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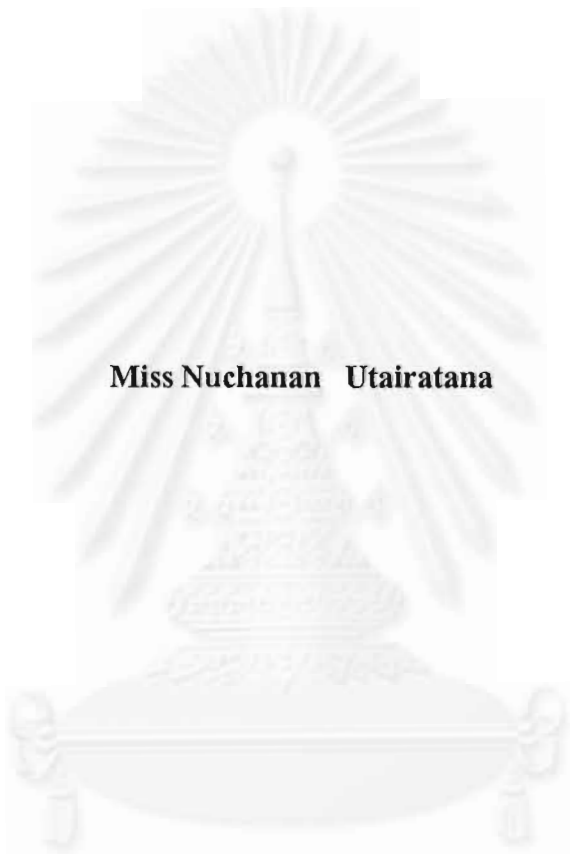
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**THERMAL AND MECHANICAL PROPERTIES  
OF HDPE/LLDPE BLENDS**



**Miss Nuchanan Utairatana**

**A Thesis Submitted in Partial Fulfillment of the Requirements  
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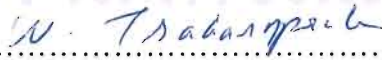
  
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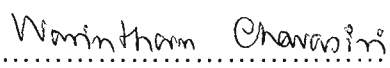
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สำหรับส่วนที่2 ของงานวิจัยเป็นการหา เอชดีพีอี/แอลแอลดีพีอีเบลนด์ ที่มีสมบัติเชิงกลเท่ากับพอลิเอทิลีนชนิดความหนาแน่นปานกลาง (เอ็มดีพีอี) สัดส่วนในการผสมที่ 0-100% โดยน้ำหนักของ เอ็ม-แอลแอลดีพีอี หรือ ซี-แอลแอลดีพีอี ถูกเตรียมโดยการผสมหลอม ด้วยเครื่องหลอมอัดรีดชนิดสกรูเดี่ยวจากพอลิเมอร์ผสมสัดส่วนต่างๆ ที่เตรียมขึ้นเล็กน้อยที่ให้ผลทดสอบของ ดัชนีการไหล และ ความหนาแน่นที่ใกล้เคียงกับเอ็มดีพีอี เพื่อทำการเป่าขึ้นรูปฟิล์ม ที่ความหนา 40, 60, และ 80 ไมครอน ฟิล์มทั้งหมดถูกนำไปทดสอบสมบัติเชิงกล ผลการวิจัยพบว่า เอชดีพีอี/เอ็ม-แอลแอลดีพีอีฟิล์ม และ เอชดีพีอี/ซี-แอลแอลดีพีอีฟิล์ม มีสมบัติเชิงกลเท่ากับเอ็มดีพีอีฟิล์ม

ภาควิชา \_\_\_\_\_  
สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์  
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## 4073412023 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEY WORD: LINEAR LOW DENSITY POLYETHYLENE / HIGH DENSITY POLYETHYLENE /  
METALLOCENE POLYETHYLENE / HEAVY DUTY FILM

NUCHANAN UTAIRATANA : THERMAL AND MECHANICAL PROPERTIES OF

HDPE/LLDPE BLENDS. THESIS ADVISOR: ASSOC. PROF. SUPAWAN

TANTAYANON, Ph.D. THESIS CO-ADISOR: PAILIN CHUCHOTTAWORN, Ph.D.

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High density polyethylene (HDPE)/metallocene linear-low density polyethylene (m-LLDPE) blends and high density polyethylene/conventional (Ziegler-Natta) linear low-density polyethylene (c-LLDPE) blends were prepared at various compositions. The first part of this study involved these blends by melt mixing in a single screw extruder with the composition of 0-100% by weight of m-LLDPE or c-LLDPE and HDPE. Thermal properties of each blend had been investigated to elucidate miscibility by using a differential scanning calorimeter (DSC) and a dynamic mechanical thermal analyzer (DMTA). The blend composed of 60-100% by weight of m-LLDPE or c-LLDPE was separately blown to the heavy duty films with 150, 165, and 180 micron thickness. All these films were subjected not only to the mechanical testing, i.e., tensile strength, elongation at break, impact resistance, and seal strength but also to optical testing for film clarity. These results indicated that HDPE/c-LLDPE and HDPE/m-LLDPE blends were miscible in both crystalline and amorphous phases. The mechanical properties of all HDPE/m-LLDPE films were superior to HDPE/c-LLDPE films at the same composition and c-LLDPE films. The downgauging of HDPE/m-LLDPE film was applicable due to the better mechanical properties of HDPE/m-LLDPE films at 90% of m-LLDPE with 150 or 165 micron thickness than c-LLDPE films at 180 micron thickness.

The second part of this study was to match the mechanical property of HDPE/LLDPE blend with medium-density polyethylene (MDPE). The compositions of 0-100% by weight of m-LLDPE or c-LLDPE were prepared by melt mixing in single screw extruder. Several blends of HDPE/m-LLDPE and HDPE/c-LLDPE blends at the composition which showed the same melt flow index (MFI) and density with MDPE were selected for blowing as the films with 40, 60, and 80 micron thickness. All these films were subjected to the mechanical testing. The results revealed that the equivalent mechanical properties of HDPE/m-LLDPE films and HDPE/c-LLDPE films to MDPE films of the same thickness can be achieved.

ภาควิชา \_\_\_\_\_

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

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# CHAPTER I

## INTRODUCTION



### 1.1 General introduction

There are many reasons for blending polymer system. However, the main reason for blending is economy. By the technique of blending, polymeric materials can be produced at a lower cost while their property specifications still meet those set by the users. The quality of blend is either the same as or superior to the existing constituent materials in the market. Users of polymer blends will enjoy the cost saving advantage.<sup>1</sup> In general, in the view of economy, reasons for blending polymers can be listed as follows:-

1. Developing materials with a full set of desired properties.
2. Formulating a high performance blend from synergistically interaction polymer.
3. Adjusting the composition of the blend to customer requirements.
4. Recycling industrial and/or municipal plastics scraps.

A vast amount of the blends in linear low-density polyethylene (LLDPE) with conventional polyolefins especially high-density polyethylene (HDPE) has been used commercially in the agricultural applications and packaging industry as a form of extrusion-blown film. LLDPE contains generally a 1-butene or 1-hexene or 1-octene comonomer controlled by the Ziegler-Natta catalyst. Recently, LLDPE is made with the higher percentage of the above-mentioned comonomer which is uniformly distributed using the metallocene catalyst. Although many research works have already been done regarding LLDPE made by the Ziegler-Natta catalyst, study of the recent modified LLDPE made by the metallocene catalyst still needs to be done.

The large segment of polyethylene usage is in the packaging area. Thick gauge, heavy duty films are used to make strong, cost-effective, and often visually appealing bags and wraps for packaging a variety of consumer and industrial items including salt, lawn and garden supplies, bulk food, fertilizers, plastic resins, and agricultural products.<sup>2</sup> The superior toughness of films made from metallocene catalyzed polyethylene is well known. Economics and environmental issues are causing converters to look for downgauging which is now possible with metallocene polyethylene. Many converters and end users have the impression that thinner and softer films give the reduced toughness. The challenge is to develop stiffer films at thinner gauges which have equal toughness as their thicker gauge version.

Films for heavy duty bag applications typically range in thickness from 100  $\mu$  to 250  $\mu$ . Since much of market growth in this application involves replacing paper construction bag with plastic, balancing the paper like stiffness with adequate physical performance is the key success for heavy duty bag film. A route to achieve this balanced performance is to add HDPE to LLDPE to increase the film stiffness to the desired level. Furthermore, replacing the conventional LLDPE (Ziegler/Natta LLDPE ; c-LLDPE) with metallocene catalyzed LLDPE (m-LLDPE) will enhance the film strength to enable significant downgauging while assuring consistent properties performance.

Recently production of new polymers with dedicated polymerization at commercial volume has disadvantage due to high value of investment and production cost. The rapid progress in the polymer blend industry is attributed to its relatively short duration associated with the development and its low investment cost. Unlike a polymerization plant for a homopolymer or a copolymer, the production of polymer blends can be a medium scale industry. This is because it requires only a few sets of equipment which are generally not too costly. Furthermore, certain equipment

nowadays offers a variety of modifications in which the equipment users can choose to best suit their particular needs. So, there are abundant opportunities to produce or to develop many kinds of polymer blends. Polyethylene has many characteristics in terms of types and contents of comonomers. The densities of polyethylenes vary among 0.910 to 0.935, 0.920 to 0.930, about 0.940, and 0.950 to 0.970 g/cm<sup>3</sup>; these are respectively designated as low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), medium-density polyethylene (MDPE), and high-density polyethylene (HDPE).<sup>3</sup> Those of different density polyethylene require many steps of polymerization. Considering the investment cost of commercial polyethylene manufacturing, it is advisable to use a production of polymer blend instead of polymerization. Therefore, blending of HDPE/LLDPE at variable range of composition has the potential to displace the costly medium density polyethylene (MDPE) in long run.

## **1.2 The objectives of the research**

This research is aimed to investigate the blending of HDPE/LLDPE by comparing the use of metallocene linear low density polyethylene (m-LLDPE) with conventional Ziegler-Natta linear low density polyethylene (c-LLDPE) with the following goals.

1.2.1 The quality demand of heavy duty film application and downgauge opportunities

1.2.2 Replacement of the commercially available medium-density polyethylene (MDPE)

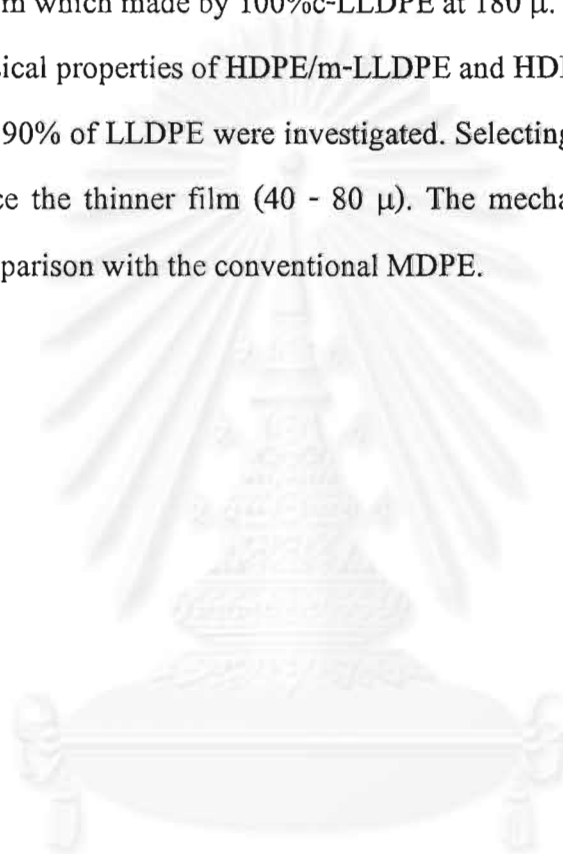


### 1.3 Scope of research

This research will focus on two topics as the following.

1.3.1 Using the blending of HDPE with m-LLDPE and c-LLDPE at the range of 60% to 90% of LLDPE produced the heavy duty film at various film thicknesses (150 - 180  $\mu$ ). The thermal behavior and mechanical properties were investigated for comparison to the film which made by 100%c-LLDPE at 180  $\mu$ .

1.3.2 The physical properties of HDPE/m-LLDPE and HDPE/c-LLDPE blend at the range of 10% to 90% of LLDPE were investigated. Selecting the ratio at desirable properties to produce the thinner film (40 - 80  $\mu$ ). The mechanical properties were investigated for comparison with the conventional MDPE.



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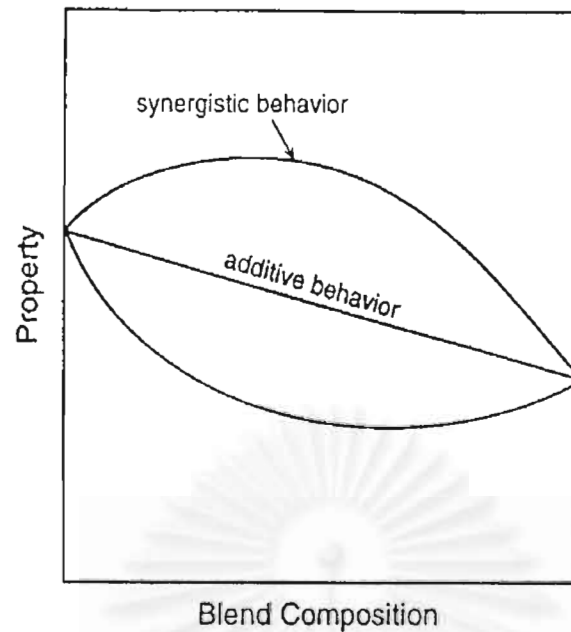
## CHAPTER II

### THEORY

#### 2.1 Polymer blend

The blending of two or more polymers has become an increasingly important technique for improving the cost-performance ratio of commercial plastics. For examples, blending may be used to reduce the cost of an expensive thermoplastics, to improve the processibility of a high temperature or heat sensitive thermoplastics, or to improve impact resistance. Commercial blends may be homogeneous, phase separated, or a bit of both. Whether a particular polymer blend will be homogeneous or phase separated depends upon many factors, such as the kinetics of the mixing process, the processing temperature, and the presence of solvent or other additives.

Properties of miscible polymer blends may be intermediate between those of the individual components (i.e., additive behavior), as is typically the case for  $T_g$ . In other cases, blend properties may exhibit either positive or negative deviation from additivity, as illustrated by Figure 2.1. For example, both modulus and tensile strength of miscible polymer blends exhibit a small maximum at some intermediate blend composition, while impact strength and permeability will normally go through a broad minimum. This latter behavior has been attributed to a loss in free volume corresponding to a negative volume change of mixing ( $\Delta V_m$ ) due to favorable interactions between blend polymers.<sup>4</sup>



**Figure 2.1:** Illustration of three types of behavior for the dependence of miscible blend composition.

## 2.2 Determination of polymer/polymer miscibility

In the thermodynamics, “miscibility” means single phase down to molecular level. In the pragmatic sense, miscibility means that system appears to be homogeneous in the type of test applied in the study, i.e., it is defined in term of degree of dispersion.

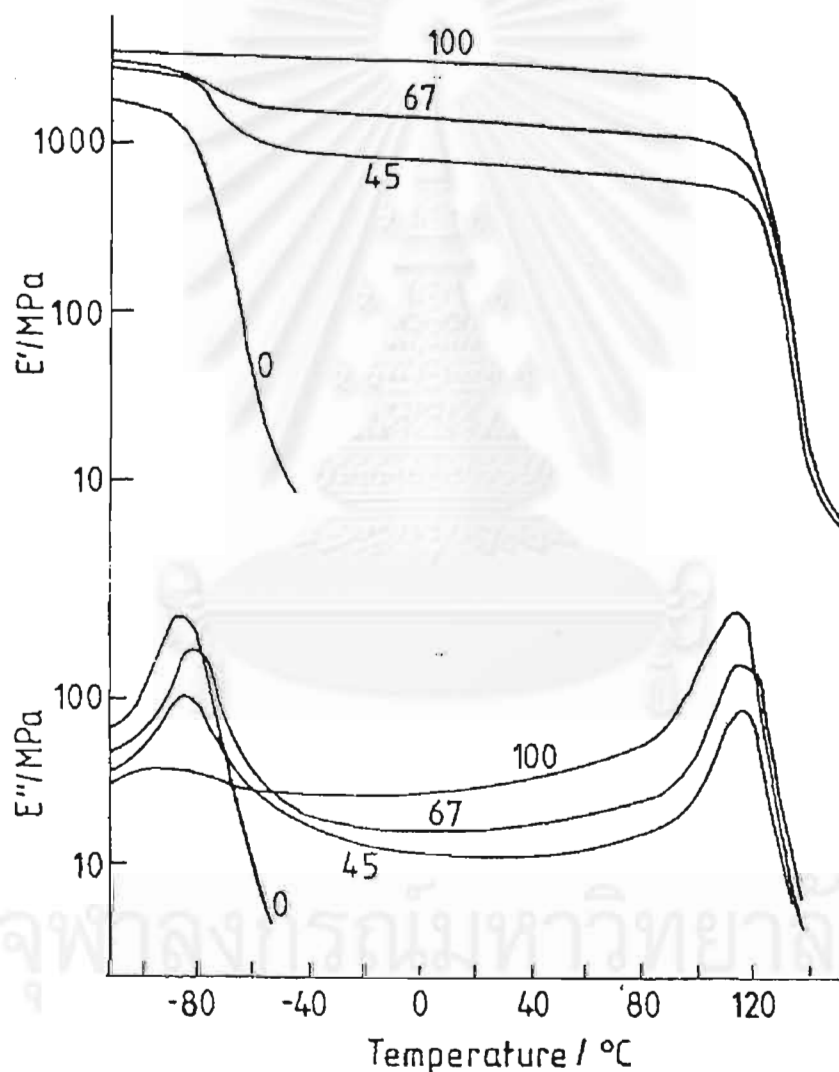
The correlations between phase equilibria, miscibility under processing conditions and  $T_g$  are elusive.  $T_g$  is a good tool for obtaining information, but as any tool, it must be used properly. The glass contains the slowly dissipating memories of the previous treatment of the system, viz. mixing and cooling. Since both the way the blend is prepared and the rate with which it is brought to the initial test condition affect the morphologies stress distribution, different conclusion can be drawn for the same

blend composition, depending on the sample treatments. To conclude the discussion on DSC/DTA determined of polymer blends it is appropriate to add that for immiscible blends very seldom were two  $T_g$ 's recorded for compositions containing less than 10 to 20 wt% of the disperse phase. This experimental range of resolution depends on the difference between  $T_g$  of the two polymers;  $\Delta T_g = T_{g1} - T_{g2}$ . In addition, since the width of the glass transition, TW, can be as large as 40 °C (for systems approaching immiscibility), as a method of assessment of miscibility should not be used for systems with  $\Delta T_g \leq TW/2 \simeq 20$  °C.<sup>5</sup>

The reasons for using the dynamic methods are much broader than the determination of  $T_g$ . Knowledge of moduli (or complex dielectric parameter) are essential for proper application of any material.<sup>5</sup> In addition, dynamic spectra allow calculation of the relaxation times providing the basic information about the mobility of affected segments.

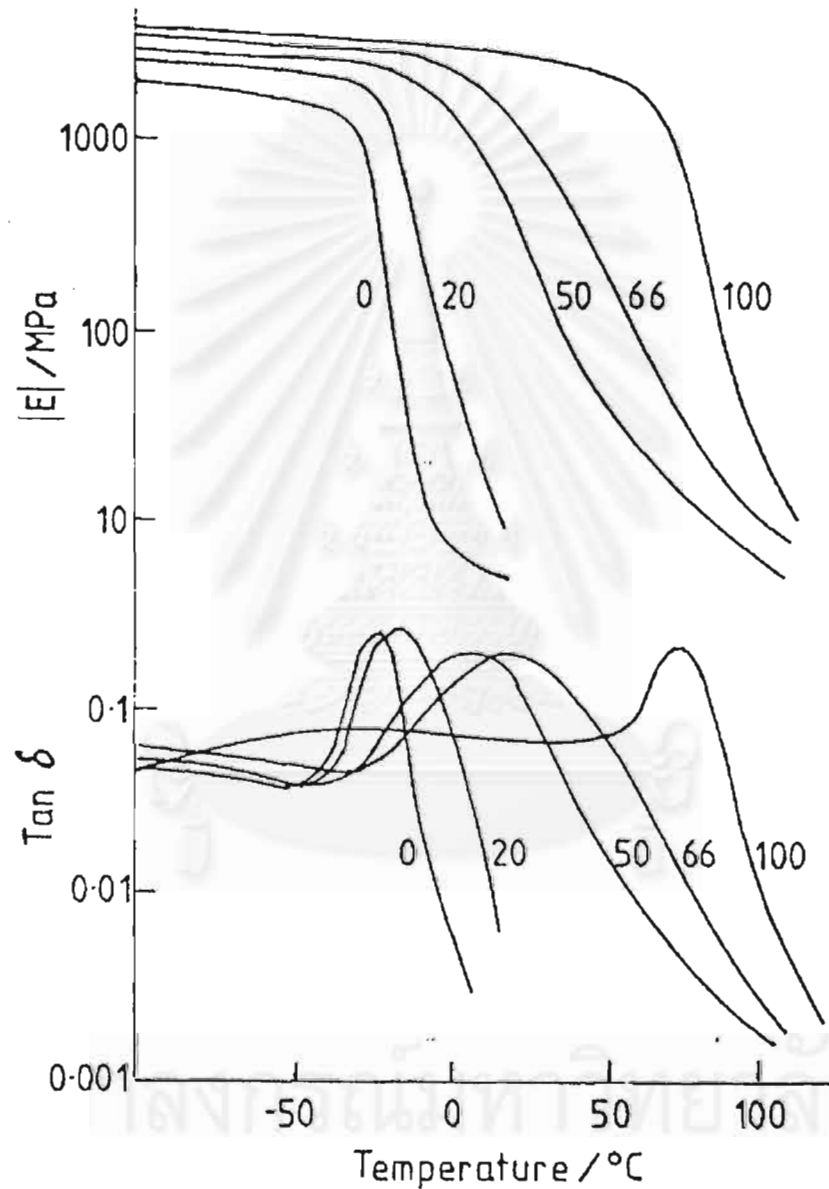
In most mechanical or dielectric spectrometers the directly measured properties are the storage modulus,  $F'$ , (or dielectric constant,  $\epsilon'$ ) and "damping factor", "phase shift" or the loss tangent,  $\tan\delta = F''/F'$ , where F stands for shear ( $F \equiv G$ ), bulk ( $F \equiv K$ ), tensile or Young's ( $F \equiv E$ ) modulus or dielectric parameter ( $F \equiv \epsilon$ ) and ' indicates storage or in-phase quantity while '' indicates loss or out-of phase quantity. While the damping factor has a direct use for some engineering applications, it only expresses the ratio of loss to store energy. The loss tangent does not have a direct molecular meaning and it should not be used as a measure of . It is quite obvious that since in the proximity of this transition both part of the complex moduli,  $F'$  and  $F''$ , change rapidly the location of the peak position of  $F''$  is different from that of  $\tan\delta$ .

Each component of the blends having its own relaxation times (and not necessarily the same one in bulk and in shear), with its characteristic activation energy, we will expect to obtain the behavior shown in figure 2.2 where phase miscibility is not perfect and the separate glass transition temperature are clearly distinguished.<sup>6</sup> The presence or absence of separate glass transition peaks is used as a measure of miscibility. We can see from the foregoing analysis that it is also a measure of the mechanical hetero- or homogeneity of the mixture.



**Figure 2.2:** The mechanical behavior, as a function of temperature, of a molecularly immiscible polymer mixture. The numbers of the curves are the percentages of the glassy component present.

In some polymer blends the mixing is at molecular level and here the phase separation is not sufficient to allow the separate phases to behave as they would in isolation. One phase affects the other in such cases and the position of  $T_g$  is described by the empirical Gordon-Taylor equation,  $T_g$  varying linearly between the values for the two phases according to the concentration of each in the mixture (Figure 2.3)



**Figure 2.3:** Schematic behavior of the molecularly miscible mixture of rubbery and glassy polymers, illustrating the Gordon-Taylor equation. Numbers indicate the percentage of the glassy component.

