

ผลของภาวะการหลอมอัดรีดต่อสมบัติทางกายภาพของคอมพาวด์พอลิเอีลีนความหนาแน่นสูงเกรดท่อ



นายอาคม ปาไส

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วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต

จุฬาลงกรณ์มหาวิทยาลัย

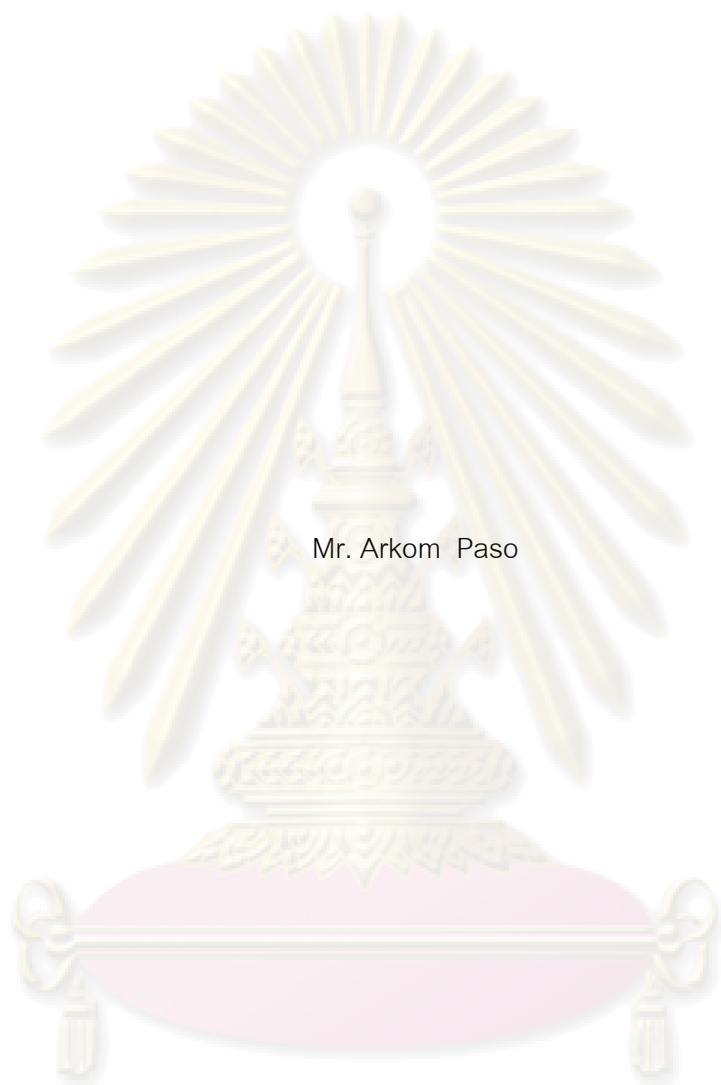
สาขาวิชาปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2551

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

EFFECT OF EXTRUSION CONDITIONS ON PHYSICAL PROPERTIES OF PIPE GRADE HIGH  
DENSITY POLYETHYLENE COMPOUND



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A Thesis Submitted in Partial Fulfillment of the Requirements  
for the Degree of Master of Science Program in Petrochemistry and Polymer Science

Faculty of Science

Chulalongkorn University

Academic Year 2008

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Thesis Title EFFECT OF EXTRUSION CONDITIONS ON PHYSICAL PROPERTIES OF PIPE GRADE HIGH DENSITY POLYETHYLENE COMPOUND

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ทิลีนความหนาแน่นสูงเกรดท่อ (EFFECT OF EXTRUSION CONDITIONS ON  
PHYSICAL PROPERTIES OF PIPE GRADE HIGH DENSITY POLYETHYLENE  
COMPOUND) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : ศ. ดร. ภัทรพรรณ ประศาสน์สารกิจ,  
75 หน้า

งานวิจัยนี้เป็นการศึกษาผลของภาวะการหลอมอัดรีดต่อสมบัติทางกายภาพของคอมพาวด์พอลิเอทิลีนความหนาแน่นสูงในงานทำท่อความดันสูง โดยเฉพาะการหลอมอัดรีดของพอลิเอทิลีนความหนาแน่นสูงที่มีการกระจายตัวของน้ำหนักโมเลกุลแบบสองโหมด ซึ่งมีตัวแปรที่ศึกษาคือการปรับเปลี่ยนอุณหภูมิกระบอบของสกรูในการหลอมอัดรีด (temperature profile) อัตราการเติมตัวอย่าง (sample feed rate) ความเร็วของสกรูในขณะการหลอมอัดรีด (screw speed) รวมถึงรูปแบบของเกลียวหนอนของสกรู (screw configuration) โดยศึกษาสมบัติทางกายภาพของคอมพาวด์พอลิเอทิลีน ซึ่งทดสอบการยืดหลังจากบากชิ้นงานสำหรับการประเมินการทนแรงกระแทกแบบห่วงซ้ำ (SCG) ทดสอบการทนแรงกระแทก ตลอดจนถึงพื้นที่จุดขาวและการวิเคราะห์พื้นฐานการกระจายตัวของจุดขาว และการทนทานต่อการออกซิเดชัน (OIT) เพื่อการทดสอบการทนทานเชิงความความร้อน โดยพบว่าภาวะการหลอมอัดรีดของพอลิเอทิลีนความหนาแน่นสูงที่มีการกระจายตัวของน้ำหนักโมเลกุลแบบสองโหมด ซึ่งแสดงให้เห็นว่าผลการจัดเรียงเกลียวหนอนของสกรูที่เหมาะสมที่อุณหภูมิการตั้งอุณหภูมิกระบอบสกรูที่ 200 องศาเซลเซียส และอัตราการเติมตัวอย่างที่ต่ำลงจะทำให้สมบัติเชิงกลทั้งด้านความแข็งแรง/เหนียว และการทนแรงกระแทกแบบทันที มีค่าสูงขึ้น และพบว่าที่ภาวะที่อุณหภูมิของกระบอบสกรูที่ 240 องศาเซลเซียสการหลอมอัดรีดที่อุณหภูมิสูงเหนียวทำให้เกิดการเสื่อมสภาพ ทำให้สมบัติการทนสภาพเชิงความร้อนและการทนแรงกระแทกของท่อความดันสูงมีค่าลดลง อย่างไรก็ตาม งานวิจัยนี้แสดงให้เห็นถึง อัตราการขับของสกรูไม่มีผลเป็นนัยสำคัญต่อสมบัติทางกายภาพของท่อความดันสูง

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จุฬาลงกรณ์มหาวิทยาลัย

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ปีการศึกษา.....2551.....ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก.....  
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## 4973422123: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE

KEYWORD: HIGH DENSITY POLYETHYLENE/ HIGH PRESSURE PIPE/ EXTRUSION/  
CRACKS RESISTANCE

ARKOM PASO: EFFECT OF EXTRUSION CONDITIONS ON PHYSICAL  
PROPERTIES OF PIPE GRADE HIGH DENSITY POLYETHYLENE COMPOUND.  
THESIS PRINCIPAL ADVISOR: PROF. PATTARAPAN PRASASSARAKICH, Ph.D.,  
THESIS CO-ADVISOR: ROMAN HELMUTH ADAM STRAUSS, Ph.D.,75 pp.

The effects of extrusion conditions on physical properties of high density polyethylene (HDPE) compound for pressurized pipe application were studied. For extrusion of HDPE with typical bimodal molecular weight distribution, the studied variables were extrusion temperature profile, feed rate and screw speed as well as screw configurations. The physical properties of HDPE compound, full notch creep test (FNCT) for evaluating slow cracking growth (SCG) resistance, impact resistance, white spot area and morphological analyses for evaluating gel dispersion, and oxidative induction time (OIT) for evaluating thermal stability were investigated. For extrusion of bimodal high density polyethylene pipe grade compound, the barrel temperature of 200°C and an optimized screw configuration were found appropriate. The decrease in material feed rate resulted in an increase in SCG resistance and impact energy of high pressure pipe. The higher barrel temperature (240°C) promoted the degradation leading to the decrease in OIT and impact resistance of HDPE pipe. However, the screw speed had no significant effect on the physical properties of high pressure pipe.

Field of Study:..Petrochemistry and Polymer Science.Student's signature:.....*Arkorn Paso*

Academic year:.....2008.....Principal Advisor's signature:.....*Pattarapan Prasassarakich*

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## ACKNOWLEDGEMENTS

The author wishes to thank Professor Dr. Pattarapan Prasassarakich, advisor, for encouragement during the research work and the thesis preparation. Sincere thanks and gratification are going to Dr. Roman Strauss, co- advisor, for valuable guidance and encouragement throughout the course of the research and during preparation of the thesis.

He is also grateful to Associate Professor Dr. Supawan Tantayanon, Associate Professor Dr. Wimonrat Trakarnpruk and Dr. Anucha Euapermkiati for serving as chairperson and members of thesis committee, respectively.

In addition, he would like to thank the Research and Development Department, IRPC (Public) Co., Ltd. for the laboratory facility and experience. Acknowledgement is also made to Graduate School, Chulalongkorn University and National Center of Excellence for Petroleum, Petrochemicals, and Advanced Materials, NCE-PPAM.

Finally, he is grateful to his family for their encouragement, and support. Many thanks are going to friends and everyone who contributed suggestions and support during the course of this research.

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## LIST OF ABBREVIATIONS

ACP	Advanced cascade process
APS	Average particle size
ASTM	American society for testing and materials
BHT	2,6-di-tert-butyl-4-methylphenol
CB	Carbon black
CEN	European committee for standardization
DSC	Differential scanning calorimeter
ESCR	Environmental tress crack resistance
MDPE	Medium density polyethylene
FNCT	Full notch creep test
FT-IR	Fourier transforms infrared spectroscopy
GPC	Gel permeation chromatography
$\Delta H_f$	Heat of fusion
ISO	International standard organization
LDPE	Low density polyethylene
MFI	Melt flow index
MFR	Melt flow ratio
MPa	Mega pascal
MRS	Minimum required strength
MWD	Molecular weight distribution
HMW	High molecular weight fraction
OIT	Oxidative induction time
PE 100	HDPE pipe ranking service 100 years old
HDPE	High density polyethylene
RCP	Rapid crack propagation
SCG	Slow crack growth
SEM	Scanning electron microscopy
TCB	1,2,4-trichlorobenzene
UV	Ultraviolet light
WSA	White spot area

# CHAPTER I

## INTRODUCTION

### 1.1 Statement of problems

Since the discovery in 1933, polyethylene has grown to become one of the most widely used plastics in the world [1]. The versatility of this thermoplastic material is demonstrated by the diversity of its uses. At present high density polyethylene (HDPE) resins are rigorous applications such as pressure-rated gas and water pipes, landfill membranes, automotive fuel tanks and other demanding applications. Polyethylene's use as a piping material was first developed in the mid 1950's when Ziegler catalyst made the synthesis of high density of linear polyethylene possible. The original use of polyethylene for pipe was in oil field where a flexible, tough and light-weight piping product was needed to fulfill the needs of rapidly developing oil and gas production industry. The performance benefits of polyethylene pipe in these original oil and gas related applications have led to its use in equally demanding piping installations such as potable water distribution, industrial and mining pipe, force mains and other critical applications.

In the late decade of last century, high density polyethylene (HDPE) grades possessing a bimodal molecular weight distribution (MWD) were successfully made with tandem reactor polymerization technology. Just very recently, Basell had launched PE grades possessing a multi-modal MWD made with an advanced cascade process (ACP). These grades benefit from their bimodality by having the strength and stiffness of HDPE, while retaining the high-stress-crack resistance and processability of unimodal medium-density polyethylene (MDPE) grades. Most of the commercial PE100 pipe grades pressure-rated to be able to withstand a minimum circumferential (hoop) stress of 10 MPa for 50 years at 20°C are typical examples of bimodality or multimodality. Such PE100 resins are ideally suited to the demanding application of pipes for gas and water distribution.

In a commercial compounding process, it is very difficult to optimize the compounding conditions, at which there is no significant degradation taken place, so that the desirable polymer structures can be maintained as close as those of original powder from reactors, and that pipe properties such as resistance to rapid crack

propagation (RCP) and to slow crack growth (SCG) for a high pressure ranking pipe can be achieved. Therefore, care must be taken to prevent material from thermal and shear damage during compounding. Levels of dispersions of high molecular weight fraction of polymer and pigments shall fall into the ranges stipulated by standards for HDPE pipe materials. Sizes of gels formed from long chain molecules, shown as white spots under optical microscope, tell whether the mechanical shear is sufficient to break down the original gel particles into small ones. Sizes of pigment, in the case of carbon black, are also measured by using an optical microscope.

Properties of HDPE resins for pipe with certain molecular weight distributions are generally governed by a property-processability trade-off. High molecular weight (HMW), high-density polyethylene exhibits good stiffness and toughness but may suffer from poor processability. Resins with bimodal molecular weight distributions offer a balance between good mechanical properties and processability [2]. Creep rupture strength and resistance to rapid crack propagation can also be achieved with additional of HMW portion present in such type of MWD. It was demonstrated that the performance of the high density polyethylene pipe material under service conditions was dependent on the nature of the microstructure of each fraction and also on its relative ratio, and that a balance of the creep rupture, stress crack resistance and resistance to rapid crack propagation can be obtained by altering the composition of the polyethylene resin.

However, it is difficult to disperse high molecular weight (HMW) and pigments in HDPE pipe compound matrix without any degradation of the polymers because, on one hand, the portion of very high molecular weight is more susceptible to shear and heat, on the other hand, addition of pigment like carbon black at percent level would tremendously lift melt viscosity of the matrix and make extrusion condition more **harsh**. In order to improve carbon black dispersion in HDPE matrix, it is needed to optimize the amount of pigment dosing, screw configuration, feed rate, temperatures profile and screw speed. Therefore, MWD plays such an important role in PE100 resin's performance, scientists and manufactures have showed a great concern on the relation of molecular structures to the rheological behaviors and physical properties of a series of high density polyethylene pipe grades with bimodal molecular structures.

Besides the requirements on features of raw materials, it was also known that extrusion conditions has significant effects on physical properties of the finished

compounds because too high screw speed (high shear rate) will partially cause chain scissions of very high molecular weight molecules, too low screw speed may not be sufficient to bring the gel size down and to achieve proper distribution. Types of pigments and additive packages also affect properties of HDPE pipe compounds. HDPE compound of pipe grades are usually prepared by using a melt extrusion process through a co-rotation twin screw extruder. Because physical properties of a HDPE (PE100) pipe grade compound are dominated both by molecular weight architecture of the polymer and by homogeneity and morphology of the finished compound, it is extremely challenging to achieve a compound of well dispersed gels and pigment, which also sustains the physical properties of the original resin without material degradation during compounding. Numerous parameters influence HDPE melt behaviors in the process of compounding and performances in their service life.

Type of carbon black and additive packages used for blocking UV light and thermal stabilization play important roles during processing and in service because thermo-mechanical degradation and thermo-oxidation during processing in a co-rotation twin screw extruder give rise to reduction of properties of the compound used for PE100 pipe if the base materials possess bimodal structural distributions. Variation of polymerization process parameters may also interfere in the degradation mechanisms. Usually, competitions take place among chain scission, chain branching and crosslinking reactions [3]. El'darov *et al.* [4] verified that these mechanisms are influenced by shear rate and temperature and they are not isolated, but concurrent. Thus, in a processing step, like extrusion, the thermo-mechanical degradation should be avoided by carefully choosing processing parameters such as feed rate, screw configuration, screw speed, barrel temperature profile and chemicals such as stabilizers, additives, type of carbon black as well [5].

In this thesis, the attention is focused on investigation of the effects of compounding parameters such as feed rate, screw configuration, screw speed, temperature profile, and additive packages on mechanical properties of HDPE pipe grade compounds. Various compounding conditions were tested in order to get a good balance between dispersion of each component and mechanical properties of the finished compounds.

## 1.2 Research objective

The purpose of this work is the preparation of the polyethylene pipe compound having optimum properties using co-rotation twin screw extruder operated at optimum conditions ( barrel temperature, screw configuration, sample feed rate, screw speed).

## 1.3 Scope of research

The scope of this research work includes

1. Literature review
2. Preparation of HDPE compound by using a co-rotation twin screw extruder. The study factors are as follows; barrel temperature, sample feed rate, screw speed, screw configuration and additional additive packages.
3. Characterization of HDPE compounds by using Gel Permeation Chromatography (GPC).
4. Characterization of thermal properties of the HDPE compounds by using Differential Scanning Calorimeter (DSC) and Fourier Transforms Infrared Spectroscopy (FT-IR).
5. Determination of physical properties of the compounds according to DIN 53453 (Charpy impact resistance) and ISO 12162 (Full notch creep test).
6. Characterization of the morphology of the compounds by using optical microscope and scanning electron microscopy (SEM).
7. Characterization of the rheology of the compounds by using rheometer.
8. Summarizing the results and discussions.
9. Writing a publicable article for an international journal and writing a thesis.



## CHAPTER II

### THEORY AND LITERATURE REVIEW

#### 2.1 PE pipe manufacturing

##### 2.1.1 Molecular structure and strength

HDPE pipes are manufactured by extruding the molten material through a specially designed die. The pipe is subsequently cooled in a water bath. Manufacturing is continuous and the pipe length is limited only by practical considerations. As already mentioned, thermoplastics consist of very long molecules, extensively, or sparsely branched, whose chains may be packed together more or less tightly, thus forming well-ordered areas called crystallite. As the chains are entangled with each other because their long length, the formation of crystallites can be inhibited to varying degrees and thus, in crystalline polymer, unordered (amorphous) areas are created between the crystallites. Similarly, extensively branched chain molecules have greater difficulty in crystallizing than sparsely branched ones. Hence, less-branched molecules give rise to more crystalline polymers with higher density (HDPE) than extensively branched molecules (LDPE). The melting point is that temperature at which the crystallite becomes amorphous. Consequently, in melted state the polymer has an amorphous structure, which is recovered to a more ordered structure upon cooling. The slower the cooling, the greater the crystalline especially in a less branched polymer. Usually, high material strength is required, which means that high density and crystallinity are also desirable. However, rising molecular weight creates a high melt viscosity which influences in its turn on the material process ability during pipe manufacture. Thus, higher temperature and pressure are required, such that extrusion technique becomes more complicated, especially for large diameter pipes of great wall thickness [6].

##### 2.1.2 The classification of PE pipe

It is well accepted that PE pipes are classified by pressure rate evaluation, where reference is made to a draft ISO Standard Extrapolation Method. The relation

between hoop stress and time to burst measured at various experimental temperatures. Brittle fracture is often characterized by a knife-sharp edge running parallel to the axis of the pipe, e.g. perpendicular to the direction of the main stress. It is supposed that ductile fracture, which requires a greater amount of stress than brittle fracture, occurs after straining of the molecules in the crystallites. As the binding forces in the crystallites are very strong, a large stress is thus necessary to result in failure. During pressure rate evaluation the modes of failure are also considered [6].

In recent years extended development work has been undertaken by PE resin manufacturer, which have resulted in materials with better long-term strength and temperature resistance. The classification is based on the minimum required strength (MRS), which has to be applied for designing long-term loaded PE pipes operating at a temperature of +20°C during at least 50 years. Thus, the first-generation pipes are named PE 32, PE 40 and PE 63. The second-generation pipes PE 63 or PE 80. The figures stand for the MRS-values expressed in bar. By dividing these values by a safety factor of 1.25. The third-generation has been developed recognized as PE 100 grade with a MRS of 100 bars.

