FIBER SPINNING PROCESS OF RECYCLED POLYOLEFINS AND POLY(ETHYLENE TEREPHTHALATE)

KANOK-ON KONGSATIT

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF
MASTER OF SCIENCE IN APPLIED CHEMISTRY
SCHOOL OF GRADUATED STUDIES
KING MONGKUT'S INSTITUTE OF TECHNOLOGY LADKRABANG
2001

ISBN 974-648-505-9

หัวข้อวิทยานิพนธ์	กระบวนการผลิตเส้นใยจากพอลิโอลิฟินส์และ พอลิเอทิลีน เทเรฟทาเลตที่ใช้แล้ว
นักศึกษา	นางสาว กนกอร คงสถิตย์
รหัสประจำตัว	41065103
ปริญญา	วิทยาศาสตรมหาบัณฑิต
สาขาวิชา	เคมีประยุกต์ (เทคโนโลยีพอลิเมอร์)
พ.ศ.	2544
อาจารย์ผู้ควบคุมวิทยานิพนธ์	ผศ.ดร.สมศักดิ์ วรมงคลชัย

บทคัดย่อ

งานวิจัยนี้ศึกษาหาอัตราส่วนและสภาวะที่เหมาะสมในกระบวนการผลิตเส้นใยสังเคราะห์แบบหลอมเหลว จากพอลิเมอร์ผสมระหว่างพอลิโอลิฟินส์ที่ใช้แล้ว (พอลิเอทิลีนชนิดความหนาแน่นสูง พอลิเอทิลีนชนิดความหนาแน่นต่ำและ พอลิพรอพิลีน) กับพอลิเอทิลีน เทเรฟทาเลตที่ใช้แล้ว โดยใช้พอลิเอทิลีนชนิดความหนาแน่นสูงเกรดเส้นใยเป็นตัวเปรียบเทียบกับพอลิเอทิลีนชนิดความหนาแน่นสูงที่ใช้แล้ว รวมทั้งศึกษาปรียบเทียบชนิดและหาอัตราส่วนที่เหมาะสมของสารช่วยผสมระหว่าง พอลิพรอพิลีนกราฟต์มาลิอิก แอนไฮดราย์ พอลิพรอพิลีนกราฟต์กรดอะคริลิค และพอลิเอทิลีนชนิดความหนาแน่นสูงกราฟต์กรดอะคริลิค ที่ส่งผลต่อสมบัติเชิงกล สมบัติทางความร้อน และสมบัติทางสัณฐานวิทยาของเส้นใยที่ได้

จากผลการวิจัยพบว่า ที่อัตราส่วนการผสมระหว่าง พอลิพรอพิลีน พอลิเอทิลีนชนิดความหนาแน่นสูง และ พอลิเอทิลีนชนิดความหนาแน่นต่ำ เท่ากับ 25/50/25 โดยทำที่อุณหภูมิ 230 องศาเซลเซียส ความเร็วสกรูและอัตราเร็วในการปั่นเก็บเป็น 20 รอบ/นาที และ 11.90 เมตร/นาที ตามลำดับ จัดเป็นสภาวะที่เหมาะสมที่สุดของระบบพอลิโอลิฟินส์ผสม โดยให้ค่าความทนต่อแรงดึง ณ จุดขาด เท่ากับ 53 เมกกะปาสคาล หรือ 0.6 กรัม/ดีเนียร์ ร้อยละของความยาว ณ จุดขาด เท่ากับ 233 และค่ามอดุลัสของความยืดหยุ่น เท่ากับ 45 เมกกะปาสคาล สำหรับในระบบพอลิเมอร์ผสมระหว่างพอลิโอลิฟินส์ กับ พอลิเอทิลีน เทเรฟทาเลต พบว่า สภาวะที่เหมาะสมคือที่อัตราส่วนระหว่างพอลิโอลิฟินส์ และพอลิเอทิลีน เทเรฟทาเลต เท่ากับ 25/75 โดยทำที่อุณหภูมิ 270 องศาเซลเซียส ซึ่งให้ค่าความทนต่อแรงดึง ณ จุดขาด เท่ากับ 60 เมกกะปาสคาล หรือ 0.7 กรัม/ดีเนียร์ ร้อยละของความยาว ณ จุดขาด เท่ากับ 39 และค่ามอดุลัสของความยืดหยุ่น เท่ากับ 68 เมกกะปาสคาล เมื่อเปรียบเทียบกับระบบที่เติมสารช่วยผสม พบว่าระบบที่เติมสารช่วยผสมจะทำให้สมบัติของเส้นใยลดต่ำลงอย่างมาก ส่วนในกรณีการเปรียบเทียบระหว่างพอลิเอทิลีนชนิดความหนาแน่นสูงเกรดเส้นใยกับพอลิเอทิลีนชนิดความหนาแน่นสูงที่ใช้แล้วที่สภาวะเดียวกัน

พบว่า การใช้เส้นใยที่ได้จากพอลิเอทิลีนชนิดความหนาแน่นสูงเกรดเส้นใยเป็นองค์ประกอบแทนพอลิเอทิลีนชนิดความหนาแน่นสูงที่ใช้แล้ว จะมีสมบัติที่ด้อยกว่าในทุกสภาวะ

Thesis Title Fiber Spinning Process of Recycled Polyolefins and Poly (ethylene terephthalate)
Name Ms. Kanok-on Kongsatit
ID. 41065103
Degree Master of Science
Programme Applied Chemistry (Polymer Technology)
Year 2001
Thesis Advisor Asst. Prof. Dr. Somsak Woramongconchai

ABSTRACT

This research studied on the synthetic fibers from recycled polyolefins (recycled high-density polyethylene (R-HDPE), low-density polyethylene and polypropylene) and recycled poly(ethylene terephthalate) blends by melt spinning process. Both fiber grade of high-density polyethylene (F-HDPE) and recycled high-density polyethylene were used as reference materials. Then the ratio and appropriate processing conditions of polymer blends were investigated with various compatibilizer types (polypropylene grafted maleic anhydride (PP-g-MA), polypropylene grafted acrylic acid (PP-g-AA) and high-density polyethylene grafted acrylic acid (HDPE-g-AA)) on mechanical, thermal and morphological properties.

From the results, it was found that the appropriate conditions of polyolefins blend were at ratio of PP/R-HDPE/LDPE as 25/50/25, temperature of 230 $^{\circ}$C, screw speed and spinning speed of 20 rpm and 11.90 m/min, respectively. The blend at this ratio had tensile strength at break of 53 MPa or tenacity of 0.6 g/denier, elongation at break of 233 and modulus of elasticity of 45 MPa. The system of polyolefin/recycled poly (ethylene terephthalate) blended at the ratio of 25/75 and mixed at temperature of 270 $^{\circ}$C showed better properties than other systems. This blend had tensile strength at break of 60 MPa or tenacity of 0.7 g/denier, elongation at break of 39% and modulus of elasticity of 68 MPa. The effects of compatibilizers were also studied. It was found that when compatibilizers were added, the mechanical and thermal properties of fibers were decreased. The system that used F-HDPE replacing R-HDPE in the components, for producing fibers at the same conditions, had worse properties.

ACKNOWLEDGEMENT

For completeness of this thesis, I would like to thank all of these following people for their supports and helpfulness in my thesis.

I would like to thank my advisor, Assistant Professor Dr. Somsak Woramongkolchai for his valuable guidance and good throughout this study. I would like to thank Dr. Jutarat Sirichaisit, Dr.Suparat Jumpa and Assistant Professor Dr. Taweechai Amornsakchai for their kindness to correct my thesis and for my committees.

I would like to thank the Bangkok Polyethylene Co., Ltd. for their support of a high-density polyethylene fiber grade.

I would like to thank the officers at the Rubber Technology Division for their helpfulness in Differential Scanning Calorimetry. In addition, my sincere thank to the technicians at the Department of Chemistry, Faculty of Science, King Mongkut' s Institute of Technology Ladkrabang and my friends for their helpfulness during the experiment. Without their supports, this research could not have succeeded.

Most importantly, I would like to express my faithful thanks to my parents for their kindness and encouragement throughout completing this thesis.

Kanok-on Kongsatit

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

TABLE OF CONTENTS (continued)

Page

LIST OF TABLES

Tables Page

LIST OF TABLES (continued)

Tables Page

LIST OF FIGURES

Figures Page

LIST OF FIGURES (continued)

Figures Page

LIST OF FIGURES (continued)

CHAPTER 1

INTRODUCTION

1.1 Motivation

Most plastics are made wholly or partly from petroleum or natural gas products or by product. The petroleum industry is the main source supply for the plastic industry. This brings two industries highly interrelated. Other sources of materials are phenol from coal tar; chlorine from salt; acetic acid from coke, limestone, and water; formaldehyde from coal, air, and water; and benzene from coal. In the future, petroleum will be in short supply and shortages of many materials according to a worldwide problem. But if petroleum products are used wisely, there should be an adequate supply of plastic products for many years to come.