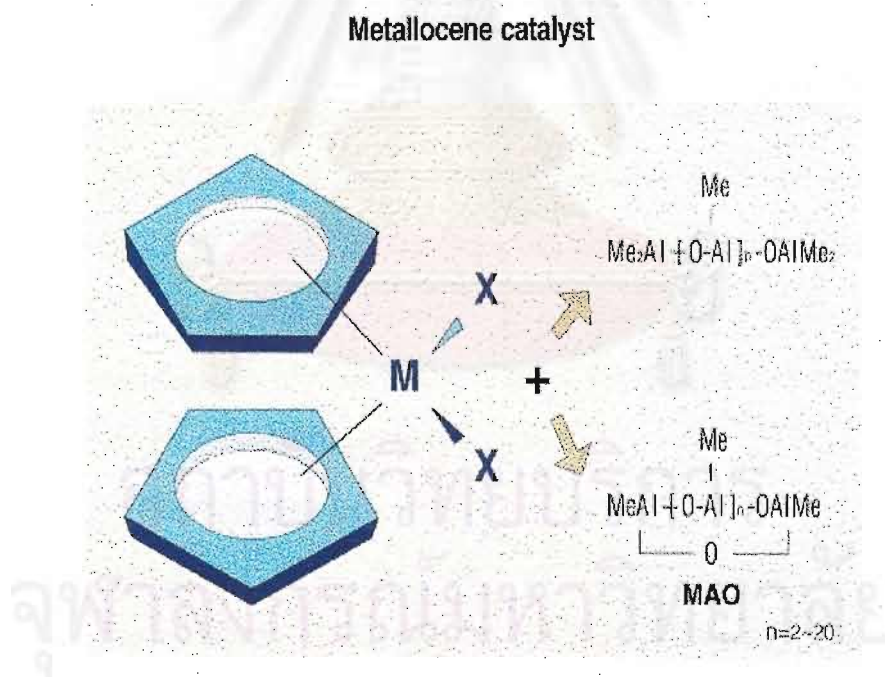
### 2.3 Grades and application of polyethylene

The original ICI process for polymerising ethylene was developed in the 1940s and produced low density polyethylene (LDPE) with a density in the range 910 to 935  $\text{kgm}^{-3}$ .<sup>7</sup> It involves compressing ethylene to very high pressures (1400 to 2400 bar) and polymerising it at a high temperature (200 to 250 °C) using free radical catalysts. There are both short and long chain branches on the molecules because of side reactions in the process. For example between 1.6% and 3% of the C atoms in the chain have ethyl ( $-\text{CH}_2\text{CH}_3$ ) or *n*-butyl ( $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) branches replacing a hydrogen atom. There are far fewer of the long chain branches but these have the effect of making the molecule into a star or comb shaped molecule. If the polymerization pressure is increased the molecular weight increases and the number of branches decreases.

From 1955 onwards a number of processes for producing high density polyethylene (HDPE), with density in the range 955 to 970  $\text{kgm}^{-3}$ , were introduced. These used organometallic catalysts which allowed polymerization at low to medium pressure of 1 to 200 bar. There are low side reactions and hence fewer short chain branches (0.5 to 1% of the C atoms) and no long chain branching. The range of polymer densities produced by low pressure processes has been extended by copolymerising ethylene with butene or hexene. When these units are incorporated in the polymer they produced ethyl and buthyl short chain branches. The copolymers produced in this way are often referred to as medium density polyethylenes (MDPE) of density about 940  $\text{kgm}^{-3}$ , and linear low density polyethylenes (LLDPE) of densities 920 to 930  $\text{kgm}^{-3}$ .

## 2.4 Conventional LLDPE and metallocene LLDPE

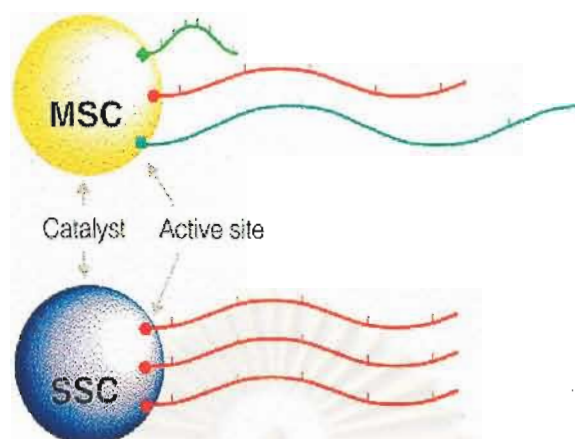
A metallocene catalyst is a “single-site catalyst” (SSC) because it has a uniform active site, in contrast with conventional, non-uniform catalysts which are known as “multi-site catalysts” (MSCs) (Figure 2.4 and 2.5). With a conventional MSC, of which the Ziegler catalyst is a typical example, it was necessary to use a solution-based manufacturing process to obtain a relatively uniform polymer with the minimal unwanted by-products. In contrast, a metallocene catalyst is characterized by a uniform active site and it therefore can be used in a gas-phase manufacturing process, without a solvent, to yield products containing no unwanted low molecular weight, low density compounds.<sup>8</sup>



**Figure 2.4 :** Metallocene catalyst



### Differences between SSC and MSC



**Figure 2.5 :** Metallocene catalyst and differences between SSC and MSC

### 2.5 Sack made from plastic film

The first commercial uses of polyethylene (PE) as a sack material were in 1958 for the packaging of 25 kg fertilizer and of polyethylene resin. These development took place in the United States, and the sack for both applications were made from what was then known as 1000 gauge material (i.e., film of 250  $\mu$  thickness). Because of technical problems, however, including those of polymer grade selection, progress was rather slow during the next two or three years.

By the early part of 1961, two large companies in Canada and the United Kingdom were using 1000 gauge (250  $\mu$ m) polyethylene film sacks for commercial dispatches of fertilizer. From then on, progress in the use of heavy duty polyethylene sacks was fairly rapid.

Most polyethylene film sacks are made from tubular blown film of the desired width and thickness, although some sacks are made from flat reeled film forming a longitudinal seam in exactly the same way as paper sacks are 'tubed'.<sup>9</sup>

The molten polyethylene is extruded upwards from a circular die and expanded outwards by internal air pressure. As will be seen in figure 2.5 the 'bubble' is held airtight by the two pinch rolls. The cooled film can then be reeled for subsequent processing, or fed directly to the printing and sack making machines.

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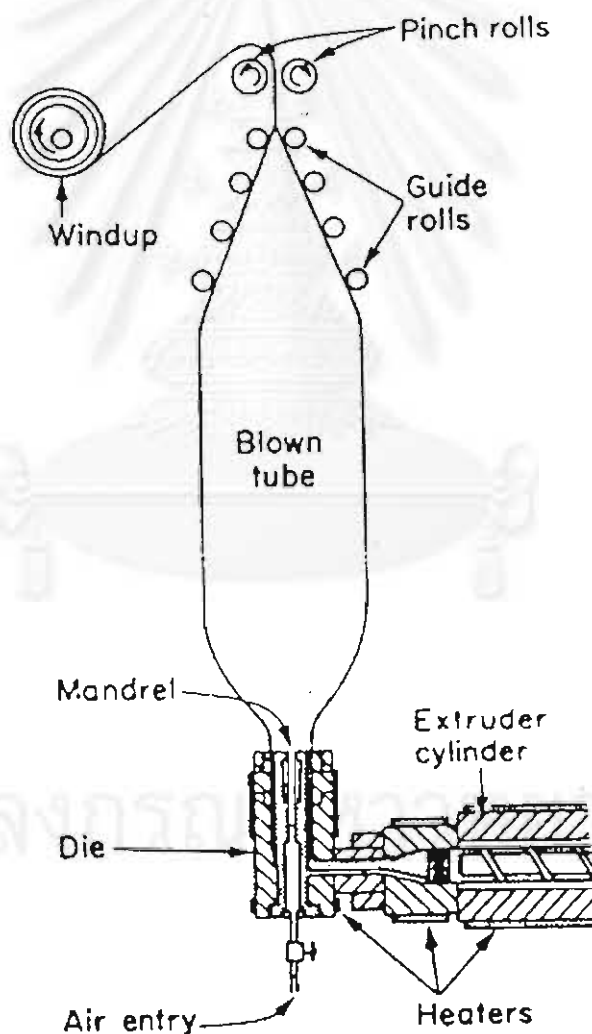


Figure 2.6 : Blow extrusion of film.

## 2.6 Literature reviews

High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are very useful material. Blends of HDPE with LLDPE have been studied by various workers. The commercial LLDPE with metallocene is now available in the market since the development of metallocene catalysts has contributed to a wide variety of available olefin polymers. The comparison of LLDPE prepared with the usual Ziegler/Natta catalysts and metallocene catalysts and also blending of HDPE with both types of LLDPE have been studied in only some applications or some compositions.

R. L. Morgan, M. J. Hill, and P. J. Barham<sup>10</sup> presented the effect of cooling rate on co-crystallization of a blend of linear polyethylene with low density polyethylene. Segregation between components was found to occur, as a result of crystallization, during cooling rate at all rates other than rapid quenching.

K. Cho et al.<sup>11</sup> reported the HDPE/LLDPE blend were miscible in the melt, but the LLDPE/LDPE and HDPE/LDPE blends exhibited two crystallization and melting temperatures indicating that those blend phases separated upon cooling from the melt. The mechanical properties of the HDPE/LLDPE blend conform to the rule of mixtures.

H. Parichutrakul<sup>12</sup> studied the properties of HDPE/m-LLDPE film for industrial bag application (typically in the thickness of 15 - 40  $\mu$ ) by comparing with HDPE/c-LLDPE. The investigations were done in the range of 0-40% LLDPE of the blends. She suggested that HDPE/m-LLDPE blends were miscible in the crystalline phase but immiscible in the amorphous phase. The mechanical properties of HDPE/m-LLDPE films were superior to HDPE/c-LLDPE films.

A.K. Gupta and others<sup>13,14,15,16</sup> who performed HDPE/Z-NLLDPE blend investigated their mechanical properties such as flexural, impact and tensile strength, etc. including the morphology. They found that the properties of HDPE and LLDPE are distinguished by three regions of blend composition, viz. (i) 0-30% LLDPE content (i.e., HDPE rich blend), (ii) 70-100% LLDPE content (i.e., LLDPE rich blend), and (iii) the middle zone. The cocrystallization of HDPE and LLDPE occurs at all compositions of their blend prepared by melt mixing in a single screw extruder. Mechanical properties of HDPE/LLDPE blend vary with the blending ratio and the variations are sufficiently linear at small deformation and nonlinear at large deformations.

H. Lee and others<sup>17</sup> suggested that HDPE/Z-NLLDPE system was miscible blend in the crystalline and amorphous phases the same as A.K. Gupta's report.

S.K. Rana<sup>18</sup> found the strong cocrystalline of HDPE/LLDPE blend when they were melt blended in a single screw extruder. Analysis showed that these constituents followed individual nucleation and combine growth of crystallites in blends. The crystallization rate is relatively independent on the blend composition. However, the number and size of crystalline greatly explain the variation of crystallization rate. It is seen that the large crystalline interface to the amorphous phase pool is either due to the presence of a large number of crystallites or is due to their bigger size and manifest faster crystallization.

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D.Rana<sup>19</sup> and others reported the thermal and mechanical properties of four binary blends, high-density polyethylene (HDPE)-metallocene polyethylene (MCPE), polypropylene (PP)-MCPE, poly(propylene-co-ethylene)(CoPP)-MCPE, and poly(propylene-co-ethylene-co-1-butene)(Ter-PP)-MCPE. All the blend systems are thermodynamically immiscible but mechanically compatible which had been understood by their thermal and mechanical behaviors.

J. Schellenberg<sup>20</sup> studied thermal, mechanical, and processing properties of polymer blend of high density polyethylene (HDPE) with homogeneous long-chain branched polyethylene (HBPE) compared to high density polyethylene (HDPE) with linear low density polyethylene (LLDPE). The reason for the different correlations in the blend properties just mentioned involved deviations in the chemical structure of HBPE and LLDPE blend components. The main difference in this structure should be the occurrence of long-chain branches in HBPE in comparison with LLDPE, which could lead to higher quantity of tie-molecules in the morphological structure of the pure HBPE as in the blends thereof.

D.J. Houska and S.A. Best<sup>21</sup> investigated the use of a bi-modal medium molecular weight high density polyethylene (MMW-HDPE) and metallocene catalyzed LLDPE in various coextrusion and blend structures as a method of increasing secant modulus and thus improving downstream conversion. The study covers a wide range of applications including thin film, clarity film and heavy duty bags. Physical property data from MMW-HDPE and metallocene blend and coextrusion studies had demonstrated that substantial performance in toughness, stiffness, and clarity can be obtained by adding low (20-40%) amounts of MMW-HDPE to metallocene LLDPE.

Y.M. Kim and others<sup>22,23</sup> had been considered the mechanical properties of blown HDPE film due to the most widely use. The most important mechanical properties of blown HDPE film are impact strength and tensile property. Blown film having a broad range of morphology were produced under several processing conditions. The mechanical properties of blown HDPE film are highly associated with their morphological feature, which are dependent on the overall characteristics of HDPE resins. Some correlations were found between the anisotropy of the tear and tensile properties of blown HDPE films and the state of orientation of the crystalline molecular chain axes and lamellae stack at the film plane.



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## **CHAPTER III**

### **EXPERIMENTAL**

#### **3.1 Materials**

##### **3.1.1 High density polyethylene (HDPE)**

HDPE (Thaizex 7000F), a product of Bangkok Polyethylene Public Company Limited, having a melt flow index of 0.04 g/10 min, a density of 0.955 g/cc, was used.

##### **3.1.2 Linear low density polyethylene (LLDPE)**

Two types of linear low density polyethylene were used. Dowlex D2045AC, a product of Dow Chemicals, was produced by using Ziegler-Natta catalyst (c-LLDPE) and octene-based copolymer, having a melt flow index of 1.0 g/10 min, a density of 0.920 g/cc. Another one is Evoluc SP 2510, a product of Mitsui Chemicals, was produced by using Metallocene catalyst (m-LLDPE) and hexene-based copolymer, having a melt flow index of 1.2 g/10 min., a density of 0.923 g/cc.

##### **3.1.3 Medium density polyethylene (MDPE)**

MDPE (GA 3245), a product of Thai Petrochemical Industry Public Company Limited, having a melt flow index of 0.08 g/10 min., a density of 0.948 g/cc.

### 3.2 Instruments and Apparatus

The instruments and apparatus used in this study are listed below:

- a) Differential scanning calorimeter, Perkin Elmer DSC-7
- b) Dynamic mechanical thermal analyzer, NETZSCH DMA 242
- c) Universal testing machine, Instron model 4501
- d) Kayaness Energy Absorption Impact Tester, Model D4092
- e) Densitometer, Macbeth/TR 927
- f) Auto melt Indexer, Tester Sankyo model TP401

### 3.3 A study of HDPE/LLDPE blend for heavy duty film application

#### 3.3.1 Blending and pelletizing

A dry blend of HDPE and LLDPE (m-LLDPE or c-LLDPE) was performed according to the formulation of 0%, 20%, 40%, 60%, 80% and 100% by weight of HDPE balance with both types of LLDPE, m-LLDPE and c-LLDPE using the high speed mixer. Mixing time for a period of 10 min., the blend was melt, extruded and pelletized by single screw extruder and pelletizer as shown in Figure 3.1. The temperature profile of the single screw extruder was 180/200/230/230/230 °C, rotor speed was kept constant at 100 rpm. The extrude was cool in water at 35 - 40 °C and subsequently cut into granules by pelletizer.

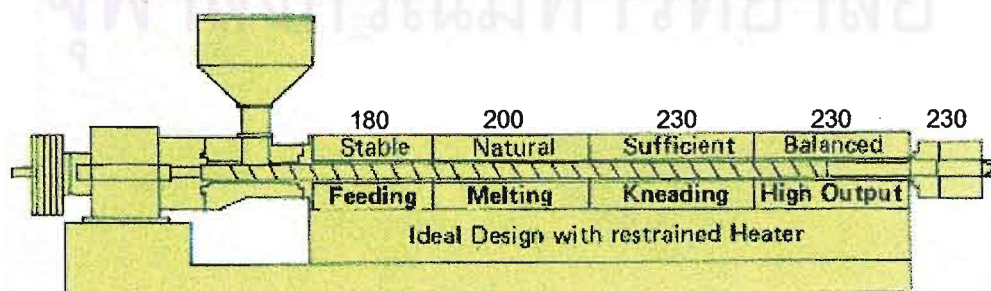


Figure 3.1 : Single screw extruder



### 3.3.2 Blown film extrusion sample

Blown film sample was processed as shown in Figure 3.2. HDPE and LLDPE (m-LLDPE or c-LLDPE) were fed to blown film extruder machine with the formulation of 0% , 10%, 20% , 30% and 40% by weight of HDPE balance with both types of LLDPE, m-LLDPE and c-LLDPE. Molten resin was extruded through a circular die into tubular extruder and blown by air until it reached to the desired width and varies the film thickness to 150  $\mu$ , 165  $\mu$  and 180  $\mu$  by adjusting the winder speed. The polyethylene film was cut to dumbbell shape for tensile and elongation testing. For dart impact testing, it was cut into approximately 200 x 200 mm. from the film. Finally, the film was sealed and tested for the seal strength.



Figure 3.2: Blown film extrusion

### 3.3.3 Testing of HDPE/LLDPE blend for Heavy duty film application

#### 3.3.3.1 Differential scanning calorimetry (DSC)

The melting point and %crystallinity of the HDPE/LLDPE blends were determined according to ASTM D 2117 by using the Perkin-Elmer Differential Scanning Calorimeter tester. Each formulation was weighed and placed in an aluminum pan, the sample was heated from 50 °C to 180 °C at a heating rate of 10 /min. A DSC scan of the specific heat flow against the temperature was obtained. The melting point was calculated from the initial temperature which the sample started to melt. The %crystallinity was calculated and base on the fact that 100% crystallinity of HDPE requires the energy of 310 J/g .

#### 3.3.3.2 Dynamic mechanical thermal analysis (DMTA)

The Tg of all HDPE/LLDPE blend compositions was measured by using dynamic mechanical thermal analyzer, NETZSCH DMA 242. Each specimen was a rectangular sheet of 1 cm. in width, 4 cm. in length and 2 mm. in thickness. The samples were cooled to -150 °C by using liquid nitrogen. Then the temperature was increased to 50 °C with the rate of 3 °C/min. The test was conducted in a single cantilever mode at a frequency of 1 Hz.

### **3.3.3.3 Tensile strength and elongation testing**

The film samples of HDPE/LLDPE blend and MDPE were prepared by blown film equipment as described in the Sections 3.2.1.2 and 3.2.2.2. The tensile and elongation properties were measured at room temperature ( $23 \pm 2$  °C) after 48 hr. of maturation time of the specimens on a Instron Universal testing machine in accordance with test procedure ASTM D 638. The gauge length was kept at 20 mm. with a crosshead speed of 500 mm/min. From the stress-strain curves, the yield strength and elongation at break (based on averages of five samples) were calculated .

### **3.3.3.4 Impact resistance by falling weight**

The same procedure as above was repeated to prepare the film samples of HDPE/LLDPE blends and MDPE. The impact resistance by falling weight was determined in order to obtain the energy required to crack or break the sample. The measurement was carried out at room temperature after 48 hr. of conditioning the samples on a Kayaness Energy Absorption Impact Tester in accordance with ASTM D 3029. The average total energy to failure was obtained from measuring five specimens of the same formulation.

### **3.3.3.5 Seal strength testing**

After sealing the film, the seal strength was tested on specimens by using Instron Universal testing machine at the same condition as tensile testing. Seal strength is the load in kg. which can break the specimen. Each specimen was a rectangular film of 1 cm. in width and 5 cm. in length. This testing is follow the standard testing method of BPE (Bangkok polyethylene public company limited). The average seal strength for each formulation was obtained from measuring five samples of that formulation.

### **3.3.3.6 Clarity of film testing**

The film specimen was tested for the clarity by using Densitometer. The light was emitted through the specimen and the detector detected the transmittance of the light. Five specimens were tested for each formulation and their average value was reported.

## **3.4 A study of comparison between HDPE/LLDPE blend and MDPE**

### **3.4.1 Blending and pelletizing**

These preparations were also performed according to Section 3.3.1.

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### **3.4.2 Molding and specimen preparation**

Sample for mechanical testing which was used for comparison between blending sample and MDPE was prepared by compression molding into plates of 2 mm. thickness for the testing of tensile and elongation. The condition of molding was set at 190 °C, 5 MPa for 6 min. The molded plate was then cooled by cooling water at the rate of 15 °C /min. then the temperature was lower. After temperature was reached to room temperature, there were conditioned in  $23 \pm 0.2$  °C and 50% humidity and then punched into the sample shape were used for testing.

### **3.4.3 Blown film extrusion sample**

A dry blend by high speed mixer of 20%HDPE balance with LLDPE (m-LLDPE or c-LLDPE) and MDPE were selected for the preparation in this Section. Blown film sample was processed. Molten resin was extruder through a circular die and blow by air until it reached the desired width (590 mm.) and a variation of the film thickness at 40  $\mu$  , 60  $\mu$  and 80  $\mu$  was obtained by adjusting the winder speed. The polyethylene film was prepared for separate testing.

### **3.4.4 Testing of HDPE/LLDPE blends and comparing to MDPE**

#### **3.4.4.1 Melt flow index (MFI)**

The weight in grams of extrudate of molten resin through an orifice of specified diameter and length for 10 min. under the prescribed weight of 2.16 kg and at a temperature of 190 °C was measured, by using the Tester Sankyo Auto Melt Indexer in accordance with ASTM D 1238.

### 3.4.4.2 Density

The density measurement of resin was performed by using the density gradient technique according to the BPE testing method which modified from the ASTM D 1505. The density of the specimen was determined by the density gradient tube. Methanol and sodium acetate were used as solvents for the density gradient study of the HDPE in the present study. The density of sample was calculated from the calibration curve which was prepared by the correlation of the distance and actual density of standard glass float in the gradient tube. Specimen preparation was done by annealing the extrudate which was prepared by the same procedure as described in Section 3.4.4.1. The specimen was heated in polyethylene glycol from room temperature to 120 °C at heating rate of 15 °C/min. and then kept constant at 120°C for 1 hr. It was subsequently cooled down to 30 °C at the cooling rate of 15 °C/min.

### 3.4.4.3 Mechanical properties

The tensile, elongation and impact resistance properties of film samples prepared by blown film extrusion as described in Section 3.4.3 were measured in accordance with the measurement of tensile and elongation in Section 3.3.3.3 and the measurement of impact resistance in Section 3.3.3.4, respectively.

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 HDPE/LLDPE blends in heavy duty film applications

##### 4.1.1 Blown film processing of HDPE/LLDPE blends

In this research, films of HDPE/LLDPE blends were produced by blown film processing. The composition of the blends was varied using HDPE 10-40% and the rest was either c-LLDPE or m-LLDPE. Extruder speed was kept constant while the winder speed was varied to achieve the required film thickness, i.e., 150  $\mu$ , 165  $\mu$  and 180  $\mu$ .