### **2.1.3 PE pipe materials**

Most standards for HDPE pipe referred rather wide range of compounds properties, emphasizing for the user the importance to make sure that the real long-term behavior does not differ significantly from the predicted one. An example of the trend to try to get one standard only, covering a wide group of materials is the recently proposed ISO and CEN standards for PE pipe. Hence, the classification is now mainly based on the minimum required strength (MRS) given as the minimum tensile circumferential stress in the pipe wall, for which pipe can be subjected during at least 50 years at a temperature of 20°C without failure. That the strength requirement is controlled by acceleration tests specified in the standard. As mentioned above, the condition for the long-term strength prediction to be valid is that the pipe has been properly processed during manufacturing.

It is particular of thermal oxidation of the inner surface layer of the pipe, which must be recognized. Therefore, a thermal stability test of the pipe is particularly important. The required “induction time”, i.e. the time it takes for the exothermal

oxygenic degradation reaction to start in the test, is normally 10 minutes at 210°C. However, for modern well stabilized PE pipes, significantly longer time periods can be met. It is recommended to utilize such a special offer particularly in the case of pipes meant for elevated water temperatures, such as pulp mill effluent transport, etc. The oxidation can then be easily be further verified by regular IR analysis.

During recent years, some PE pipe failures have been recognized particularly in the case of pipes used for natural gas supply. At the failure, the sudden pressure loss of the compressed gas has given rise to an explosive type of process which has caused the pipe to fail rapidly with very long crack extensions in the axial direction. The phenomenon has been called “rapid crack propagation” and has been subject to a draft ISO standard (ISO/DIS 13477 and 13478) for determining the critical hoop stress, at which such a phenomenon might occur. In the case of pressure pipes for water supply, due to the high compression modulus of water compared with gas, the same type of failure gives rise only to a rather short axial crack. This phenomenon called “slow crack growth” has been subject to a corresponding ISO proposal for determining the pipe’s resistance to crack propagation susceptibility (ISO/DIS 13479). The pipe has been subject to a thermal oxidation of the internal pipe wall surface already during the manufacturing.

In the case of natural gas, condensation of the gas into the liquid phase may certainly further weaken the oxidized internal pipe surface and consequently hasten the failure to show up. The risk for thermal oxidation during the manufacturing is greatest when extruding thick-walled or large diameter PE pipes. Pipe failures due to oxidation have been recognized both for first and second generation of PE pipes. A somewhat less crack susceptibility is claimed to be expected for the “third generation” PE pipes, when subjected to thermal oxidation. However, a safe technique for preventing any type of oxidation of the internal surface of PE pipe is achieved by using an inert gas (nitrogen) in the pipe during the extrusion, instead of air [6].

#### **2.1.4 The strength and durability of plastics pipe**

Most structural materials used in the building industry are elastic solid materials or almost so. Thus, on one hand, independently of loading time, the relation between stress and strain is linear up to a certain stress level.(Hook’s law is valid)

and, on the other, the material can recover original shape immediately after unloading. A large number of building materials certainly differ considerably from the ideal elastic material. However, conditions for plastics are different. Thus, strain is not proportional to stress nor independent of loading time and creep will occur in the material under load. Creep increases with increasing temperature. The consequence of creep is dependent of the magnitude of the stress [6].

In addition, the failure is preceded by a large elongation. Brittle fracture is assumed to occur as result of failure in the non-crystalline or amorphous regions of the molecules between the crystallites. The amount of these tie molecules in relative terms is not very great. Consequently, little stress is required to stretch these molecules and bring them to failure. Simultaneously, there is a creep rate –dependent mechanism involved in the process, in which the lower creep rate, e.g. the smaller the stress, the smaller the elongation at burst. The brittle burst mechanism is not entirely clear, but it has been indicated that water absorption by the plastics may hasten the process.

The risk of premature fracture as a result of stress cracking is greatest in the case of polyethylene with a high density and high melt flow rate, where tie molecules are small in number and length. The risk of premature fracture can, however, be entirely eliminated by a suitable combination of melt flow rate and density. Hence, it may generally be observed that steep section of the curve in the stress/time diagram will be displaced further to the right, the higher the average molecular weight of the resin used. It should be added that a narrowing of the molecular weight distribution, where this implies a decrease in the number of short molecules, may compensate for low mean molecular weight to certain extent, as the long term strength is concerned.

## **2.2 Long term strength control of pipe**

The long term behavior, the long –term behavior, and by that the long-term strength of the plastics pipe must be recognized in detail. This will of course be more difficult if several resin grades are incorporated in one and the same standard. A risk is at least that it will be the weakest grade which determines the strength test requirements, implying that the degree of superiority of the better grades are not fully recognized or tested, and consequently the benefit of these grades will not be utilized in an optimum way. An attempt to come out of this dilemma may be the ISO Standard

Extrapolation Method (SEM) specified in ISO 9080. The attempt is to provide a definite procedure to find the long-term strength of the pipe, incorporating extrapolation by using stress/time test data at different temperatures. The task is to find out how long a pipe system will last when subjected to a defined tensile hoop stress at a given temperature. This means that the stress is chosen as independent variable when calculating the long-term hydrostatic strength. The test data are statically analyzed by using curve fitting techniques and linear regression analysis. Certainly, SEM will help very much in the understanding of the long-term strength of plastics pipes.

The significance of taking the creep behavior into consideration appears also when performed strength quality control of large diameter PE pipe. In such cases it is just the relation between linear strain and time, which will help to predict the long-term strength quality within a reasonable testing time. Thus, it may be plausible that a badly processed pipe or a pipe with some latent injuries should be recognized as having a strain/time relation suddenly or smoothly deviating upwards from the rectilinear course. The ambition has been to collect knowledge about the capability of the pipe material to fulfill requirements also from a practical engineering point of view. The actual problem connected to the fact long-term strength of the new material has so far only been studied according to the traditional relation between hoop tensile stress and time to burst. As the stresses referred to rise primary to the ductile type of failure which will be preceded by large relative strains, it is obvious that also the relation between strain and loading time has to be recognized [6].

## **2.2 Pipe properties**

Polyethylene exhibits the property known as creep, i.e. over a period of time it undergoes deformation, even at room temperature and under relatively low stress. After removal of stress, a more or less regains their originals shape, depending on the time under stress and magnitude of the stress. The recoverable deformation is known as elastic deformation and permanent deformation as plastic deformation. The mechanical properties of a plastic are dependent on the three most important parameters: time, temperature and stress [6].



### 2.2.1 Behavior at low testing rates

The brittle fracture observed here is initiated by small defects or notches. Temperature increase accelerates this process. The fracture diagram shows a small crack running lengthwise along the pipe. The failure mechanism depends mainly on molecular parameters of the PE grade such as average molecular weight, molecular weight distribution, and copolymer content and copolymer distribution. As a partially crystalline polymer, polyethylene reacts to the stress concentration at the crack tip (notch root) by forming a crazing zone. The start of the crazing zone is referred to as the nucleation zone. The crazing zone consists of highly oriented craze fibrils. The craze fibrils absorb the stress and are stretched further and further until failure occurs. As a result of the increasing stress in the notch root new craze fibrils that absorb the stress are formed from the nucleation zone. At a microscopic level, the so-called tie molecules play an important role, as they link the crystalline regions. The tie molecules disentangle slowly under the tensile stress so that the crystalline regions can separate.

In first-generation pipe materials, failures due to slow crack propagation resulting from point loads (e.g. from sharp-edged stones or notches caused by relatively severe external damage) have occasionally been known [6].

### 2.3.2 Behavior under impact stress (high deformation rate)

Information on the toughness characteristics of polymer materials at high deformation rates is provided by flexural and tensile impact strength tests. The results of impact, notched impact strength and tensile impact strength are considerably influenced by the conditions under which the test specimen prepared. Injection molded test specimens, because of their rapid cooling rate, are less crystalline on solidifying and therefore more impact-resistance than those prepared from compression molded sheet. The orientation produced by injection molding also has an effect. The toughness of pipe materials under shock or impact stress is influenced by a number of factors such as crystallinity (density), molecular weight and molecular weight distribution as well as the nature and content of the co-monomer or additives. With increasing molecular weight and narrowing molecular weight distribution, toughness also increases [6].

By rapid crack propagation, the following phenomenon is meant: if a gas pipe during operation is damaged by an external force (e.g. by construction machinery) or there is a stress-induced crack (for example in a defective weld), then, under the action of internal pressure and hence of the potential energy stored in the gas, the crack can spread over an extended length at almost the speed of the sound. This phenomenon, also known by the abbreviation RCP (Rapid Crack Propagation), has so far mainly been studied in steel pipelines. The way in which HDPE pipes have been designed has made the RCP risk irrelevant until now. But if, as in the case of PE 100, the range of application is widened to include higher operating pressures, pipe designers must be given highly reliable assurances for this.

## **2.4 Production of PE pipe**

### **2.4.1 Flow properties**

Flow properties are of crucial importance in processing polymer melts. During pipe extrusion, the high-molecular weight PE melt is subjected to shear stress. To design the extruder and die, it is necessary to know the viscosity function which describes the viscosity / shear curve with increasing shear rate. Shear means that a cubic volume element of the melt is deformed by force acting on its top surface. This force produces a shear stress in the surface. For a given extrusion die geometry, the shear stress can be calculated using the operating pressure and the shear rate from the volumetric flow rate. To determine the viscosity function, capillary rheometers are used. There are two different methods of measurement: the discontinuous method, in which pressure is applied with a plunger (high pressure capillary rheometer), and the continuous, in which the melt is prepared in an extruder and constant fed to measuring die (continuous rheometer). The advantage of the continuous method is that the influence of processing conditions on flow behavior can also be studied. By plotting a graph of viscosity as a function of shear rate or shear stress, the viscosity curve is obtained.

The most frequently used method for characterizing the flow behavior of polymer melts is MFR (melt mass flow rate) measurement according to ISO 1133. In this method, the material is heated to the melt state (190° C for HDPE compound) in a

cylinder of diameter 9.5 mm. It is then forced through an annular die of diameter  $D = 2.095$  mm and length  $L = 8$  mm by a piston loaded with a weight (2.16, or 5 or 21.6 kg). From the measured melt mass-flow rate value (MFR) or the volume flow rate value (MVR) and density of the melt\* ( $\rho = 0.76$  g/cm<sup>3</sup> for HDPE at 190°C). If two melt mass rate values are measured, for example MFR 190°C/ 21.6 kg and MFR 190°C /5 kg, then the ratio of these tells us something about the slope of the flow curve and hence about molecular weight distribution. The higher this ratio is, the wider the molecular weight distribution [6].

#### **2.4.2 Gentle processability**

The simplest and quickest way to ascertain materials stress in extrusion is to test the oxidation induction time (OIT, EN 728), which is determined by the stabilizer system. For this purpose, specimens are taken from the pipe inside wall and then the OIT value measured at 200°C or 210°C is compared with the OIT value measured on unprocessed pellets. In processing pipe materials, the melt temperatures were between 210°C and 219°C. Bimodal PE pipe compound can even be thermally stressed up to 260°C for short periods without detriment to the stabilizer system [6].

#### **2.4.3 PE pipe application**

In gas supply sector, HDPE and MDPE pipes and fittings have been very successfully used for over 30 years. Their main field of application has been local gas distribution with operating pressures of up to 1 bar, 4 bars and in some cases even 5 bars. Long – distance lines with operating pressures of 10 bars can be produced without any problem from PE 100. PE gas pipes have gained increasing importance in recent years because of their low cost and technical advantages over pipes made from more traditional materials. Of course, PE lines meet all safety requirements without any problems.

The production, quality assurance and testing of PE gas pipes, including joint, are carried out according to international standards, such as prEN 1555 and ISO 4437, and in Germany according to the regulations of the German Association of Gas and Water Engineering (DVGW) in its Work Sheets G 477, G 472 and VP 608 and the

German Quality Association for Plastics Pipe (GKP) Guideline (14.3.1.G) In term of quality requirements, the PE gas pipes used in Germany, like other HDPE pressure pipes, have to conform with DIN 8075. To ensure that gas lines are clearly indentifiable as such, yellow PE pipes have been widely used for gas lines in recent years. For higher operating pressures, orange-yellow PE 100 pipes are used. The German Association of Gas and Water Engineering (DVGW) Guideline G 472 stipulates 10 bar as the highest permissible operating pressure for PE 100 pipeline systems. For drinking water were used international standard in ISO 4427 (12/96) in the context of European standardization.

## 2.5 Degradation of PE materials

The reaction of a polyolefin with oxygen will lead to the formation of oxygen-containing functionalities through a sequence of reactions, known as auto-oxidation. During outdoor exposure, light initiated breakdown (photo-degradation or photo-oxidation) predominantly takes place, followed by thermally initiated reactions. High temperatures are usually not encountered during normal exposure and temperatures above the crystalline melting points are not encountered for extended periods of time. Irradiation can also lead to the degradation of polymers.  $\gamma$ -Irradiation may result in crosslinking or scission of polyethylene chains, depending on the conditions of degradation. Polyolefins may degrade in the absence light if they are exposed to extreme temperatures. The general degradation mechanism of polyolefins will now be reviewed. The degradation reactions can be divided into initiation, propagation, branching and termination reactions.

Chain scission will result in a decrease in the molar mass averages and the molar mass distribution. This will dramatically affect the rheological properties, as well as tear strength and other mechanical properties. Under oxidative breakdown of polyethylene, the optical properties will also be negatively affected. In the review of article by Gugumus [7,8,9], the influence of several factors on the degradation of polyethylene is considered. He reviews the work by Rideal and Padget [10], who considered the thermo-mechanical degradation of high density polyethylene. A nitrogen blanketed Brabender extruder was used for the experiments and several temperature regions were considered. They found that there were two distinct

temperature regions with respect to the effect on the polymer. Below 290°C the melt viscosity increased. This is indicative of cross-linking and chain branching. Above 290°C the melt viscosity decreased. This is indicative of chain scission. They attributed the increase in viscosity in lower temperature region to the formation of long-chain branching. This was confirmed by measuring the melt elasticity and intrinsic viscosity. The mechanism proposed for this phenomenon postulates that at lower temperature the chains undergo scission due to shear and will yield two radicals in a cage structure. Due to the relatively higher melt viscosity at lower temperatures, the cage structure will be disrupted. These radicals will not recombine but rather abstract a hydrogen atom from another polymer chain and will form a secondary alkyl radical. This alkyl radical will combine with another alkyl radical to form long-chain branching.

With regards to the degradation during melt processing, the conversion of a thermoplastic polymer to a finished article normally involves heating it to the liquid state followed by extrusion through a die. The polymer is mixed continuously by means of a screw which conveys it to the extrusion port. During this processing operation, considerable shear is applied to the viscous polymer melt which causes some of polymer chains to undergo hemolytic scission at the carbon –carbon bonds with the formation of macro-alkyl radicals. Radicals produced are highly active chemicals species which, like lower molecular weight radical, initiate the radical chain reaction. There are a number of quite conclusive pieces of evidence which suggest that mechanical rupture of polymer chains result in radicals. Firstly, radical scavengers have a profound effect on the reaction. Thus, at ordinary temperatures no appreciable change in molecular weight occurs during compounding in the absence of oxygen. Different hydrocarbon polymers behave differently during processing. For polyethylene melt flow index (MFI) during processing in the shearing mixer decreases due to cross-linking. That mean in PE the cross-linking will dominant the shearing induced reactions. Optimizing ingredients and optimizing compounding equipment are not necessarily independent tasks.



## **2.6 Homogenization**

### **2.6.1 Effect of feed rate in HDPE homogenization**

As feed stocks are frequently in pellet form, polymers pass through the following aggregate conditions in the extruder: solid to solid/melt to melt. For polymer melts, one-dimensional modeling has been available since the 1970s in the form of a dimensionless description of the pressure build-up for filled and partially filled zones in the twin screw extruder and barrel temperature. It is due to the fact that plasticization in the extruder is a very complex process, dominated by viscous energy dissipation. In the process, friction and plastic deformation of the individual granules on the walls (of the barrel and the screws) and between individual granules produce heat which cause melting. On the other hand, the quantity of heat introduced through the barrel's wall by thermal conduction is usually quite small in practice. Homogeneous melts can only be covered in a later account of pressure build-up and power input in the extruder.

In order to achieve HDPE pipe grade compounds meeting with PE100 requirements, the role of elongational flow of the melt has to be emphasized. Elongational flow is more favorable than shear flow for a safe compounding by extrusion because elongational flow dissipates less energy into the material through heat. Elongational flow improves both distributive and dispersive mixing. Processors are finding that an additional benefit of highly dispersive mixing is the improved dispersion that allows them to reduce additive levels but maintain properties and stability. Pellet density is a direct indicator of the levels of dispersion. The melt temperature in the extruder will increase to a point where the density of the finished pellets is "out of specification" in density. When it happens, the only thing one can do is to start reducing the feed rate. Obviously, that is negative to the productivity [11].

### **2.6.2 Effect of screw configuration on HDPE homogenization**

Tasks of compounding are breaking down solid, polymer particles and fluid droplets and mixing them evenly incorporated together. The key setting parameters of extrusions are screw speed, throughput, screw geometry. The degree of distribution



and the degree of dispersion is dependent on the kinematic parameters of flow. However, along the axial radial velocities in the screw channel, the dispersion process is also dependent on viscosity and is therefore affected by shear stress in screw channel. The dispersion effect is dependent on the shear stress as well as on the duration of the load. Which of the two variables has the most influence depends on the material to be dispersed. Together with a sufficient residence time in the stress zone, effective dispersion is also encouraged by high screw speed, low throughput, narrow shearing gaps and high melt viscosity. Wide –disc kneading blocks achieve the most effective dispersion because they generate the greatest shear stresses. This also leads to high energy input, hence increases the melt temperature and reduces the viscosity of the predominantly shear-thinning polymer melts, which in turn leads to a reduction of shear stress. Therefore, dispersive mixing is resulted from the optimization among these conditions [11].

## 2.7 Literatures review

Pinherio *et al.* [3] studied the thermo-mechanical and thermo-oxidative degradation of high density polyethylene (HDPE) in a twin screw extruder using various processing conditions. Two types of HDPE, Philips and Ziegler-Natta, having different levels of terminal vinyl unsaturation were analysed. Mild screw profiles, having mainly conveying element, have shorter mean residence times than profiles with kneading disc and left hand elements. Carbonyl and trans-vinylene group concentrations increased, whereas vinyl group concentration decreased with number of extrusions. Higher temperature profiles intensified these effects. The thermo-mechanical degradation mechanism began with chain scission in the longer chains due to their higher probability of entanglements. These macroradicals then reacted with the vinyl terminal unsaturations of other chains producing chain branching. Shorter chains were more mobile, not suffering scission but instead being grafted by the macroradicals, increasing the molecular weight. Increase in the levels of extrusion temperature, shear and vinyl end groups content facilitated the thermo-mechanical degradation reducing the amount of both, longer chains via chain scission and shorter chains via chain branching, narrowing the polydispersity. Philips HDPE produced a higher level of chain branching than does the Ziegler- Natta type.

Baird *et al.* [5] studied a kinetic model of polymer degradation during extrusion. Investigations and numerical representation of chemical transformation mechanisms occurring during polymer processing had recently become a very important problem. In this study a model put forward to describe the interrelation of mechanical degradation and thermal oxidation phenomena during polyethylene extrusion. The model permitted the determination of changes in molecular weight, amounts of reacted oxygen and the quantities of accumulated peroxide together with amount of the inhibitor used during extrusion. These parameters had a significant effect on the physical and mechanical properties of the polymer and made it possible to extend its lifetime in finished products under operating condition.