The convenience and design aspects of plastics many times overshadow the less obvious benefits of plastics. The use of plastics as a replacement for glass, metal, paper, and other materials often results in such benefits as these:

1. Lighter weight packaging,
2. Reduced shipping costs,
3. Reduced breakage,
4. Improved product distribution,
5. Reduced solid waste load,
6. Increased safety,
7. Improved health,
8. Improved consumer convenience,
9. Aid to truth in packaging,
10. Reduced contamination and infection through medical disposable,
11. Easier disposal by sanitary landfill or incineration.

Many of these tend to reduce costs of consumer products [1].

Today, plastics are more popular materials for industry and the world's consuming of plastics is reaching a magnitude where disposal is becoming a major problem, an increasing volume of plastic wastes needs to be recycled for both environmental and economical reasons. Recycling processes generally produce fewer environmental effluents than do processes that produce virgin resins, so the use of recycled plastics usually results in a decrease in air and water pollution. Recycling processes can result in significant energy saving (recycling plastics saves 88% of the energy required to produce plastics from raw materials) and help to protect resources. Obviously, the use of recycled plastics also results in less depletion of natural resources, while the major motivations for the business community have been the cost saving and marketing advantage that can be gained by enhancing the efficiency of plastic materials. In recent years there has been a significant increase in the amount of plastic recycling that being done around the world. Reasons for recycling plastics are as these:

Recycling of waste is a currently believed to be the most acceptable from disposal in the long run; however, this route is known to be difficult for plastics. Recycling would be easier if the various generic types present in solid waste could be isolated.

According to American Plastics Council (APC), 1994 recycling rates were about 21 percent for plastic bottles and about 17 percent for plastic containers-substantial growth since 1989, when the recycling rate was just over 4 percent. Total tonnage recycled in 1994 in the United States, by APC estimate, was 1 billion pounds. For some types of bottles, the rate was much larger-nearly 49 percent for PET soft drink bottles (PET is the only one that already has achieved high a recycling rate) and nearly 26 percent for natural HDPE bottles [2].

Table 1.1 Volume of plastic wastes in Thailand, 1996 [3].

Details	Tonnes	Percent
Total wastes	13,140,000	100
Plastic wastes	1,156,000	9
Recycled plastic wastes	245,000	2
Non-recycled plastic wastes	911,000	89

Nowadays, Thai people have used plastics for 219 kg/person/year or 0.6 kg/person/day and the rate of consumption increases for 25 to 30 percent in each year. Thus, that no surprising, we can find plastic wastes everywhere in Thailand. Table 1.1 shows the volume of plastic wastes of the year 1996 in Thailand [3].

Polymer blends are of considerable interest for recycling plastic waste, in which plastics of different polymer types are mixed to form reusable materials with acceptable properties. They are also important for improving the properties of virgin materials such as impact strength and tensile strength.

This research studied on the mechanical, thermal and morphological properties, ratio and processing conditions of blends of recycled polyolefins (recycled high-density polyethylene (R-HDPE), low-density polyethylene (LDPE) and polypropylene (PP)) and recycled poly(ethylene terephthalate) (R-PET) on spun fibers by melt spinning process. This research is motivated by the fact that polyolefins and poly(ethylene terephthalate) are the most commonly used in plastic industry and in recycling process.

1.2 Objectives of this study

1.2.1 To study ratio and processing conditions of recycled polyolefins and polyolefins with R-PET blends on spun fibers by melt spinning process.

1.2.2 To compare fibers of recycled polyolefins and polyolefins with R-PET.

1.2.3 To compare properties of fibers from blends that used fiber grade material of high-density polyethylene instead of R-HDPE in the components.

1.3 Scope of this work

1.3.1 To find appropriate optimum processing conditions of recycled polyolefins and polyolefins blends with R-PET by melt spinning process as following variables:

1.3.1.1 Spinning speed and screw speed

1.3.1.2 Temperature

1.3.1.3 Ratio of polyolefins and polyolefins with R-PET blends

1.3.2 To study the effect of compatibilizer types.

1.3.3 To investigate the mechanical, thermal and morphological properties of fibers.

1.4 Expected results

1.4 1 Plastic wastes resources are to be dumped.

1.4.2 The spun fibers have the good properties and are suitable for applications of products.

1.4.3 Cost productions are low because of recycled materials.

1.4.4 Appropriate compatibilizer improves properties of blends on fibers.

1.4.5 Performances of recycled plastic wastes are expanded widely.

1.4.6 The spun fibers from recycling material blends are an alternative in recycling process.

CHAPTER 2

LITERATURE REVIEWS AND THEORETICAL CONSIDERATION

2.1 Literature reviews

Daw F. M., *et al* [4] used recycled poly(ethylene terephthalate) (R-PET) blends with a fiber grade material poly(ethylene terephthalate) (F-PET). As spun fibers of R-PET, F-PET and R/ F-PET blends were made at winding speeds ranging from 1000 to 4000 m/min. The results indicated that: (1) mechanical properties: the high speed spinning improved the tensile strengths of as-spun fibers. (2) The birefringence property: the orientation of as-spun fiber was increased with the increasing of spinning speed. Less orientation for the fibers was found by the incorporation of R-PET component. (3) Crystallinity properties: the results of DSC showed that the degree of crystallinity was higher for F-PET as spun fibers than for R-PET fibers spun at the same speed. (4) The thermal properties: DSC studies had shown that increased spinning speed gave a higher melting temperature (T_m). For the R-/F-PET blends T_m was proportionally decreased with incorporating of R-PET component.

Vallilatos *et al.* [5] suggested that high spinning speed improves mechanical properties. It was explained that by increasing spinning speed, the level of molecular orientation that develop were high enough to induce crystallization on the spinning line.

Ravi S. K., *et al* [6] investigated structural development during melt spinning of syndiotactic polypropylene and determined that the fibers were distinctly semi-crystalline with well and high crystal orientation at low spinning speeds (up to 1000 m/min), but were not as well crystallized at higher speeds (greater than 1000). The tensile properties, the breaking stress increased and elongation at break decreased with increasing speed.

Rakesh G. K., *et al* [7] investigated the crystallization behavior of poly(ethylene terephthalate) (PET) melt spun into fiber monofilaments. It was found that while the filaments that had been spun non-isothermally were essentially amorphous, those that had been made under isothermal conditions at temperatures ranging from 180 to 240 °C were oriented and crystalline. The shapes of the stress-strain curves of the non-isothermal fibers varied with spinning speed with the low speed curves exhibiting ductile behavior and long elongation before break and even though the mechanical strength increased with spinning speed but the ultimate strength remained low. This was a typical of an amorphous fiber. For stress-strain curves of the isothermal spun fibers at higher spinning speeds, the fiber gains molecular orientation and crystallinity and its mechanical improvement. The fiber became much less ductile, the modulus increased and so did the ultimate strength. In addition, the rate of oriented crystallization was much greater than that under quiescent conditions at the same temperature.

Napolitano M. J. and Moet A. [8] studied the variation of the modulus with gauge length of melt spun poly(ethylene terephthalate) fibers and the modulus achieved a stable, reproducible value for gauge length above 150 mm. A gauge length of 170 mm was selected to minimize grip effects. It was found that the denier of fibers increased as the spinning speed decreased. The results of DSC showed that fibers spun at lower speeds display higher cold crystallization temperature.

Edgar T. R., *et al* [9] studied the processing of blends of poly(ethylene terephthalate) (PET) and high-density polyethylene (HDPE). It was determined that at 270 °C, the blends showed good homogenization and were easy to process. The tensile modulus for non-compatibilized blends of PET and HDPE increased with increasing PET composition in the blend and when the processing temperature increased from 230 to 260 °C. Blend compatibilization using Kraton (triblock copolymer, styrene end block and a hydrogenated butadiene midblock) showed lower modulus than equivalent non-compatibilized blends under the same conditions.

Krasnikova N. P., *et al* [10] using blends of polyethylene and polystyrene studied the conditions for fibre formation during melt extrusion through a capillary die. It was determined that the optimum conditions for fibre formation was parity of the viscosity between the components.

Bo-Run L., *et al* [11] investigated phase morphology of polypropylene and nylons 6 blends. The PP/N6 blends show polypropylene islands in nylons 6 sea. Both

75/25 and 50/50 blends show nylon 6 islands in a polypropylene sea. The cross sections of the discrete island depend on composition.

