สมบัติและความสามารถในการนำกลับมาใช้ใหม่ของลังพอลิเอทิลีนชนิดความหนาแน่นสูง สำหรับขนส่งขวดน้ำอัดลมที่ผ่านการใช้งานมาแล้ว

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PROPERTIES AND RECYCLABILITY OF USED HIGH DENSITY POLYETHYLENE CRATES FOR SOFT DRINK BOTTLE TRANSPORTATION

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ศุภชัย งามศิลปเสถียร : สมบัติและความสามารถในการนำกลับมาใช้ใหม่ของลังพอลิเอทิลีนชนิดความหนาแน่นสูงสำหรับขนส่งขวดน้ำอัดลมที่ผ่านการใช้งานมาแล้ว (PROPERTIES AND RECYCLABILITY OF USED HIGH DENSITY POLYETHYLENE CRATES FOR SOFT DRINK BOTTLE TRANSPORTATION). อ. ที่ปรึกษา : ผศ.ดร.ศิริพร ดำรงค์ศักดิ์กุล, 160 หน้า. ISBN 974-13-0173-1

งานวิจัยนี้มุ่งเน้นที่จะศึกษาความเป็นไปได้ในการนำขยะพลาสติกที่เกิดจากลังพลาสติกชนิดพอลิเอทิลีนชนิดความหนาแน่นสูง (HDPE) สำหรับขนส่งขวดน้ำอัดลมที่ผ่านการใช้งานมาแล้วกลับมาใช้ใหม่ โดยใช้ลังพลาสติกที่ผลิตภายใต้กระบวนการผลิตเดียวกันแต่มีอายุการใช้งานต่างกันกล่าว คือ 8 ปี, 3 ปี และลังที่ยังไม่ผ่านการใช้งาน จากการศึกษาสมบัติทางกลและทางกายภาพ, ความสามารถในการขึ้นรูป และการเสื่อมสภาพของพอลิเมอร์อย่างเป็นระบบ พบว่าดัชนีการไหล, เปอร์เซ็นต์การยืดตัวที่จุดแตกหัก, การทนต่อแรงกด และการทนต่อแรงกระแทกของลัง HDPE มีค่าลดลง เมื่ออายุการใช้งานเพิ่มขึ้น โดยการเปลี่ยนแปลงดังกล่าวเกิดจากการเสื่อมสภาพจากแสงที่เกิดขึ้นในระหว่างการใช้งานซึ่งส่งผลต่อการเปลี่ยนแปลงโครงสร้างของพอลิเมอร์ สมบัติด้อยของลัง HDPE ที่หมดอายุการใช้งานแล้วสามารถถูกปรับปรุงให้ดีขึ้นได้โดยการผสมกับสารเพิ่มความเสถียร “Recyclossorb 550” (R550) และเอทิลีนไวนิลอะซิเตดโคโพลิเมอร์ (EVA) โดยพบว่าการเติม EVA (ที่อัตราส่วนการผสมโดยน้ำหนักเท่ากับ 5% และ 15%) มีประสิทธิภาพในการปรับปรุงสมบัติของลังที่หมดอายุการใช้งานได้ดีกว่า R550 (ที่อัตราส่วนการผสมโดยน้ำหนักเท่ากับ 0.2% และ 0.4%) โดยเฉพาะอย่างยิ่งการเติม EVA จะช่วยในการปรับปรุงเปอร์เซ็นต์การยืดตัวที่จุดแตกหัก, และการทนแรงกระแทกได้อย่างดียิ่ง นอกจากนั้นพอลิเมอร์ผสมของลัง HDPE ที่หมดอายุการใช้งานแล้วกับสารปรับสภาพ (R550 และ EVA) สามารถนำมาทำการขึ้นรูปเป็นฝาครอบถังเบียร์โดยกระบวนการฉีด ฝาครอบที่ผลิตได้ผ่านการตรวจสอบพบว่ามีมาตรฐานตามความต้องการใช้งานของลูกค้า

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต...
สาขาวิชา วิศวกรรมเคมี ลายมือชื่ออาจารย์ที่ปรึกษา......................................
ปีการศึกษา 2543 ลายมือชื่ออาจารย์ที่ปรึกษาร่วม.............................

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KEY WORD: RECYCLING / HIGH DENSITY POLYETHYLENE / CRATES / MODIFYING AGENTS / ETHYLENE VINYL ACETATE / STABILIZER / RECYCLOSSORB 550

SUPACHAI NGAMSINLAPASATHIAN : PROPERTIES AND RECYCLABILITY OF USED HIGH DENSITY POLYETHYLENE CRATES FOR SOFT DRINK BOTTLE TRANSPORTATION. THESIS ADVISOR : ASSISTANT PROFESSOR SIRIPORN DAMRONGSAKKUL, Ph.D., 160 pp. ISBN 974-13-0173-1.

The aim of this research is to study the possibility in recycling plastic wastes of high density polyethylene (HDPE) crates used for soft-drink bottle transportation. The raw materials are HDPE crates produced under the same condition, which has been used for bottle transportation for 8, 3 and 0 years, respectively. The properties of plastic crates including the mechanical and physical properties, the processability and the degradation of polymer were studied systematically. It was found that the melt flow index, %elongation at break, flexural strength at yield and impact resistance were decreased with increasing utilization time. This could be a result from the photo-oxidative degradation occurred, leading to changes in the structure of polymer molecules. The poor properties of post-used HDPE crates can be improved by blending with two types of modifying agents, stabilizer “Recyclossorb 550” (R550) and ethylene vinyl acetate copolymer (EVA). The addition of EVA (5% and 15% by weight) in post-used HDPE crates has stronger property improvement than that of R550 (0.2% and 0.4% by weight) in post-used HDPE crates. The blends of post-used HDPE crates with EVA showed a remarkable increase in %elongation at break and impact resistance. Furthermore, the blends of post-used HDPE crates with modifying agents had been recycled to produce caps for beer keg by injection process. These products were inspected and shown to satisfy the customer requirement standard.

Department	Chemical Engineering	Student’s signature..
Field of study	Chemical Engineering	Advisor’s signature...
Academic year	2000	Co-advisor’s signature....................................

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Finally, the author wishes to convey his deep appreciation to his family.

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CHAPTER I

INTRODUCTION

1.1 Introduction

High density polyethylene (HDPE) is a commodity plastic, which is used to produce a wide range of plastic containers used in daily life. This is due to the advantage properties of HDPE in high impact strength, toughness, good chemical resistance, excellent moisture and water resistance, and recyclability. Plastics crates used for bottle transportation is one of the major products manufactured from HDPE. Because of the popularity in soft-drink consumption, the growth of soft drink industries in Thailand has been increased continuously. The average demand of plastic crates is around 200,000 – 300,000 containers per year (or 300 – 450 ton per year). The average lifetime of plastic crates is about eight years. As a result, a huge amount of waste from plastic crates has been generated that should be handled properly in order not to cause any environmental pollution. One method used to reduce plastic waste is a recycling, which is of high interest nowadays.

At present, the company that manufactures plastic crates has to collect all used plastic crates returned from their customers. The used plastic crates have been randomly used to mix with virgin grade of HDPE and process to be new recycled plastic crates. However, the quality of recycled plastic crates is down and problems on color property and strength are always faced. This work, therefore, aims to study the possibility in recycling plastic wastes of HDPE crates used for soft drink bottle transportation. The properties of plastic crates including the mechanical and physical properties, the processability and the degradation of polymers were studied systematically. The raw materials are the HDPE crates, produced under the same condition, which have been used for bottle transportation for 8, 3 and 0 years ,respectively. In addition, the post-used HDPE crates were blended with two types of modifying agents, stabilizer “Recyclossorb 550” and ethylene vinyl acetate copolymer (EVA), in an attempt to improve properties of post-used HDPE crates for recycling purpose. After that, blends of post-used HDPE crates were taken to process by injection molding to produce caps for beer keg. Other applications for the waste of post-used HDPE crates have also been suggested.

1.2 Objectives

1.2.1 To study the mechanical properties, processability and polymer degradation of HDPE crates at various utilization time.

1.2.2 To improve properties of post-used HDPE crates for recycling purpose by the methods of polymer blending.

1.2.3 To produce new products from the blends of post-used HDPE crates with modifying agents.

1.3 Scope of work

1.3.1 To study the properties of new HDPE crates and HDPE crates at the utilization time of 8 years, 3 years, including virgin HDPE granule. The study will be focused on the effects of the utilization time of HDPE crates on the properties of HDPE, which can be divided into 3 groups.

a) The characteristics and the degradation of the polymer, e.g. molecular weight, molecular weight distribution, melting temperature, degree of crystallinity and density.

b) The processability of the polymer, e.g. melt flow index and viscosity.

c) The mechanical properties of the polymer, e.g. tensile properties, flexural properties, impact resistance and Rockwell hardness.

1.3.2 To improve the poor properties of post-used HDPE crates by polymer blending with two modifying agents, stabilizer “Recyclossorb 550” and EVA. The effects of each modifying agent on the processability and the mechanical properties of blended post-used HDPE crates will be investigated and discussed. The influence of both modifying agents will be compared.

1.3.3 The blends of post-used HDPE crates will be tested for manufacturing a practical product which is, in this case, a cap for beer keg by injection process. The products are inspected according to the customer requirement standard. In addition, other applications for the waste of post-used HDPE crates will be suggested.

CHAPTER II

THEORY

2.1 High density polyethylene

High density polyethylene (HDPE) is a thermoplastic polyolefin synthesized from the polymerization of ethylene monomer. The density of HDPE is in the range of 0.94 – 0.96 g/cm^3. The polymerization process is performed at low reaction pressure and temperature by using Zeigler-type or Phillips-type catalysts.

HDPE is a semi-crystalline polymer at about eighty degree of crystallinity. Semi-crystalline polymers have amorphous regions connecting among crystalline regions. The crystalline part plays an important role in the structural strength of polymers. Decreasing in crystallinity results in lowering the stiffness and yield stress of crystalline polymers. The amorphous part normally exhibits rubbery or glassy state depending on the glass transition temperature. For HDPE, the glass transition temperature is –110 ^{0}C and the melting temperature is 135 ^{0}C [Daniels, 1989]. The combination of amorphous and crystalline structures in HDPE gives it high toughness at room temperature, which tends to decrease at low temperature. At well below the glass transition temperature, HDPE behaves more like glassy material that is rather brittle.

The growth and size of crystals in crystalline region greatly depend on the cooling rate. Quenching of HDPE can lead to a material with only 50% degree of crystallinity. In contrast, slow cooling or annealing HDPE at a suitable temperature can produce material with higher degree of crystallinity [Zahavich *et al*., 1997].

HDPE is used for many applications because it provides excellent moisture barrier properties, good chemical resistance, good stiffness and recyclability. Applications for HDPE are summarized in Table 2.1, classified by the processing technique [Edenbaum, 1996].

Table 2.1 Applications for HDPE with various processing techniques [Edenbaum, 1996].

Processing Technique	Products
Extrusion	● Pipe and tubing ● Wire and cable ● Film and sheet
Blow molding	● Fuel tanks ● Containers for industrial chemicals; milk, water, and juices; household chemicals; agricultural chemicals
Injection molding	● Tote boxes, buckets, beverage crates, housewares, toys, pallets, containers
Rotational molding	● Large hollow containers (e.g., gas tanks), toys

In Table 2.2, the disposition of eight commodity plastics in 1990 has been shown [Bisio and Xanthos, 1994]. It can be seen that the total production of HDPE in 1990 is 7,793 million pounds but only 134 million ponds of HDPE waste (1.7%) has been recycled. This amount is very small comparing to other methods used to manage HDPE waste; for example landfill (71.6%) and incineration (12.6%). Plastic waste recycling offers a significant opportunity to reduce the amount of plastic waste and conserves the environment. It can also eliminate the problems of landfill crisis and air pollution from incineration.

Table 2.2 Disposition of eight commodity plastics in 1990[a] [Bisio and Xanthos, 1994].

	Millions of pounds					
	Total[b] production	Fabrication[c] Losses	Addition to[d] inventory	Recycled[e]	Incinerated	Landfilled[f]
LDPE film	6,507	65	0	19	963	5,459
LDPE non-film	4,289	43	920	1	499	2,826
PVC	8,136	81	6,091	5	294	1,665
HDPE	7,793	78	1,014	134	985	5,582
PP	6,592	66	1,173	67	793	4,493
PS	4,941	49	607	13	641	3,631
PU	3,265	33	1,565	6	249	1,413
Thermoplastic Polyester	2,069	21	113	233	255	1,448
ABS	1,014	10	370	4	94	535
Totals	44,606	446	11,853	482	4,773	27,052

[a] The development of this table is documented in Volume 2., Appendix I of the ODE Report.

[b] From January 1992 issue of Modern Plastics, a McGraw-Hill publication.

[c] The disposition of fabrication losses is uncertain; however, they are often sold to a reprocessor.

[d] A significant fraction of the plastics produced in 1990 were used in applications that have a life greater than 1 year (see Table 2-4) or have been abandoned in place; often the final disposition of these objects is not clear. Unfortunately, all errors in the numbers are cumulated in this column.

[e] Plastics actually returned to the market as products made from recycled resins.

[f] Plastics are landfilled in both municipal and industrial (private) landfills.

2.2 Recycling of plastics

A huge amount of plastic waste generated in residential, commercial and industrial sectors has become a serious problem for environment because of the non-biodegradable characteristic of plastics. Recycling of plastic waste can relieve this problem. The advantage of plastic recycling are energy saving, reduction in disposal costs and resource conservation. However, management procedures for plastic waste recycling are not straightforward and could be costly in some cases so that recycled plastics can not well complete with virgin plastics. In addition, the properties of recycled plastics might be poor and the application for recycled plastics is still limited.

Plastic recycling can be classified into four categories; primary recycling, secondary recycling, tertiary recycling and quaternary recycling. The classification is based on ASTM D5033–90.

- Primary recycling

  Primary recycling is the recycling of scrap plastics by standard processing methods into products having performance characteristics equivalent to the original products made of virgin plastics.

- Secondary recycling

  Secondary recycling is the recycling of scrap or waste plastics by one or a combination of process operations into products having less demanding performance requirements than the original products.

- Tertiary recycling

  Tertiary recycling is the recycling process of producing chemicals, monomers and fuel from scrap or waste plastics by depolymerization reactions.

- Quaternary recycling

  Quaternary recycling is the recycling process of recovering energy from scrap or waste plastics by incineration.

2.2.1 Plastic recycling technologies

Generally, the basic procedures of plastic recycling are composed of five steps; collection, shredding, cleaning, separations and regranulation. This refers only to polymers recovered from products and parts in waste streams. Scrap polymers that are recovered and reused during production processes are excluded.

2.2.1.1 Collection

Most plastics can be recycled but a proper collection method is needed in order to make recycling easy. There are several alternative methods of collection for discarded plastic objects such as drop-offs, deposit return and curbside collection. Main problem for plastic recycling is mixed plastic waste since various types of plastics melt at different temperatures. If a plastic melting at a high temperature is mixed with another plastic that melts at a lower temperature, the appearance and properties of recycled material is altered so that the reprocessing ability would be poor or impossible. A collection method can be used for preliminary sorting plastic wastes, for example, plastic objects can be source separated by both households and commercial groups. The international code system for recycling, provided by the Society of the Plastic Industry Inc. (SPI), is widely used to identify different types of plastics. The code is a three-sided triangular arrow with a number in the center and letters underneath. This code is intended for molding into or imprinting on plastic product. Details of code numbers are as follows:

1. Polyethylene terephthalate (PET)

Polyethylene terephthalate has good barrier properties, clarity and toughness. The main applications for PET are in food packaging, carbonated beverages and noncarbonated beverages.

2. High density polyethylene (HDPE)

High density polyethylene is used for many packing applications because it provides good stiffness, excellent moisture barrier properties and excellent chemical resistance. The applications for HDPE are rigid bottles, food container, buckets and crates.

3. Polyvinyl chloride (PVC)

Polyvinyl chloride is the most versatile among all plastics because it can be compounded with stabilizers, plasticizers, and other additives. Major applications for PVC are pipes, conduits, wires, bottles, and packaging films.

4. Low density polyethylene (LDPE)

Low density polyethylene has good toughness and flexible characteristics. Major applications for LDPE are packaging, agricultural and squeezed consumer bottles.

5. Polypropylene (PP)

Polypropylene has high temperature resistance, good chemical resistance and medium gloss. It is often used in the industries of food container, straws, pipes and household appliances.

6. Polystyrene (PS)

Polystyrene is a hard, transparent and brittle thermoplastic polymer. It is being widely used in many applications because of its low cost and easy processability, for example, in packaging industry, disposable products, house-wares and toys.

7. Other plastics

Besides six commodity plastics classified above, other plastics and thermoset resins are in this group.

2.2.1.2 Shredding

Shredding is required as a basic operation for reducing size of plastic objects and parts. Granulators can be used to shred almost all types of plastics and they are suitable to use in shredding tough and resilient plastics. Metal impurities should be detected and separated form plastic wastes, by means of air classification or magnets, before shredding in order not to damage cutting blades.

2.2.1.3 Cleaning

The quality of scrap is determined by the degree of residual impurities. Generally, classifications of impurities are as follows [Bittner and Michaeli, 1992].

- Mineral impurities (clay, earth, sand, etc.): These are not water soluble but can be released because of their higher specific weight comparing to water.
- Particles capable of floating (peat, small pieces of wood, slips of paper, cigarette ends, etc.): Floating methods can be used to eliminate these impurities.
- Soluble components (salts, milk powder, oils, paint residues, grease, etc.): Hot water or washing solutions are frequently used for cleaning these impurities.

Normally, intensive pre-cleaning of soiled plastic wastes is essential. In most cases, plastic wastes are sprayed with water and then cleaned in a water bath with a high level of friction between the polymer pieces.

2.2.1.4 Separation

Separation or sorting processes are necessary for plastic recycling since different resins must usually be reprocessed or recycled separately due to the difference in melting temperatures, as mentioned earlier. Sortation can be practiced in a household and commercial firm (source separation). Hand sorting has basically been used almost exclusively for separation of plastic parts from waste streams. Separation technologies are developed based on the differences in polymer characteristics. Separation methods for plastic wastes are as follows:

- Density-based separation

  Separation in a hydrocyclone works on the basis of sorting in a centrifugal force field. The cyclone geometry produces an upwards-directed inside vortex to separate out the lightweight fraction and a downwards-directed outside vortex to separate out the heavy fraction.

- Sink/float separation

  Generally, commodity plastic waste is composed of polyolefins, polyvinyl chloride and polystyrene. These plastics have slightly different densities. The difference in density can be used to separate a mixture of plastics into generic groups using a sink/float separator. The schematic diagram of sink-float separation is shown in Figure 2.1 [Leidner, 1981]. The separation is achieved by using four liquid media composed of water ($d = 1$ g/cm^3), two mixtures of water and alcohol ($d = 0.93$ g/cm^3 and 0.91 g/cm^3) and an aqueous salt solution ($d = 1.2$ g/cm^3).

- Electrostatic sorting

  Electrostatic sorting can be used to separate plastics on the basis of the dissimilarity in electrical conductivity of polymer. The device employed this technique called corona roll separator is shown in Figure 2.2 [Bittner and Michaeli, 1992].

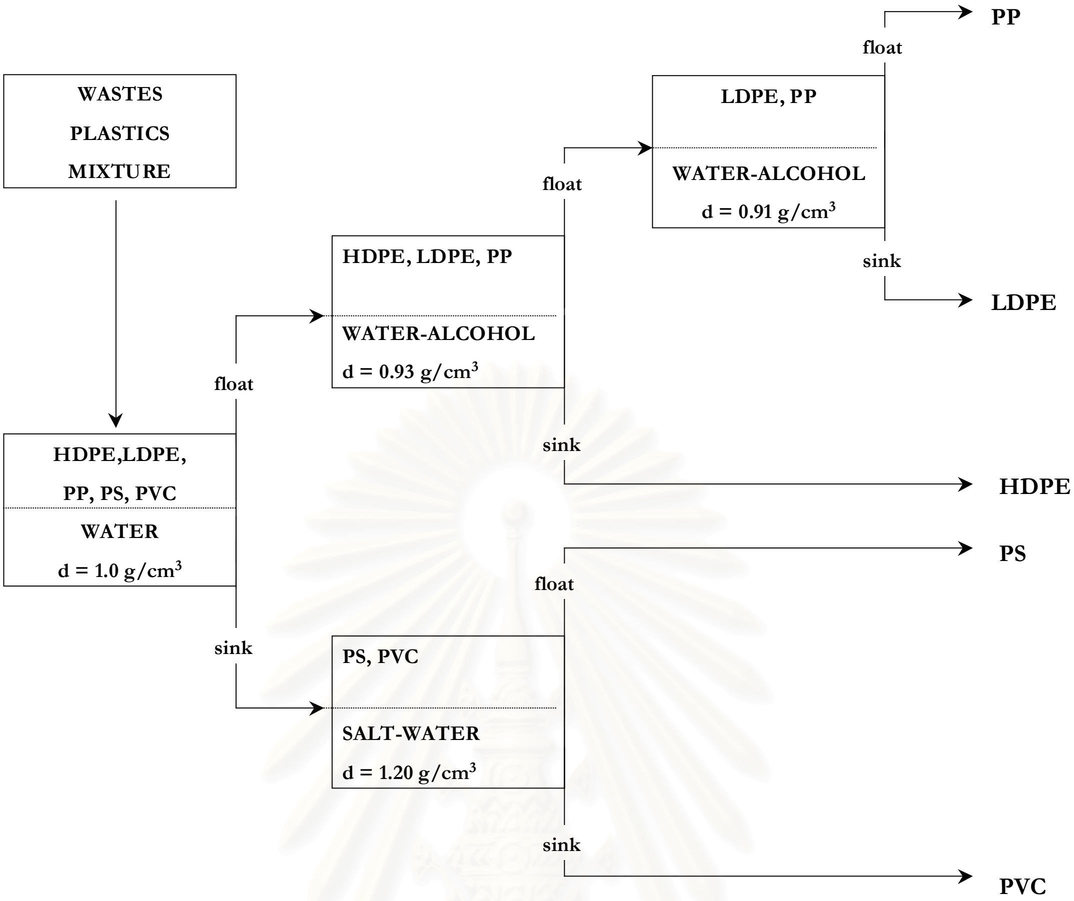


Figure 2.1 Schematic diagram of sink-float separation [Leidner, 1981].

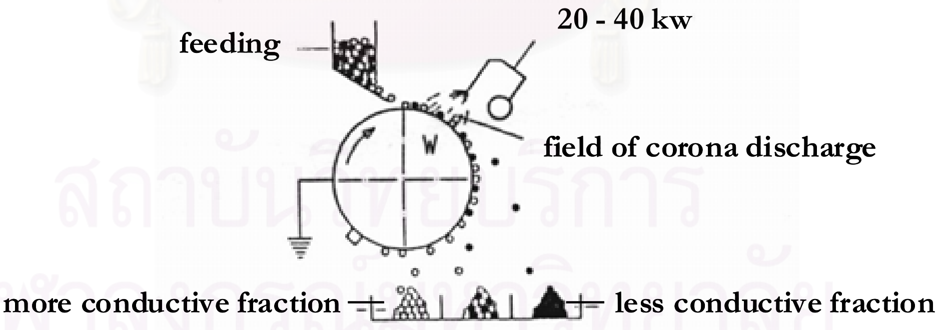


Figure 2.2 Corona roll separator [Bittner and Michaeli, 1992].

2.1.2.5 Regranulation

Regranulation is generally performed in an extruder, which can thoroughly mix and prepare recycled materials in a pellet form. During extrusion, melted plastics must be free of gaseous components (moisture, air and monomer). Thus a vented extruder is used. Degassing of the melt is important in the reprocessing of plastic wastes into high-grade pellet. Moreover, recycled materials can be mixed with virgin materials and additives to obtain desired properties.

An example on recycling process of soft drink bottle made from PET is schematically shown in Figure 2.3 [Ehrig, 1992]. Generally, the base cup, label, and closure on the plastic soft drink bottle are polyolefins, which must be separated from PET. The process is composed of sorting, shredding, cleaning, separation by hydrocyclone and regranulation.

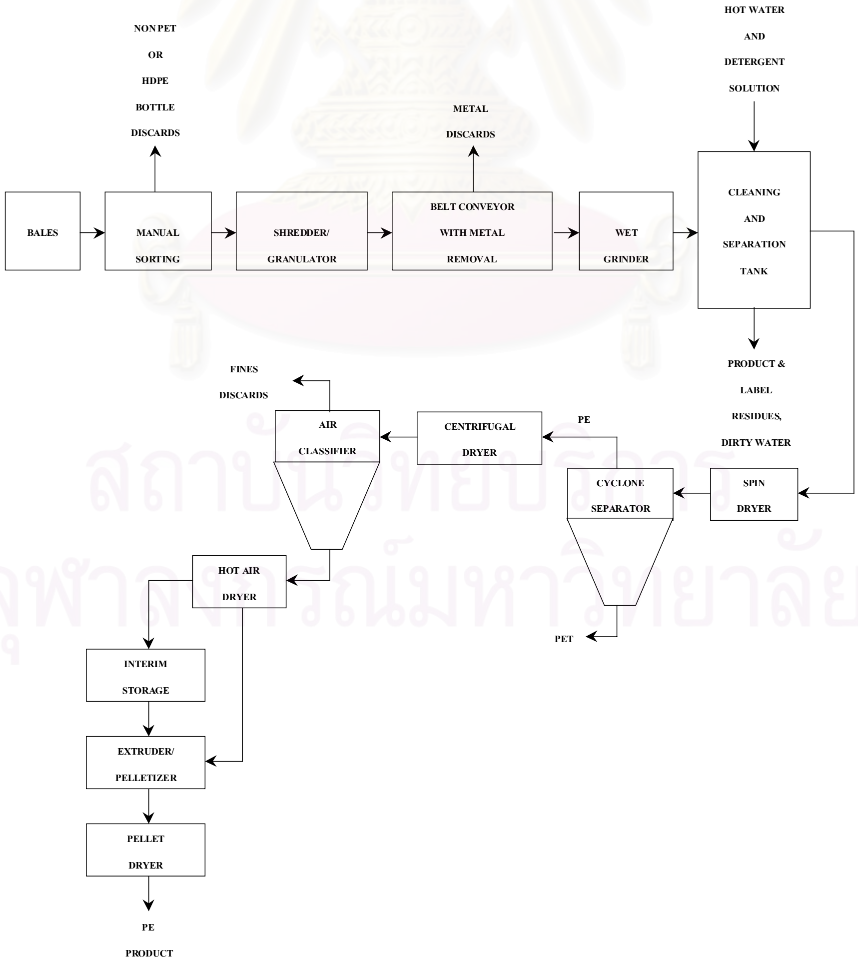


Figure 2.3 Recycling process of soft drink bottle from PET [Ehrig, 1992].

2.3 Polymer degradation

The main technical problems faced in plastic recycling is the degradation of material, resulting in a loss in such properties as appearance, chemical resistance, processability and mechanical properties. The properties of polymers deteriorate because of environmental effects. Stress applied during processing and application, UV light, heat and moisture enhance the degradation. In this section, we will concern with the effects of degradation during processing (thermal-oxidative degradation) and degradation during uses caused by UV radiation (photo-oxidative degradation).

2.3.1 Degradation during processing

During processing, plastics can undergo preliminary molecular damage. These changes may occur in the molecular structure such as decrease in the average molecular weight due to chain scission, increase in the average molecular weight due to crosslinking and formation of unsaturated species due to side-chain reaction. Thermal-oxidative degradation of polymer during processing is composed of initiation, propagation and termination steps.

Initiation

Under the influence of shear forces together with the high processing temperature, free radical (R•) can be formed [eqn (2.1)].

$$\text{Polymer (RH)} \longrightarrow R\bullet \qquad (2.1)$$

Propagation

The free radicals react quickly with oxygen to form peroxy radical (ROO•) [eqn (2.2)] which can abstract hydrogen radicals (H•) from the polymer to form hydroperoxide (ROOH) [eqn (2.3)]. Hydroperoxide (ROOH) can be decomposed by heat into alkoxy radicals (RO•) and hydroxy radicals (•OH) [eqns (2.4) and (2.5)]. Both species, RO• and •OH, will react with a hydrogen radical abstracted from the polymer backbone [eqns (2.6) and (2.7)].

$$R\bullet + O_2 \longrightarrow ROO\bullet \tag{2.2}$$

$$ROO\bullet + RH \longrightarrow ROOH + R\bullet \tag{2.3}$$

$$ROOH \longrightarrow RO\bullet + \bullet OH \tag{2.4}$$

$$2ROOH \longrightarrow ROO\bullet + RO\bullet + H_2O \tag{2.5}$$

$$RO\bullet + RH \longrightarrow ROH + R\bullet \tag{2.6}$$

$$\bullet OH + RH \longrightarrow R\bullet + H_2O \tag{2.7}$$

Termination

Termination step can take place in two ways between combination [eqns (2.8) and (2.9)] and disproportionation [eqn (2.10)], depending on the concentration of oxygen. When the oxygen access is limited by diffusion, for example during processing of polymers, the reaction (2.8) and (2.9) may play an important role.

$$2\,R\bullet \longrightarrow R\text{-}R \tag{2.8}$$

$$R\,OO\bullet + R \longrightarrow ROOR \tag{2.9}$$

$$2ROO\bullet \longrightarrow ROOR + O_2 \tag{2.10}$$

2.3.2 Degradation caused by UV radiation

Plastic products used outdoor are exposed to hostile environment. Sunlight, oxygen, humidity, and physical stresses can create changes in the chemical composition of polymeric material. These changes may include molecular weight reduction due to main chain cleavage, the formation of cross-links, or the formation of other functional groups. When plastics are used outdoors, they are exposed to solar radiation. Ultraviolet (UV) from sunlight is perhaps the most significant factor causing degradation for polymers. The first reason is that the UV lights add thermal energy to the polymer. The other is that the UV lights excite the electrons in the covalent bonds of the polymer to be at a higher energy level. The excited electrons are less restricted to the particular covalent bond in which they are located. The energy content of UV radiation compared to the dissociation energies of some typical bonds is provided in Table 2.3 [Olayan *et al.*, 1996]. The energy of the photons in the UV region at the wavelength of 290 to 400 nm is in the range of 479 to 297 kJ/Einstein^{-1} (Einstein^{-1} = 1 mol photons = 6 × 10^{23}), which is significantly higher than the bond energy of typical bonds in the polymers [Hoyle and Karsa, 1997]. Hence, the bond is weaker and can be broken more readily. Bond breaking can occur only if the photon exceeds the disassociation energy of one of covalent bonds in the polymer. One major difference between the energy from sunlight and the energy from thermal heat is that sunlight is made up of a wider energy spectrum of different intensities. The different intensities are characterized by different frequencies of vibration of the light energy. The energy of light is directly proportional to the frequency of radiation given by

$$E = h\nu \qquad (2.11)$$

where E is the energy of a photon, h is a constant (call Planck's constant) and ν is the frequency of the light vibrations. UV light has more intense energy than the others part of sunlight (visible and infrared light). UV light is especially damaging to plastics because the energy intensity closely matches the energy levels in the bonds between most of the atoms. This degradation process is called photo-oxidative degradation of which the mechanism is the same as the thermal-oxidative degradation in section 2.3.1.

Table 2.3 Energy content of some radiation compared to the dissociation energy of some typical bonds [Olayan *et al.*, 1996].

Wavelength of Radiation (nm)	Energy (kJ/Einstein)	Bond Type	Bond Dissociation Energy (kJ/mol)
250 - 290	479	C – H	380 – 420
275	436	O – H	420
300	399	C – OH	380
300 – 325	368 – 398	C – C	340 – 350
320 – 350	342 – 375	C – O	320 – 380
350 – 375	319 – 339	C – Cl	300 – 400
400	299	RO – O	150
400	297	C – N	320 – 330
500	239	RO – OR	140

2.4 Properties modification by additives

A common method which is used to modify the properties of the polymers is by blending polymers with additives. Additives can be classified into several types mainly depending on the function of the additives such as stabilizer, plasticizer, pigment, etc. In this section, we will focus on two modifying agents, stabilizers and ethylene vinyl acetate copolymer, that are used in this work.

2.4.1 Stabilizers

Stabilizers are necessary to prevent polymers from oxidative degradation during processing or the exposure to UV lights. Stabilizers can be classified by the causes of degradation, heat stabilizers and UV stabilizers. Not only first time use must be considered to add stabilizer but recycled materials should also be anticipated. Because recycled plastics often do not contain enough heat and light stabilizers. It is rare that a single antioxidant can provide all of the varied functions of protection required affording complete polymer stability. Consequently, combinations of antioxidants are used as stabilizer formulations to effectively protect polymers from thermally induced degradation during storage, processing and final service life.

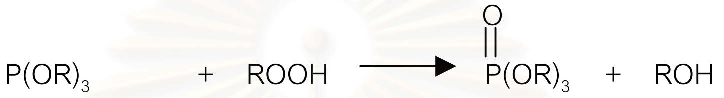
Most organic polymers are susceptible to attack by oxygen. Generally, antioxidants for polymers can be classified by the mode of action during degradation such as primary antioxidant and secondary antioxidant. Primary antioxidants act by trapping or deactivating radicals. Hindered phenols (AH) are the most widely used primary antioxidants. Hindered phenols react with the peroxy radical in the propagation step, leading to the formation of hydroperoxides but without releasing a new free radical [eqn (2.12)].

$$\mathrm{ROO\bullet} \quad + \quad \mathrm{AH} \quad \longrightarrow \quad \mathrm{ROOH} \quad + \quad \mathrm{A\bullet} \qquad (2.12)$$

Secondary antioxidants are used to enhance the performance of the primary antioxidants. Secondary antioxidant such as phosphites and thioethers can act as hydroperoxides decomposers to prevent further damage.

Phosphites

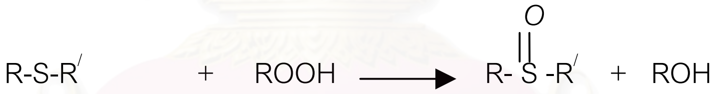
Phosphites ($P(OR)_3$) reduce the hydroperoxides to alcohols and are converted to inactive phosphates [eqn (2.13)].



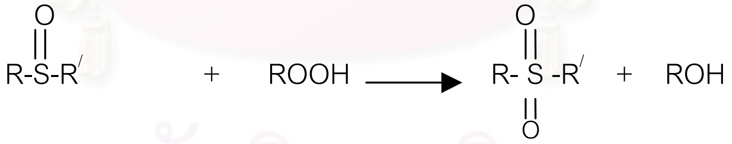
$$P(OR)_3 \quad + \quad ROOH \longrightarrow \overset{\overset{O}{\|}}{P}(OR)_3 \quad + \quad ROH \qquad (2.13)$$

Thioethers

Thioethers ($R\text{-}S\text{-}R^{/}$) can decompose hydroperoxides, leading to the formation of alcohols and sulfoxides [eqn (2.14)]. In addition, the latter can further react with hydroperoxides again, leading to the formation of alcohols and inactive sulfones [eqn (2.15)].



$$R\text{-}S\text{-}R^{/} \quad + \quad ROOH \longrightarrow R\text{-}\overset{\overset{O}{\|}}{S}\text{-}R^{/} \quad + \quad ROH \qquad (2.14)$$



$$R\text{-}\overset{\overset{O}{\|}}{S}\text{-}R^{/} \quad + \quad ROOH \longrightarrow R\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}R^{/} \quad + \quad ROH \qquad (2.15)$$

In addition, the possible way of protecting polymer from the effects of UV is to coat the surface with a non-transmitting film or to add UV stabilizers. Adding of UV stabilizers or UV absorbers is a simple way to avoid degradation caused by UV since UV absorbers can reduce the rate of photo-initiation and the kinetic chain length in the propagation stage of the oxidative degradation mechanism.

2.4.2 Ethylene vinyl acetate copolymer

Ethylene vinyl acetate copolymer (EVA) is a thermoplastic polymer manufactured by the polymerization of ethylene and vinyl acetate (VAc). EVA has vinyl acetate contents varied from 1.5% to about 50%. EVA can provide a wide range of rubberlike properties because of the elasticity of VAc contents. Small amounts of VAc reduce crystallinity and melting point, but increase toughness and flexibility. In addition, the softening point of EVA decreases with increasing VAc content.