Hubert *et al.* [12] studied on the physical and mechanical properties of polyethylene for pipe in relation to molecular architecture via microstructure and crystallization kinetics. Ethylene/ $\alpha$ -olefin copolymers having bimodal molecular weight distribution were investigated in comparison with unimodal copolymer in order to understand the incidence of the molecular architecture on the stress cracking resistance. The preferred introduction of the co-units in the longest chains of bimodal copolymer was suggested to favour the occurrence of inter-crystalline tie molecules during crystallisation. The more complex was the molecular architecture, the greater was the difficulty for crystallization by regular chain folding. Intermolecular chemical heterogeneity resulting from preferred incorporation of the co-units in the long chain enhanced the co-unit disturbing effect on crystallization without reducing crystallinity. Intra-molecular heterogeneity of the co-unit distribution was also suggested to be an efficient means to generate tie molecule and random chain folding at the expense of regular chain folding. Isothermal crystallisation was used to probe the effect of molecular architecture on the crystallization kinetics. It appeared that the correlations between kinetics, molecular architecture and molecular topology of unimodal copolymers were no longer held when considering bimodal copolymers. In contrast, the crystal surface free energy was proved to be sensitive to topological changes resulting from molecular architecture modifications.

Pinherio *et al.* [13] evaluated the Philips and Ziegler- Natta high density polyethylene degradation during processing in an internal mixer by using the chain

scission and branching distribution function analysis. The oxidative and thermal-mechanical degradation of HDPE was studied during processing in an internal mixer under two conditions: totally an partially filled chambers, which provided lower and higher concentrations of oxygen, respectively. Two types of HDPEs, Philips and Ziegler-Natta, having different levels of terminal vinyl unsaturations were analyzed. Materials were processed at 160°C, 200°C, and 240°C. Standard rheograms using a partial filled chamber showed that the torque was much more unstable in comparison to a totally filled chamber which provided an environment depleted of oxygen. Carbonyl and trans-vinylene group concentrations increased, whereas vinyl group concentration decreased with temperature and oxygen availability. Average number of chain scission and branching ( $n_s$ ) was calculated from MWD curves and its plotting versus functional groups' concentration showed that chain scission or branching took place depending upon oxygen content and vinyl group consumption. Chain scission and branching distribution function (CSBDE) values showed that longer chains undergo chain scission easier than shorter ones due to their higher probability of entanglements. This yielded macro-radicals that reacted with the vinyl terminal unsaturation of other chains producing chain branching. Shorter chains were more mobile not suffering scission but instead were used for grafting the macro-radicals, increasing the molecular weight. Increase in the oxygen concentration, temperature, and vinyl end groups' content facilitated the thermo-mechanical degradation reducing the amount of both, longer chains via chain scission and shorter chains via chain branching, narrowing the polydispersity. Philips HDPE produced a higher level of chain branching than Ziegler –Natta's type at the same processing condition.

Fayolle *et al.* [14] studied the mechanism of degradation induced embrittlement in polyethylene. The thermal oxidation of polyethylene films in air at 80°C and 90°C was studied with tensile testing. IR spectroscopy and molar mass determination were from rheometric measurements. In the conditions under studied, the polymer predominantly underwent chain scission and embrittles suddenly when the weight average molar mass reached a critical value ( $90 \text{ kg mol}^{-1}$ ), far before significant damage of the entanglement network ( $M_e=1.9 \text{ kg mol}^{-1}$ ) in the amorphous phase. The em-brittlement mechanism was proposed via chain scission in the amorphous phase induced chemi-crystallization. The thickness of the inter-lamellar

amorphous layer ( $l_a$ ) decreased unit a critical value of the order of 6-7 nm, below which plasticity could not be activated and the polymer behaved in a brittle manner, as previously shown for virgin polyethylene. Using ( $l_a$ ,  $M_w$ ) maps, it was possible to explain the differences observed in the embrittlement behavior of semi-crystalline polymers predominantly undergoing chain scission.

Rische *et al.* [15] studied the method to evaluate the homogenization of bimodal PE in a co-rotating twin screw extruder. Recent progress in technology of polyolefin synthesis led to development of a new generation of polyolefin materials with broad molecular weight distributions. In contrast to conventional products these bimodal polyolefins were distinguished by a high strength and good processability. Due to the very different molecular weights of the different fractions the viscosity ratio of these fractions was usually well above 100. Apparently, this phenomenon was the reason that bimodal materials after the homogenization by use of conventional extruders still contained a relative high amount of undesired in homogeneities. Both the development of special function elements which could realize a strong elongational flow and the optimization of specific extruder conditions were required to solve the technological problem encountered in compounding bimodal products. An important desire at the processing of bimodal polyethylene was the achievement of good product homogeneity in combination with a low specific energy input. To do so, a step-wise optimization of certain zones of the extruder was required to realize this goal. In their study, a method was developed which enabled the evaluation of the morphology in defined function zones of co-rotating twin screw extruders. Using this technique, the effect of specific function elements which realized a strong elongational flow could be determined. These techniques could be also applied to evaluate the morphology developed during the processing of other disperse systems.

Brown *et al.* [16] studied the dependence of rapid crack propagation in polyethylene pipes on the plane stress fracture energy of the resin. The critical temperature (CT) for rapid crack propagation (RCP) was measured in 11 polyethylene (PE) 200 mm diameter gas pipes each with different resins. The plane stress fracture energy (PSFE) in thin Charpy impact specimens of the resin was found to correlate with the critical temperature (CT). This result was related to the observation that the plane stress fracture energy (PSFE) decreased as the temperature decreased. It was

found that the impact energy of specimens from compression molded pipe re-melted at 180°C gave a better correlation with the critical temperature than specimens that were machined from the inner wall of the pipe. Consequently, it is now possible to predict the critical temperature of a pipe by measuring the plane stress fracture energy (PSFE) of the resin without making the pipe.

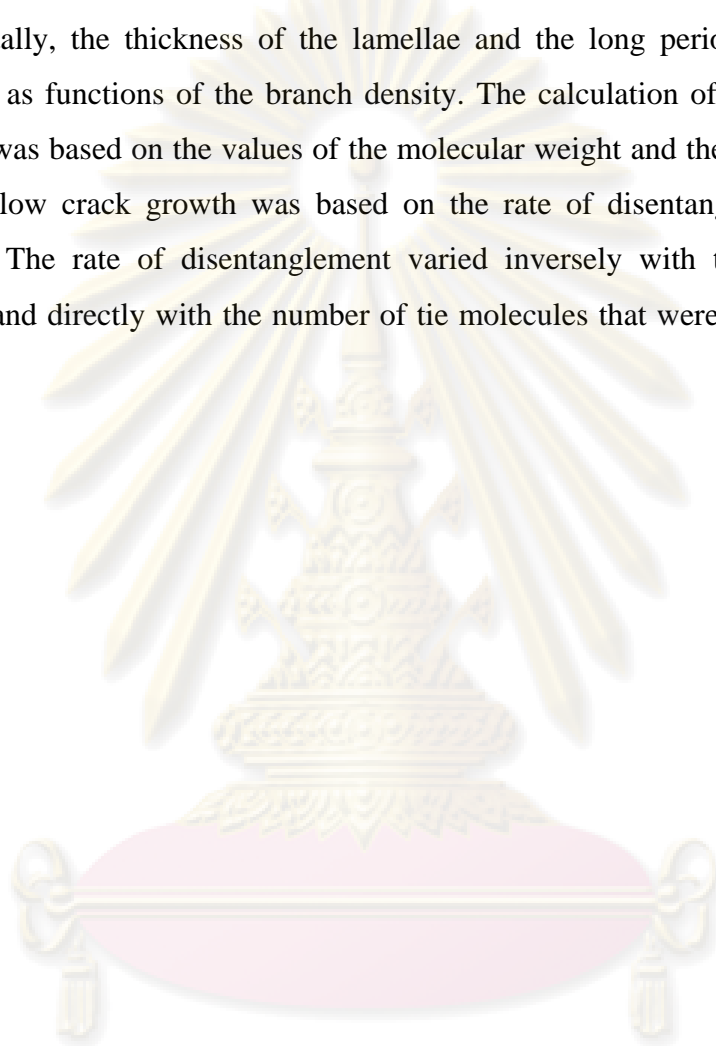
Fleissner *et al.* [17] used a laboratory method to measure the stress crack resistance of polyethylene. The creep rupture test of circumferentially notched specimens cut from plaques or pipes has proven to be a rapid and reliable method to evaluate the stress crack performance. Surfactant-assisted stress cracking was employed to accelerate testing. The stress crack resistance of several polyethylene samples was studied with respect to its dependence on stress, temperature, and environment. The creep rupture behavior at different temperatures could be superposed by horizontal shifting when they were normalized in proportion to the respective bulk yield stresses. The notch tip radius turned out not to be very crucial, and variation of the nominal concentration of the surfactants, nonylphenolpolyglycoethers, scarcely affected slow crack growth. Acceleration of testing by surfactants equalized property differences to a noticeable extent but did not influence the ranking of the materials. The activation energy of crack growth was in the expected range. Defects introduced into the line by butt joint welding were precisely modeled by the full notch creep test.

O'Connell *et al.* [18] studied the failure mode of a number of polyethylene under predominantly plane strain conditions. Square section samples, notched on all sides, were tested in tension to failure over a range of crosshead speeds and temperatures. Integration under the subsequent load displacement curve had allowed the total energy, energy to peak load, and energy after peak loaded to be determined. The data were analyzed in terms of the ratio of the energy at the peak loaded to the total energy. The results showed that the materials could change from brittle to ductile failure as a function of test speed. At a suitable temperature, brittle-like failure at the highest and lowest test speeds and ductile failures at intermediate speeds were observed. The resulting failure surface features correlated very strongly with the energy ratio analysis flat smooth surfaces where low energy ratios were seen large



ductile tearing where high ratios were seen. The effect of molecular weight and polydispersity was shown and possible failure mechanisms were discussed.

Yan-Ling *et al.* [19] studied the parameters of spacing of the butyl branches, number of tie molecules, and the thickness of the lamellar crystal of HDPE. Experimentally, the thickness of the lamellae and the long period of crystal were determined as functions of the branch density. The calculation of the number of tie molecules was based on the values of the molecular weight and the long period. The model of slow crack growth was based on the rate of disentanglement of the tie molecules. The rate of disentanglement varied inversely with the number of tie molecules and directly with the number of tie molecules that were not pinned by the branched.



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## CHAPTER III

### EXPERIMENTAL

#### 3.1 Materials

1. Matrix polymer: high density polyethylene power (Bimodal molecular weight: AM 3050) supplied by IRPC Co.,Ltd., Rayong Thailand, MFI 190°C at 5 kg loading = 0.40 g/10min) and density of 0.948 g/ cm<sup>3</sup>.
2. Additive: tetrakis[methylene 3-(3',5'-di-t-butyl-4'-hydroxyl) propanoate, Irganox1010, B215 (Irganox1010/Irganox168, ratio 2:1), Irgafos168, Tinuvin<sup>®</sup> 622 and calcium stearate as primary, secondary antioxidant, UV stabilizer and acid scavenger in commercial grade supplied by Ciba Geigy Co.,Ltd.
3. Carbon black: furnace black; 2.3 % of Printex P (Particle size 20 nm, ash content 0.2% and sieve residue 0.05 % max.) supplied by Degussa Ltd.

#### 3.2 Instruments

1. LTE 26-40 system twin screw co-rotating extruder (LAB TECH Engineering Co.,Ltd., Thailand).
2. LZ-120/VS Pelletizing unit (LAB TECH Engineering Co.,Ltd., Thailand).
3. Pendulum impact tester, ZWICK Co., Germany.
4. Full notch creep test (TECH Engineering Co.,Ltd., Thailand).
5. Melt flow Indexer (Gottfert MPX 62.92, Gottfert Co., Ltd., Germany).
6. Automatic viscometer (Luada PVS1, Lauda Co., Ltd., Germany).
7. GPC 220, Polymerlab, Gel permeation chromatography (GPC), United Kingdom.
8. DSC1, Mettler Toledo, Differential scanning calorimeter (DSC), Switzerland.
9. Cone and Plate Rheometer (Physica MCR 301, Anton Paar Co., Austria).
10. RH-10D, Bohlin Twin Bore Capillary Rheometer, United Kingdom.
11. Fourier- transform infrared spectrophotometer (FTIR), Vertex 70, Bruker, Germany.

12. Microscope with polarized, Nikon, Optaphol, Japan.
13. JSM-5800LV JEOL, Scanning electron microscope (SEM), Japan.
14. Microtome, RM2265 Leica, Germany.

### **3.3 Experimental**

High density polyethylene compound was processed by melt compounding of HDPE powder, pigment (2.3 % carbon black) and additives including stabilizers via a co-rotating twin-screw extruder (26 mm screw diameter; L/D=40/1) equipped with hopper screw feeder, water bath and strand cutter. Feeding rates were varied in the range of 4-12 kg/h. The main screw speeds were varied in the range of 100-300 rpm. The barrel temperature settings were varied from 140°C, 180°C, 200°C, 220°C and 240°C with the constant profile along processing zones. Four screw configurations were utilized, screw 2KB; two kneading blocks, screw 3KB; three kneading blocks, screw 4KB; four kneading blocks, screw 4 KBRH; four kneading block with additional reverse element.

### **3.4 Characterization methods**

#### **3.4.1 Gel permeation chromatography (GPC)**

A Polymerlab GPC 220 instrument equipped with a viscotek 150R viscometer and Refractive index detector were used with 1,2,4-trichlorobenzene (TCB) stabilized with 0.0125% 2,6-di-tert-butyl-4-methylphenol (BHT) as an eluent. A set of two mixed bead (trade name PLgel: Mixed B 13µm: operation range of MW (500-13,000,000)) columns was used and operated at 160°C. The information of the number average, weight average and Z-average molecular weights ( $M_n$ ,  $M_w$  and  $M_z$ ) were calculated using universal calibration curve based on narrow polystyrene standards. Approximately 1-2 mg/ml sample was prepared. To achieve complete sample dissolution, the samples were heated at 160°C and subjected to occasional gentle agitation using a PL-SP-260 sample preparation device. Complete dissolution was

achieved after a period of approximately 3 hours. Immediately prior to injection, the sample vials (which contained precipitated polymer) were heated to 160°C for 3 hours within the auto-sampler component of a GPC 220 in order to re-dissolve the sample. The 200µL sample solution was automatically injected with the flow rate of 1.0 mL/min. (TCB as the eluent) into the injection port and subsequently passed through the column set. The experiments were repeated twice and average values were reported. The error for the GPC instrument used in this study was estimated to be around 10% for number average and weight average molecular weights. For this study, the number average and weight average molecular weights were fairly reproducible and within this error range.

### **3.4.2 Differential scanning calorimetry (DSC)**

Thermal analysis was performed on a differential scanning calorimeter (DSC 1, Mettler-Toledo) under nitrogen atmosphere. Samples were heated from ambient to 200°C at 10°C/min. Melting temperature ( $T_m$ ) was recorded in the second scan analysis with the same heating rate. The melting enthalpy ( $\Delta H_m$ ) was determined by integration between heat flow curve and the linear interpolation of the baseline between the clear-cut end of the endothermic melting and its onset. Oxidative induction time (OIT) values of the samples were measured at 200°C according to ASTM D3350. Total crystallinity was calculated from the specific heat of fusion of perfect crystalline PE of 289 J/g [4].

### **3.4.3 Fourier transform infrared spectroscopy (FTIR)**

Three 100-150 µm thick hot pressed (160°C) films were tested. Infrared spectroscopy (IR) was carried out on Vertex 70, Bruker model, quantifying carbonyl and unsaturated group concentration using a resolution of 0.5 cm<sup>-1</sup>. Spectra were recorded using vertex 70 software and 64 scans were acquired for each spectrum. The resolution was set at 2 cm<sup>-1</sup>.

### 3.5 Physical properties testing

#### 3.5.1 Charpy impact testing

Testing specimens of 64 mm x 12.7 mm x 3.2 mm for the measurement of Charpy impact were prepared by following ASTM D 4101. They were tested on Pendulum impact tester according to the standard method of DIN 53453. A pendulum swung on its track and struck a notched, cantilevered plastic sample. The energy lost (required to break the sample) as the pendulum continued on its path was measured from the distance of its follow through. This energy absorbed by the specimen, as it breaks, can qualitatively be related to its fracture mode (ductile or brittle.) Ductile fracture, which involves substantial plastic deformation, would require much more energy than brittle fracture. Note that the fracture energy measured in a Charpy impact test is a relative energy and can only be used to compare dimensionally identical specimens; it cannot be easily used directly in engineering calculations.

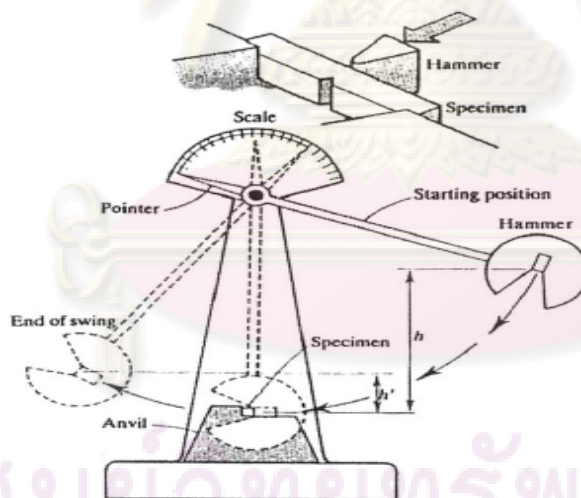


Figure 3.1 Charpy Impact tester.

#### 3.5.2 Full notch creep test (FNCT)

The samples were tested on full notch creep test according to the standard method of ISO 13479. The test specimen was prepared in the form of square section bar molded

on a hot press at 190°C and pressurized at 175 kN for 15 min. Specimen was cut in dimensions of 100x 10x10 mm. It was notched at room temperature with coplanar notches in each face at its center with notch depth of 1.60 mm and pre-conditioned for 1 h in an ethylene glycol bath at 80±1.0°C. Then sample was subjected to different static tensile loads at 80±1.0°C until rupture. The failure time of test specimens under different loading and the cross section ligament areas of the fractured surfaces were recorded.

### **3.6 Morphology of HDPE compound**

#### **3.6.1 White spot area**

White spot area (WSA) was analyzed by using optical microscope in accordance with ISO 4427, a Nikon optical microscope “Optaphol” at 100x magnification. The image analysis system “Optimas” was used for the quantitative characterization of obtained images. Dispersion of the white spots of the samples can be evaluated by their sizes compared to the total area of micrographs. Microtome sections of 20±5 µm thickness were used. The fibril intensity of fracture surface of HDPE compound was investigated using scanning electron microscopy (SEM). The fracture surfaces were cut and stitched on a SEM stub using double-side tape. The samples were then sputter-coated with gold and examined using an electron microscope, JEOL model JSM-5800 LV operated at 15 kV.