Shimizu J., *et al* [12] studied of the extent of crystallization in poly(ethylene terephthalate). The results have identified the relative effects of the increase in crystallization rate resulting from the increase in flow-induced orientation at higher speeds and the decrease in the duration of crystallization in the treadline resulting from the increased rate of cooling. In fiber formation at low speeds, the crystallization is negligible owing to the extremely low rate of crystallization. At very high speeds, crystallization is limited by extremely short residence time in the crystallization zone.

Abhiraman S. a., et al [13] describe the evolution of orientation order in melt spinning of polymer. In the case of crystallizable polymers, with $T_g<T_r$, the fiber at room temperature is still above its glass transition temperature and it continues to under go additional crystallization.

Traugott D.T., et al [14] studied the properties of melt blends of poly(ethylene terephthalate) (PET) and HDPE. Blend compatibilization using Kraton 1652G(triblock copolymer, styrene end block and a hydrogenated butadiene midblock) adheres fairy well to both materials. As a little as 5 percent addition to the 50/50 blend converts to it a reasonably ductile material, and at the 20 percent addition level the blends do not break to strains higher than the 200 percent. The blend modulus and yield strength are reduced somewhat as the rubbery agent is added, but the decline in these properties is small relative to the improvements in ductility achieved.

Somsak W., *et al* [15] studied optimum conditions for processing of recycled polyolefins (PP, LDPE and R-HDPE) and recycled poly(ethylene terephthalate) blends using polypropylene grafted maleic anhydride (PP-g-MA) as compatibilizer. It was determined that the adding of compatibilizer increased the mechanical properties and then decreased when exceeded compatibilizer was added to polymer blends. The optimum conditions of recycled polyolefins and recycled poly(ethylene terephthalate) blends from single-screw extruder used screw speed of 50 rpm, temperature of 230 °C and added 1% by weight of compatibilizer to the ratio of polyolefins/recycled poly (ethylene terephthalate) as 50/50.

Gupta P., *et al* [16] have also studied melt-blended polypropylene (PP) and high density polyethylene (HDPE) samples containing 5 to 25 wt % HDPE. They have observed that the addition of HDPE to PP results in an increased degree of crystallinity of PP, a faster rate of nucleation and a reduction in the crystallite size distribution.

2.2 Polymer blend

Polymer blending has entered the plastics industry a half century ago. Since then it has been growing so rapidly that it is becoming an increasingly important portion of the entire plastics industry, 20-40% of the total plastics market by various estimates. With growing understanding and command of the science and engineering involved, it may well continue to offer increasing contributions to plastics and the other polymer industries.

Polymer blends have commercial importance because they offer properties, or a balance of properties, not available in a single polymer. These properties depend very much on the microstructure of the blend [17].

A polymer blend will be defined here as a physical mixture of two polymers; however, frequently some grafting of one polymer on to the other is also present as a result of the method of blend preparation e. g. mixing of two polymers in the molten state etc. These preparation methods do not usually lead to chemical bonding between the components [18]. Sometimes the term refers specifically to such two-phase mixtures, single phase mixtures then being called alloys.

2.2.1 Types of Polymer blend

Polymer blend can be classified in 3 types.

2.2.1.1 Miscible polymer blend

Polymer blend is homogeneous down to the molecular level, associated with the negative value of the free energy of mixing, as shown in equation (2.1) [19].

$$\Delta G_{mix} \approx \Delta H_{mix} \leq 0 \quad \text{from} \quad \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (2.1)$$

There are rare cases of miscible (or compatible) polymers, the blend properties are intermediate (roughly average) between those of the individual unblended polymers [18].

When two polymers are completely miscible down to the segmental level, they form a single homogeneous phase, and properties are generally proportional to the ratio of the two polymers in the blend. On a molecular level, polymer A molecules intermingle with polymer B molecules, as shown in Figure 2.1 (a). Miscible polymer blend is much like a random copolymer in properties and processing [20].

Figure 2.1 Morphologies of a blend of polymer A (solid lines) and polymer B (dashed lines); (a) partially miscible (b) immiscible (c) miscible [20].

Miscibility of polymer blend, being defined in terms of the equilibrium thermodynamics, must be considered only within the range of independent variables (temperature, pressure, molecular weight, chain structure, etc.) under which the free energy of mixing is negative. The condition for $\Delta G_m < 0$ can exist only if the binary polymer-polymer interaction coefficient, χ_{12}, is negative. There are three contributions to χ_{12}: dispersion forces, free volume and the specific interactions.

The χ_{12} relative magnitude and the temperature dependence are shown schematically in Figure 2.2. In the figure the dependency on the left is most frequently observed in low molecular weight solutions, while that on the right found in polymer blends. The UCST and LCST indicate the upper and the lower critical solution temperature respectively. For UCST < T < LCST the mixture is miscible, i. e. for polymer alloy and blend the miscibility vanishes above the LCST. In consequence, blending polymer blend above LCST leads to a state of miscibility in the finished product, which depends on the kinetics of phase separation during the post-processing cooling stage [19]. In Figure 2.3 shown relationship between temperature and composition of phase diagram for two-component blends [21].

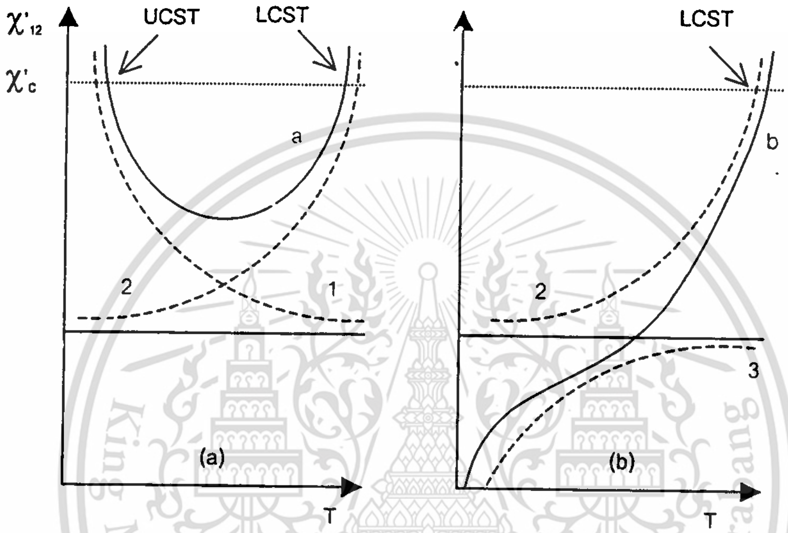


Figure 2.2 Schematic representation of the temperature variation of the interaction parameter, χ_{12} (solid line) and its components: 1. dispersion forces, 2. free volume, and 3. specific interactions. The resulting graph (a) represents interactions encountered mostly in solutions with upper and lower solution temperature, UCST and LCST respectively, whereas graph (b) is more typical of polymer blends where only LCST is visible [19].

2.2.1.2 Immiscible polymer blend

Any polymer blend whose, follows equation (2.2) and in Figure (2.1) (b).

$$\Delta G_{mix} \approx \Delta H_{mix} > 0 \quad \text{from} \quad \Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{2.2}$$

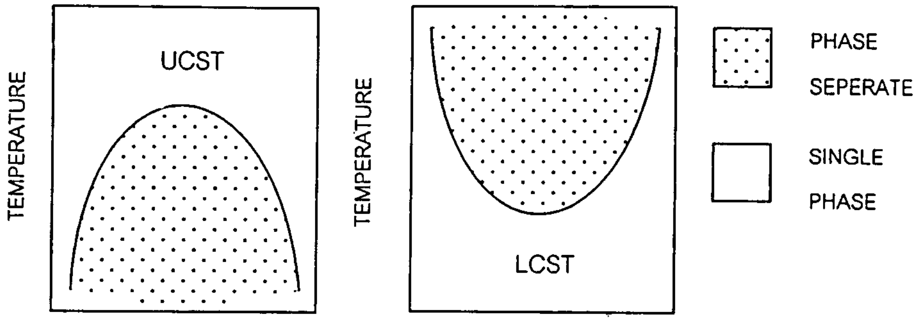


Figure 2.3 Schematic phase diagrams for binary blends showing LCST and UCST behavior [21].

From Figure 2.1 (b) when two polymers are immiscible, phase rule explains quantitatively the extent to which they separate and the extent to which each phase is actually-not pure polymer A and pure polymer B, but rather-a solution of B in A and a solution of A in B. Generally the major phase will form the continuous matrix and control most properties, while the minor phase will form dispersed microdomains and contribute certain specialized properties to the blend. Another factor is rheology: the less viscous phase tends to form the continuous matrix (even if it is present in rather minor amount), while the more viscous phase tends to form the dispersed domains. The structure of the dispersed domains is refered to as the morphology. The properties of immiscible blend depend on the amount, size, shape and interfacial adhesion of the disperse phase, but are primarily those of the continuous phase.