The EVA can be processed by all thermoplastic methods such as injection molding, extrusion, blow molding and calendering. In injection molding, the EVA must be injected at the lowest possible temperature that will yield a satisfactory molded part. Normally, the cooling time will be excessively long in order to prevent penetration and deformation caused by ejector pins.

The EVA can be used as a modifying agent which can be blended and compounded with other materials to produce a variety of adhesives, color concentrates and coating product. Moreover, additives and fillers are possible in a mixture of EVA and a compatible polymer because of high polarity of VAc.

2.5 Processing technique

2.5.1 Compression molding

Compression molding is one of the most common methods used to produce thermoset plastics. The process can also be used for thermoplastics but this is less common. General compression molding used for polymers is illustrated in Figure 2.4 [Billmeyer, 1984]. The polymer is placed in the lower half of a heated mold, the upper half is then moved down and the pressure is applied. The pressure and temperature can be varied considerably depending upon the thermal and rheological properties of the polymers. In practice, the polymer is often preheated to reduce the temperature different from the mold and to assist early flow in the mold. In addition, a slight excess of material is usually placed in the mold to insure its being completely filled. The rest of the polymer is squeezed out to take the shape of the mold. The advantages of compression molding over other processing techniques are:

- Polymers flow over shorter distances thus reducing frozen-in stresses.
- Polymers are not forced through small gates, which can lead to reduction in mechanical properties.
- Mold maintenance cost is low.
- Tooling costs are inexpensive because of the simplicity.
- Material is not wasted because of the absence of sprues and runners.

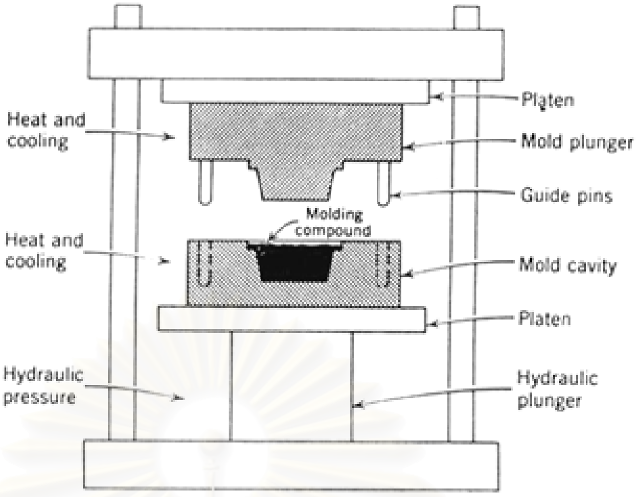


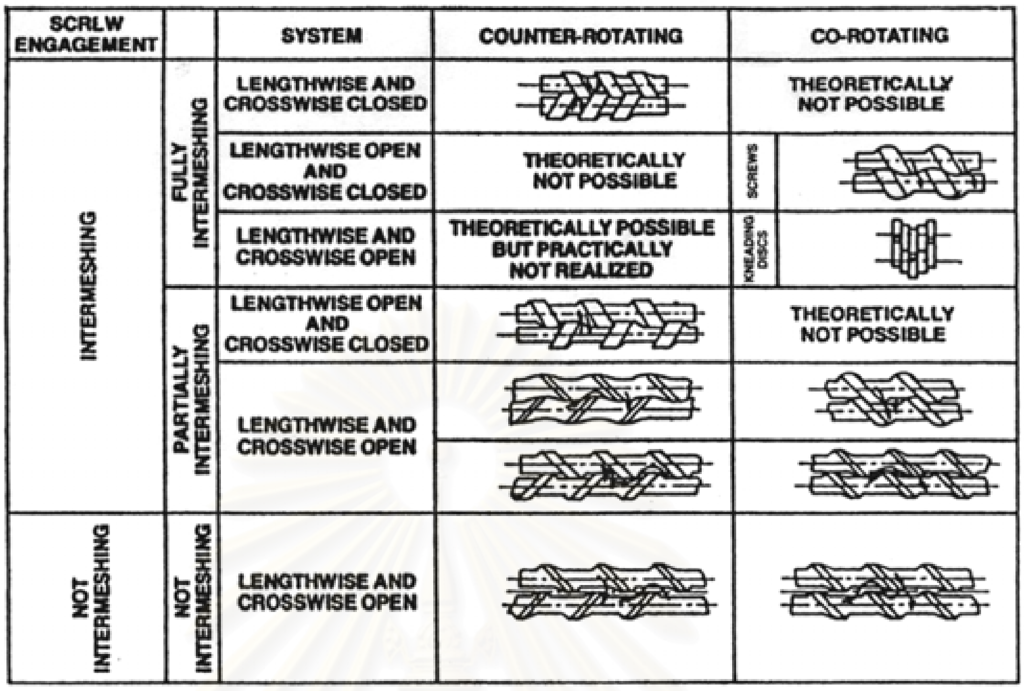
Figure 2.4 Principle of compression molding [Billmeyer, 1984].

2.5.2 Twin-screw extrusion

Polymer compounding is defined as upgrading of polymers. Compounding processes range from single additive incorporation to multi-additive processing. A twin-screw extruder is effective compounding equipment, which plays an important role in processing steps. The primary advantages of using twin-screw extruders are:

- Greater ability to control the mixing action, both dispersive mixing and distributive mixing.
- High conveying capacity at low screw speed.
- An ability to feed normally difficult feeding materials such as powders.
- Low frictional heat generation and low contact time in the extruder.

However, the disadvantage of the twin-screw extruder is that it is a relatively expensive machine. The meshing of the screws and the high pressure built up in the final flights give rise to severe wear of screws and barrel.



SCRLW ENGAGEMENT		SYSTEM	COUNTER-ROTATING	CO-ROTATING	
INTERMESHING	FULLY INTERMESHING	LENGTHWISE AND CROSSWISE CLOSED		THEORETICALLY NOT POSSIBLE	
		LENGTHWISE OPEN AND CROSSWISE CLOSED	THEORETICALLY NOT POSSIBLE	SCREWS	
		LENGTHWISE AND CROSSWISE OPEN	THEORETICALLY POSSIBLE BUT PRACTICALLY NOT REALIZED	KNEADING DISCS	
	PARTIALLY INTERMESHING	LENGTHWISE OPEN AND CROSSWISE CLOSED		THEORETICALLY NOT POSSIBLE	
		LENGTHWISE AND CROSSWISE OPEN			
NOT INTERMESHING	NOT INTERMESHING	LENGTHWISE AND CROSSWISE OPEN			

Figure 2.5 Twin-screw extruder classification [Todd, 2000].

Twin-screw extruders can be classified into intermeshing or non-intermeshing, and co-rotating or counter-rotating, as summarized in Figure 2.5 [Todd, 2000]. The intermeshing twin-screw extruders are self-cleaning. The main characteristic of this configuration is that the screw surfaces slide pass each other, constantly removing polymers stuck to the screw.

An interesting feature of non-intermeshing twin-screw extruder is the possibility of running the two screws at different speeds, thus creating functional relationships between them, which in some instances can be exploited for the rapid melting of powders.

Co-rotating twin-screw extruder transfers the melt from the channel of one screw to that of the other screw. This type is particularly suitable for heat sensitive materials because the material is conveyed through the extruder quickly with little possibility of entrapment. Co-rotating intermeshing twin-screw extruders are most widely used for commercial processing as shown in Figure 2.6 [Todd, 2000].

In a counter-rotating twin-screw extruder, the material is sheared and pressurized in a mechanism similar to calendering. The counter-rotating twin-screw extruder generates high temperature pulses, making them efficient machines to disperse pigments.

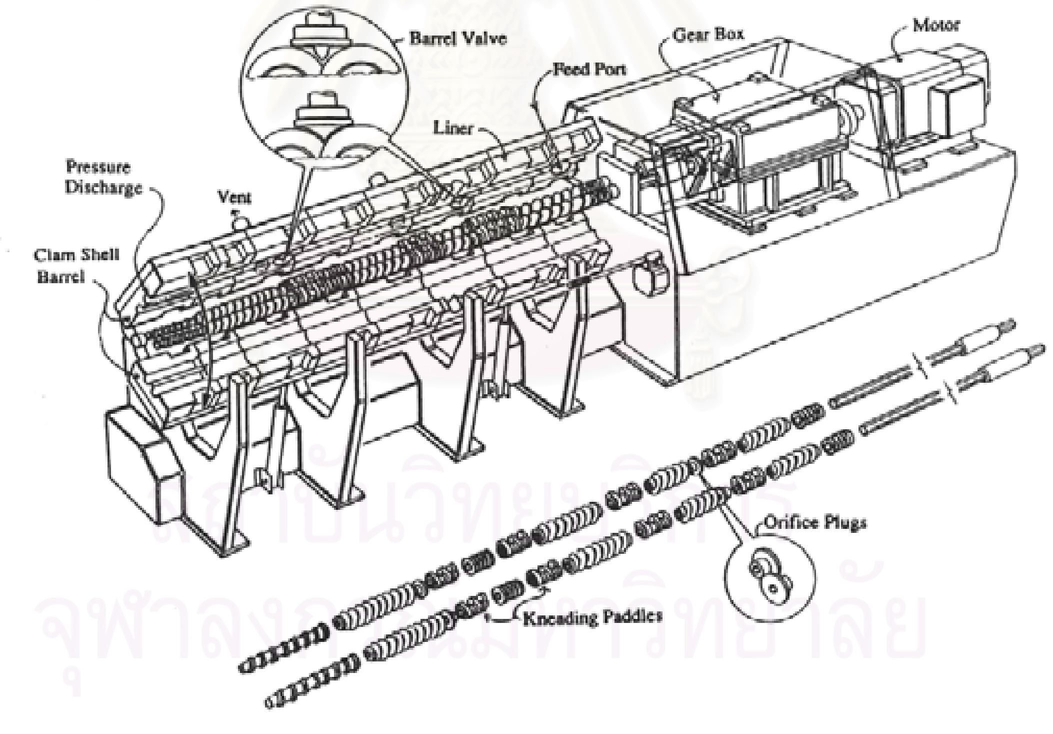


Figure 2.6 Co-rotating intermeshing twin-screw extruder [Todd, 2000].

2.5.3 Injection molding

One of the most common processing methods for plastics is injection molding. Nowadays, more than one-third of all thermoplastic objects is injection molded and more than half of all polymer processing equipment is for injection molding. The injection molding process is ideally suited to produce parts of complex shapes requiring precise dimension. The complete injection molding equipment is composed of injection molding machine and injection mold.

2.5.3.1 Injection molding machine

The reciprocating screw injection molding machine, shown in Figure 2.7 [McCrum *et al.*, 1988], illustrates two essential components of the injection molding machine which are injection unit and clamp unit.

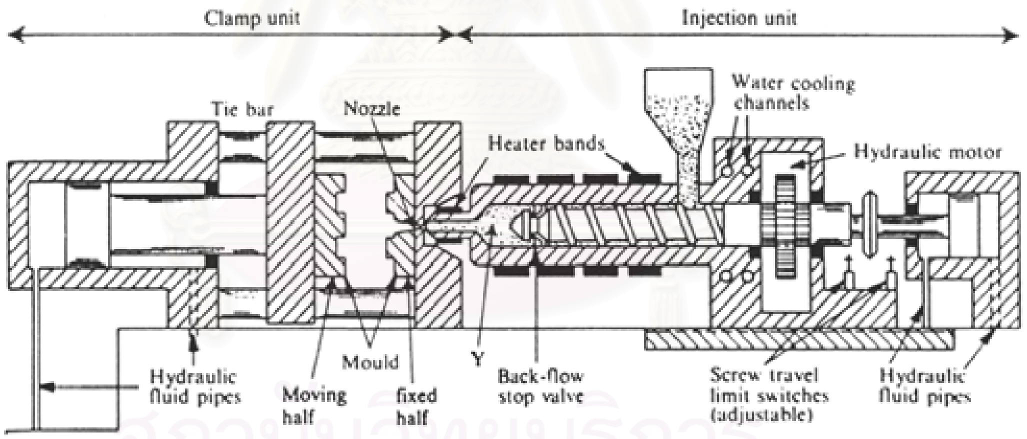


Figure 2.7 A reciprocating screw injection machine [McCrum *et al.*, 1988].

2.5.3.1.1 Injection Unit

The function of injection unit is to melt the polymers, to accumulate the melt in the screw chamber, to inject the melted polymers into the mold cavity and maintain the holding pressure during cooling. An injection unit is shown in Figure 2.8 [Osswald, 1998]. The main components of the injection unit are screw, heaters, check valve and nozzle.

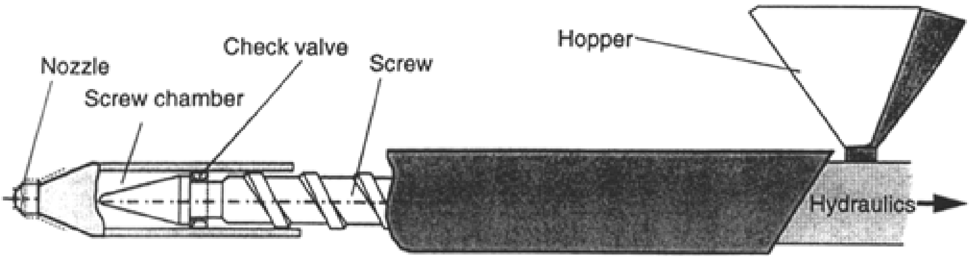


Figure 2.8 Injection unit [Osswald, 1998].

- Screw

  The screw is basically the same as a single screw extruder, except that the screw in injection molding machine can be moved backwards and forwards to allow for melted accumulation and injection.

- Check valve

  The check valve or non-return valve is at the end of the screw. The purpose of this valve is to stop any back flow across the flights of the screw during injection.

- Nozzle

  The nozzle is at the end of the injection unit and fits tightly against the mold during injection. The contact between the nozzle and the mold causes heat transfer from the nozzle to the mold. Therefore, the nozzle must be withdrawn from the mold during the screw moved backwards. Otherwise the plastic may freeze off in the nozzle.

- Heaters

  The heaters are normally of the electrical resistance type and are thermostatically controlled using thermocouples. Typically, heaters are designed to withstand a maximum pressure of 50,000 to 60,000 psi.

2.5.3.1.2 Clamp unit

The function of a clamping unit in an injection molding machine is to open and close the mold. In addition, the auxiliary mechanisms needed for part removal are in most cases located in the clamp unit. Modern injection molding machines have two predominant clamping types: toggle clamp unit and hydraulic clamp unit.

- **Toggle clamp unit**

Figure 2.9 presents a toggle mechanism in the closed (a) and opened positions (b) [Osswald, 1998]. The toggle clamp unit uses a small hydraulic cylinder to open and close a toggle mechanism, which slides the moving plate on tie bars. The two main advantages of the toggle clamp unit are that it is more economical to run the small hydraulic cylinder and since the toggle is self-locking, it is not necessary to maintain the hydraulic pressure throughout the molding cycle. On the other hand, the toggle clamp unit has a disadvantage on that there is a more complicated mold set up than a hydraulic clamp unit and regular maintenance for the link pins is required.

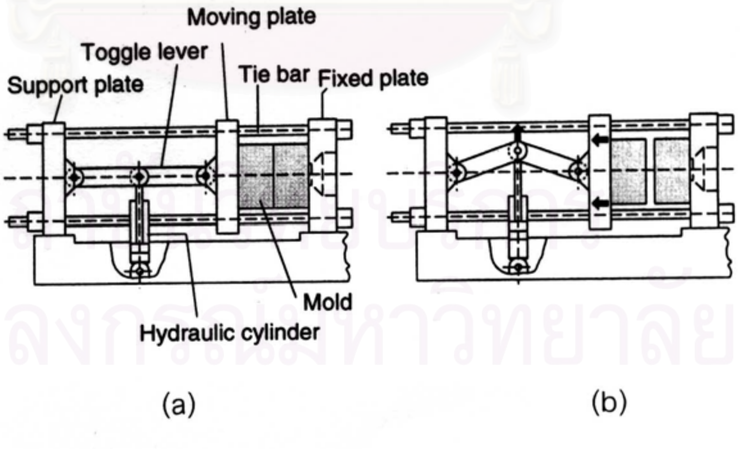
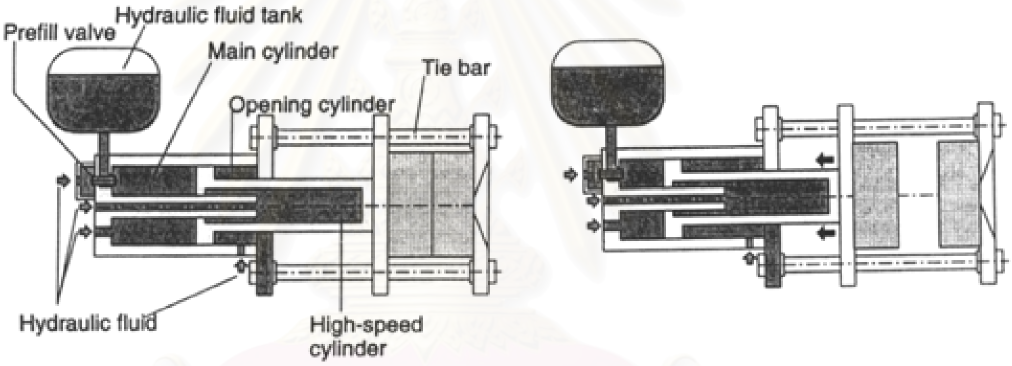


Figure 2.9 Toggle clamp unit; (a) closed position; (b) opened position [Osswald, 1998].

- Hydraulic clamp unit

Figure 2.10 shows a hydraulic clamp unit in the closed (a) and opened positions (b) [Osswald, 1998]. Hydraulic clamp unit uses a large hydraulic cylinder and piston to move the movable plate. Clamping force is built up by a direct hydraulic pressure. The clamping force can be adjusted so that there is no leakage of melted plastic from the mold. The advantage of the hydraulic system is that as a maximum clamping force is attained at any mold closing positions and that the system can take different mold sizes without major system adjustments. However, hydraulic system requires high energy to compress oil.



(a) (b)

Figure 2.10 Hydraulic clamp unit; (a) closed position; (b) opened position [Osswald, 1998].

2.5.3.2 Injection mold

The injection mold must be considered as one of the most important pieces of production equipment in processing plants. The mold comprises two halves; the fixed half attached to a stationary platen and the moving half attached to a moving platen.

Two-plate mold is illustrated in Figure 2.11 [Morton-Jones, 1989]. The gate of two-plate mold is at the side of the molded parts and the melted polymer will have to flow round a core to join up on the far side.

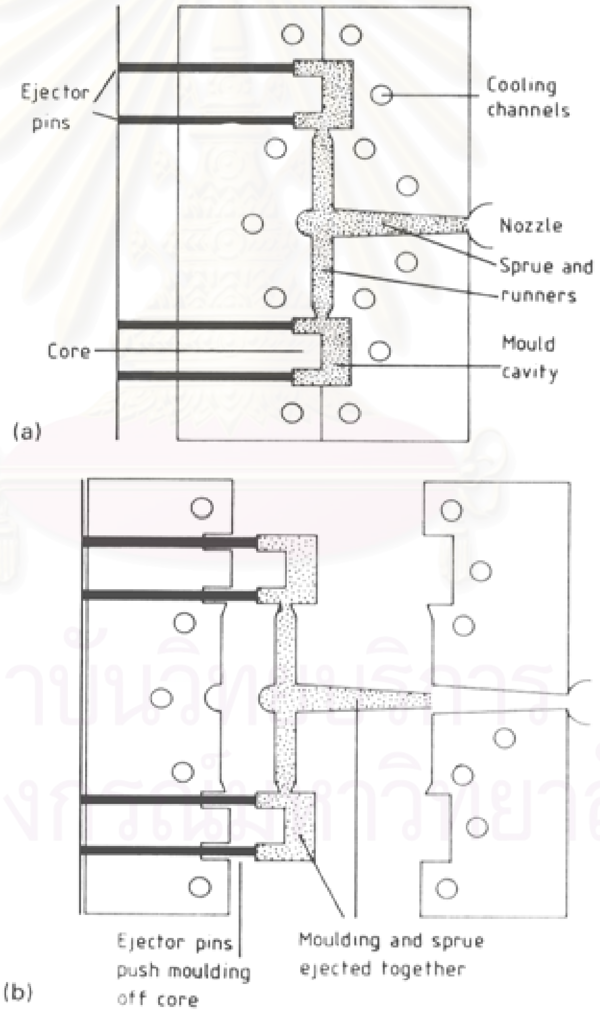


Figure 2.11 Two-plate mold; (a) closed mold; (b) opened mold [Morton-Jones, 1989].

Figure 2.12 shows a three-plate mold [Morton-Jones, 1989]. This mold is needed when the runner system and the cavities are in different planes. Two openings of the three-plate mold are required to eject the molded parts and the sprue separately. The gate of three-plate mold stays at the bottom of the molded parts and the melted polymer can flow evenly to form the walls of the molded part. This type will give a molded part with better properties.

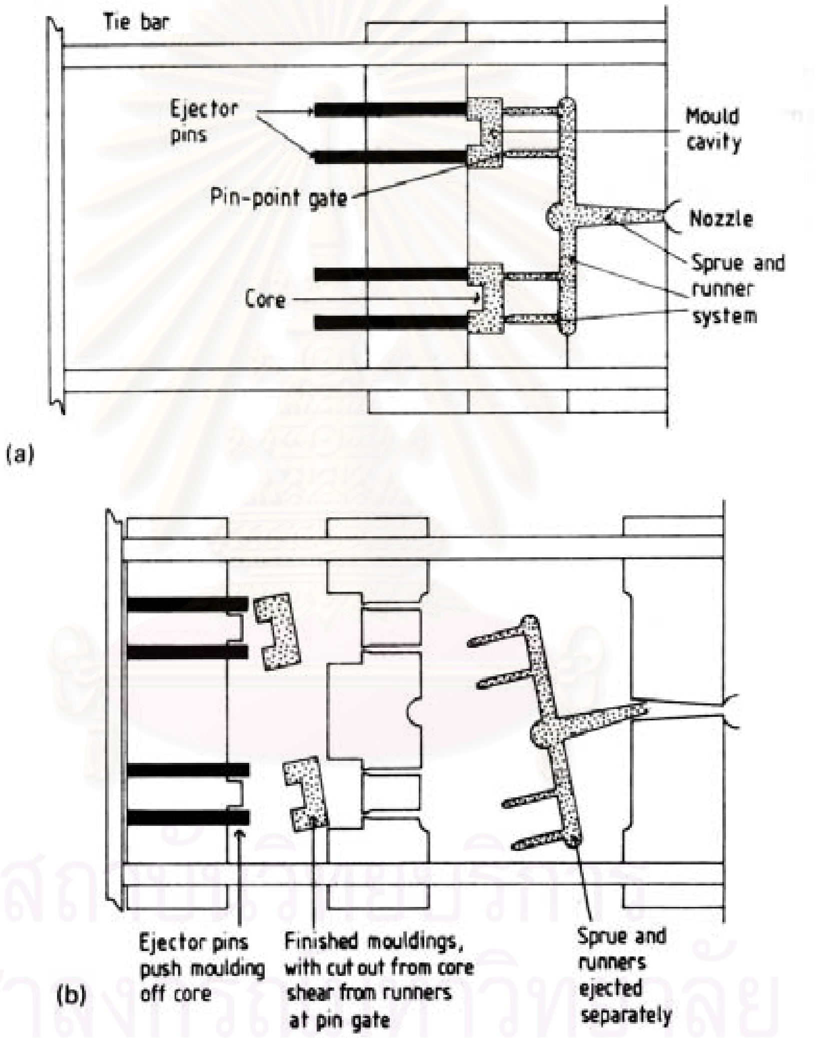


Figure 2.12 Three-plate mold; (a) closed mold; (b) opened mold [Morton-Jones, 1989].

Figure 2.13 shows the feed system of multi-cavity mold [McCrum *et al.*, 1988]. In the filling of multi-cavity molds, the melted polymer runs from the nozzle into the sprue, and then flows along runners. Finally, melted polymer passes through a gate into cavity. Generally, the design of multi-cavity mold should use balanced runners to ensure that all mold cavities are filled at the same rate. If this is not done, incomplete molding filling will occur.

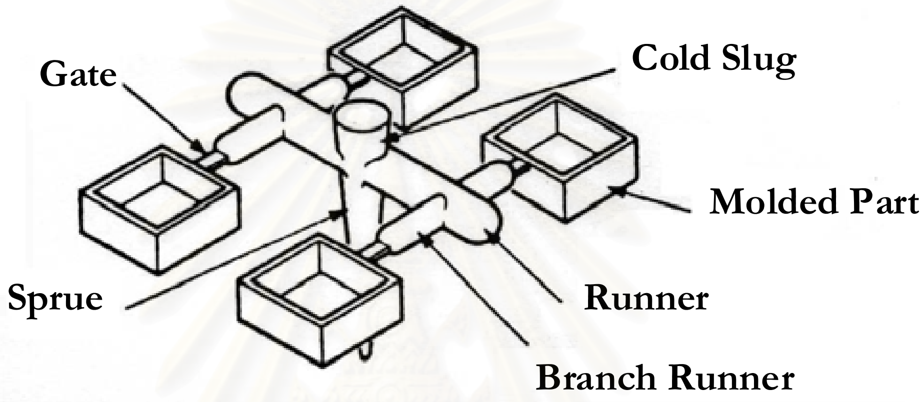


Figure 2.13 Feed systems of multi-cavity mold [McCrum *et al.*, 1988].

2.5.3.3 Injection molding cycle

The sequence of events during the injection molding of a plastic part, as shown in Figure 2.14, is called an injection molding cycle [Osswald, 1998]. The cycle begins when the mold closes, followed by the injection of polymers into the mold cavity (step A). After the cavities are full, pressure on the plastic is maintained until the gates freeze (step B). Meanwhile, the gates have frozen, plastic is cooled in the mold and at the same time the injection unit moves backward and screw rotates to retract for the next shot of plastics (step C). After the molded part is frozen, the mold opens and ejects the molded parts (step D). Finally, the mold closes again and ready for the next cycle.

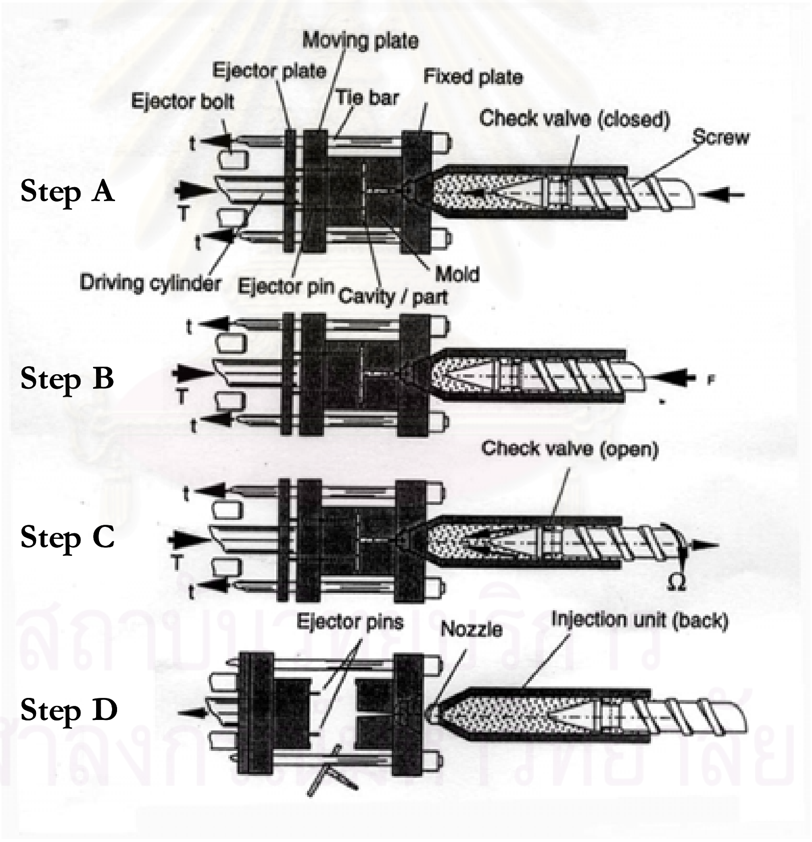


Figure 2.14 Sequence of events during injection molding cycle [Osswald, 1998].

Figure 2.16 summarized the sequence of events during the injection molding cycle [Osswald, 1998]. This figure shows that the cycle time is dominated by the cooling of the molded part inside the mold cavity. Consequently, cooling rates are an important concern for injection molding. The total cycle time can be calculated by:

$$t_{\text{cycle time}} = t_{\text{mold closing}} + t_{\text{cooling}} + t_{\text{mold opening / ejection}} \qquad (2.16)$$

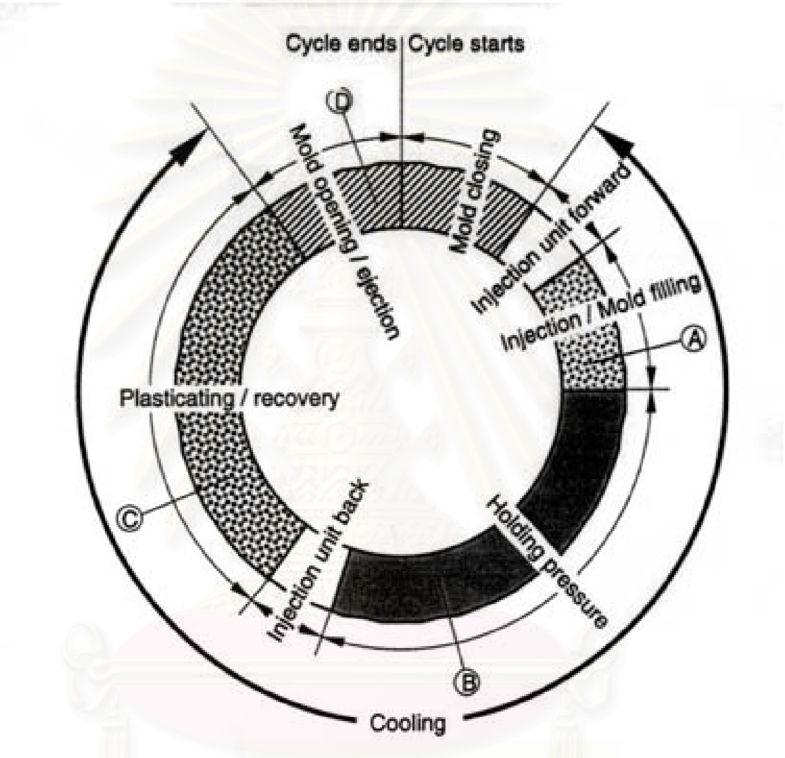


Figure 2.15 Injection molding cycle [Osswald, 1998].

2.6 Characterization of molecular weight and molecular weight distribution

One of the most important characteristics of a polymer is molecular weight and molecular weight distribution that significantly affect the processing and the strength of polymer. The molecular weight of a polymer is expressed as an average due to the heterogeneous nature of the molecules that comprise the polymer. There are two basic ways calculating the size of the molecules in the number; the number average molecular weight, M_n (based on the number of molecules present) and the weight average molecular weight, M_w (based on the total weight of the molecules of each size). These relationships are defined in equation (2.16) and (2.17). The ratio of the weight average molecular weight to the number average molecular weight gives a good indication of the molecular weight distribution (MWD).

$$M_n = \frac{\text{Total weight of all molecules}}{\text{Total number of molecules}} \tag{2.16}$$

$$M_w = \frac{\sum(\text{weight of all molecules of each size} \times \text{its molecular weight})}{\text{Total weight of all molecules}} \tag{2.17}$$

Gel permeation chromatography (GPC), or size exclusion chromatography (SEC) is the choice for determining the molecular weight and molecular weight distribution of polymers. The separation of polymer molecules by GPC is based on the differences in their molecular sizes in solution. A schematic diagram of a typical GPC is shown in Figure 2.16 [Painter and Coleman, 1994]. GPC column is filled with beads, which have several pores with various and distribution, commonly made from different types of glass (or crosslinked polystyrene).

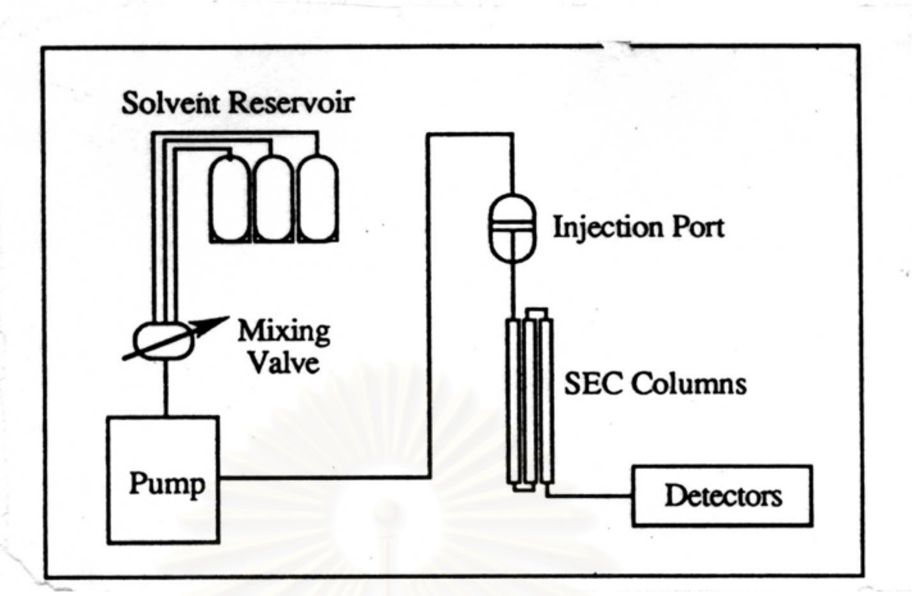


Figure 2.16 Schematic diagram of a typical GPC [Painter and Coleman, 1994].

A sample of polymer solution is pumped through the set of columns and then through the detector which measures the amount of different species. Figure 2.17 illustrates the schematic of size separation in GPC [Hadad *et al.*, 1988]. While the small molecules diffuse quickly into the pores, large species may be excluded from the pores and will be swept through the column first, followed by others of decreasing size.

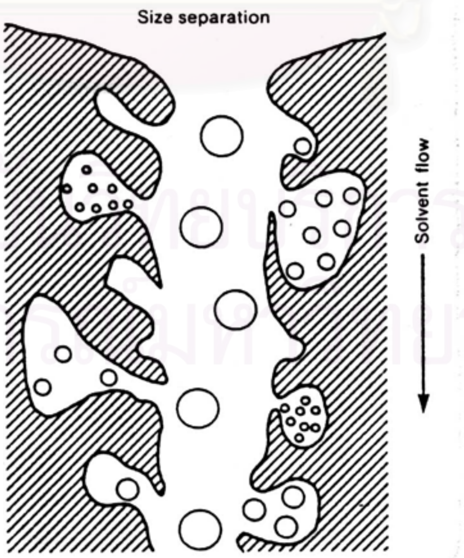


Figure 2.17 Schematic of polymer size separation in GPC [Hadad *et al.*, 1988].

2.7 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is generally used for determining the melting temperature, glass transition temperature, degree of crystallinity, and heat of fusion of polymers. This test measures the thermal energy absorbed (endothermic) or given off (exothermic) by the sample. Figure 2.18 illustrates the operating principle of DSC [Cheremisinoff, 1990]. The sample and the reference are placed in thin metal (aluminum) pans, with the thermocouple sensor below the pans. DSC measurements can be made in two ways: by measuring the electrical energy provided from heaters below the pans necessary to maintain the two pans at the same temperature or by measuring the heat flow as a function of sample temperature. Either type of DSC is performed at a constant heating rate under a nitrogen atmosphere.

