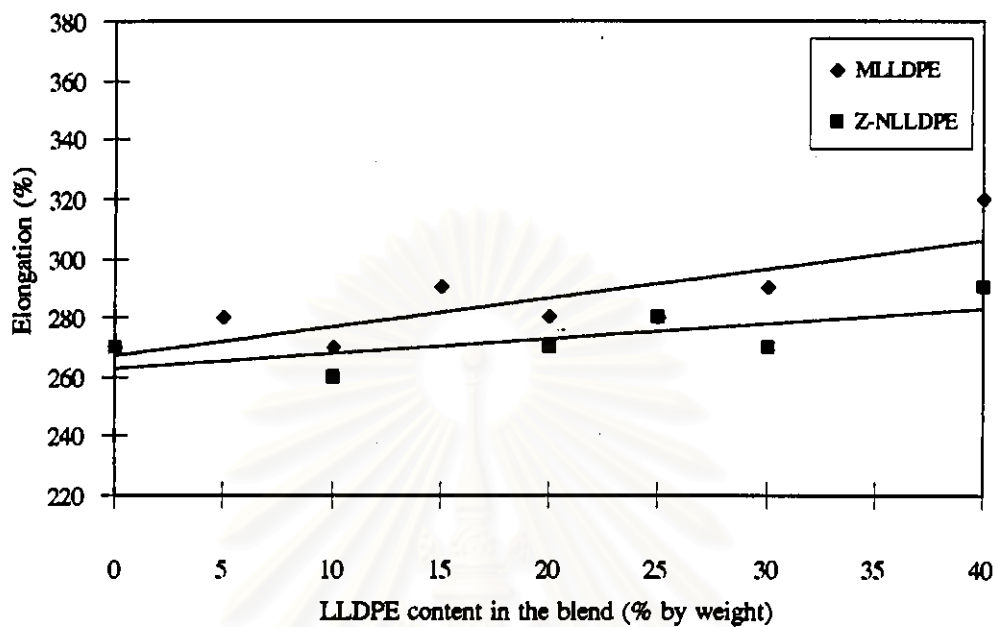


Figure 4.3 : Elongation at break in machine direction of HDPE/LLDPE film

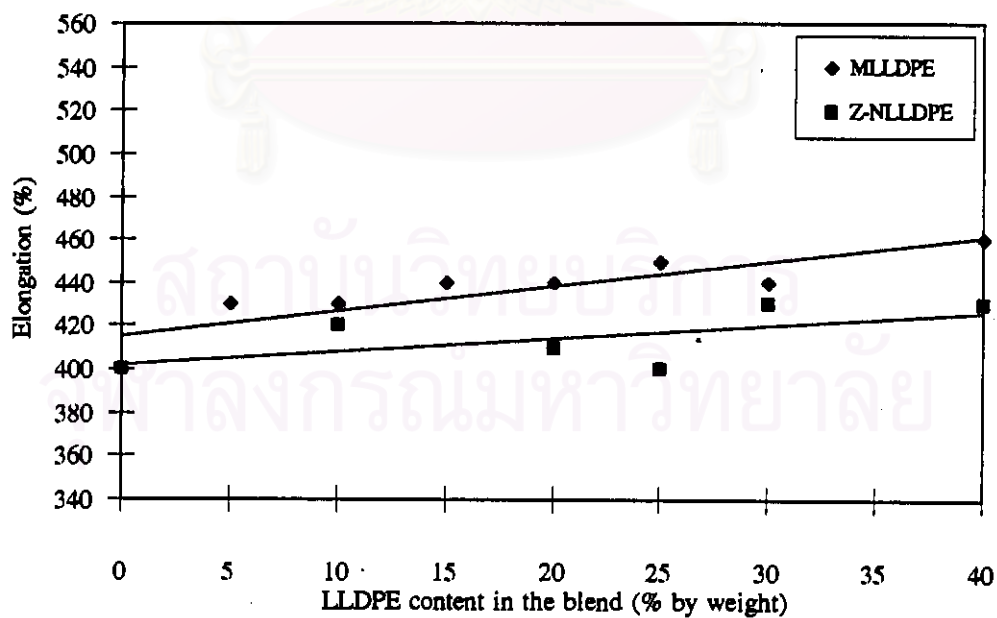


Figure 4.4 : Elongation at break in transverse direction of HDPE/LLDPE film

MLLDPE has higher volume fraction of amorphous phase than Z-NLLDPE as explained in section 4.3.2. HDPE/MLLDPE film should thus have higher elongation at break than HDPE/Z-NLLDPE. Indeed, such behavior Figure 4.3 and 4.4 illustrates.

It can be said that perfect orientation is obtained in the machine direction which is reflected by the lower elongation in the machine direction relative to transverse direction. This explanation can also be applied accounted for the difference in elongation at break of both directions. The higher orientation of molecules along machine direction is stronger than the lower orientation along the transverse direction. Therefore, elongation at break in machine direction is usually lower than the transverse direction.

The industrial film usage does not need the high elongation, therefore, HDPE/MLLDPE film which has higher elongation than HDPE/Z-NLLDPE is exceed the industrial film requirement.

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#### 4.2.3 Film impact strength

When MLLDPE or Z-NLLDPE content in the blend increased, the film impact strength decreased gradually until the LLDPE content reached 30%, the film impact strength seemed almost unchanged with further increasing LLDPE content as shown in Figure 4.5. The other research work reported by A.K.Gupta and et al[15] suggested that LLDPE might not contribute much impact modification of HDPE, because the cohesion between the crystalline and amorphous interphase was poor and the large number of such interphases would need low energy to break the sample.

This illustration corresponded to this study as well Zhao-Y[24] found that both HDPE/MLLDPE and HDPE/Z-NLLDPE can be cocrystallized. The formation of cocrystalline thus may result from the merging of the individual crystalline in the growth process of the crystallization. In this present study, HDPE/Z-NLLDPE film has lower impact strength than HDPE/MLLDPE film, the cause should be said that HDPE/MLLDPE has more complete cocrystallization than HDPE/Z-NLLDPE. The complete cocrystallization come from the branches of MLLDPE can be more included in the crystal lattice during the cocrystallization process[24] while the HDPE/Z-NLLDPE, the side group containing segments of Z-NLLDPE would remain outside the cocrystalline regions in HDPE/Z-NLLDPE blend[25]. Since cocrystallization reduced the quantity of the crystalline due to the merging of the crystalline, then HDPE/MLLDPE has less the crystalline amorphous interphase than HDPE/Z-NLLDPE and confirm in the section 4.3.3. Yong-Man suggested that the impact strength of the blown HDPE films was highly dependent of on the network structure of lamella stacks[20]. As referred in section 4.2.1, HDPE/MLLDPE had less lamella stacks than HDPE/Z-NLLDPE, then HDPE/MLLDPE film should have

higher impact strength than HDPE/Z-NLLDPE film. The impact strength at 30% LLDPE content remained almost unchanged on further addition of LLDPE up to 40%, probably due to the maximum cocrystallization between HDPE and LLDPE. Same as tensile strength, HDPE/MLLDPE film is exceed impact strength for the industrial film.

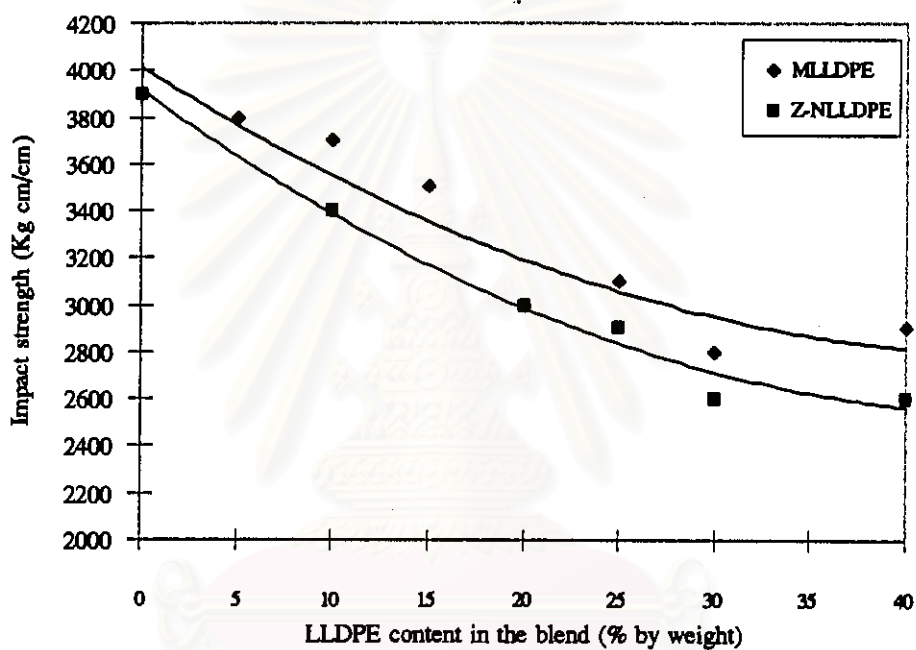


Figure 4.5 : Film impact strength of HDPE/LLDPE film



#### 4.2.4 Stiffness testing

MLLDPE film has been reported to be softer than Z-NLLDPE film[26] but no equipment for softness measurement is available. Instead, the stiffness of the sheet was determined in the present study as shown in the Figure 4.6. With the increase in LLDPE content, the stiffness of blend sheet decreased. In term of softness, this means that the film has more softness. This is true because the amorphous phase in the MLLDPE or Z-NLLDPE contains the flexible chain segment which can respond quickly to the applied stress or load. MLLDPE has higher volume fraction in amorphous phase than Z-NLLDPE, therefore, HDPE/MLLDPE film is softer than HDPE/Z-NLLDPE film.

The stiffness of industrial film is the most important requirement then HDPE/MLLDPE film that is softer than HDPE/Z-NLLDPE film has the profit for industrial film requirement.