#### **3.6.2 Carbon black dispersion**

Carbon black dispersion was analyzed by using optical microscope in accordance with ISO 18553. The small sample pellets were heated and compressed between microscope slides. A scalpel was used for cutting six specimens, each of mass 0.6 mg±0.10mg for assessing carbon black dispersion, from different parts of the product were analyzed. Then they were placed on one or more cleaned microscope slides, which each specimen were approximately equidistant from its neighbor and from adjacent edges of the slide. Cover with another (or other) cleaned slide(s). By oven, the two slides were

clamped together with spring clip. Placed the clamped slides in the oven, for instance maintained at a temperature between 150°C and 210°C and leave for at least 10 minutes until each specimen was pressed out to a film of thickness of at least  $60\mu\text{m} \pm 20\mu\text{m}$  for assessment of pigment dispersion or to a thickness of  $20\mu\text{m} \pm 10\mu\text{m}$  for assessment of carbon black dispersion. Removed the slides from the oven and, when they were cool enough to be handled, removed the clips. The particles and agglomerates in each of the six specimens were examined in turn through the microscope under transmitted light with a recommended magnification of 100x. Measured and recorded the largest dimension of each particle and agglomerate, ignoring those less than 5  $\mu\text{m}$ .

### **3.6 Rheology properties**

#### **3.6.1 Small amplitude oscillation shear analysis**

For these analyses, the melt rheological behavior of HDPE compound was determined using an Anton Paar instrument MCR 301 rheometer. The measurement was carried out under nitrogen atmosphere at 220°C using parallel plate geometry. It was tested that the measurements were in linear range so that the results were independent on the used strain amplitude, which was within 6-10%. The disk specimens for measurements were cut from the plate pressed from the HDPE compound pellet at 170°C in the compression molded to be sheet of 2 mm in thickness. By preheating time mold for 6 minutes, the HDPE sample was compressed at the 1<sup>st</sup> step at 50kN for 1 minute the 2<sup>nd</sup> step at 100 kN hold for 1 minute and the 3<sup>rd</sup> at 175 kN hold for 2 minutes. The sheet was de-molded by cooling water (<40°C). The sheet was cut into disc with a diameter of 25 mm. In these measurements storage modulus ( $G'$ ), loss modulus ( $G''$ ) and complex viscosity ( $\eta^*$ ) were obtained as a function of frequency ( $\omega$ ) or complex modulus ( $G^*$ ). From viscosity function ( $\eta^*$ ) versus ( $G^*$ ) at low shear viscosity ( $\eta_{5\text{kPa}}$ ) and shear thinning index  $\text{SHI}_{5/355}$  ( $= \eta_{5\text{kPa}}/\eta_{355\text{kPa}}$ ) were calculated.



### 3.6.2 Capillary rheometer

An RH 10D Bohlin twin bore capillary was used to characterize shear flow properties in terms of shear stress and shear viscosity of each compound. The tests were carried out at a wide range of shear rate (20 to 400s<sup>-1</sup>) at a test temperature of 463 K. Dimensions of the capillary die used were 1 mm diameter, 16 mm length and 180° entry with an aspect angle with an aspect ratio ( $L/D$ ) of 16:1. The material was first preheated in barrel for 5 minutes under a pressure of approximately 0.5 MPa to get a compact mass. The excess material was then carried out at a set shear rate in a program via a microprocessor. During the test, the pressure drop across capillary channel and melt temperature was captured via a data acquisition system. The apparent values of shear stress, shear rate and shear viscosity were calculated using the derivation of the Poiseuille law for capillary flow:

$$\text{Apparent wall shear stress (Pa); } \tau = \frac{R\Delta P}{2L} \quad (3.1)$$

$$\text{Apparent wall shear rate (s}^{-1}\text{); } \dot{\gamma}_{app} = \frac{4Q}{\pi R^3} \quad (3.2)$$

$$\text{Apparent shear viscosity (Pa s); } \eta_s = \frac{\tau}{\dot{\gamma}_{app}} \quad (3.3)$$

where  $\Delta P$  is a pressure drop across the channel (Pa),  $Q$  is volumetric flow rate (m<sup>3</sup>s<sup>-1</sup>),  $R$  is the capillary radius (m), and  $L$  is the length of the capillary (m). The values of  $R$  and  $L$  used in this work were 1 mm and 16 mm, respectively.

### 3.6.3 Melt flow index

Melt flow index is the output rate (flow) in grams that occurs in 10 minutes through a standard die of  $2.0955 \pm 0.00051$  mm diameter and  $8 \pm 0.025$  mm in length when a fixed pressure is applied to the melt via a piston and a load of total mass 5 and 21.6 kg at a temperature of 190°C. Melt flow index is an assessment of average molecular

mass and is an inverse measure of the melt viscosity; In other words, the higher a MFI, the more polymer flows under test conditions.

For this study melt flow indices of HDPE compound were measured by using MPX 62.92 Gottfert followed DIN ISO1133 (the plunger with its rod which carries two circular reference markings at a distance of 30 mm from each other).

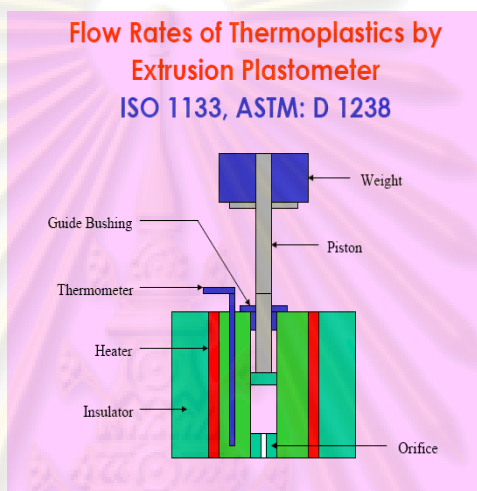


Figure 3.2 Melt Flow Indexer.

### 3.6.4 Viscosity number

The viscosity number referred to the molecular weight of the HDPE compound, was analyzed by Automatic Viscometer, Lauda PVS1 model. The instrument equipped with Ubbelohde “Schott-Geratte” type capillary no.O<sub>a</sub>, K=0.05 measuring range 1.2-1.8 cst. by comparing the flow time of polymer solution ( $t$ ) and flow time of solvent ( $t_0$ ) divided by concentration. Polymer samples were dissolved in 50 ml Decahydronaphthalene (Decalin). Approximately 0.001g/ ml and dissolution period was 2 hours periodic shaking at temperature of 140°C. Irganox 1010 was added to prevent further decomposition of the solution under high-temperature conditions (instrument temperature set at 135°C). The clear solution was transferred to the Ubbelohde set compared with the flow time of solvent by infra red sensor system. The error for the Automatic Viscometer instrument used in this study was estimated to be around 10 % RSD.

## CHAPTER IV

### RESULTS AND DISCUSSION

In this study, the effect of extrusion condition such as screw configuration, screw speed, feed rate and temperature profile on thermal properties of HDPE compound was investigated. The mechanical properties, the morphology and white spot area of the HDPE compounds representing the homogenization of each component were described. The rheological behavior of HDPE melt and the effect of extrusion conditions on melt flow index and viscosity number were presented.

#### 4.1 Molecular weight and molecular weight distribution of HDPE powder

A typical GPC chromatogram of bimodal HDPE is shown in Figure 4.1. The molecular weight distribution (MWD) curve of a PE 100 pipe grade (pressure class) base resin was a function of extrapolated molecular weight. The chromatogram revealed two peaks, corresponding to low molecular weight (first peak) and high molecular component (second peak).

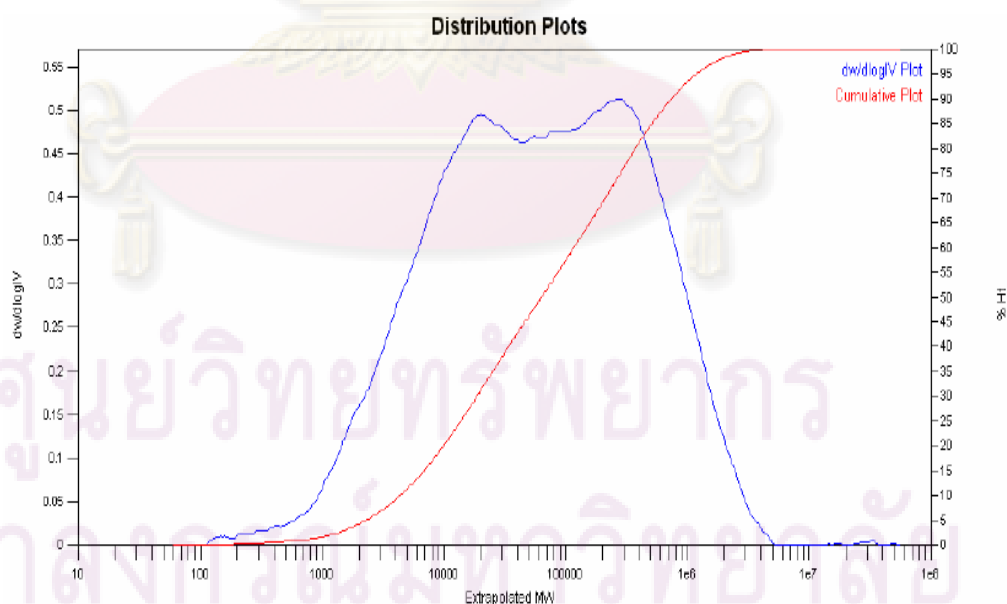


Figure 4.1 GPC chromatogram of PE 100 pipe grade HDPE base resin having bimodal molecular weight distribution.

The physical properties and molecular weight of HDPE powder are presented in Table 4.1.

Table 4.1 Analysis of PE 100 pipe grade HDPE base resin powder

Properties	Unit	HDPE
MFI 5/190°C	g/10min	0.4
MFI 21.6/190°C	g/10min.	12
MFR 21.6/5		30.0
Density	g/cm <sup>3</sup>	0.948 ± 0.001
Viscosity number	cm <sup>3</sup> /g	370
Average powder size	µm	191
Fine powder content	% wt	7.3
Mn	g/mol	15,200
Mw	g/mol	409,000
Mz	g/mol	2,196,500
MWD		28.2

## 4.2 Thermal properties of HDPE compound

### 4.2.1 Oxidative induction time and melting temperature

The influence of extrusion conditions on thermal properties are presented in Table 4.2. It was found that HDPE compounded at 140°C barrel temperature had the lowest oxidative induction time (OIT) value as shown in Figure 4.2. It can be explained that the high shear stress caused the formation of more radicals resulting in the consuming more antioxidant in the compound. At barrel temperature above 220°C, the oxidative induction time (OIT) of HDPE tended to decrease and leveled off at ca. 96 min. at 240°C barrel temperature. It implied that the high barrel temperature resulted in more severe polymer degradation. The increasing shear stress due to higher screw filling levels (4 kg/h to 12 kg/h as shown in Figure 4.3), OIT was

not significantly affected. Also the melting temperature and enthalpies of fusion showed no substantially change compared with neat HDPE powder as seen from Table 4.2.

Table 4.2 Effect of extrusion conditions on thermal properties of HDPE compounded at constant 200 rpm screw speed

Sample	Screw configuration	Barrel temperature (°C)	Feed rate (kg/h)	Melting temperature ( $T_m$ ) (°C)	Oxidative induction time (OIT, min)	Heat of fusion ( $\Delta H_f$ ) (J/g)	Crystallinity ( $\chi_c$ ) (%)
1	4KBRH	140	8	129.3	92.8	166.8	57.7
2	4KBRH	180	8	129.4	113.1	172.6	59.7
3	4KBRH	200	8	131.5	113.1	167.7	58.0
4	4KBRH	220	8	129.5	99.6	174.4	60.3
5	4KBRH	240	8	128.1	96.5	156.1	54.0
6	4KBRH	200	4	131.1	94.0	175.9	60.9
7	4KBRH	200	8	130.1	87.5	172.3	59.6
8	4KBRH	200	12	130.6	90.3	172.0	59.5
9	2KB	200	8	130.5	130	160.9	55.7
10	3KB	200	8	129.5	130	166.5	57.6
11	4KB	200	8	130.6	>140	159.7	55.3
12*	-	-	-	128.5	1	166.0	57.4

\* neat powder

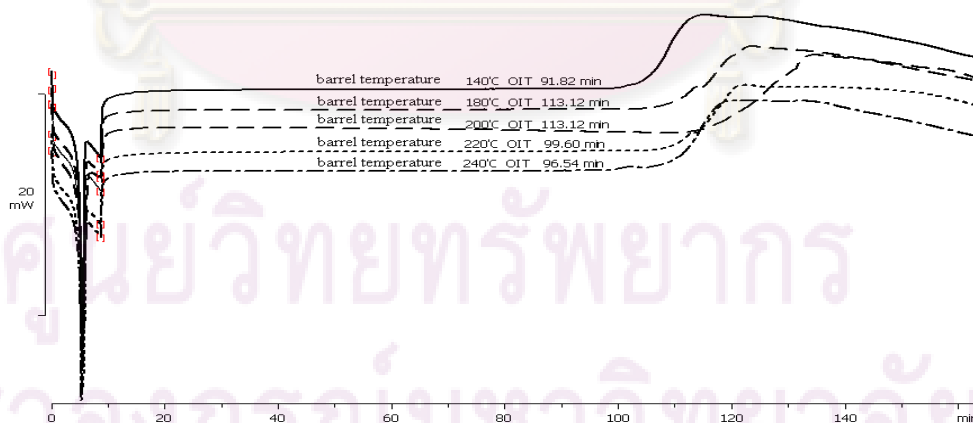


Figure 4.2 DSC thermograms of the oxidative induction time (OIT) of HDPE compounded at various barrel temperature.

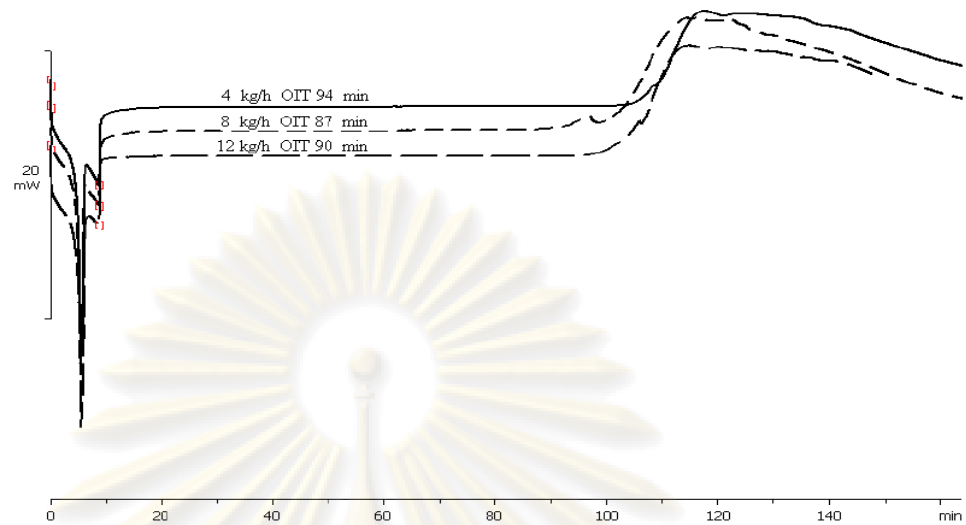


Figure 4.3 DSC thermograms of the oxidative induction time (OIT) of HDPE compounded at various feed rate conditions.

The behavior of shear rate and stress of the molten polymer in the extruder is shown in Figures 4.4-4.5. As the polymer melt moves in the intermeshing area from one screw to the other screw, one screw cleans out the other one and almost no polymer melt remains sticking onto the screw surface as shown in Figure 4.4.

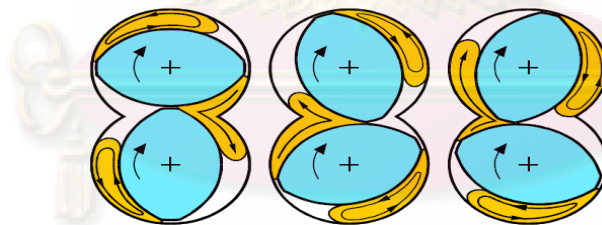


Figure 4.4 Molten polymer flow path in the intermeshing zone of twin screw extruder [11].

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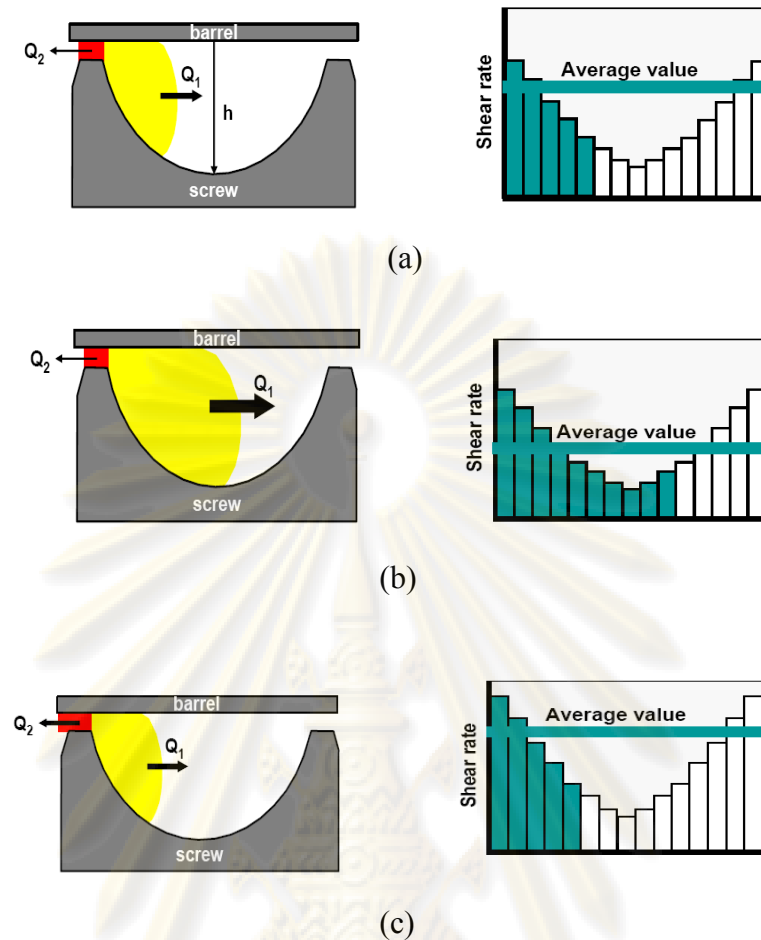


Figure 4.5 Melt flow path in extruder screw channel at: (a) Low feed rates and low screw speed, (b) High feed rate and low screw speed, (c) High screw speed [11].

#### 4.2.2 Heat of fusion and crystallinity

From Table 4.2, heat of fusion and total crystallinity of HDPE compound increased considerably with the reduction in feed rate and reached a maximum value at a feed rate of 4 kg/h. Heat of fusion increased by ca. 9.9 J/g and total crystallinity increased by ca. 3.5 % compared with neat powder. Feed rate would influence the degree of screw filling, shear rate, shear stress, viscosity and residence time, and hence the homogeneity of polymer melts as well. It can be noted that the increase in heat of fusion of 6-10 J/g related to about 1-1.5 wt % change in crystallinity. Such change in total crystallinity correlates to an approximately 1.0-1.2 MPa increase in tensile yield stress of HDPE [20]. Therefore, the increase in crystallinity through maximum homogeneity without degradation would result in an improvement of the hydrostatic pressure performance of HDPE pipes.