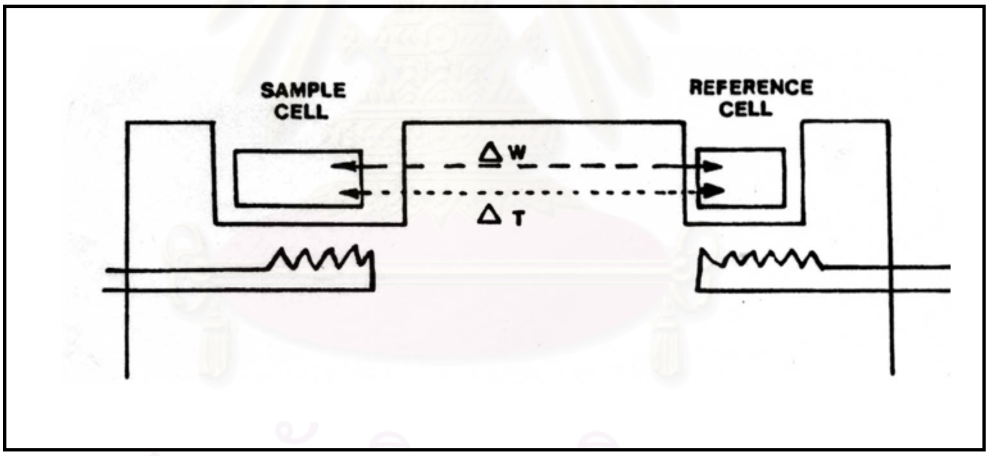


Figure 2.18 Operation principle of DSC; differential energy (dashed line); differential temperature (dotted line) [Cheremisinoff 1990].

Although DSC is used routinely in polymer characterization studies, the analyst needs to be aware of variable factor that can distort the results. It is well known that the first heating curve is significantly influenced by the thermal history of the sample that the polymer is subjected to during processing. Therefore, the second heating scan must be performed to introduce constant thermal history to the samples.

2.7.1 Melting temperature

Melting temperature data can be used to determine the processing temperature. Figure 2.19 illustrates melting temperature of HDPE [Rosato and Rosato, 1990]. The melting temperature is often broad due to variations in crystal thickness.

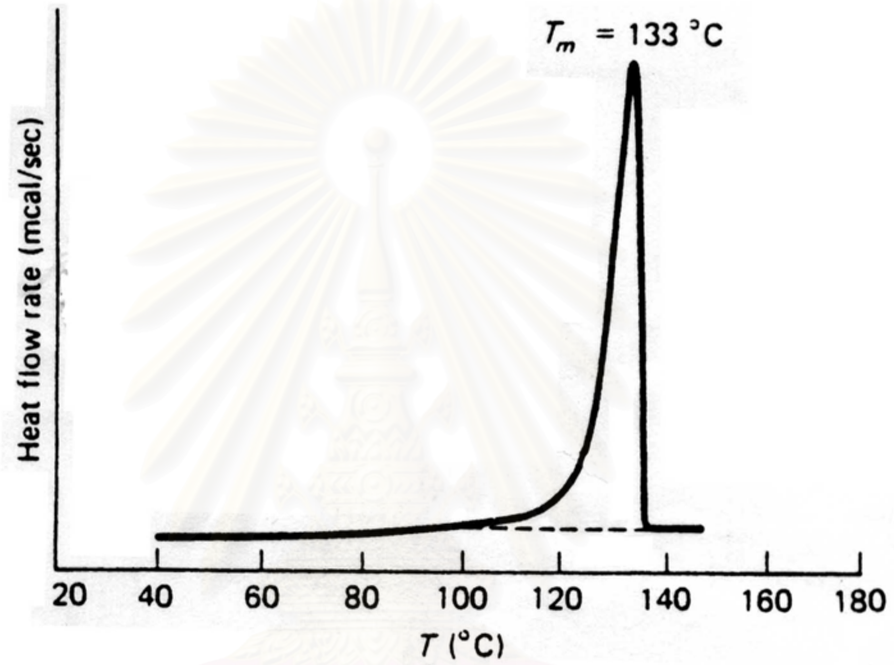


Figure 2.19 Melting temperature of HDPE [Rosato and Rosato, 1990].

2.7.2 Degree of crystallinity

The degree of crystallinity of sample is simply measured by dividing the heat of fusion required to melt a polymer sample (the area under the DSC melting curve) by the heat of fusion for a 100% analogue. It needs to be remembered that the heat of fusion is also dependent on the degree of orientation in the polymer sample.

2.8 Tensile properties

One of the most widely used testing methods for mechanical properties of polymer is the tensile or stress-strain test. This test is usually done by measuring the force that generates as the sample is elongated at a constant rate of extension. The force and the extension of samples can be converted to stress and strain by calculations using the original dimensions and the increase in length. The standard tensile test for plastic is outlined in ASTM D638. Test specimens for tensile tests can be prepared in many different ways such as injection molding and compression molding. Injection molded specimens may exhibit different tensile properties from those of compression molded specimens because of polymer orientation. Preferably, the specimen is made by compression molding and cut into the standard shape to reduce internal stress.

Tensile properties are generally highly sensitive to both temperature and strain rate. As temperature increases, a material results in more free volume and a weakening of the bonding forces that hold the material together. In polymers this is mainly manifested in a reduction in the van der Waals forces between molecules. Therefore, all polymers have less internal strength with increasing temperature, which is reflected in a decreased in maximum strength. As the strain rate is increased, leading to increase in tensile strength and modulus.

Figure 2.20 shows the transition of stress-strain curves, when temperature decreases or strain rate increases [Gruenwald, 1993]. The graphs vary from the rubbery behavior at the high temperature to that of the glassy behavior brittle at the low temperature. The change in tensile behavior with increasing strain rate is also similar to the tensile behavior of a polymer with decreasing temperature. By varying either temperature or strain rate, polymer is possible to exhibit tensile behavior form brittle through ductile for most polymers. Generally, tensile properties are usually measured at a constant strain rate of 50 mm/min.

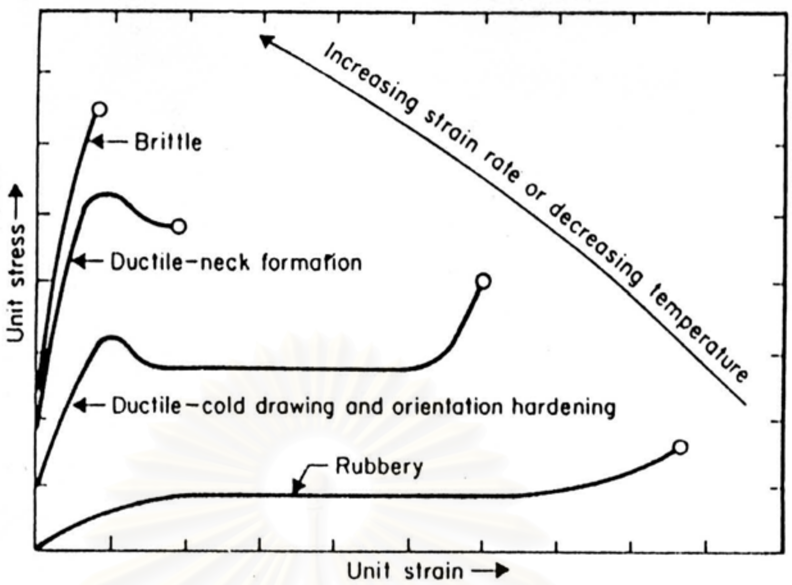


Figure 2.20 The effect of temperature and strain rate on stress-strain curves [Gruenwald,1993].

A typical stress-strain curve for plastics is shown in Figure 2.21 [Haung, 1988]. For a better understanding of this curve, it is necessary to define a basic terms that are associated with the stress-strain curves.

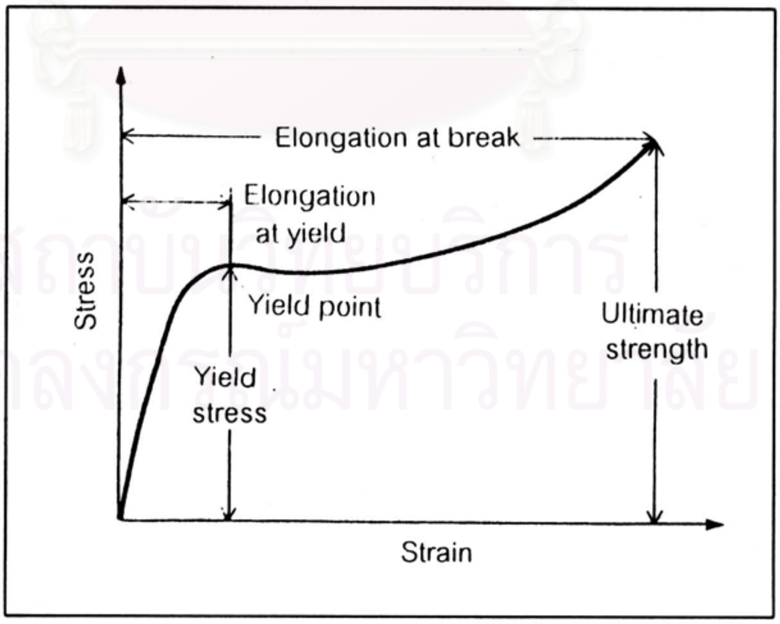


Figure 2.21 A typical stress-strain curve for plastics [Haung, 1988].

2.8.1 Stress

Stress is the force applied to produce deformation in a unit area of a test specimen. If the test specimen eventually breaks then the load at break divided by the cross-sectional area will give us the “ultimate tensile strength“ or “ultimate tensile strength at break”.

2.8.2 Strain

Strain is the ratio of elongation or deformation to the gauge length of the test specimen, that is, the change in length per unit of original length. This term is also used in a broader sense to denote a dimensionless number (mm/mm or in/in) that characterizes the change in dimensions of a specimen during a deformation.

2.8.3 Young’s modulus

Modulus is defined as the stress divided by the strain (slope of stress-strain curve). If the specimen consists of a linear elastic material then the stress-strain curve should be a straight line and the value of the modulus will be a constant value. However, plastics are generally nonlinear. Therefore, modulus values for plastics are determined at very low extension which the stress-strain curve is often reasonably straight line. The slope in the range is known as “Young’s modulus” or “modulus of elasticity”. Young’s modulus is applied to describe the stiffness or rigidity of plastic.

2.8.4 Yield point

The yield point is the first point on the stress-strain curves at which an increase in strain occurs without an increase in stress. After the yield point the specimen exhibits non-recoverable behavior. Thus, this point would normally represent the limit of elasticity. The stress at the yield point is specified as the tensile strength at yield or yield stress. Tensile strength at yield is an often-quoted property, especially if it has a higher value than the ultimate tensile strength at break.

2.8.5 Elongation

The increase in the length of a test specimen that is expressed as a percentage of the original gauge length is called the percentage of elongation.

2.8.6 Area under the stress-stain curve

Generally, the area under the stress-strain curve from the origin to the breaking point is proportional to the energy required to break the plastic and is sometimes referred to the toughness of the plastic. Figure 2.22 illustrates typical stress-strain curves for several types of polymers [Haung, 1988]. Plastics can be classified according to the stress-strain behavior.

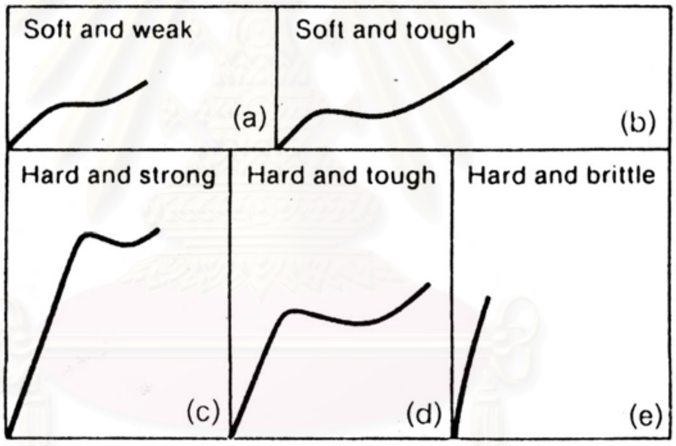


Figure 2.22 Typical stress-strain curves for several types of polymers [Haung, 1988].

In Figure 2.22, a soft and weak material is characterized by low modulus, low yield strength and moderate elongation at break (a). A soft and tough material such as polyethylene shows low modulus, low yield stress, but very high elongation at break (b). A hard and strong material such as polyacetal has high modulus, high yield stress, usually high ultimate strength, and low elongation (c). A hard and tough material such as polycarbonate is characterized by high modulus, high yield stress, high elongation at break and high ultimate strength (d). A hard and brittle material such as general purpose phenolic is characterized by high modulus and low elongation (e).

2.9 Flexural properties

Flexural properties are the ability of the material to withstand bending forces applied perpendicular to the beam. The stresses induced due to the flexural load are the combination of compressive and tensile stresses, as illustrated in Figure 2.23 [Rosato and Rosato, 1991]. The results from this test give the flexural modulus and flexural strength. Explanation of the terminology used in flexural testing is as follows:

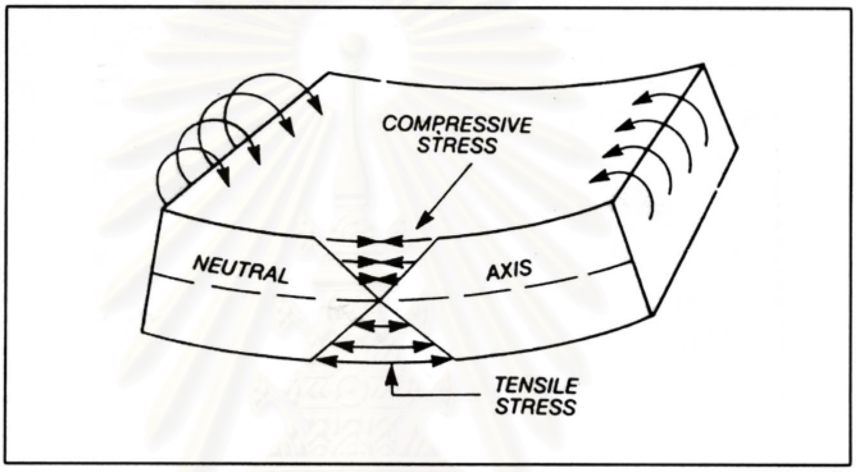


Figure 2.23 A Flexural test specimen being subjected to compressive and tensile stress [Rosato and Rosato, 1991].

2.9.1 Flexural modulus

The flexural modulus is represented by the slope of the initial straight line portion of the stress-strain curve. In addition, flexural modulus gives a good indication of the stiffness.

2.9.2 Flexural strength

Flexural strength is equal to the maximum stress in the outer fibers at the moment of break. However, many polymers do not break under the flexural test even after a large deflection. For this case (In such case), flexural strength at yield is reported when the maximum strain in the outer fiber of the specimen has reached five percent.

2.10 Impact properties

Impact properties represent the ability of plastic to absorb impact energy very rapidly. These properties can be measured in several ways. The most common method is the Izod impact. Other methods of testing are not directly comparable to this test. Even when the same testing technique is used, the results may vary considerably since the test is sensitive to sample thickness, surface roughness and surface flaws. Using a notched sample for testing helps to limit the surface effects but adds a stress concentration at the tip of the notch that may not simulate service conditions.

The objective of Izod impact test is to measure the notch sensitivity of the different polymers to the impact energy and not the toughness. The results are expressed in terms of kinetic energy. The energy required to break a standard specimen is actually the sum of energies needed to deform the specimen, to initiate fracture of specimen, and to propagate the fracture across the specimen.

Impact properties are strongly dependent upon the temperature, degree of crystallinity and molecular weight. At lower temperature, the impact resistance is reduced drastically, especially at the glass transition temperature. Increasing the percentage of crystallinity and decreasing the molecular weight decreases the impact resistance.

2.11 Hardness

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation, or scratching. Hardness is purely a relatively term and should not be confused with wear and abrasion resistance of plastics material. For example, polystyrene has a high Rockwell hardness value but a poor abrasion resistance. Two of the most common used hardness tests for plastics are the Rockwell hardness and Durometer hardness test. Rockwell hardness is used for relatively hard plastics such as polystyrene, nylons, acetals and acrylics. For softer materials such as flexible PVC and thermoplastic rubbers, Durometer hardness is often used.

Rockwell hardness test measures the net increase in depth impression as the load on an indenter is increased from a fixed minor load to a major load and then returned to a minor load. The reason for using both minor and major loads is as follows. When the indenter is forced into the specimen both elastic and plastic deformation occurs. But hardness is a measurement of permanent plastic deformation. Therefore the load must be removed before the hardness is taken. However, the minor load is left on the specimen. This ensures that the indenter remains in full contact with the specimen when the reading is taken.

CHAPTER III

LITERATURE REVIEW

In this chapter, the literature reviews on recycled HDPE are summarized.

Dintcheva *et al.* [2001] studied the characterization and reprocessing of greenhouse films mainly made of polyethylene. They found that the degree of crystallinity of post-consumer film is higher than that of virgin film. The viscosity, the tensile strength and the elongation at break of post-consumer film is lower than that of virgin film. They claimed that this is due to the decrease of the molecular weight of post-consumer film, caused by photo-oxidative degradation during use. In addition, the mechanical properties decrease with the number of reprocessing steps and with increasing level of photo-oxidative degradation. However, the mechanical properties of the recycled post-consumer film is rather good even after many extrusion passes.

Boldizar *et al.* [2000] studied the recycling of post-used, uncolored HDPE bottles. The lifetime of bottle is expected to be between 1 and 2 years. The recycled materials were examined by a testing procedure consisting of reextrusion and subsequently accelerated by thermo-oxidative ageing. It was found that the HDPE material did not degrade to any significant degree during 10 cycles of stimulated recycling. In addition, the effect of addition of stabilizer “Recyclostab 411” (R411) from Ciba Specialty Chemicals, Ltd. was also studied. The addition of 0.1 wt% R441 in the post-used HDPE at each extrusion step in a series of 10 cycles of stimulated recycled indicated an increases in oxygen induction temperature, average molecular weight and stress at break. This might be the result of crosslinking and/or molecular enlargement, which occurred in HDPE during processing at low oxygen concentration and high temperatures as R411 can react with oxygen leading to a decrease in the oxygen concentration in the melt.

Kartalis *et al.* [2000] studied the effect of artificial weathering on the properties of post-used, yellow-pigmented HDPE crates, using Recyclossorb 550 (R550) from Ciba Specialty Chemical, Ltd. as the stabilizer. They found that tensile impact strength of the nonrestabilized grade dramatically decreases after 1000 hours of exposure, because of severe photo-oxidative degradation. On the other hand, the addition of the R550 improves the light stability of the recycled HDPE crates, resulting in excellent retention of tensile impact strength for at least up to 8000 hours in artificial exposure. Therefore, it was elucidated that the light stability of restabilized post-used HDPE crates was improved, ensuring its reuse in the original application.

Kartalis *et al.* [1999] studied the mechanical recycling of post-used, yellow-pigmented HDPE crates using restabilization technique. Recyclossorb 550 (R550) from Ciba Specialty Chemicals, Ltd. was used as the stabilizer. During the reprocessing procedure, the melt flow index of post-used HDPE crates is decreased with an increasing in the melting temperature and the number of extrusion, caused by branching phenomena along the polymer structure. The addition of R550 significantly improves processability during repeated remelting cycle. Moreover, the mechanical tests have shown that the addition of R550 is mandatory for elongation at break improvement. This can be explained by the well-known fact that the %elongation at break decreases with branching of the nonrestabilized post-used HDPE crates, leading to limitation in the free volume between the polymer chains and to an embrittlement increase. Tensile strength and tensile impact strength of restabilized HDPE crates are more or less the same as post-used HDPE crates.

Pfaendner *et al.* [1998] presented the concept for the improving of recycled polymer by restabilization. They suggested that all products from outdoor applications intended to reuse require an adjusted restabilization according to the active stabilizer residues. For the HDPE waste bins, results on natural weathering tests have shown a decrease in tensile impact strength of post-used HDPE bins without R550 within very short time. Addition of R550 can prevent degradation offering the opportunity to fulfill existing standard.

Dintcheva *et al.* [1997] studied the recycling of plastics from packaging. The recycled material is a blend of low density polyethylene (LDPE) and linear low density polyethylene (LLDPE). It was found that the mechanical and rheological property of the recycled polymer depending on the processing condition, temperature and apparatus. The elongation at break and the viscosity of the recycled materials prepared in a closed mixer is lower than those of the samples reprocessed in a single-screw extruder and a twin-screw extruder. High processing temperature and high residence times strongly enhance the degradation processes and reduce the mechanical properties, particularly the elongation at break. The addition of ethylene vinyl acetate copolymer (EVA) in the recycled materials resulted in an improvement of the elongation at break. A possible use of this recycled plastic is for the production of low pressure pipes but the properties are lower than those of virgin pipe grade polyethylene.

Loultcheva *et al.* [1997] studied the recycling of HDPE containers. The rheological and mechanical properties of recycled HDPE depend on the reprocessing conditions. They found that the viscosity of recycled HDPE at low shear rate increased with an increasing number of extrusions, because of the formation of chain branching. High residence times in the extruder lead to a decrease of mechanical properties, particularly the %elongation at break. In addition, the %elongation at break and tensile strength of the HDPE recycled in a twin-screw extruder is higher than those of HDPE recycled in a single-screw extruder. The addition of stabilizer (Irganox 1010, Irganox 1076 and Irgafos 168) in HDPE has shown to maintain the initial properties of HDPE even after several recycling cycles.

Zahavich *et al.* [1997] studied the effects of multiple extrusion passes on the properties of recycled HDPE from blow molded bottle resin. The complex viscosity at low frequency of recycled HDPE was increased with an increasing number of extrusions. They used the cross over point of G' and G'' (elastic storage and loss modulus) to measure relative changes in the molecular weight distribution (MWD). It was indicated that MWD of both recycled and virgin HDPE increased with an increase in extrusion passes. Form the results on DSC, the degree of crystallinity of recycled HDPE decreased as increasing the extrusion passes from zero to four passes. It was reported that the degradation mechanisms such as chain scission and chain branching could be considered to be responsible for this behavior.

Pages *et al.* [1996] studied the structural changes and the mechanical properties variation of HDPE when exposed to weathering aging in Canadian winter. Results on FTIR spectroscopy have shown that the changes in HDPE micro-structure occurred in the polymer chains causing the degradation. The alterations of micro-structure are defined by a series of mechanisms composed of the chain breaking, chain branching and oxidation phenomena. The configuration changes obviously influence the degree of crystallinity caused by the formation of bulky groups, which leads to an increase of the amorphous content. Therefore, the degree of crystallinity was decreased with increasing exposure times. The impact energy is remarkable affected by aging phenomena which has caused by the formation of bulky groups, imparting stiffness of polymeric chains. Other mechanical properties evaluated (tensile strength and Young's modulus) do not vary significantly with exposure times.

Takahashi [1996] studied the performance of the blend of 25% post-consumer recycled HDPE blow molded bottles and 75% virgin HDPE. He found that the addition of 25% recycled HDPE to the virgin polymer slightly decreases melting temperature, heat of fusion, dynamic modulus and tensile impact energy. The small changes in properties of blended material with 25% recycled content was not expected to significantly affect the performance of the base polymer.

Jabarin and Lofgren [1994] studied the effects of photooxidation on the properties and structure of HDPE. Extruded sheets of HDPE samples were exposed to natural Arizona sunlight for 1 month to 6 months. It was found that weathering exposure time has an extremely effects on a decrease in the %elongation at break of HDPE and a decrease in the molecular weight as a result of photo-oxidative degradation. In addition, the results on FTIR spectroscopy can be elucidated that photo-oxidative degradation occurred during weathering exposure time because of the formations of carbonyl and vinyl groups.

Pardon *et al.* [1993] studied the viscoelasticity and structure of reextruded HDPE melts. They observed that when a polymer is reextruded at 190 ^{0}C, the melt viscosity increased steadily. HDPE basically contains a significant amount of vinyl end-groups but few methyl units and no trans-unsaturation within the chain. Therefore, chain branching is significant phenomena occurred during extrusion because it would lead to the reduction in vinyl content noted in the infrared absorption experiments. From the results on die-swell, the die-swell of HDPE increased with an increasing number of extrusions. This can be explained by the fact that die-swell increases with chain branching. It was concluded that chain branching and crosslinking have occurred during the reprocessing.

Hinsken *et al.* [1991] studied the degradation of HDPE during melt processing by multiple extrusion. They reported that the melt flow index was decreased with an increasing number of extrusion. In addition, the average molecular weight (by GPC technique) and the low shear viscosity were increased with an increasing number of extrusions. Results on FTIR spectroscopy have shown that the concentration of vinyl groups in the virgin resin has dropped after an increasing number of extrusions. It can be indicated that alkyl radicals react with vinyl groups. This reaction leads to an increase in the molecular weight due to chain branching and crosslinking. Therefore, it was concluded that chain branching and crosslinking must be considered to be dominant when this polymer is processed.

Pattanakul *et al*. [1991] studied the effects of the composition of recycled HDPE from milk bottles on the physical and mechanical properties changes. From the results on GPC, the number average molecular weight of HDPE from milk bottles was slightly decreased while the weight average molecular weight was increased comparing with virgin HDPE, resulting in a broadening in the molecular weight distribution. It was suggested that chain scission and crosslinking reactions have probably occurred during molding process. In addition, it was shown that no change in the flow properties occurred and no effect of recycled HDPE composition on tensile strength was seen. But, the elongation at break was the mechanical property mostly affected by the composition of recycled HDPE. Moreover, they suggested that the recycled HDPE from milk bottles was a material with useful properties not largely different from those of virgin materials and could be used, at an appropriate concentration in virgin HDPE, for different applications.

CHAPTER IV

PROPERTIES OF POST-USED HDPE CRATES

4.1 Materials

High density polyethylene used in this study is from plastic crates for soft drink bottle transportation supplied by Srithai Superware Public Co., Ltd. and Thai Pure Drinks Co., Ltd. They are red HDPE crates used for 10-ounce soft drink bottle, as shown in Figure 4.1.

Figure 4.1 HDPE crates for soft drink bottle transportation.

All materials can be classified according to different utilization time as shown in Table 4.1, including virgin HDPE granule.

Table 4.1 Classification of HDPE samples.

Code	Material	Source
VIRGIN	Virgin HDPE	Srithai Superware Public Co., Ltd.
HDPE#0	New HDPE crates	Srithai Superware Public Co., Ltd.
HDPE#3	3-year used HDPE crates	Thai Pure Drinks Co., Ltd.
HDPE#8	8-year used HDPE crates	Thai Pure Drinks Co., Ltd.

Post-used HDPE crates were washed in water, dried and then shredded into granule as shown in Figure 4.2. The size of the HDPE granule is about 5 mm.

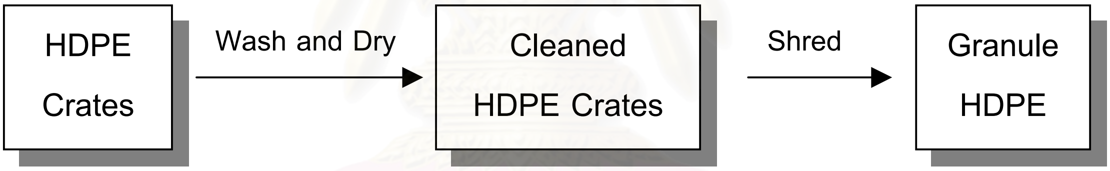


Figure 4.2 Material preparation of HDPE crates for soft drink bottle transportation.

4.2 Samples preparation

Specimens for mechanical property testing were prepared by compression molding technique. The size of the mold is 16 cm in width, 24 cm in length and 3 mm in depth. The granule of HDPE crates was heated up to 190 °C for 7 min, compressed at the pressure of 160 kg/cm^2 for 5 min, and then cooled down with water to 25 °C for 10 min. Finally, the HDPE compressed sheet was cut into a standard size for mechanical testing.

Specimens for viscosity measurement were prepared by compression molding. The size of the mold is 1 cm in diameter and 1 mm in depth. Materials were heated up to 190°C for 5 min, compressed at the pressure of 160 kg/cm^2 for 5 min, and cooled down in atmosphere.

Samples for density measurement were extruded from the die of the melt flow index equipment. Four gram of HDPE granule was charged to the heated barrel at 190 °C. A piston was placed inside the barrel. Load of 2.16 kg was placed on top of the piston. The melted HDPE granule was extruded from the die and collected. Samples for density measurement were annealed in ethylene glycol at 120 °C for 1 hour and cooled to 30°C at the cooling rate of 1.5 °C/min. Annealed samples were cut into pieces with the length of 5 mm.

4.3 Experimental procedure

4.3.1 Characterization of HDPE

4.3.1.1 Molecular weight and molecular weight distribution

The molecular weight and molecular weight distribution of HDPE samples were determined by gel permeation chromatography (GPC) carried out on "Waters HT-GPC150C" instrument (Bangkok Polyethylene Public Co., Ltd.) at 135 ^{0}C. The solvent used was 1,2,4-trichlorobenzene (TCB). The instrument is composed of three μ styragel columns shown in Table 4.2. The three columns were calibrated by using nine monodisperse polystyrene standards (molecular weight = 5970, 9100, 28500, 66000, 96400, 156000, 834000, 1290000 and 2880000). The mobile phase (TCB) flow rate of 1 mL/min was maintained throughout the work. Resin samples were dissolved in the solvent (0.1 % w/v) at 100 ^{0}C and kept in the GPC injector compartment for 1 hour before injection. The molecular weight and molecular weight distribution of soluble fractions were determined by computer software.

Table 4.2 Efficiency of μ styragel columns.

Column	Effective Molecular Weight
HT3	500 – 30,000
HT4	5,000 – 600,000
HT5	50,000 – 4,000,000

4.3.1.2 Melting temperature and degree of crystallinity

The melting temperature (T_m) and the degree of crystallinity of all materials were evaluated by differential scanning calorimetry (DSC) technique, using a “NETZSCH DSC 2000” (Scientific and Technological Research Equipment Center, Chulalongkorn University). About 5 mg of the sample was placed in an open aluminum pan. Each sample was subjected to a two-stage heating process. The first stage is to heat the sample from 30 to 180°C at the heating rate of 10 °C/min and cool down to 30 °C at the rate of 10 °C/min. This was done to remove any inconsistencies in the samples in terms of thermal history. The second stage was a repeat of the first stage heating cycle. Experiments were performed under a nitrogen atmosphere to prevent oxidative degradation. Melting temperature and heat of fusion (ΔH) were analyzed from the second run of each sample. Degree of crystallinity, based on a value of 293 J/g as the heat of fusion of 100% crystalline polyethylene [Wunderlich, 1973], can be calculated by the following equation:

$$\text{Degree of crystallinity of the sample} = \frac{[\Delta H \text{ sample}] \times 100}{[\Delta H \text{ 100\% crystalline polyethylene}]} \quad (4.1)$$

4.3.1.3 Density

The density of plastic materials is defined as the weight per unit volume. The density gradient technique was used to determine the density of plastics very accurately (carried out at Bangkok Polyethylene Public Co., Ltd.), by observing the level of test specimen which sinks in a liquid column exhibiting a density gradient, in comparison with standard specimens of known density. Density gradient columns are columns of miscible liquid with various concentrations, the densities of which increase uniformly from top to bottom. Specimen of unknown density is dropped into the column at 23 °C. After 10 min, the specimen would float steadily in the column. The height of the test specimen and the two standard floats with certain densities will be recorded. The density can be calculated using following equation. Schematic diagram of density gradient technique is shown in Figure 4.3.

$$\text{Density at } x = a + [(x - y)(b - a)/(z - y)] \qquad (4.2)$$

where: a and b = the densities of the two standard floats,

y and z = the height of the two standard floats above the reference level and

x = the height of the sample above the reference level.

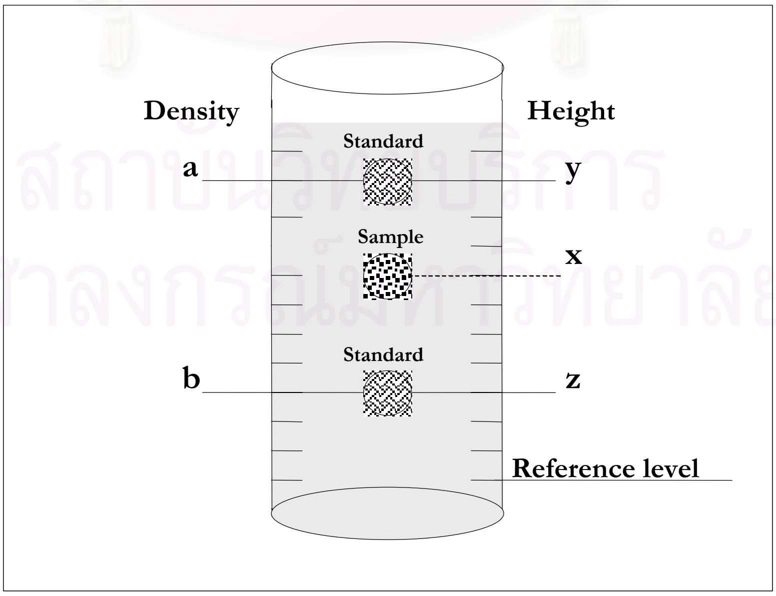


Figure 4.3 Schematic diagram of density gradient technique.

4.3.2 Processability

4.3.2.1 Melt flow index

Melt flow index was measured by using “KAYNESS GALAXY I” extrusion plastometer (Department of Material Science, Faculty of Science, Chulalongkorn University) with a piston load weight of 2.16 kg at 190 °C. The dimension of the die is 1.18 mm in diameter and 8 mm in length. The test conditions are set according to ASTM D1238. The schematic diagram of melt flow indexer is shown in Figure 4.4.

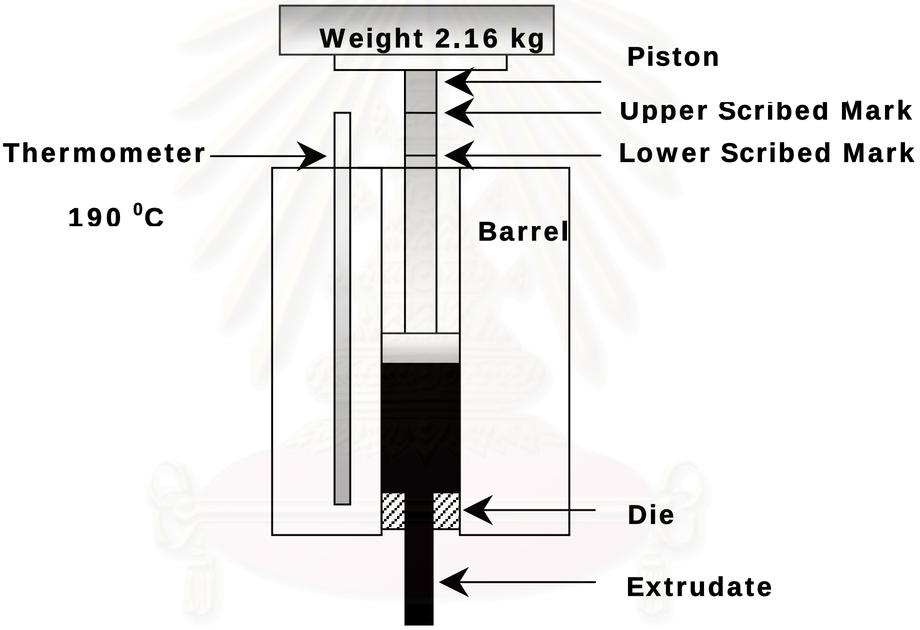


Figure 4.4 Schematic diagram of melt flow indexer.

Eight gram of HDPE was charged to the heated barrel. A piston was placed inside the barrel with a load of 2.16 kg on top of the piston. The initial extrudate were discarded. The experiment was started when the lower scribed mark reached the top of the barrel and stopped when upper scribed mark reached the top of the barrel. The extrudate was collected every 1 minute and left to cool down before being weighted accurately. The melt flow index was calculated from the weight of material extruded for 10 minutes. The results of the test are the average values of five samples. Raw measured data are provided in Appendix.

4.3.2.2 Viscosity

The viscosity of scrap HDPE crates was measured by using "HAAKE RHEOMETER RS 75" (Department of Chemical Engineering, Faculty of Engineering, Burapha University). The tests were performed in dynamic mode using a parallel-plate geometric head. The parallel-plate geometric head is shown in Figure 4.5. The compressed sample disc (1 cm in diameter and 1 mm in height) was placed between the parallel-plate and the frequency sweep experiment was performed between 100 to 0.01 Hz at 190 °C. All measurements were carried out in the linear viscoelastic zone, which was at the applied stress of 1000 Pa.