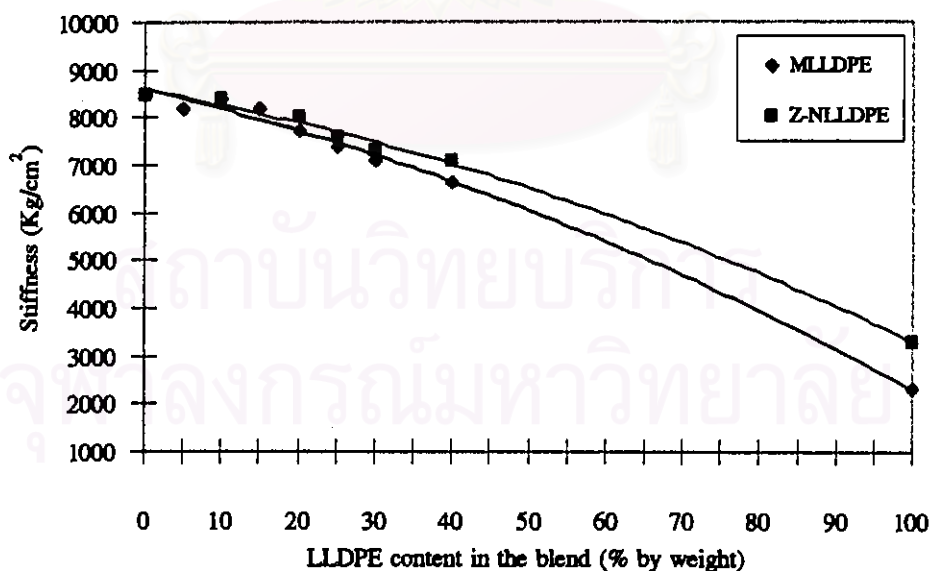


Figure 4.6 : Stiffness of HDPE/LLDPE sheet

#### 4.2.5 Seal strength

HDPE/MLLDPE and HDPE/Z-NLLDPE films were sealed at different temperatures, i.e., 130°C, 140°C and 150°C and subject to the seal strength testing. Figure 4.7 shows the seal strength of each film at different seal temperature. At 5 to 15% of LLDPE content, the higher seal temperature, the more seal strength because it is HDPE rich blend and HDPE film use high seal temperature, normally is 170°C. Thereafter, at 20-25% of LLDPE content, the highest seal strength is about 140°C of seal temperature. With 30-40% of LLDPE content, the highest seal strength is about 130°C due to high LLDPE content. The causes of low seal strength are incomplete seal process and too high temperature which make the resin melt at the seal.

HDPE/MLLDPE has the few advantage in seal strength when compare with HDPE/Z-NLLDPE. Since MLLDPE has small lamella size, the industrial film that is sealed at the bottom of bag will use lower seal temperature if it is made from HDPE/MLLDPE than HDPE/Z-NLLDPE used.

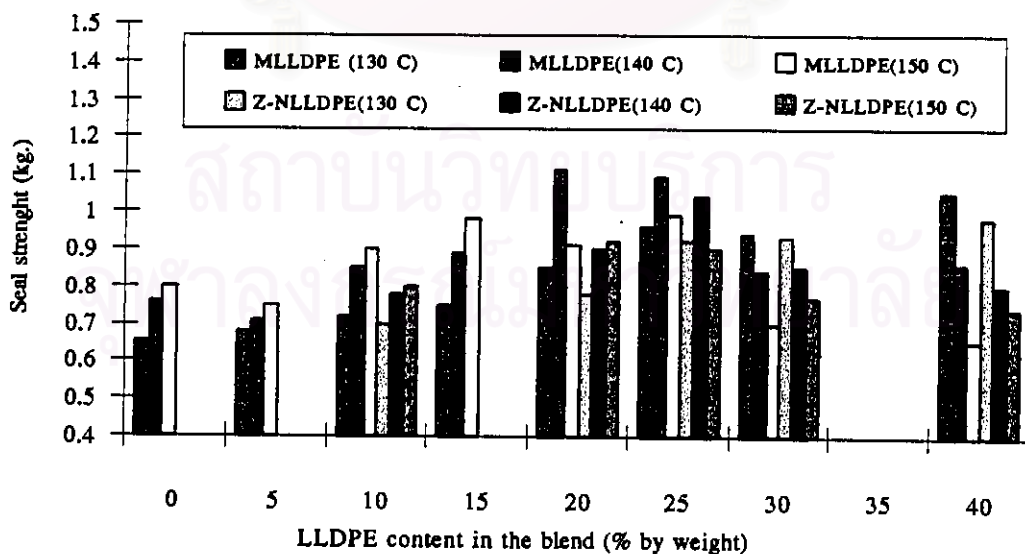


Figure 4.7 : Seal strength of HDPE/LLDPE film

### 4.3 Clarity of film testing

Table 4.1 shows the clarity of HDPE/LLDPE films in terms of light transmittance. The higher transmittance indicates more clarity of the film.

Table 4.1 : The transmittance of HDPE/LLDPE film.

Blend composition (HDPE/LLDPE)	Transmittance of film (%)	
	with MLLDPE	with Z-NLLDPE
100/0	91	91
95/5	91	91
90/10	91	91
85/15	91	91
80/20	91	91
75/25	91	91
70/30	92	92
60/40	92	92

In general the higher density of film is, the less clarity and transmittance of the film shall be. However, the results of both type of films indicate that LLDPE content in the range of this study (0-40%) does not affect the clarity of the film by comparing with HDPE film. It can be stated that all HDPE/MLLDPE blends are rich in HDPE and the cocrystallization that occurs during the film processing is effect to the transmittance of light. The clarity of film cannot be improved with the increasing of MLLDPE content.

To blend HDPE with Z-NLLDPE is to improve the clarity of industrial film and it is satisfy. HDPE/MLLDPE film has the same clarity as HDPE/Z-NLLDPE film, it means that HDPE/MLLDPE clarity can accept for the industrial film using.



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#### 4.4 Sample characterization

This section shows the trend of compatibility, percentage of crystallinity and morphology of the HDPE/MLLDPE blends.

##### 4.4.1 Melt flow index and density

MLLDPE has the higher melt flow index than HDPE, therefore, the increase of MLLDPE content should increase the melt flow index of HDPE/MLLDPE blend. Figure 4.8 shown the influence of MLLDPE content, the melt flow index of the blends increased as the MLLDPE content increased. In principle for mixing materials with different melt flow index, the melt flow index of the blend can be calculated using the equation 4.1[27].

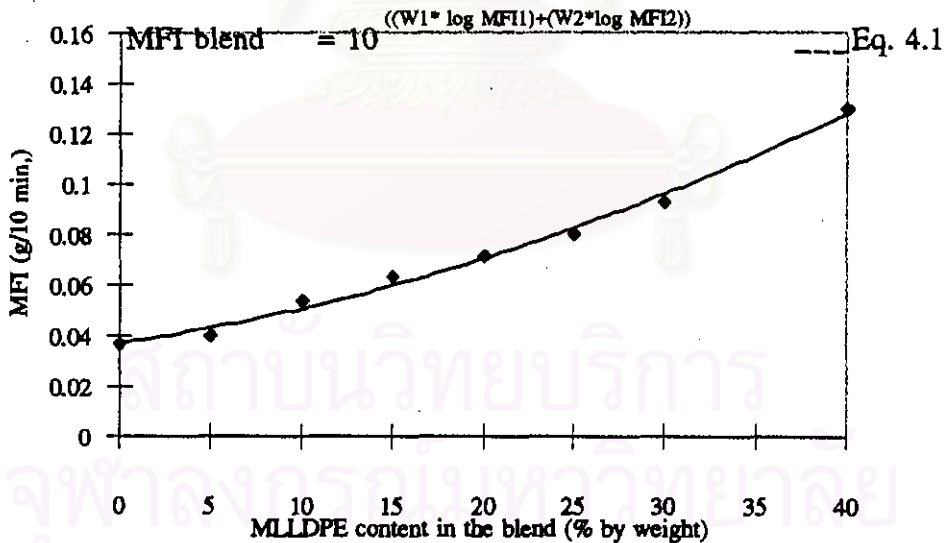


Figure 4.8 : MFI of HDPE/MLLDPE blend

From the data, the melt flow index was in accordance with that from the calculation. Theoretically, it seem to be that the blending was homogenized because the melt flow index was according to the equation as shown in the Table 4.2.

Table 4.2 : Melt flow index of HDPE/MLLDPE blend from measurement and calculation

MLLDPE (% by weight)	Melt flow index (g/10 min.)	
	From measurement	From calculation
0	0.037	0.037
5	0.040	0.043
10	0.054	0.051
15	0.063	0.059
20	0.071	0.069
25	0.080	0.081
30	0.093	0.095
40	0.130	0.129

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The Figure 4.9 shown the density of HDPE/MLLDPE blend. With the increasing of MLLDPE content, the density of HDPE/MLLDPE decreased because MLLDPE has lower density than HDPE. Same as melt flow index, the density of blending can calculate from the equation 4.2[28], as stated by the “rule of mixture”

$$1/D_{\text{blend}} = W_1*(1/D_1) + W_2*(1/D_2) \quad \text{---Eq. 4.2}$$

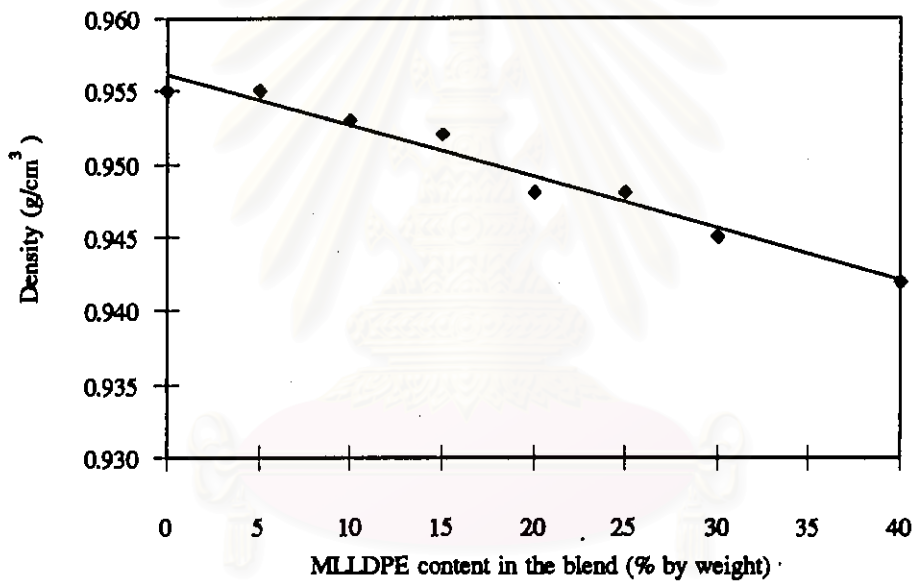


Figure 4.9 : Density of HDPE/MLLDPE blend

The difference between calculated value and empirical value was very small as shown in the Table 4.3, it shown that the blending may be homogenized which confirmed the melt flow index data.