##### 4.1.2 Effect of blend composition on thermal behavior

###### 4.1.2.1 Study by dynamic mechanical thermal analysis (DMTA)

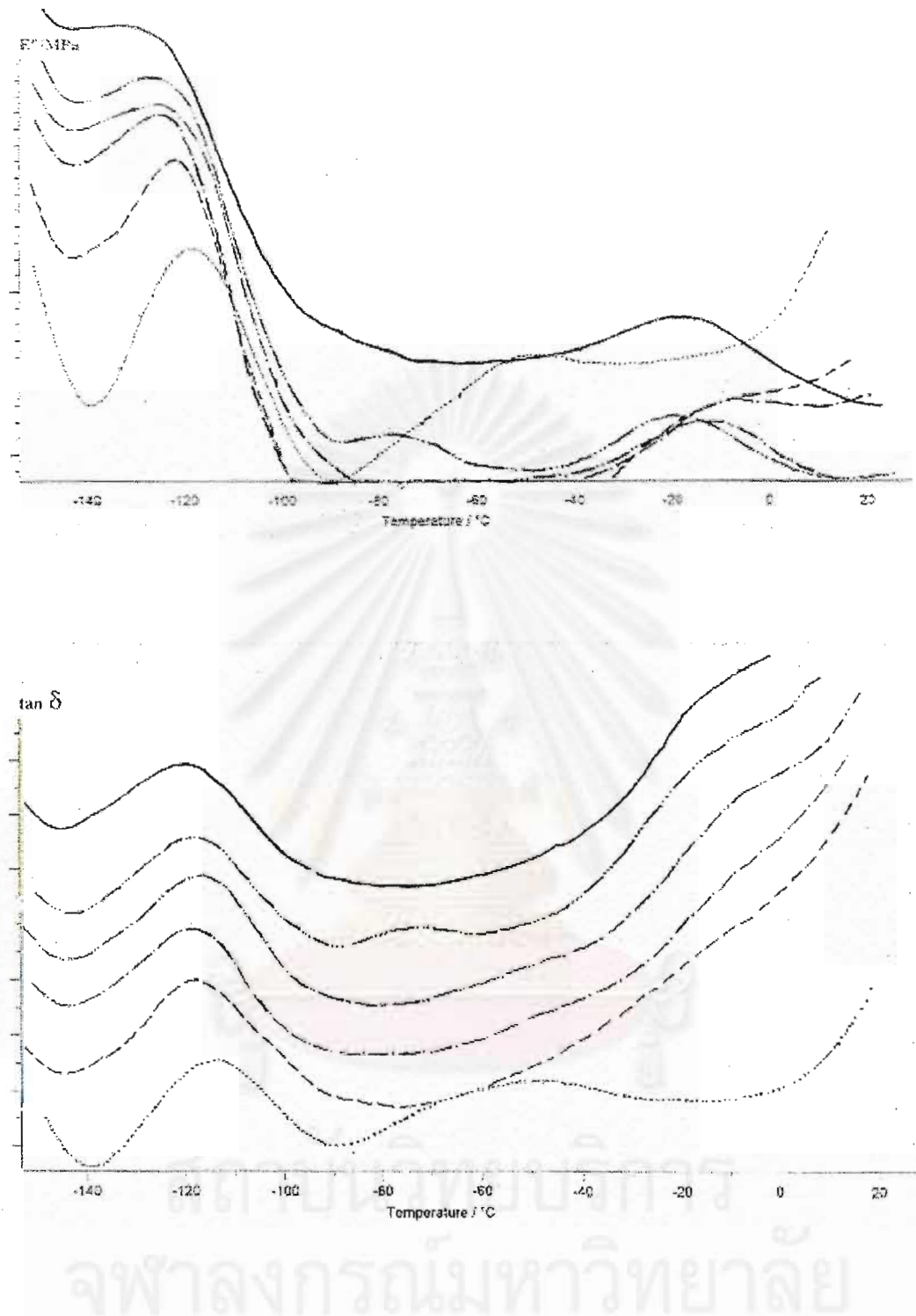
A representative dynamic mechanical relaxation in the tensile storage modulus  $E'$ , tensile loss modulus  $E''$ , and a tensile  $\tan \delta$  versus temperature for HDPE, m-LLDPE, c-LLDPE, and HDPE/LLDPE (m-LLDPE and c-LLDPE) at 20%, 40%, 60%, and 80% of LLDPE are seen in Appendix B. Dynamic mechanical relaxation in tensile loss modulus  $E''$  and a tensile  $\tan \delta$  versus temperature for the HDPE/m-LLDPE and HDPE/c-LLDPE were plotted in Figures 4.1 and 4.2, respectively. Below the temperature of 20 °C by the order of descending temperature, the peaks are designated as the  $\beta$  and  $\gamma$  relaxation.

The glass transition temperature ( $T_g$ ) of those samples can be investigated by the presence of damping peak at  $\gamma$  relaxation region.<sup>24</sup> Normally, in completely amorphous polymer blends, miscibility has often been accepted when a single composition-dependent is observed. By applying the same concept, the HDPE/m-LLDPE and HDPE/c-LLDPE system are believed to be miscible in the amorphous phase. The  $T_g$  of HDPE/LLDPE blend system in Figures 4.1 to 4.2 were linearly shifted from  $-114$  °C (designated the  $T_g$  of HDPE) to  $-120$  °C (designate the  $T_g$  of LLDPE). However, these two  $T_g$ s are too close therefore there may be no meaning to distinguish each  $T_g$  and discuss miscibility. The  $\gamma$  relaxation occurs in amorphous regions and therefore its magnitude is a function of the volume of amorphous polymer and the intensity of  $\gamma$  relaxations depends on the amorphous. The intensities of  $\gamma$  relaxation of m-LLDPE is higher than that of c-LLDPE (see Appendix B). Thus, m-LLDPE has higher volume fraction of amorphous than c-LLDPE. This behavior is related to the excellent of impact property of m-LLDPE.

The similar result was also observed by P. Hatairat<sup>12</sup> and Hoseok Lee et al.<sup>17</sup> They found the  $T_g$  of HDPE/LLDPE blends was linearly shifted from  $-114$  °C to  $-117$  °C and  $-117$  °C to  $-119$  °C, respectively. Matthews, Ward, and Capaccio<sup>25</sup> reported the  $T_g$  by the  $\gamma$  relaxation process at approximately  $-130$  °C. The difference of each  $\gamma$  relaxation temperature depends on the type of comonomer of HDPE or LLDPE that they used. The glass transition in polyethylene has been discussed by several workers i.e., Hoseok Lee et al.<sup>17</sup> presented that in HDPE/LLDPE system, the dynamic mechanical  $\alpha$ ,  $\beta$ , and  $\gamma$  relaxations of the blends display an intermediate behavior that indicates miscibility in both the crystalline and amorphous phases. They suggested that HDPE/LLDPE system was miscible in the crystalline and amorphous phases.

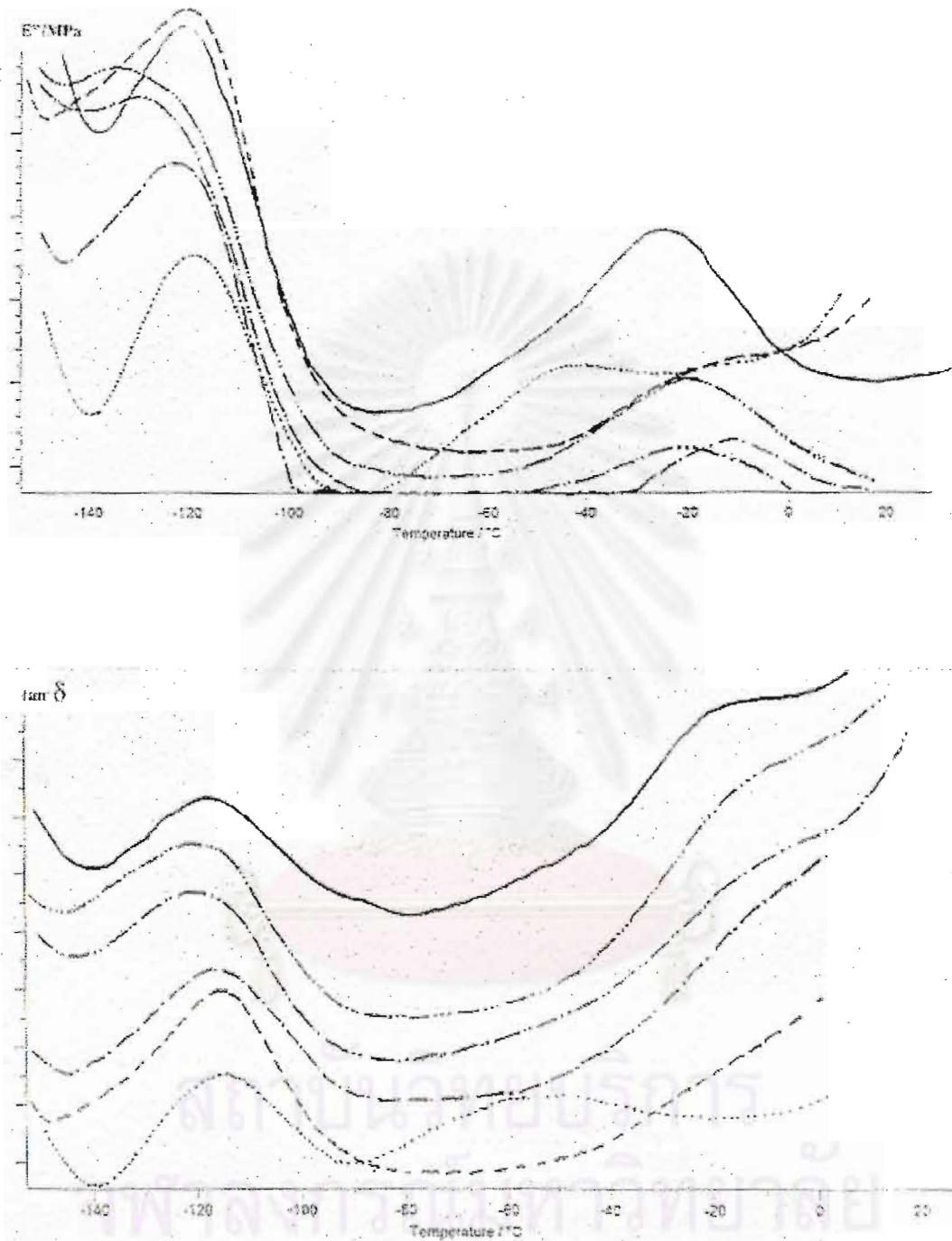


The  $\beta$  transition normally describes motion in flexible side chains of polymer.<sup>24</sup> The  $\beta$  relaxation of HDPE, c-LLDPE, m-LLDPE and HDPE/LLDPE blends systems were also presented in Figures 4.1 to 4.2. In the  $\beta$  region, small shoulder was observed in the HDPE reflection at about  $-60\text{ }^{\circ}\text{C}$  due to the small amount of 1-butene comonomer. For either m-LLDPE and c-LLDPE it exhibits a broad  $\beta$  relaxation at about  $-20\text{ }^{\circ}\text{C}$  which may arise due to the segmental motion of the 1-hexene comonomer and 1-octene comonomer, respectively. For the blends, only one  $\beta$  relaxation was observed for HDPE/m-LLDPE and HDPE/c-LLDPE at all formulations (Figures 4.1 and 4.2). These indicated that the HDPE/m-LLDPE and HDPE/c-LLDPE are miscible in the amorphous region. The different results have been reported by P. Hatairat,<sup>12</sup> i.e., the DMTA spectrum of HDPE/m-LLDPE blend (75/25) showed two  $\beta$  relaxations which indicated the immiscibility of amorphous region. The miscibility in amorphous region of the blends are related to the systematic change of corresponding mechanical property such as impact resistance in the total range of the blends. The different results may be affected by the different type of m-LLDPE in the blends.



**Figure 4.1 :** Dynamic mechanical relaxation in tensile loss modulus  $E''$ (above) and a tensile  $\tan \delta$  (below) versus temperature of HDPE/m-LLDPE blends.

..... 0% m-LLDPE,      - - - - - 20% m-LLDPE,      - . - 40% m-LLDPE,  
 - - - - - 60% m-LLDPE,      - . . . 80% m-LLDPE,      \_\_\_\_\_ 100% m-LLDPE



**Figure 4.2 :** Dynamic mechanical relaxation in tensile loss modulus  $E''$  (above) and a tensile  $\tan \delta$  versus temperature of HDPE/c-LLDPE blends.

..... 0% c-LLDPE,      - - - - - 20% c-LLDPE,      \_ . \_ 40% c-LLDPE,  
 \_ . . \_ 60% c-LLDPE,      \_ . . . \_ 80% c-LLDPE,      \_\_\_\_\_ 100% c-LLDPE

#### 4.1.2.2 Study by differential scanning calorimeter (DSC)

The melting endotherms and crystallization exotherms of HDPE, m-LLDPE, c-LLDPE, HDPE/m-LLDPE blends, and HDPE/c-LLDPE blends are shown in Figures 4.12 and 4.13. Single peak of melting is observed in both HDPE/m-LLDPE and HDPE/c-LLDPE blends and shifts to the middle point between the melting points of HDPE and m-LLDPE or c-LLDPE. In crystallization process, the total heat of fusion ( $\Delta H$ ) of the blends decreasing linearly with LLDPE content followed the simple rule of mixture. The single peak character in these exotherms of the blend is an indication of cocrystallization for the blend of HDPE with both m-LLDPE and c-LLDPE. This system is thought to be miscible in the crystalline phase.

Each DSC of both m-LLDPE and c-LLDPE shows the shoulder peak which is influenced by the long chain branch content in LLDPE. Therefore the same shoulder peak still exists in HDPE/m-LLDPE and HDPE/c-LLDPE blends which may be observed at the high content of LLDPE.

Furthermore, the decrease in melting temperature with increasing LLDPE content decreases the rate of nucleation of cocrystallization which might be responsible for the formation of large crystallites. Consequently, the crystalline size of HDPE/m-LLDPE blend is larger than HDPE/c-LLDPE blend. Several works<sup>10,15,18,25,26</sup> were presented the same behavior.

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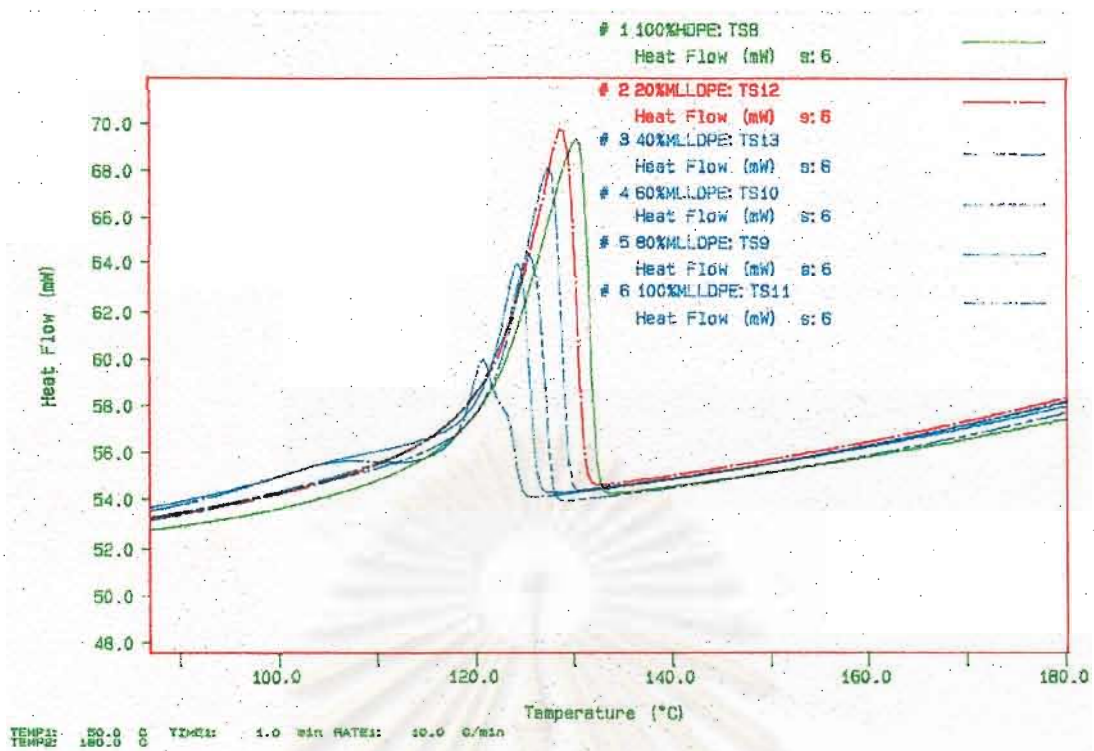


Figure 4.3 : DSC of HDPE, m-LLDPE, and HDPE/m-LLDPE blends

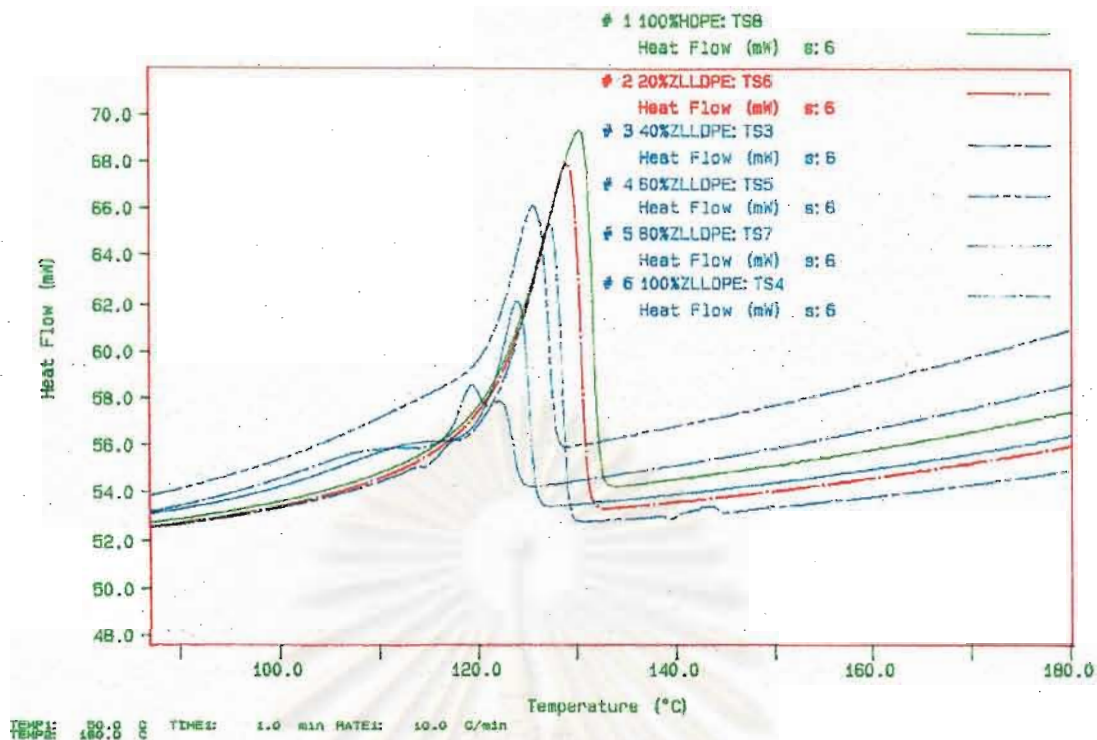


Figure 4.4 : DSC of HDPE, c-LLDPE, and HDPE/c-LLDPE blends

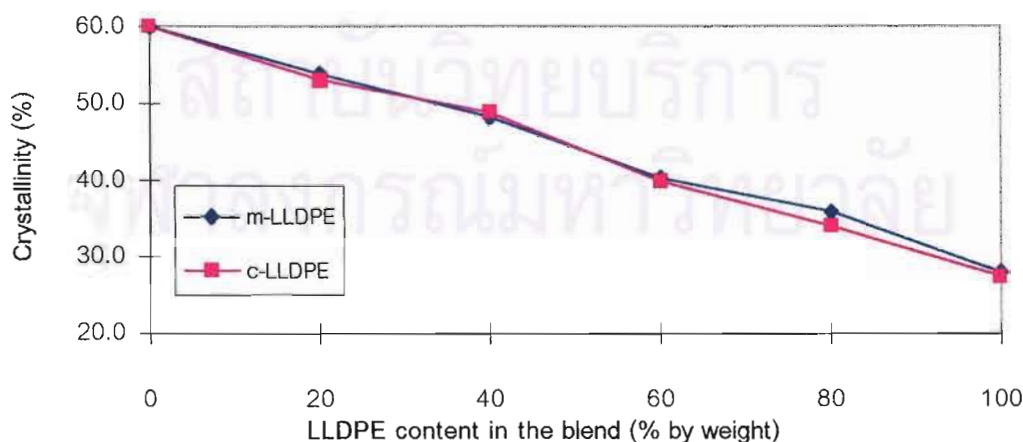
The %crystallinity of the blend which is calculated from total energy of heat of fusion<sup>15,17,24,25</sup> by using the Equation 4.1<sup>24</sup> (see details in Appendix B).

$$\% \text{crystallinity} = (\Delta H / \Delta H^0) * 100 \quad \text{----- Equation. 4.1}$$

where :  $\Delta H^0$  is the enthalpy of fusion for infinite polyethylene crystal = 310 J/g<sup>25</sup>

$\Delta H$  is the enthalpy of fusion for sample

The %crystallinity decreases with increasing LLDPE content as shown in Figure 4.5. The decrease in crystallinity may be attributed to the obstruction of mobility of HDPE chains by the LLDPE chains, which might reduce the ease of crystallization. The comparison between %crystallinities of HDPE/m-LLDPE and HDPE/c-LLDPE indicated that the former has a few higher %crystallinity than the latter. The difference of %crystallinity is related to the type of comonomer by hexene comonomer in m-LLDPE and octene comonomer in c-LLDPE. The branch chain of the former is shorter than makes a few obstruction to form cocrystallization than the latter. Because of cocrystallization, then higher %crystallinity is the indication of the more miscibility. Therefore, HDPE/m-LLDPE is a little bit more miscible in the crystalline phase than HDPE/c-LLDPE.



**Figure 4.5 : %Crystallinity of HDPE/m-LLDPE and HDPE/c-LLDPE**

### 4.1.3 Effect of blend composition on mechanical properties

#### 4.1.3.1 Effect of LLDPE content on tensile strength

Figures 4.6 to 4.8 give the mechanical property of HDPE/LLDPE blends as measured by tensile test. From the regression line, it can be seen that tensile strength at yield in both machine and transverse directions decrease linearly with an increasing LLDPE content in the blend. The decrease of this characteristic parameter caused by crystallinity and orientation. The decrease of crystallinity may be attributed to the obstruction of mobility of HDPE chains by side chain branching of LLDPE chains, which might reduce the ease of crystallization. It thus affects on the reduction of tensile properties with increasing %LLDPE in the blend. Considering the deformation process of the blown film, it seems to be strongly influenced by the orientation of the lamellar stack, as well as their interconnection, with respect to the tensile direction. When LLDPE content in the blend increases, its side chain branching will disturb the orientation of the molecule in the blend. Consequently, the tensile strength of the film was decreased.