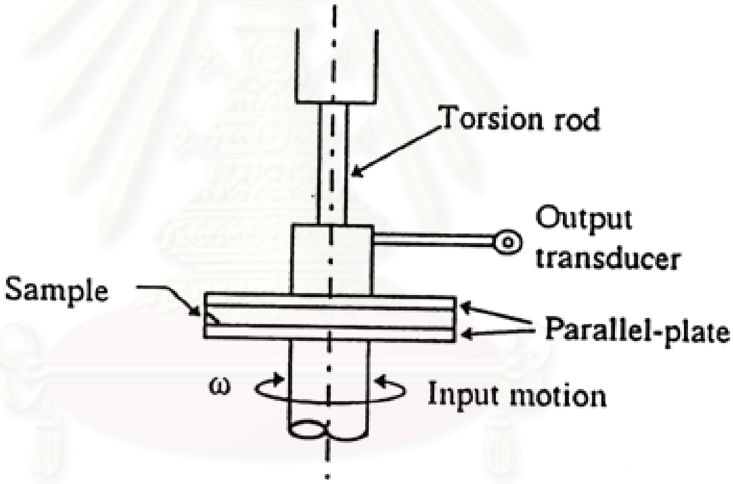
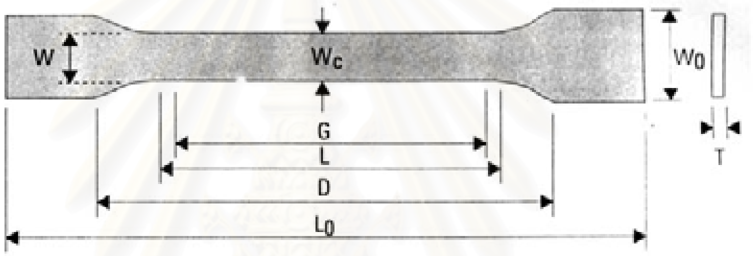


Figure 4.5 Parallel-plate geometric head.

4.3.3 Mechanical properties

4.3.3.1 Tensile testing

Tensile testing was measured using “HOUNSFIELD” universal testing machine (Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala Institute of Technology). The test conditions follow ASTM D638. For tensile test, dumbbell shaped samples type II were cut with the dimensions shown in Figure 4.6. Specimen dimensions of type II are suitable for material that does not break in the narrow section.



Dimensions	Type II, mm
W - Width of narrow section	6
L - Length of narrow section	57
W_0 - Width overall	19
L_0 - Length overall	183
G - Gage length	50
D - Distance between grips	135
T - Thickness	7 or under

Figure 4.6 Tensile test specimen and dimensions followed ASTM D638.

The determination of tensile properties was done at constant crosshead speed of 50 mm/min with a 1000 N load cell. The results from the tests include Young's modulus, tensile strength at yield, elongation at break and stress–strain curves. Average value of five specimens is reported. Raw measured data are provided in Appendix.

4.3.3.2 Flexural testing

Flexural testing was measured by using "HOUNSFIELD" universal testing machine (Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala Institute of Technology). The test conditions follow ASTM D790. The specimen dimensions are 4.5 mm in thickness, 10 mm in width and 90 mm in length. The specimens arranged in a three-point bending configuration with L/D ratio = 16 were tested at a constant crosshead speed of 19.2 mm/min and 72 mm for supported span. The flexural testing is shown in Figure 4.7.

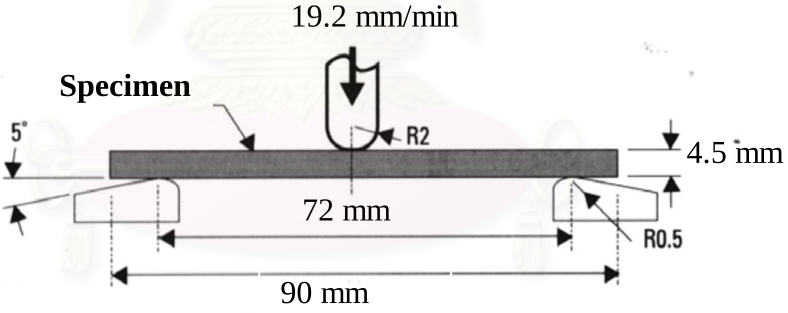


Figure 4.7 Flexural testing.

For flexural test, procedure B of ASTM D790 was selected for HDPE which undergoes large deflections during testing. The test would be terminated when the mid-span deflection has reached 9.6 mm. The results of the tests are the average values of five samples. Raw data are provided in Appendix.

4.3.3.3 Impact testing

Izod impact test was carried out according to ASTM D256 on a “CEAST” pendulum impact tester (Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala Institute of Technology). The dimensions of test specimens are 12.75 mm in width and 63.5 mm in length. Notching machine was used to make a notch at the depth of 2.54 mm. The specimen of Izod type test is shown in Figure 4.8.

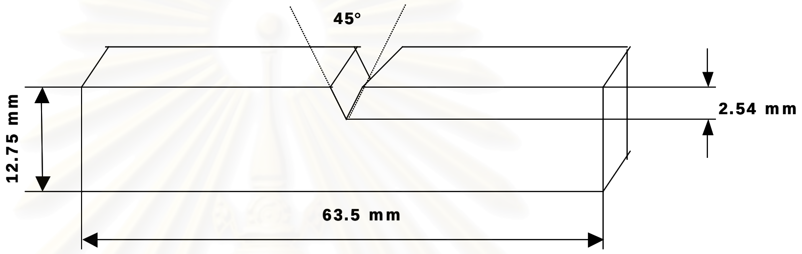


Figure 4.8 Dimensions of Izod impact test.

The apparatus for Izod impact test is shown in Figure 4.9. The test specimen was clamped into the position that the notched end of the specimen faced the striking edge of the pendulum. The pendulum hammer was released, allowed to strike the specimen. The lightest potential energy of pendulum hammer was first used as expected to break each specimen. In this case, the proper potential energy of pendulum hammer is 2 J. Impact resistance results are defined as the recorded impact energy (in joules) used to break the test specimen, divided by the specimen area at the notch. The results of the tests are the average values of ten samples. Raw data of Izod impact test are given in Appendix.

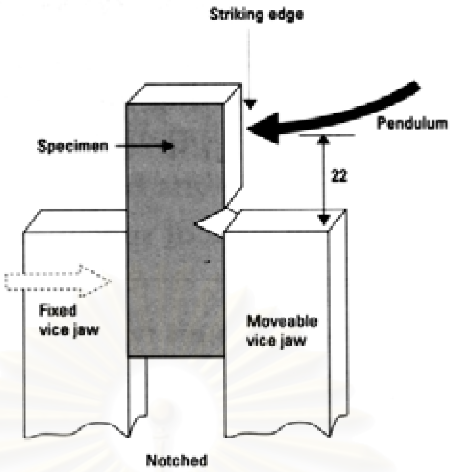


Figure 4.9 The apparatus for Izod impact test.

4.3.3.4 Hardness testing

The Rockwell hardness of samples was determined by using the "MATSUZAWA" Rockwell hardness (Department of Materials and Metallurgical Engineering, Faculty of Engineering, Rajamangala Institute of Technology). The test follows ASTM D785. The test specimen is a square sheet of 50 mm in length, 50 mm in width and 7.3 mm in depth. The Rockwell hardness tester is shown in Figure 4.10.

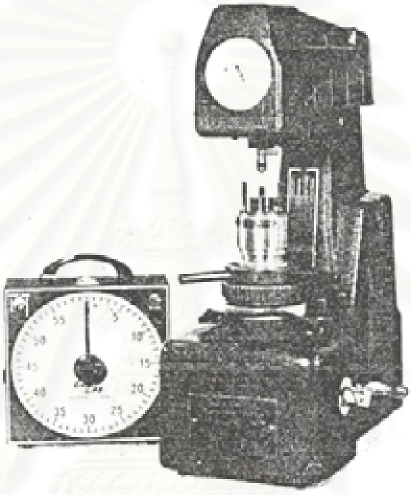
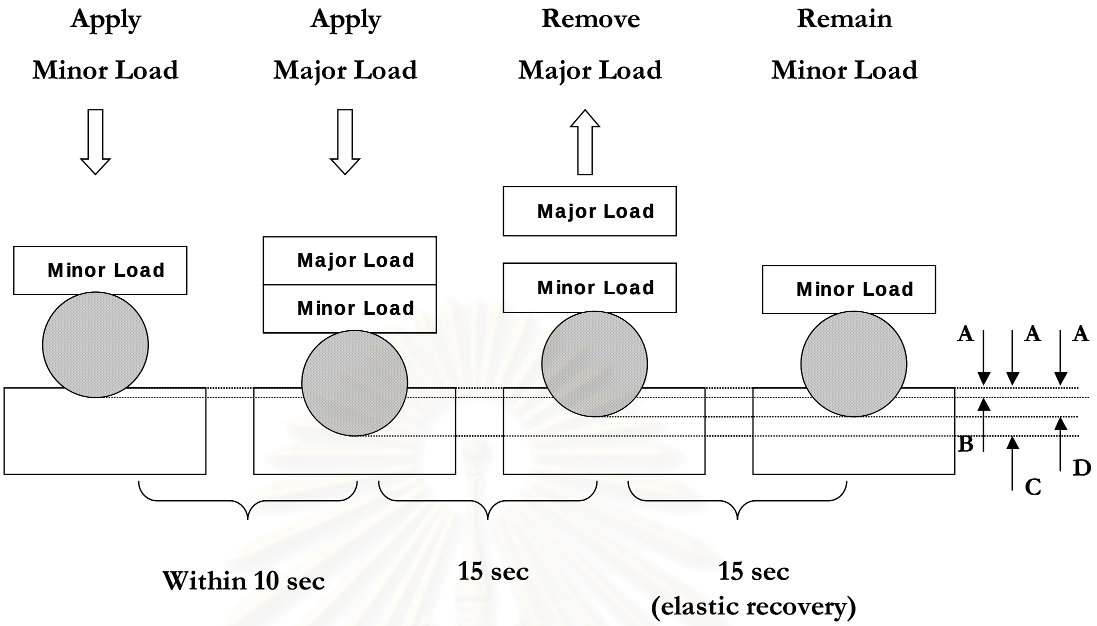


Figure 4.10 Rockwell hardness tester.

The value of Rockwell hardness should be between 30 to 100. Rockwell hardness of HDPE was determined in "R" scale. The diameter of the ball is 12.7 mm (0.5 inch). Test procedures of Rockwell hardness in "R" scale are shown in Figure 4.11. A minor loading ball of 10 kg was applied to a specimen (AB), following by a major load of 60 kg within 10 sec to set off the maximum reading (AC). After 15 sec, the major load was removed while the minor load was still applied for 15 sec before the final depth of penetration (AD) was recorded. The Rockwell hardness number equals to the difference between the final depth of penetration and the depth of penetration resulting from minor load (AD–AB). The Rockwell hardness measurement was reported for 5 times at different areas of the same specimen. The results of test are the average values of five samples. Raw data are given in Appendix.



Rockwell Hardness	Minor Load	Major Load	Indenter Diameter
Scale	Kg	kg	inch
R	10	60	0.5
Rockwell Hardness = AD-AB			

Figure 4.11 Test procedures of the Rockwell hardness in “R” scale.

4.4 Results and discussion

4.4.1 Characterization of HDPE

4.4.1.1 Molecular weight and molecular weight distribution

Table 4.3 presents the results on weight average molecular weight (M_w), number average molecular weight (M_n) and molecular weight distribution (MWD) of virgin HDPE and HDPE crates at various utilization time obtained from GPC technique. The molecular weight distribution curve of virgin HDPE and HDPE crates at various utilization time is plotted in Figure 4.12. From Table 4.3, the M_w of new HDPE crates is higher than that of virgin HDPE granule by 2.3% while the M_n of new HDPE crates is lower than that of virgin HDPE granule by 14.2%. It can be seen that a slight increase in M_w and a decrease in M_n, resulted in a broadening in the MWD. The result corresponds to the work on HDPE from milk bottles compared to virgin HDPE by Pattanakul *et al.* [1991]. It was reported that after molding process, a slight decrease in the M_n and an increase in the M_w had occurred, resulting in a broadening in the molecular weight distribution. They have suggested that chain scission and crosslinking mechanism probably has occurred during the processing. Further study by Epacher *et al.* [1999] on the effects of chemical reactions during the processing of stabilized polyethylene found that chemical reactions of the polyethylene can proceed in two main directions namely chain scission and crosslinking. The ratio of the two reactions depends on the amount of oxygen and amount of stabilizer added. In the absence of excessive oxygen, polyethylene has strongly tendency to crosslink.

Table 4.3 Molecular weight and molecular weight distribution of virgin HDPE and HDPE crates at various utilization time.

Code	M_w	M_n	MWD
VIRGIN	204,504	48,684	4.2
HDPE#0	209,245	41,744	5
HDPE#3	208,445	35,996	5.8
HDPE#8	208,451	37,152	5.6

From Table 4.3, the M_w of HDPE crates at various utilization time is, more or less, consistent, but the M_n of HDPE crates at the utilization time of 3 and 8 years is lower than that of new crates by 13.8% and 11%, respectively. Therefore, the MWD of HDPE crates at the utilization time of 3 and 8 years is broader than that of new HDPE crates by 16% and 12%, respectively. The broadening in the MWD can be obviously noticed in Figure 4.12. This indicates that the utilization time of HDPE crates has an effect on the molecular weight of HDPE crates, in particular M_n. This indicated that there is a change occurred in polymeric molecules during the use of the crates for bottle transportation, leading to changes in molecular weight. A change in HDPE molecules could be due to the degradation process of HDPE which is a result of competing reactions of crosslinking and chain scission that lead to molecular weight changes [Hinsken *et al.*, 1991]. Other reports related to the molecular weight and degradation process are the work of Jabarin *et al.* [1994] who found that weathering exposure time has an extremely effects on a decrease in M_n and M_w of HDPE film as a result of photo-oxidative degradation. Valadez-Gonzalez, A., *et al.* (1999) reported that irradiated HDPE, during the first 300 hours of exposure in an accelerated weathering chamber, the viscosity average molecular weight (M_v) decreases slightly and after that it drops abruptly in the irradiation time interval between 300 and 800 hours. It is evident from the results that there is chain scission reaction during the degradation of material.

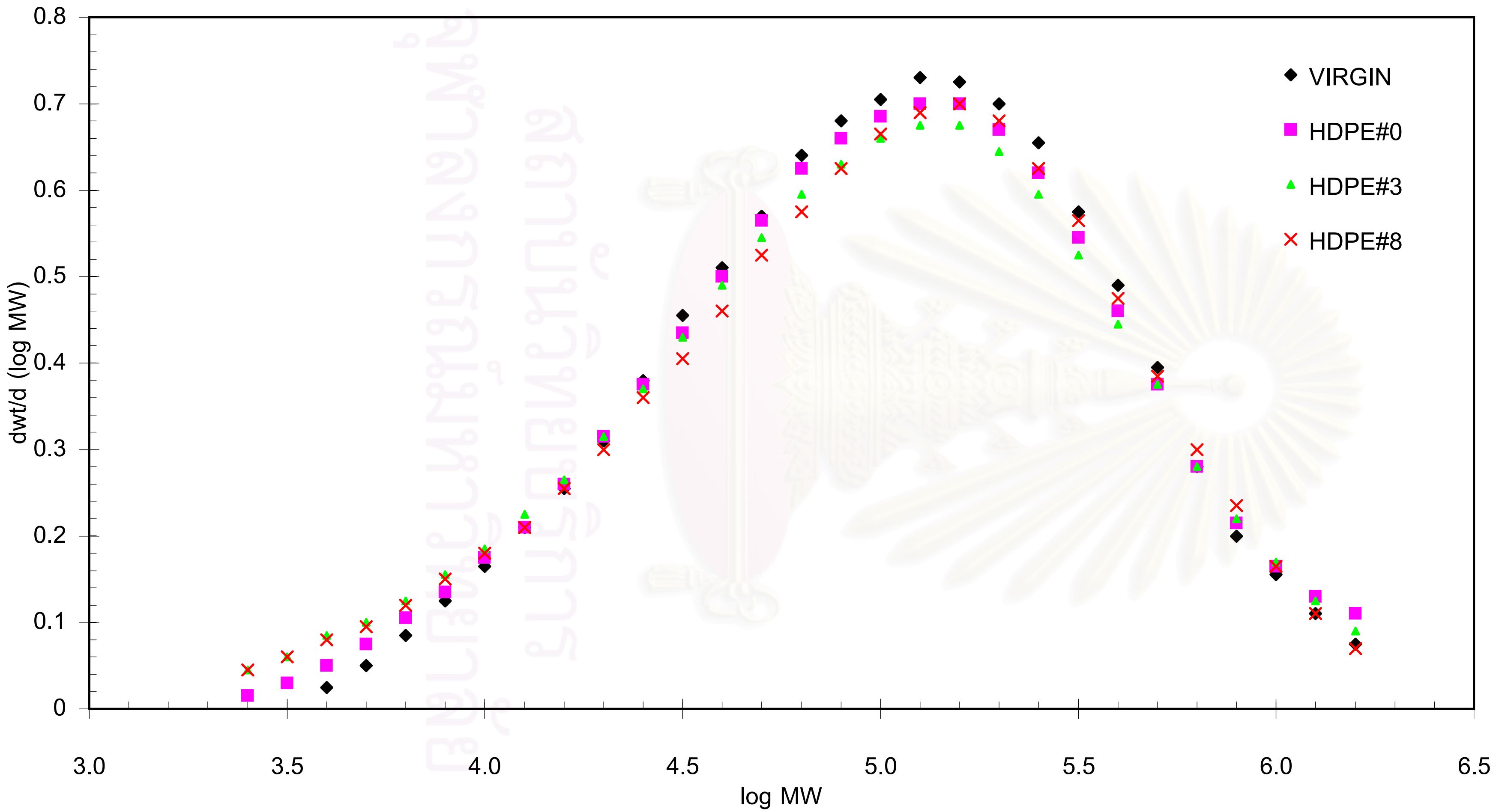


Figure 4.12 The molecular weight distribution curves of virgin HDPE and HDPE crates at various utilization.

4.4.1.2 Melting temperature and degree of crystallinity

From differential scanning calorimetry measurement, the melting temperature (T_m) and heat of fusion were determined. The heat of fusion can be converted to the degree of crystallinity. Figure 4.13 shows the melting temperatures of virgin HDPE and HDPE crates at various utilization time. The melting temperatures vary in a narrow range of 132 – 135 ^{0}C. It can be indicated that the melting temperatures of post-used HDPE crates does not change during the utilization time.

Normally, the degree of crystallinity can have tremendous influence on polymer properties. Figure 4.14 shows the degree of crystallinity of virgin HDPE and HDPE crates at various utilization time. Degree of crystallinity of virgin HDPE granule is higher than that of HDPE crates. The degree of crystallinity of HDPE crates at the utilization time of 3 and 8 years is lower than that of new crates by 9% and 6%, respectively. Degree of crystallinity of HDPE crates tends to decrease after a period of the utilization time. A decrease in the degree of crystallinity indicates that the crystallized region or the ordered structure in the HDPE chains has decreased while the amorphous part has increased.

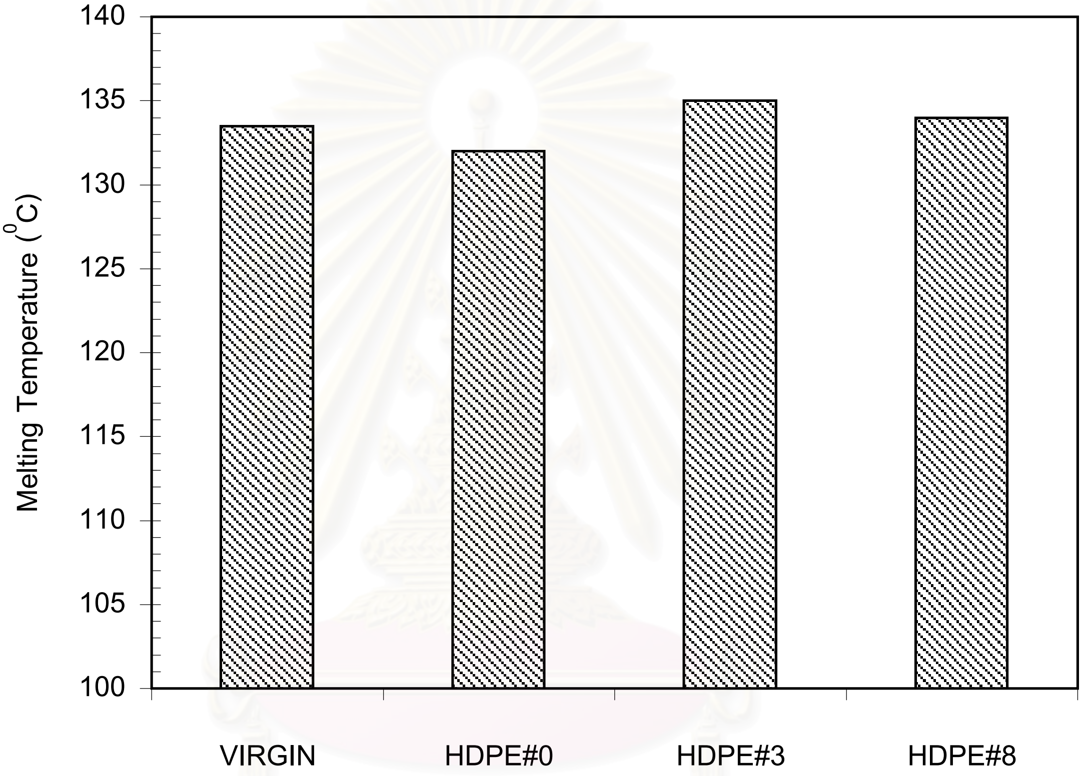


Figure 4.13 Melting temperature of virgin HDPE and HDPE crates at various utilization time.

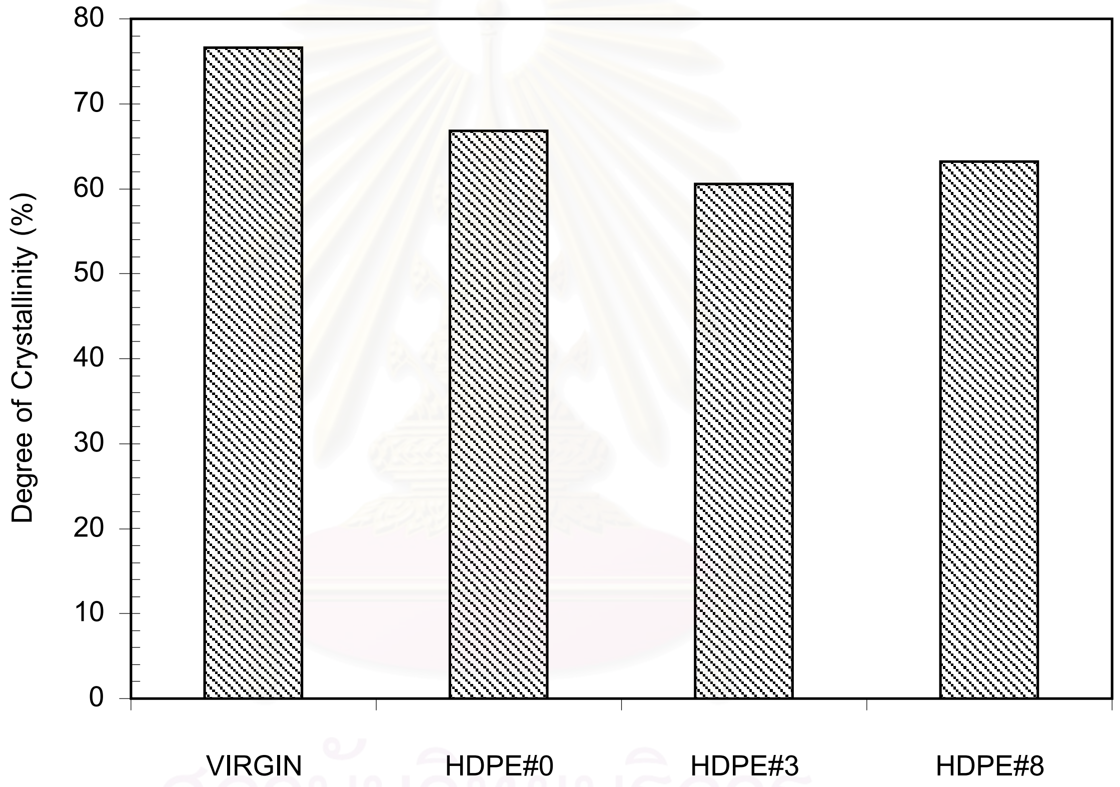


Figure 4.14 Degree of crystallinity of virgin HDPE and HDPE crates at various utilization time.

4.4.1.3 Density

Figure 4.15 shows the density of virgin HDPE and HDPE crates at various utilization time. The density of virgin HDPE and HDPE crates varies in a narrow range of 0.962 – 0.966 g/cm^3. It can be noticed that the density of virgin HDPE tends to be slightly lower than that of HDPE crates since there are many additives added during the processing of HDPE crates. The density of HDPE crates at various utilization time is, more or less, consistent.

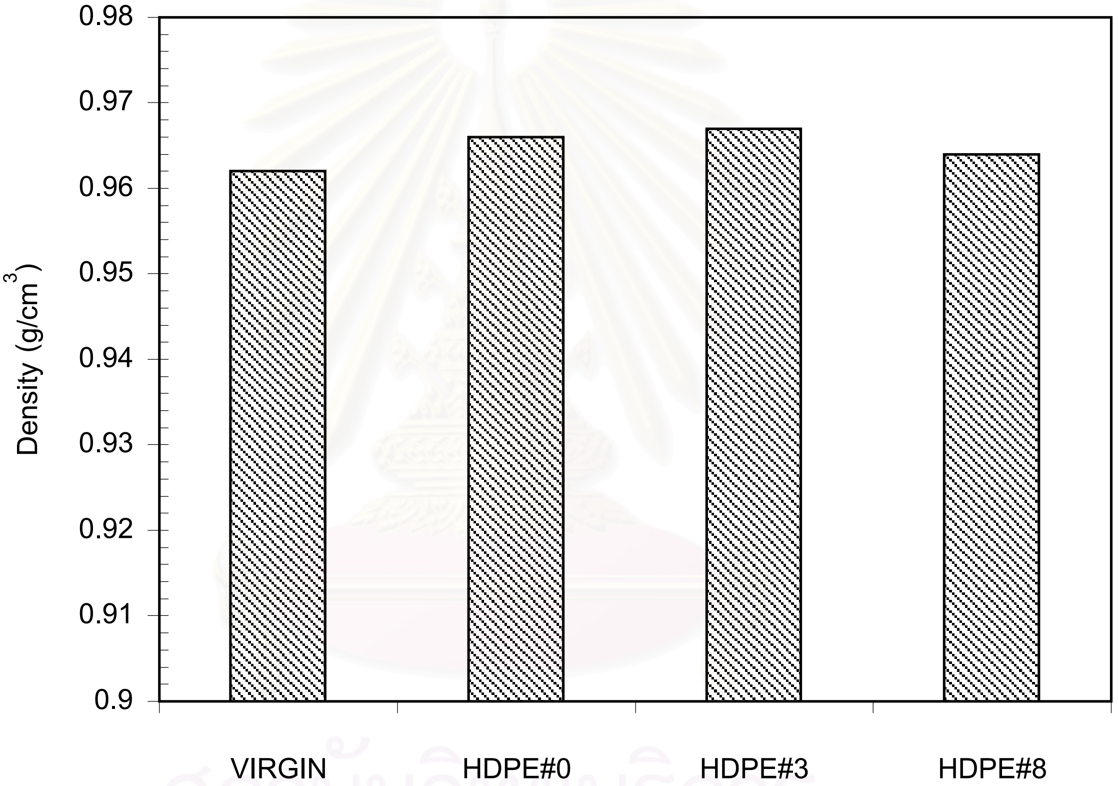


Figure 4.15 Density of virgin HDPE and HDPE crates at various utilization time.

4.4.2 Processability

4.4.2.1 Melt flow index

The melt flow index of virgin HDPE and HDPE crates at various utilization time is shown in Figure 4.16. The melt flow index of new HDPE crates is higher than that of virgin HDPE granule by 6.4%. This could be the result from several additives added during the injection process.

The utilization time of HDPE crates has an effect on the melt flow index of HDPE. In Figure 4.16, it can be seen that the melt flow index of HDPE crates is decreased with an increasing in the utilization time. HDPE crates after 3 and 8 years of utilization shows a decrease in melt flow index by 15.7% and 14.1%, respectively, in comparison with the melt flow index of new HDPE crates. This behavior could possibly be related to changes in the polymer chain structure since HDPE crates were exposed to a very hostile environment such as sunlight, heat, physical stress and impact during the use for bottle transportation. A drop in melt flow index could due to photo-oxidative degradation which might occur during the service life.

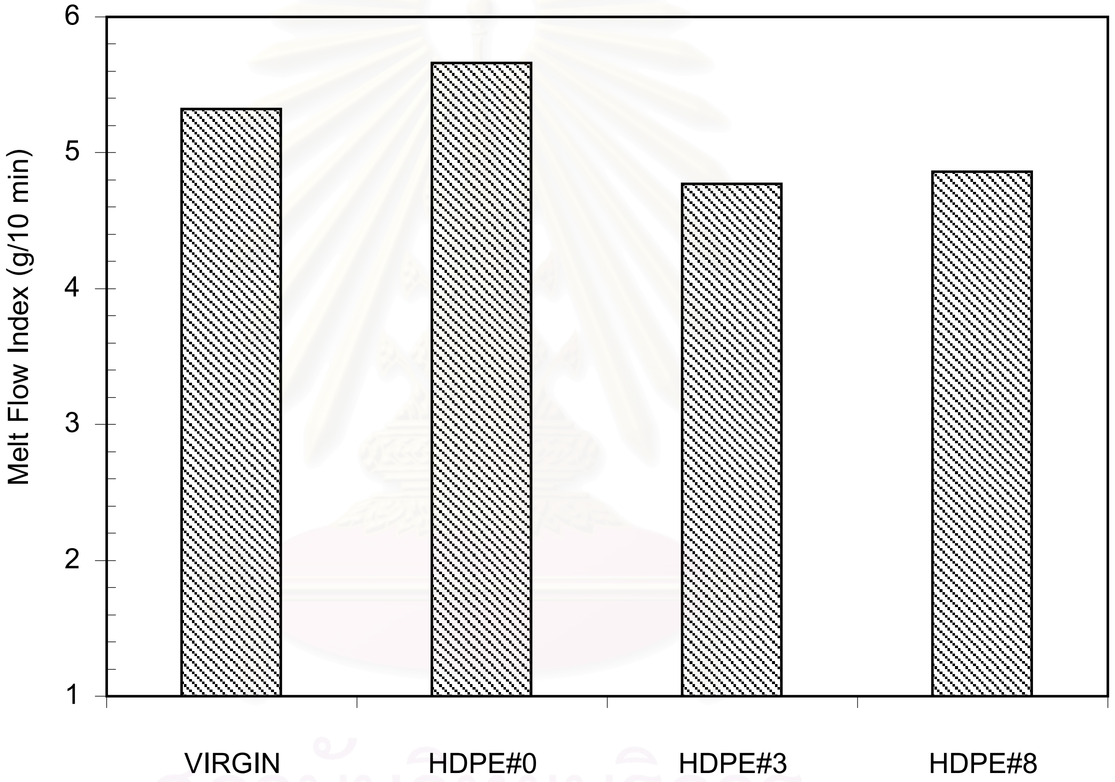


Figure 4.16 Melt flow index of virgin HDPE and HDPE crates at various utilization time.

4.4.2.2 Viscosity

The complex viscosity of virgin HDPE and HDPE crates at various utilization time is shown in Figure 4.17. The constant complex viscosity at very low frequency corresponds to the zero shear viscosity of the polymer which represents the flow ability in the melted state. At low frequency range (near 0.01 Hz), the complex viscosity tends to be consistent with reducing the frequency representing the zero shear viscosity. For clear comparison, the zero shear viscosity of virgin HDPE and HDPE crates at various utilization time is plotted in Figure 4.18.

It can be seen that the zero shear viscosity of new HDPE crates is lower than that of virgin granule by 5.6% and increasing in utilization time tends to increase the zero shear viscosity of HDPE. The zero shear viscosity of HDPE crates at the utilization time of 3 and 8 years increases by 33.6% and 21.7% from that of the new HDPE crates, respectively. Comparing with the previous results on melt flow index, increasing in the viscosity of used HDPE crates is in agreement with decreasing in the melt flow index of used HDPE crates. This is resulted from changes in polymer chain structure from photo-oxidative degradation as discussed earlier. Chain scission, chain branching and crosslinking would occur during the degradation process. Theoretically, increasing in M_w results in increasing in zero shear viscosity or steady shear viscosity. Unfortunately, our results on viscosity did not agree with the theory mainly due to changes in chain structure.

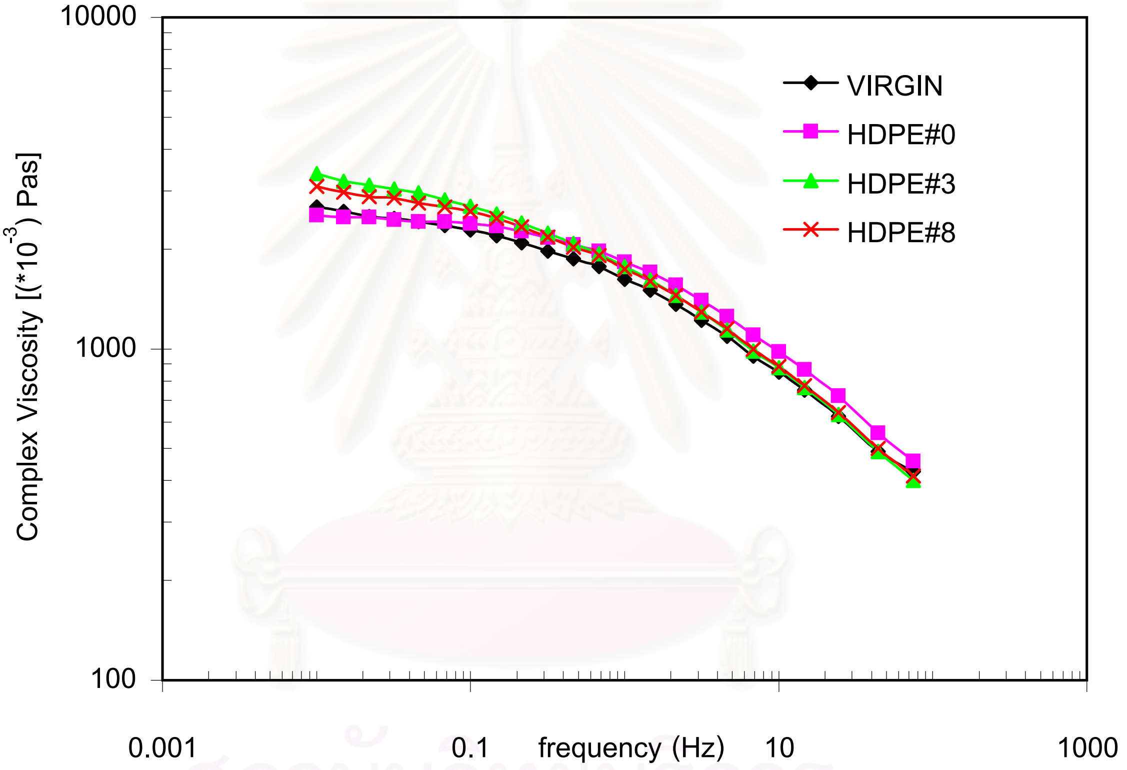


Figure 4.17 Complex viscosity of virgin HDPE and HDPE crates at various utilization time.