Most polymer pairs are immiscible and separate into two-phase systems. If they are very immiscible, the domain size is coarse, irregular, and unstable, and the interface is sharp and weak, giving poor properties and practical incompatibility.

2.2.1.3 Partially miscible polymer blend

Two-phase blend has naturally good properties and practical compatibility, the reason is usually to be sought in partial miscibility. Such an interphase is able to resist stress and deliver useful properties. In many naturally compatible polymer blends, such partial miscibility is the most likely explanation for their good properties [17] (see Figure 2.1 (c)).

2.2.2 Factors of miscibility and immiscibility

These may be listed in order of commercial importance:

1. Polarity: polymers that are similar in structure or, more generally, similar in polarity are less likely to repel each other and more likely to form miscible blends. Diverging polarities generally produce immiscibility.

2. Specific group attraction: polymers that are drawn to each other by hydrogen bonding, acid-base, charge transfer, non-dipole, donor-acceptor adducts, or transition metal complexes are less common, but when such attractions occur they are very likely to produce miscibility.

3. Molecular weight (M_w): Lower M_w permits greater randomization on mixing and therefore greater gain entropy, which favors miscibility. Polymers of similar M_w are more miscible, while polymers of very different M_w may be immiscible, even if they have the same composition.

4. Ratio: evens through two polymers appear immiscible at a fairly equal ratio, it is quite possible that a small amount of one polymer may be soluble in a large amount of the other polymer.

5. Crystallinity: when a polymer crystallizes, it already forms two-phase system, with important consequences for practical compatibility. In a polymer blend, when a polymer crystallizes, this adds another phase to the system. If both polymers in a blend crystallize, they will usually form two separate crystalline phases; it is quite rare for the polymers to cocrystallize in a single crystalline phase [17].

The general relation between blends and alloys is shown in Figure 2.4. Virtually all high performance engineering blends are alloys. For practical reason polymer alloy can be subdivided into two categories: (A) those in which the compatibilization leads to very fine (usually sub-micron) dispersion so the molded part will show neither streaking nor excessive weld-line weakening, and (B) those where some compatibilizer is added in order to facilitate the formation of the desired morphology in a subsequent processing step.

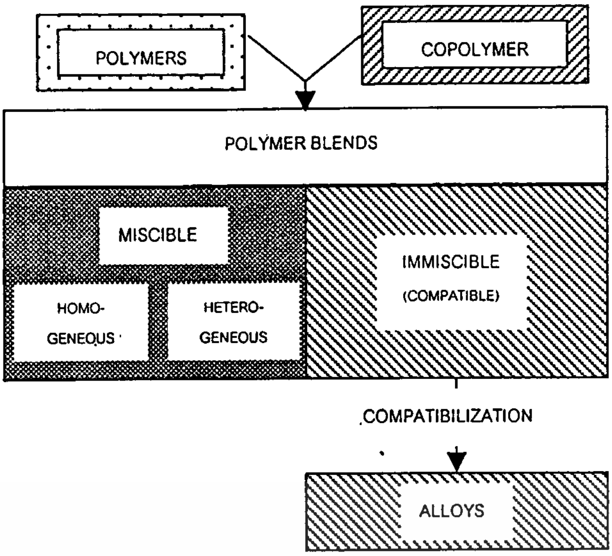


Figure 2.4 Interrelations in polymer blend nomenclature [19].

2.2.3 Compatibilization

The achievement of compatibilization, whether by addition of a third component (a so-called 'compatibilizer') or by inducing *in situ* chemical reaction between blend components (reactive blending), has played an important role in the development of polymer blends. Compatibilization can produce the optimum level of phase separation, morphology, and interfacial attraction.

Morphology of immiscible blends depends on thermodynamics, interphase, and flow history. At high dilutions and low flow rates, the morphology of polymer blends is controlled by the three micro-rheological dimensionless parameters:

1. The viscosity ratio, $\lambda = \eta_A / \eta_B$ where η_A is the viscosity of the dispersed phase and η_B is that of the matrix.

2. The capillary number, $K = \tau R / \sigma$, where τ is the shear stress, σ/R is the interfacial stress (σ is the interfacial tension coefficient and R is the initial drop radius).

3. The reduced time, $t' = t \dot{\gamma} / K$, where $\dot{\gamma}$ is the rate of deformation, and t' is its duration.

To ascertain high performance of immiscible blends, usually, compatibilizers need to be added. There are three aspects of compatibilization:

1. Reduction of the interfacial tension (better dispersion).
2. Stabilization of the morphology against changes during the processing.
3. Enhancement of adhesion between the phases, facilitating the stress transfer, hence improving the mechanical properties of the product [17].

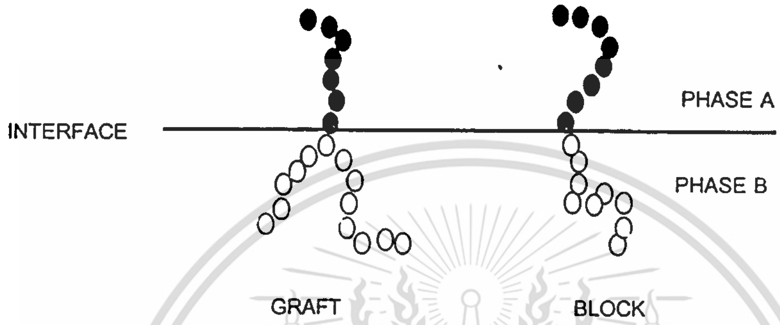


Figure 2.5 Schematic diagram showing location of block and graft copolymers at phase interfaces [21].

2.2.3.1 Compatibilization has two basic strategies:

1) Addition of block and graft copolymers (non-reactive blending)

Block and graft copolymers containing segments chemically identical to the blend components are obvious choices as compatibilizers, given the miscibility between the copolymer segments and the corresponding blend component is assured, provided the copolymer meets certain structural and molecular weight requirements, and that the copolymer locates preferentially at the blend interfaces. The classical view of how such copolymers locate at the interfaces is shown in Figure 2.5 [21].

2) Reactive blending

Reactive blending differs from non-reactive blending routes in that the blend components themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibilizer.

Since primary covalent bonds may be the most effective way to strengthen the interface, most currently research is concerned with chemical reactions that the processor can accomplish during the blending process. These may be reactions directly between the two polymers in the blend, or they may be produced by adding a third polymer that can react with one or both of the primary polymers [17]. This research used polypropylene grafted maleic anhydride (PP-g-MA), polypropylene grafted acrylic acid (PP-g-AA) and high-density polyethylene grafted acrylic acid (HDPE-g-AA) as compatibilizer and their structures are shown in Figure 2.6.

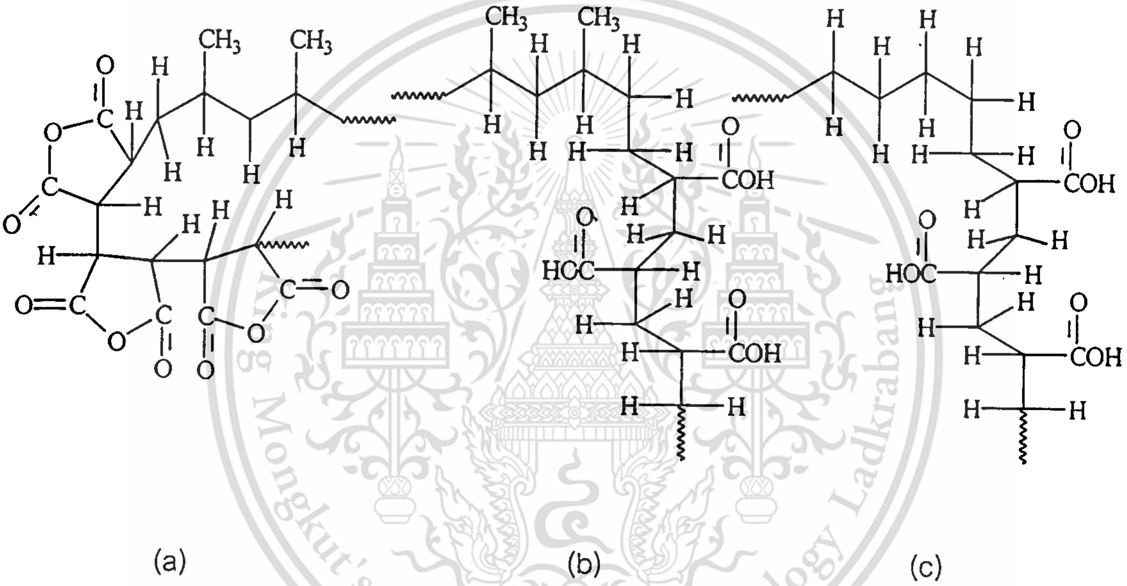


Figure 2.6 Structures of compatibilizers: (a) PP-g-MA, (b) PP-g-AA, (c) HDPE-g-AA [22].