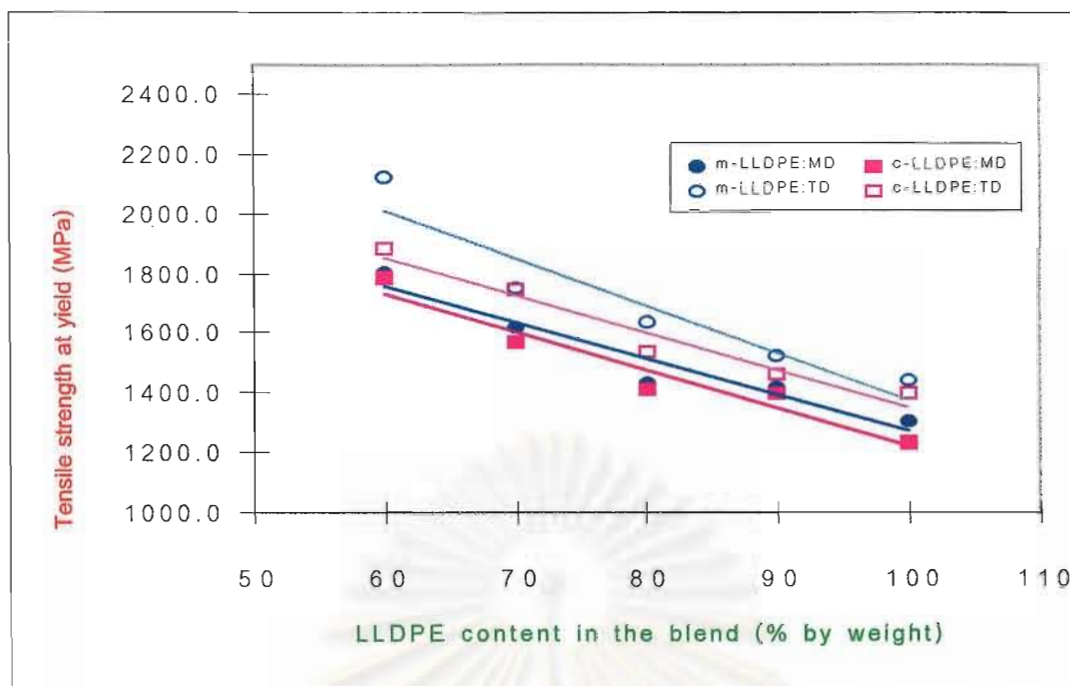
Combination with the previous research of this blend in the range of HDPE-rich blend (0 - 40% LLDPE) by Hatairat<sup>12</sup>, it was found that the tensile strength of HDPE/LLDPE decreased with increasing LLDPE content at the total range of the blends (0 - 100% LLDPE). The present study shows the tensile strength in transverse direction is equivalent to machine direction. In contrast, the study by P.Hatairat<sup>12</sup> showed the different result which can be explained by the difference of film preparation. In blown film process, most molecular chains are preferably aligned in the machine direction. The reason of which is that the stress pulled vertically by haul-off unit is much greater than the hoop stress generated by blow pressure. Therefore, the degree of orientation in both two directions could be optimised to the properties



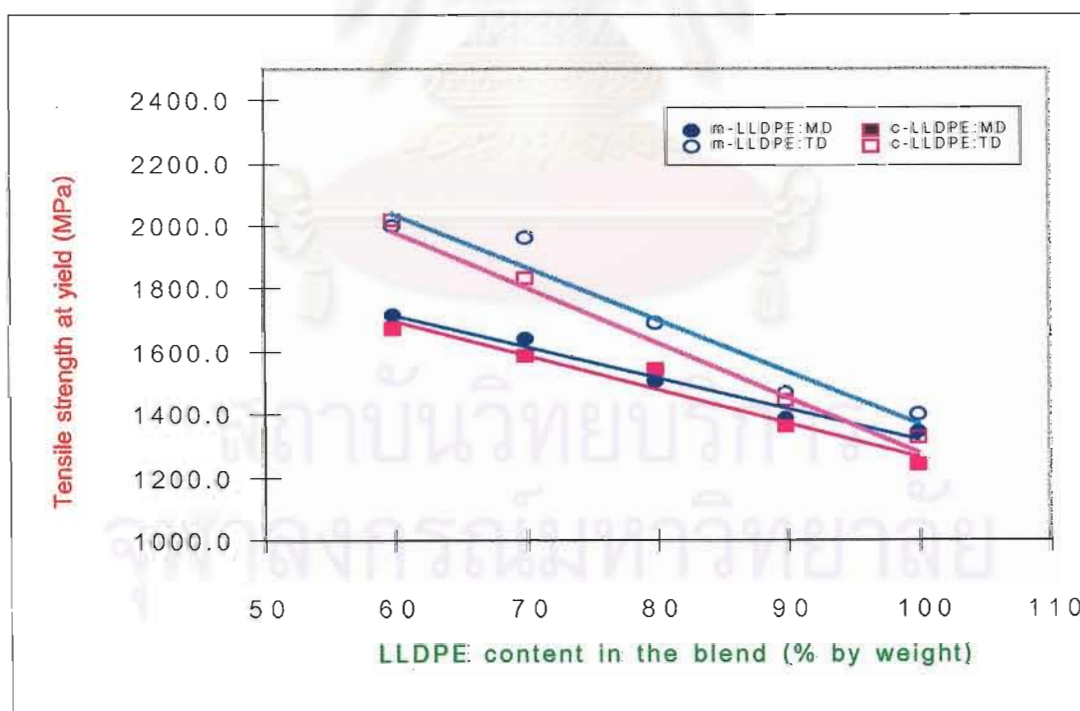
according to end-use demand. The present study prepared the heavy duty film which thickness is higher and requires the strength in both machine and transverse directions, then orientation in both directions could be optimised to similar level. The study by P. Hatairat<sup>12</sup> prepared the thinner film which requires the high tension to pull the film, then influenced on the orientation in machine direction is higher than transverse direction.

Solid state relaxation study in LLDPE , LDPE and HDPE by L. Huseok et al.<sup>17</sup> was shown the larger the lamellae thickness, the higher the melting. In semicrystalline polymers the melting temperature  $T_m$  is a linear function of the lamellae thickness through the gibbs Thompson equation<sup>26</sup> and a relationship between the crystallinity and the peak melting temperature, which implies a relationship between the crystallinity and the lamellar thickness. Moreover, yield stress which depends on the crystallinity is also depended on the lamellar thickness. Since the melting point of m-LLDPE is higher than that of c-LLDPE, thus lamellae of m-LLDPE is thicker. These results are attributed to the higher crystallization of HDPE/m-LLDPE than that of HDPE/c-LLDPE. Consequently, tensile strength of HDPE/m-LLDPE film is higher than HDPE/c-LLDPE film.

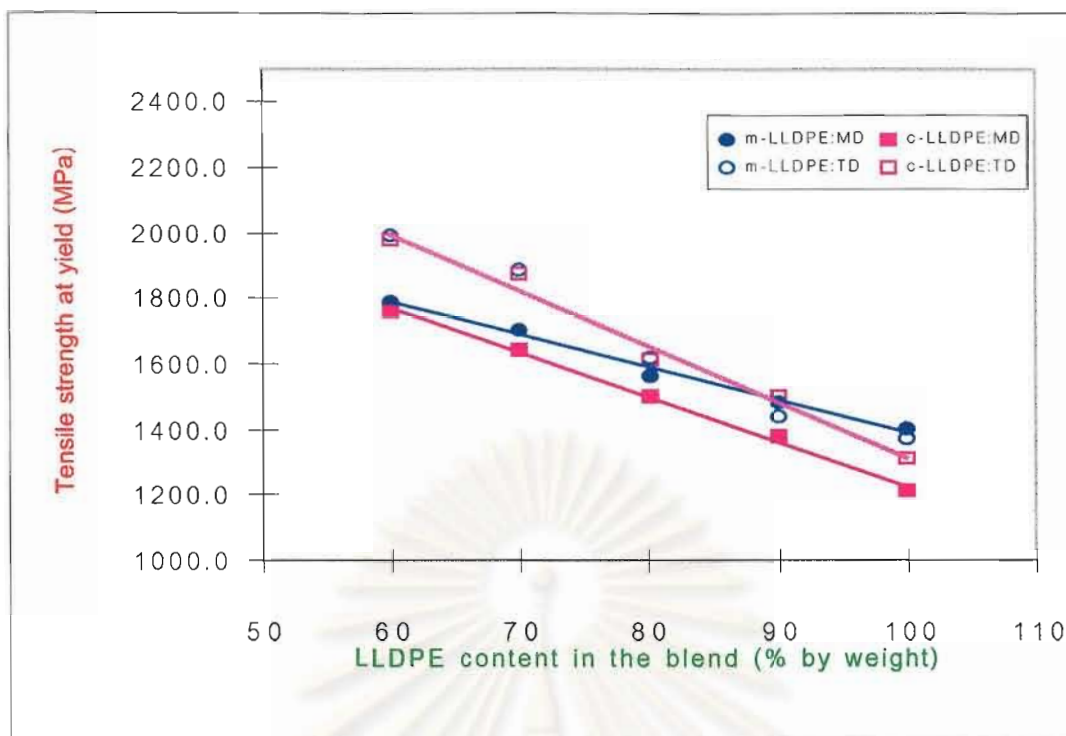
Similar observations were also reported by Kyuchol<sup>27</sup> and co-workers, Rana et al.<sup>19</sup>, Schellenberg<sup>20</sup>, Houska and best<sup>21</sup>, and Gupta<sup>16</sup>. They found that the enhancement in tensile properties of the blend was crystallinity and orientation dependent.



**Figure 4.6 :** Tensile strength at yield in machine and transverse directions of HDPE/LLDPE film at 150 μ thickness



**Figure 4.7:** Tensile strength at yield in machine and transverse directions of HDPE/LLDPE film at 165 μ thickness



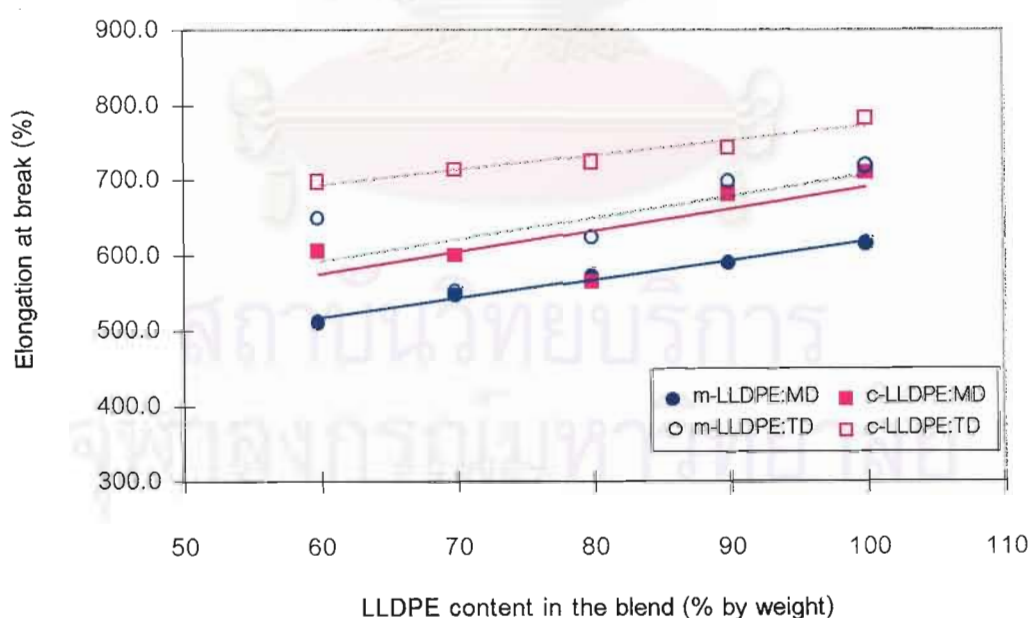
**Figure 4.8:** Tensile strength at yield in machine and transverse directions of HDPE/LLDPE film at 180  $\mu$  thickness

Tensile strength of film represents the film stiffness, then higher tensile strength, higher the film stiffness. These properties provide the strength of film bubble during blown film processing. Since the increase of tensile strength has a positive effect on processibility of heavy duty film, therefore all compositions of HDPE/m-LLDPE films and HDPE/c-LLDPE films in this work meet the requirement of heavy duty film application.

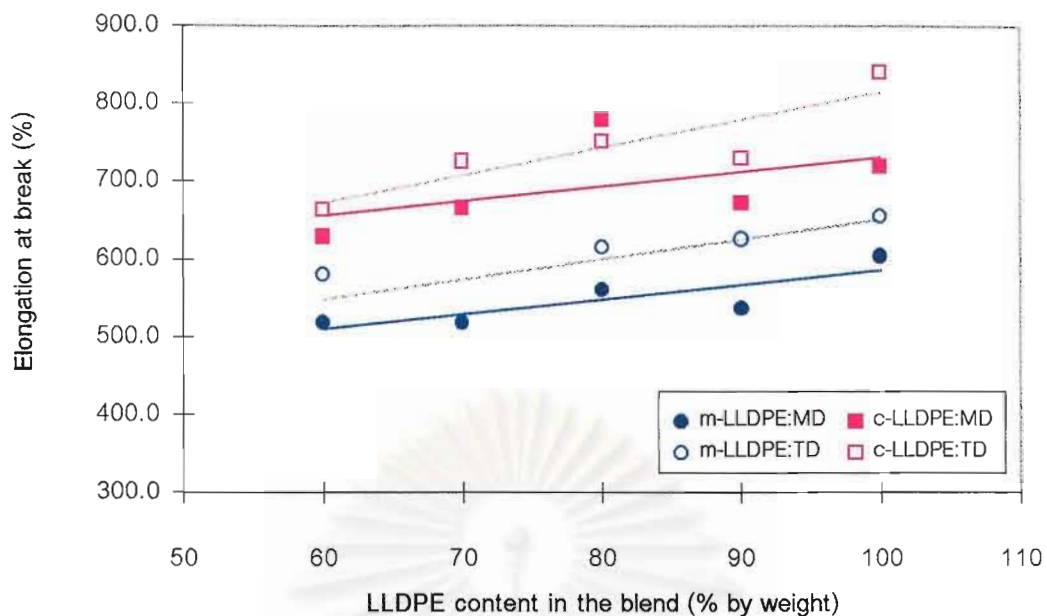
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#### 4.1.3.2 Effect of LLDPE content on elongation

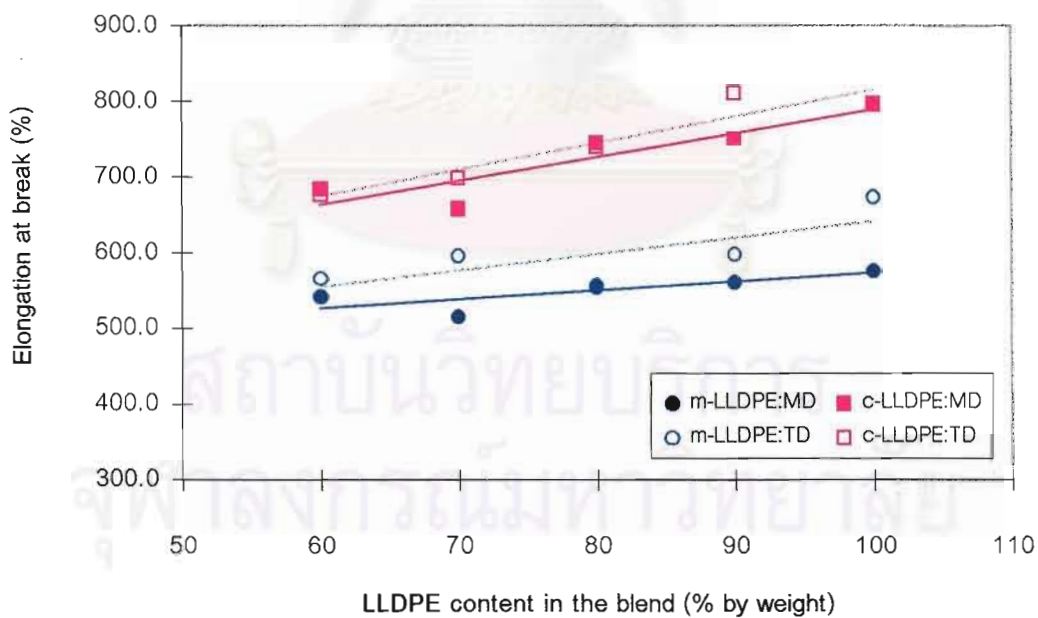
Elongation at break (Figures 4.9 to 4.11) increases with increasing LLDPE content in the blend. Because the comonomer units present in LLDPE act to increase the free volume, and, thus, the flexibility or extensibility is increased. The LLDPE, which has greater extensibility than does HDPE, contributes very little to the increasing of the elongation at break of the blend. Entrapment of molecular segment in cocrystallites leaves quite small lengths of LLDPE segments in the amorphous region, which might account for the low elongation at break of the blend samples. This indicates that breaking occurs before the LLDPE content contributes to the elongation of the sample beyond the limit of maximum elongation of HDPE. The lower value of elongation at break for the blend than pure LLDPE suggest that the major portion of the LLDPE gets involve into cocrystallized regions and the boundary region of crysatlline and amorphous phase and, hence does not produce any significant variation of the elongation at break as a function of LLDPE content.



**Figure 4.9 :** Elongation at break in machine and transverse directions of HDPE/LLDPE film at 150  $\mu$  thickness



**Figure 4.10 :** Elongation at break in machine and transverse directions of HDPE/LLDPE film at 165  $\mu$  thickness



**Figure 4.11 :** Elongation at break in machine and transverse directions of HDPE/LLDPE film at 180  $\mu$  thickness

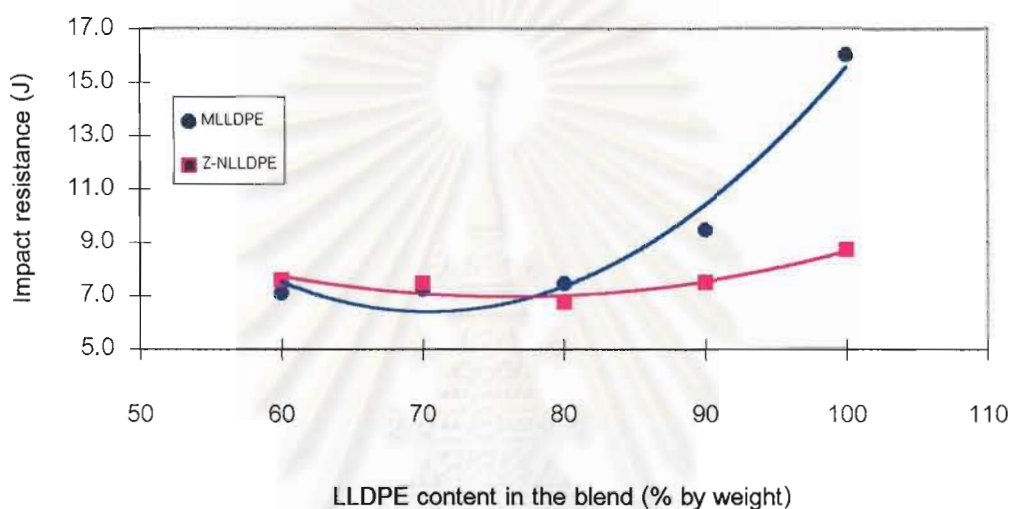
Combination of the previous study by Hatairat<sup>12</sup> with our present study, elongation at break of HDPE/LLDPE blends increase with increasing of LLDPE content in the blend at the total range of the blend composition. The several workers were also reported the similar result.<sup>11,16,19,27</sup> Gupta<sup>16</sup> reported the elongation at break decrease with increasing LLDPE content of the blend up to 35% LLDPE content and then remains almost unchanged on further addition of LLDPE up to 100% LLDPE content and, thereafter, its increase is very sharp up to the value of pure LLDPE that is similar to our present study.

Thermal behavior of HDPE/LLDPE blends in the present study and the study by Rana<sup>19</sup> gives the relation of segmental motion of the comonomer which is corresponded to volume fraction of amorphous phase by the representative DMA spectrum trace of the tensile storage modulus  $E'$ , tensile loss modulus  $E''$  and tensile  $\tan\delta$  versus temperature. The exhibition of high intensity of a  $\gamma$  relaxation due to the higher volume fraction of segmental motion in amorphous region while HDPE have the lowest of the  $\gamma$  relaxation intensity compared to m-LLDPE and c-LLDPE. The intensity of  $\gamma$  relaxation of m-LLDPE and c-LLDPE in section 4.1.2 has been compared. The lower segmental motion of m-LLDPE than that of c-LLDPE is observed. This behavior is attributed to lower elongation at break of HDPE/m-LLDPE than HDPE/c-LLDPE (Figures 4.9 - 4.11) .

However, the elongation at break is not the critical parameter of the requirement of heavy duty film application as tensile strength which related to film stiffness and also dart impact strength which related to film toughness. Therefore, all compositions of HDPE/m-LLDPE films and HDPE/c-LLDPE films in this work also meet the requirement of heavy duty film application.

### 4.1.3.3 Effect of LLDPE content on impact resistance

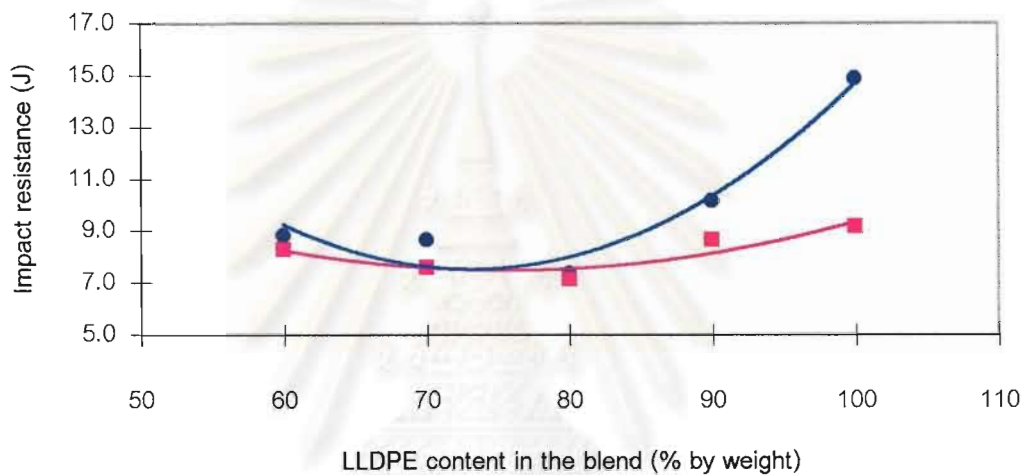
The results of impact test with three different film thickness are depicted in Figures 4.12 to 4.14. As expected, impact resistance of the films increases through the additional of LLDPE to the range of LLDPE rich blend because of high amorphous content which is attributed from higher LLDPE content in the blend.



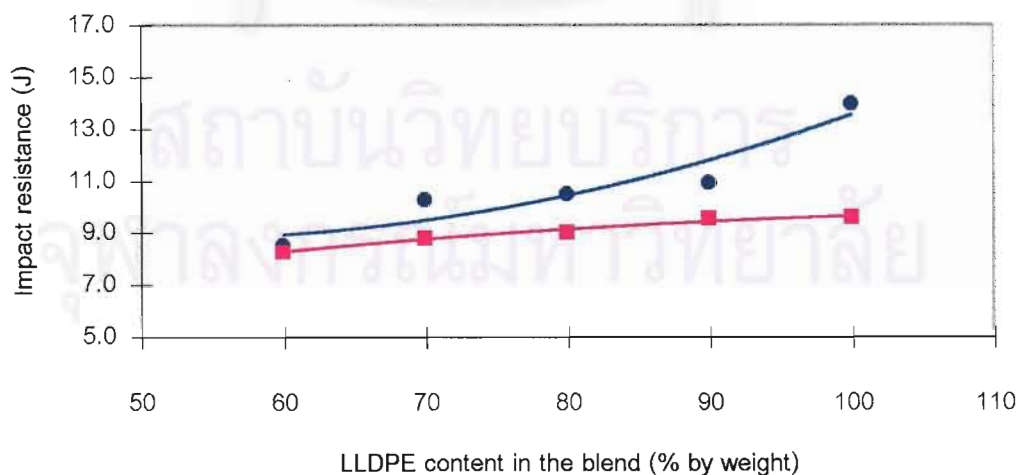
**Figure 4.12** : Energy absorption impact strength of HDPE/LLDPE film at 150  $\mu$  thickness

Impact resistance data show interesting trends in comparison of the HDPE/m-LLDPE and HDPE/c-LLDPE film performance. The HDPE/m-LLDPE film tends to high dart impact compared to HDPE/c-LLDPE film. This result can be explained by the superior impact resistance of m-LLDPE to c-LLDPE and perfectly cocrystallization of HDPE/m-LLDPE than that of HDPE/c-LLDPE. The formation of cocrystallization was described in the section of thermal behavior by DSC (Section 4.1.2). The previous study of A.K. Gupta<sup>14,16</sup> was also found the systematic variation of impact strength with blend composition which is similar to the variation of the total amorphous content of the blend.

The impact resistance is important property of heavy duty film application as well as the tensile strength. In the commercial producing of heavy duty film requires typically more than 9 joule of impact resistance which is equivalent to 100% c-LLDPE film at 180  $\mu$  thickness, therefore HDPE/m-LLDPE films with 90-100% m-LLDPE content at the film thickness of 150  $\mu$  or higher are exceed impact resistance of heavy duty film as well as HDPE/m-LLDPE film with 80% m-LLDPE content at only 180  $\mu$  thickness.



**Figure 4.13 :** Energy absorption impact strength of HDPE/LLDPE film with 165  $\mu$  thickness



**Figure 4.14 :** Energy absorption impact strength of HDPE/LLDPE film with 180  $\mu$  thickness



#### 4.1.3.4 Effect of LLDPE content on seal strength of film

The seal strength of HDPE/m-LLDPE and HDPE/c-LLDPE film samples at various seal temperatures (that is 130°C, 140°C and 150°C) and 2 levels of film thickness (that is 150  $\mu$  and 180  $\mu$ ), presented in Figure 4.15, the higher LLDPE content, the lower seal strength at every seal temperature. This result can be explained by too high temperature that makes the weaker seal when content of LLDPE in the blend is increased. Therefore adding of HDPE to the blend can be improved the seal strength of the film. Since the level of seal temperature of heavy duty film application normally is 130°C to 150 °C, therefore those sets of blending in this work are met the requirement of heavy duty film application.