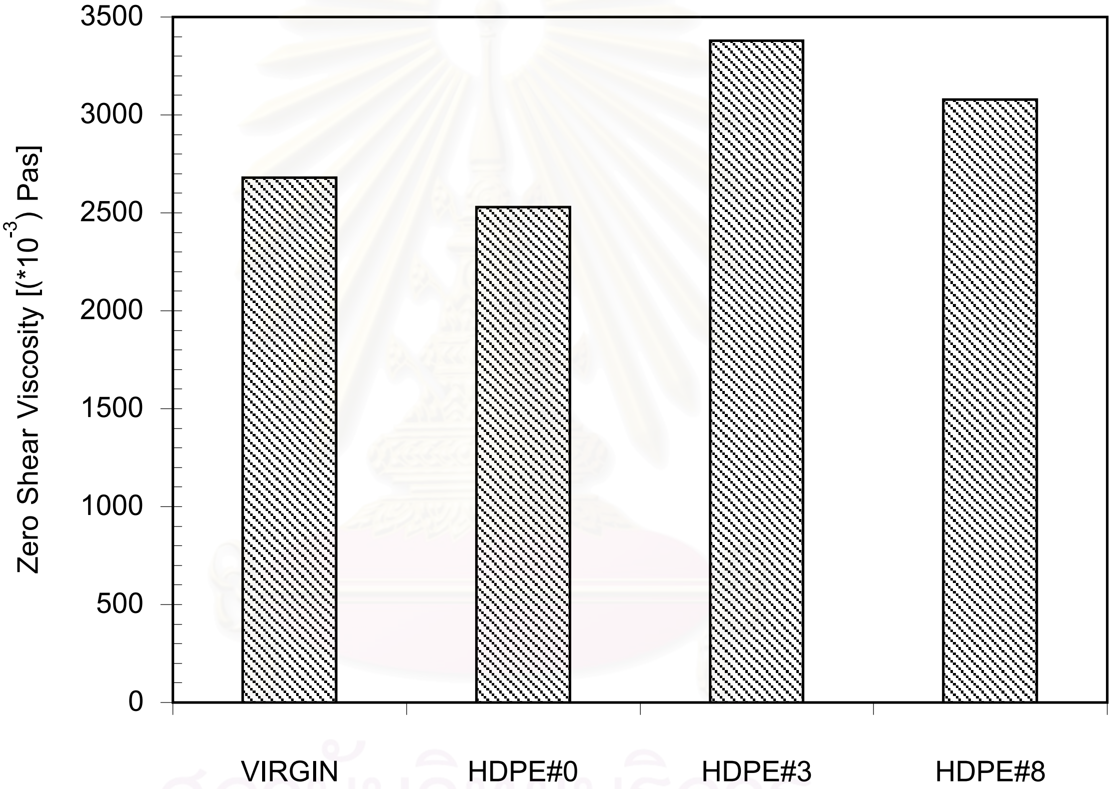


Figure 4.18 Zero shear viscosity of virgin HDPE and HDPE crates at various utilization time.

4.4.3 Mechanical properties

4.4.3.1 Tensile properties

Tensile properties are the most important indication of strength in a material to withstand tension. Table 4.4 presents the results of tensile properties of virgin HDPE and HDPE crates at various utilization time at a deformation rate of 50 mm/min. Figure 4.19 shows Young's modulus of virgin HDPE and HDPE crates at various utilization time. Young's modulus of new HDPE crates is higher than that of virgin HDPE granule by 10% while Young's modulus of HDPE crates at the utilization time of 3 and 8 years is higher than that of new HDPE crates by 66.7% and 63.7%, respectively. It is noticed that Young's modulus of HDPE crates is rapidly increased after uses.

Table 4.4 Tensile properties of virgin HDPE and HDPE crates at various utilization time.

Code	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	% Elongation at break (%)
VIRGIN	1474	24.91	>600
HDPE#0	1622	25.17	147
HDPE#3	2704	25.25	74
HDPE#8	2656	25.08	93

Figure 4.20 shows tensile strength at yield of virgin HDPE and HDPE crates at various utilization time. The results show that the tensile strength at yield of virgin HDPE is lower than that of HDPE crates. From Figure 4.20, the tensile strength at yield of HDPE crates varies in a very narrow range during their utilization time. In other words, the tensile strength at yield of HDPE crates at various utilization time is more or less the same as that of new HDPE crates.

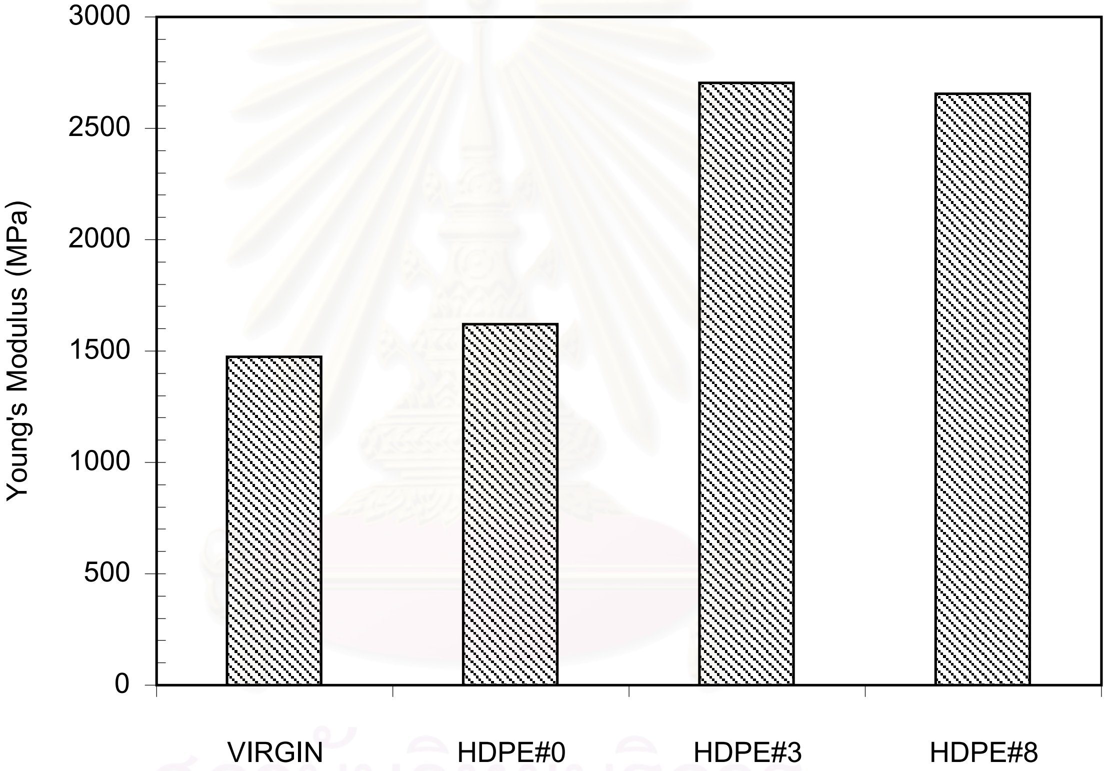


Figure 4.19 Young's modulus of virgin HDPE and HDPE crates at various utilization time.

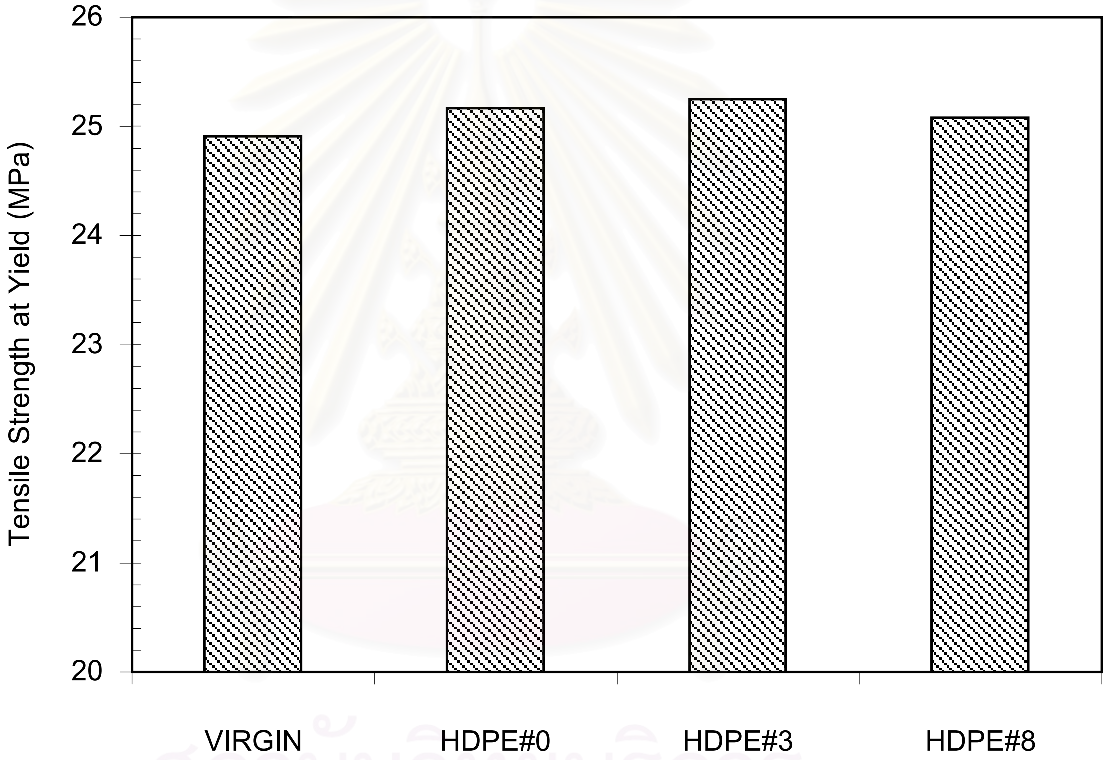


Figure 4.20 Tensile strength at yield of virgin HDPE and HDPE crates at various utilization time

The %elongation at break of virgin HDPE and HDPE crates at various utilization time is shown in Figure 4.21. Virgin HDPE granule can be elongated more than 600%. In all cases, decreasing in %elongation at break was observed for HDPE crates. The %elongation at break of HDPE crates at the utilization of 3 and 8 years is decreased by 49.7% and 36.7% from that of new HDPE crates, respectively. These results clearly indicate that the elongation at break is significantly decreased after uses, which could be resulted from outdoor exposure. The result is in agreement with the work of Jabarin and Lofgren [1994] who have studied the photo-oxidative degradation effects on the properties and structure of HDPE are found that weathering exposure time has an extremely effects on a decrease in the %elongation at break of HDPE. Their results indicated that HDPE embrittlement is influenced by chain scission.

Figure 4.22 shows stress-strain curves of virgin HDPE and HDPE crates at various utilization time. Generally, the stress-strain curves can be referred to the toughness of the plastic. The area under the curves can represent the softness, brittleness, hardness and toughness of polymers. In Figure 4.22, high Young’s modulus and high tensile strength at yield indicates that HDPE crates are hard and rather tough. Stress after the yield point has sharply decreased because some parts of the samples broke but some still extended. As a result, the tensile strength at break is low. It may be indicated that scrap HDPE crates were not thoroughly mixed due to the deflect mixing during processing and the irregular changes of properties in different parts of the crates during uses. In addition, the area under stress-strain curve which is proportional to the energy required to break for HDPE crates decreases for 3 and 8 years used HDPE crates compared to the new HDPE crates. This implies that the new HDPE crates are tougher than the used HDPE crates.

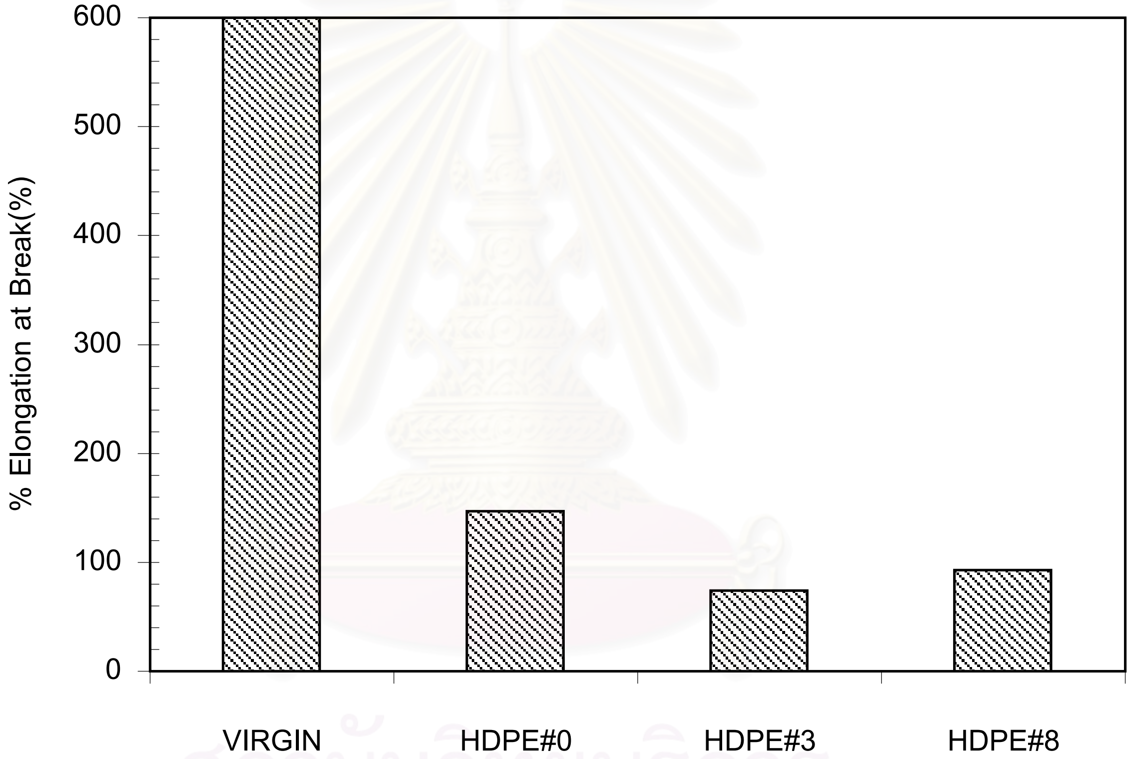


Figure 4.21 %elongation at break of virgin HDPE and HDPE crates at various utilization time.

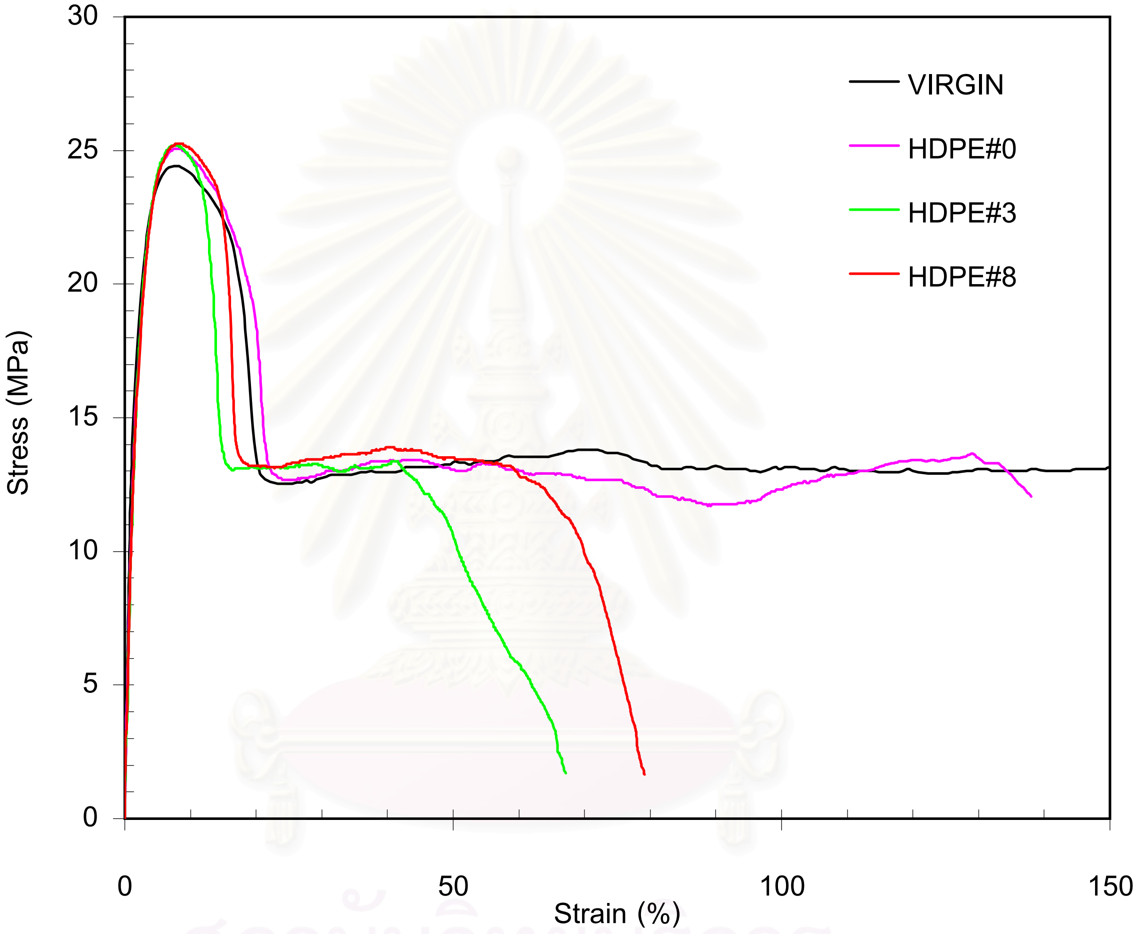


Figure 4.22 Stress-stain curves of virgin HDPE and HDPE crates at various utilization time

4.4.3.2 Flexural properties

Generally, flexural test is suitable for brittle polymers. HDPE used in this work seems to be too tough to rupture with in 5% strain limit suggested in ASTM D790. Therefore, the results presented in this section are the flexural modulus and the flexural strength at yield. Figure 4.23 shows the flexural modulus of virgin HDPE and HDPE crates at various utilization time. The flexural modulus of virgin HDPE and HDPE crates varies in a narrow range of 910 – 973 MPa. It can be indicated that the flexural modulus of post-used HDPE crates does not change during the utilization time.

Figure 4.24 shows the flexural strength at yield of virgin HDPE and HDPE crates at various utilization time. The flexural strength at yield of virgin HDPE is about the same as that of new HDPE crates. The flexural strength at yield of HDPE crates at the utilization of 3 and 8 years decreases by 7.5% and 9.6% from that of new HDPE crates, respectively. It can be said that the flexural strength at yield of HDPE crates is decreased with an increasing in the utilization time that could be a result of decreasing in the degree of crystallinity of HDPE crates (section 4.4.1.2). Generally, the crystalline part of polymer structure represents the strength of the polymer. Decreasing in crystalline part lowers the strength of the polymer.

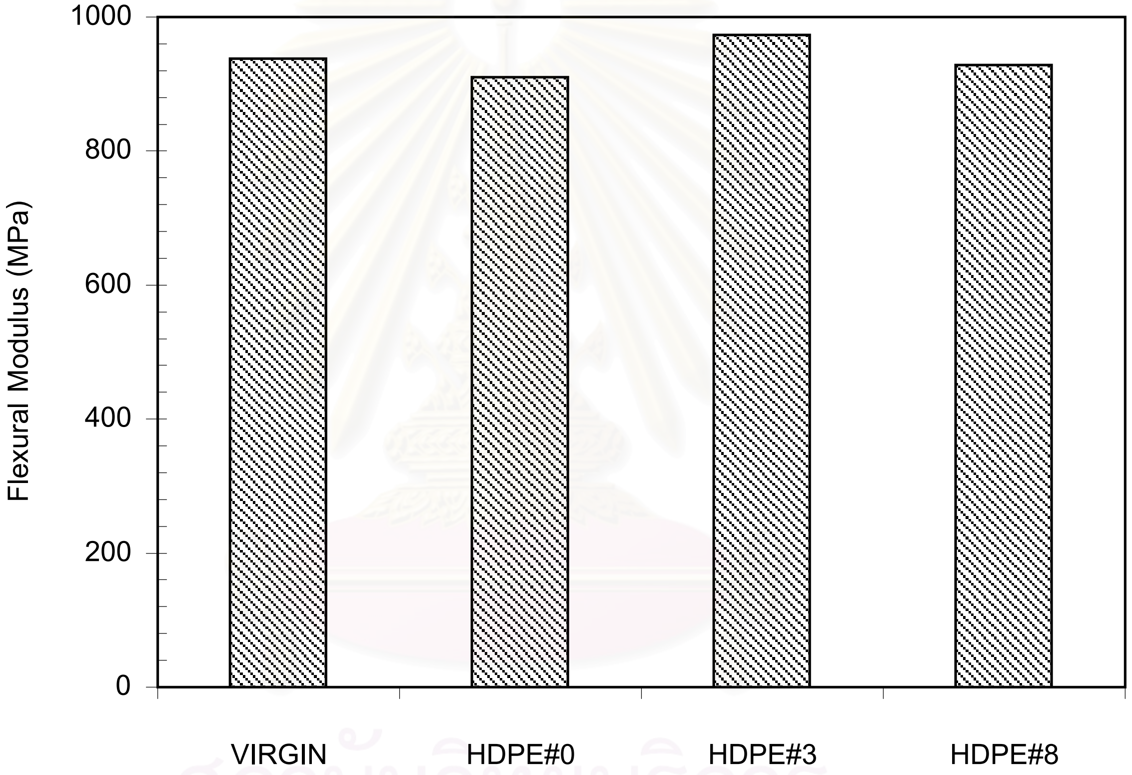


Figure 4.23 Flexural modulus of virgin HDPE and HDPE crates at various utilization time.

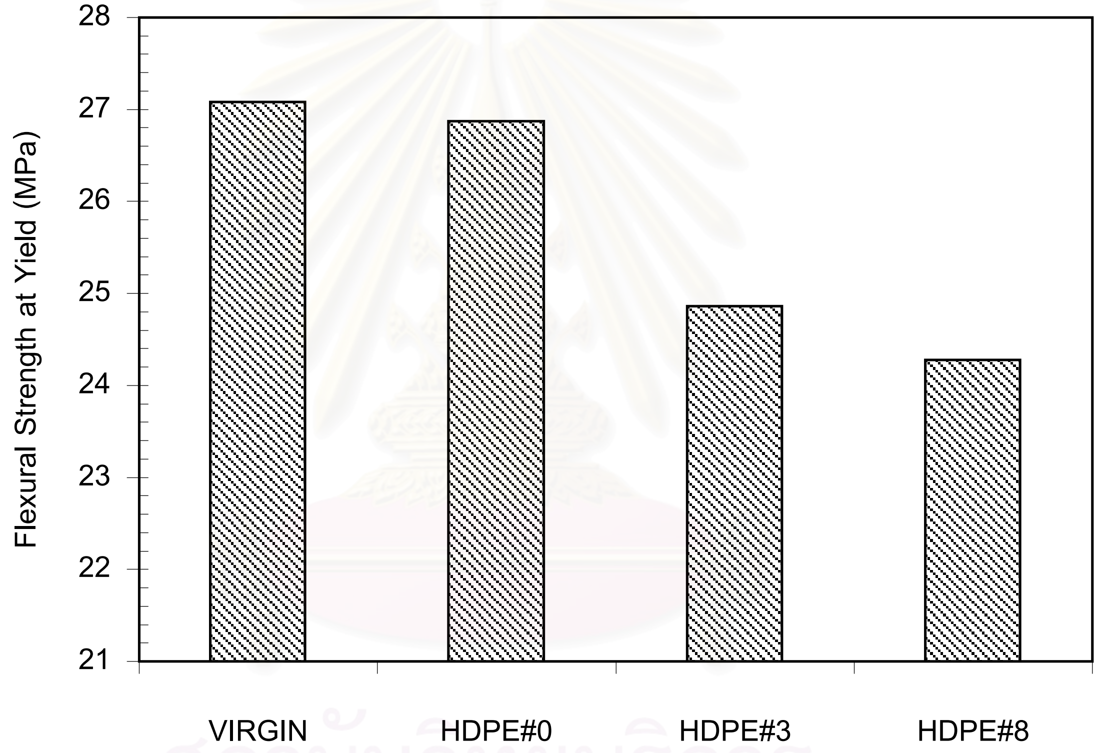


Figure 4.24 Flexural strength at yield of virgin HDPE and HDPE crates at various utilization time.

4.4.3.3 Impact properties

Figure 4.25 shows the impact resistance of virgin HDPE and HDPE crates at various utilization time. The impact resistance of virgin HDPE is higher than that of new HDPE crate by 8.3% while the impact resistance of HDPE crates at the utilization time of 3 and 8 years is lower than that of new HDPE crates by 16.7% and 25%, respectively. The utilization time of HDPE crates has an effect on impact resistance of HDPE. The results are similar to the previous work by Pages *et al.* [1996] on weathering aging of HDPE. This article has demonstrated that long exposure time in Canadian winter has caused specific chemical transformations undergone in the polymer chain. These reactive phenomena decrease the linear character of the polymer chains caused by the formation of bulky groups, which leads to an increase of the amorphous content and a decrease in the impact resistance. This also corresponds to our results on the degree of crystallinity.

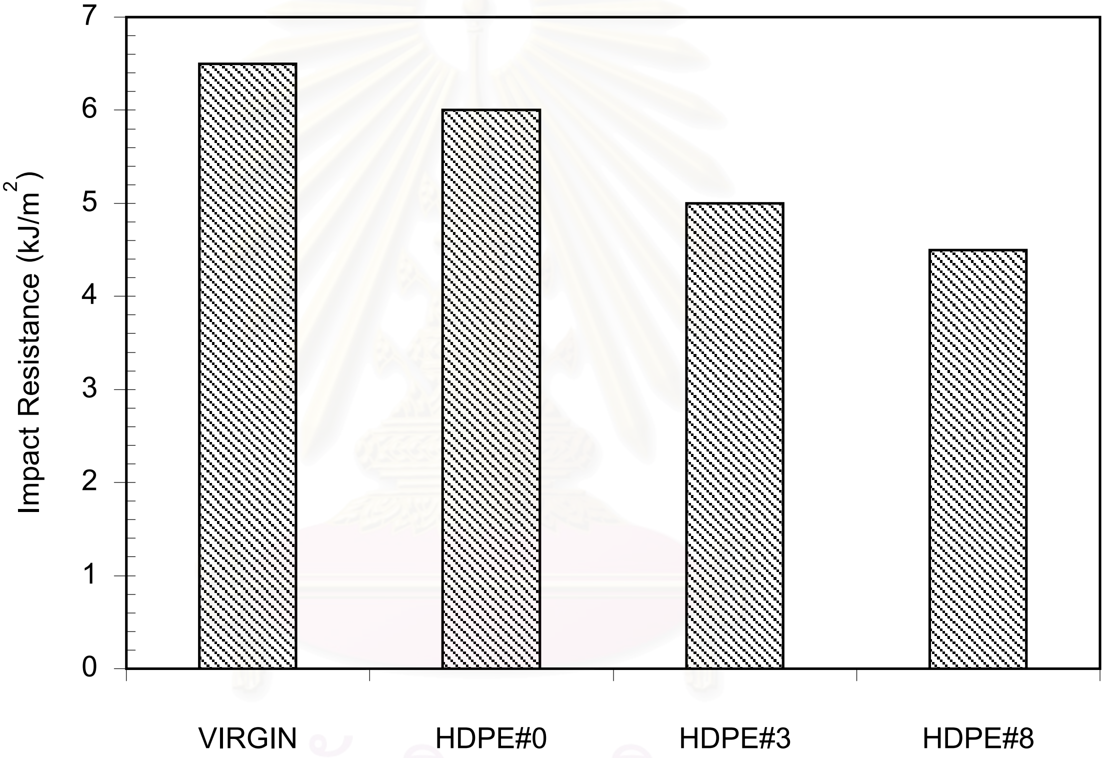


Figure 4.25 Impact resistance of virgin HDPE and HDPE crates at various utilization time.

4.4.3.4 Rockwell hardness

Figure 4.26 shows the Rockwell hardness of virgin HDPE and HDPE crates at various utilization time. The Rockwell hardness of new HDPE crates is higher than that of virgin HDPE by 3.9% which could be due to many additives added during the processing. The Rockwell hardness of HDPE crates does not significantly vary along the utilization time.

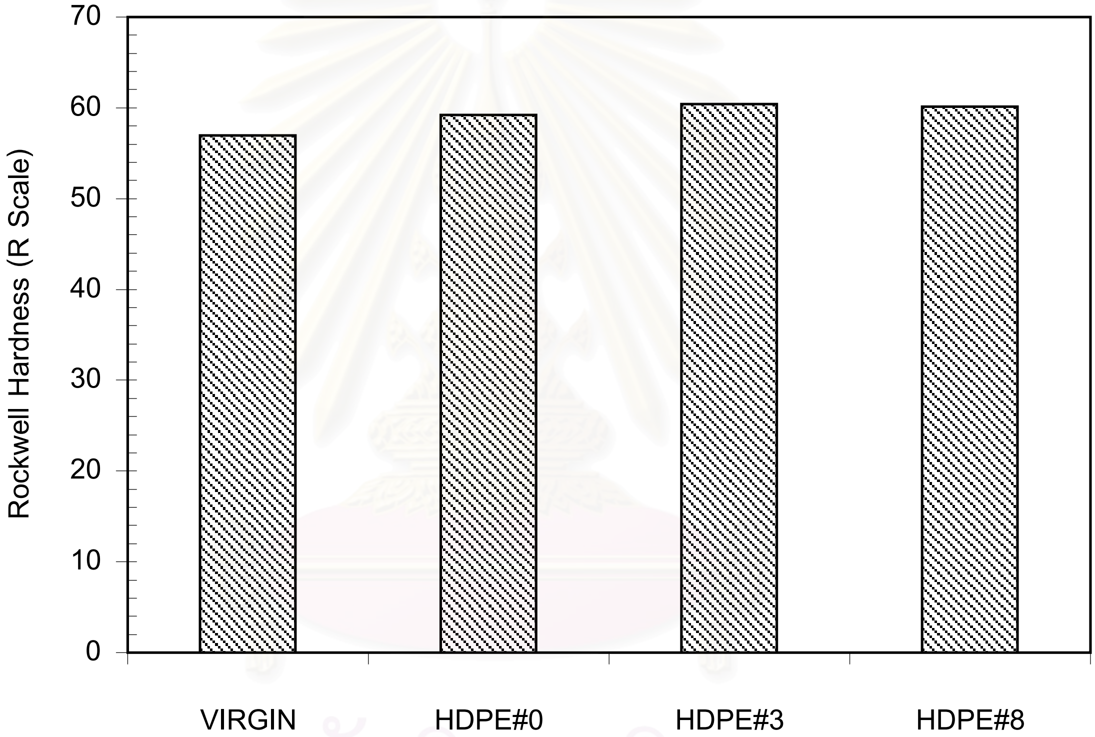


Figure 4.26 Rockwell hardness in "R" scale of virgin HDPE and HDPE crates at various utilization time

4.5 Conclusions

From the study of the properties of post-used HDPE crates at various utilization time, several points can be concluded as follows:

1) The utilization time of HDPE crates has strongly effect on the M_n but the M_w of HDPE crates does not change during the utilization time, resulting in a broadening MWD. This might be because the photo-oxidative degradation has occurred during the use of the crates for bottle transportation, leading to change in molecular weight.

2) The melting temperature of post-used HDPE crates does not change during the utilization, while degree of crystallinity of HDPE crates tends to decrease after a period of the utilization time.

3) Increasing in utilization time tends to decrease the processability of HDPE crates. Particularly, the zero shear viscosity of HDPE crates tends to increase at longer utilization time.

4) Increasing in the utilization time of HDPE crates remarkably decreases %elongation at break, flexural strength at yield and impact resistance. This could be a result of decreasing in the degree of crystallinity found that implies the occurrence of photo-oxidative degradation during the service life, leading to changes in polymer chain structures.

5) The mechanical properties of post-used HDPE crates at the utilization time of 8 years are general worse than those of new HDPE crates, particularly the %elongation at break and the impact resistance. This could be because the photo-oxidative degradation occurred in HDPE crates as exposed to hostile environment during uses.

However, the variable factors that cannot be controlled in the experiment are the condition of services of HDPE crates. Some crates might be exposed to the sunlight for sometimes, some were heavily pressed and some were crashed for different periods of time. For these reasons, the results of the experiment exhibit in a wide range.

CHAPTER V

Property Modification of Post-used HDPE Crates

From Chapter IV, the results indicate that the mechanical properties and processability of post-used HDPE crates are decreased with an increasing utilization time, in particular the %elongation at break and impact resistance. The property modification of recycled post-used HDPE crates become the important factors for a second life of these materials. Therefore, the aim of this chapter is to find out the ways to improve the properties of recycled post-used HDPE crates by polymer blending with modifying agents.

5.1 Materials

5.1.1 Post-used HDPE crates

Post-used HDPE crates, i.e. 8 years used HDPE crates (HDPE#8), which were studied in Chapter IV were taken to modify their poor properties. Properties of HDPE#8 investigated in Chapter IV are summarized in Table 5.1.

Table 5.1 The properties of post-used HDPE crates.

Properties	HDPE#8
Melt Flow Index	4.86 g/10 min
Young's Modulus	2656 MPa
Tensile Strength at Yield	25.08 MPa
% Elongation at Break	93 %
Flexural Modulus	928 MPa
Flexural Yield Strength	24.28 MPa
Impact Resistance	4.5 kJ/m^2
Rockwell Hardness, R Scale	R 60.1

5.1.2 Stabilizer (Recyclossorb 550)

The stabilizer under the trade name of “Recyclossorb 550”, obtained from Ciba-Specialty Chemical Ltd., was used to mix with HDPE#8. This additive developed for recycling of HDPE. R550 is the blend of light stabilizers, antioxidants and co-stabilizers. The components of R550 are summarized in Table 5.2.

Table 5.2 The components of Recyclossorb 550.

Trade Name	Concentration
IRGANOX 1010	8.0 – 12.0 %
IRGAFOS 168	18.0 – 22.0%
CHIMASSORB 944 FD	22.5 – 27.5%
TINUVIN 622 FB	22.5 – 27.5%
CALCIUM STEARATE	18.0 – 22.0%

5.1.3 Ethylene vinyl acetate copolymer (EVA)

Ethylene vinyl acetate copolymer obtained from Thai Petrochemical Industry Public Co., Ltd., was used to blend with HDPE#8. The properties of EVA are shown in Table 5.3.

Table 5.3 The properties of ethylene vinyl acetate copolymer.

Properties	EVA
Melt Flow Index	2.3 g/10 min
Density	0.941 g/cm^3
Tensile Strength at Yield	4 MPa
Tensile Strength at Break	18 MPa
% Elongation at Break	700%
Vinyl Acetate (VA) content (% Max)	18%

5.2 Blending by twin-screw extruder

R550 and EVA were used as modifying agents for post-used HDPE crates. Each modifying agent was blended with post-used HDPE crates at two different compositions. Four blend formula can be summarized in Table 5.4.

Table 5.4 Blend formula of post-used HDPE crates.

Code	Weight ratio	Code	Weight ratio
R550,0.2%	HDPE#8 : R550 = 99.8 : 0.2	EVA5%	HDPE#8 : EVA = 95 : 5
R550,0.4%	HDPE#8 : R550 = 99.6 : 0.4	EVA15%	HDPE#8 : EVA = 85 : 15

Each formula was firstly prepared by dry blending in “BOSCO” Pot for 15 min and then melt blending by “COLLIN co-rotating twin screw Kneader ZK-25” (25 mm in diameter × 750 mm in length). The temperature profiles of the twin-screw extruder during the processing are shown in the Figure 5.1.

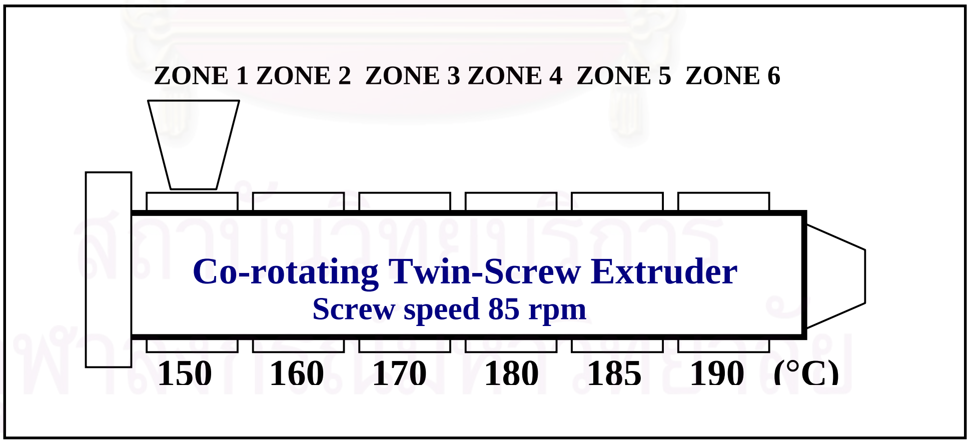


Figure 5.1 The temperature profiles of co-rotating twin-screw extruder.

The extrudate was cooled in the water bath at the temperature around 25 °C and fed to a “PLANETROL 075D2” pelletizer to cut into pellet form. All equipment used in blending procedure is at Petroleum and Petrochemical College, Chulalongkorn University. The samples were collected for further testing on processability and mechanical properties. In addition, the influence of reprocessing of post-used HDPE crates was investigated by extruding HDPE#8 (coded as RE1) in order to compare with blended post-used HDPE crates.