2.3 Extrusion

Extrusion is a very widely used plastic process. More plastic is processed by extrusion than any other way. The various products made by extrusion including pipe, garden hoses, coatings for paper and foil, fibers, filament, yarns, tapes, and a wide array of profiles.

Extrusion is an excellent process for the recycling of scrap thermoplastics. Cutoffs and scrap from thermoforming and injection molding may be reground and pelletized for use in the extruder or injection molder. Scrap thermoplastics from the home or school may also be recycled. This is an excellent way to help control pollution and reduce the cost of materials. Margarine tube and lids, plastic spoons, detergent bottles, and other similar scrap plastic products may be used. These plastics must be cleaned (label also removed) and sorted before recycling.

Plastic powder or pellets are loaded into the hopper funnel (1) of the extruder, as shown in Fig 2.7, and dropped by gravity into the barrel (3). The plastic is moved forward by the turning of the screw (2). The screw works like a grain auger or meat grinder screw. It turns all the time while the extruder is working. It does not start and stop like the one in the screw type injection molder. As the material moves forward in the barrel (3) it is heated. The heat comes from two sources: outside heating bands (4) and inside frictional heat. The heat from the heating bands is controlled by temperature controllers (thermostats). The frictional heat is caused by the screw pressing and rubbing the plastic particles together in the barrel. Seventy-five percent (75%) or more of the heat added to the plastic in extrusion is from friction.

The screw is designed to compress the plastic as it moves forward. Trapped air and gases escape back through the hopper or a vent in the barrel. The screw usually turns about 20 to 2000 revolutions per minute (rpm). The last section of the screw (metering section) meter measures the flow of the melted plastic. The metering section makes sure that there is enough back pressure on the material in the barrel to give an even melt. The metering section also helps keep an even flow of plastic going through the die. Pressure inside the barrel of up to 5,000 pounds per square inch (psi) (34,500 KPa) is common. The melted plastic passes through a screen pack and breaker plate (5) which traps impurities in the plastic and the straightens out the flow. The screen pack keeps the die from clogging. Without the breaker plate, the plastic tends to spiral as it comes out of the barrel. The breaker plate and screen pack also provides some back pressure.

The plastic enters the die (6) and takes on the shape of its opening. The plastic that comes through the die is call extrudate (7). The die adapter section (8) and die are also heated with heating bands. The heating bands are usually electrical power.

The extrudate (extruded plastic) coming from the die is taken away and cooled by a take-off system. This system is regulated to take the plastic away from the extruder at just the right speed. The speed of both the take-off system and extruder are variable [1].

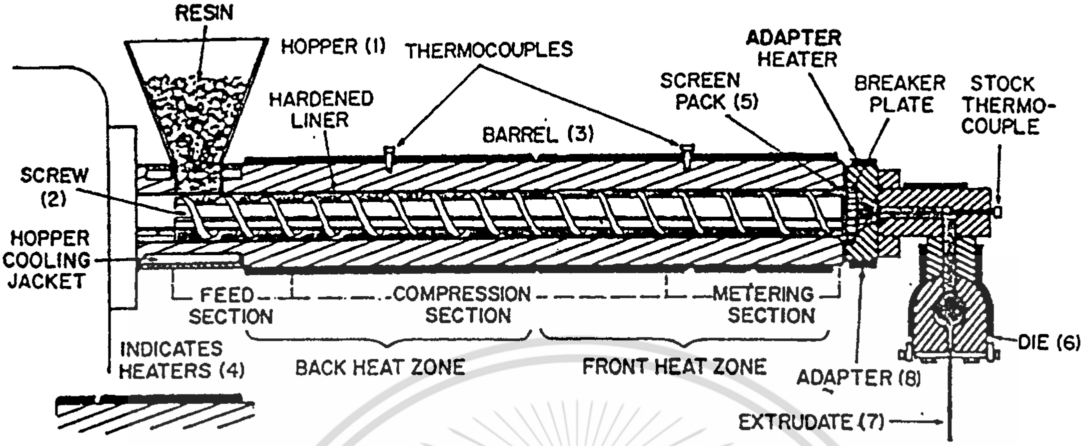


Figure 2.7 Extruder with flat sheet die [1].

2.4 Fiber Spinning Process

2.4.1 Synthetic fibers

A fiber can be defined as a material whose length is at least 100 times its diameter. Synthetic fibers are organic or inorganic materials that have been processed (spun) into the fiber form (thread lines).

Organic synthetic fibers can be formed from polymer in a variety of ways depending on the nature of the materials. In ease case, however, the fiber forming process (spinning) is similar (see Figure 2.8) in that a polymer melt or solution is forced or extruded through a small orifice, called a spinneret or jet, which shapes it into the fiber form. Next, the material undergoes a phase transformation to the solid form, after which it is wound up, or "taken up", on a bobbin. The processed or spun yarn can then pass through other operation so that it is brought to some final performance level.

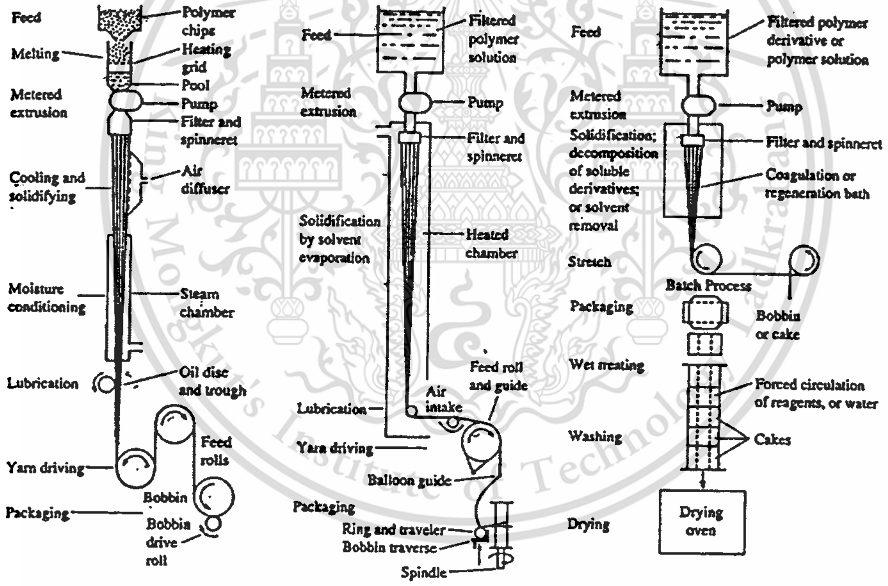
The principal forms of spinning are listed in Table 2.1, together with the phase-transformation process as well as the principal commercial fibers formed by each technique. Generally, the selection of a particular type of spinning process is related to the material being spun.

Table 2.1 Spinning Types [23]

Spinning Process	Type of Phase Transformation	Material Spun
Melt	Solidification from molten mass	Nylon, polyester, polypropylene, glass
Dry	Evaporation of solvent with solidification	Cellulose acetate, Cellulose triacetate, polyacrylonitrile (Orlon[a])
Wet	Countercurrent diffusion in a bath with solidification	Polyacrylonitrile (Acrilan[b])
Reaction	Material reacts and solidifies	-

[a] Trademark: E I. Dupont DeNemours & Co., Inc.

[b] Trademark: Monsanto Coporation.



(a) (b) (c)

Figure 2.8 Schematic diagrams of spinning processes: (a) melt spinning (b) wet spinning (c) dry spinning [23].

2.4.2 Fiber Requirements

Synthetic fibers must have certain characteristics in order to be useful materials. They should, for example, have a high thermal softening point, to permit processing or ironing; a high initial modulus of elasticity or stiffness; and reasonable tensile strength over a wide temperature range. Tensile strength is expressed as grams/denier. The denier is a measure of the size of fibers and is defined as the weight in grams of 9000 m of fiber length.

Approximate property ranges for synthetic fibers are:

1. Tensile strengths should be about 5 g/denier for textile applications to 7-8 g/denier for industrial applications.
2. Initial modulus should be 30-60 g/denier for textile applications and 50-80 g/denier for industrial applications.
3. Elongation at break should not less be than 10% for textile use and 8-15% for industrial use.
4. Temperature at which creep or softening occurs should be lower than 215 $^{\circ}$C for textile applications or 250 $^{\circ}$C for industrial applications
5. Fibers should have good abrasion resistance, moisture resistance for textile applications, and chemical resistance for industrial use.