Table 4.3 : Density of HDPE/MLLDPE blend from measurement and calculation

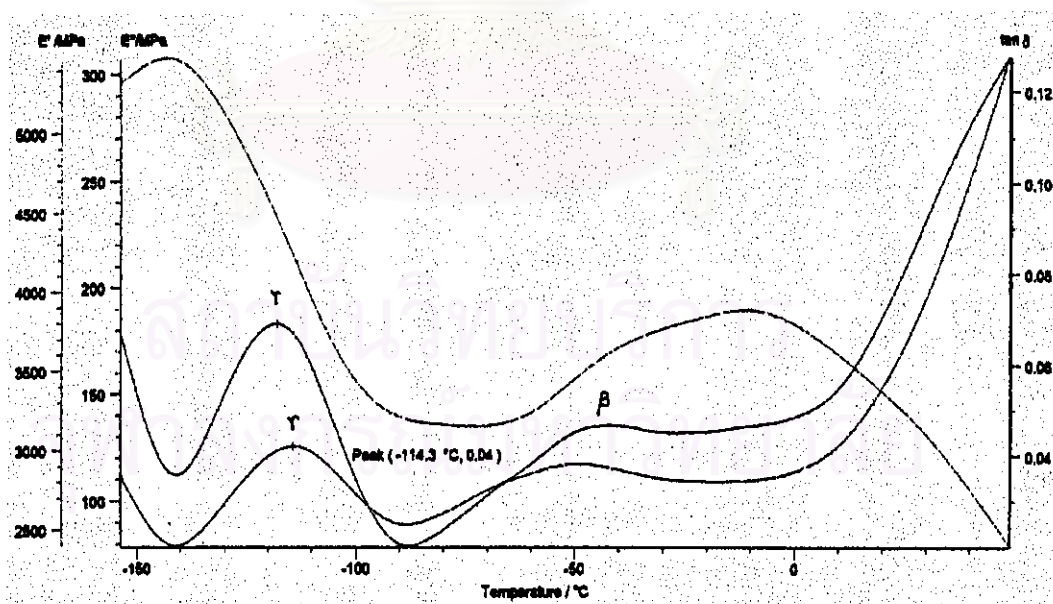
MLLDPE (% by weight)	Density (g/cm <sup>3</sup> )	
	From measurement	From calculation
0	0.955	0.956
5	0.955	0.954
10	0.953	0.952
15	0.952	0.951
20	0.948	0.949
25	0.948	0.947
30	0.945	0.945
40	0.942	0.942

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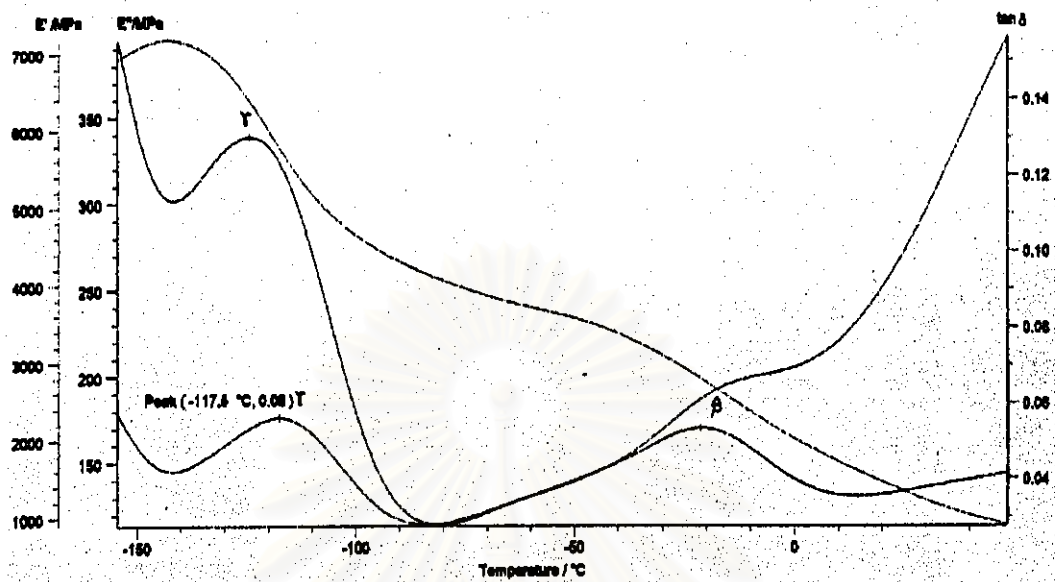
#### 4.4.2 Dynamic mechanical thermal analysis (DMA)

The glass transition temperatures of HDPE, MLLDPE, Z-NLLDPE, HDPE/MLLDPE blend (75/25), and HDPE/Z-NLLDPE (75/25), were investigated by the plots of  $\tan \delta$  versus temperature as shown in Figure 4.10 to 4.14. Their glass transition temperatures are  $-114.3^{\circ}\text{C}$ ,  $-117.5^{\circ}\text{C}$ ,  $-117.1^{\circ}\text{C}$ ,  $-115.4^{\circ}\text{C}$  and  $-114.3^{\circ}\text{C}$ , respectively. In case of HDPE/MLLDPE and HDPE/Z-NLLDPE only one  $T_g$  was observed for each blend. Similar result had been reported by Hoseok Lee and others[19], i.e., the glass transition of HDPE/LLDPE blends were linearly shifted from  $-117^{\circ}\text{C}$  (designated the  $T_g$  of HDPE) to  $-119^{\circ}\text{C}$ . They assumed the miscible blend in the amorphous phase. However, in this research the glass transition temperatures of HDPE, MLLDPE and Z-NLLDPE are very close to each other. It is difficult to discuss miscibility of these blends with this information.



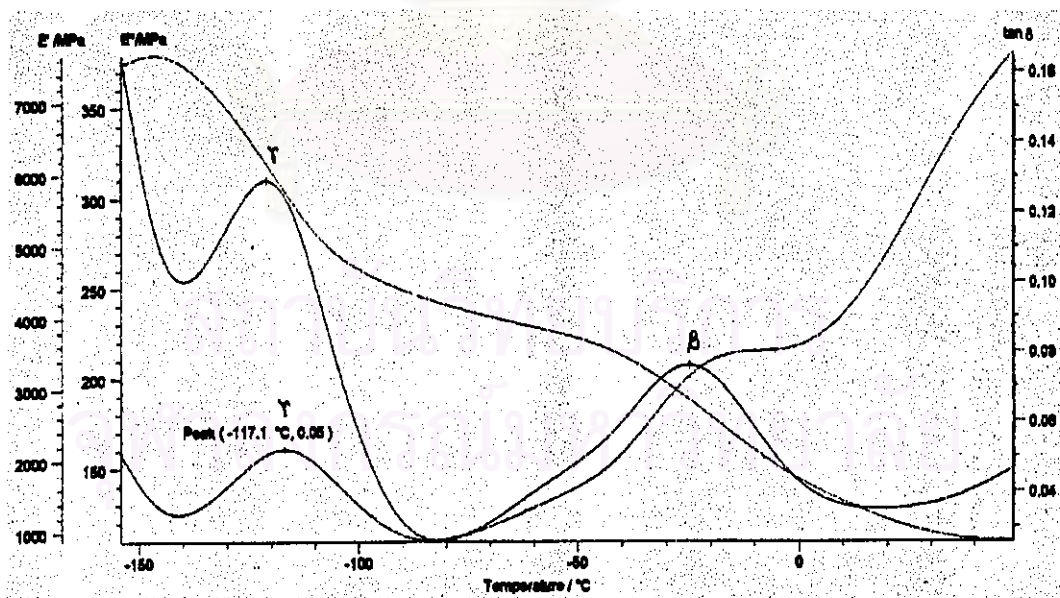
red =  $\tan \delta$ , blue =  $E''$ , and green =  $E'$

Figure 4.10 : DMA of HDPE



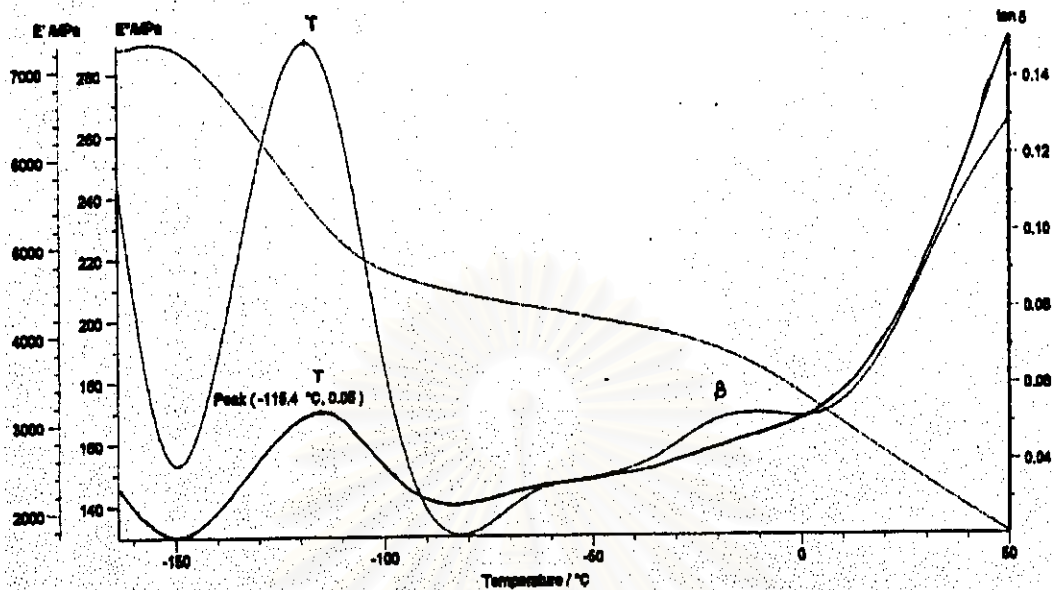
red =  $\tan \delta$ , blue =  $E''$ , and green =  $E'$