5.3 Sample preparation and experimental procedure

Four sets of blended post-used HDPE compounds and the reextruded post-used HDPE were taken to prepare and test for processability and mechanical properties, following the procedures described in Section 4.2, 4.3.2 and 4.3.3 in Chapter IV.

5.4 Results and discussion

Results on processability and mechanical properties of blended post-used HDPE compounds are presented and the effects of Recyclossorb 550 and ethylene vinyl acetate copolymer are discussed comparing to the post-used HDPE crates (HDPE#8) and the reextruded ones (RE1).

5.4.1 Processability

5.4.1.1 Melt flow index

The melt flow index of blended post-used HDPE crates with modifying agents is shown in Figure 5.2. Reprocessing of post-used HDPE crates (RE1) shows an effect on melt flow index. The melt flow index of RE1 is lower than that of HDPE#8 by 3.1%. Generally, thermal-oxidative degradation of polyethylene results in chemical structure changes. The reaction of long chain branching and crosslinking are much more important than chain scission [Gachter *et al*., 1993]. Therefore, reextruded post-used HDPE crates may degrade and chain structure has been changed, resulting in lowering melt flow index. Kartalis *et al.* [1999] have found that the melt flow index of post-used Heineken HDPE crates was decreased with an increasing number of reprocessing in the single screw extruder and in the twin-screw extruder. They indicated that during the processing step, the HDPE crates material suffered from degradation, caused by branching phenomena along the polymer structure.

In Figure 5.2, it can be seen that the melt flow index of blended post-used HDPE crates with 0.2% and 0.4% of stabilizer (R550) seems to be consistent comparing with post-used HDPE crates. In addition, melt flow index of blended post-used HDPE crates with 0.2% and 0.4% of stabilizer is higher than that of re-extruded HDPE crates by 4.9% and 6.4%, respectively. This indicates that the addition of R550 can be retained the melt flow stability of post-used HDPE crates during the processing step. R550 could also inhibit or retard oxidation and prevent degradation that might occur during the processing step. Moreover, Increasing in melt flow index could be caused by the component of calcium stearate in R550 which is normally used as an external lubricant [Edenbaum, 1996].

For blends of post-used HDPE crates with EVA, it can be noticed that post-used HDPE crates after blending with 5% and 15% of EVA have lower melt flow index than that of post-used HDPE crates by 2.3% and 8% respectively. This could because of the low melt flow index of EVA (2.3 g/10 min).

Comparing the effects of R550 and EVA on the melt flow index of post-used HDPE crates, it can be concluded that R550 can slightly increase the melt flow index of the post-used HDPE crates, whereas EVA at a significant amount make the melt flow index remarkably decreased. These results will be compared with the viscosity in the next section.

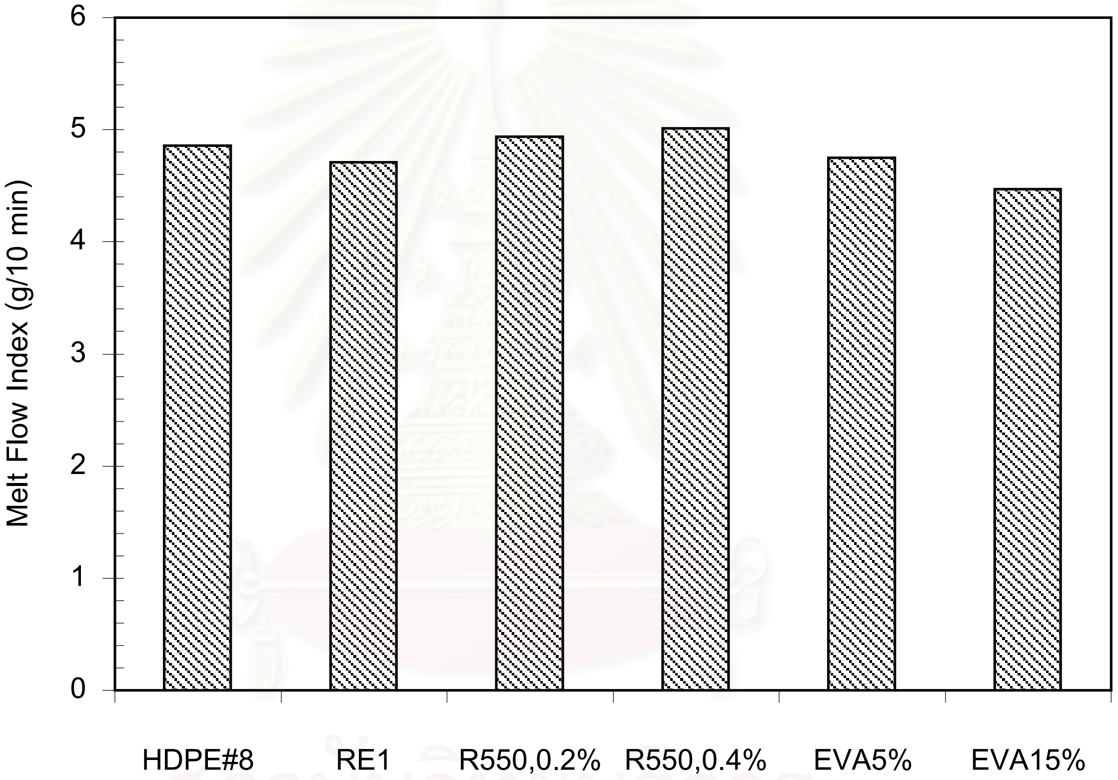


Figure 5.2 Melt flow index of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

5.4.1.2 Viscosity

Figure 5.3 shows the complex viscosity of blended post-used HDPE crates with R550 and EVA. For clear comparison, the zero shear viscosity (constant complex viscosity at low frequency) of all samples is plotted in Figure 5.4. It can be seen that the viscosity of reextruded post-used HDPE crates is slightly increased comparing to that of HDPE#8.

Comparing the zero shear viscosity of the blends of post-used HDPE crates and R550 with the unblended sample, it can be found that the zero shear viscosity of restabilized HDPE crates at the concentration of R550 at 0.2% and 0.4% is lower than that of HDPE#8 by 4.5% and 7.1%, respectively. Further reduce in viscosity is noticed when increasing the amount of R550 added.

Comparing the zero shear viscosity of the blends of post-used HDPE crates and EVA with the unblended sample, it is shown that the zero shear viscosity of post-used HDPE crates is increased by increasing the concentration of EVA. The viscosity of the blends of HDPE#8/EVA at the EVA concentration of 5% and 15% is higher than that of HDPE#8 by 3.9% and 13.6%, respectively. The results indicate that EVA has a remarkably effect on the processability of the post-used HDPE crates. The results on viscosity of the blends of HDPE#8 with either R550 or EVA are in agreement with the melt flow index results discussed in previous section (5.4.1.1).

Comparing the effects of R550 and EVA on the viscosity of post-used HDPE crates, it can be concluded that the viscosity of the blend of HDPE#8/EVA at the weight ratio of 85/15 is rapidly increased from the unblended HDPE#8, whereas the addition of R550 results in a decrease in the viscosity of post-used HDPE crates.

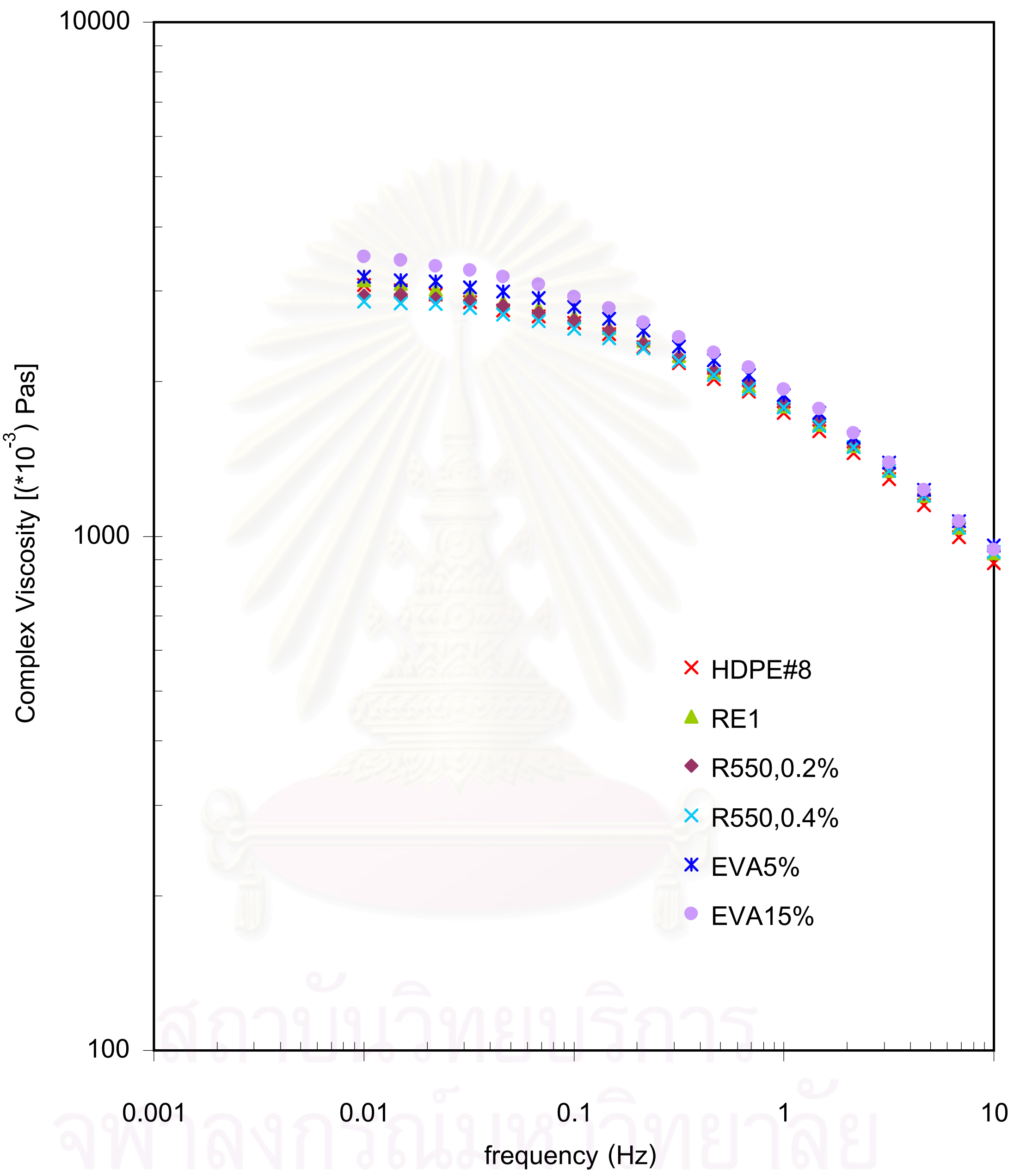


Figure 5.3 Complex viscosity of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

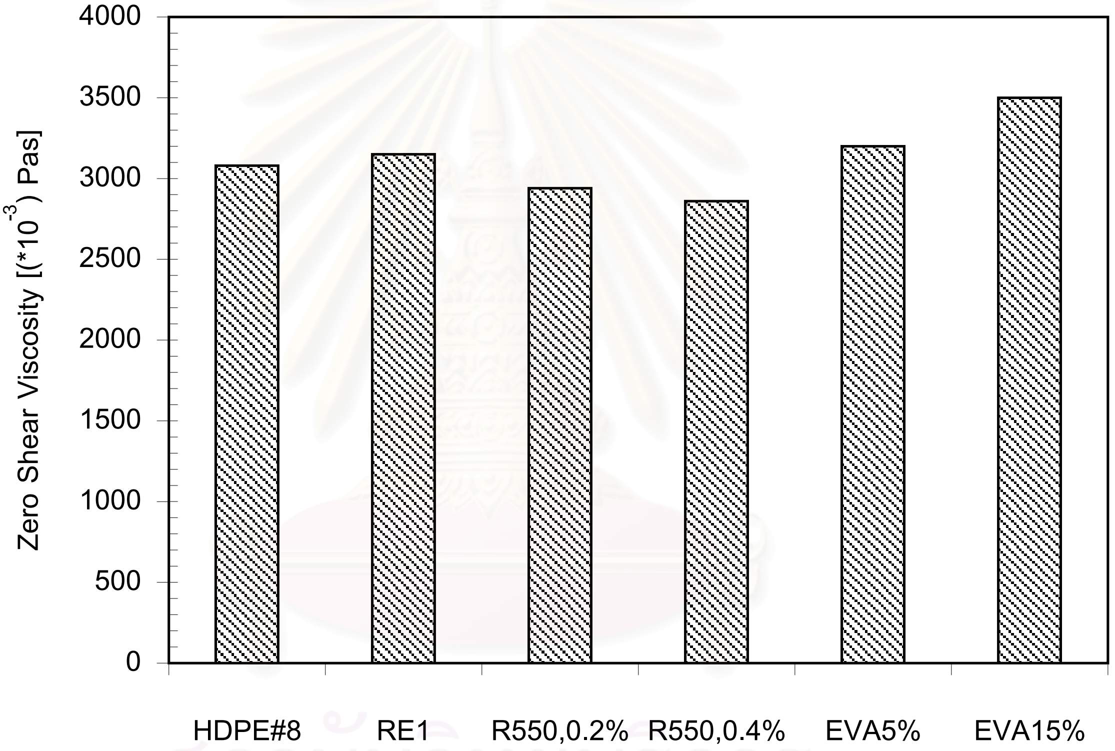


Figure 5.4 Zero shear viscosity of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

5.4.2 Mechanical properties

5.4.2.1 Tensile properties

The results on tensile properties of blended post-used HDPE crates with both modifying agents, R550 and EVA, are shown in Table 5.5. Figure 5.5 presents the Young's modulus of all post-used HDPE crates samples. It can be noticed that reprocessing of all post-used HDPE crates (with modifying agents and without modifying agents) have a significantly effect on Young's modulus. Young's modulus of RE1 is lower than that of HDPE#8 by 41.2%.

Table 5.5 Tensile properties of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

Code	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	% Elongation at Break (%)
HDPE#8	2656	25.08	93
RE1	1561	25.67	244
R550,0.2%	1573	25.27	318
R550,0.4%	1496	24.77	473
EVA5%	1389	23.52	>600
EVA15%	1192	19.90	541

In Figure 5.5, it can be seen that Young's modulus of restabilized HDPE crates at the concentration of R550 at 0.2% and 0.4% is lower than that of HDPE#8 by 40.8% and 43.7%, respectively, while Young's modulus of restabilized HDPE crates seems to be consistent comparing with RE1.

In Figure 5.5, it can be seen that the Young's modulus of blended HDPE#8 with EVA at the EVA concentration of 5% and 15% is lower than that of HDPE#8 by 47.7% and 55.1%, respectively. In addition, Young's modulus of blended HDPE#8 with EVA at the EVA concentration of 5% and 15% is lower than that of RE1 by 11% and 23.6%, respectively. The results indicate that Young's modulus of post-used HDPE crates is further decreased when increasing EVA concentration in the blends.

Figure 5.6 shows the stress–strain curves of post-used HDPE crates and blended HDPE crates with modifying agents in the range of small strain which includes the elastic region. It can be obviously noticed that, at very low strain range, the stress-strain characteristic of HDPE#8 which was not reprocessed in the twin-screw extruder is different form these of the rest of the samples which were reextruded. All reextruded samples can sustain an applied load to a higher linear proportional limit of stress and strain comparing to HDPE#8. A drop in Young's modulus of all reextruded samples is also found as mentioned earlier. This could possibly be effected by better compatibility induced in the twin-screw extruder.

Tensile strength at yield of blended post-used HDPE crates with R550 and EVA is shown in Figure 5.7. Tensile strength at yield of reprocessed HDPE crates and restabilized HDPE crates with R550 varies in a very narrow range of 24.77 – 25.67 MPa. In other words, the tensile strength at yield of reprocessed HDPE crates and restabilized HDPE crates is more or less the same as that of post-used HDPE crates.

In Figure 5.7, it can be seen that the tensile strength at yield of post-used HDPE crates after blending with EVA at the EVA concentration of 5% and 15% is lower than that of post-used HDPE crates by 6.2% and 20.7%, respectively. The results indicate that tensile strength at yield of post-used HDPE crates is slightly decreased at the EVA concentration of 5% and continues to be rapidly decreased when increasing the amount of EVA content in the blend. This behavior could be due to the softness of EVA comparing to HDPE. Adding EVA in HDPE has leaded to the reduction of tensile strength at yield and Young's modulus of post-used HDPE crates.

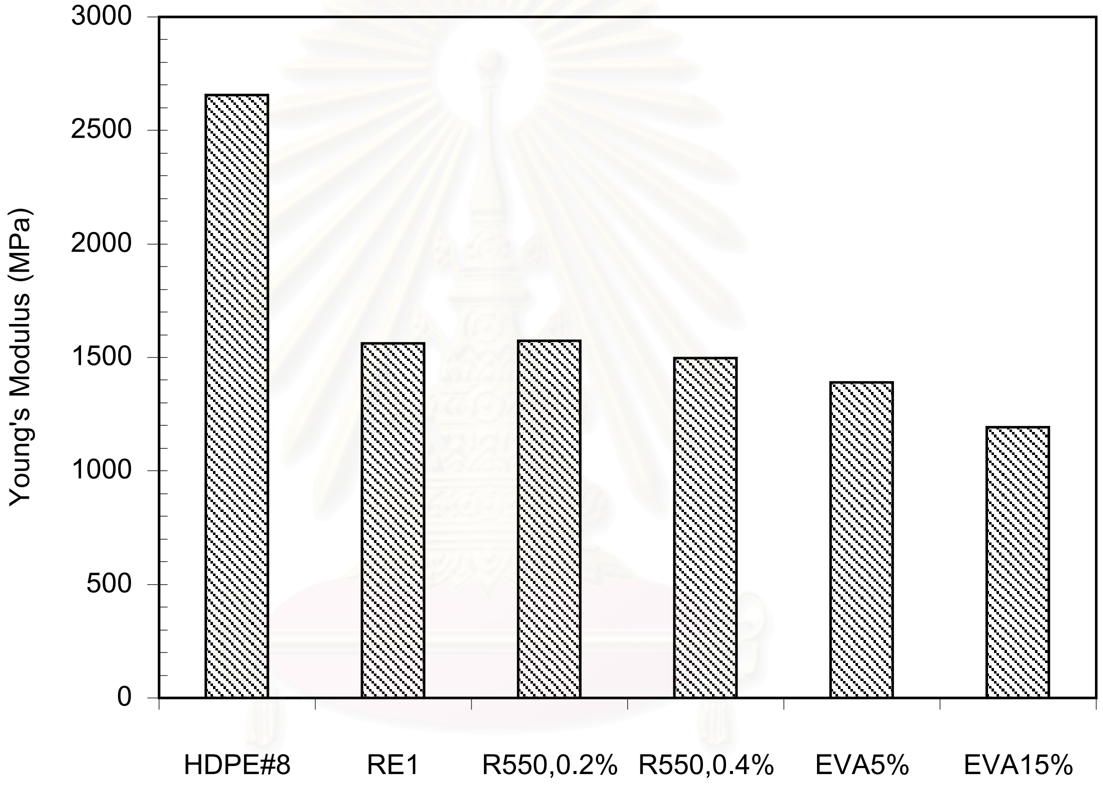


Figure 5.5 Young's modulus of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

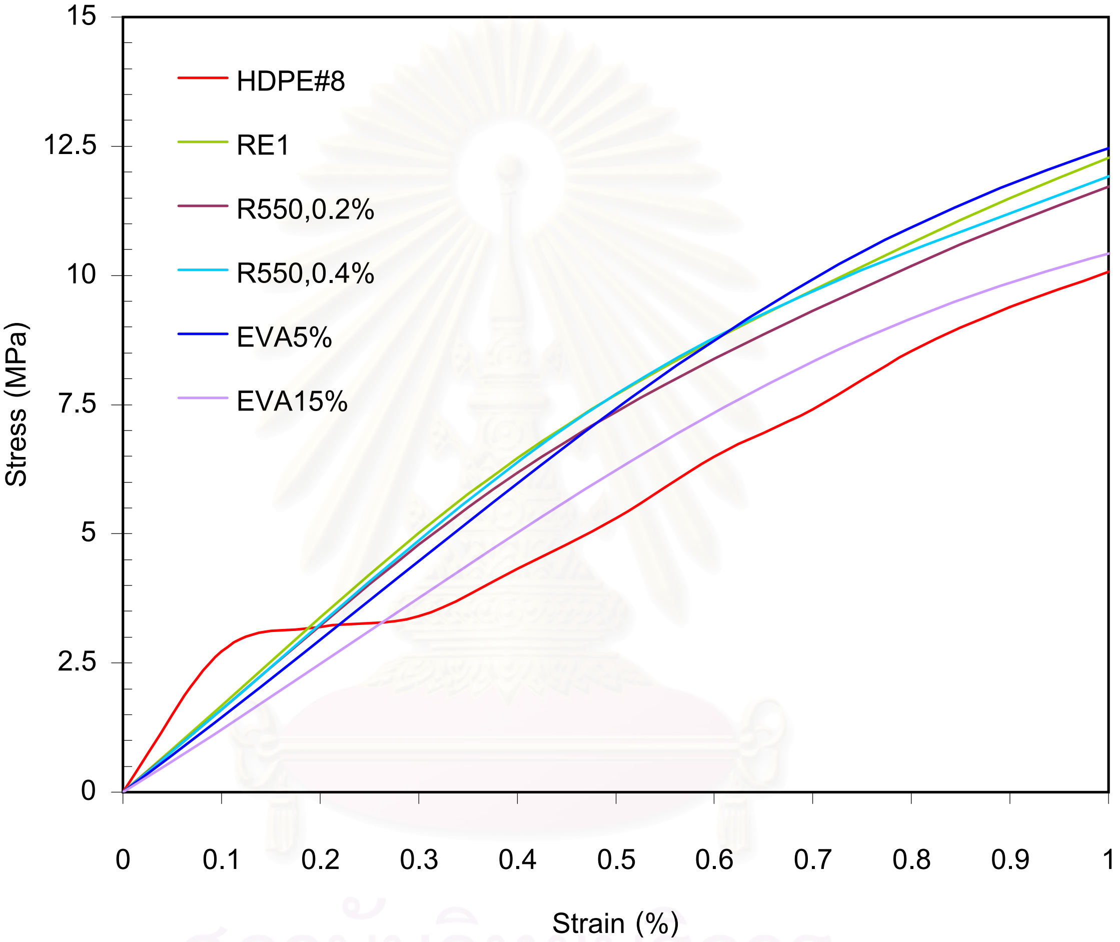


Figure 5.6 Stress-strain curves of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates in the range of small strain.

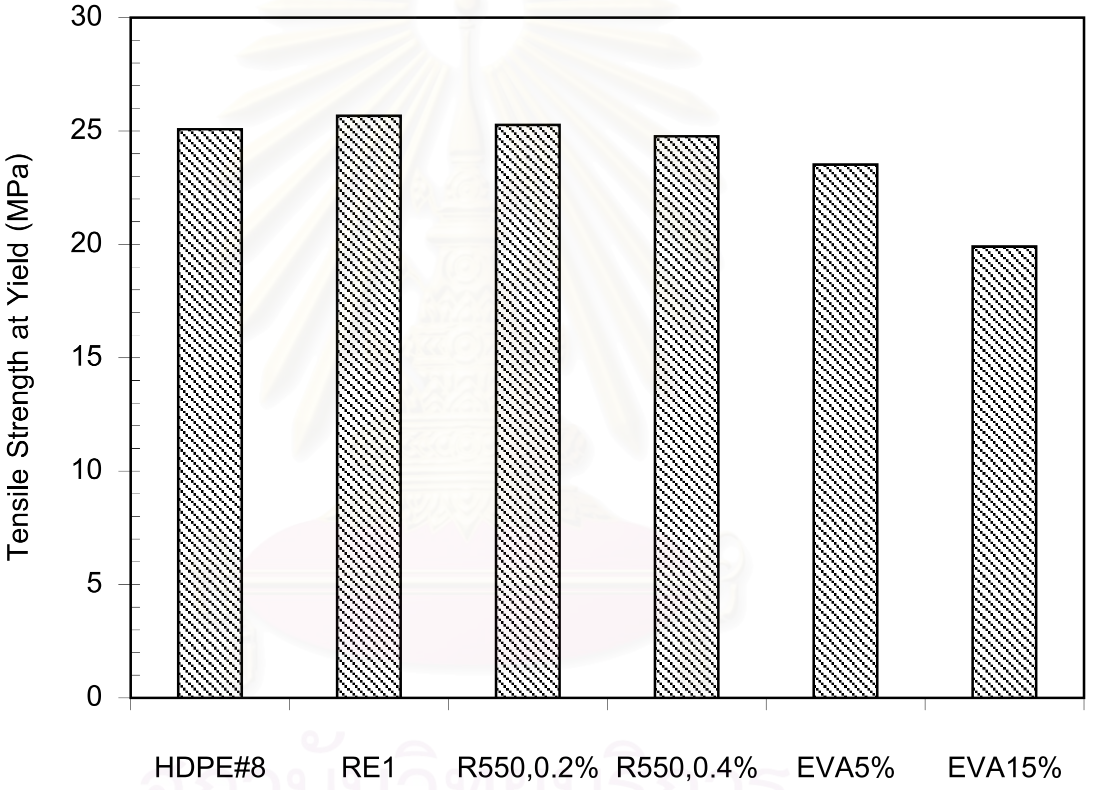


Figure 5.7 Tensile strength at yield of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

The %elongation at break of blended post-used HDPE crates with R550 and EVA is shown in Figure 5.8. The %elongation at break of RE1 is higher than that of HDPE#8 by 162.4%. This suggests that reprocessing by twin-screw extruder of post-used HDPE crates improve %elongation at break of the HDPE crates. Better homogenization and better dispersion of the additives in HDPE could be responsible for this behavior.

In Figure 5.8, it can be noticed that the %elongation at break of post-used HDPE crates after blending with R550 at the R550 concentration of 0.2% and 0.4% is higher than that of HDPE#8 by 241.9% and 408.6%, respectively. The %elongation at break of post-used HDPE crates is effectively increased while increasing the amount of stabilizer from 0.2% to 0.4%. R550 might play a role to improve the resistance of thermal degradation during reprocessing. This might correspond to the work of recycled HDPE crates using the Recyclossorb 550 [Kartalis *et al*., 1999]. It was reported that %elongation at break of recycled HDPE crates are further increased after adding R550 in recycled HDPE crates. This was indicated that the addition of R550 decreased the effects of crosslinking and branching phenomena, caused by the degradation reaction.

Comparing the blends of HDPE#8 and EVA with the unblended sample in Figure 5.8, the blend of HDPE#8/EVA at the weight ratio of 95/5 (EVA5%) can be elongated more than 600%. The ability on the %elongation at break of EVA5% exceeds the detection limit of the testing machine at the crosshead speed of 50 mm/min, similar to that found in the case of virgin HDPE granule (see Figure 4.21). This point will be further clarified. For the blend of HDPE#8/EVA at 85/15 (EVA15%), the %elongation at break of EVA15% is higher than that of HDPE#8 by 481.7%. It could be suggested that the addition of EVA improve the elasticity of HDPE.

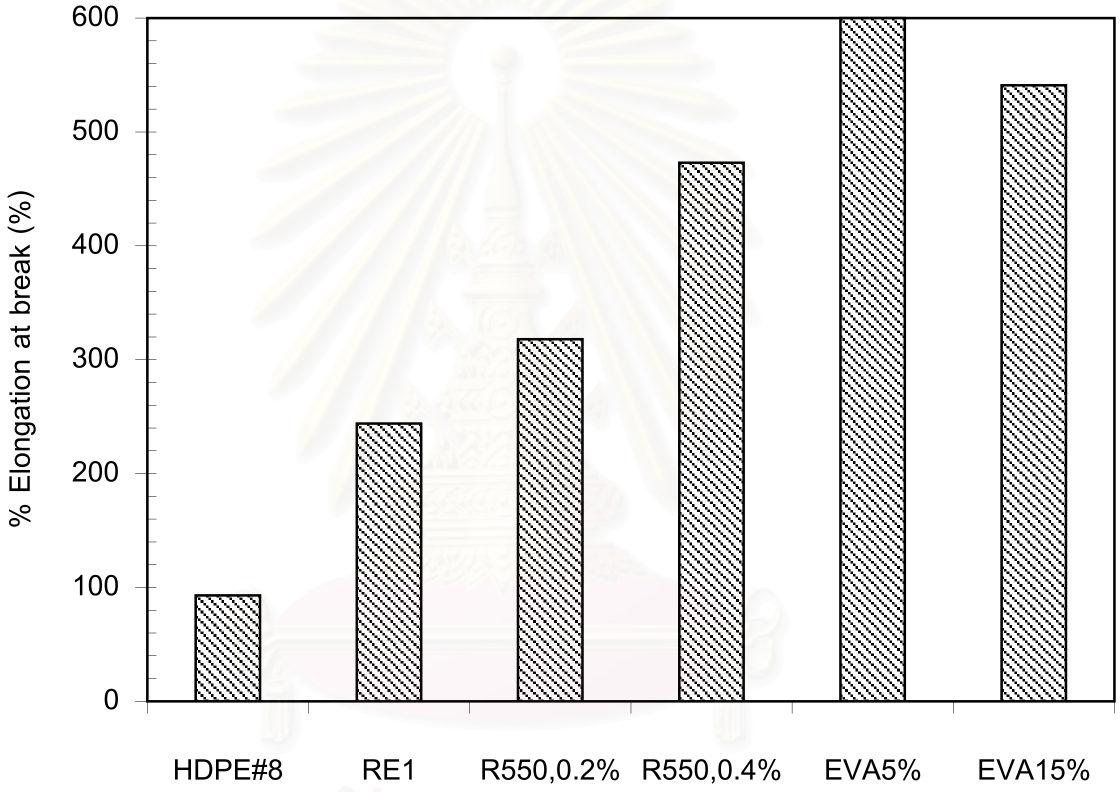


Figure 5.8 %Elongation at break of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

Tensile stress–strain curves of recycled post-used HDPE crates with modifying agents are shown in Figure 5.9. It can be seen that toughness of blended post-used HDPE crates with R550 and EVA is strongly improved, especially for the case of EVA. Adding EVA can dramatically reduce tensile strength at yield and Young's modulus. This indicates that blends of post-used HDPE crates with EVA are softer and much tougher than post-used HDPE crates. In addition, the tensile strength at break of blended post-used HDPE crates with EVA is higher than that of restabilized HDPE crates and post-used HDPE crates. This indicates that blending of EVA with HDPE could have a good compatibility and result in high tensile strength at break.

Since the EVA5% and virgin HDPE granule can be elongated more than 600%, at this point, the tensile properties of both samples are rechecked at the higher crosshead speed of 100 mm/min (Previous test was done at the crosshead speed of 50 mm/min). The results on tensile properties of virgin HDPE and EVA5% at crosshead speed of 50 mm/min and 100 mm/min are shown in Table 5.6. Increasing strain rate from 50 mm/min to 100 mm/min, Young's modulus increases with a corresponding decrease in elongation at break. At the speed of 100 mm/min, it is clearly noticed that the %elongation at break of EVA5% is lower than that of virgin by 26.6%.

Stress–strain curves of virgin HDPE and EVA5% at crosshead speed of 100 mm/min shown in Figure 5.10 confirms that blend of post-used HDPE crates with 5% of EVA is not as hard and tough as the virgin HDPE. However, the blend of post-used HDPE crates with 5% of EVA generally gives the most improved tensile property comparing with other blend formulae.

Comparing the effects of R550 and EVA on the tensile properties of post-used HDPE crates, it can be concluded that EVA has stronger effects than R550. The large amount of EVA added in post-used HDPE crates decreases Young's modulus and tensile strength at yield but increase %elongation at break.

Table 5.6 Tensile properties of virgin HDPE and EVA5%.

Code	Young's Modulus (Mpa)	Tensile Strength at Yield (MPa)	% Elongation at Break (%)
Crosshead speed 50 mm/min			
VIRGIN	1474	24.91	>600
EVA5%	1389	23.52	>600
Crosshead speed 100 mm/min			
VIRGIN	2140	24.98	124
EVA5%	2298	23.16	91

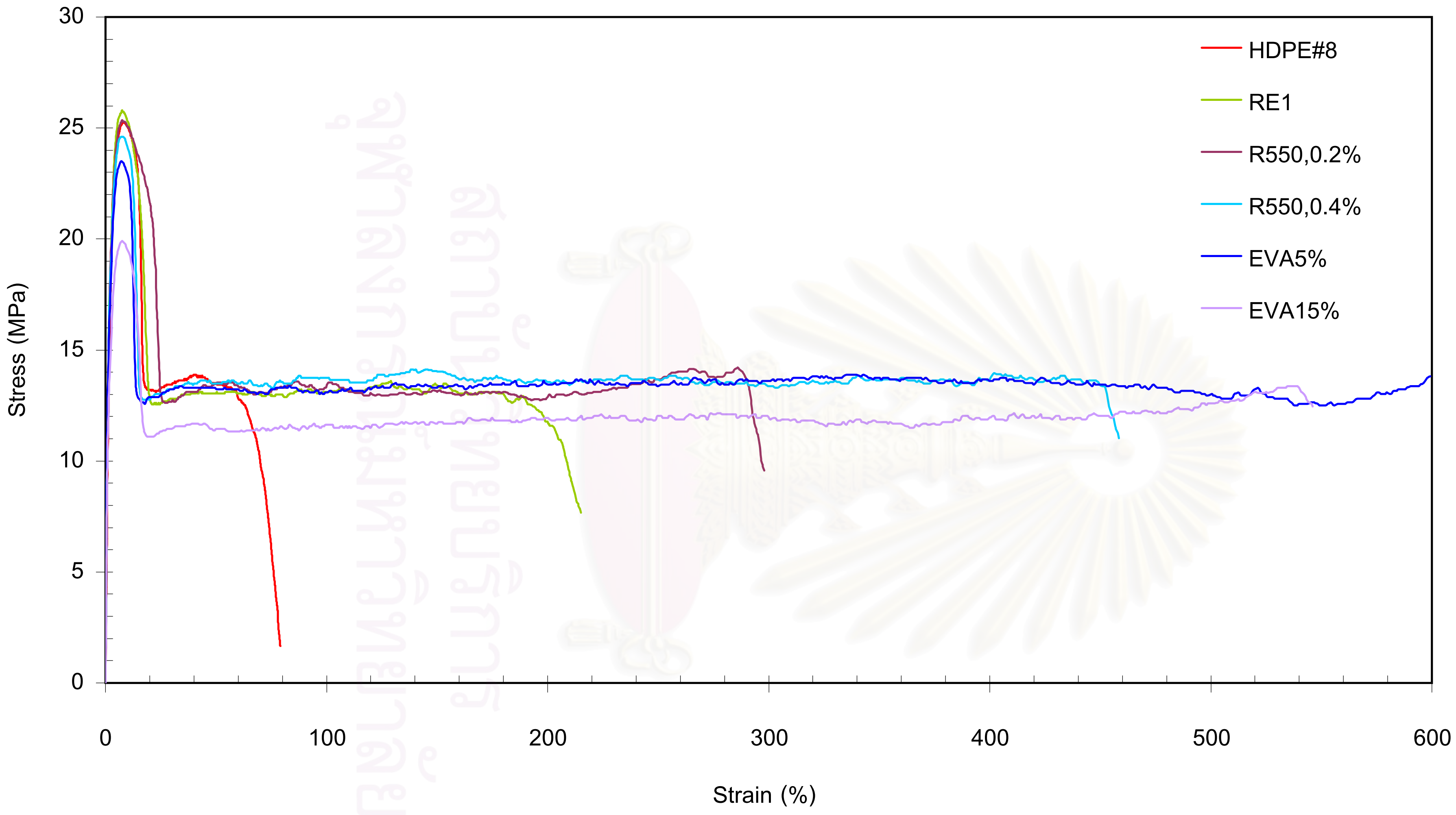


Figure 5.9 Stress-strain curves of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded HDPE crates.