### 4.3 Degradation of HDPE compound

Table 4.3 and Figure 4.6 show the effect of extrusion on carbonyl index of HDPE compound under various extrusion conditions. FTIR was employed to study the changes of un-saturation during degradation of HDPE. The carbonyl index (C.I.) is defined as the ratio of the absorbance band of the carbonyl group around  $1714\text{ cm}^{-1}$  and that of the polyethylene at  $2920\text{ cm}^{-1}$ . It was found that a barrel temperature of  $200^\circ\text{C}$  at feed rate of  $8\text{ kg/h}$  and screw speed of  $200\text{-}300\text{ rpm}$  resulted in the lowest carbonyl index and therefore the least oxidative degradation of HDPE compound in presence of air. At other conditions, such as lower or higher barrel temperature, lower or higher feed rate and especially lower screw speed, oxidation degradation was more pronounced due to excessive shear or thermal stress. Higher antioxidant levels led to reduction in C.I. due to primary radical scavenger and hydroperoxyl decomposition [21].

Mendes *et al.* [22] also found the significant increase in the carbonyl concentration during the serious extrusion conditions. It was also found that the maximum value of carbonyl index ca. 0.037 at  $100\text{ rpm}$  screw speed. It can be explained that the molten compound had longer residence time with oxygen gas in the atmosphere.

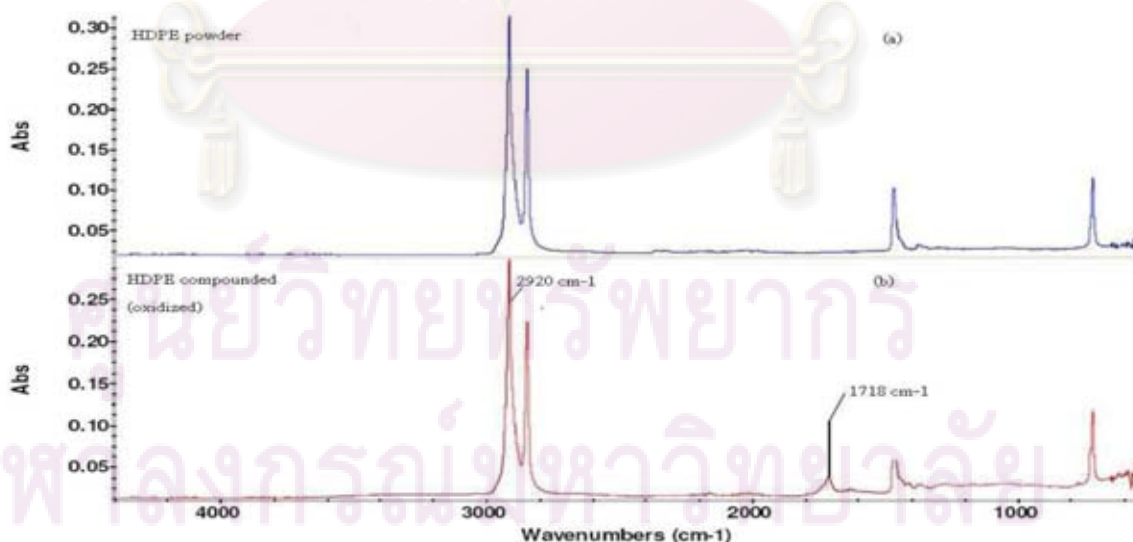


Figure 4.6 FT-IR spectra of HDPE at: (a) neat powder (b) oxidized HDPE compound.

Table 4.3 Effect of extrusion conditions on carbonyl index of HDPE compound.

Sample	Screw configuration	Barrel temperature (°C)	Feed rate (kg/h)	Screw speed	Absorbance 1718 cm <sup>-1</sup>	Absorbance 2920 cm <sup>-1</sup>	Carbonyl Index
1	4KBRH	140	8	200	0.040	3.7	0.011
2	4KBRH	180	8	200	0.057	4.1	0.014
3	4KBRH	200	8	200	0.037	4.1	0.009
4	4KBRH	220	8	200	0.047	3.3	0.014
5	4KBRH	240	8	200	0.051	3.6	0.014
6	4KBRH	200	4	200	0.052	4.0	0.013
7	4KBRH	200	8	200	0.035	4.3	0.008
8	4KBRH	200	12	200	0.052	3.4	0.015
9	2KB	200	8	200	0.051	4.0	0.013
10	3KB	200	8	200	0.039	4.2	0.009
11	4KB	200	8	200	0.035	4.8	0.007
12	4KBRH	200	8	100	0.130	3.5	0.037
13	4KBRH	200	8	300	0.061	5.4	0.011
14 <sup>a</sup>	4KBRH	200	8	200	0.041	4.1	0.010
15 <sup>b</sup>	4KBRH	200	8	200	0.038	3.9	0.010
16 <sup>c</sup>	4KBRH	200	8	200	0.033	3.9	0.008

Remark : a= additional 0.1 phr primary antioxidant, Irganox 1010, b= additional 0.1 phr secondary antioxidant Irgafos 168, c= 0.1 phr of UV stabilizer Tinuvin® 622.

## 4.4 Mechanical properties

### 4.4.1 Charpy impact resistance

The higher the charpy impact resistance, the tougher the materials. The effect of extrusion conditions on impact energy of the HDPE compound are shown in Table 4.4 and Figures 4.7-4.9. Feed rate, screw speed and barrel temperature were found to have significant effect on impact energy of the compound. Increasing the feed rate at lower screw speed significantly decreased impact energy of the compound. The increasing barrel temperature was also observed to result in the decrease in impact energy because the degradation of Ziegler –Natta HDPE.

According to Figure 4.7, the impact energy of the HDPE compound was considerably increased with decreasing material feed rates and reached a maximum value at 4 kg/h and screw speed of 100 rpm. It was anticipated that the low feed rate would promote better homogenization of high and low molecular weight fractions leading to superior strength in HDPE compound. For HDPE compound at screw speed of 300 rpm and 12 kg/h feed rate, the impact energy was as low as 15 mJ/mm<sup>2</sup>. It can be explained that the melt in the barrel was subjected to high shear forces exceeding a critical value. Consequently, this led to shear degradation resulting in lower impact energy of HDPE compound.

As shown in Figure 4.8, the extrusion at 140°C barrel temperature resulted in high impact energy of HDPE compound between 20-35 mJ/mm<sup>2</sup> but low values (ca. 15-17 mJ/mm<sup>2</sup>) for extrusion at 180°C barrel temperature. For the extrusion at higher barrel temperature, the decreasing impact energy of HDPE compound might be caused by the thermal degradation due to the chain scission of the polyethylene molecules.

According to Figure 4.9, the charpy impact strength of HDPE compound with 4KBRH screw configuration was higher than other screw configurations at all feed rates. Maximum charpy impact resistance of HDPE compound was observed at 4 kg/h feed rate with 4KBRH screw configuration. The charpy impact dramatically decreased when the number of kneading blocks decreased and leveled off at ca. 10 mJ/mm<sup>2</sup> with 2KB screw configuration at 12 kg/h feed rate. It can be explained that the increasing number of kneading blocks promoted better homogenization of high and low molecular weight polymer fractions resulting in higher impact resistance.

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Table 4.4 Effect of extrusion conditions on charpy impact energy at 23°C of HDPE compound.

Sample	Screw configuration	Barrel temperature (°C)	Feed rate (kg/h)	Screw speed (rpm)	Charpy impact energy at 23°C (mJ/mm <sup>2</sup> )
1	4KBRH	140	8	200	25
2	4KBRH	180	8	200	16
3	4KBRH	200	8	200	18
4	4KBRH	220	8	200	18
5	4KBRH	240	8	200	16
6	4KBRH	200	4	200	30
7	4KBRH	200	8	200	22
8	4KBRH	200	12	200	17
9	2KB	200	8	200	12
10	3KB	200	8	200	12
11	4KB	200	8	200	16
12	4KBRH	200	8	100	33
13	4KBRH	200	8	300	21
14 <sup>a</sup>	4KBRH	200	8	200	25
15 <sup>b</sup>	4KBRH	200	8	200	22
16 <sup>c</sup>	4KBRH	200	8	200	23

Remark : a = additional 0.15 phr Irgafos 168, b= additional 0.15 phr Tinuvin<sup>®</sup> 622

c = 0.25 phr Tinuvin<sup>®</sup> 622

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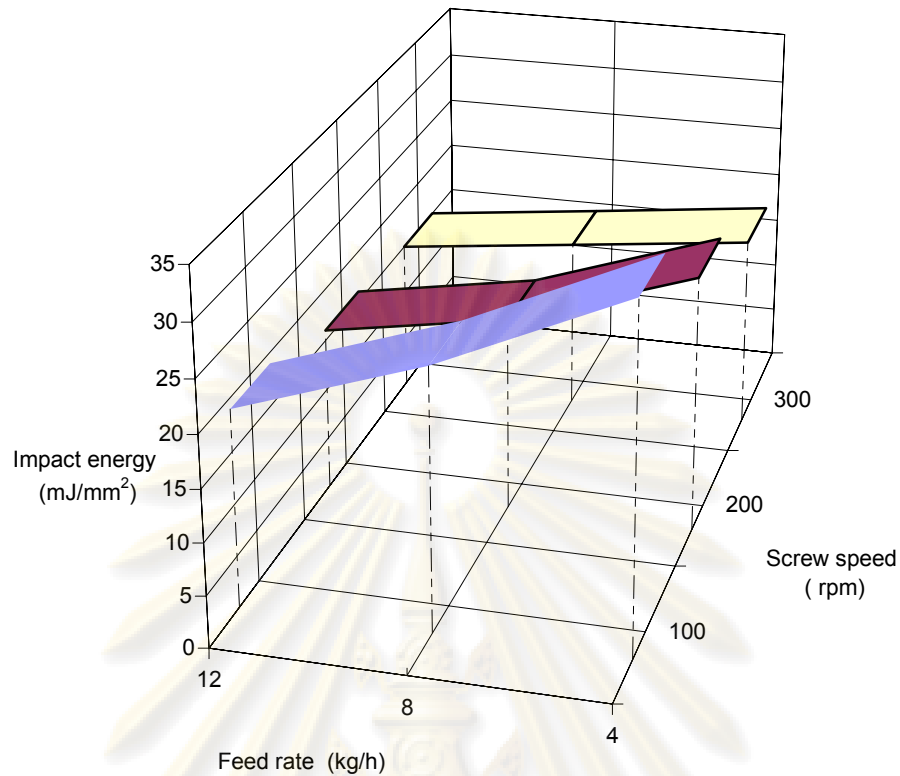


Figure 4.7 Charpy impact energy at 23°C of HDPE compound as function of feed rate and screw speed. Extrusion with 4KBRH screw configuration at 200°C barrel temperature.

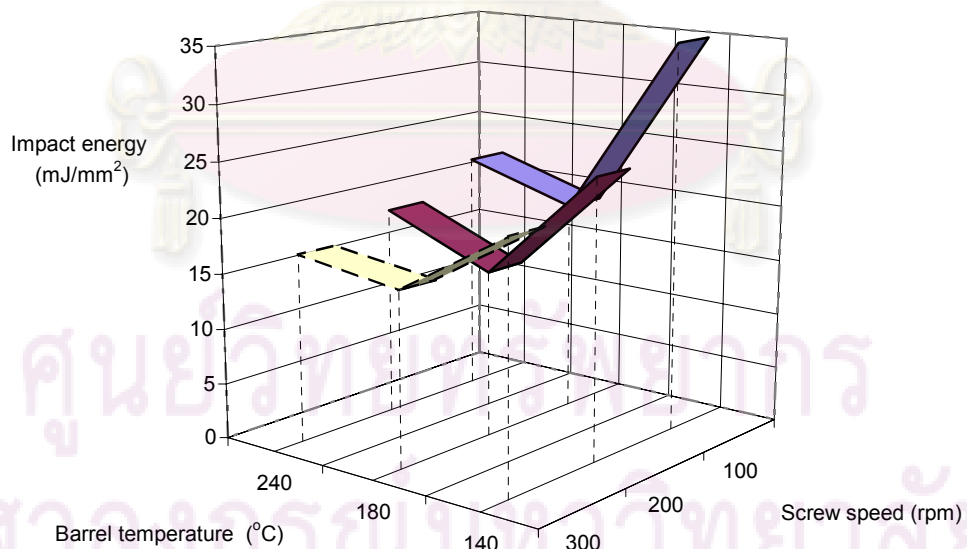


Figure 4.8 Charpy impact energy at 23°C of HDPE compound as function of barrel temperature. Extrusion with 4 KBRH screw configuration at 8 kg/h feed rate.



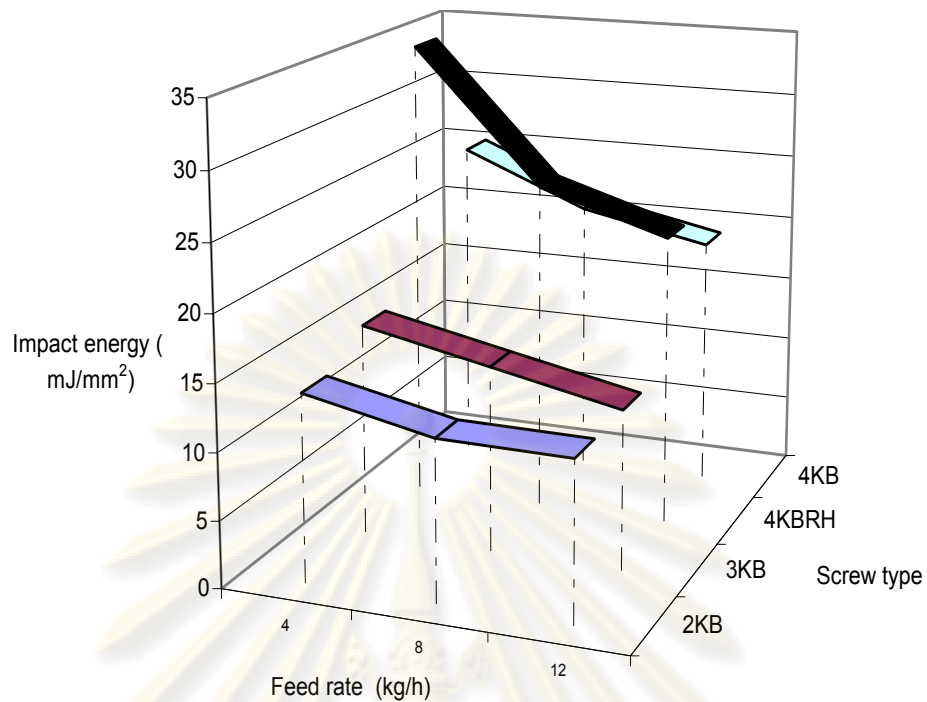


Figure 4.9 Charpy impact energy at 23°C of HDPE compound as various of screw configurations and feed rates at 200°C barrel temperature and 200 rpm screw speed.

#### 4.4.2 Full notch creep test (FNCT)

As shown in Table 4.5, the FNCT failure time of HDPE compound was considerably increased with decreasing white spot area (%WSA) due to better homogeneity of the compound components. It was also found that the optimized screw configuration of extrusion was 4KBRH, the longer FNCT failure time and the lower white spot area. The longest failure time of 4,826 hours at a load of 6 MPa at 80°C with white spot area below 1% was obtained at this optimum extrusion condition.

For HDPE high pressure pipe, the brittle failure at relatively low stress loading is the common mode of failure. External factors that initiate or accelerate the slow crack growth (SCG) in pipe are the indentation of sand and rocks, squeezing and loading stress including bending of the pipe. The early occurrence of brittle pipe failures is related with lower failure times for SCG evaluation via FNCT test [23]. During the FNCT test, when the notched specimen is subjected to a constant load stress, the failure is composed of three sequential deformation regimes (1) fracture initiation (2) slow crack growth (3) post-yielding tensile stretching.

Figure 4.10 shows that the decrease in compounding feed rate leads to a sharp increase in FNCT failure time of HDPE compounded at 200 °C with 4 KBRH screw configuration due to good homogenization. The maximum FNCT value was obtained for HDPE compounded at 4 kg/h feed rate for all screw speeds.

The results in Figure 4.11 show that higher feed rate caused lower FNCT failure times of HDPE compound. The FNCT failure time of the HDPE compounded at 4 kg/h feed rate was higher than that at 8 kg/h because of the better homogenization due to longer residence time at low feed rate. The effect of screw speed was not substantially significant.

Table 4.5 White spot area and FNCT failure time of HDPE compound. Extrusion at 200°C barrel temperature, feed rate of 8 kg/h and 200 rpm screw speed.

Sample ( screw configuration)	WSA (%)	Failure Time FNCT (80°C) at 6 MPa ( h )
2KB	3.2	558
3KB	3.0	887
4KB	1.6	1228
4KBRH	0.9	4826

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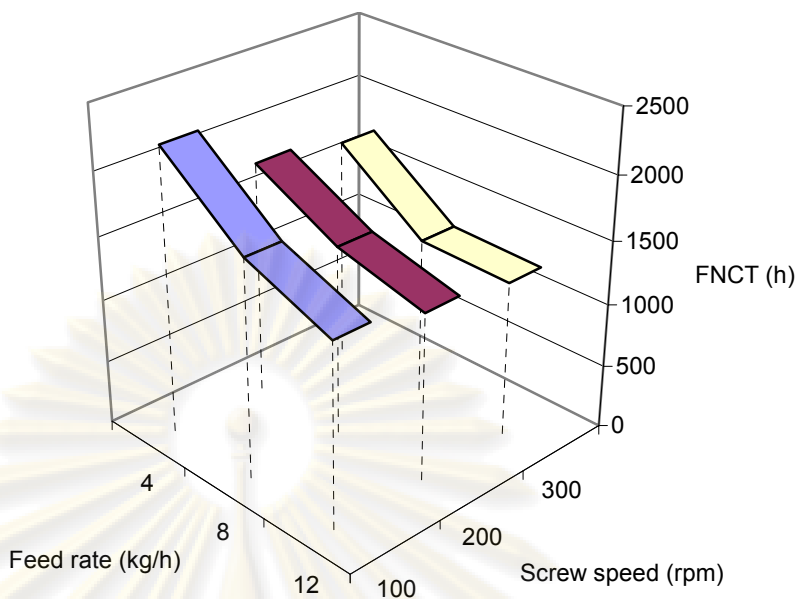


Figure 4.10 FNCT failure time of HDPE compounds as function of feed rate and screw speed. Extrusion with 4KBRH screw configuration and 200°C barrel temperature.

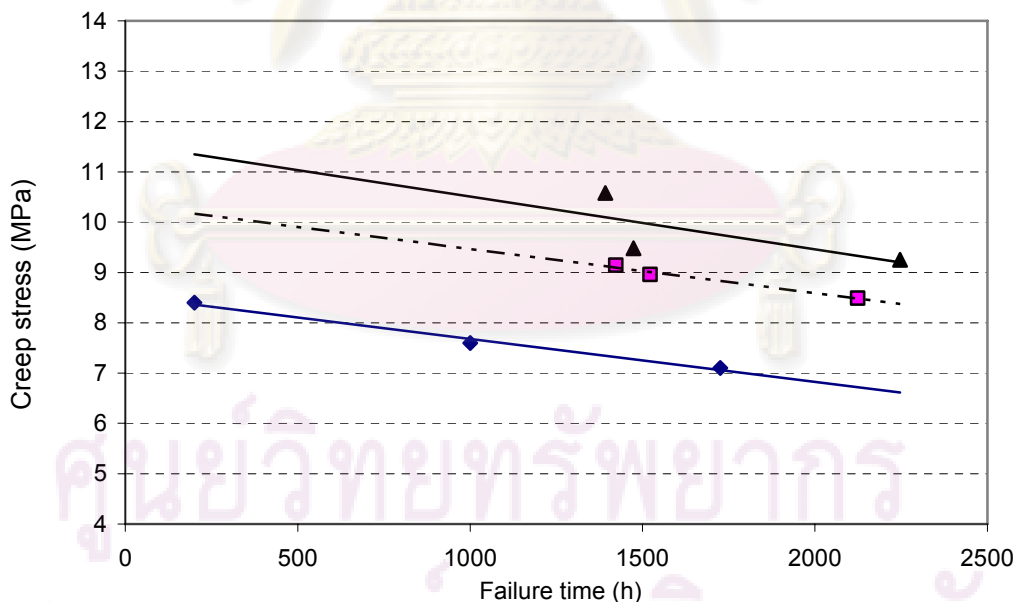


Figure 4.11 Applied creep stress versus time to FNCT failure time at 80°C of HDPE compound.: (◆) PE 100 commercial; (■) compounded at 8 kg/h; (▲) compounded at 4 kg/h. Extrusion with 4KBRH screw configuration at 200°C barrel temperature and 200 rpm screw speed.