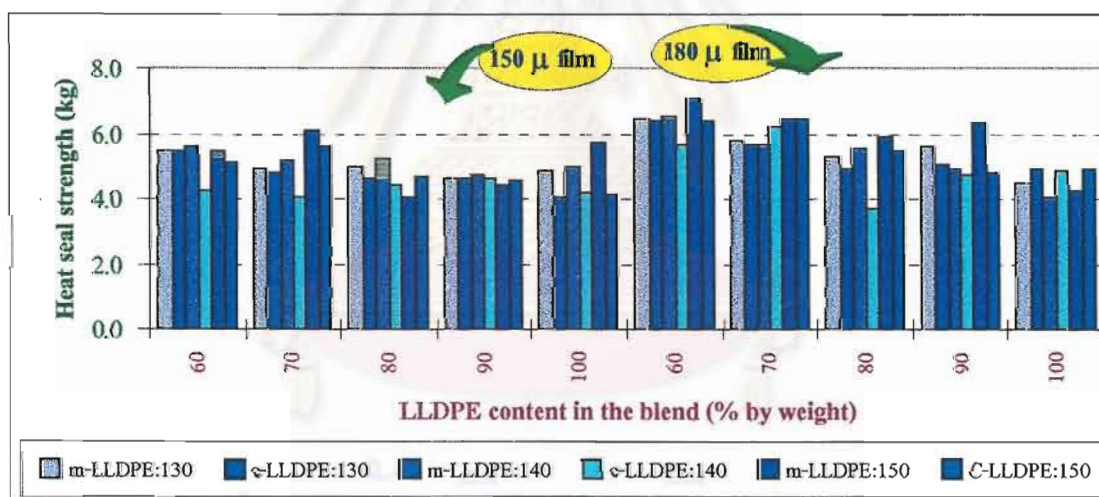


Figure 4.15 : Heat seal strength of HDPE/LLDPE film

#### 4.1.4 Downgauging of heavy duty film

Normally, LLDPE is used in heavy duty film application. It is typically not run at very thin gauge due to the low melt strength of LLDPE which cause bubble instability. The studies of thermal and mechanical properties of HDPE/LLDPE blend with m-LLDPE and c-LLDPE from the section 4.1.2 - 4.1.3 are very useful for heavy duty film application. The most important properties in heavy duty film application are tensile strength and impact resistance. Since the most important for downgauging of heavy duty film is to develop stiffer film which is performed by increasing in tensile property. The stiffer film provides greater melt strength which improves bubble stability yielding a more stable blown film operation at thinner film gauges. The balance property of stiffness with adequate impact resistance is the key for a successful heavy duty film.

The comparing of tensile strength and impact resistance of HDPE/m-LLDPE films and HDPE/c-LLDPE with c-LLDPE films have been done by calculation the percent change in impact resistance and tensile strength at yield for HDPE/m-LLDPE and HDPE/c-LLDPE film at various thickness with 100% of c-LLDPE film at 180  $\mu$  thickness. The results are shown in Figure 4.16 and 4.17 respectively. There were revealed that the impact resistance decreases with the small number as 10 - 25 % while the tensile strength increases with the large number as 10 - 50 % when decreases the LLDPE content in the blends with the lower film thickness.

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By this study, a route to achieve this balance performance is to add HDPE to LLDPE to increase the film stiffness at thinner gauges which have equal toughness performance of their heavier gauge versions. Also as the excellent mechanical properties of m-LLDPE to make the HDPE/m-LLDPE films that are stronger and thinner. Through the use of HDPE/m-LLDPE blend, downgauging of 9 - 17 % is possible. These can be shown by the blend of 10% HDPE with 90% m-LLDPE have equal dart impact and enhance tensile property when downgauge to 165  $\mu$  and 150  $\mu$ .

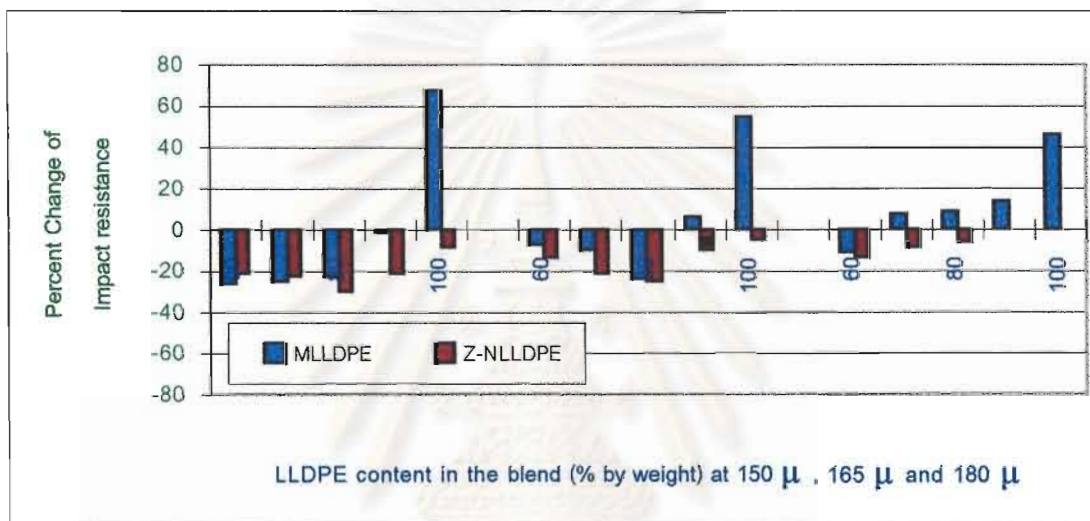


Figure 4.16 : Percent change in impact property of HDPE/m-LLDPE and HDPE/c-LLDPE film

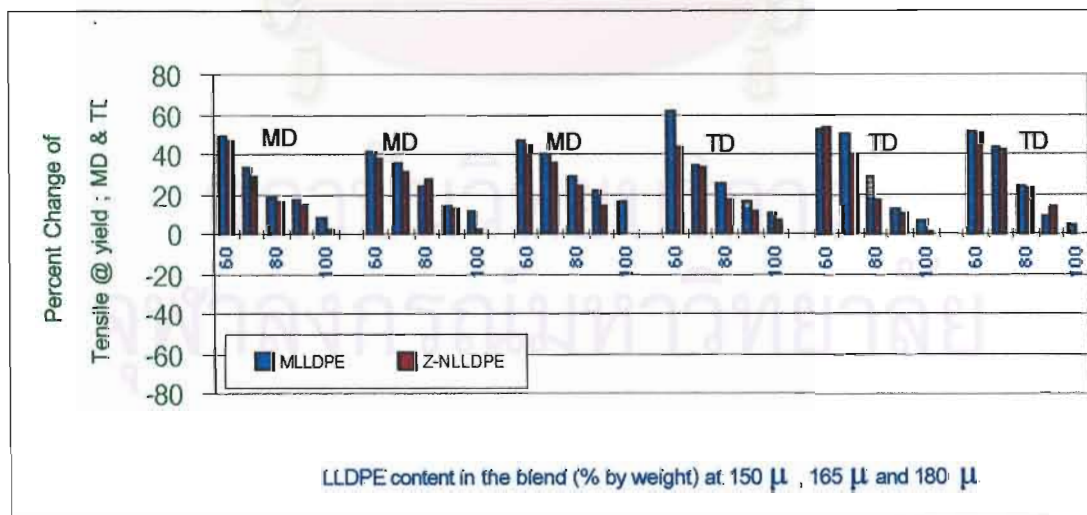


Figure 4.17 : Percent change in tensile property of HDPE/m-LLDPE and HDPE/c-LLDPE film

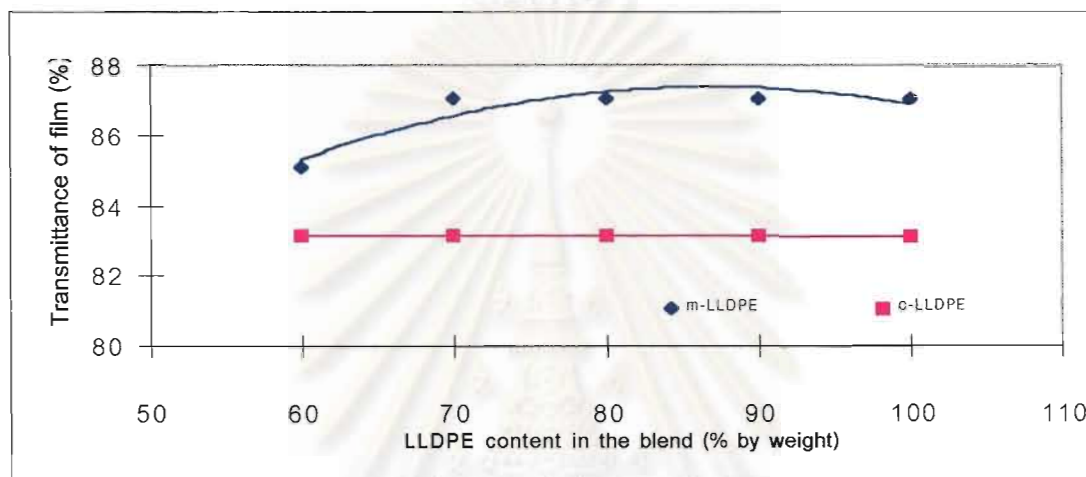
For ensuring the reproducibility of the testing and blending preparation in this work, the second attempt was made with the same formulation as the first attempt by preparing HDPE/m-LLDPE film containing 90% m-LLDPE at 165  $\mu$  thickness for mechanical properties investigation. The properties of HDPE/m-LLDPE film from first and second attempt are presented in Table 4.1. The similar properties represent a good reproducibility of our preparation and testing in the present study.

**Table 4.1** Properties of HDPE/m-LLDPE (10/90) film with 165  $\mu$  thickness

Film properties	165 $\mu$ of HDPE/m-LLDPE(10/90) film	
	First attempt	Second attempt
1. Tensile strength at yield in machine direction ( $\text{kg}/\text{cm}^2$ )	141.5	145.3
2. Tensile strength at yield in transverse direction ( $\text{kg}/\text{cm}^2$ )	150.1	152.1
3. Elongation at break in machine direction (%)	537.1	534.1
4. Elongation at break in transverse direction (%)	627.5	599.4
5. Impact resistance (J)	10.19	11.02

#### 4.1.5 Effect of blend composition on film clarity

The optical properties of polymer film such as gloss, haze, transparency or clarity being quite important for packaging film. Figure 4.18 shows the clarity of HDPE/LLDPE films in terms of light transmittance. The clarity of HDPE/LLDPE films are constant while the LLDPE content is increased in both m-LLDPE and c-LLDPE which is different in MFR and density.



**Figure 4.18 : The transmittance of HDPE/LLDPE film at 150  $\mu$  thickness**

In principle, polymer crystal dominates the reflection and transmission of light passing through the film. If small crystal structure is exist, the good of clarity can be obtained. Factors dominating the optical properties are low density (low crystal quantity), high MFI (small crystal size) or molecular weight distribution; MWD (uniform crystal size). The HDPE/m-LLDPE film has better clarity than HDPE/c-LLDPE because m-LLDPE has narrow MWD than c-LLDPE. By this result MWD is high influence on the film clarity than the density or MFI.

Even though the film clarity is not the important parameter in this application but higher film clarity is preferable by several users. Therefore all compositions of HDPE/m-LLDPE films and HDPE/c-LLDPE films still meet the requirement of heavy duty film application.

## 4.2 The comparison of HDPE/LLDPE blends with MDPE

### 4.2.1 Effect of blend composition on density

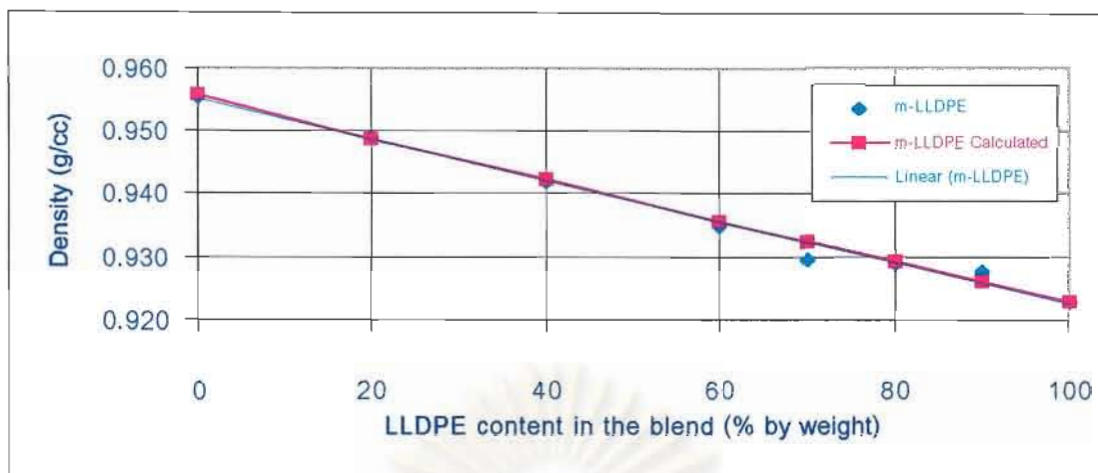
To study the effect of the blend composition on the density of the HDPE/LLDPE blend, both m-LLDPE and c-LLDPE were separately blended with HDPE at various ratios and compared with conventional MDPE. Figure 4.19 presents the relationship between the density of the HDPE/LLDPE blends both m-LLDPE and c-LLDPE and LLDPE content. By linear regression, it shows a linear relationship between the density of the blend and LLDPE content. When more LLDPE content is in the blend, its density decreases. This can be explained that the branches of LLDPE disrupt the close packing of the polymer chains. High content of LLDPE in the blend thus results in lower density of the blend.

In general, the density of the blends can be calculated from the Equation 4.2<sup>4</sup> which is the simple rule of mixing. According to the equation 4.2, the calculated density of each blend was made (see details in Appendix B) and then plotted to compare with the measuring density. The results are shown in Figure 4.19. Therefore, these results offer a good way to predict the density of blended materials.

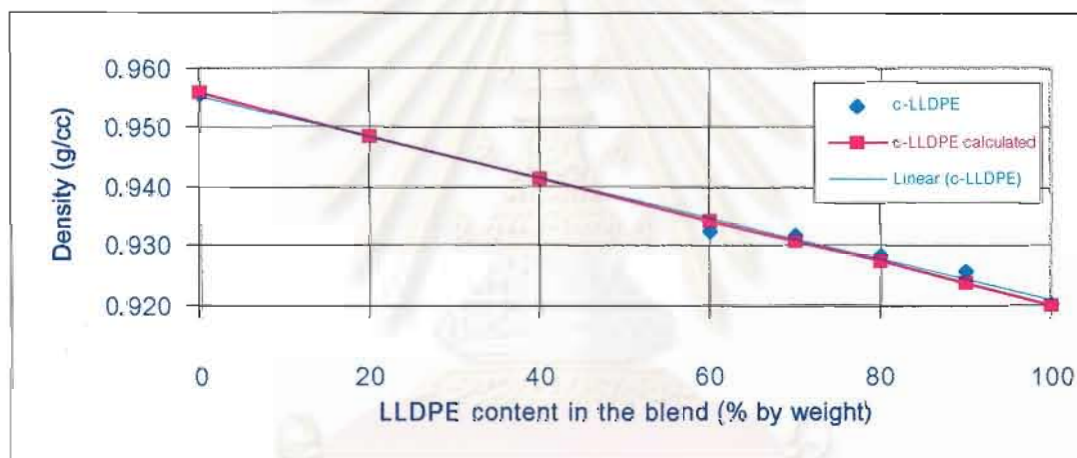
$$1/D_b = W_1 \times (1/D_1) + W_2 \times (1/D_2) \quad \text{----- Equation 4.2}$$

Furthermore, the homogeneity of the blends can be evaluated from the similarity of measuring density and calculated density of the blends. The result in this study is identified the homogeneous of the blending system. The similar relationship between density and blend ratio of binary polyethylene blends which studied by Anthony chi-ying wong<sup>28</sup> and Sellenberg.<sup>20</sup> were also reported.

(A)



(B)



**Figure 4.19** : Density of HDPE/LLDPE blends for: (A) m-LLDPE : and (B) c-LLDPE

In order to replace for MDPE, the blend with similar density to MDPE is selected which is 20% by weight of LLDPE in both HDPE/m-LLDPE and HDPE/c-LLDPE blends. The selected blends were used to study the mechanical properties in the section 4.2.

### 4.2.2 Effect of blend composition on melt flow index (MFI)

The dependence of the MFI, as a function of the LLDPE content, are plotted in Figure 4.20. From the curve it can be seen that the MFI of HDPE/LLDPE blends increases linearly in the semilogarithmic scale over the entire composition range. The MFI of the blends was calculated using the Equation 4.3<sup>29</sup> (see also Appendix B).

$$(W_A + W_B, \text{ etc.}) \log \text{MFI}(\text{blend}) = W_A \log \text{MFI}_A + W_B \log \text{MFI}_B, \text{ etc.} \quad \text{----- Equation 4.3}$$

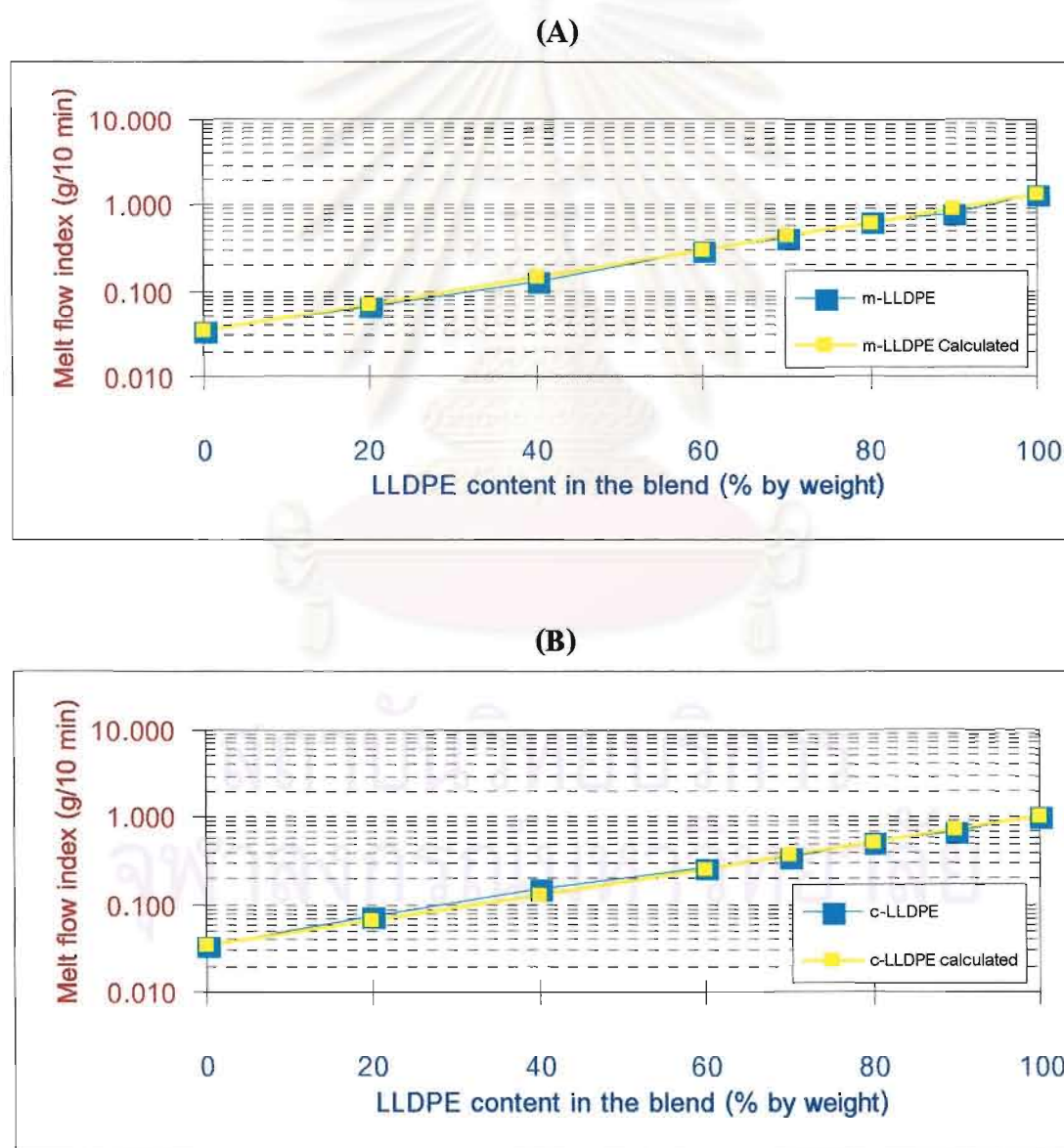


Figure 4.20 : Melt flow index of HDPE/LLDPE blends for: (A) m-LLDPE : and (B) c-LLDPE

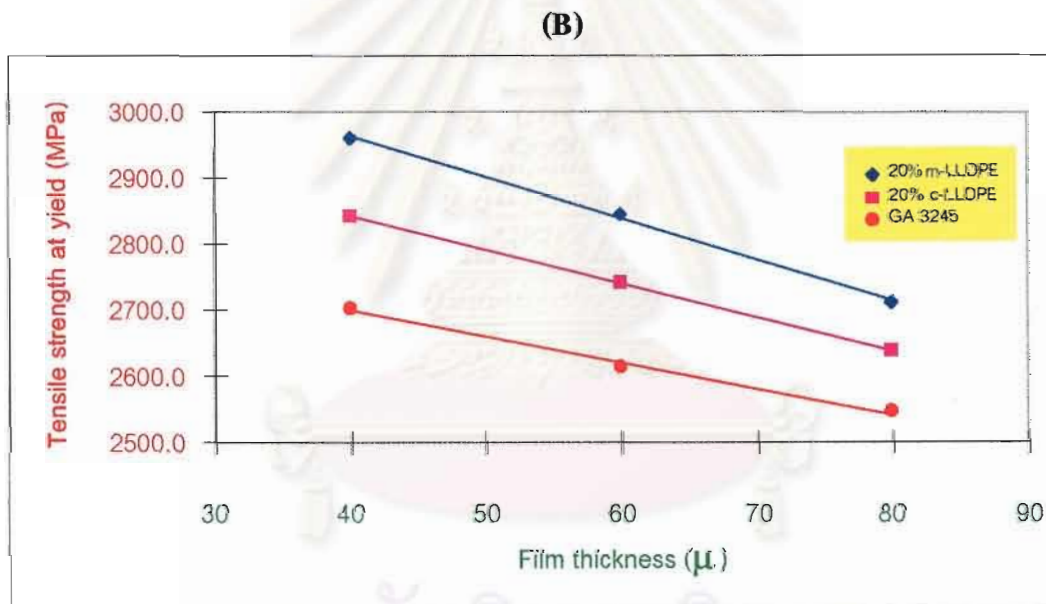
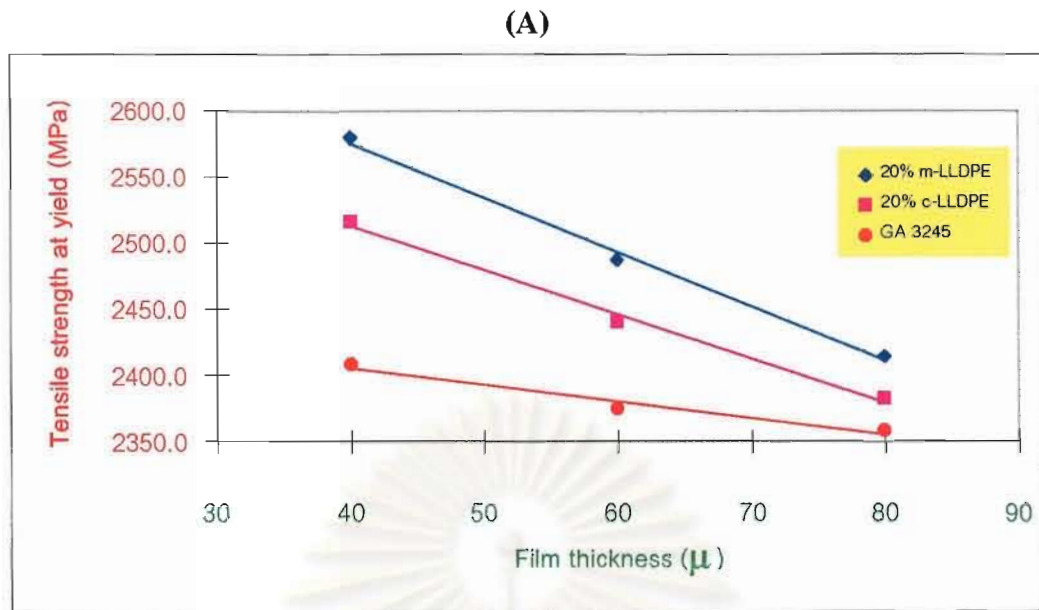


By the same concept for evaluation of homogeneity, the calculated MFI was reported to compare with measuring MFI in Figure 4.20. From the plotted data, the similarity of the measuring MFI and the calculated MFI of the blends are supported for the conclusion of our blending system is good of homogeneity. Several equations were proposed to predict the MFI of the blend by Anthony chi-ying wong.<sup>28</sup> However, the equation 4.3 was shown to give the better estimation of the values of blended MFI. The similar result has been reported by Schellenberg.<sup>20</sup> He found the increasing of MFI with HBPE (Homogenous branched polyethylene) content in HDPE/HBPE blends.