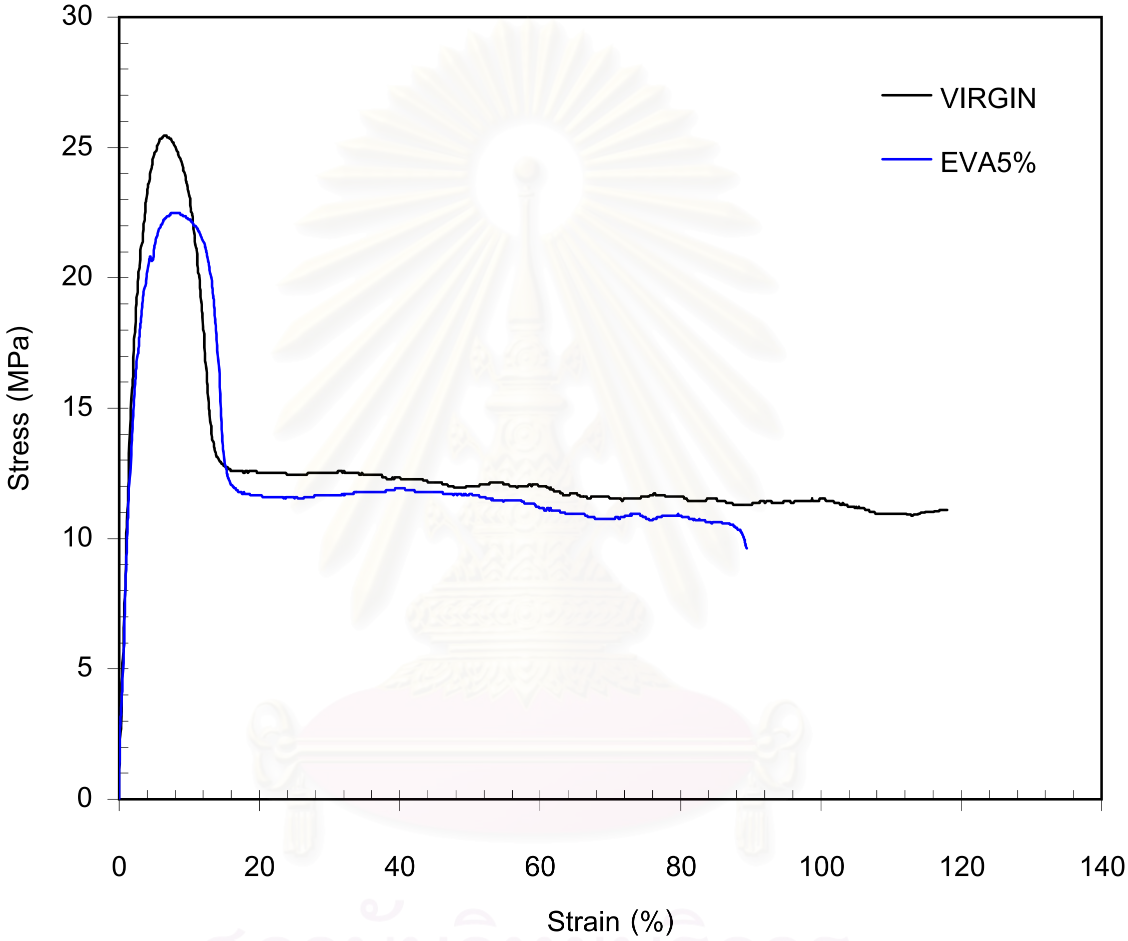


Figure 5.10 Stress-strain curves of virgin HDPE and EVA5% at crosshead speed of 100 mm/min.

5.4.2.2 Flexural properties

Figure 5.11 shows flexural modulus of recycled HDPE crates with both modifying agents, R550 and EVA. Flexural modulus of RE1 is slightly higher than that of HDPE#8 by 5.9%. Flexural modulus of restabilized post-used HDPE crates with 0.2% and 0.4% of R550 varies in a narrow range of 911 – 940 MPa. It can be said that the flexural modulus of post-used HDPE crates does not change after adding R550 at the concentration of 0.2% and 0.4%.

In Figure 5.11, it can be seen that the flexural modulus of blended post-used HDPE crates with EVA at the EVA concentration of 5% and 15% is lower than that of HDPE#8 by 7.1% and 19.4%, respectively. Flexural modulus of post-used HDPE crates is dramatically decreased when the EVA content in the blend is increased.

Figure 5.12 shows flexural strength at yield of recycled HDPE crates with both modifying agents, R550 and EVA. Flexural strength at yield of RE1 is higher than that of HDPE#8 by 6.9%. After adding R550, the flexural strength at yield of post-used HDPE crates tends to be slightly decreased.

In Figure 5.12, it can be seen that the flexural strength at yield of blended post-used HDPE crates with EVA at the EVA concentration of 5% and 15% is lower than that of HDPE#8 by 2.9% and 13.7%, respectively. Flexural strength at yield of post-used HDPE crates is slightly decreased at the low concentration of EVA and continues to be gradually decreased when increasing the amount of EVA concentration in the blend.

Comparing the effects of R550 and EVA on the flexural properties of post-used HDPE crates, it can be concluded that EVA has a stronger effect than R550.

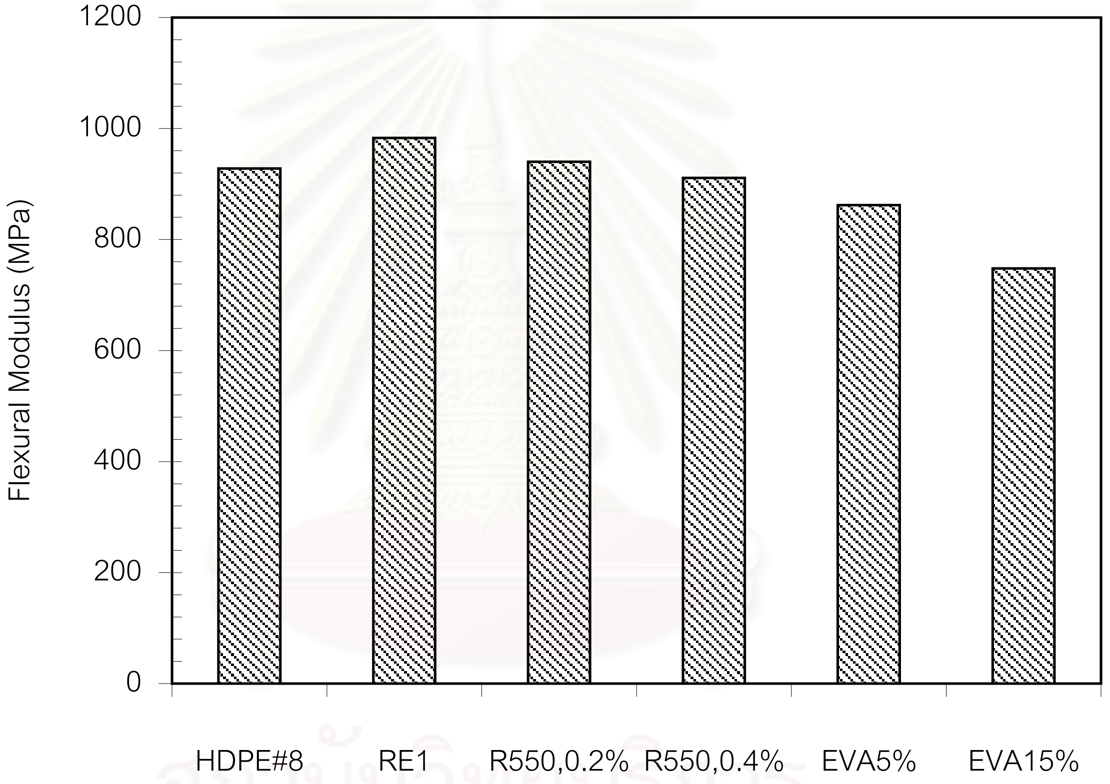


Figure 5.11 Flexural modulus of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

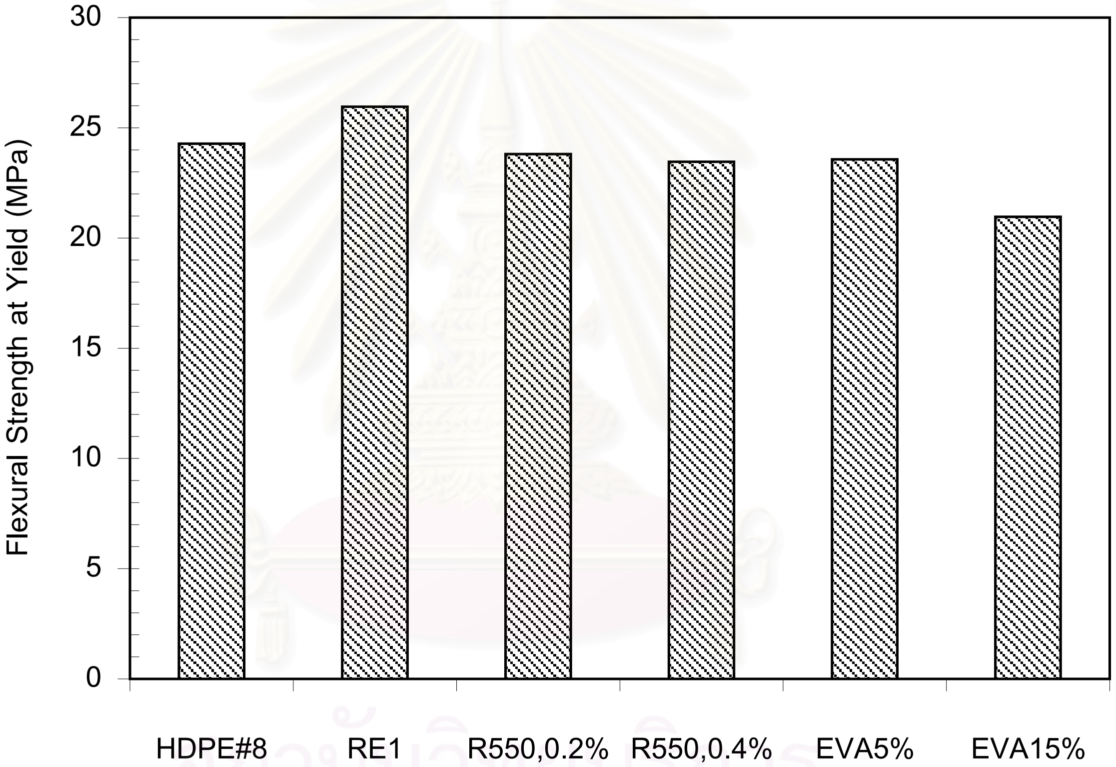


Figure 5.12 Flexural strength at yield of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

5.4.2.3 Impact properties

Figure 5.13 shows the impact resistance of recycled HDPE crates with both modifying agents, R550 and EVA. The impact resistance of post-used HDPE crates is almost the same after reprocessing. In the case of restabilizer, the impact resistance of post-used HDPE crates does not improve when adding R550 at the concentration of 0.2% and 0.4%. The impact resistance of restabilized HDPE crates at the R550 concentration of 0.2% and 0.4% is lower than that of HDPE#8 by 11.1% and 6.7%, respectively.

In Figure 5.13, it can be noticed that the impact resistance of post-used HDPE crates is rapidly increased with an increasing in the concentration of EVA. The impact resistance of EVA5% and EVA15% is higher than that of HDPE#8 by 37.8% and 348.9% respectively. The impact resistance of post-used HDPE crates is much improved after blending with EVA at the concentration of 15% comparing with post-used HDPE crates. This could be because EVA has a rubberlike property. Good compatibility of the blends of EVA and HDPE could thus result in a much better impact resistance.

Comparing the effects of R550 and EVA on the impact resistance of post-used HDPE crates, it can be concluded that EVA has stronger effects than R550.

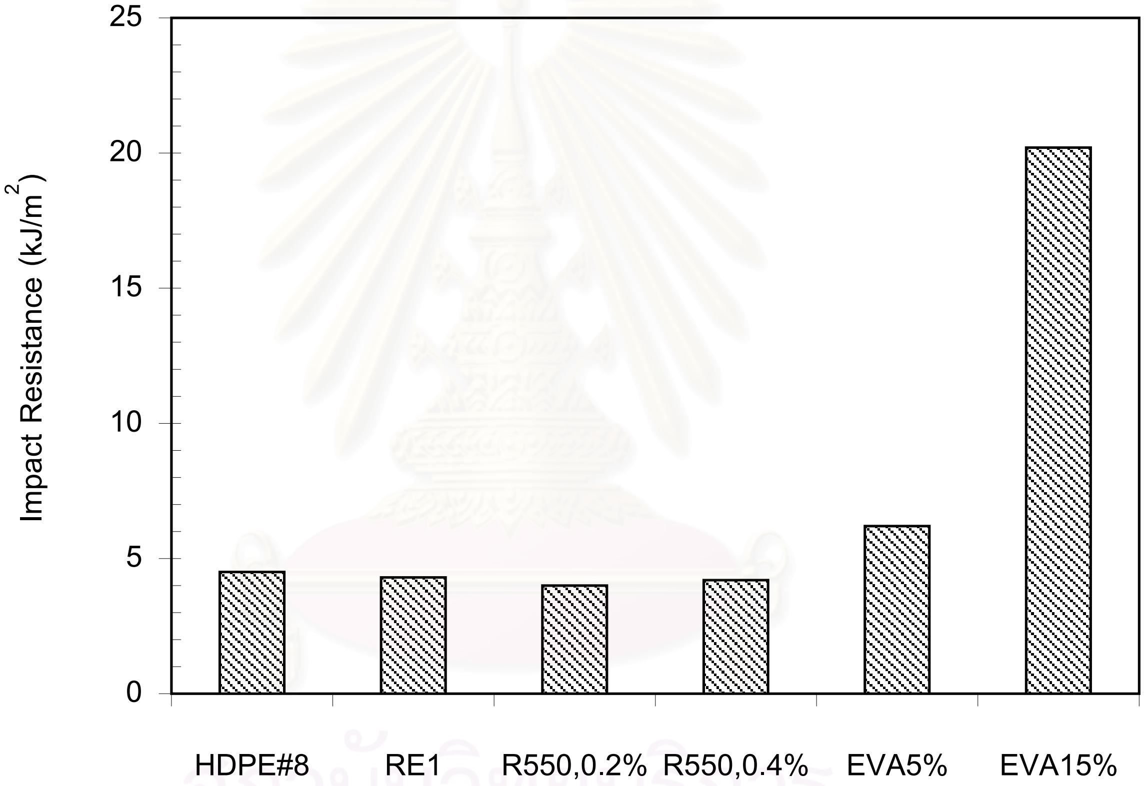


Figure 5.13 Impact resistance of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

5.4.2.4 Rockwell hardness

Figure 5.14 shows the Rockwell hardness in “R” scale of recycled HDPE crates with both modifying agents, R550 and EVA. The Rockwell hardness of reprocessed post-used HDPE crates is closed to that of HDPE#8. In the case of R550, it can be seen that the Rockwell hardness of post-used HDPE crates does not change after blending with R550 at the concentration of 0.2% and 0.4%. In other words, R550 gives no effect on the Rockwell hardness of post-used HDPE crates.

In Figure 5.13, it can be noticed that the Rockwell hardness of post-used HDPE crates is decreased with an increasing in the concentration of EVA. The Rockwell hardness of EVA5% and EVA15% is lower than that of HDPE#8 by 4.7% and 21.6%, respectively. Generally, loss of crystallinity is the factor of decreasing in hardness. The degree of crystallinity of EVA is lower than that of HDPE. This could result in decreasing in the Rockwell hardness of HDPE/EVA blends.

Comparing the effects of R550 and EVA on the Rockwell Hardness of post-used HDPE crates, it can be concluded that EVA has stronger effects than R550.

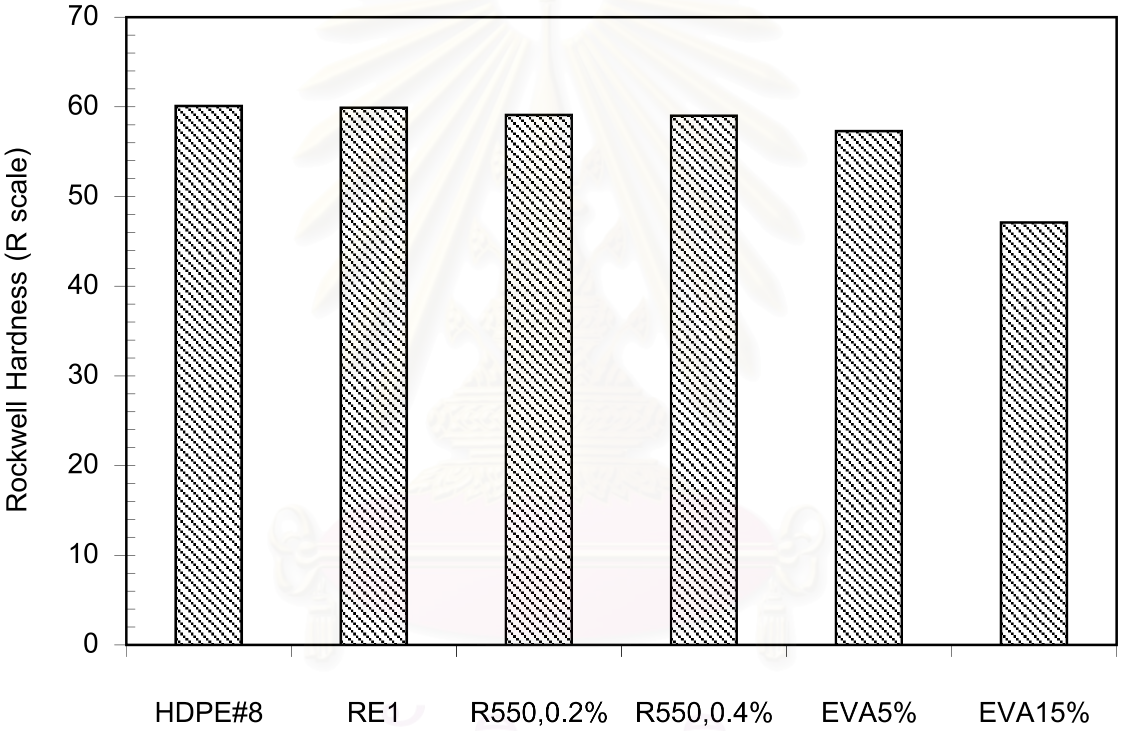


Figure 5.14 Rockwell hardness in "R" scale of blended post-used HDPE crates with R550 and EVA comparing to post-used HDPE crates and reextruded post-used HDPE crates.

5.5 Conclusions

From the property modification of post-used HDPE crates by polymer blending with R550 and EVA, the effects of each modifying agent on the processability and the mechanical properties of blended post-used HDPE crates can be concluded as follows:

1) The addition of a small amount (0.2% and 0.4%) of stabilizer “R550” to post-used HDPE crates resulted in a decrease in the zero shear viscosity. This might imply that R550 could inhibit oxidation degradation and the component of calcium stearate in R550 can act as an external lubricant.

2) The %elongation at break and toughness of post-used HDPE crate are effectively increased while increasing the amount of R550 from 0.2% and 0.4%. This might be due to restabilized HDPE crates can resist the thermal-oxidative degradation during reprocessing.

3) The blended of post-used HDPE crates with R550 at the concentration of 0.2% and 0.4% has negligible effects on tensile strength at yield, flexural modulus, flexural strength at yield, impact resistance and Rockwell hardness.

4) The addition of EVA at the concentration of 5% and 15% to post-used HDPE crates has an effect on processability. Increasing the concentration of EVA increases the zero shear viscosity and lowers the melt flow index of post-used HDPE crates.

5) The addition of EVA at the concentration of 5% to 15% to post-used HDPE crates resulted in a continuing decrease in Young’s modulus, tensile strength at yield, flexural modulus, flexural strength at yield and Rockwell hardness. On the other hand, the impact resistance of post-used HDPE crates is rapidly increased with an increasing in the concentration of EVA. This could be because EVA has a rubberlike property. This also implies that EVA continually disperses in HDPE phase.

6) The blend of post-used HDPE crates with 5% of EVA generally gives the most improved tensile and elongation property comparing with other blend formulae. These results could be suggested that the EVA improves the elasticity of HDPE and gives a good compatibility with HDPE.

7) Comparing the effects of R550 and EVA on the properties of post-used HDPE crates, it can be concluded that EVA (5 – 15%) generally has stronger effects than R550 (0.2 – 0.4%).

CHAPTER VI

NEW APPLICATIONS FOR POST-USED HDPE CRATES

From the study of processability and mechanical properties of post-used HDPE crates in Chapter IV, it was shown that some properties were decreased mainly due to the degradation that started to occur after a long time of utilization. In Chapter V, post-used HDPE crates were blended with two types of modifying agents, stabilizer “R550” and EVA copolymer, in an attempt to improve poor properties and processability of HDPE waste for recycling purpose. In this chapter, blended post-used HDPE crates were taken to process by injection molding to produce caps for beer keg. Caps for beer keg were practically tested in a real situation according to their uses. This application was chosen to test for the waste of post-used HDPE crates because of a limit in the amount of raw material and the availability of processing machine. However, other applications for the waste of post-used HDPE crates have been surveyed and presented in this chapter too.

6.1 Materials

Pellets of blends of post-used HDPE crates with either R550 or EVA, as classified in Table 6.1, were used to produce caps for beer keg.

Table 6.1 Classification of HDPE for injection process.

Code	Amount of material	Modifying agent	Method of Compounding
R550,0.2%	1.5 kg	Recyclossorb 550	Twin-Screw Extruder
R550,0.4%	1.5 kg	Recyclossorb 550	Twin-Screw Extruder
EVA5%	1.5 kg	EVA Copolymer	Twin-Screw Extruder
EVA15%	1.5 kg	EVA Copolymer	Twin-Screw Extruder

6.2 Equipment

6.2.1 Injection molding machine

Since the original products, HDPE crates, were manufactured by injection process, a further processing of this plastic waste should be suitable to the characteristic and processablity of the material. Form the results of processability of blended post-used HDPE crates with R550 and EVA in Chapter V, the melt flow index of these materials varied in range of 4.47 – 5.01 g/10 min, which is closed to the melt flow index required for injection process, which is about 5 – 100 g/10 min [Rosato and Rosato, 1990]. Hence, the injection molding process is chosen for the waste of HDPE crates.

The injection molding machine used in this study is at Srithai Superware Public Co., Ltd. The size of machine is 100 ton. Each formula of the blend of post-used HDPE crates performed at the injection pressure of 95 kg/cm^2 and back pressure of 15 kg/cm^2. Temperature conditions for injection molding are shown in Figure 6.1.

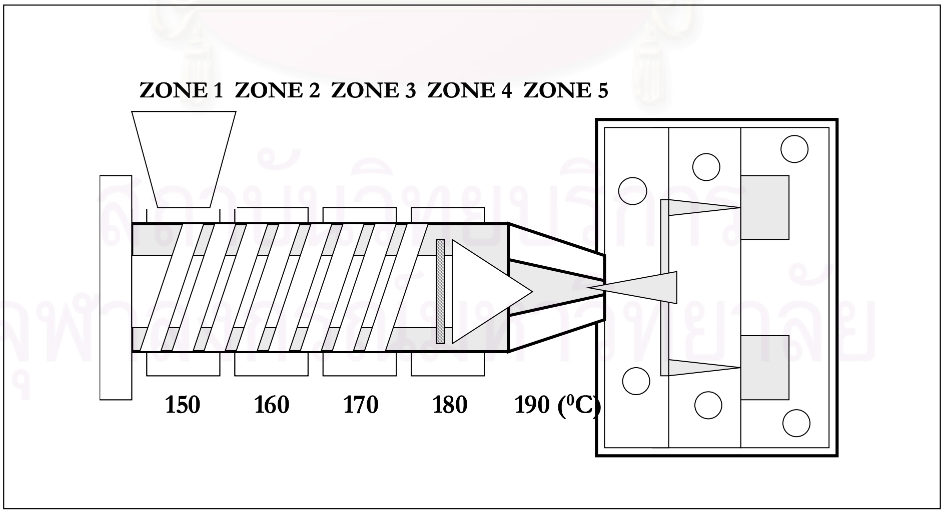


Figure 6.1 Temperature conditions for injection molding process.

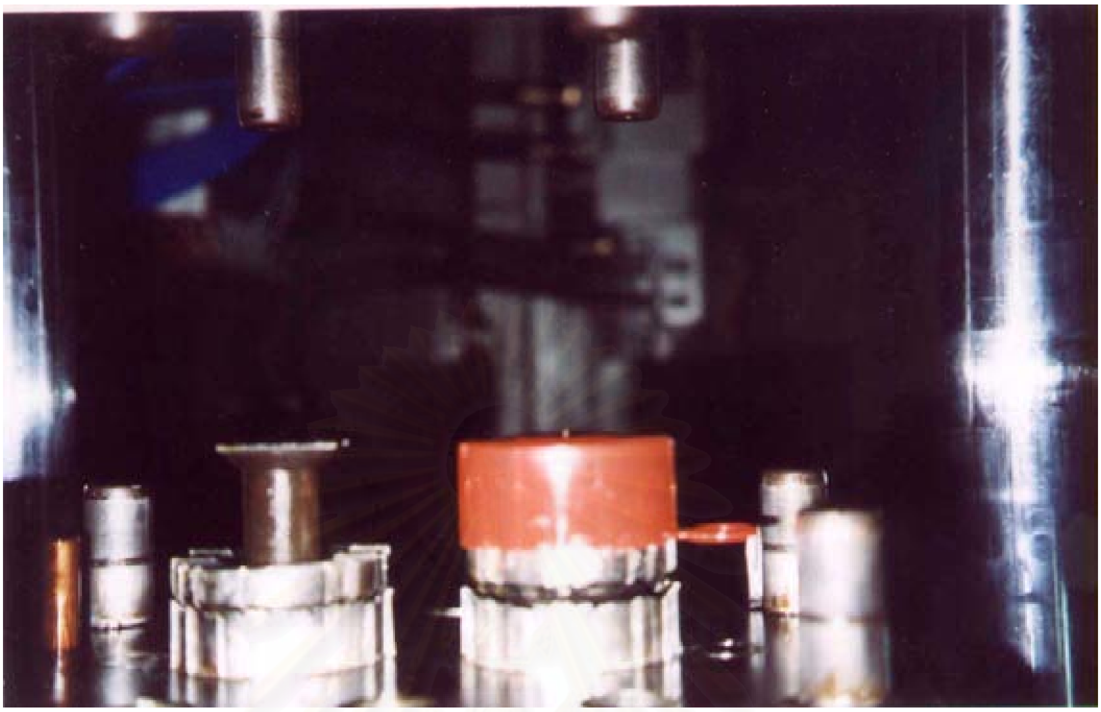
The cycle time to inject one lot of caps for beer keg is composed of mold closing time, cooling time, mold opening time and ejection time. The total cycle time of all samples is fixed at 39 sec. Details of the cycle time are shown in Table 6.2. The caps of blended post-used HDPE crates were then cooled in water at 25 ^{0}C. These process conditions are based on the production data from Srithai Superware Public Co., Ltd.

Table 6.2 Details of cycle time for injection molding process.

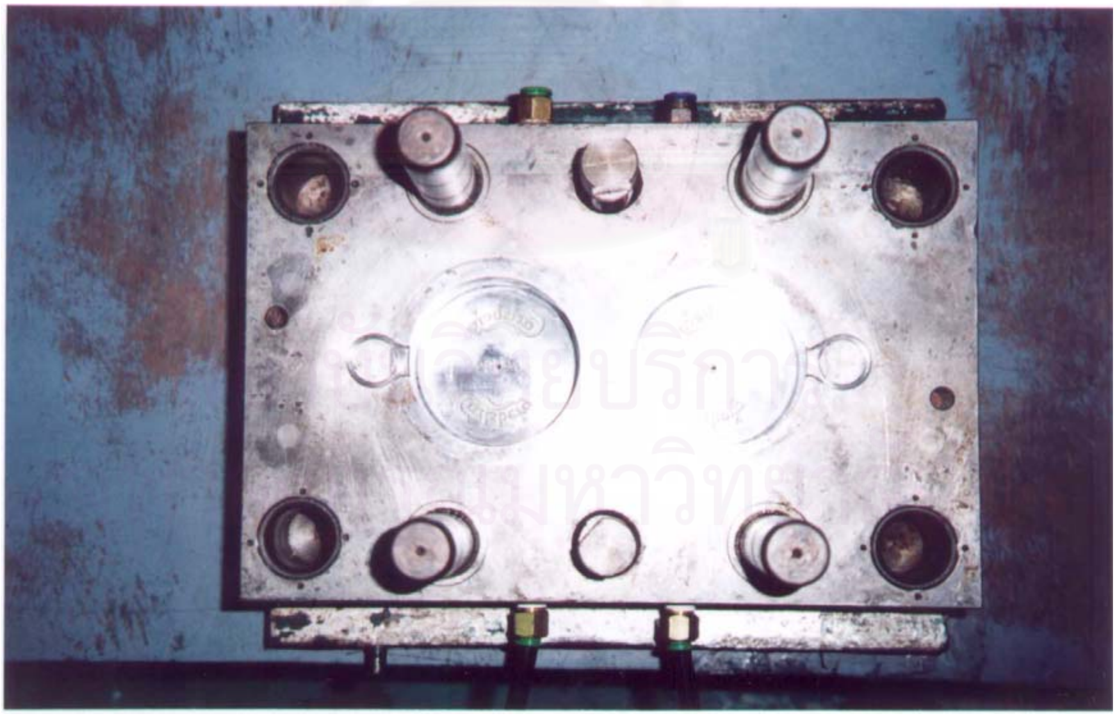
Cycle Time	Time (sec)
Mold closing time	3
Cooling time	28
Mold opening time	3
Ejection time	5
Total cycle time	**39**

6.2.2 Injection mold

The mold of a cap for beer keg, kindly offered by Srithai Superware Public Co., Ltd., is a three-plate injection mold. The plates automatically detach from each other so that the products and the runner are separated. Pin gate was used in injection mold design. The advantages of pin gate are low defects in finished products and the melted polymer in the gate can be frozen quickly. The injection mold of a cap for beer keg is shown in Figure 6.2.



(a)



(b)

Figure 6.2 Injection mold of a cap for beer keg; (a) moving plates; (b) fixed plate.

6.3 Inspection test

After a cap for beer keg has been produced from the injection process, the product was requested to pass the inspection test according to the customer requirement standard. The product was inspected following the check sheet shown in Table 6.3. Two important checkpoints, shown in Figure 6.3, are the “hook” and the “pin gate”. Good appearance of the finished caps is shown in Figure 6.4. Moreover, for each lot of production, a couple of caps were randomly taken to have a tear test. This is done by putting a cap on a beer keg and pulling it up. It is a practical test made by an operator in order to make sure that the cap can be functioned properly. The test on tear characteristic of a cap is shown in Figure 6.5.

Table 6.3 Details of the check sheet for a cap.

Checkpoints	Standard
Gate	None
Flash	None
Contamination	None
Hook	Complete
Shape and dimension stability	Complete
Fitness to the beer keg	Loosen or tighten

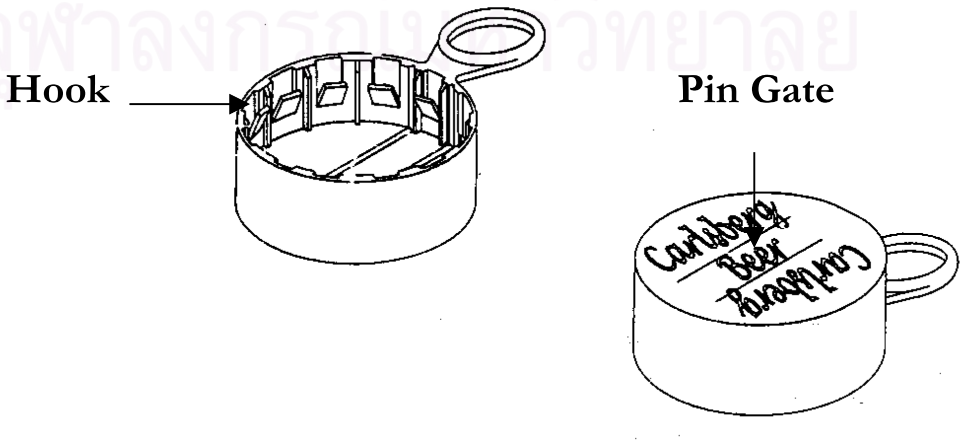


Figure 6.3 Checkpoints of a cap for beer keg.

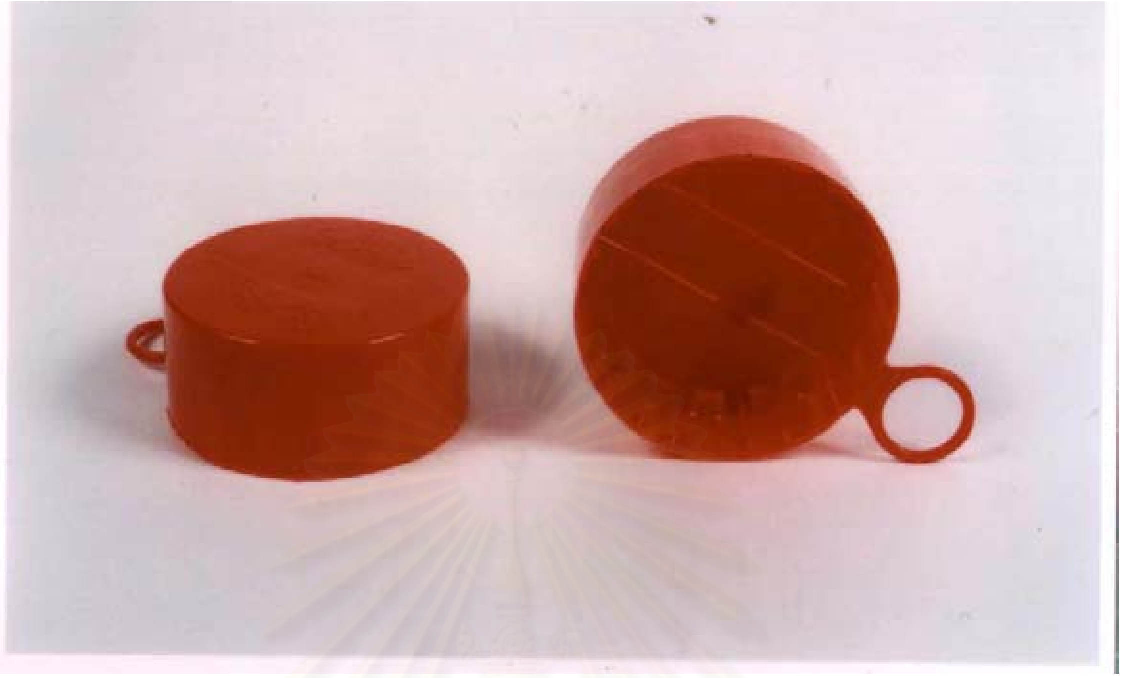


Figure 6.4 Good appearance of caps produced by injection process.

Figure 6.5 Tear characteristic of a cap.

6.4 Results and discussion

The data of check points for the caps produced from blends of post-used HDPE crates is presented in Table 6.4. When the finished products were cooled at 25 ^{0}C, caps made from blends of post-used HDPE crates and R550 have a good shape and appearance but caps made from blends of post-used HDPE crates and EVA have incomplete hook parts. This could possibly due to two reasons. The first reason is that the cooling time and temperature is insufficient. The other could be the lower heat deflection temperature of EVA, which is about 62 ^{0}C at 66 psi. However, increasing cycle time was not suitable for injection because it could affect the productivity. The problem was then solved by reducing cooling temperature from 25 ^{0}C to around 18 ^{0}C. The good caps were produced without any deflects in hook parts. All caps for beer keg have been tested on tear characteristic. The caps were easily ripped by pulling up when the beer keg was needed to open.

Table 6.4 The data of checkpoints for the caps.