Figure 4.12 (a) shows the picture of ductile failure at 285 hours of high pressure pipe after hydrostatic pressure test of pipe specimen (32 mm diameter, 3 mm thickness, at 12.4 MPa / 20°C). From Figure 4.12 (b), the specimen was cut from ductile area and aged follow [25], the high density and longer fibrils (Figure 4.12 (c)) was observed relating to the ductile phenomena.

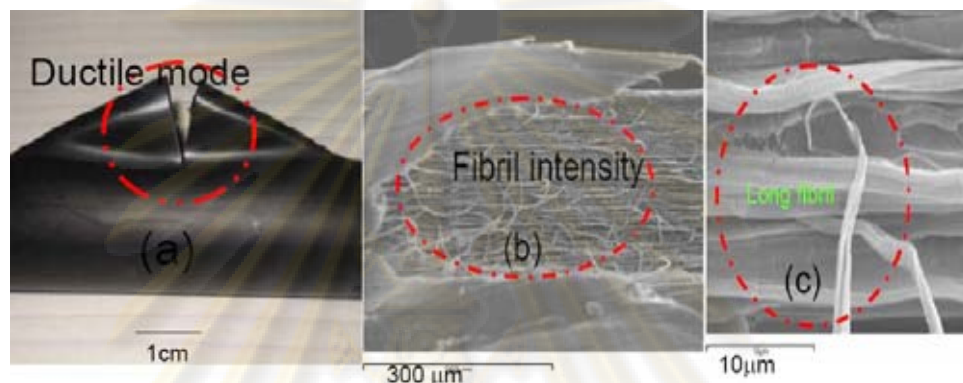


Figure 4.12 (a) picture of side view ductile pipe failure of hydrostatic pressure test. SEM micrographs taken at 5,000x magnification (b) fibril density (c) longer fibril. Extrusion with 4KBRH screw configuration at 200°C barrel temperature and 8 kg/h feed rate.

Figure 4.13 shows the indirect effect of properties of the HDPE compound on the deterioration of FNCT of the HDPE pipe grade. Figure 4.13 (a) shows the dimple of contaminate solid particle that is starting point of slow crack growth of pipe. Figure 4.13 (b) shows that the un-dispersed additive also caused the reduction of physical properties of high pressure pipe.

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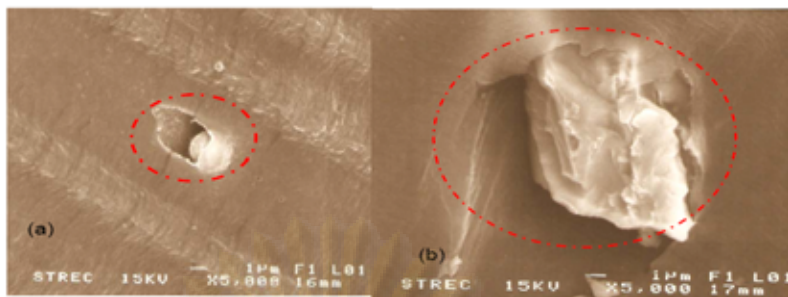


Figure 4.13 SEM micrographs taken at 5,000x magnification of: (a) dimple from solid particle (b) dimple from un-dispersed additive.

## 4.5 Morphology of HDPE compound

### 4.5.1 Morphology by SEM

The fracture surface of HDPE compound can be visualized using SEM technique. Figure 4.14 shows the comparison of a micrograph of a sample homogenized using 4 KBRH screw configuration at various barrel temperatures at 8 kg/h feed rate. The SEM morphology of in-homogeneities gels of HDPE compounded at different barrel temperature showed the decrease in white spot size (gels) with increasing barrel temperature.

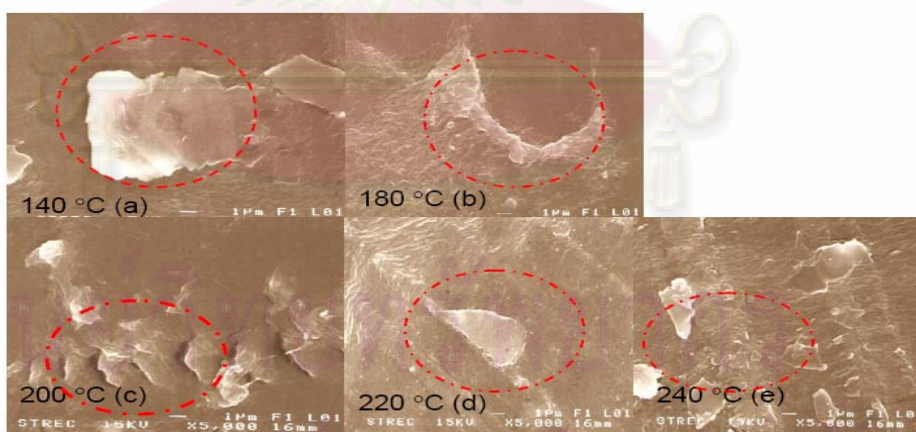


Figure 4.14 SEM micrographs taken at 5,000x magnification of undispersed high molecular weight fraction (white spot area) at various barrel temperature, with 4KBRH screw configuration and 200 rpm screw speed (a) 140°C, (b) 180°C, (c) 200°C, (d) 220°C and (e) 240°C, respectively.



Figures 4.15-4.16 show the fracture surfaces of the HDPE compounded at 4 and 8 kg/h compared with the commercial PE 100 reference compound. The results presented in Figures 4.16a and 4.16c indicate that a higher fibril density appeared on the fracture surface of the homogenous specimen. Compounding at 1000 kg/h of PE 100 commercial compound from large scale production had lower fibril density (Figure 4.16 b).

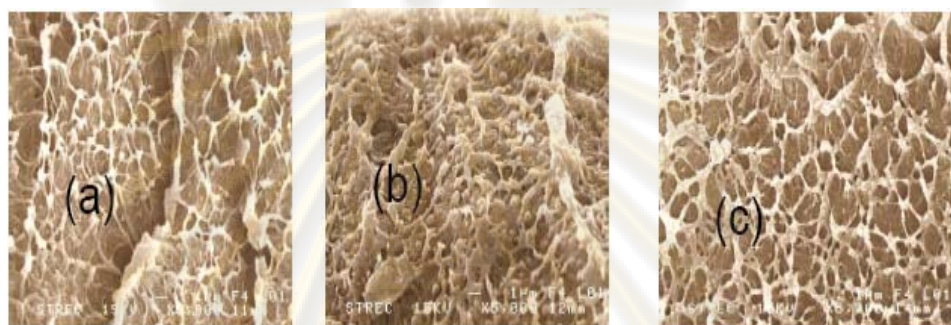


Figure 4.15 SEM micrographs taken at 5,000x magnification of HDPE compounded with 4KBRH screw configuration at 200°C and 200 rpm screw speed. Feed rate: (a) 4 kg/h; (b) plant production (c) 8 kg/h.

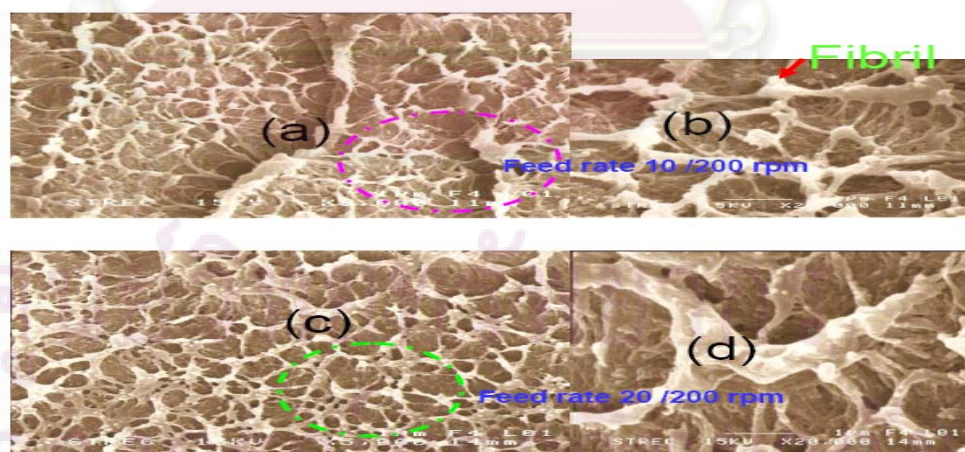


Figure 4.16 SEM micrographs of HDPE compounded with 4KBRH screw configuration at 200°C and 200 rpm screw speed. Feed rate: 4 kg/h (a) magnification 5,000x and (b) magnification 20,000x; 8 kg/h (c) magnification 5,000x and (d) magnification 20,000x.



#### 4.5.2 Carbon black dispersion (CB dispersion)

ISO 4427 pipe industry standard required the carbon black dispersion ISO rating  $\leq 3$ . This degree of carbon black dispersion was only achieved with 4 KBRH screw configuration (ISO rating ca. 1.9). Figure 4.17 shows big agglomerates of carbon black dispersion in the HDPE matrix compounded with 4 KB configuration (ISO rating 3.2). It can be explained that the screw 4KB could not provide sufficient dispersion of carbon black particles in the HDPE compound. Figure 4.18 showed that carbon black dispersion obtained with 4KBRH screw configuration resulted at ISO rating ca. 1.9. The reverse element screw promoted the distribution and dispersion of carbon black pigment in the HDPE compound by increasing residence time in kneading blocks.

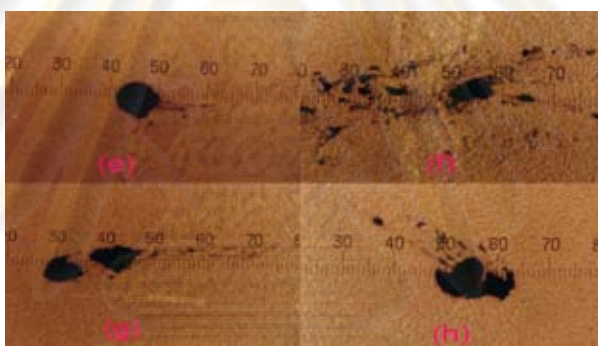


Figure 4.17 Carbon black dispersion taken at 100x magnification of HDPE compounded with 4KB screw configuration at 200°C barrel temperature, 200 rpm screw speed and 8 kg/h feed rate.



Figure 4.18 Carbon black dispersion taken at 100x magnification ( ISO rating 1.9 ) of HDPE compounded with 4KBRH screw configuration at 200°C barrel temperature, 200 rpm screw speed and 8 kg/ h feed rate.

### 4.5.3 White spot area (% WSA) of HDPE compound

White spots are non-dispersed high molecular weight fractions (gels), not impurities in the HDPE matrix [15]. Optical micrographs (Figures 4.19-4.22) showed the white spot area of HDPE compounded at various conditions. Figure 4.19 shows that white spot areas were strongly dependent on screw configurations. The white spot area was drastically reduced when the number of kneading blocks of extrusion screw increased. It can be explained that the additional kneading blocks promoted the dispersion and homogenization of low and high molecular weight components of bimodal HDPE compound and resulted in the reduction of white spot area by incorporating the highly viscous high molecular weight gels into the polyethylene matrix.

Figure 4.20 shows the comparison of a micrograph of a HDPE compounded using a screw consisting of 4 kneading block with additional reverse element (4KBRH). The average number of in-homogeneities (white spot area) increased significantly from Figure 4.20b to Figure 4.20d. Increasing feed rate from 4 kg/h to 12 kg/h caused more white spot. Figure 4.20a is an example for homogeneity of commercial scale compound (rate 1 ton/h) and shows much higher number and larger size of white spot (gels). Longer residence time in extruder (low feed rate) is more important for good homogeneity (low white spot area) than high shear rates (high screw speed).

The micro-cut (Figure 4.21) were made from pellets compounded in commercial scale extruder at 1 ton/h direction. The microtome cuts were made perpendicular (Figure 4.21a) to melt flow direction in extruder die-hole and parallel to flow direction (Figure 4.21b). Whereas the shape of the in-homogeneities in the image of the perpendicular cut (a) is almost circular and parallel cut (b) shows very high elongated particles. This finding indicates that highly elongated in-homogeneities in bimodal high density polyethylenes do not break up due to high difference in viscosities. It also shows that for bimodal polyethylene there is no interfacial tension present between matrix and in-homogeneities (gels) because it is the same material but with different viscosities. For further dispersion of elongated gels, they must be elongated to virtually zero thickness by mixing elements that generate elongation not shear.

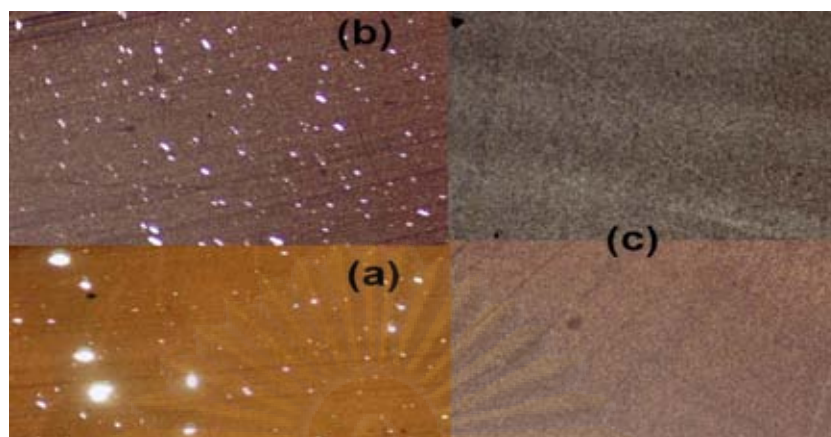


Figure 4.19 Optical micrographs taken at 100x magnification of HDPE compounded at 200°C, 200 rpm screw speed and 8 kg/h feed rate. Screw configuration: (a) 3KB, (b) 4KB, (c) 4KBRH.

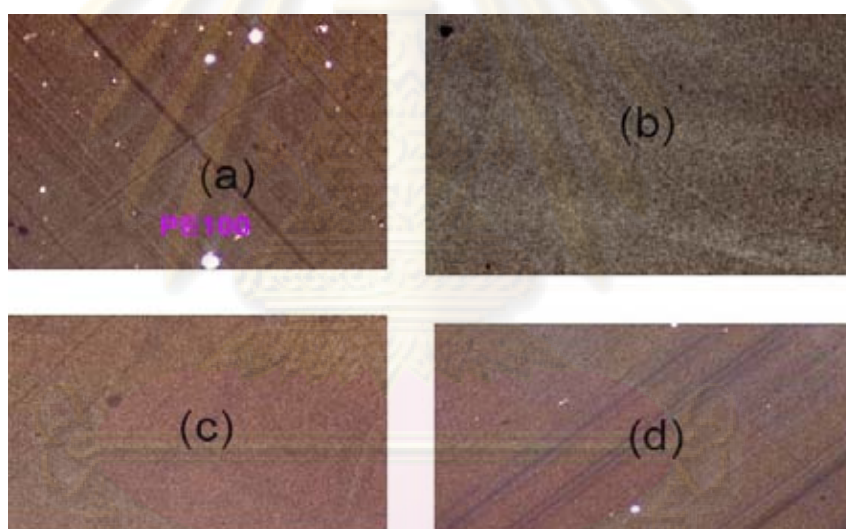


Figure 4.20 Optical micrographs taken at 100x magnification of HDPE compounded with 4KBRH screw configuration at 200°C and 200 rpm screw speed compared to commercial reference. Feed rate: (a) plant production, (b) 4 kg/h, (c) 8 kg/h, and (d) 12 kg/h.

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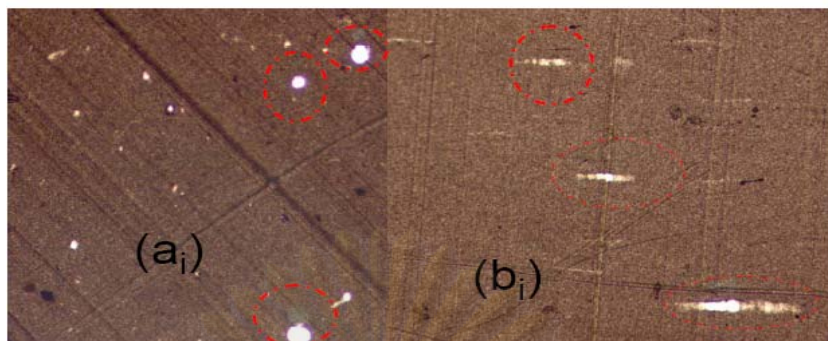


Figure 4.21 Optical micrographs taken at 100x magnification of PE 100 reference sample compounded at 1 ton/h (a) perpendicular cut (b) parallel cut to extruder die melt flow direction.

Figure 4.22 shows that the average percent white spot area (%WSA) decreased with increasing the number of kneading blocks in the screw configuration at all feed rates. The decrease in white spot area is due to better homogenization of HDPE compound. The lowest white spot area of HDPE compound of less than 0.5% was found when additional reverse screw element was inserted after each kneading blocks at low feed rate of 4 kg/h. It can be explained that the reverse element would lead to better homogeneity of the HDPE compound.

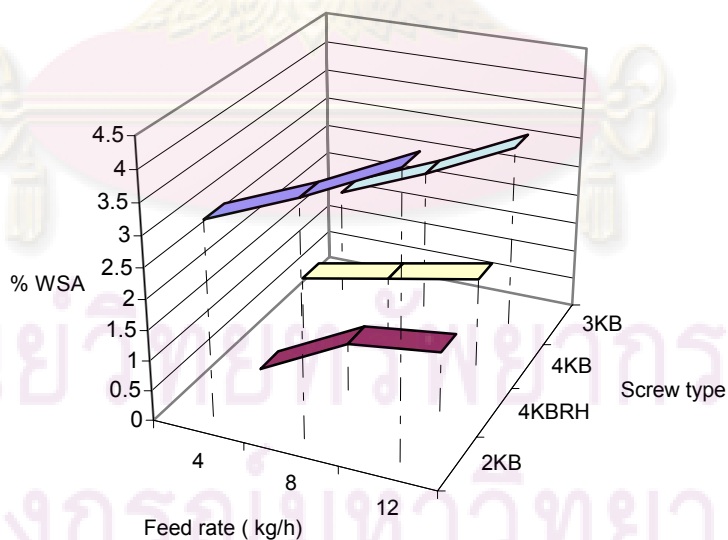


Figure 4.22 Percentage of white spot area (gels) of HDPE compounded as function of screw configuration and feed rate 8 kg/h at 200°C barrel temperature, 200 rpm screw speed.