Figure 4.11 : DMA of MLLDPE



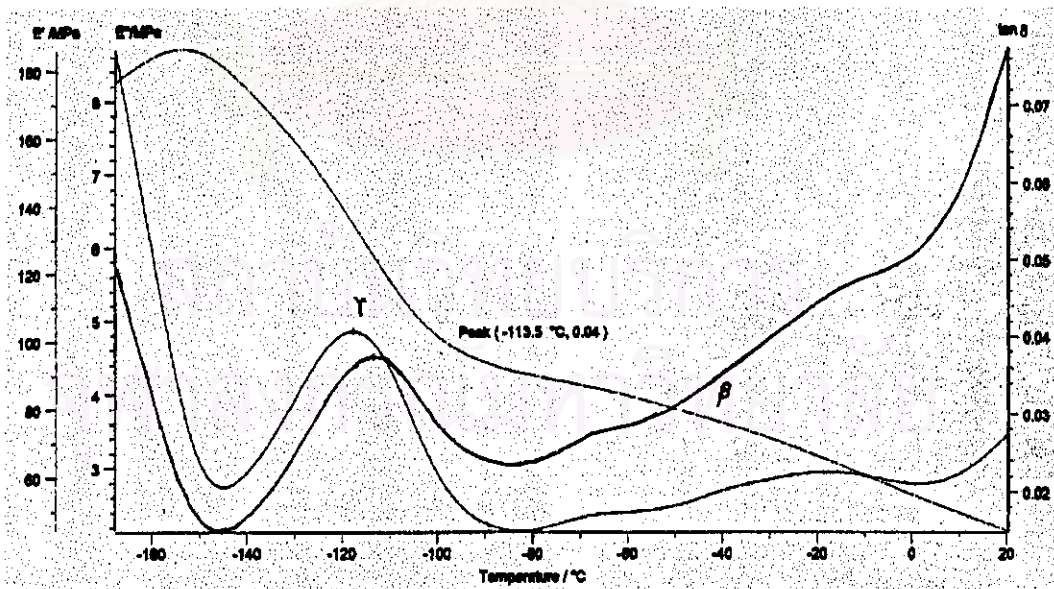
red =  $\tan \delta$ , blue =  $E''$ , and green =  $E'$

Figure 4.12 : DMA of Z-NLLDPE



red =  $\tan \delta$ , blue =  $E''$ , and green =  $E'$

Figure 4.13 : DMA of HDPE/MLLDPE blend (75/25)



red =  $\tan \delta$ , blue =  $E''$ , and green =  $E'$

Figure 4.14 : DMA of HDPE/Z-NLLDPE blend (75/25)

The  $\gamma$  peak of the  $\tan \delta$  maximum peak is the glass relaxation of the  $(\text{CH}_2)_n$  group. That is, the  $\gamma$  relaxation occurs in the amorphous regions and therefore its magnitude is a function of the volume of amorphous polymer[29] with the incorporation of more amorphous species. With the intensity of  $\gamma$  peak, MLLDPE has higher volume fraction of the amorphous than Z-NLLDPE.

The  $\beta$  peak is attribute to the rotation of the side-branching group, specially of the portion of the molecule containing group. On the contrary, the  $\beta$  peak can be observed in Figure 4.10 to 4.14 but their presences are not so obvious visually. To clarify this behavior,  $E''$  should be also analyzed. HDPE/MLLDPE blend has two  $\beta$  peaks, one peak is due to HDPE at about  $-60^\circ\text{C}$  and the other belongs to MLLDPE at about  $-20^\circ\text{C}$ . The  $\beta$  peak of HDPE is due to butene-1, the comonomer and the  $\beta$  peak of MLLDPE belongs to octene-1, the comonomer. If the blend is miscible, only one  $\beta$  peak shall appear. Consequently, it can be concluded that HDPE/MLLDPE blend is immiscible in the amorphous phase.

### 4.3.3 Differential scanning calorimeter (DSC)

DSC studies were carried out for all the blends. Figure 4.15 to 4.21 for HDPE/MLLDPE blends and Figure 4.22-4.24 for HDPE/Z-NLLDPE blends comparing to its individual material, Figure 4.25 to 4.27. The HDPE/MLLDPE and HDPE/Z-NLLDPE appeared only one crystalline peak the same as the previous study by E. Karbasheswoki[30]. He concluded that the HDPE/Z-NLLDPE blending operation was successful because it appeared to be only one “crystalline” peak by using DSC. Consequently, HDPE/MLLDPE and HDPE/Z-NLLDPE blend in this present study are homogenous at every composition.