Checkpoints	**Cooling Temperature at 25 ^{0}C**			
	R550,0.2%	**R550,0.4%**	**EVA5%**	**EVA15%**
Gate	None	None	None	None
Flash	None	None	None	None
Contamination	None	None	None	None
Hook	Complete	Complete	Incomplete	Incomplete
Dimension stability	Complete	Complete	Incomplete	Incomplete
Fittness to a beer keg	Tighten	Tighten	-	-
Tear test	Easy	Easy	-	-
Checkpoints	**Cooling Temperature at 18 ^{0}C**			
	R550,0.2%	**R550,0.4%**	**EVA5%**	**EVA15%**
Gate	-	-	None	None
Flash	-	-	None	None
Contamination	-	-	None	None
Hook	-	-	Complete	Complete
Dimension stability	-	-	Complete	Complete
Fittness to a beer keg	-	-	Tighten	Tighten
Tear test	-	-	Easy	Easy

6.5 Conclusion

Scrap of post-used HDPE crates can be recycled by mixing with either stabilizer R550 or EVA copolymer using the injection molding method. The blend can be used to produce the cap for beer keg. The appearance and shape of caps depend on the cooling temperature. It was found that the cooling temperature of 25^0C is suitable for the mixture of post-used HDPE crates and R550, while for the blend of post-used HDPE crates and EVA, the suitable cooling temperature is 18^0C. So far this is a satisfied example of the reused HDPE crates. It is much likely that the blended post-used HDPE crates can be further used to manufacture other larger products such as plastic carpet and stall walkway.

6.6 Recommendations

From property modification in Chapter V, R550 and EVA can be used to improve the properties of post-used HDPE crates. Especially, properties of EVA5% are not much different from virgin HDPE granule. The improved HDPE waste could possibly be used to produce a range of new products. Generally, applications of recycled products made from HDPE are animal pens, plastic lumber, pallets, drums and pails, traffic barrier cones, flower pots, bins, stall walkways and carpets. In this work, caps for beer keg were chosen as the application for recycled HDPE crates due to a small amount of material provided. Other applications for this case are plastic carpets and stall walkways. However, the problems of large injection machine, high operating cost and a huge amount of material required were faced so that a test for large product injection is impossible to perform, especially in the laboratory.

Plastic carpet used for anti-slip in bathroom and toilet, produced from Srithai Superware Public Co., Ltd, is an example of the products that can be manufactured from recycled HDPE, shown in Figure 6.6. The dimension of the product is 25 cm in length, 25 cm in width and 1.5 cm in thickness. The product weight is 230 g. From Chapter V, the properties of blended post-used HDPE crates with EVA is rather soft and tough, which is closed to the characteristic of plastic carpet. Therefore, the blend of post-used HDPE crates with EVA should be a suitable formula to produce plastic carpet.

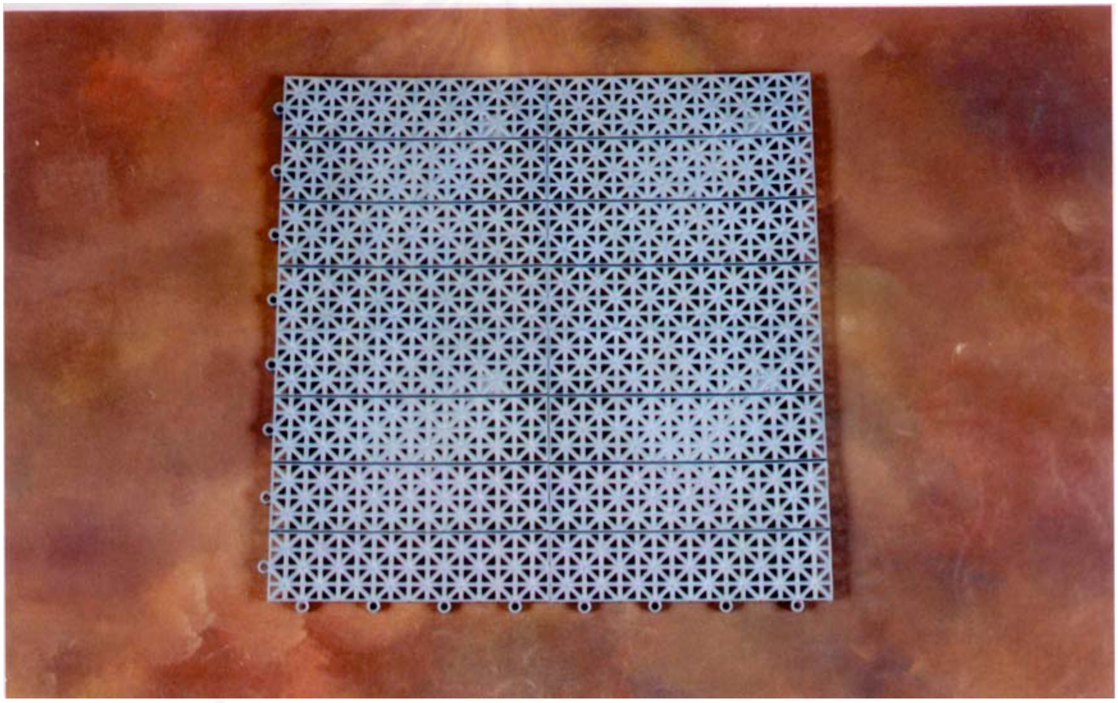


Figure 6.6 Plastic carpet.

Another high potential application for blended post-used HDPE waste is a stall walkway generally used in a farm, produced by T.K.T. Plastic Industrial Co., Ltd. The example of the product is shown in Figure 6.7. The dimension of the product is 100 cm in length, 25 cm in width and 4 cm in thickness. The product weight is 2.2 kg. From Chapter V, the blended post-used HDPE crates with 5% of EVA could possibly be used to produce stall walkway. Moreover, stall walkways have many ribs in the structure, which can support excessive load. The production of stall walkway from blended post-used HDPE crates and EVA should be preformed at a low cooling temperature to rapidly remove heat from the melted polymer. This application needs a huge amount of material per one lot of production. The production of stall walkway could be an effective way to reduce a huge amount of waste from plastic crates.

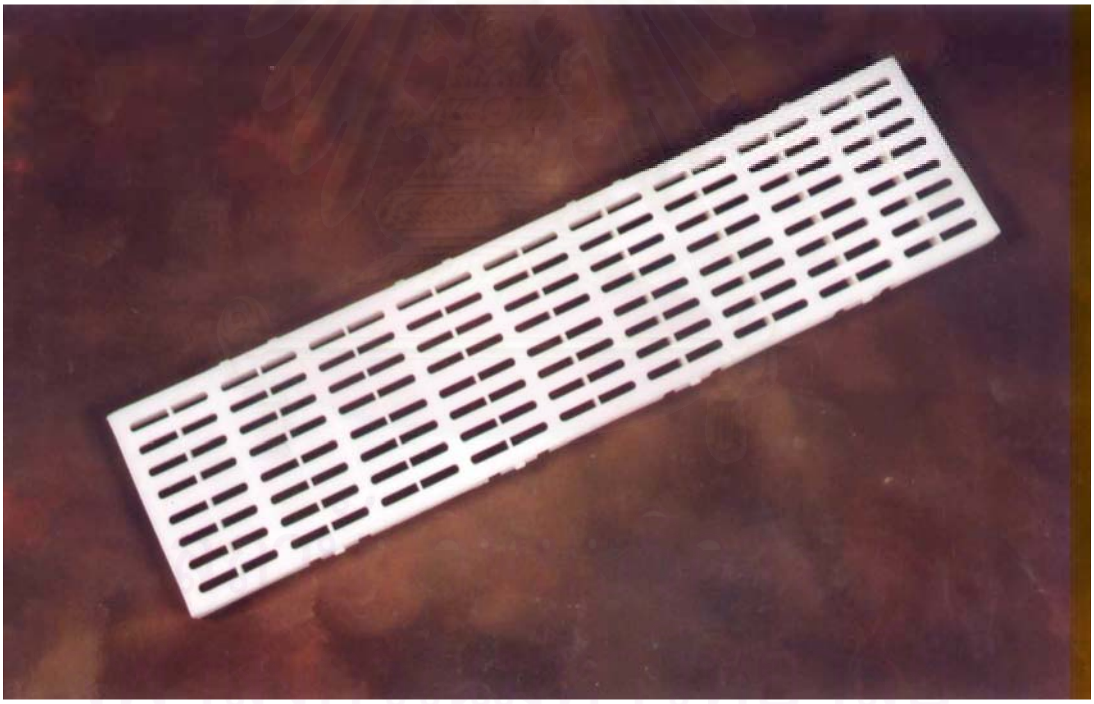


Figure 6.7 Stall walkway.

CHAPTER VII

CONCLUSIONS

7.1 Properties of post-used HDPE crates

From the study of the properties of used HDPE crates, it can be concluded that the period of utilization time of HDPE crates has affected the melt flow index, viscosity, %elongation at break, flexural strength at yield and impact resistance of the HDPE crates

- Increasing in the utilization time tends to increase the zero shear viscosity and decrease the melt flow index.
- Increasing in the utilization time decrease the %elongation at break, flexural strength at yield and impact resistance.

This should be a result of changes of the polymer chain structure, molecular weight and degree of crystallinity because of photo-oxidative degradation. Chain scission, chain branching and crosslinking mechanism would occur during photo-oxidative degradation.

7.2 Property modification of post-used HDPE crates

From the study of the mechanical properties and processability of the blends of post-used HDPE crates and either stabilizer “R550” or EVA, it can be concluded that stabilizer “R550” and EVA can be used to improve the poor properties of post-used HDPE crates for recycling purpose.

For the effects of R550, it can be concluded that the addition of a small amount (0.2% and 0.4%) of stabilizer “R550” to post-used HDPE crates resulted in an improvement in %elongation at break of post-used HDPE crates but had no effects on the tensile strength at yield, flexural modulus, flexural strength at yield, impact resistance and Rockwell hardness of post-used HDPE crates. This might be due to restabilized HDPE crates can resist the thermal-oxidative degradation during reprocessing.

For the effects of EVA, it can be concluded that the addition of EVA at the concentration of 5% and 15% to post-used HDPE crates has an effect on processability and mechanical properties. Increasing the concentration of EVA increases the zero shear viscosity, %elongation at break, and impact resistance of post-used HDPE crates but decreases the Young’s modulus, tensile strength at yield, flexural modulus, flexural strength at yield and Rockwell hardness. Particularly, the blend of post-used HDPE crates with 5% of EVA generally gives the most improved tensile and elongation property comparing with other blend formulae.

7.3 New applications for post-used HDPE crates

The blend of post-used HDPE crates with either stabilizer “R550” or EVA can be recycled to produce the caps for beer keg using the injection molding method. The appearance and shape of the caps depend on the cooling temperature in the injection process. It was found that the cooling temperature of 25^0C is suitable for the mixture of post-used HDPE crates and R550, while for the blend of post-used HDPE crates and EVA, the suitable cooling temperature is 18^0C. So far this is a satisfied example of the recycled HDPE crates. It is much likely that the blended post-used HDPE crates further used to manufacture other larger products such as plastic carpet and stall walkway. From Chapter V, the blend of post-used HDPE crates with EVA copolymer should be a suitable formula to produce plastic carpet and stall walkway.

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APPENDIX

APPENDIX

A. Raw data on experimental results of virgin HDPE and HDPE crates at various utilization time.

Table A-1 Molecular weight and molecular weight distribution of virgin HDPE and HDPE crates at various utilization time.

Code	M_w	M_n	MWD
VIRGIN	204,504	48,684	4.2
HDPE#0	209,245	41,744	5.0
HDPE#3	208,445	35,996	5.8
HDPE#8	208,451	37,152	5.6

Table A-2 Melting temperature and degree of crystallinity of virgin HDPE and HDPE crates at various utilization time.

Code	Melting Temperature (^{0}C)	Degree of Crystallinity (%)
VIRGIN	134	77
HDPE#0	132	67
HDPE#3	135	61
HDPE#8	134	63

Table A-3 Density of virgin HDPE and HDPE crates at various utilization time.

Code	Density (g/cm^3)		
	1	2	Average
VIRGIN	0.962	0.962	0.962
HDPE#0	0.966	0.966	0.966
HDPE#3	0.967	0.967	0.967
HDPE#8	0.964	0.964	0.964

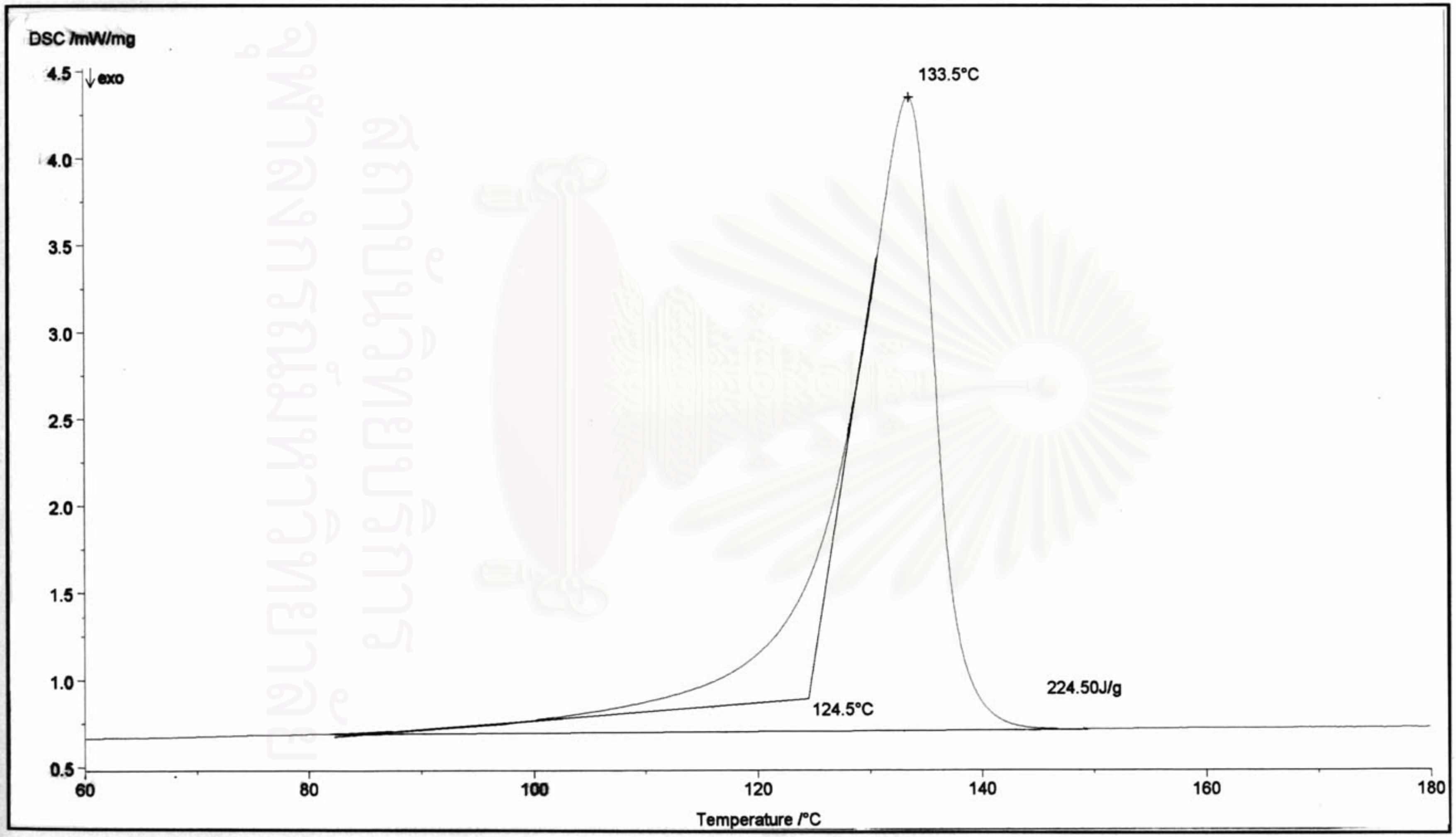

Figure A-1 Melting temperature and heat of fusion of virgin HDPE.

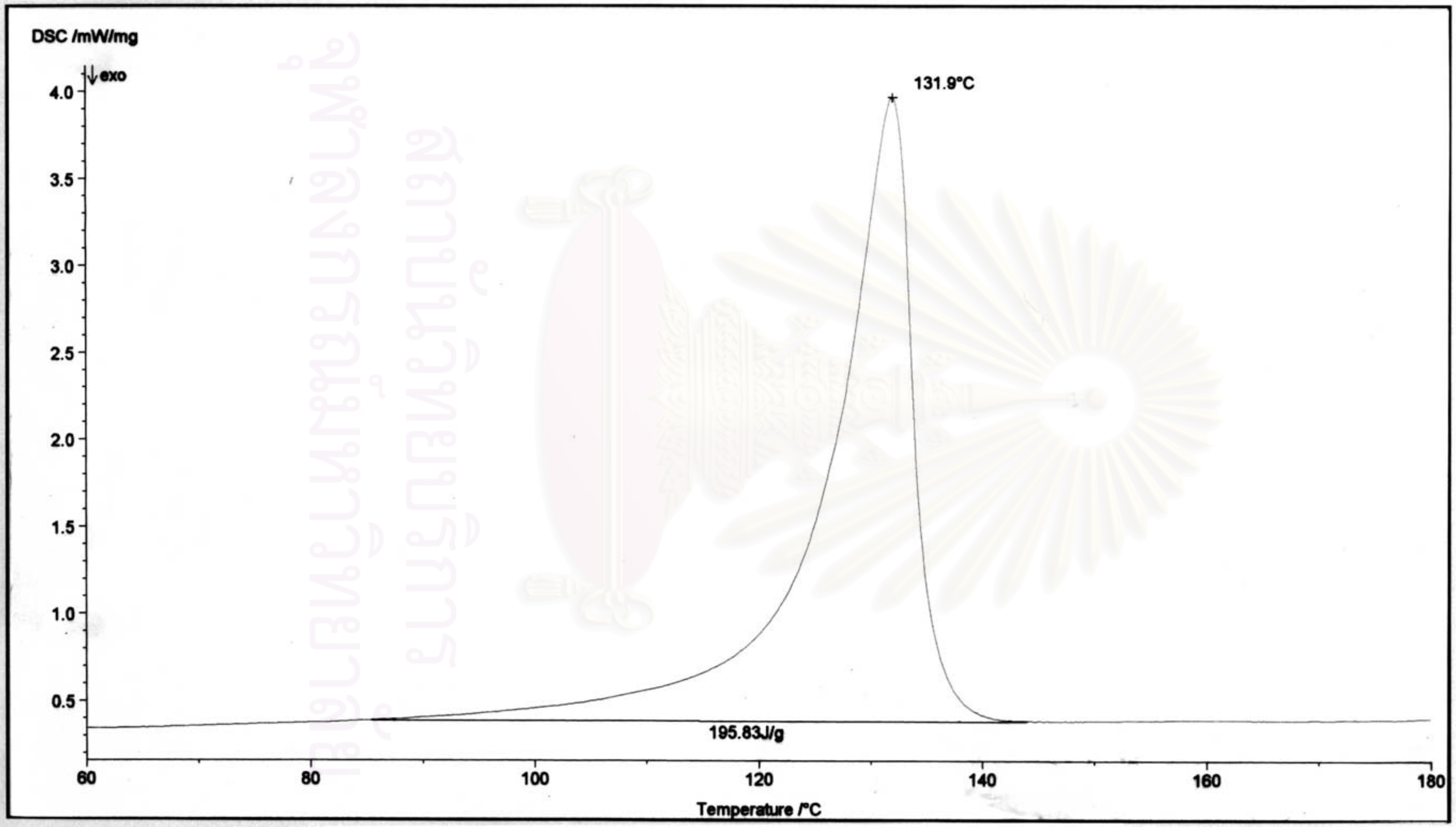

Figure A-2 Melting temperature and heat of fusion of new HDPE crates.

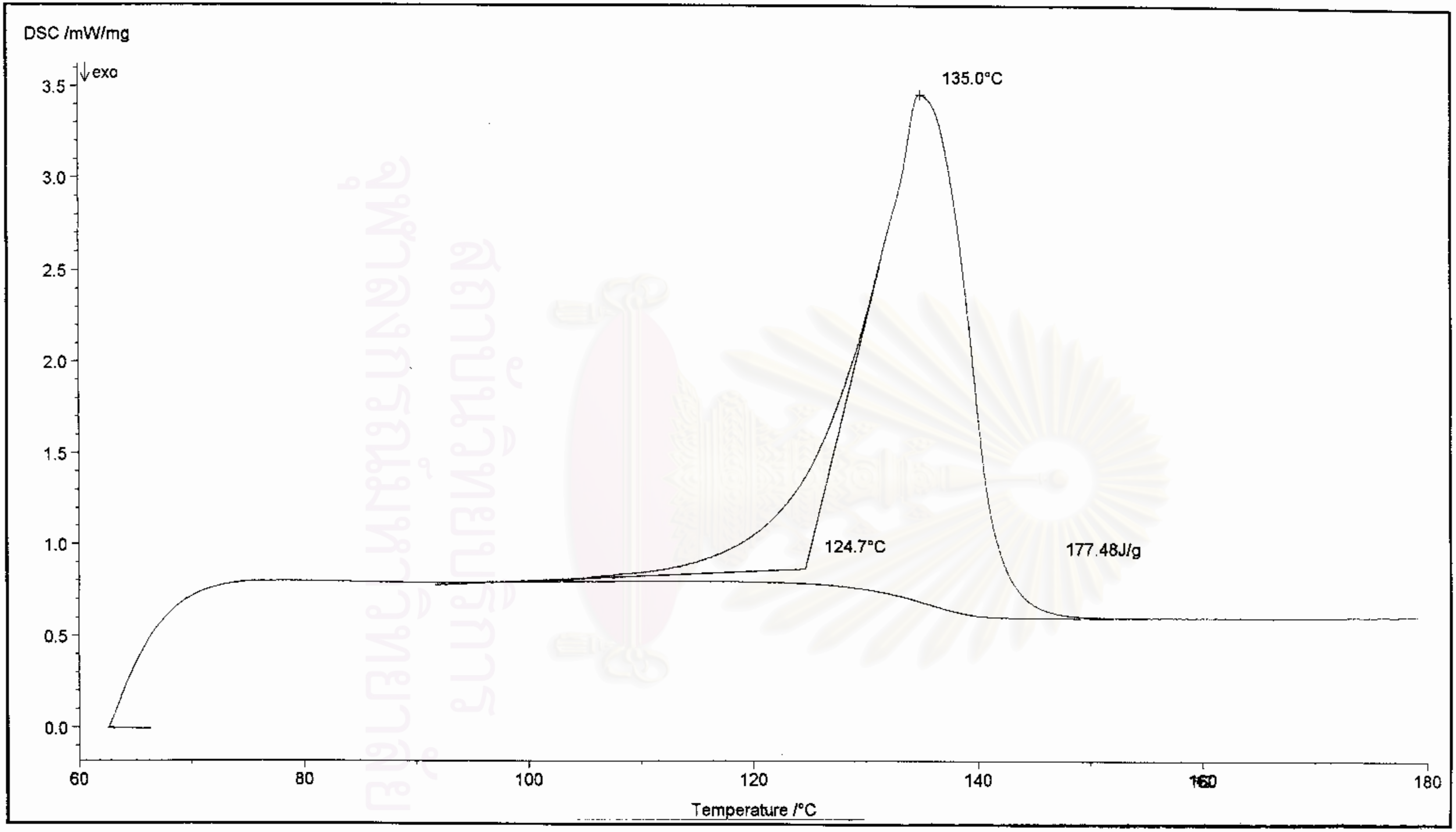

Figure A-3 Melting temperature and heat of fusion of 3 year used HDPE crates.

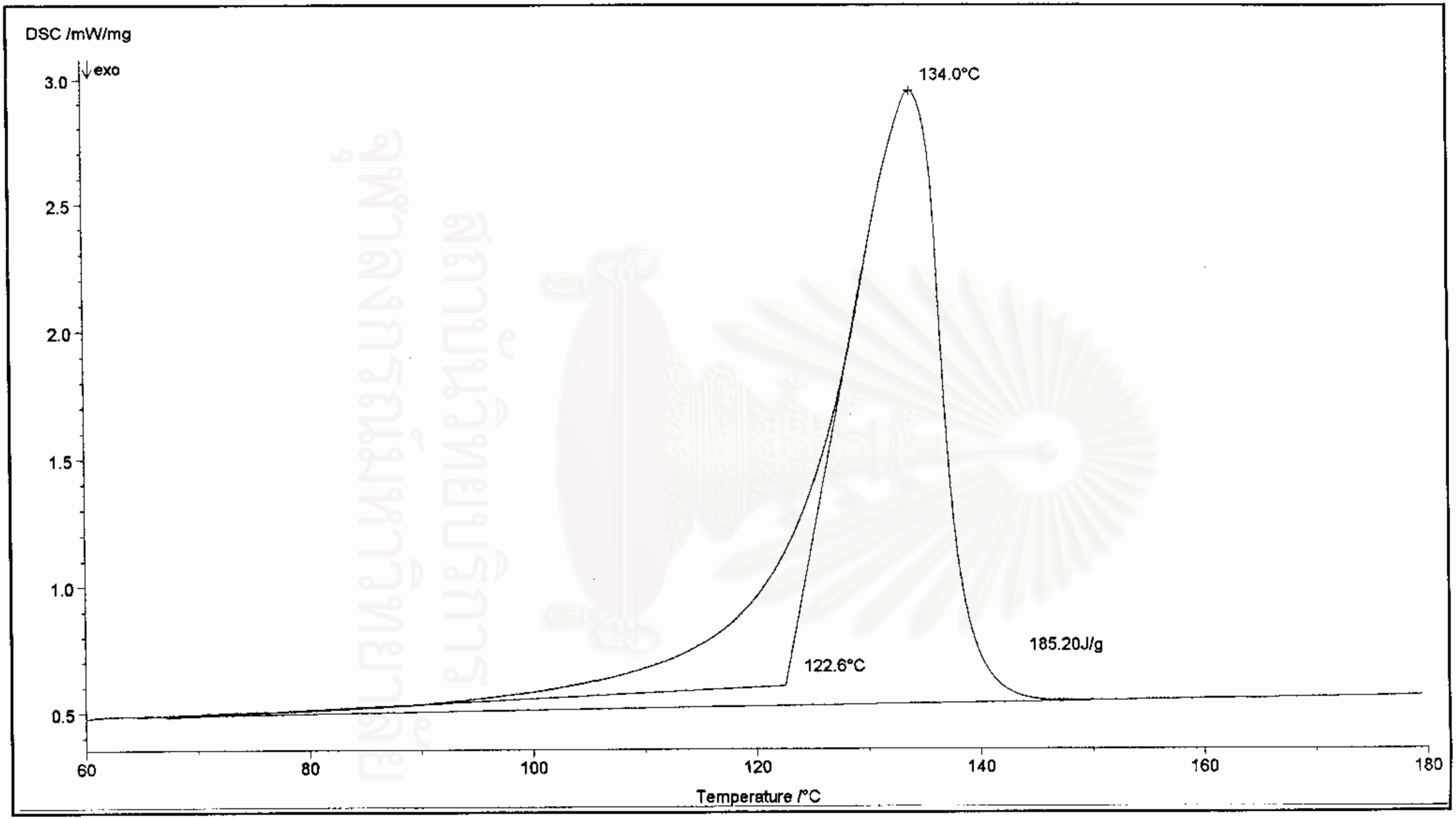

Figure A-4 Melting temperature and heat of fusion of 8 year used HDPE crates.

Table A-4 Melt flow index of virgin HDPE and HDPE crates at various utilization time.

Code	Melt Flow Index (g/10 min)					
	1	2	3	4	5	Average
VIRGIN	5.16	5.23	5.33	5.42	5.48	5.32
HDPE#0	5.49	5.66	5.68	5.72	5.77	5.66
HDPE#3	4.69	4.71	4.77	4.77	4.93	4.77
HDPE#8	4.67	4.85	4.90	4.93	4.94	4.86

Table A-5 Zero shear viscosity of virgin HDPE and HDPE crates at various utilization time.

Code	Zero Shear Viscosity (*10^{-3} Pas)
VIRGIN	2680
HDPE#0	2530
HDPE#3	3380
HDPE#8	3080

Table A-6 Tensile properties of virgin HDPE.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1456	24.26	>600
2	1516	25.48	>600
3	1441	24.98	>600
4	1489	24.50	>600
5	1469	25.32	>600
Average	1474	24.91	>600

Table A-7 Tensile properties of virgin HDPE (at crosshead speed of 100 mm/min).

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	2360	25.54	110
2	1970	24.07	137
3	2498	24.55	95
4	2235	25.28	160
5	1638	25.47	118
Average	2140	24.98	124

Table A-8 Tensile properties of new HDPE crates.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1610	25.24	138
2	1652	25.36	126
3	1631	24.46	184
4	1625	25.42	176
5	1592	25.37	113
Average	1622	25.17	147

Table A-9 Tensile properties of HDPE crates at the utilization time of 3 years.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	2540	25.78	66
2	2783	25.83	85
3	1528	25.60	97
4	3547	23.83	57
5	3123	25.19	67
Average	2704	25.25	74

Table A-10 Tensile properties of HDPE crates at the utilization time of 8 years.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	2367	25.14	110
2	2822	24.60	79
3	2498	25.09	110
4	3174	25.60	60
5	2421	24.96	109
Average	2656	25.08	93

Table A-11 Flexural properties of virgin HDPE.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	1006	27.96
2	905	27.53
3	934	25.66
4	899	27.36
5	947	26.89
Average	938	27.08

Table A-12 Flexural properties of new HDPE crates.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	905	26.59
2	908	27.25
3	929	26.82
4	927	27.26
5	880	26.45
Average	910	26.87

Table A-13 Flexural properties of HDPE crates at the utilization time of 3 years.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	965	25.62
2	1024	25.18
3	991	24.75
4	922	25.23
5	965	23.53
Average	973	24.86

Table A-14 Flexural properties of HDPE crates at the utilization time of 8 years.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	944	24.21
2	904	23.17
3	947	25.09
4	903	24.21
5	942	24.72
Average	928	24.28

Table A-15 Impact resistance of virgin HDPE and HDPE crates at various utilization time.

No. of sample	Impact Resistance (kJ/m^2)			
	VIRGIN	HDPE#0	HDPE#3	HDPE#8
1	6.8	5.8	4.7	4.7
2	6.9	5.8	4.9	4.6
3	6.2	4.5	5.3	4.8
4	6.3	6.0	4.9	4.5
5	6.2	5.8	5.3	4.4
6	6.5	7.8	4.9	4.3
7	6.6	5.8	4.7	4.4
8	6.4	5.6	5.3	4.3
9	6.6	6.0	5.7	4.1
10	6.5	6.9	4.5	4.8
Average	6.5	6.0	5.0	4.5

Table A-16 Rockwell hardness of virgin HDPE and HDPE crates at various utilization time.

No. of sample	Rockwell Hardness (R Scale)			
	VIRGIN	HDPE#0	HDPE#3	HDPE#8
1	54.90	56.30	58.20	59.00
2	55.70	59.40	58.30	59.50
3	57.20	59.90	60.50	59.70
4	57.50	60.10	61.50	61.00
5	59.40	60.20	63.50	61.50
Average	56.94	59.18	60.40	60.14

B. Raw data on experimental results of reextruded post-used HDPE crates and blended post-used HDPE crates with two types of modifying agents, R550 and EVA.

Table B-1 Melt flow index of reextruded post-used HDPE crates and blended post-used HDPE crates with R550 and EVA.

Code	Melt Flow Index (g/10 min)					
	1	2	3	4	5	Average
RE1	4.66	4.67	4.71	4.76	4.77	4.71
R550,0.2%	4.88	4.90	4.97	4.98	4.98	4.94
R550,0.4%	4.97	4.99	5.01	5.04	5.05	5.01
EVA5%	4.70	4.72	4.77	4.77	4.77	4.75
EVA15%	4.45	4.46	4.46	4.47	4.52	4.47

Table B-2 Zero shear viscosity of reextruded post-used HDPE crates and blended post-used HDPE crates with R550 and EVA.

Code	Zero Shear Viscosity (*10^{-3} Pas)
RE1	3150
R550,0.2%	2940
R550,0.4%	2860
EVA5%	3200
EVA15%	3500

Table B-3 Tensile properties of reextruded post-used HDPE crates.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1507	25.99	215
2	1516	25.08	276
3	1574	25.45	201
4	1616	26.35	267
5	1591	25.50	261
Average	1561	25.67	244

Table B-4 Tensile properties of blended post-used HDPE crates with R550 at the R550 concentration of 0.2%.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1581	25.95	298
2	1473	25.18	325
3	1602	25.64	326
4	1633	25.93	294
5	1575	23.66	347
Average	1573	25.27	318

Table B-5 Tensile properties of blended post-used HDPE crates with R550 at the R550 concentration of 0.4%.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1436	24.49	540
2	1516	25.82	575
3	1470	24.44	379
4	1542	24.61	471
5	1517	24.47	398
Average	1496	24.77	473

Table B-6 Tensile properties of blended post-used HDPE crates with EVA at the EVA concentration of 5%.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1420	24.10	>600
2	1388	23.43	>600
3	1408	23.81	>600
4	1361	23.20	>600
5	1370	23.07	>600
Average	1389	23.52	>600

Table B-7 Tensile properties of blended post-used HDPE crates with EVA at the EVA concentration of 5% (at crosshead speed of 100 mm/min).

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1942	23.27	107
2	2333	23.31	95
3	2232	22.47	89
4	2095	23.52	87
5	2889	23.23	77
Average	2298	23.16	91

Table B-8 Tensile properties of blended post-used HDPE crates with EVA at the EVA concentration of 15%.

No. of sample	Young's Modulus (MPa)	Tensile Strength at Yield (MPa)	%Elongation at Break (%)
1	1181	20.09	550
2	1118	18.29	480
3	1120	19.06	546
4	1262	20.23	575
5	1278	21.82	553
Average	1192	19.90	541

Table B-9 Flexural properties of reextruded post-used HDPE crates.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	982	26.18
2	978	26.51
3	971	25.07
4	985	26.47
5	1001	25.56
Average	983	25.96

Table B-10 Flexural properties of blended post-used HDPE crates with R550 at the R550 concentration of 0.2%.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	888	23.86
2	934	23.24
3	1005	24.38
4	999	24.04
5	876	23.55
Average	940	23.81

Table B-11 Flexural properties of blended post-used HDPE crates with R550 at the R550 concentration of 0.4%.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	921	22.82
2	854	23.17
3	959	23.69
4	939	24.23
5	884	23.4
Average	911	23.46

Table B-12 Flexural properties of blended post-used HDPE crates with EVA at the EVA concentration of 5%.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	867	23.39
2	849	23.44
3	851	23.79
4	880	23.76
5	864	23.48
Average	862	23.57

Table B-13 Flexural properties of blended post-used HDPE crates with EVA at the EVA concentration of 15%.

No. of sample	Flexural Modulus (MPa)	Flexural Strength at Yield (MPa)
1	730	21.02
2	713	20.26
3	810	22.23
4	746	20.61
5	743	20.70
Average	748	20.96

Table B-14 Impact resistance of reextruded post-used HDPE crates and blended post-used HDPE crates with R550 and EVA.

No. of sample	Impact Resistance (kJ/m^2)				
	RE1	R550,0.2%	R550,0.4%	EVA5%	EVA15%
1	4.3	4.1	3.8	5.3	18.8
2	4.0	3.9	4.2	5.2	20.0
3	4.3	3.8	4.4	5.5	18.5
4	4.5	3.8	4.7	5.6	18.4
5	4.2	3.8	4.2	6.0	18.8
6	3.9	3.8	4.3	5.2	16.1
7	4.0	4.2	4.3	8.4	17.9
8	4.2	4.7	4.0	5.5	26.9
9	4.9	4.1	3.9	8.0	20.5
10	4.2	4.2	4.5	6.8	26.4
Average	4.3	4.0	4.2	6.2	20.2

Table B-15 Rockwell hardness of reextruded post-used HDPE crates and blended post-used HDPE crates with R550 and EVA.

No. of sample	Rockwell Hardness (R Scale)				
	RE1	R550,0.2%	R550,0.4%	EVA5%	EVA15%
1	59.2	58.2	58.2	56.7	46.5
2	59.5	58.9	58.5	56.9	46.6
3	60	59.4	59.1	57.2	47.2
4	60.3	59.5	59.5	57.7	47.5
5	60.5	59.5	59.8	57.8	47.6
Average	59.9	59.1	59.0	57.3	47.1

CURRICULUM VITAE

Mr. Supachai Ngamsinlapasathian was born in Bangkok, Thailand on February 7, 1974. He graduated the secondary school from Yannawait Wittayakom School in Bangkok and received the Bachelor degree of Engineering (Plastic Technology), Rajamangala Institute of Technology, Thailand in 1996. He entered the Master of Engineering in Chemical Engineering Program at Chulalongkorn University in 1997.