#### **4.2.3 Mechanical properties of HDPE/LLDPE films and MDPE**

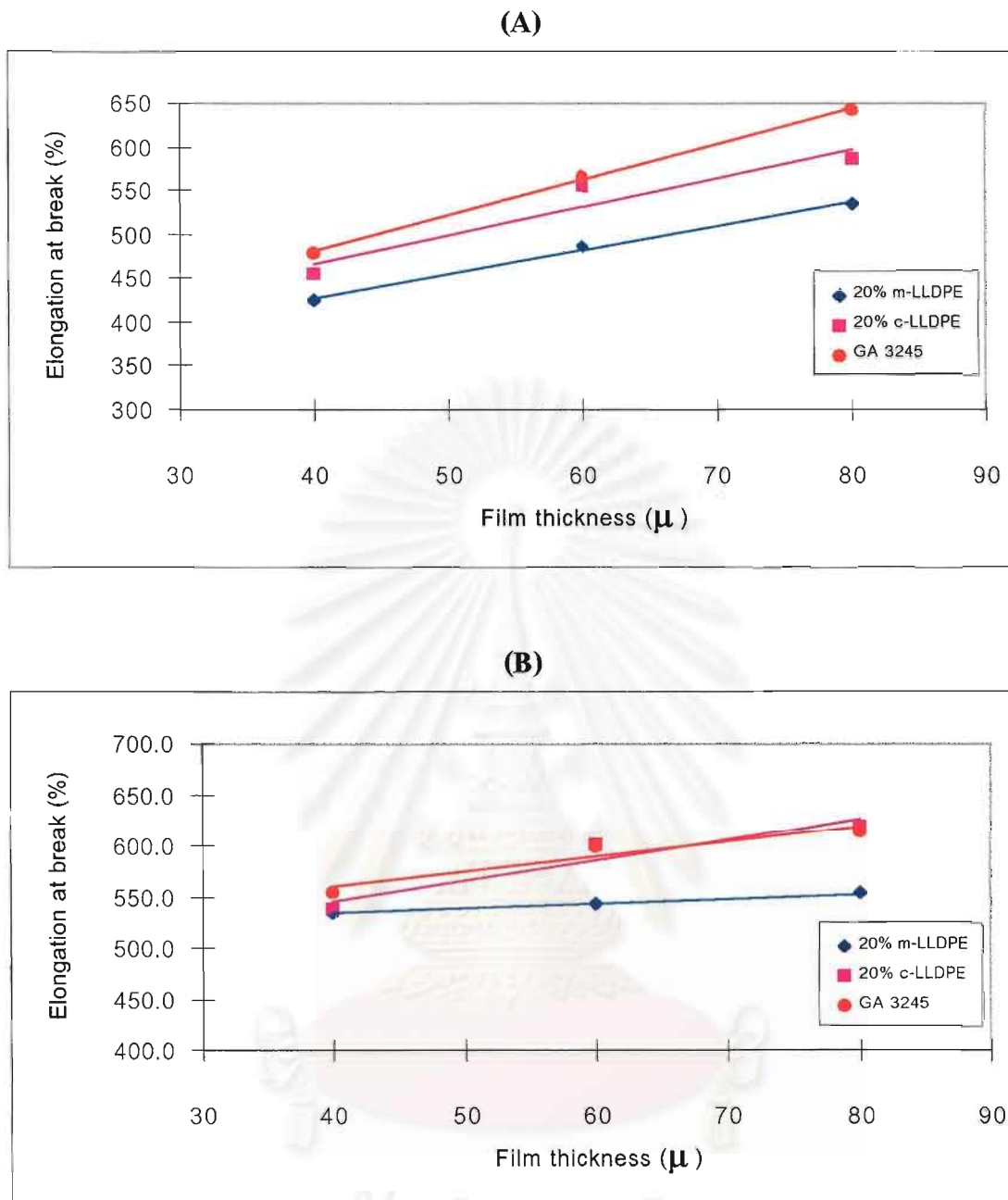
According to the one application of MDPE is the industrial film application which has the typical range in 40 - 80  $\mu$  thickness. Therefore the expected blend composition (20% LLDPE ) which has MFI and density nearly the same as MDPE was used to make an industrial film. The MFI of 20%LLDPE for HDPE/c-LLDPE and HDPE/m-LLDPE is 0.075 g/10 min and 0.068 g/10 min respectively while the MFI of MDPE is 0.080 g/10 min. The density of 20%LLDPE for HDPE/c-LLDPE and HDPE/m-LLDPE is 0.948 g/cc and 0.949 g/cc respectively while the density of MDPE is 0.948 g/cc. The comparison of mechanical properties between HDPE/m-LLDPE films and HDPE/c-LLDPE films with MDPE films is presented in Figures 4.21, 4.22 and 4.23.

It was found that both HDPE/m-LLDPE and HDPE/c-LLDPE films with 20% LLDPE have tensile strength at yield about the same as MDPE film.(Figures 4.21 (A) and (B))



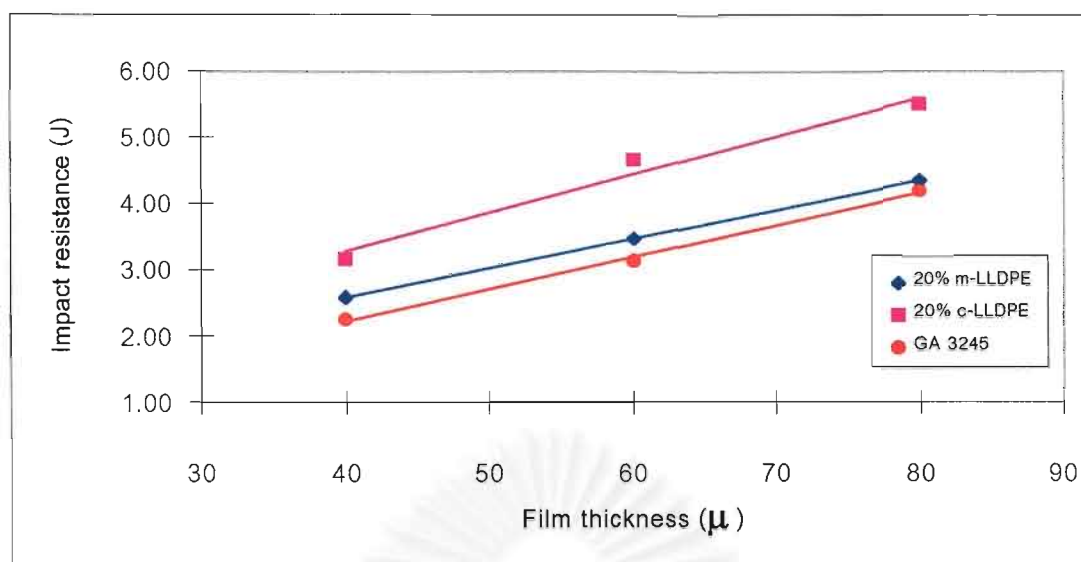
**Figure 4.21** : Tensile strength at yield of film sample for: (A) machine direction : and  
(B) transverse direction

The comparison of elongation at break of HDPE/LLDPE films with MDPE film is depicted in Figure 4.22. The equivalent elongation at break of HDPE/LLDPE films to MDPE films is achieved.



**Figure 4.22** : Elongation at break of film sample for: (A) machine direction : and (B) transverse direction

In Figure 4.23, impact resistance of HDPE/m-LLDPE film , HDPE/c-LLDPE film at selected formulation and MDPE film are shown with different film thickness. The equivalent impact resistance of HDPE/LLDPE film to MDPE film is also achieved.



**Figure 4.23 :** Impact resistance of film sample

Most properties of HDPE/LLDPE blend are equivalent to those of MDPE. The enhanced properties may be obtained from the successful blending system from the good performance of homogeneity and miscibility. The homogeneity was presented by equivalent of MFI and density data from the experimental and calculation in section 4.2.1 and 4.2.2, respectively. The miscibility was performed by thermal behavior of the blends which had been described in Section 4.1.2.

It can be seen that, the use of HDPE/LLDPE blend to replace the application of MDPE is available. Because the equivalent properties of estimated blend were achieved from the estimation of MFI and density with the proposed equation (Equation 4.2 or 4.3) which is equivalent to the value of interested MDPE. The advantage is the lower investment cost between HDPE/LLDPE blend and MDPE production. Moreover, this study provides the challenge of polyethylene producing at desired MFI and density for several applications by no requirement of specific polymerization concerning.

## CHAPTER V

### CONCLUSION AND SUGGESTION

#### 5.1 Conclusion

The thermal behavior of HDPE/c-LLDPE and HDPE/m-LLDPE shows miscible in both crystalline and amorphous phases over the total range of the blend.

Mechanical property data from HDPE/LLDPE blends for both c-LLDPE and m-LLDPE have demonstrated that substantial performance improvement in particular stiffness and toughness can be obtained by adding low amount, in the range of 10 - 30%, of HDPE to LLDPE. By the superior impact property of HDPE/m-LLDPE film to HDPE/c-LLDPE film, adding higher amount of HDPE in HDPE/m-LLDPE film for improving the stiffness without sacrificing impact property can be achieved.

The improvement of stiffness with enhanced tensile property of HDPE/LLDPE film makes downgauging in heavy duty film application possible. The HDPE/m-LLDPE films at 90% of m-LLDPE which can be downgauged from 180  $\mu$  to 165  $\mu$  and even to 150  $\mu$  still exhibit slightly higher impact resistance than c-LLDPE film and HDPE/c-LLDPE film at 90% of c-LLDPE with the thickness of 180  $\mu$ . Moreover, tensile strength of HDPE/m-LLDPE film at 90% of m-LLDPE is also higher than c-LLDPE film which improves the stiffness and stable film at lower thickness during blown film processing. For heavy duty film application, HDPE/m-LLDPE film with 90% of m-LLDPE at 150 or 165  $\mu$  thickness can thus be replaced c-LLDPE film at 180  $\mu$  thickness. With this result, it obviously shows that 9 - 15% of the amount of the resin can be saved for heavy duty film production.

The MFI and density of HDPE/LLDPE blend show a correlation with the LLDPE content. The mechanical properties of HDPE/LLDPE films show synergistic effect on tensile strength and impact resistance comparing to MDPE films at the same thickness, 40 -80  $\mu$  thickness, with the same MFI and density. By this study, blending of HDPE and LLDPE at desired ratio according to the Equation 4.2 and 4.3 can be employed to make resin which can replace the conventional MDPE resin. Moreover, this study can be applied for producing the mixed resins which meet the individual requirement of commercial application instead of using the dedicated MDPE.

## 5.2 Suggestion for further study

The blending of HDPE and LLDPE has the advantage of low value of investment cost to produce the various properties of the resin without using the dedicated polymerization process. If the properties of several blends can be estimated by the selection of the resin and composition of the blend, it becomes very useful. Therefore, this research can be extended to study on the prediction method of the desired properties of HDPE/LLDPE blend with the blend composition by formulating the equation which is combined not only of MFI and density but also the other factors such as molecular weight distribution, etc.

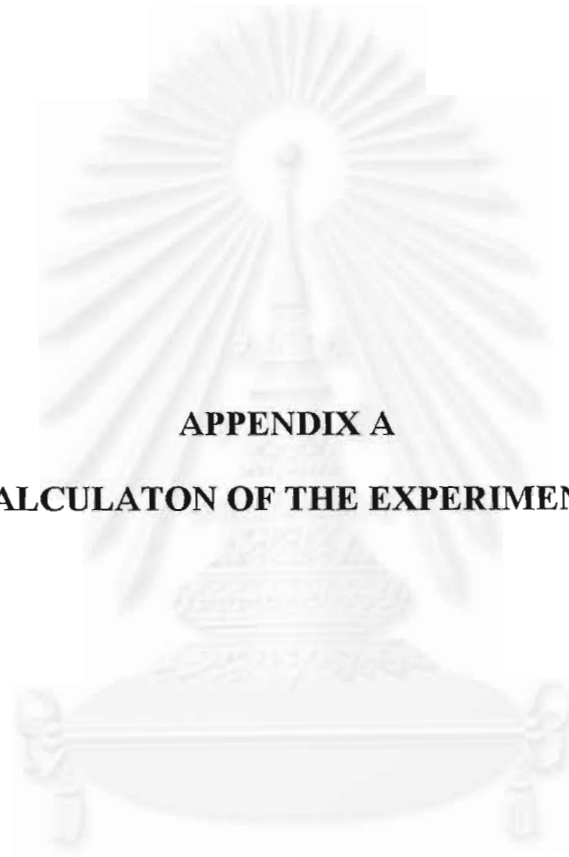
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**APPENDIX A**  
**CALCULATON OF THE EXPERIMENT**

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### **1. Calculation for density of the blend**

The density of the blend can be calculated with the simple rule of mixing by the following equation.

$$1/D_{\text{blend}} = W_A * (1/D_A) + W_B * (1/D_B) \text{ ----- Equation 4.2}$$

where ;  $D_{\text{blend}}$  = Density of the blend  
 $D_A$  = Density of component A  
 $D_B$  = Density of component B  
 $W_A$  = Weight fraction of component A  
 $W_B$  = Weight fraction of component B

### **2. Calculation for melt flow index of the blend**

The melt flow index of the blend from the mixing materials with different melt flow index can be calculated according the Equation 4.3 with the following

$$(W_A + W_B, \text{etc}) \log \text{MFI}(\text{blend}) = W_A \log \text{MFI}_A + W_B \log \text{MFI}_B, \text{etc} \text{ ---- Equation 4.3}$$

where;  $\text{MFI}(\text{blend})$  = Melt flow index of the blend  
 $\text{MFI}_A$  = Melt flow index of component A  
 $\text{MFI}_B$  = Melt flow index of component B  
 $W_A$  = Weight fraction of component A  
 $W_B$  = Weight fraction of component B

### 3. Calculation for film clarity

The light was transmitted through the sample and the density of film is measured. Thereafter, calculated the transmittance of film with the Equation 4.4.

$$\log 1/T = D$$

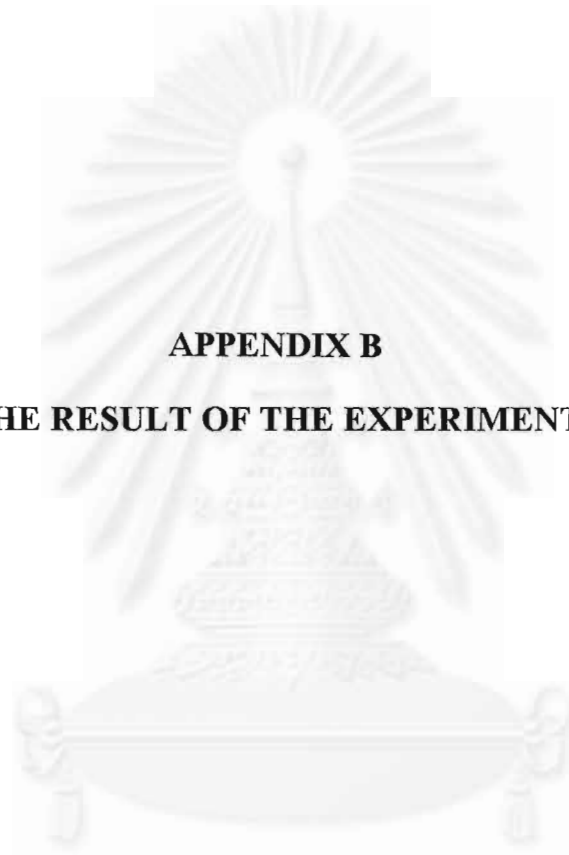
$$T = (1/10^D) * 100 \quad \text{----- Equation 4.4}$$

where; T = transmittance of film (%)

D = Density of film



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**APPENDIX B**  
**THE RESULT OF THE EXPERIMENT**

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The results of HDPE/LLDPE blends in heavy duty film application

Table A1 : Tensile strength at yield of HDPE/LLDPE film

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	Film direction	Tensile strength at yield of HDPE/m-LLDPE film ( $\text{kg/cm}^2$ )							Tensile strength at yield of HDPE/c-LLDPE film ( $\text{kg/cm}^2$ )							
			#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$	
150.0	60.0	MD	184.5	181.9	178.8	188.9	187.2	184.3	4.1	183.1	181.6	179.6	182.1	187.3	182.7	2.9	
		TD	215.1	218.0	214.5	216.3	220.0	216.8	2.2	194.1	192.3	191.7	190.0	193.7	192.4	1.6	
	70.0	MD	156.3	168.9	165.3	171.2	166.4	165.6	5.7	156.2	164.3	160.0	155.3	164.7	160.1	4.4	
		TD	152.7	180.4	183.0	194.5	185.1	179.1	15.7	177.7	178.3	173.8	183.3	176.7	178.0	3.4	
	80.0	MD	145.5	149.9	146.4	143.0	147.2	146.4	2.5	139.7	146.2	143.9	145.8	146.2	144.4	2.8	
		TD	205.4	168.7	160.9	141.1	159.3	167.1	23.7	165.6	154.2	157.7	158.8	148.9	157.0	6.1	
	90.0	MD	141.6	144.1	145.7	144.2	147.7	144.7	2.2	136.9	148.7	147.1	138.4	143.3	142.9	5.2	
		TD	155.7	156.1	156.4	159.9	152.3	156.1	2.7	142.7	152.7	146.5	154.2	152.2	149.7	4.9	
	100.0	MD	133.5	132.3	132.5	134.0	135.4	133.5	1.3	127.9	127.6	126.0	126.5	123.8	126.4	1.6	
		TD	148.8	145.9	149.2	147.7	145.3	147.4	1.7	145.0	142.1	143.2	138.8	144.5	142.7	2.5	
	165.0	60.0	MD	171.2	170.2	187.5	174.3	172.0	175.0	7.1	172.7	170.9	165.7	172.9	170.2	170.5	2.9
			TD	208.8	201.9	201.4	203.2	204.0	203.9	2.9	209.8	201.0	200.0	204.2	216.2	206.2	6.8
70.0		MD	168.5	166.3	169.7	167.4	166.5	167.7	1.4	162.5	161.1	166.2	160.3	160.1	162.0	2.5	
		TD	199.0	194.2	209.9	205.7	194.2	200.6	7.0	191.6	183.5	184.7	185.9	189.6	187.1	3.4	
80.0		MD	150.8	154.2	155.3	152.8	154.1	153.4	1.7	156.4	162.0	157.1	151.8	160.8	157.6	4.0	
		TD	172.2	170.6	177.7	172.7	170.7	172.8	2.9	157.3	160.1	155.1	157.3	158.2	157.6	1.8	
90.0		MD	146.3	143.4	140.6	140.0	137.3	141.5	3.4	132.3	145.5	132.5	141.7	144.6	139.3	6.5	
		TD	146.5	148.2	154.0	148.5	153.4	150.1	3.4	145.2	140.6	154.7	148.5	147.3	147.3	5.1	
100.0		MD	134.7	152.8	131.4	134.4	134.0	137.5	8.7	125.4	121.5	128.1	131.2	125.7	126.4	3.6	
		TD	147.2	141.7	147.2	140.9	138.4	143.1	4.0	135.8	133.0	138.2	133.2	135.8	135.2	2.2	
180.0		60.0	MD	181.0	183.9	183.6	178.6	186.5	182.7	3.0	178.7	172.6	180.7	186.6	178.5	179.4	5.0
			TD	205.1	200.0	201.8	205.5	203.7	203.2	2.3	211.2	171.6	209.5	210.5	205.9	201.7	17.0
	70.0	MD	170.1	175.2	173.6	172.4	177.5	173.8	2.8	168.0	174.3	165.8	167.7	163.6	167.9	4.0	
		TD	192.3	193.3	195.8	191.2	190.1	192.5	2.2	192.9	191.3	187.4	193.9	190.9	191.3	2.5	
	80.0	MD	158.8	160.2	159.4	158.6	161.7	159.7	1.3	163.1	150.6	149.6	145.5	157.7	153.3	7.0	
		TD	164.0	166.4	164.6	163.4	168.4	165.4	2.0	172.4	152.0	174.2	149.6	174.6	164.6	12.6	
	90.0	MD	154.2	147.8	152.3	150.1	151.1	151.1	2.4	138.1	141.1	145.7	138.3	139.8	140.6	3.1	
		TD	146.3	147.8	146.7	149.1	144.5	146.9	1.7	152.6	149.1	155.3	152.0	155.8	153.0	2.7	
	100.0	MD	140.8	144.5	139.9	147.9	144.3	143.5	3.2	125.2	120.7	123.9	125.7	124.4	124.0	2.0	
		TD	142.6	138.1	139.6	141.7	139.3	140.3	1.8	135.3	134.4	134.2	132.2	133.6	133.9	1.1	

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Table A2 : Elongation at break of HDPE/LLDPE film

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	Film direction	Elongation at break of HDPE/m-LLDPE film (%)								Elongation at break of HDPE/c-LLDPE film (%)							
			#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$		
150.0	60.0	MD	499.0	518.4	524.2	509.4	605.1	511.2	10.1	587.2	615.1	601.5	630.2	595.6	605.9	17.0		
		TD	626.8	651.3	656.4	652.0	658.0	646.9	12.7	679.9	689.6	704.2	705.7	711.8	698.2	13.1		
	70.0	MD	577.8	576.7	519.5	578.2	485.1	547.5	43.0	684.6	606.0	583.0	578.7	542.1	598.9	53.1		
		TD	591.9	515.9	616.1	510.7	527.8	562.5	48.2	748.3	758.7	726.5	662.4	671.5	713.5	44.2		
	80.0	MD	568.6	597.8	537.6	565.3	602.3	574.3	26.4	534.9	574.8	587.4	563.2	569.8	566.0	19.5		
		TD	674.6	610.1	517.1	658.9	668.4	625.8	65.9	688.2	788.5	761.1	654.0	738.4	726.0	54.6		
	90.0	MD	613.1	594.2	625.6	578.3	546.5	591.5	31.0	767.4	666.4	699.3	596.0	694.6	684.7	62.0		
		TD	684.6	588.1	699.5	753.1	772.1	699.5	72.1	715.6	785.3	708.0	722.5	792.6	744.8	40.7		
	100.0	MD	667.0	535.6	563.2	673.1	668.4	617.5	63.2	714.2	696.3	689.9	724.5	725.8	709.9	16.6		
		TD	740.6	700.8	702.0	756.4	702.3	720.4	26.2	770.5	776.5	769.5	799.3	801.4	783.4	15.7		
	165.0	60.0	MD	561.6	491.9	470.3	489.8	580.0	518.7	48.7	715.4	643.9	611.1	565.4	611.7	629.5	55.6	
			TD	575.3	539.3	678.8	563.9	544.1	580.3	57.0	662.7	606.9	713.1	737.9	605.7	663.3	60.5	
70.0		MD	404.2	528.8	566.4	565.2	540.1	518.9	65.7	725.8	569.7	740.6	660.1	642.5	665.7	72.5		
		TD	548.8	507.7	499.7	518.8	511.7	517.3	18.9	797.3	691.6	710.7	722.8	712.7	727.0	40.9		
80.0		MD	611.7	600.7	472.5	559.7	560.4	561.0	54.7	629.2	785.2	889.2	909.7	683.2	779.3	123.4		
		TD	607.4	687.6	607.0	618.4	558.9	615.9	46.2	648.3	721.1	765.1	798.3	828.2	752.2	70.4		
90.0		MD	624.1	425.8	463.1	534.1	638.2	537.1	94.4	749.3	605.4	635.2	715.1	657.0	672.4	58.8		
		TD	561.2	720.8	599.0	658.7	598.0	627.5	62.8	704.7	790.3	775.5	700.0	686.2	731.3	47.8		
100.0		MD	621.8	551.5	736.9	560.9	556.9	605.4	78.9	747.0	830.2	778.2	689.6	560.9	721.2	103.1		
		TD	540.6	675.0	702.0	749.0	612.1	655.9	81.2	802.0	873.1	835.6	829.5	867.8	841.5	29.3		
180.0		60.0	MD	630.9	576.8	522.6	500.5	479.2	542.0	61.6	709.0	697.6	757.4	699.0	660.7	684.7	59.7	
			TD	547.8	500.2	581.7	625.8	569.3	565.0	46.1	669.7	780.9	654.3	687.2	602.7	677.0	65.6	
	70.0	MD	532.4	532.2	563.9	449.3	501.8	515.9	43.2	704.7	624.1	638.9	584.0	740.3	658.4	63.1		
		TD	642.6	601.3	592.1	613.9	531.7	596.3	40.8	699.0	707.4	701.1	718.1	668.1	698.7	18.7		
	80.0	MD	592.9	522.5	513.9	548.1	609.4	557.4	42.3	720.5	711.2	721.5	839.2	734.2	745.3	53.1		
		TD	509.1	592.1	514.9	590.9	573.8	556.2	41.0	792.9	662.1	701.7	705.7	829.2	738.3	69.7		
	90.0	MD	528.5	539.9	580.7	616.1	537.7	560.6	37.0	795.6	786.3	657.7	774.8	736.6	750.2	56.4		
		TD	614.8	576.7	575.7	643.9	579.5	598.1	30.3	830.2	753.3	817.1	797.6	861.1	811.9	40.1		
	100.0	MD	569.1	595.3	521.1	629.2	570.3	577.0	39.7	796.3	788.4	811.2	784.5	799.8	796.0	10.4		
		TD	649.7	719.5	685.9	657.9	654.4	673.5	29.3	736.6	763.7	839.9	796.0	850.3	797.3	48.6		