2.4.3 Melt Spinning

Melt spinning is one of the most widespread of all the fibers-processing operation. The process involves either melting polymer pellet in, or pumping molten polymer to, an appropriate spinning unit, which carefully meters the flow of the polymer. The molten polymer passes through a screen pack and then through a spinneret or jet, where the fibers are formed and extruded. After the extrusion, the filaments are quenched and cool in some fluid medium (air, other gases, or even water) and eventually taken up on an appropriate mechanical device. In some case, the fibers are then processed further, that is drawn, separately. In others, the process is continuous in that the polymer is spun and drawn on one overall apparatus. This final processing-structuring step significantly enhances fiber strength.

If the overall process of melt spinning is analyzed, three distinct regions or zones become apparent [23]. These are (see Figure 2.9):

1. The experience or behavior of the melt prior to extrusion,
2. The region after extrusion until solidification,
3. The behavior from solidification until take-up

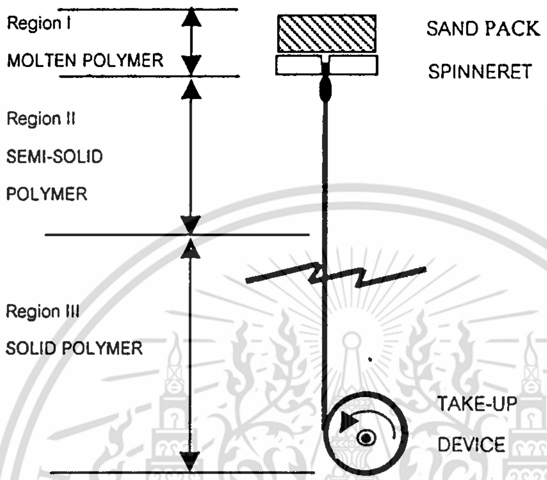


Figure 2.9 Melt Spinning zones [23].

2.5 Classification of blend fibers by phase morphology

The phase morphology of individual fibers made from two or more polymers is grouped into major categories. Typically these structural features can be observed through the conventional microscopy techniques normally used to prepare and examine fibers cross and longitudinal sections.

2.5.1 Types of phase morphology

The phase morphology can be classified in 2 types

2.5.1.1 Homogeneous Blends

In an ideal sense, this category is characterized by a single phase of miscible polymers, most polymer pairs are not miscible, but an important number of exceptions exist, particularly among polymers that are closely related members of a copolymer family. In a real sense, most fibers made from only one polymer are not homogeneous because of crystallinity, porosity, additives, etc. Consequently, a homogeneous-blend fiber does not have composition inhomogeneities because it is a blend; however, this does not preclude these other types of heterogeneities. Miscible mixtures may be expected to behave in some way like a single polymer, for example, a single glass transition temperature (T_g), similar to a copolymer of the parent polymers. Its homogeneity would give it optical properties important to fibers. This type of blend fiber is not common first because of the lack identified miscible polymer pairs suited for fibers and second because two phases are essential to achieve some of the effects sought by blending.

2.5.1.1 Heterogeneous blends

In this common category the two polymers are segregated into spatial regions that are composed essentially of one or the other pure component. Usually, the two polymers are immiscible but in principle they could be miscible but not mixed. Ordinarily, the phase morphologies of interest can be readily observed in fiber cross or longitudinal sections. The possible morphologies could be divided further into structured and random, but there is not a clear boundary between these extremes. The number of potential phase arrangements is almost unlimited; thus, in the following only the major types that are generally recognized are classified and possible variants suggested.

In heterogeneous structures, adhesion between the two phases is a critical concern. Adhesion is essential for the integrity of some structures but not others. Poor adhesion is a requirement for some applications, but usually good adhesion is required for many important blend fiber properties.

1) Side-by-side

Here the two polymers lie side by side within the fibers as the name suggests and as shown schematically in Figure 2.10 (a). The components must adhere or two fibers of different composition would result. Some variations from the ideal shown in the upper part are shown in the lower part of Figure 2.10 (a). These include cases in which there are unequal amounts of the two polymers, curved interfaces, two regions of one polymer, and the many possibilities when the fiber cross section is nonround, as in wet or dry spun fibers.

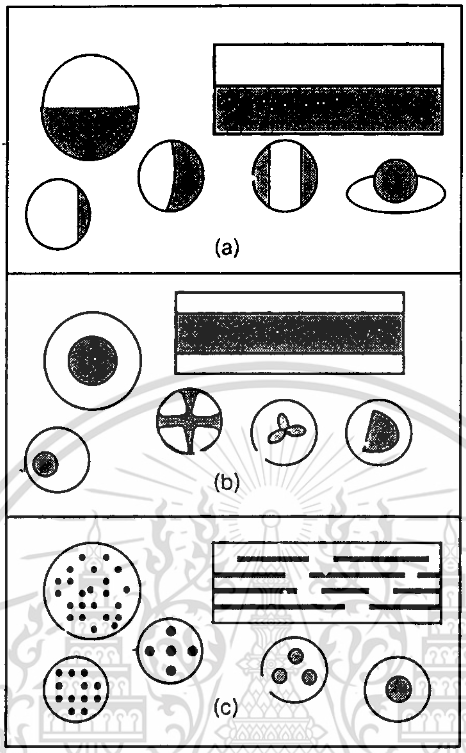


Figure 2.10 Typical phase arrangements in heterogeneous-blend fibers: (a) side-by-side; (b) sheath-core; (c) matrix-fibril. Both cross sectional and longitudinal views are shown for three major categories, while some possible variations within each category are shown in cross section only [24].

2) Sheath-Core

Here both polymers are not usually exposed to the fiber surface but rather one polymer is encased (core) by the other (sheath) as shown in Figure 2.10 (b). Adhesion is not always essential for fiber integrity. A selection of variations is shown in the lower part of Figure 2.10 (b). A highly contorted interface between sheath and core with undercuts can lead to mechanical interlocking that may be desirable in the absence of good adhesion.

3) Matrix-Fibril

The ideal situation is illustrated in the upper part of Figure 2.10 (c), where many fine fibrils of one polymer are dispersed in a matrix of another. In a cross section, the fibrils appear random in size and location; however, because of inherent orientation processes in all fiber processes. These fibrils are aligned in the axial direction. Adhesion is not essential to fiber integrity, and because of the finer dispersion and high interfacial area, a lack of adhesion may not be as apparent in this formation as in sheath-core structures. The size and number of fibrils depend on proportions and the rheological conditions of fiber formation (24).

2.6 Polymer blend characterization

2.6.1 Scanning electron microscopy (SEM)

This is a very popular technique, which can provide 10X better resolution than light microscopy and surfaces are easy to prepare. The large depth of field is the major advantage as uneven surfaces with vertical differences 100X the resolution still produce focused images. Specimens must be coated with a conductive layer, which is achieved by sputter coating the surface with gold. However sputtered gold produces its own texture with particles of ~3 to 5 nm. The electron beam damage can alter the surface morphology (uneven loss of mass, blister, cracks). Contrast in SEM is formed by the surface relief, which must therefore be related to the bulk structure. This can be achieved in a number of ways.

1. Cutting is the only suitable technique available for the study of bulk polymer blends. Cutting can produce some inhomogeneities if the cutting properties are different phase. This can be used for immiscible blends where the phase size is much larger than the scratches produced by cutting. For blends with a poor interfacial strength debonding can occur and the structure can be more difficult to analyze.

2. Fracture surfaces can also show inhomogeneities, but only for a special case when the phases can debond easily and the debonding surface has a recognizable shape (e.g. spherical). This can only be used for immiscible blends, as the objects must be large.

3. Solvent extraction can be used to remove a selected phase and observe the holes left. The application of this technique is again for immiscible blends, with suitable components for extraction. There is however a high probability that the extracted polymer will not be washed away and will form a gel, which will, after solvent evaporation, produce voided structure. This can easily lead to confusion and wrong interpretation.

4. Solvent swelling is a technique, which is simpler and more reliable. Most polymers cannot be dissolved at room temperature but will swell as a result of partial miscibility. It is possible to find for a given polymer blends a suitable compound that is a solvent for one phase and a non-solvent for the second [25].