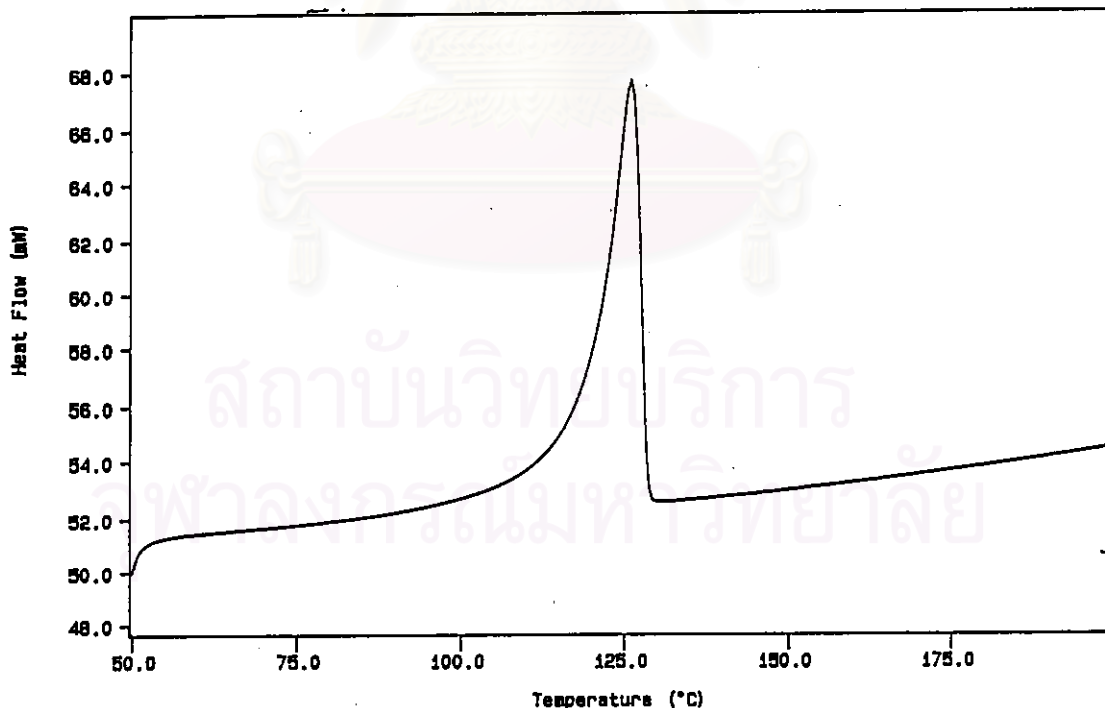


Figure 4.15 : DSC of HDPE/MLLDPE blend 95/5

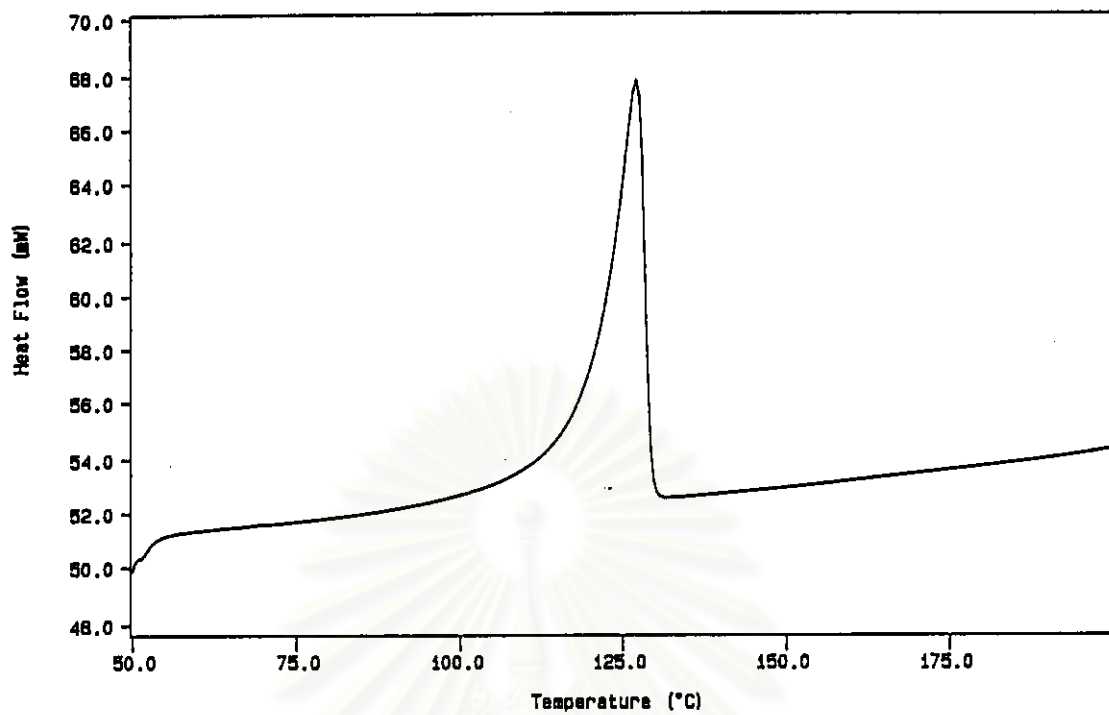


Figure 4.16 : DSC of HDPE/MLLDPE blend 90/10

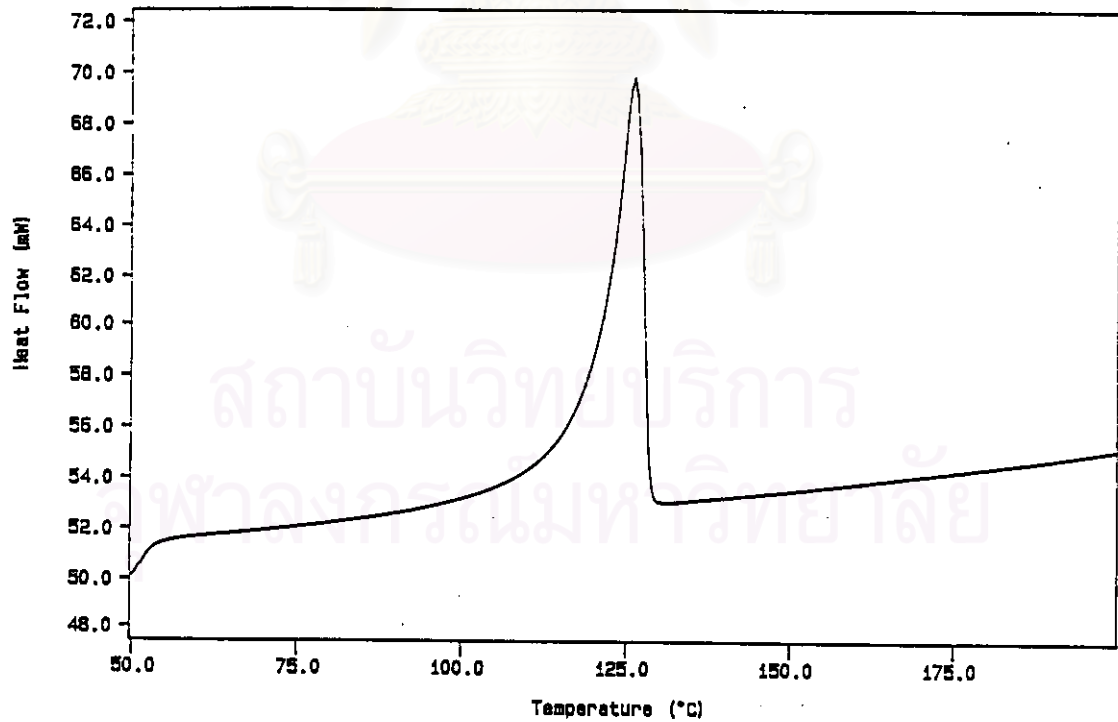


Figure 4.17 : DSC of HDPE/MLLDPE blend 85/15

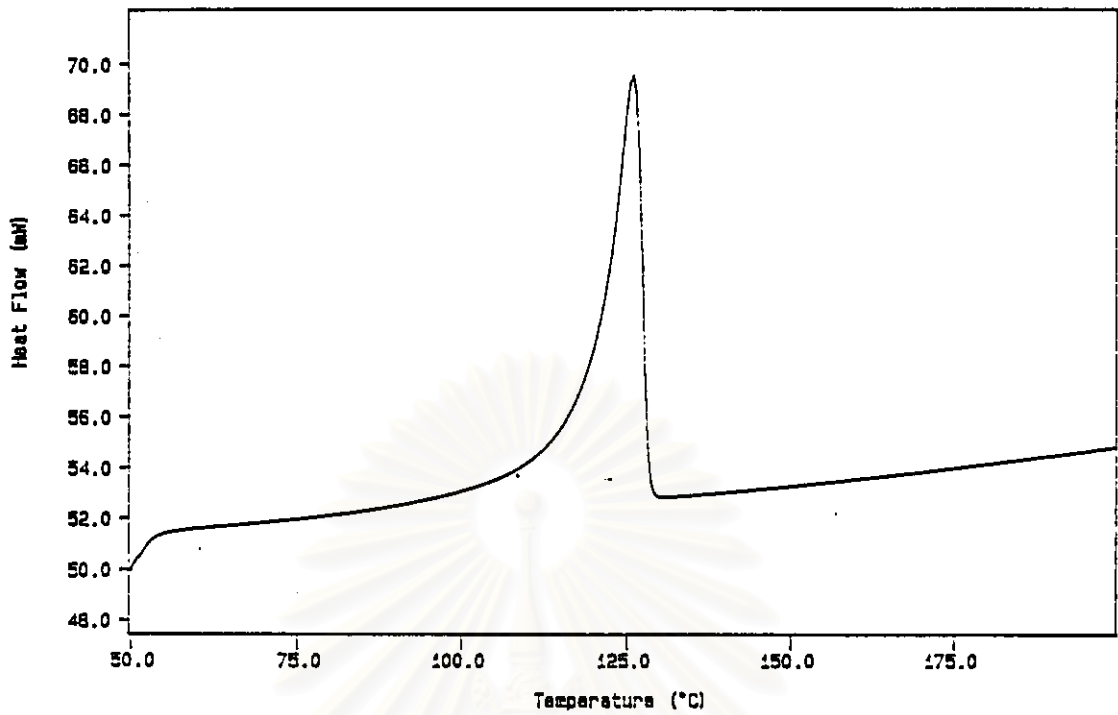


Figure 4.18 : DSC of HDPE/MLLDPE blend 80/20

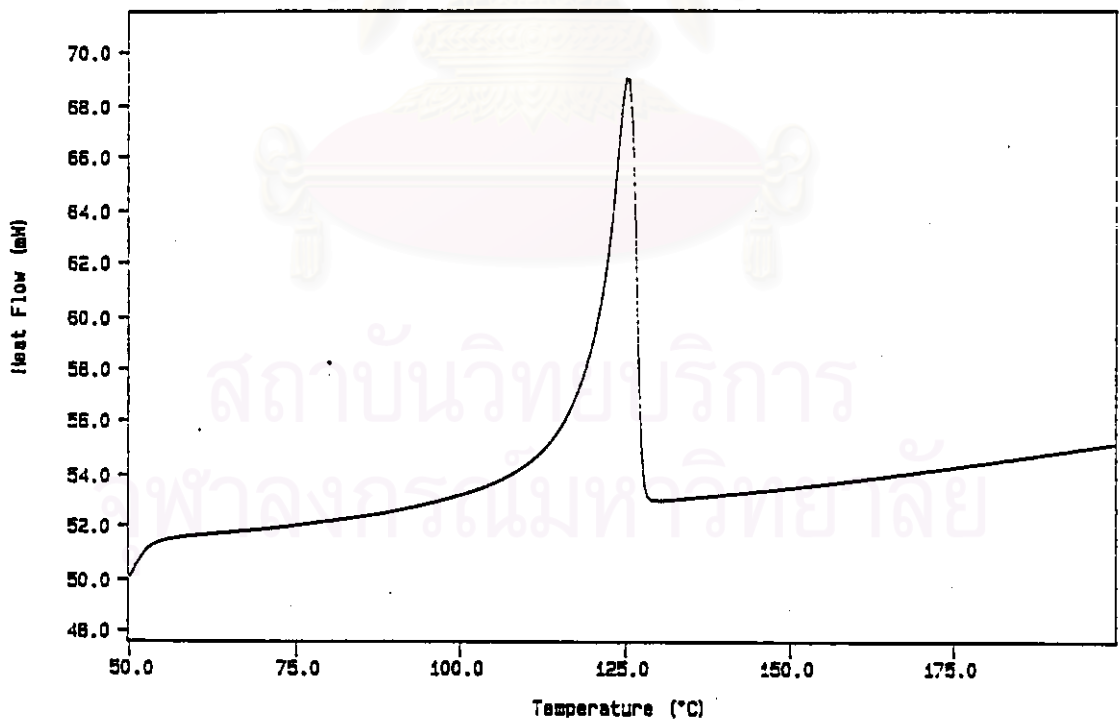


Figure 4.19 : DSC of HDPE/MLLDPE blend 75/25

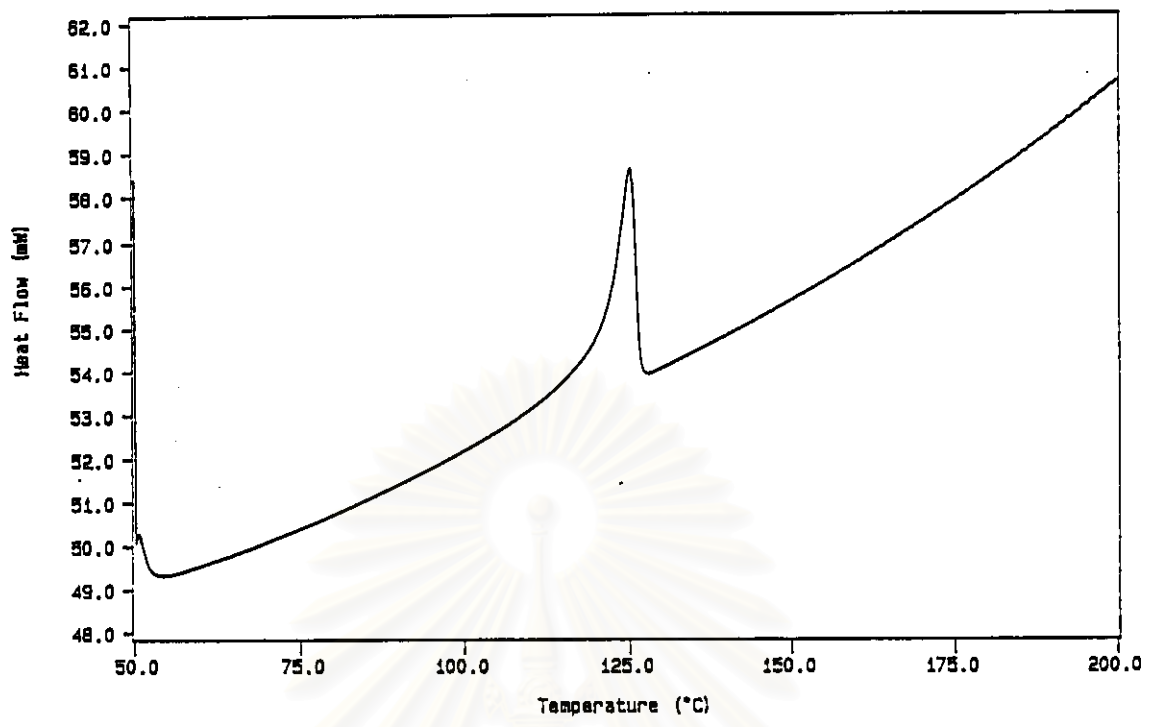


Figure 4.20 : DSC of HDPE/MLLDPE blend 70/30

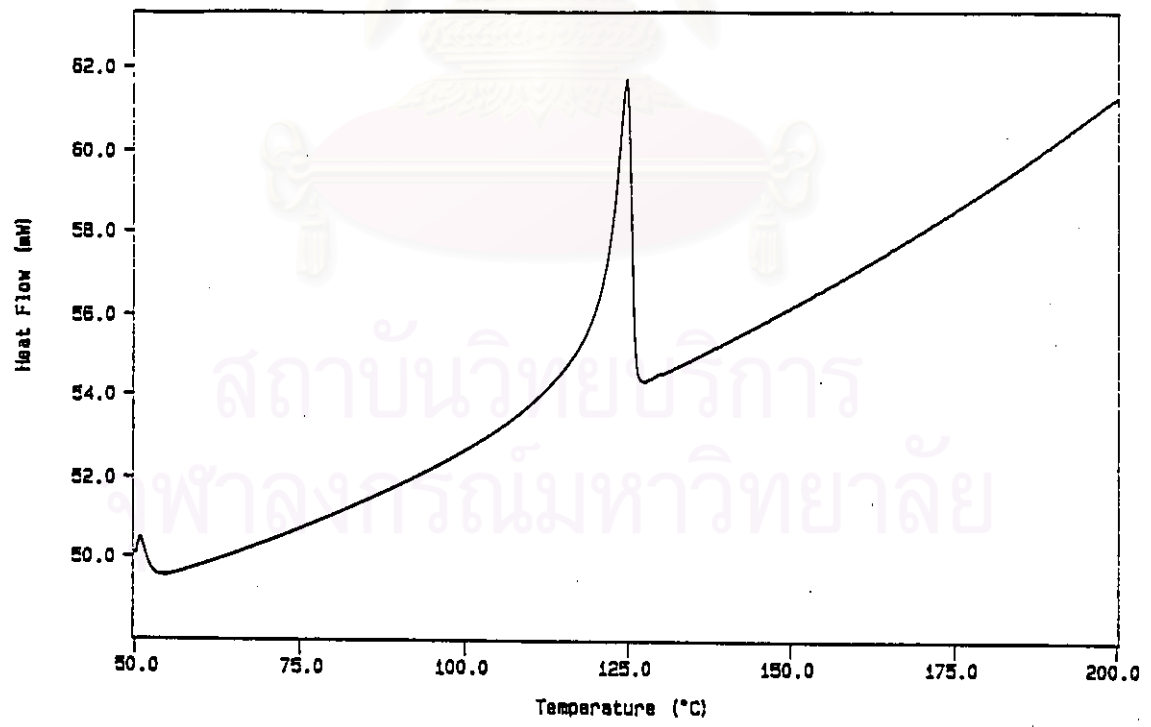


Figure 4.21 : DSC of HDPE/MLLDPE blend 60/40



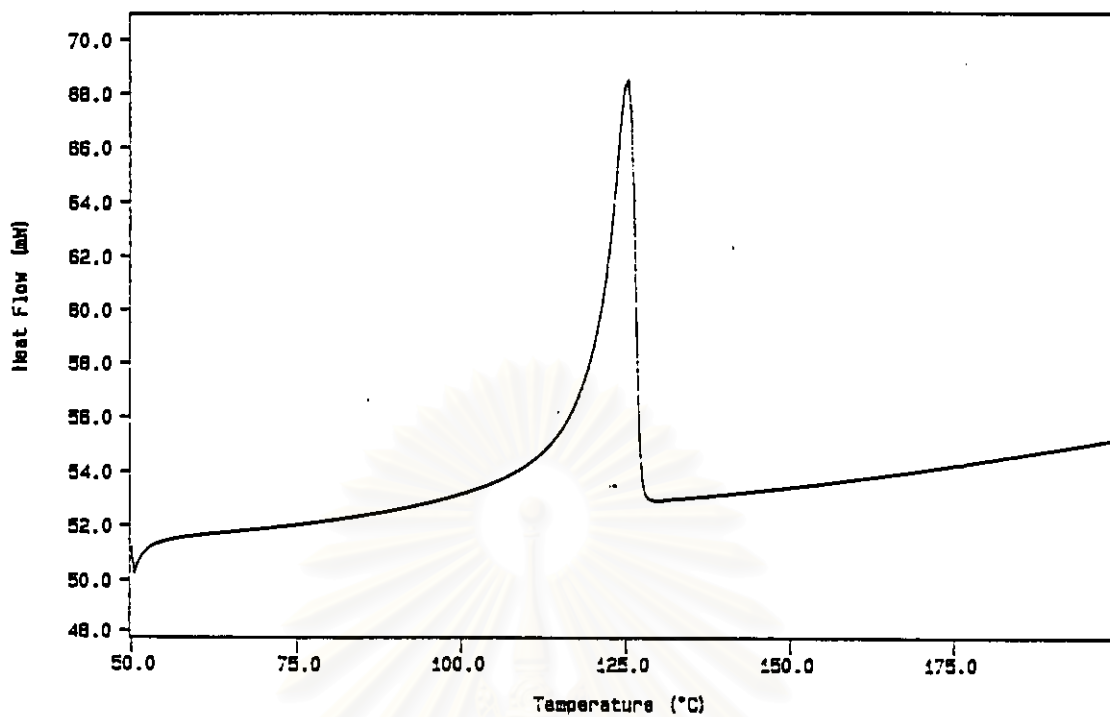