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Table A3 : Impact resistance of HDPE/LLDPE film

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	Impact resistance of HDPE/m-LLDPE film (J)								Impact resistance of HDPE/c-LLDPE film (J)							
		#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$		
150.0	60.0	6.37	6.36	8.55	7.15	7.02	7.09	0.89	7.16	8.10	7.51	7.66	7.52	7.59	0.34		
	70.0	6.48	6.83	8.43	7.54	6.98	7.25	0.76	7.85	6.70	7.80	7.23	7.67	7.45	0.49		
	80.0	9.45	6.57	6.35	8.11	6.81	7.46	1.31	6.55	7.31	6.43	7.15	6.38	6.76	0.43		
	90.0	9.72	9.78	8.93	8.55	10.40	9.48	0.74	7.53	7.61	7.38	6.95	8.06	7.51	0.40		
	100.0	15.34	14.79	17.98	16.25	15.82	16.04	1.22	9.69	7.34	9.12	7.22	10.21	8.72	1.37		
165.0	60.0	9.86	7.90	8.76	8.63	9.05	8.84	0.71	8.48	8.50	7.92	7.54	9.06	8.30	0.59		
	70.0	9.26	8.13	8.60	9.56	7.77	8.66	0.75	6.94	7.94	7.95	6.23	8.99	7.61	1.06		
	80.0	7.60	7.13	7.37	7.45	7.28	7.37	0.18	6.93	6.97	7.56	6.39	7.92	7.15	0.60		
	90.0	9.56	10.69	10.30	9.87	10.50	10.18	0.46	8.15	9.29	8.51	8.46	8.84	8.65	0.43		
	100.0	14.01	16.79	13.9	15.11	14.69	14.90	1.17	9.07	8.83	9.63	9.11	9.24	9.18	0.29		
180.0	60.0	7.72	10.14	7.71	9.21	7.84	8.52	1.10	7.82	8.38	8.59	8.45	8.08	8.26	0.31		
	70.0	9.10	10.86	10.86	9.67	10.88	10.27	0.84	9.25	8.68	8.45	9.13	8.46	8.79	0.38		
	80.0	10.67	10.58	10.04	11.63	9.35	10.49	0.86	8.93	9.21	8.89	9.58	8.44	9.01	0.42		
	90.0	9.10	11.88	11.83	10.38	11.49	10.94	1.19	9.06	10.25	9.37	10.54	8.58	9.56	0.82		
	100.0	15.45	14.74	11.76	13.21	14.76	13.98	1.49	8.94	9.26	10.60	10.25	8.95	9.60	0.77		



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**Table A4** : Impact resistance of HDPE/LLDPE film and %Change  
while comparing with 100%c-LLDPE film at 180 micron thickness

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	Impact resistance of HDPE/LLDPE film (J)		% Change of impact resistance	
		m-LLDPE	c-LLDPE	m-LLDPE	c-LLDPE
150.0	60	7.09	7.59	-26.1	-20.9
	70	7.25	7.45	-24.5	-22.4
	80	7.46	6.76	-22.3	-29.5
	90	9.48	7.51	-1.3	-21.8
	100	16.04	8.72	67.0	-9.2
165.0	60	8.84	8.30	-7.9	-13.5
	70	8.66	7.61	-9.8	-20.7
	80	7.37	7.15	-23.3	-25.5
	90	10.18	8.65	6.0	-9.9
	100	14.90	9.18	55.2	-4.4
180.0	60	8.52	8.26	-11.2	-13.9
	70	10.27	8.79	7.0	-8.4
	80	10.49	9.01	9.3	-6.1
	90	10.94	9.56	13.9	-0.4
	100	13.98	9.60	45.7	0.0

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**Table A5** : Tensile strength at yield of HDPE/LLDPE film and %Change  
while comparing with 100%c-LLDPE film at 180 micron thickness

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	Film Direction	Tensile strength at yield of HDPE/LLDPE film (kg/cm <sup>2</sup> )		% Change of tensile strength at yield	
			m-LLDPE	c-LLDPE	m-LLDPE	c-LLDPE
150.0	60	MD	184.3	182.7	48.6	47.4
		TD	216.8	192.4	61.8	43.6
	70	MD	165.6	160.1	33.6	29.1
		TD	179.1	178.0	33.7	32.9
	80	MD	146.4	144.4	18.1	16.4
		TD	167.1	157.0	24.7	17.2
	90	MD	144.7	142.9	16.7	15.2
		TD	156.1	149.7	16.5	11.7
	100	MD	133.5	126.4	7.7	1.9
		TD	147.4	142.7	10.0	6.6
165.0	60	MD	175.0	170.5	41.2	37.5
		TD	203.9	206.2	52.2	54.0
	70	MD	167.7	162.0	35.2	30.7
		TD	200.6	187.1	49.8	39.7
	80	MD	153.4	157.6	23.8	27.1
		TD	172.8	157.6	29.0	17.7
	90	MD	141.5	139.3	14.1	12.4
		TD	150.1	147.3	12.1	9.9
	100	MD	137.5	126.4	10.9	1.9
		TD	143.1	135.2	6.8	0.9
180.0	60	MD	182.7	179.4	47.4	44.7
		TD	203.2	201.7	51.7	50.6
	70	MD	173.8	167.9	40.2	35.4
		TD	192.5	191.3	43.8	42.8
	80	MD	159.7	153.3	28.8	23.6
		TD	165.4	164.6	23.5	22.9
	90	MD	151.1	140.6	21.9	13.4
		TD	146.9	153.0	9.7	14.2
	100	MD	143.5	124.0	15.7	0.0
		TD	140.3	133.9	4.7	0.0

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Table A6 : Melting point and % Crystallinity of HDPE/LLDPE blend and MDPE (GA3245)

LLDPE content (% by weight)	HDPE/m-LLDPE blend			HDPE/c-LLDPE blend		
	Melting temperature (°C)	ΔH (J/g)	% Crystallinity	Melting temperature (°C)	ΔH (J/g)	% Crystallinity
0	130.4	186.14	60.05	130.4	186.14	60.05
20	129.9	166.76	53.79	129.2	164.61	53.10
40	127.6	149.38	48.19	127.4	151.28	48.80
60	125.6	124.41	40.13	125.7	123.44	39.82
80	124.4	110.93	35.78	124.1	104.97	33.86
100	120.8	86.16	27.79	119.4	84.59	27.29
GA3245	128	173.8	56.06			

Table A7 : Seal strength of HDPE/LLDPE film

Film Thickness (μ)	LLDPE content (% by weight)	Seal temperature (°C)	Seal strength of HDPE/m-LLDPE film (kg)								Seal strength of HDPE/c-LLDPE film (kg)							
			#1	#2	#3	#4	#5	average	σ	#1	#2	#3	#4	#5	average	σ		
150.0	60.0	130.0	4.43	5.08	5.25	5.58	5.70	5.47	0.16	5.09	6.07	4.97	5.19	6.66	5.60	0.74		
		140.0	5.09	6.07	4.97	5.19	6.66	5.60	0.74	3.84	4.00	3.70	3.87	5.85	4.25	0.90		
		150.0	5.03	5.28	5.81	5.17	6.40	5.50	0.55	4.51	5.45	4.36	5.83	5.37	5.10	0.64		
	70.0	130.0	5.11	4.62	4.99	4.97	4.88	4.91	0.18	5.53	4.99	4.60	4.63	6.01	5.15	0.61		
		140.0	5.53	4.99	4.60	4.63	6.01	5.15	0.61	3.66	4.56	3.57	3.91	4.66	4.07	0.51		
		150.0	6.16	6.18	6.24	5.58	6.44	6.12	0.32	6.09	6.30	5.26	5.93	5.31	5.58	0.40		
	80.0	130.0	4.85	5.17	5.13	4.97	4.91	5.01	0.14	5.18	5.11	5.11	5.35	5.52	5.25	0.18		
		140.0	5.18	5.11	5.11	5.35	5.52	5.25	0.18	4.13	4.83	4.24	4.41	4.65	4.45	0.29		
		150.0	4.04	4.11	3.84	4.15	4.02	4.03	0.12	4.73	4.95	4.97	4.15	4.69	4.70	0.33		
	90.0	130.0	5.28	5.56	5.59	5.75	5.25	4.62	0.26	4.90	4.81	4.58	4.54	4.85	4.73	0.16		
		140.0	4.90	4.81	4.58	4.54	4.85	4.73	0.16	4.76	4.91	4.65	4.53	4.34	4.64	0.22		
		150.0	5.84	2.56	5.35	4.60	3.84	4.44	1.30	4.83	4.31	4.75	4.47	4.55	4.58	0.21		
100.0	130.0	4.695	4.513	4.719	5.01	5.24	4.84	0.29	5.14	4.97	4.75	5.01	4.93	4.96	0.14			
	140.0	5.138	4.966	4.749	5.01	4.93	4.96	0.14	4.22	4.09	4.13	4.16	4.32	4.18	0.09			
	150.0	5.36	4.89	6.33	5.85	6.10	5.71	0.58	4.23	4.29	3.95	3.96	4.11	4.11	0.15			
180.0	60.0	130.0	6.30	6.91	6.87	6.21	5.92	6.44	0.43	6.37	5.00	6.92	6.88	7.51	6.54	0.95		
		140.0	6.37	5.00	6.92	6.88	7.51	6.54	0.95	5.54	6.04	5.03	5.90	5.88	5.68	0.40		
		150.0	7.44	7.15	7.21	6.88	6.82	7.10	0.25	6.48	6.81	6.20	5.96	6.43	6.38	0.32		
	70.0	130.0	6.67	5.51	5.71	5.59	5.45	5.79	0.50	5.40	5.70	5.85	5.44	5.80	5.64	0.21		
		140.0	5.40	5.70	5.85	5.44	5.80	5.64	0.21	5.94	6.06	6.45	5.85	6.71	6.20	0.37		
		150.0	5.52	4.52	5.35	6.02	5.45	6.49	0.34	6.06	6.83	6.19	6.75	6.81	6.49	0.34		
	80.0	130.0	4.49	5.59	5.44	5.43	5.51	5.29	0.45	5.48	5.69	6.17	5.12	5.28	5.55	0.41		
		140.0	5.48	5.69	6.17	5.12	5.28	5.55	0.41	3.76	3.59	3.26	3.72	4.28	3.72	0.37		
		150.0	6.21	5.46	6.52	5.80	5.46	5.89	0.47	4.84	6.13	5.67	5.33	5.39	5.47	0.48		
	90.0	130.0	5.96	5.26	5.61	5.66	5.51	5.60	0.25	4.83	5.55	4.98	5.19	4.66	5.04	0.35		
		140.0	4.55	5.62	4.96	4.78	4.85	4.95	0.40	5.22	4.52	4.80	4.76	4.41	4.74	0.31		
		150.0	6.57	5.68	5.86	6.56	7.13	6.36	0.59	5.00	4.73	4.72	4.55	5.02	4.80	0.20		
100.0	130.0	4.77	4.43	4.44	4.70	4.24	4.51	0.22	4.76	5.54	4.90	4.72	4.72	4.93	0.35			
	140.0	3.88	4.27	3.75	3.85	4.49	4.05	0.32	4.22	5.63	5.09	5.12	4.11	4.83	0.65			
	150.0	4.00	4.263	4.242	4.59	4.19	4.26	0.21	5.03	4.86	4.79	5.22	4.75	4.93	0.20			

Table A8 : Clarity of HDPE/LLDPE film

Film Thickness ( $\mu$ )	LLDPE content (% by weight)	HDPE/LLDPE Film	Density of film							Clarity						
			#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$
150.0	60.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	70.0	HDPE/m-LLDPE	0.06	0.06	0.06	0.06	0.06	0.06	0.00	87	87	87	87	87	87	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	80.0	HDPE/m-LLDPE	0.06	0.06	0.06	0.06	0.06	0.06	0.00	87	87	87	87	87	87	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	90.0	HDPE/m-LLDPE	0.06	0.06	0.06	0.06	0.06	0.06	0.00	87	87	87	87	87	87	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	100.0	HDPE/m-LLDPE	0.06	0.06	0.06	0.06	0.06	0.06	0.00	87	87	87	87	87	87	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
165.0	60.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	70.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	80.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	90.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	100.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
180.0	60.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.09	0.09	0.09	0.09	0.09	0.09	0.00	81	81	81	81	81	81	0.00
	70.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	80.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	90.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00
	100.0	HDPE/m-LLDPE	0.07	0.07	0.07	0.07	0.07	0.07	0.00	85	85	85	85	85	85	0.00
		HDPE/c-LLDPE	0.08	0.08	0.08	0.08	0.08	0.08	0.00	83	83	83	83	83	83	0.00

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The results of the comparison between HDPE/LLDPE blend and MDPE

Table A9 : MFR<sub>2.16</sub> at 190 °C of HDPE/LLDPE blends

LLDPE content (% by weight)	MFR <sub>2.16</sub> at 190 °C of HDPE/m-LLDPE blends								MFR <sub>2.16</sub> at 190 °C of HDPE/c-LLDPE blends							
	#1	#2	#3	#4	#5	average	σ	#1	#2	#3	#4	#5	average	σ		
0.0	0.037	0.029	0.035	0.031	0.036	0.034	0.00	0.037	0.035	0.029	0.028	0.039	0.034	0.00		
20.0	0.069	0.065	0.063	0.062	0.070	0.066	0.00	0.075	0.075	0.072	0.078	0.071	0.074	0.00		
40.0	0.129	0.126	0.126	0.130	0.125	0.127	0.00	0.157	0.154	0.153	0.151	0.160	0.155	0.00		
60.0	0.306	0.300	0.302	0.308	0.301	0.303	0.00	0.265	0.261	0.259	0.254	0.269	0.262	0.01		
70.0	0.420	0.411	0.414	0.422	0.410	0.415	0.01	0.369	0.367	0.346	0.381	0.340	0.361	0.02		
80.0	0.676	0.619	0.639	0.647	0.642	0.645	0.02	0.512	0.502	0.517	0.501	0.516	0.510	0.01		
90.0	0.825	0.823	0.824	0.829	0.820	0.824	0.00	0.699	0.698	0.719	0.712	0.695	0.705	0.01		
100.0	1.316	1.318	1.323	1.325	1.315	1.319	0.00	1.013	1.011	1.014	1.010	1.011	1.012	0.00		

Table A10 : Density of HDPE/LLDPE blend

LLDPE content (% by weight)	Density of HDPE/m-LLDPE blends								Density of HDPE/c-LLDPE blends							
	#1	#2	#3	#4	#5	average	σ	#1	#2	#3	#4	#5	average	σ		
0.0	0.956	0.955	0.955	0.956	0.956	0.956	0.001	0.956	0.955	0.955	0.956	0.956	0.956	0.001		
20.0	0.949	0.948	0.949	0.949	0.950	0.949	0.001	0.948	0.949	0.949	0.949	0.948	0.949	0.001		
40.0	0.942	0.942	0.941	0.943	0.943	0.942	0.001	0.941	0.941	0.942	0.941	0.941	0.941	0.000		
60.0	0.935	0.935	0.935	0.935	0.935	0.935	0.000	0.932	0.934	0.933	0.931	0.932	0.932	0.001		
70.0	0.930	0.929	0.929	0.930	0.930	0.930	0.001	0.933	0.932	0.932	0.930	0.932	0.932	0.001		
80.0	0.929	0.929	0.929	0.928	0.929	0.929	0.000	0.930	0.928	0.927	0.928	0.929	0.928	0.001		
90.0	0.928	0.927	0.928	0.927	0.928	0.928	0.001	0.924	0.926	0.926	0.926	0.926	0.926	0.001		
100.0	0.923	0.923	0.922	0.924	0.923	0.923	0.001	0.921	0.920	0.920	0.921	0.920	0.920	0.001		

Table A11 : Tensile strength at yield of HDPE/LLDPE film and MDPE film

Film Thickness ( $\mu$ )	Film direction	Tensile strength at yield of HDPE/m-LLDPE film at 20% m-LLDPE (kg/cm <sup>2</sup> )								Tensile strength at yield of HDPE/c-LLDPE film at 20% c-LLDPE (kg/cm <sup>2</sup> )							
		#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$		
40.0	MD	268.7	258.9	257.8	270.5	260.2	263.2	5.9	252.5	256.7	254.8	265.1	255.0	256.8	4.9		
	TD	303.3	296.8	305.9	297.9	306.9	302.2	4.6	285.0	283.6	302.6	283.0	295.6	290.0	8.7		
60.0	MD	252.2	252.3	253.6	257.6	253.4	253.8	2.2	244.7	251.9	254.3	244.0	250.4	249.1	4.5		
	TD	293.2	274.5	291.4	303.1	289.0	290.2	10.3	296.5	301.5	300.9	245.5	255.0	279.9	27.3		
80.0	MD	253.5	249.2	251.7	226.3	251.5	246.4	11.4	242.4	244.6	243.7	241.7	243.6	243.2	1.1		
	TD	291.6	286.4	288.3	235.8	281.4	276.7	23.2	237.0	276.4	279.1	274.9	278.9	269.3	18.1		

Table A12 : Elongation at break of HDPE/LLDPE film and MDPE film

Film Thickness ( $\mu$ )	Film direction	Elongation at break of HDPE/m-LLDPE film at 20% m-LLDPE (kg/cm <sup>2</sup> )								Elongation at break of HDPE/c-LLDPE film at 20% c-LLDPE (kg/cm <sup>2</sup> )							
		#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$		
40.0	MD	441.6	402.8	403.7	442.6	443.5	426.8	21.5	506.9	419.6	396.8	468.1	491.9	456.7	47.0		
	TD	534.9	535.7	508.0	501.0	597.1	535.3	37.9	602.0	545.3	509.6	503.2	530.7	538.2	39.4		
60.0	MD	504.4	433.0	528.0	506.9	474.5	489.4	36.8	535.7	558.4	520.0	582.0	583.9	556.0	28.1		
	TD	592.9	602.3	531.0	439.3	551.5	543.4	65.1	613.7	618.8	589.4	600.7	589.6	602.4	13.5		
80.0	MD	583.5	504.7	493.6	520.5	582.7	537.0	43.2	575.5	586.7	562.6	611.4	601.0	587.4	19.5		
	TD	558.0	533.0	551.0	525.2	602.1	553.9	30.0	617.8	588.1	627.2	631.2	637.6	620.4	19.4		

Table A13 : Impact resistance of HDPE/LLDPE film and MDPE film

Film Thickness ( $\mu$ )	Impact resistance of HDPE/m-LLDPE film at 20% m-LLDPE (kg/cm <sup>2</sup> )								Impact resistance of HDPE/c-LLDPE film at 20% c-LLDPE (kg/cm <sup>2</sup> )							
	#1	#2	#3	#4	#5	average	$\sigma$	#1	#2	#3	#4	#5	average	$\sigma$		
40.0	1.39	1.46	3.16	3.06	3.99	2.61	1.14	2.88	3.76	2.65	3.31	3.36	3.19	0.43		
60.0	3.85	3.76	3.04	3.60	3.23	3.50	0.35	4.90	4.74	4.60	4.57	4.47	4.66	0.17		
80.0	3.91	4.66	4.05	5.09	4.10	4.36	0.50	4.89	5.62	5.24	5.72	6.10	5.51	0.46		

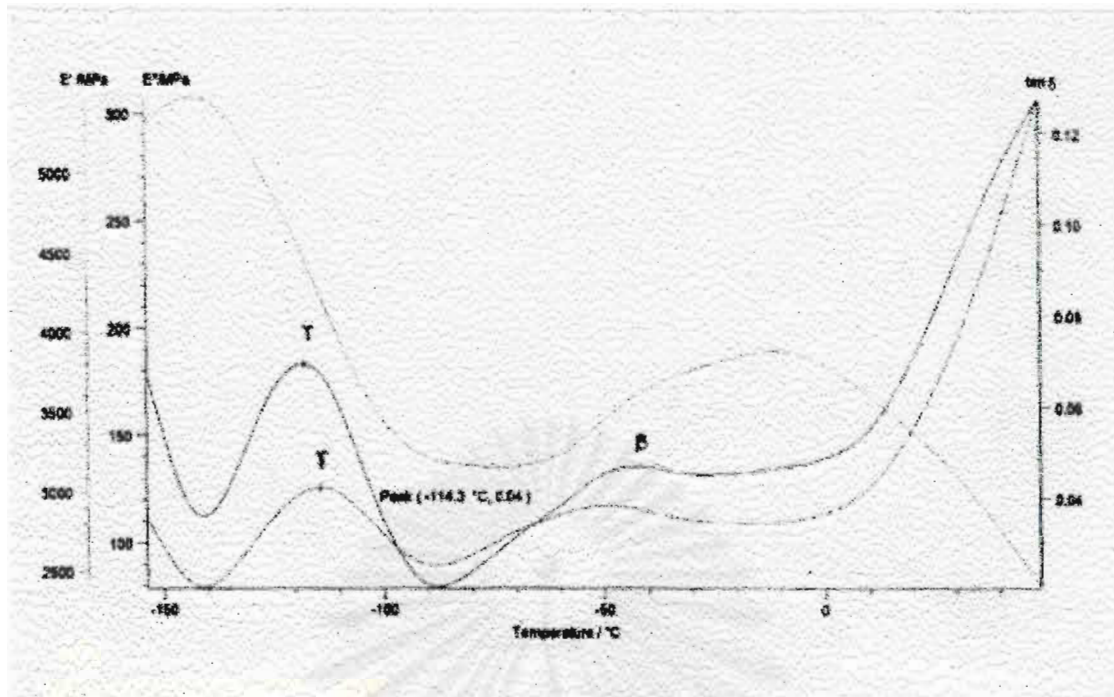


Figure A1 : Dynamic mechanical relaxation of HDPE

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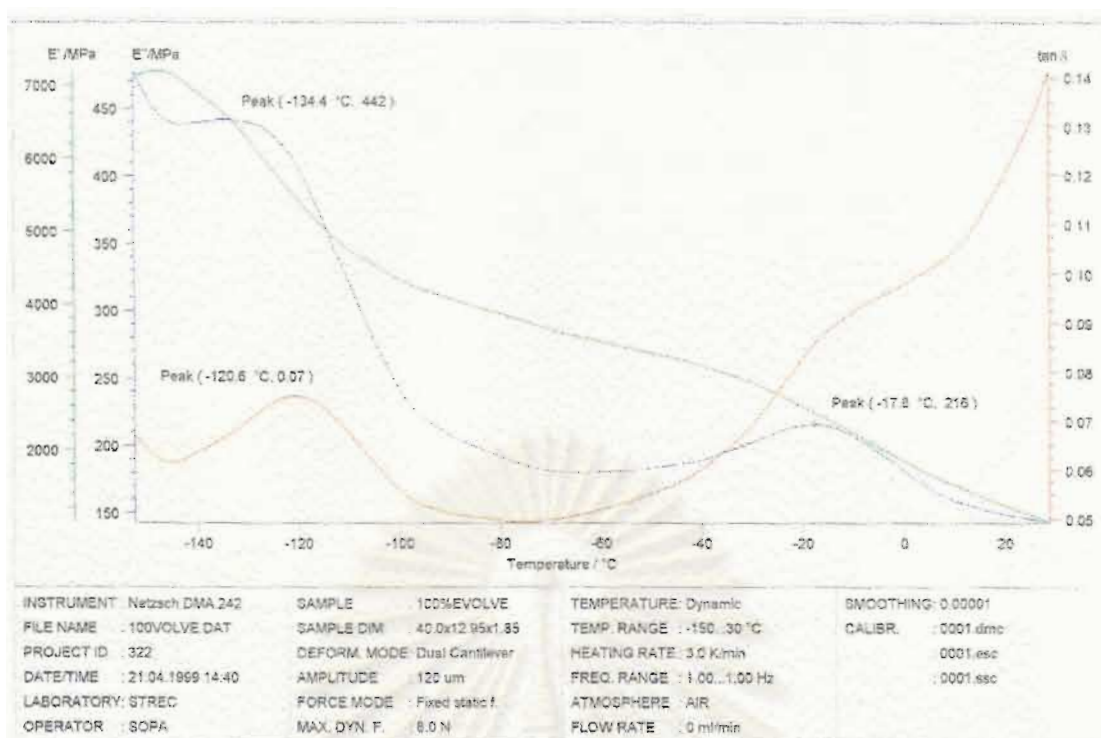