The principal of SEM (Figure 2.11) is as follows. A small electron probe is formed by an electron gun and a set of three or more electromagnetic lenses. The electron gun consists of a heated tungsten filament, an anode attracting the emitted electrons and a focusing electrode (gun bias). The important parameter of the gun is its brightness which is given by the total number of electrons coming from a unit area of the source into a unit solid angle. In order to increase the brightness, it is possible to increase the emission current by replacing tungsten with lantanum hexaborite. Alternatively, the area of the source can be reduced with a pointed filament or the emission angle can be reduced by field emission. The last source is the best for resolution, as a very small probe of less than a nanometer with a very high current can be formed. Unfortunately, ultra-high vacuum is required for this source and the cost is very high.

The probe size is reduced by demagnification of the filament image using two electromagnetic lenses and then focusing onto the specimen surface by using a final (or objective) lens. The probe scans on the specimen by two sets of scanning coils controlled by the same scan generator as the cathode ray tube used to observe the image. The signal is detected by a low noise scintillator-photomultiplier-amplifier system and modulates the display signal. Each point of the scanned raster on the sample thus has a corresponding point on the display screen. Once the probe is focusing and corrected for astigmatism, the magnification can be changed by changing the size of the scanned area without refocusing [21].

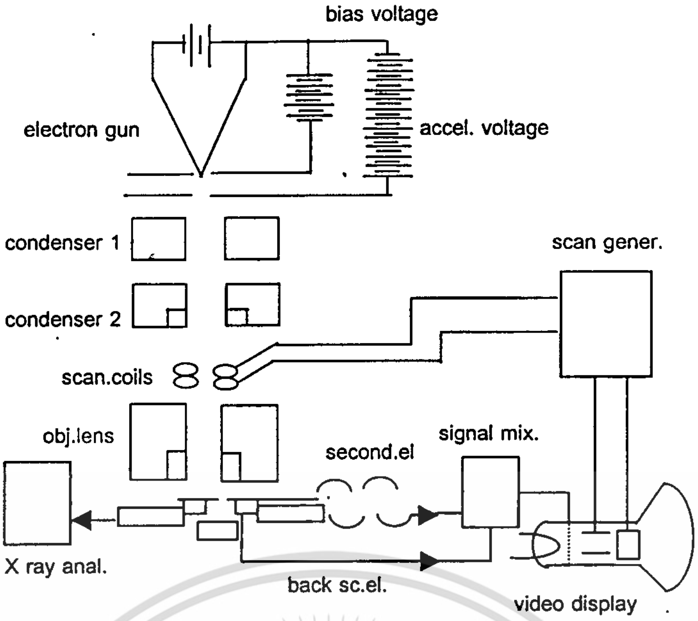


Figure 2.11 Schematic diagram of a scanning electron microscope [21].

2.5.2 Differential scanning calorimetry (DSC)

Application areas of DSC technique are as follows:

1. Heat capacity versus temperature or time allows measurement of heats of fusion, identification of crystalline and liquid crystalline phases, degree of crystallinity, etc.

2. Glass transition measurement allows characterization of aging, blend compatibility.

3. Heats of reaction allow cure and degradation studies [25].

Structural changes are usually associated with changes in heat absorption or emission and are measured using calorimetry. Scanning calorimetry can also measure changes at constant heating or cooling rates. The differences in heat loss or gain between the sample and the reference cells are measured in a differential scanning calorimeter. In this case the heat input needed to maintain both cells at the same temperature is measured. The principal of this technique is schematically illustrated in Figure 2.12. The cells are placed in a metal block, which can be cooled for more efficient heat stability. The thermocouples measure the temperature as well as differences in the temperature. The difference is quickly compensated by the heat controller and the amount of compensation is measured. From these measurements the rate of heat absorbed by or evolved from the sample can be computed [21].

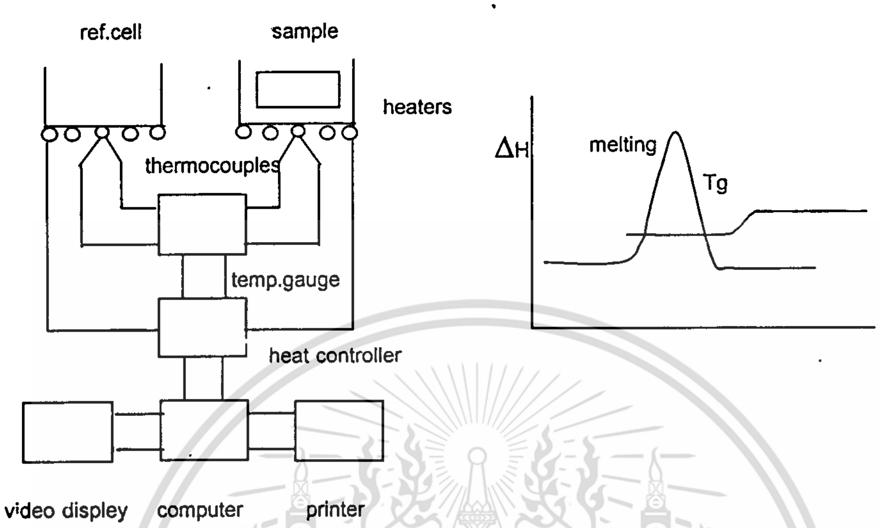
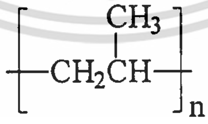


Figure 2.12 Schematic diagram of DSC [21].

2.7 Materials

2.7.1 Polyolefins

2.7.1.1 Polypropylene



$$\left[-CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}H- \right]_n$$

Polypropylene (PP) have better resistance to heat (heat distortion temperature at 0.455 MPa: 93-121 °C) and resist more chemicals than do other thermoplastic materials of the same cost. Also, polypropylenes have negligible water absorption and excellent electrical properties, and they are easy to process

The stereoregularity (related to the repeated units in the stereoregular molecular chain) of a polypropylene very often determines the characteristics of the material. The hardness, stiffness, and tensile strength of polypropylene also increase.

On the other hand, the stereoregularity decreases as elongation and impact strength increase.

The ability to carry light loads for long periods and over wide temperature ranges is one of the properties that make polypropylene valuable in engineering applications. Like all polyolefins, polypropylenes have excellent water solution that is destructive to metals. They also are resistant to organic solvents and alkalis. Above 79 °C, polypropylene is soluble in aromatic substances such as toluene and xylene, and in chlorinated hydrocarbons such as trichloroethylene.

Polypropylene has excellent electrical resistivity (both volume and surface), and their dielectric strength is high.

The greatest commercial uses for homopolymer PP are in fibers and filaments. PP fibers are woven into fabrics and carpets, and they also are used to produce nonwoven fabrics for disposable. Slit tape-filaments are used as jute replacements in carpet backings and sacks [27].

2.7.1.2 Polyethylenes

$$\left[-CH_2CH_2- \right]_n$$

Polyethylenes are characterized by thoughness, near zero-moisture absorption, excellent chemical resistance, excellent electrical insulating properties, low coefficient of friction, and ease of processing. In general, they are not outstanding load-bearing materials, but high-density polyethylene can be used for some short-term light loads. Few thermoplastics have the excellent chemical resistance and dielectrical properties of polyethylenes. Polyethylenes resist bases and acids at room temperature, soluble in some organic solvents above 60 °C Their resistivity (both volume and surface) and dielectric strength are high. Polyethylenes are classified by density as in Table 2.2.

The primary differences among the types are in rigidity, heat resistance, stiffness, and ability to sustain loads. In general, as density increases, hardness, heat resistance, stiffness, and resistance to permeability increase.

Table 2.2 Classification of polyethylenes by density [21].

Types of polyethylenes	Density (g/cm^3)
(a) ultra- or very low density (ULDPE and VLDPE)	0.880-0.915
(b) low-density (LDPE)	0.910-0.925
(c) medium density (MDPE)	0.926-0.940
(d) high-density (HDPE)	0.941-0.965

1) Low-Density Polyethylene

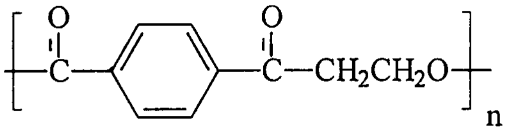
The low-density polyethylene (LDPE) is often called "regular" or "branched" polyethylene because they are produced in high-pressure reactors. Such polymers have highly branched structures with moderate crystallinity (50-60%).

Low-density polyethylene are quite flexible, with high impact strength and relatively low heat resistance (maximum recommended service temperature is 60-79 °C), although grades are available with heat resistance up to 93 °C.

2) High-Density Polyethylene

Linear high-density polyethylene (HDPE) can be produced via a slurry process or in gas phase reactors. HDPE are highly crystalline, tough material that can be formed by most processing methods. Much HDPE is blow-molded into containers for household and industrial chemicals. It is injection-molded into items such as crates, housewares, pails, and dunnage containers; extruded into pipe, tubing, and wire insulation; blown into film for packaging; and rotationally molded into containers, toys, and sporting goods [28].