Figure 4.22 : DSC of HDPE/Z-NLLDPE blend 75/25

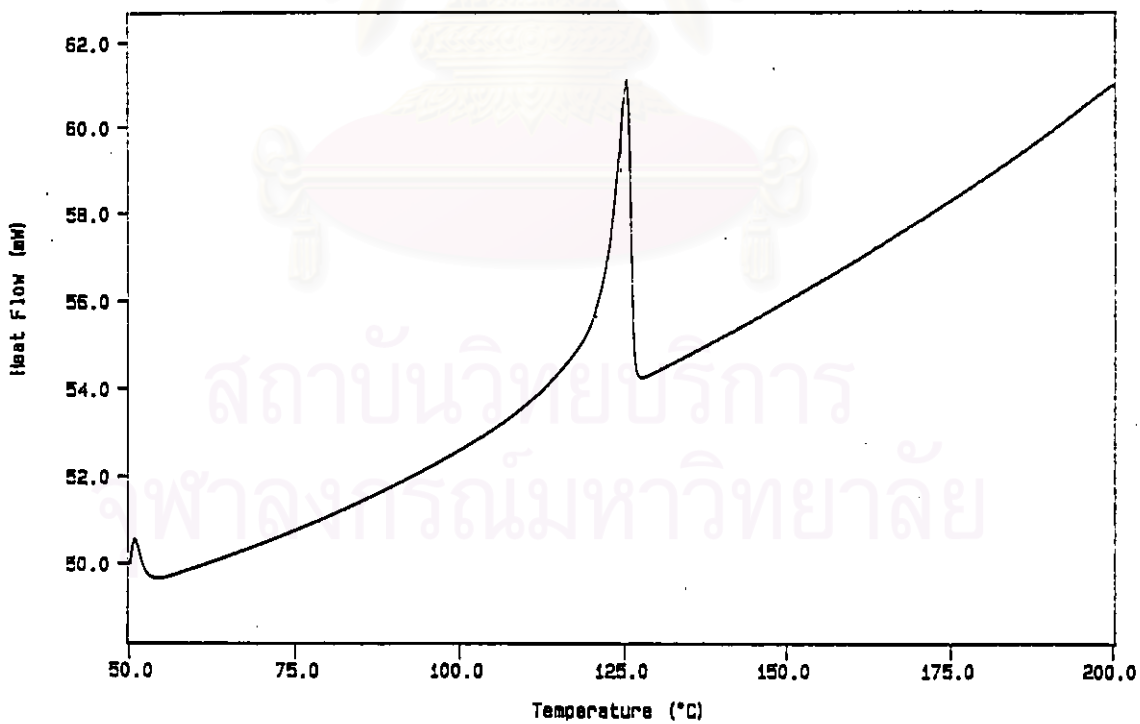


Figure 4.23 : DSC of HDPE/Z-NLLDPE blend 70/30

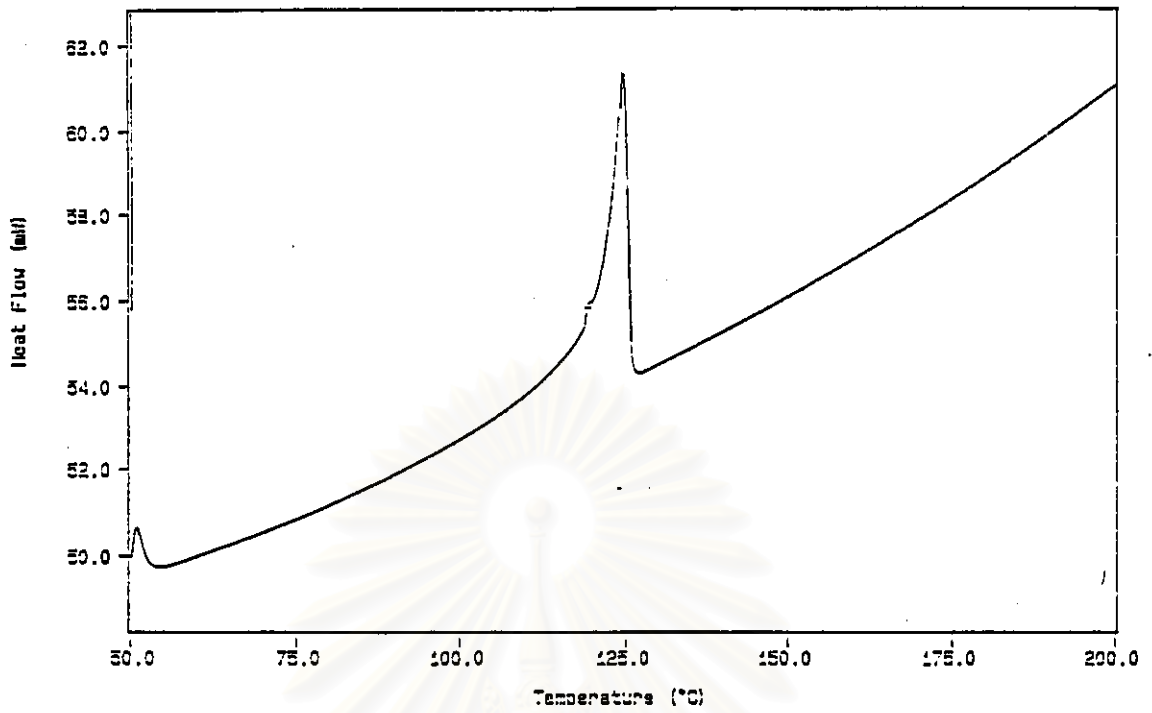


Figure 4.24 : DSC of HDPE/Z-NLLDPE blend 60/40

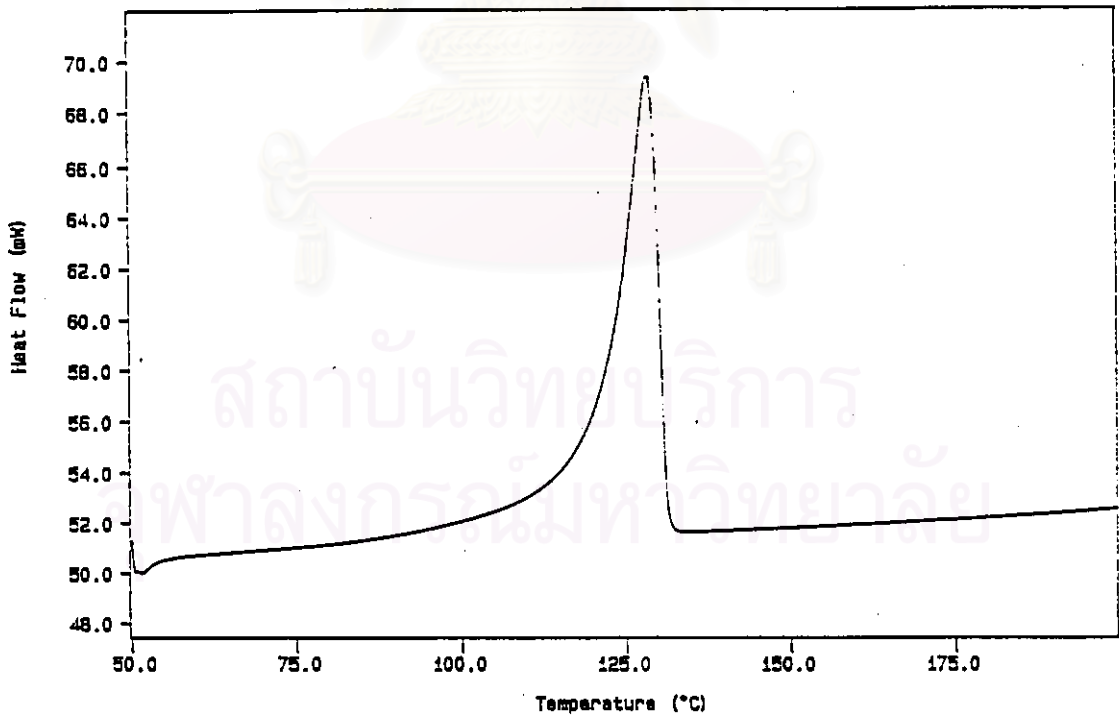


Figure 4.25 : DSC of HDPE

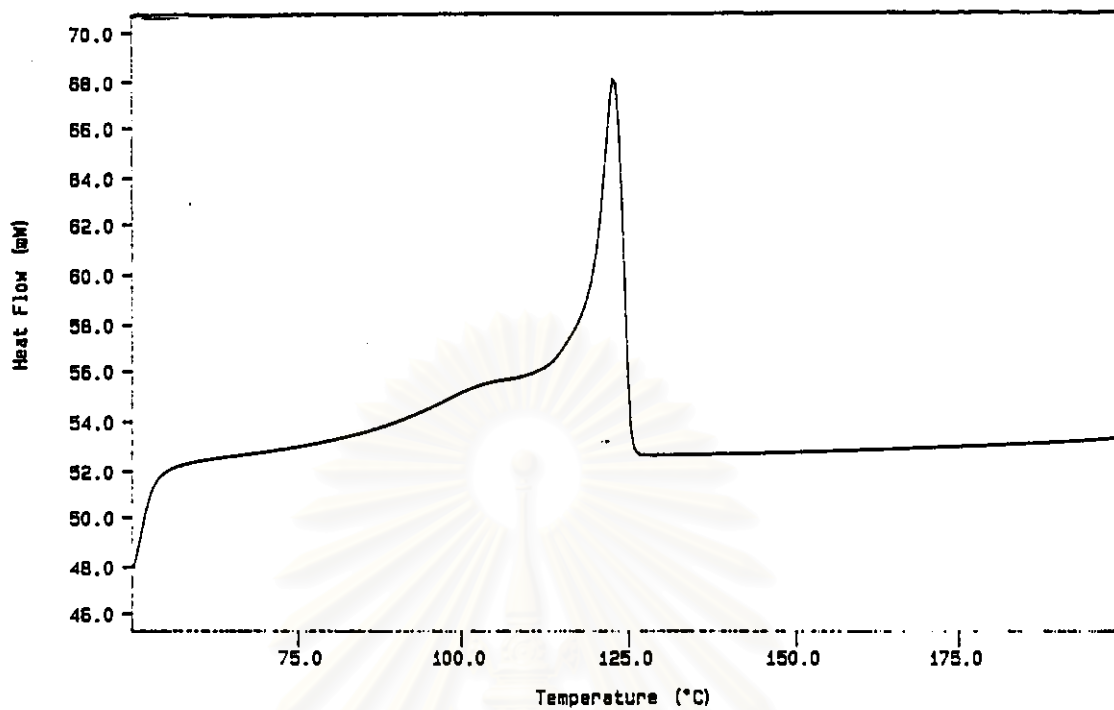


Figure 4.26 : DSC of MLLDPE

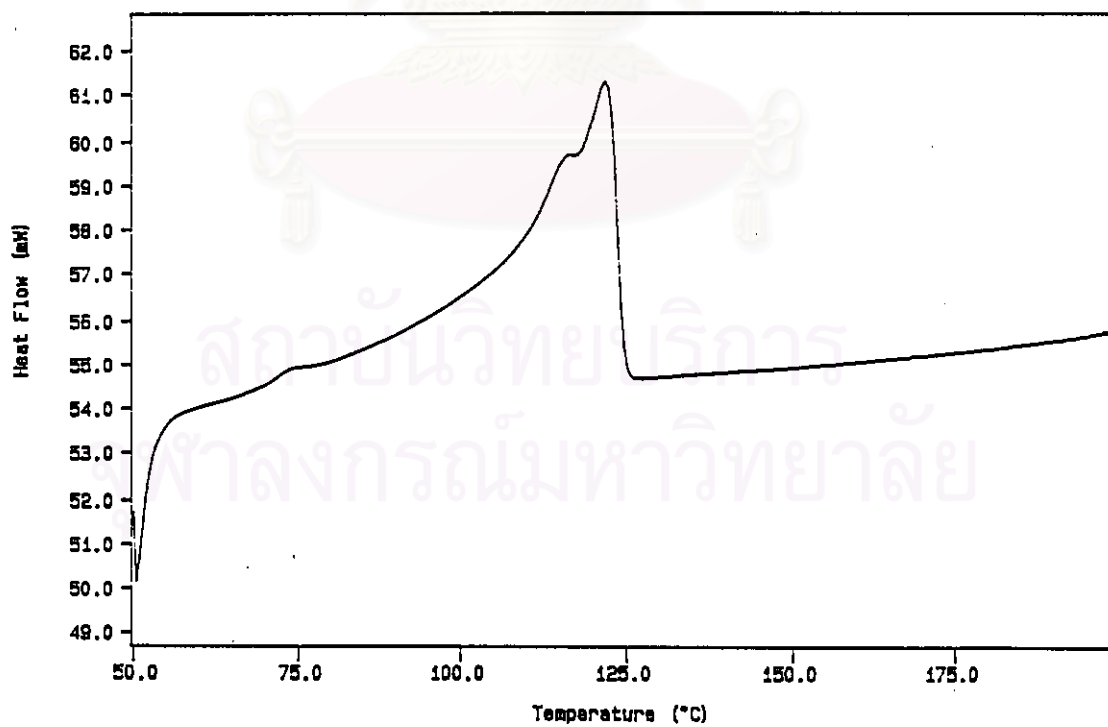


Figure 4.27 : DSC of Z-NLLDPE

The single crystallization exotherm characterizes cocrystallinity of HDPE/MLLDPE or HDPE/Z-NLLDPE. The cocrystallinity of HDPE and LLDPE had been supported by Rana-SK[16]. He revealed that the HDPE/LLDPE (MLLDPE or Z-NLLDPE) blend manifests a single crystallization exotherm which was ascribed to the cocrystallization between two constituting component. The similarity in their chemical structure may be accountable for their affinity toward % crystallinity. With the increasing of MLLDPE content, a single peak was shifted to intermediate between the melting point of the components, thus melt temperature of HDPE/MLLDPE blend decreased linearly by following a simple mixture rule as shown in Figure 4.28. This result is the same as other separate study by Hoseok Lee[19] that HDPE/Z-NLLDPE blend was thought to be miscible in the crystalline phase. In this present study, the conclusion is that HDPE/MLLDPE is miscible blend in crystalline phase.