Figure A2 : Dynamic mechanical relaxation of m-LLDPE

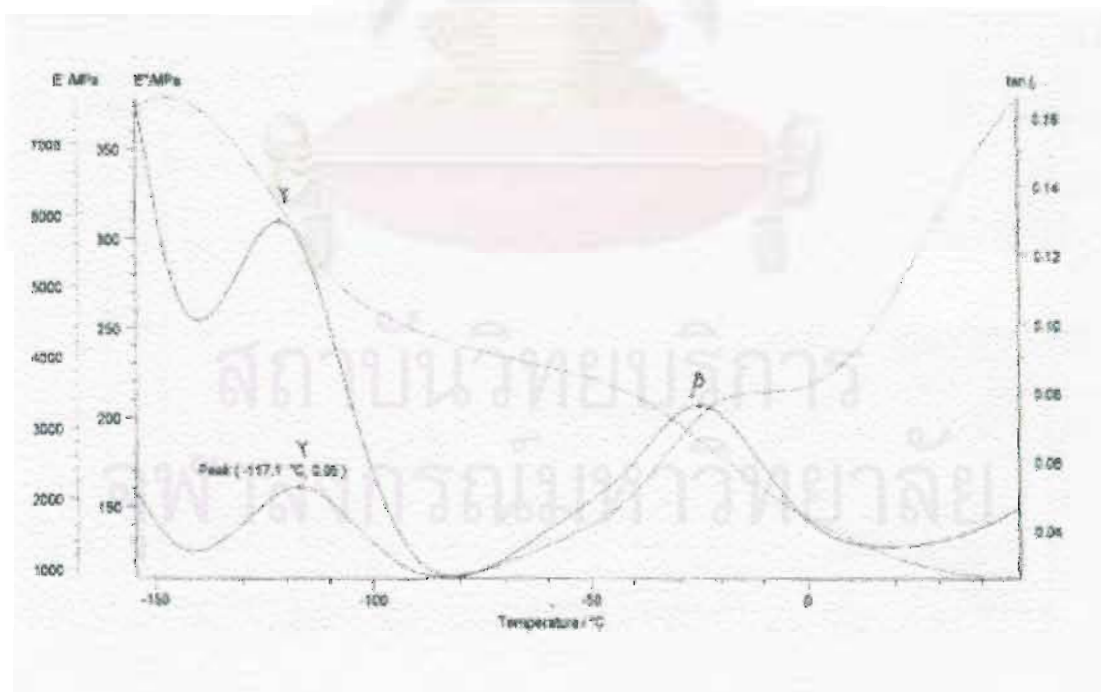


Figure A3 : Dynamic mechanical relaxation of c-LLDPE



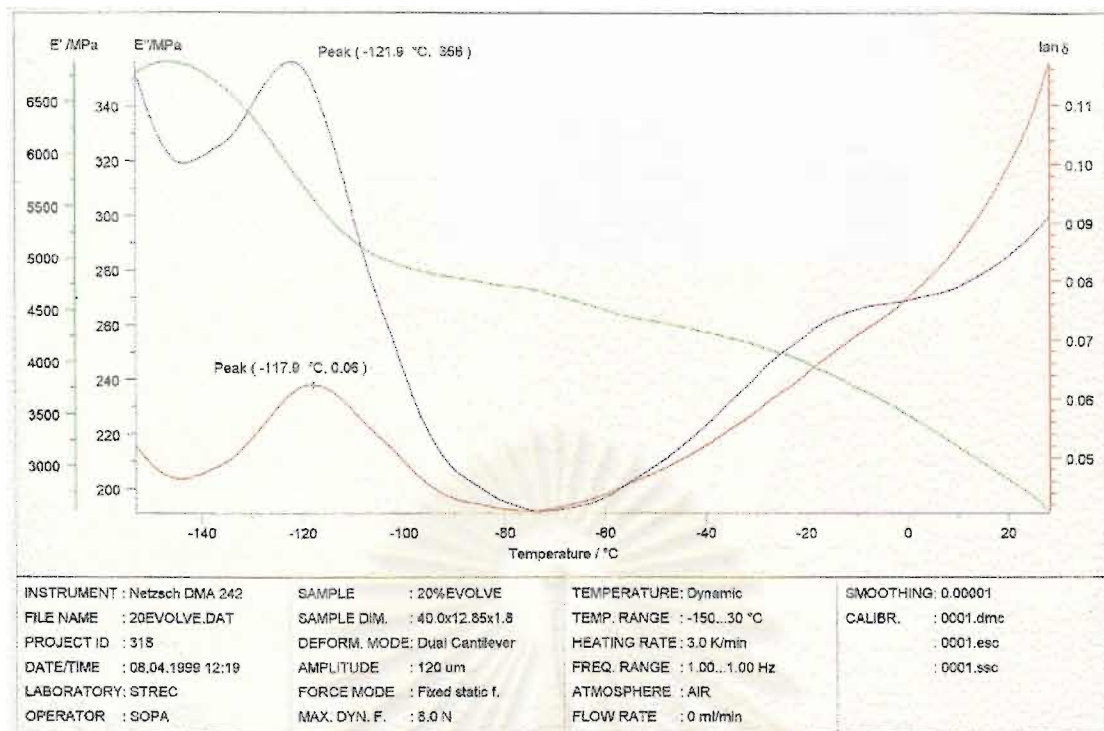


Figure A4 : Dynamic mechanical relaxation of 20% m-LLDPE in HDPE/m-LLDPE blend

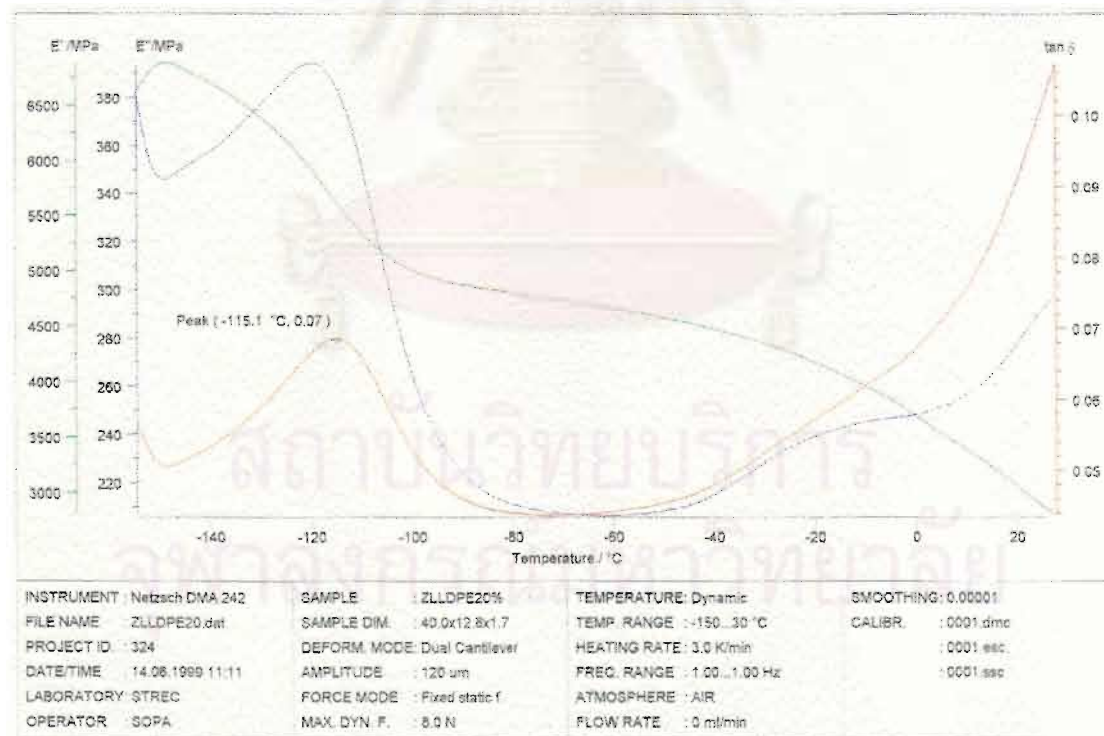


Figure A5 : Dynamic mechanical relaxation of 20% c-LLDPE in HDPE/c-LLDPE blend

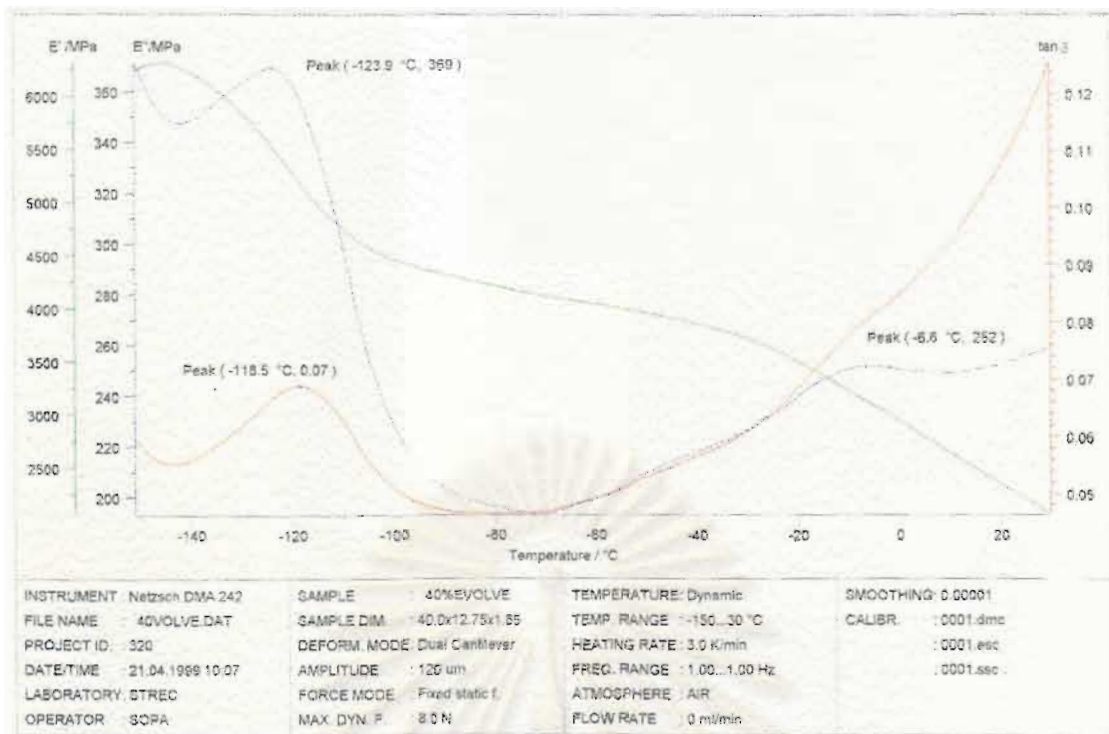


Figure A6 : Dynamic mechanical relaxation of 40% m-LLDPE in HDPE/m-LLDPE blend



Figure A7 : Dynamic mechanical relaxation of 40% c-LLDPE in HDPE/c-LLDPE blend

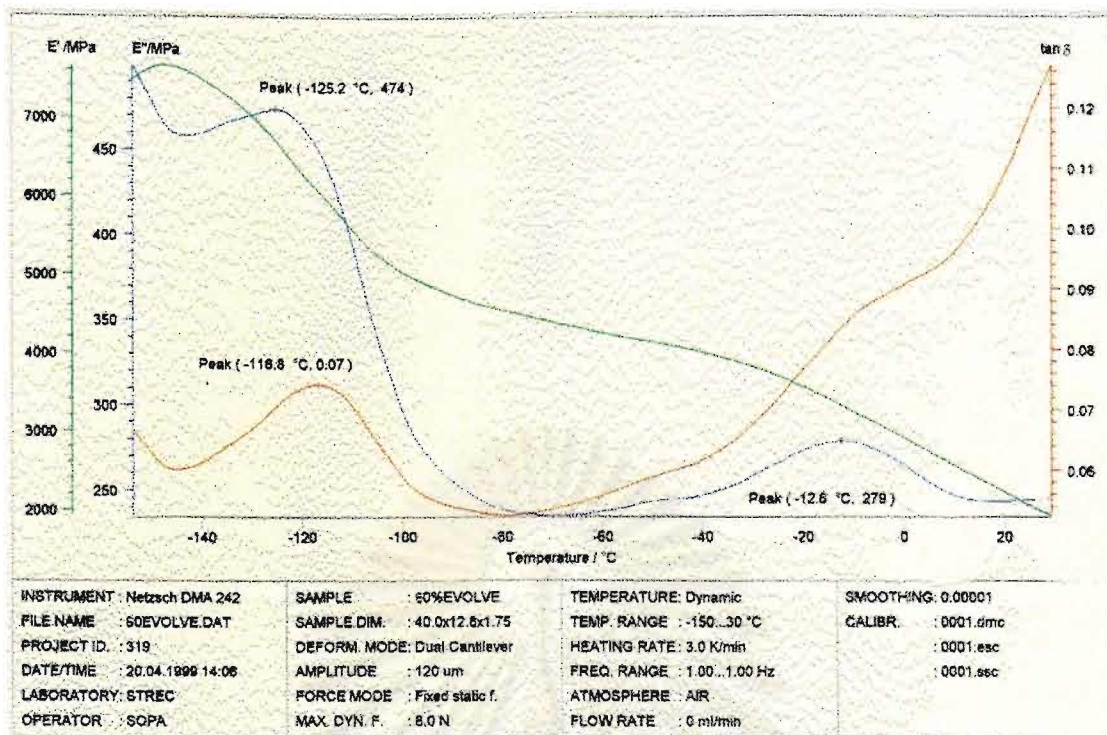


Figure A8 : Dynamic mechanical relaxation of 60% m-LLDPE in HDPE/m-LLDPE blend

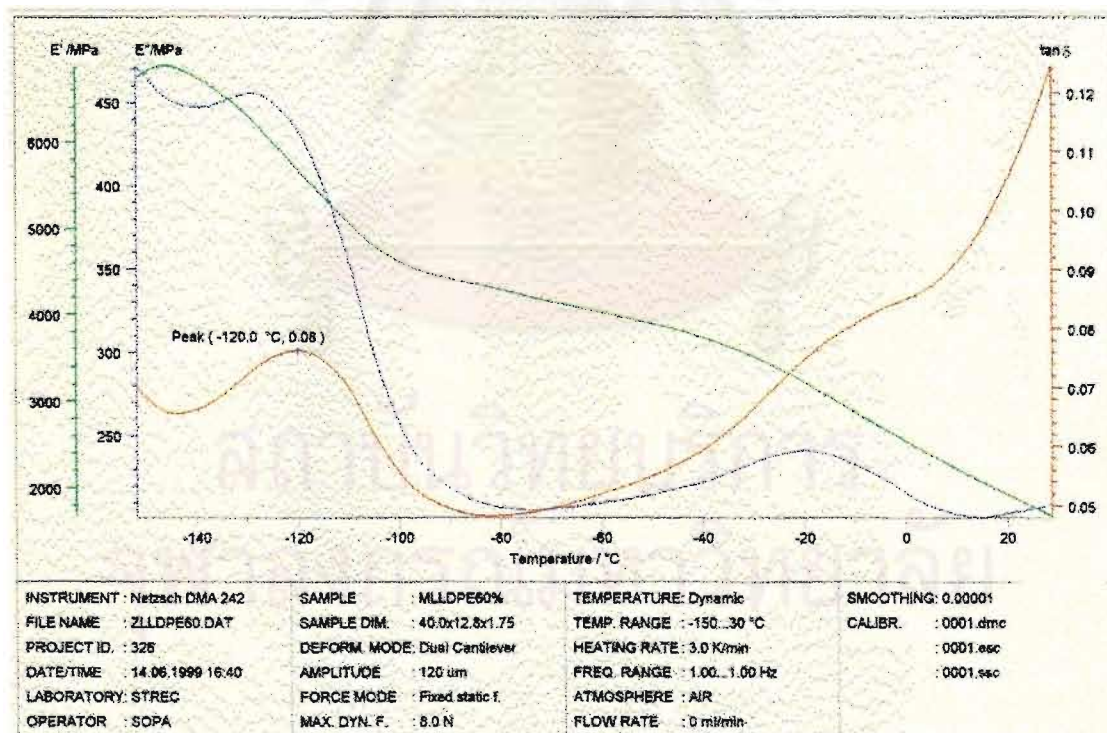


Figure A9 : Dynamic mechanical relaxation of 60% c-LLDPE in HDPE/c-LLDPE blend

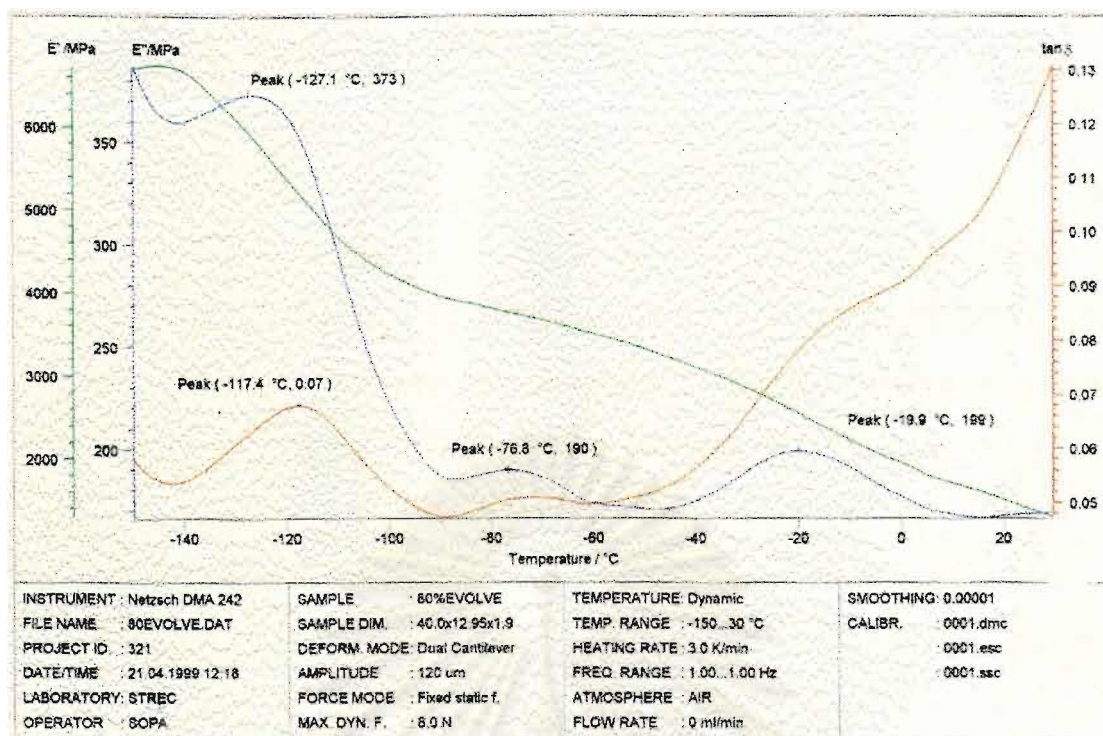


Figure A10 : Dynamic mechanical relaxation of 80% m-LLDPE in HDPE/m-LLDPE blend

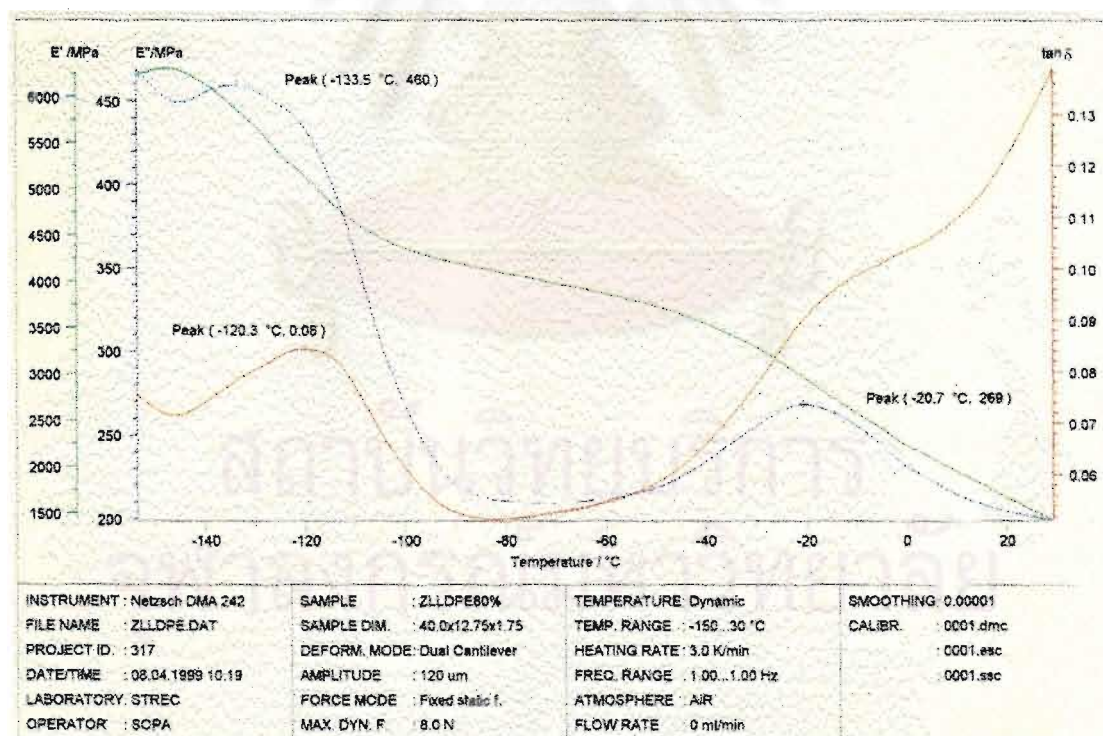


Figure A11 : Dynamic mechanical relaxation of 80% c-LLDPE in HDPE/c-LLDPE blend

## BIOGRAPHY

Miss Nuchanan Utairatana was born on February 7,1969 in Songkla. She received her Bachelor's degree of Science in Chemistry from Department of Chemistry, Faculty of Science, Prince of Songkla University in 1986. She is working in Quality Assurance, Research and Development Section, Technical Division, Production and Engineering Department, Bangkok Polyethylene Public Company Limited. She is pursuing a Master's Degree in Petrochemistry and Polymer Science, Graduate School, Chulalongkorn University, in 1998.



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