#### 4.6 Rheological behavior of HDPE compound

HDPE pipe compound is commercially processed to form a pipe at high output rates and extrusion pressures. Therefore, the processing properties are of the great importance. In this work, the rheological measurements were made with an oscillating cone & plate rheometer under dynamic frequency sweep mode. The complex viscosities of HDPE compounded under various extrusion conditions are quite similar as shown in Figure 4.23. Variation of feed rate within the studied range had no significant effect on the melt rheology. It is expected that these HDPE compounds can be processed under same condition as the commercial PE 100 reference sample.

Figure 4.24 shows the influence of barrel temperature on the complex viscosity of compound. It was found that the complex viscosity of HDPE compounded at 240°C barrel temperature had a much lower shear viscosity compared to other conditions including commercial sample. The high barrel temperature and therefore high melt temperature led to the chain scission by thermal degradation for HDPE compound which resulted in reduction of the complex viscosity.

Figure 4.25 shows the complex viscosity of HDPE compound at various screw speeds. The results are not significantly different with the exception of the commercial reference samples which show similar behavior in the flow curve as well.

On the other hand, the results of different screw configurations in Figure 4.26 reveal the dominating effect on the low to medium viscosity of compounds. The complex shear viscosity increased considerably with number of kneading blocks using 2KB, 3KB and 4KB screw configuration and reached a maximum value using 4 KBRH configurations at 144000 Pas. Again, the additional reverse element led to better homogeneity of HDPE compound.

Figure 4.27 shows the effect of additional antioxidant additive of commercial recipe on shear viscosity. The complex viscosities of the compounds do not show any significant difference. It can be concluded that additional antioxidant levels have no influence on thermal and mechanical degradation under the selected compounding conditions.

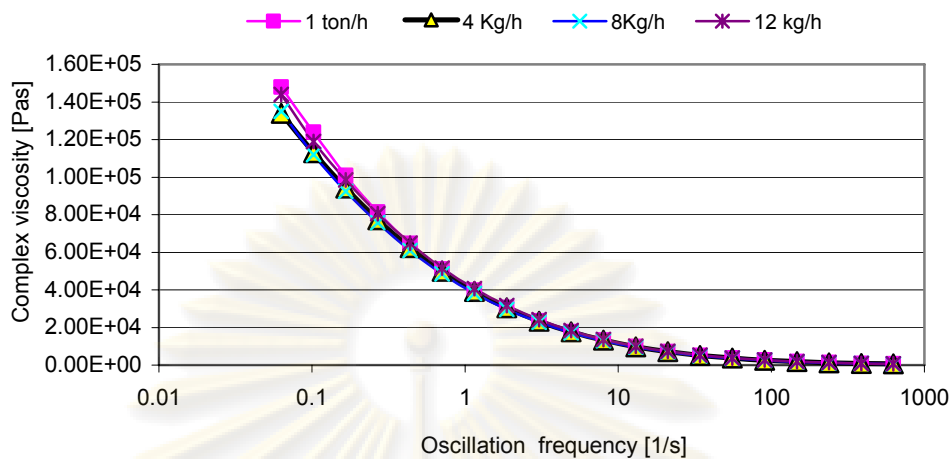


Figure 4.23 Complex viscosity versus oscillation frequency of HDPE compounded at various feed rate. Extrusion with 4KBRH screw configuration at 200°C barrel temperature and 200 rpm screw speed.

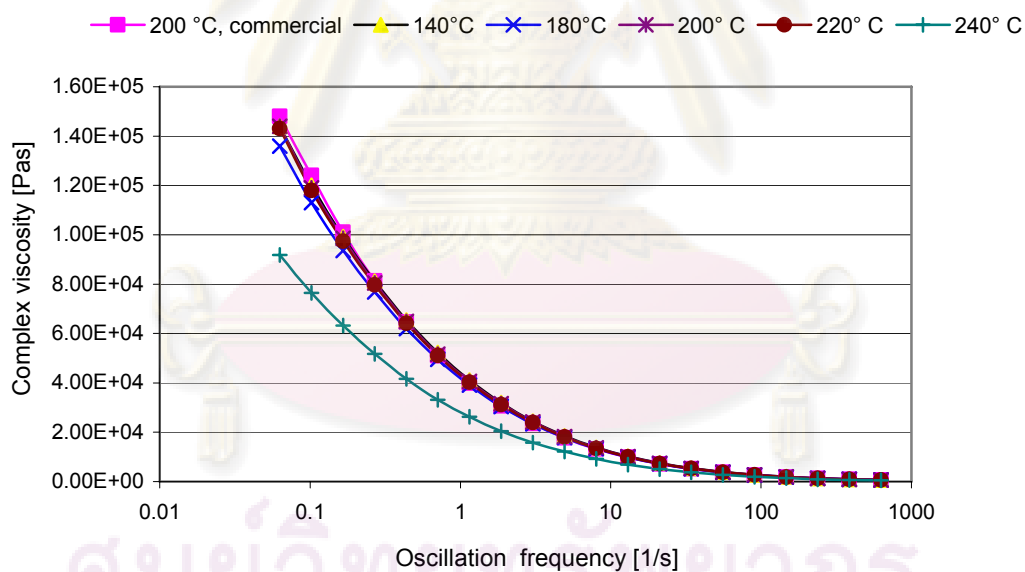


Figure 4.24 Complex viscosity versus oscillation frequency of HDPE compounded at various barrel temperatures. Extrusion with 4KBRH screw configuration at 8 kg/h feed rate and 200 rpm screw speed.



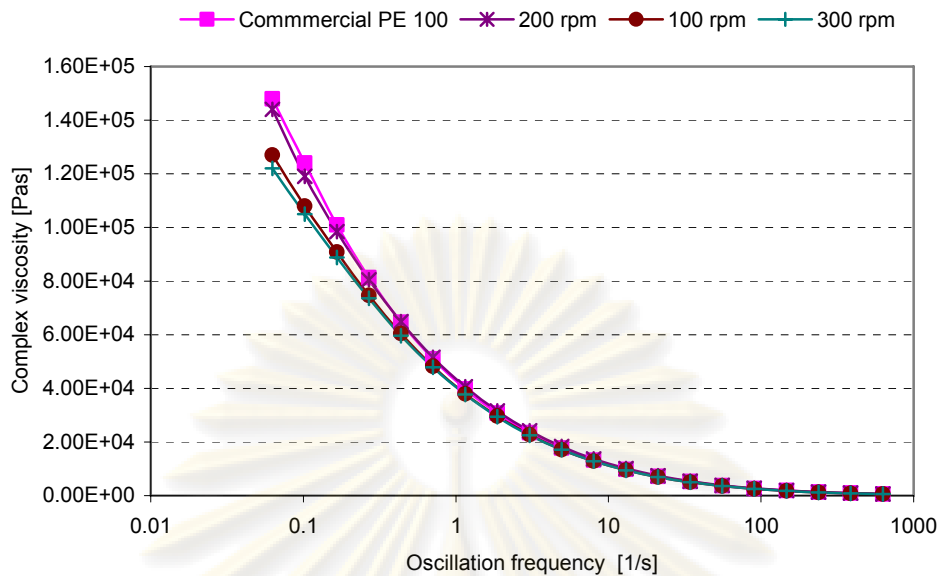


Figure 4.25 Complex viscosity versus oscillation frequency of HDPE compounded at various screw speeds. Extrusion with 4KBRH screw configuration at constant 8 kg/h feed rate and 200°C barrel temperature.

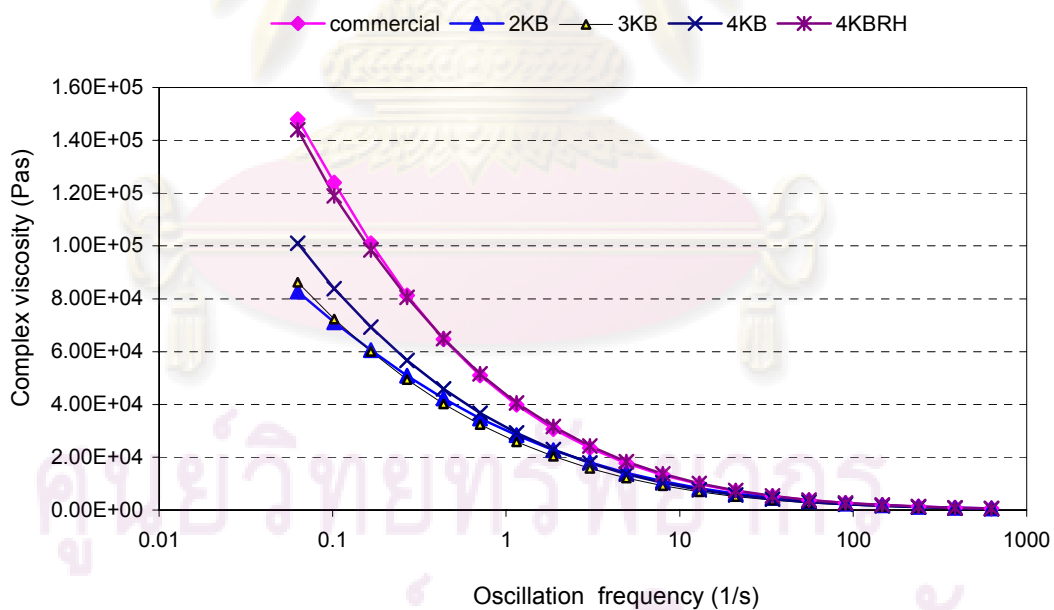


Figure 4.26 Complex viscosity versus oscillation frequency at various screw configurations. Extrusion with constant 8 kg/h feed rate, 200°C barrel temperature and 200 rpm screw speed.

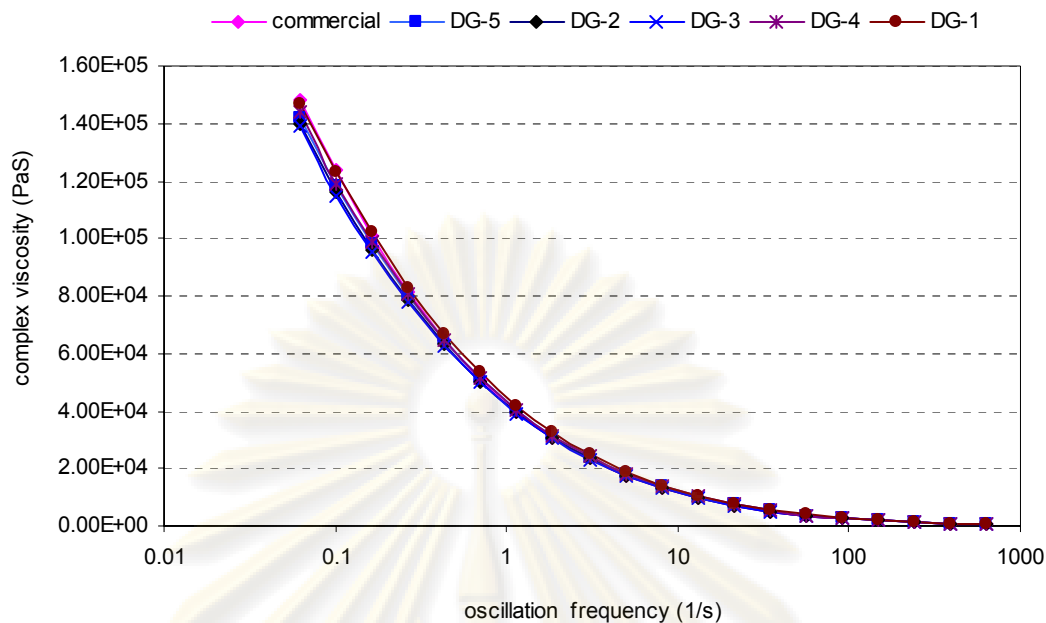


Figure 4.27 Complex viscosity versus oscillation frequency of HDPE compounded with additional of additive. Extrusion with constant 8 kg/h feed rate, 200°C barrel temperature, 200 rpm screw speed. (commercial: plant sample with commercial recipe, DG-1: plus 0.15 phr Irganox 1010, DG-2: plus 0.25 phr Irganox 1010, DG-3: 0.15 phr Irgafos 168, DG-4 : 0.15 phr Tinuvin<sup>®</sup> 622, DG-5 : 0.25 phr Tinuvin<sup>®</sup> 622.

#### 4.7 Melt flow index (MFI) and viscosity number (VN)

As shown in Table 4.5, the viscosity number of HDPE compound was not significant different due to better homogeneity of the compound components. It was also found that the optimized screw configuration of extrusion was 4KBRH. The viscosity number of the compound close to powder with lower melt flow index at this extrusion condition.

Figure 4.28 shows the significant effect of barrel temperature on %WSA and viscosity number. At 140°C barrel temperature, viscosity number leveled off ca. 405 cm<sup>3</sup>/g, thus low barrel temperature caused mechanical shear of bimodal HDPE lead to chain branching higher viscosity than the neat powder. Above 180°C barrel temperature, the viscosity number and melt flow indexer do not substantially change with increasing barrel temperature. It can be explained that optimized extrusion

condition for 4 KBRH screw configuration resulted in the balance of HDPE compound properties as well.

Table 4.6 Effect of various screw configuration on melt flow index and viscosity number of HDPE compounded at 200 rpm screw speed and 8 kg/h feed rate

Sample	Viscosity Number ( $\text{cm}^3/\text{g}$ )	MFR ( $190^\circ\text{C}/5\text{ kg}$ )
2KB	320	0.23
3KB	333	0.21
4KB	340	0.17
4KBRH	368	0.14
Powder	370	0.4

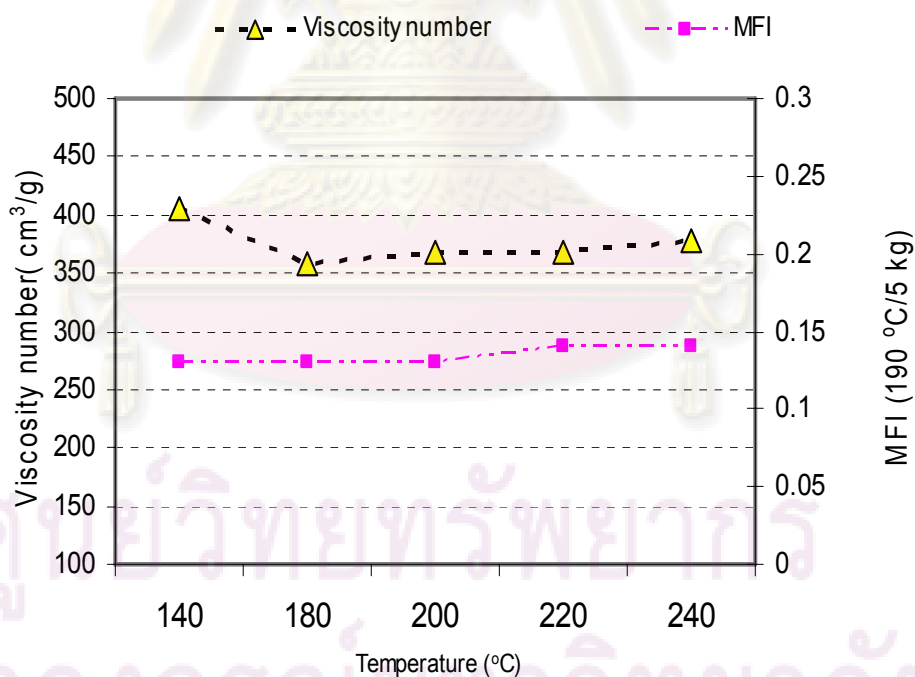


Figure 4.28 Viscosity number and MFI ( $190^\circ\text{C}/5\text{ kg}$ ) of HDPE compounded versus barrel temperature. Extrusion with 4 KBRH screw configuration at 8 kg/h feed rate,  $200^\circ\text{C}$  barrel temperature and 200 rpm screw speed.

As the effect of extrusion condition were investigated, the effect results of various extrusion conditions are summarized in Table 4.7.

Table 4.7 Summary of extrusion conditions affecting the physical properties of HDPE compound

Extrusion parameter	$\chi_c$ (%)	OIT	Impact energy	FNCT	(%) WSA	Carbon black dispersion	Complex viscosity	MFI	C.I.	VN
Feed rate ↑	0	0	-	-	++	++	-	+	0	0
Barrel temperature ↑	-	-	-	-	-	-	-	+	+	-
Screw speed ↑	0	-	0	0	0	0	0	0	-	0
*Kneading block ↑	+	+	+	+	-	--	+	-	0	0
Additive ↑	0	+	+	+	0	0	+	0	-	0
Feed rate ↓	+	-	+	+	-	-	+	-	+	0
Barrel temperature ↓	0	-	+	+	0	0	+	-	+	0
Screw speed ↓	0	-	0	0	0	0	0	-	+	0
*Kneading block ↓	0	0	-	-	+	+	-	+	0	-
Additive ↓	0	-	-	-	0	0	-	+	+	-

Remark: (+) positive effect, (-) negative, (0) not significant effect and \* (2KB -4KBRH)

Table 4.7 shows that the main important factor is the number of the kneading block resulting in better homogenization of the compound. The decrease in feed rate caused the higher impact resistance and FNCT failure time of HDPE compound because of good homogenization. The high barrel temperature lowered the final properties of the HDPE compound because of thermal degradation.

#### 4.8 PE Pipe from HDPE compounded at optimized extrusion conditions

##### 4.8.1 Hydrostatic pressure testing

Quality control testing according to ISO 4427:2007 of PE pipe grade, the hydrostatic pressure testing was performed according to ISO 1167: 2006. At 20 and 80°C water was pressurized on the inside and on the outside of the pipe specimens. The accuracy for the temperature and pressure are  $\pm 1^\circ\text{C}$  and  $+2/-1\%$ , respectively. The measurements of the wall thickness are accurate within  $\pm 0.1$  mm. The pipes were

fitted with commercial brass fittings, type A. From Table 4.8, the results show that all pipe from optimized compounded can be passed the PE 100 classification requirement. At 20°C temperature the hoop stress of 12.4 MPa, shortest failure time was greater than 200 h for 100 h test time.

Table 4.8 Summary of test results (Hoop stress)

Temperature (°C)	No of pipes	Hoop stress MPa	Shortest failure time	Required test time
20	3	12.4	Ductile >200 h	100 h
80	3	5.4	Ductile > 500 h	165 h
80	3	5.0	Ductile >1000 h	1000 h

#### 4.8.2 Rapid crack propagation – critical pressure

An evaluation of the critical pressure for rapid crack propagation was performed according to ISO 13477 of the PE pipe grade. Three pipe specimens of the PE pipe grade were tested according to the Small –Scale –Steady-State (S4 test), ISO 13477. The testing was performed at 0°C and different internal pressures.

The pipes were cut into lengths of 840 mm. The pipes were conditioned for at least 16 h at  $-1 \pm 1^\circ\text{C}$  in air. The internal and external medium was air during test. The testing followed ISO 13477:1997. The highest pressure where crack arrest was obtained was at 12 bars which is the highest pressure level of the testing equipment. Therefore, the PE pipe has a critical pressure  $p_{c,S4}$  at 0°C of  $\geq 12$  bar.