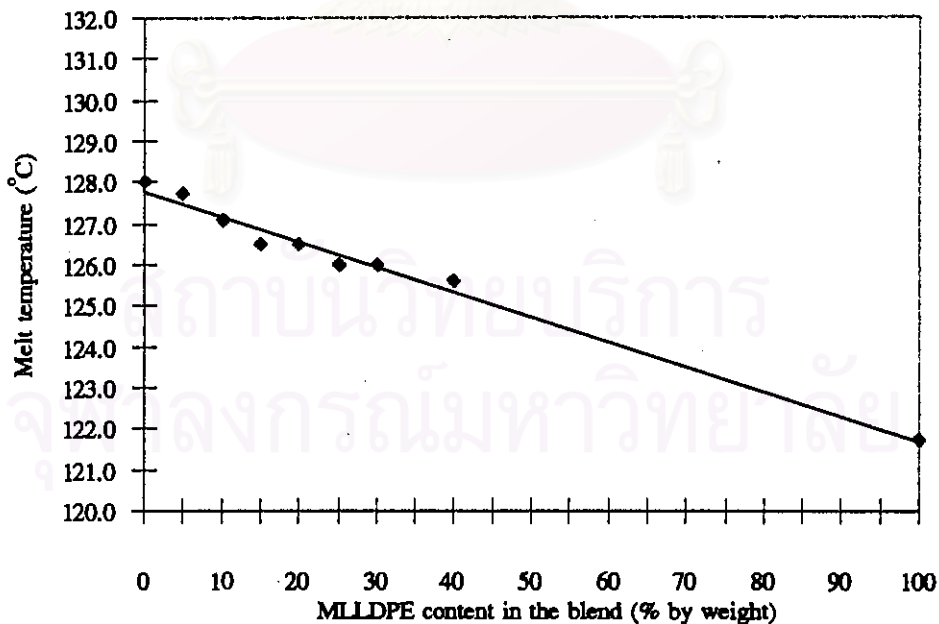


Figure 4.28 : Melt temperature of HDPE/MLLDPE blend

Each DSC of both MLLDPE and Z-NLLDPE, shows two peaks of melt temperature. One of these two peaks probably arises from the other component, the long chain branch compound, which is added to mix with MLLDPE or Z-NLLDPE to improve the processability of LLDPE. MLLDPE has lower melt temperature because MLLDPE has smaller lamella size than Z-NLLDPE which requires lower energy to melt the crystalline. HDPE has higher melt temperature than LLDPE because it has higher crystallinity.

From DSC, the % crystallinity of the blend can be calculated by using the equation 4.3 as shown below.

$$\% \text{ crystallinity} = (\Delta H \text{ of the sample} / \Delta H \text{ of polyethylene}) * 100 \quad \text{--- Eq. 4.3}$$

$$\text{where : } \Delta H \text{ of polyethylene} = 293 \text{ J/g}$$

$\Delta H$  can be calculated from the ratio of area under the endotherm and mass of the sample of DSC scan. The % crystallinity of HDPE/MLLDPE blend decreased with increasing MLLDPE content as shown in Figure 4.29 due to the increase of amorphous phase. By comparing HDPE/MLLDPE to HDPE/Z-NLLDPE with 25% LLDPE content, the former has higher % crystallinity than the latter. It is believed that HDPE/MLLDPE has more cocrystallization than HDPE/Z-NLLDPE.

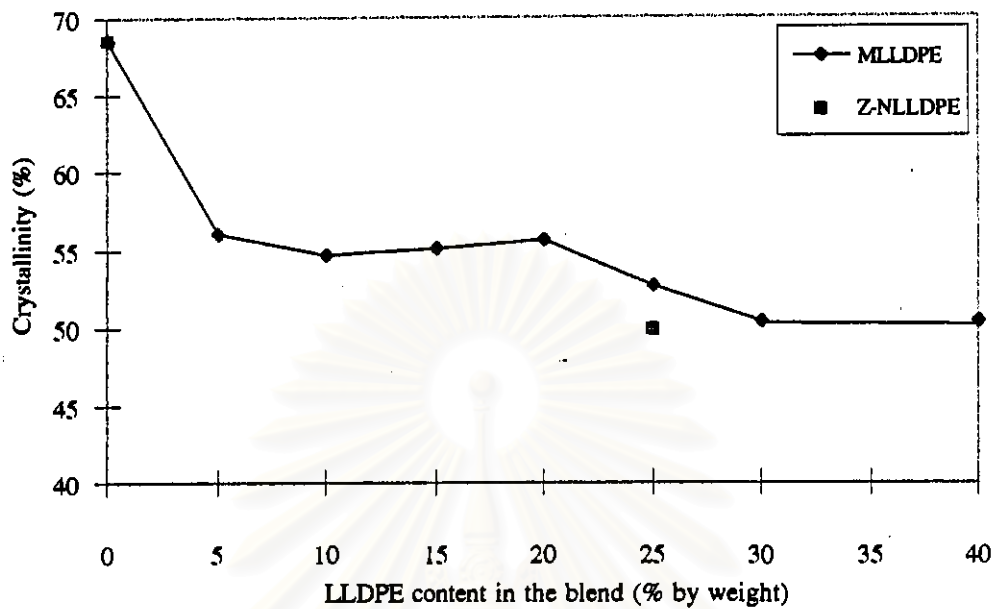


Figure 4.29 : % crystallinity of HDPE/LLDPE blend

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#### **4.5 Downgauging of HDPE/MLLDPE film.**

From section 4.2 and 4.3, HDPE/MLLDPE offered better film performance, including higher tensile strength, elongation and softness than HDPE/Z-NLLDPE. Since MLLDPE has much higher mechanical property than Z-NLLDPE, HDPE/MLLDPE shall be able to blown as thin film. The downgauging of HDPE/MLLDPE film from 25 micron to 15 micron thickness was thus produced. The mechanical properties of HDPE/MLLDPE at 15 micron have been compared with HDPE/Z-NLLDPE film at 25 micron thickness as shown in Table 4.4. HDPE/MLLDPE film at 15 micron thickness still has slightly better mechanical properties than HDPE/Z-NLLDPE film at 25 micron thickness.

From economic point of view, the downgauging film will reduce the amount of the resin for production about 40 percent. In other words, more products can be obtained with the same amount of resins. Although the price of MLLDPE is about 44 US\$/ton higher than Z-NLLDPE or approximately 4 percent different, as shown in Figure 4.30[31]. The production cost of HDPE/MLLDPE film at 15 micron thickness will decrease about 37 percent comparing to HDPE/Z-NLLDPE film at 25 micron thickness. It is not necessary to modify the machine for processing of HDPE/MLLDPE film at 15 micron thickness. Beside with 15 micron thickness, the industrial film will be thinner than usual, this will make it easier to either tying or sealing to the industrial bag produced from such a film.

Table 4.4 : Comparison the mechanical properties of HDPE/MLLDPE at 15 micron thickness to HDPE/Z-NLLDPE at 25 micron thickness.

Blend composition HDPE:LLDPE (% wt)	Film Thickness	Tensile Strength (Kg/cm <sup>2</sup> ) (MD/TD)	Elongation at break (%) (MD/TD)	Impact Strength (Kg cm/cm <sup>2</sup> )
90:10	HDPE/MLLDPE (15 microns)	520/290	240/370	3300
	HDPE/Z-NLLDPE (25 microns)	490/300	260/420	3400
80:20	HDPE/MLLDPE (15 microns)	440/250	280/370	2800
	HDPE/Z-NLLDPE (25 microns)	470/270	270/410	3000
70:30	HDPE/MLLDPE (15 microns)	440/240	310/380	2400
	HDPE/Z-NLLDPE (25 microns)	400/250	270/430	2600



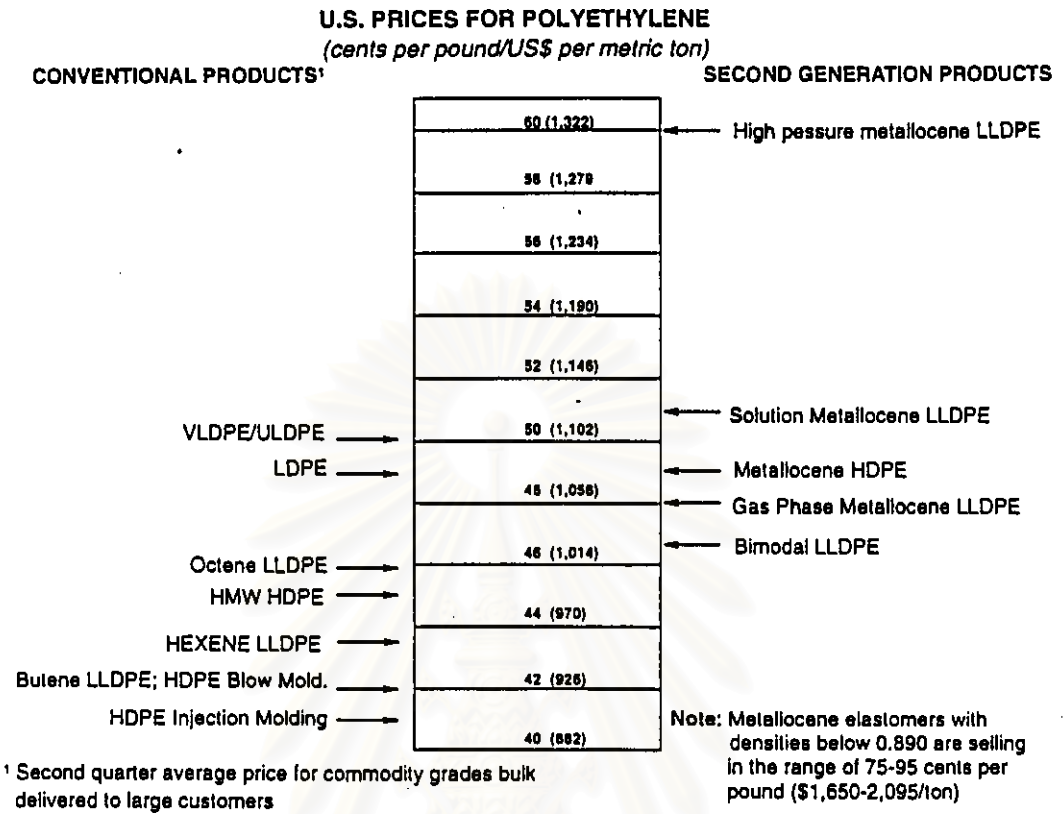


Figure 4.30 : U.S. prices for polyethylene[31]

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