Table 4.9 Summary of test results (RCP)

Material	Dimension	Critical pressure $p_{c,S4}$ at 0°C
HDPE pipe	110 mm (SDR 11)	$\geq 12$ bar

For the PE 100 classification, the critical pressure  $p_{c,S4}$  at 0°C is  $\geq 12$  bar. From Table 4.9, HDPE pipe from HDPE optimized compound passed the PE 100 classification for RCP evaluation.

#### 4.8.3 Slow crack growth by FNCT test

A notch specimen testing program was also performed. Three specimens were notched and tested. The testing conditions were at 80°C of ethylene glycol. From Table 4.9, HDPE pipe from HDPE optimized compound passed the PE 100 classification for SCG evaluation.

Table 4.10 Summary of test results (SCG)

Material	Minimum failure time (h)	Shortest failure Time (h)
HDPE pipe	> 1000	Ductile >4,800

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## CHAPTER V

### CONCLUSIONS AND SUGGESTIONS

#### 5.1 Conclusions

1. The screw configurations of a twin-screw co-rotating extruder are decisive for successful homogenization of a bimodal high density polyethylene compound having pressure rate at 10MPa (PE100 pipe classification). High quality compounds possessing balanced properties between slow crack growth (SCG) resistance and impact resistance at the sustained pressure rate could be achieved by using extruder 4KBRH screw configuration together with other optimized conditions (white spot area less than 1%, failure time test of FNCT more than 1,000 hours and impact resistance more than 16 mJ/mm<sup>2</sup>).

2. Sample feeding rate to the extruder has a significant effect on distribution of the high molecular weight fraction (white spot area or gels) in the HDPE matrix and homogeneity of the compound as a whole. Increasing feed rate led to increase white spot area, hence deteriorates physical properties of the high pressure HDPE pipes such as impact resistance, surface appearance and pressure rating as well.

3. The optimum barrel temperature for extruding HDPE (Ziegler–Natta catalyst system) was 200°C barrel temperature, at which the high total crystallinity, long OIT (more than 100 minutes) and good balance between SCG and impact resistance properties were observed.

4. The barrel temperatures above 220°C promoted the material degradation resulting in the low dispersion and homogeneity.

5. The sufficient dispersion and homogeneity allowed the compounding with minimum level of stabilizers while the mechanical properties and stability of the materials were maintained.

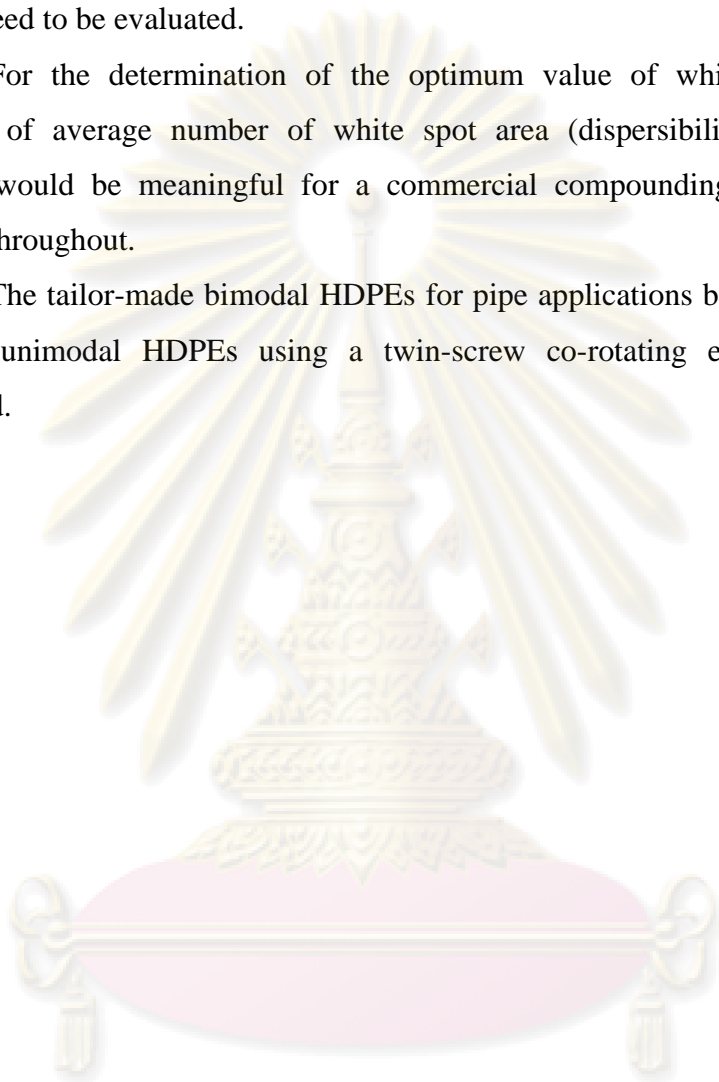
6. Rheological study revealed that the compound made under optimized conditions had good processability as the commercial PE100 pipe grade.

## 5.2 Suggestions for further work

1. The pipes for different applications can be visually distinguished by colors, thus, the effects of pigments used for this purpose on the physical properties of pipe materials need to be evaluated.

2. For the determination of the optimum value of white spot area, the percentage of average number of white spot area (dispersibility) and the final properties would be meaningful for a commercial compounding process, with a maximum throughput.

3. The tailor-made bimodal HDPEs for pipe applications by blending several grades of unimodal HDPEs using a twin-screw co-rotating extruder could be investigated.



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**APPENDIX**

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## APPENDIX

Table A1. High molecular weight fraction (% WSA) of HDPE compound

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	(% WSA)
1	4KBR	140	200	8	0.65
2	4KBR	180	200	8	0.56
3	4KBR	200	200	8	0.85
4	4KBR	220	200	8	0.90
5	4KBR	240	200	8	0.75
6	4KBR	200	200	4	0.30
7	4KBR	200	200	8	0.50
8	4KBR	200	200	12	0.90
9	2KB	200	200	8	4.3
10	3KB	200	200	8	3.3
11	4 KB	200	200	8	2.5
12	4KBR	200	200	8	0.90
13	4KBR	200	100	8	0.56
14	4KBR	200	200	8	0.67
15	4KBR	200	300	8	0.89
16 <sup>1</sup>	4 KBR	200	200	8	0.78
17 <sup>2</sup>	4KBR	200	200	8	0.85
18 <sup>3</sup>	4KBR	200	200	8	0.90

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Table A2. Carbon black ranging of HDPE compound

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Carbon black dispersion
1	4KBR	140	200	8	1.8
2	4KBR	180	200	8	2.1
3	4KBR	200	200	8	1.8
4	4KBR	220	200	8	1.8
5	4KBR	240	200	8	1.8
6	4KBR	200	200	4	1.9
7	4KBR	200	200	8	1.8
8	4KBR	200	200	12	1.8
9	2KB	200	200	8	4.2
10	3KB	200	200	8	3.8
11	4 KB	200	200	8	3.2
12	4KBR	200	200	8	1.8
13	4KBR	200	100	8	1.9
14	4KBR	200	200	8	1.7
15	4KBR	200	300	8	1.8
16 <sup>1</sup>	4 KBR	200	200	8	1.8
17 <sup>2</sup>	4KBR	200	200	8	1.8
18 <sup>3</sup>	4KBR	200	200	8	1.8

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Table A3. MFR of HDPE compounds

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	MFI 190°C/5 kg	MFI 190°C/21.6 kg	MFR
1	4KBR	140	200	8	0.12	3.4	28.3
2	4KBR	180	200	8	0.11	3.1	28.1
3	4KBR	200	200	8	0.13	4.0	30.8
4	4KBR	220	200	8	0.13	4.0	30.8
5	4KBR	240	200	8	0.13	3.9	30
6	4KBR	200	200	4	0.13	3.9	30.0
7	4KBR	200	200	8	0.13	4.0	30.8
8	4KBR	200	200	12	0.14	4.6	32.9
9	2KB	200	200	8	0.26	7.7	33.6
10	3KB	200	200	8	0.24	6.3	26.9
11	4 KB	200	200	8	0.22	5.7	27.2
12	4KBR	200	200	8	0.13	4.0	30.8
13	4KBR	200	100	8	0.11	3.1	28.2
15	4KBR	200	300	8	0.15	4.7	31.3
16 <sup>1</sup>	4 KBR	200	200	8	0.13	3.9	30
17 <sup>2</sup>	4KBR	200	200	8	0.13	3.9	30
18 <sup>3</sup>	4KBR	200	200	8	0.13	3.9	30

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Table A4. Rheological properties of HDPE compound at various extrusion conditions by Cone & Plate rheometer

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Low shear viscosity	High shear viscosity	SHI
1	4KBR	140	200	8	155,000	665	233.0
2	4KBR	180	200	8	144000	619	232.6
3	4KBR	200	200	8	146000	633	230.6
4	4KBR	220	200	8	152000	648	234.6
5	4KBR	240	200	8	147000	641	229.3
6	4KBR	200	200	4	151000	650	232.3
7	4KBR	200	200	8	146000	633	230.6
8	4KBR	200	200	12	136000	642	211.8
9	2KB	200	200	8	82700	640	129.2
10	3KB	200	200	8	86200	478	180.3
11	4 KB	200	200	8	101000	534	189.1
12	4KBR	200	200	8	146000	633	230.6
13	4KBR	200	100	8	156000	647	241.1
14	4KBR	200	200	8	146000	633	230.6
15	4KBR	200	300	8	136000	634	214.5
16 <sup>1</sup>	4 KBR	200	200	8	151000	650	232.3
17 <sup>2</sup>	4KBR	200	200	8	145000	623	232.7
18 <sup>3</sup>	4KBR	200	200	8	147000	636	231.1

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Table A5. Rheological properties of HDPE compound at various extrusion conditions by Capillary Rheometer

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Shear viscosity (Pas)
					at 20 s <sup>-1</sup> / 40 s <sup>-1</sup> / 60 s <sup>-1</sup> / 80 s <sup>-1</sup> / 100 s <sup>-1</sup> / 200 s <sup>-1</sup> / 300 s <sup>-1</sup> / 400 s <sup>-1</sup>
1	4KBR	140	200	8	7117 / 3606 / 2400 / 2205 / 1859 / 1059 / 629 / 461
2	4KBR	180	200	8	6585 / 4091 / 3023 / 2482 / 2128 / 831 / 582 / 463
3	4KBR	200	200	8	6742 / 4157 / 3061 / 2500 / 2131 / 928 / 596 / 479
4	4KBR	220	200	8	6831 / 4166 / 3060 / 2497 / 2133 / 899 / 592 / 470
5	4KBR	240	200	8	5606 / 3520 / 2662 / 2172 / 1831 / 1134 / 843 / 583
6	4KBR	200	200	4	7008 / 4206 / 3049 / 2482 / 2116 / 919 / 572 / 458
7	4KBR	200	200	8	6711 / 4145 / 3061 / 2515 / 2146 / 1139 / 579 / 461
8	4KBR	200	200	12	6314 / 3831 / 2845 / 2279 / 1939 / 1167 / 697 / 504
9	2KB	200	200	8	5440 / 3723 / 2566 / 2087 / 1737 / 1038 / 567 / 486
10	3KB	200	200	8	5620 / 4235 / 3072 / 2615 / 2347 / 1210 / 590 / 482

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Shear viscosity (Pas)
					at 20 s <sup>-1</sup> / 40 s <sup>-1</sup> / 60 s <sup>-1</sup> / 80 s <sup>-1</sup> / 100 s <sup>-1</sup> / 200 s <sup>-1</sup> / 300 s <sup>-1</sup> / 400 s <sup>-1</sup>
11	4 KB	200	200	8	5934 / 4109 / 2793 / 2415 / 1884 / 1117 / 587 / 487
12	4KBR	200	200	8	6742 / 4157 / 3061 / 2500 / 2131 / 928 / 596 / 479
13	4KBR	200	100	8	7215 / 3715 / 2480 / 2210 / 1870 / 1070 / 680 / 510
14	4KBR	200	200	8	6334 / 4380 / 2914 / 2187 / 1949 / 970 / 678 / 508
15	4KBR	200	300	8	6070 / 4109 / 2766 / 2154 / 1832 / 900 / 687 / 512
16 <sup>1</sup>	4 KBR	200	200	8	6758 / 4065 / 2953 / 2386 / 2010 / 923 / 737 / 494
17 <sup>2</sup>	4KBR	200	200	8	6353 / 4338 / 2897 / 2315 / 1951 / 927 / 754 / 505
18 <sup>3</sup>	4KBR	200	200	8	6372 / 4357 / 2892 / 2298 / 1952 / 863 / 748 / 507

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Table A6. Viscosity number of HDPE compound at various extrusion conditions

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Viscosity number (cm <sup>3</sup> /g)
1	4KBR	140	200	8	381
2	4KBR	180	200	8	375
3	4KBR	200	200	8	377
4	4KBR	220	200	8	368
5	4KBR	240	200	8	370
6	4KBR	200	200	4	372
7	4KBR	200	200	8	366
8	4KBR	200	200	12	379
9	2KB	200	200	8	329
10	3KB	200	200	8	333
11	4 KB	200	200	8	334
12	4KBR	200	200	8	377
13	4KBR	200	100	8	397
14	4KBR	200	200	8	365
15	4KBR	200	300	8	358
16 <sup>1</sup>	4 KBR	200	200	8	373
17 <sup>2</sup>	4KBR	200	200	8	440
18 <sup>3</sup>	4KBR	200	200	8	370

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Table A8. Molecular weight of HDPE compound

Sample	Screw configuration	Barrel temperature (°C)	Screw speed (rpm)	Feed rate (kg/h)	Molecular weight			
					Mn	Mw	Mz	MWD
1	4KBR	140	200	8	9,600	255,200	1,405,700	26.6
2	4KBR	180	200	8	10,900	224,600	1,133,200	20.6
3	4KBR	200	200	8	12,400	309,800	1,713,500	25.0
4	4KBR	220	200	8	10,600	277,600	1,394,300	26.2
5	4KBR	240	200	8	14,500	303,800	1,455,000	21.8
6	4KBR	200	200	4	13,400	325,400	1,715,000	24.3
7	4KBR	200	200	8	11,500	220,000	1,403,000	19.1
8	4KBR	200	200	12	8,900	196000	1,470,000	22.0
9	2KB	200	200	8	11,900	216,300	979,000	18.2
10	3KB	200	200	8	13,000	248,200	1,064,000	19.1
11	4 KB	200	200	8	14,200	222,000	1,170,000	15.6
12	4KBR	200	200	8	12,400	309,000	1,713,500	24.9
13	4KBR	200	100	8	11,500	333,000	1,823,000	29.0
14	4KBR	200	200	8	12,400	309,000	1,713,500	24.9
15	4KBR	200	300	8	12,100	324,000	1,570,000	26.9
16 <sup>1</sup>	4 KBR	200	200	8	15,400	325,000	1,742,000	21.1
17 <sup>2</sup>	4KBR	200	200	8	13,400	303,000	1,872,000	22.6
18 <sup>3</sup>	4KBR	200	200	8	14,100	298000	1,624,000	21.1

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**Extruder Data****Configuration**

Diameter of screw:	26mm L: D = 40: 1
Mode of operation:	Screw co-rotating
Screw operation speed:	0-800 rpm
Screw configuration:	Refer to the enclosed drawing of screw/barrel
Motor power:	11.0 KW
Heater power:	500 W per cartridge
Maximum barrel temperature:	400°C
Minimum water pressure:	2 bars
Water flow rate:	20 liters per minute at 2 bars

Table A8. The screw configuration for normal polyolefin of the twin screw co-rotation extruder

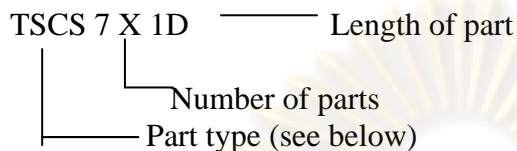
Labtech twin screw 2x26 L = 40D			
Screw configurations : Configuration for normal polyolefin			
Screw parts	Offset angle	Length (D)	Sum of D
TSCS 13x1D		13	13
IKD 1x 0.25 D	0	0.25	13.25
IKD 12x 0.25 D	30	3	16.25
TSCS 4x 1D		4	20.25
IKD 1x 0.25D	0	0.25	20.5
IKD 4x 0.25D	60	1	21.5
TSCS 2x 1D		2	23.5
IKD 1x 0.25D	0	0.25	23.75
IKD 7x 0.25D	60	1.75	25.5
TSCS 3x 1D		3	28.5
IKD 1x 0.25D	0	0.25	28.75
IKD 5x 0.25D	60	1.25	30
IKD 4x 0.25D	90	1	31
TSCS 7x 1D		7	38
TSCS 1x 0.5D		0.5	38.5
SSMS 1x1.5D		1.5	40

Vent: To atmosphere at 26D

: To vacuum at 34D

D = diameter

Coding for screw parts:



TSCS = Twin –start conveying screw

TSCS (R) = Twin –start conveying screw reverse angle

IKD = Individual kneading disc.

IKD (R) = Individual kneading disc, reverse offset angle.

SSMS = Single-start metering screw

Table A9. The screw configuration (Invention configuration) of twin screw co-rotation extruder

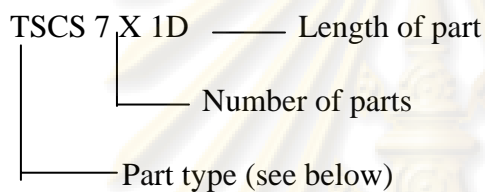
Labtech twin screw 2x26 L = 40D			
Screw configurations : invention 1 configuration			
Screw parts	Offset angle	Length (D)	Sum of D
TSCS 13x1D	-	13	13
IKD 1x 0.25 D	0	0.25	13.25
IKD 12x 0.25 D	60	2.5	15.75
TSCS (R) 1x 0.5 D	-	0.5	16.25
TSCS 4x 1D	-	4	20.25
IKD 1x 0.25D	0	0.25	20.5
IKD 4x 0.25D	60	1	21.5
TSCS 2x 1D	-	2	23.5
IKD 1x 0.25D	0	0.25	23.75
IKD 5x 0.25D	60	1.25	25.0
IKD 8x 0.25D	90	2	27
IKD 7x 0.25D	60	1.75	25.5
TSCS 1x 1D	-	1.0	28.5
IKD 1x 0.25D	0	0.25	28.75
IKD 5x 0.25D	60	1.25	30
IKD 4x 0.25D	90	1	31

Labtech twin screw 2x26 L = 40D			
Screw configurations : invention 1 configuration			
Screw parts	Offset angle	Length (D)	Sum of D
TSCS 7x 1D	-	7	38
TSCS 1x 0.5D	-	0.5	38.5
SSMS 1x1.5D	-	1.5	40

Vent : To atmosphere at 26D  
: To vacuum at 34D

D = diameter

Coding for screw parts:



- TSCS        = Twin-start conveying screw  
TSCS (R)   = Twin-start conveying screw reverse angle  
IKD         = Individual kneading disc.  
IKD (R)    = Individual kneading disc, reverse offset angle.  
SSMS       = Single-start metering screw

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## VITA

Mr. Arkom Paso was born on November 2, 1972 in Roi-Et province. He graduated with a bachelor degree of Science (Chemistry) from Khon Kaen University in 1993. Since then he has joined Charoen Pokphan Food Public Co. Ltd. as a chemist for 2 years. And then he joined the Research and Development Department, IRPC Public Co., Ltd. in 1998, he was accepted as graduate student in the program for M.Sc. in Petrochemistry and Polymer Science, Chulalongkorn University. He received a Master's degree of Science in 2008.

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