2.7.2 Poly(ethylene terephthalate)



Poly(ethylene terephthalate), PET is formed through step growth polymerization of terephthalic acid or dimethyl terephthalate with ethylene glycol at 250-300 °C in the presence of a catalyst of a dicumyl peroxide.

PET is a water–white polymer and is made into fibers, film and sheets, and blow-molded and thermoformed containers for soft drinks and foods. Glass-reinforced PET compounds can be injection-molded into parts for automotive, electrical/electronic, and other industrial and consumer products. PET is the most recycled plastic, largely due to recycling of soft-drink bottles. Packaging is the largest source of PET in municipal solid waste [28].

2.8 Fibers

2.8.1 Polyolefin fibers

Polyolefin fibers are those fibers produced from polymers formed by chain growth polymerization of olefins (alkenes) and which contain greater than 85% polymerized ethylene, propylene, or other olefin units. In general, linear high-density stereoregular polyethylene and polypropylene are used in textile applications, with polypropylene predominating due to its superior temperature stability. These fibers have good strength, toughness, abrasion resistance, and low cost. The fibers are difficult to dye and have relatively low melting point, but they are effectively used in a wide variety of textile applications.

The spinning of suitable polyolefins into fibers presents no basic difficulties. The molten polymers are extruded through spinnerets in much the same fashion as polyamides and polyester, the filaments hardening as they cool. The nature of the polyolefins imposes special conditions on the extrusion process, but the technique is fundamentally the same as that used in melt-spinning other polymers [29]. The properties of polyolefin fibers are shown in Tables 2.3 and 2.4.

2.7.2 Poly(ethylene terephthalate) fibers

Poly(ethylene terephthalate), PET polyester is the leading man-made fibers in production volume and owes its popularity to its versatility alone or as blended fibers in textile structure. PET is used extensively in woven and knitted apparel, home furnishing, and industrial applications. Modification of the molecular structure of the fibers through texturizing and/or chemical finishing extends its usefulness in various applications. PET fibers are melt-spun at 250-300 °C, followed by fiber orientation and stretching [27]. The properties of poly(ethylene terephthalate) fibers are shown in Table 2.5.

Table 2.3 Properties of polyethylenes fibers [29].

Properties	COURENE [a]	
	LDPE fibers (conventional)	HDPE fibers (Courene X3 [a])
Specific gravity	0.91	0.95
Moisture regain (%)	0	0
Tenacity (g/denier)	0.9-1.7	4.0-7.0
Breaking extension (%)	25-50	15-35
Knot strength (g/denier)	1.0-1.5	3-5.0
Tensile strength (MPa)	Up to 172.36	Up to 551.6
Elastic recovery (%)	Good	Good
Softening point	Above 90 °C	120 °C
Melting point	110-120 °C	135 °C
Flammability	Slow burning	
Resistance to strong acids	Resistance (above 60 °C some acid attacks)	
Resistance to weak acids	Resistance	
Resistance to strong alkalis	Resistance	
Resistance to weak alkalis	Resistance	
Effect of organic solvents	Resistance (above 60 °C soluble in carbon tetrachloride, toluene, chlorinated or aromatic hydrocarbon	
Effect of sunlight	Loses strength (pigmented more resistant)	
Identification	Low melting point, floats on water, soluble in toluene and aromatic solvents above 60 °C	
Producer	British Celanese Ltd.	

[a] Trademark of polyethylene fibers

Table 2.4 Properties of polypropylene fibers [29].

Properties	PP fibers (DLP51 [a])
Specific gravity	0.90
Moisture regain (%)	0
Tenacity (g/denier)	4.8-5.7
Breaking extension (%)	15-25
Knot strength (g/denier)	About 40,000
Elastic recovery (%)	Good
Stiffness (g/denier)	Similar to nylon
Softening point	160 °C
Melting point	167 °C
Flammability	Supports combustion but burns slowly
Resistance to strong acids	Resistance (slowly attacked by oxidizing)
Resistance to weak acids	Resistance
Resistance to strong alkalis	Resistance
Resistance to weak alkalis	Resistance
Effect of organic solvents	Resistance (below 66 °C)
Effect of sunlight	Loses strength on prolonged exposure
Identification	Low melting point, floats on water
Producer	Dawbarn Brother Inc., USA. (filament)

[a] Trademark of polypropylene Fibers.

Table 2.5 Properties of poly(ethylene terephthalate) fibers [29].

Properties	DACRON [a]PET fibers (Regular)
Specific gravity	1.38
Moisture regain (%)	0.4-0.8
Tenacity (g/denier)	4.4-5.0
Dry Loop tenacity (g/denier)	4.0-4.6
Tensile strength (MPa)	531.0-606.7
Elastic recovery (%)	98 at 2% stretch
Stiffness (g/denier)	21
Thermal properties	Excellent strength retention on prolong exposure to heat
Softening point	Sticks at 235 °C
Melting point	Melts at 249 °C
Flammability	Slow burn
Resistance to strong acids	Resistance, but disintegrates in 96% H_2SO_4
Resistance to weak acids	Resistance
Resistance to strong alkalis	Moderate resistance at room temperature
Resistance to weak alkalis	Resistance
Effect of oxidizing agents	Resistance
Effect of sunlight	Weakens, resistance behind glass
Identification	Melts before burning, soluble in hot metacresol, insoluble in concentrated formic acid

[a] Trademark of poly(ethylene terephthalate) fibers

CHARPTER 3

EXPERIMENTAL DETAILS

3.1 Materials

The physical properties of materials; LDPE, PP and F-HDPE are shown in Table 3.1 and some properties of compatibilizers are shown in Table 3.2.

3.1.1 Low-density polyethylene (LDPE): Polene JJ 321®, Thai Petrochemical Industry Co., Ltd.

3.1.2 Polypropylene (PP): Pro-Fax 6331®, HMC Polymers Co., Ltd..

Table 3.1 Physical properties of LDPE, PP and F-HDPE

Properties	Typical values		
	LDPE*	PP**	F-HDPE*
Melt Flow Rate (g/10min)	0.50	12.00	0.80
Density (g/cm^3)	0.92	0.90	0.95
Tensile Strength at Yield (MPa)	>11	34.47	25.49
Tensile Strength at Break (MPa)	>11	-	38.24
Elongation at Break (%)	>600	-	> 500
Elongation at Yield (%)	-	10.00	-
Flexural Modulus (MPa)	-	1620	-
Stiffness (Olsen) (MPa)	-	-	784.50
Notched Izod Impact Strength (J/m)	-	2.67	19.61
Rockwell Hardness (R Scale)	-	97	62
Deflection Temperature at 0.455 MPa., (°C)	-	96	-
Environmental Stress Cracking Resistance, F_{50} (hours)	-	>500	30
Melting Point (°C)	-	-	131
Softening Point (°C)	95	-	126

Notices: * at 190 °C

** at 230 °C

3.1.3 Recycled poly(ethylene terephthalate) bottles (R-PET), various sources

3.1.4 Recycled high-density polyethylene bottles (R-HDPE), various sources

3.1.5 High-density polyethylene fiber grade (F-HDPE): Thai-zex® 5000S, Bangkok Polyethylene Co., Ltd.

3.1.6 Polypropylene grafted maleic anhydride: polybond 3150®, TOA Uni Royal Chemical

3.1.7 Polypropylene grafted acrylic acid: polybond 1001®, TOA Uni Royal Chemical

3.1.8 High-density polyethylene grafted acrylic acid: polybond 1009®, TOA Uni Royal Chemical

Table 3.2 Some properties of compatibilizers

Properties	Type of compatibilizers		
	PP-g-MA (polybond 3150)	PP-g-AA (polybond 1001)	HDPE-g-AA (polybond 1009)
Melt flow index (g/10 min)	50 *	40.0 *	6.0 **
Melting Point (°C)	168.7	168.3	131.4
Other	0.5% Maleic anhydride,	6% Acrylic acid	6% Acrylic acid

Notices : * at 230 °C

** at 190 °C

3.2 Instruments

Lists of instruments are shown in Table 3.3

Table 3.3 Lists of instrument

Instrument	Model
Single-screw Extruder	Axonab BX-18
Grinder	Bosco A6000
Universal Testing Machine	LLOYD LR30K
Differential Scanning Calorimeter (DSC)	Perkin Elmer DSC7
Scanning Electron Microscope (SEM)	JEOL JSM - 6400

3.3 Flow chart of the experiment

The overall experiment is shown in Figure3.1

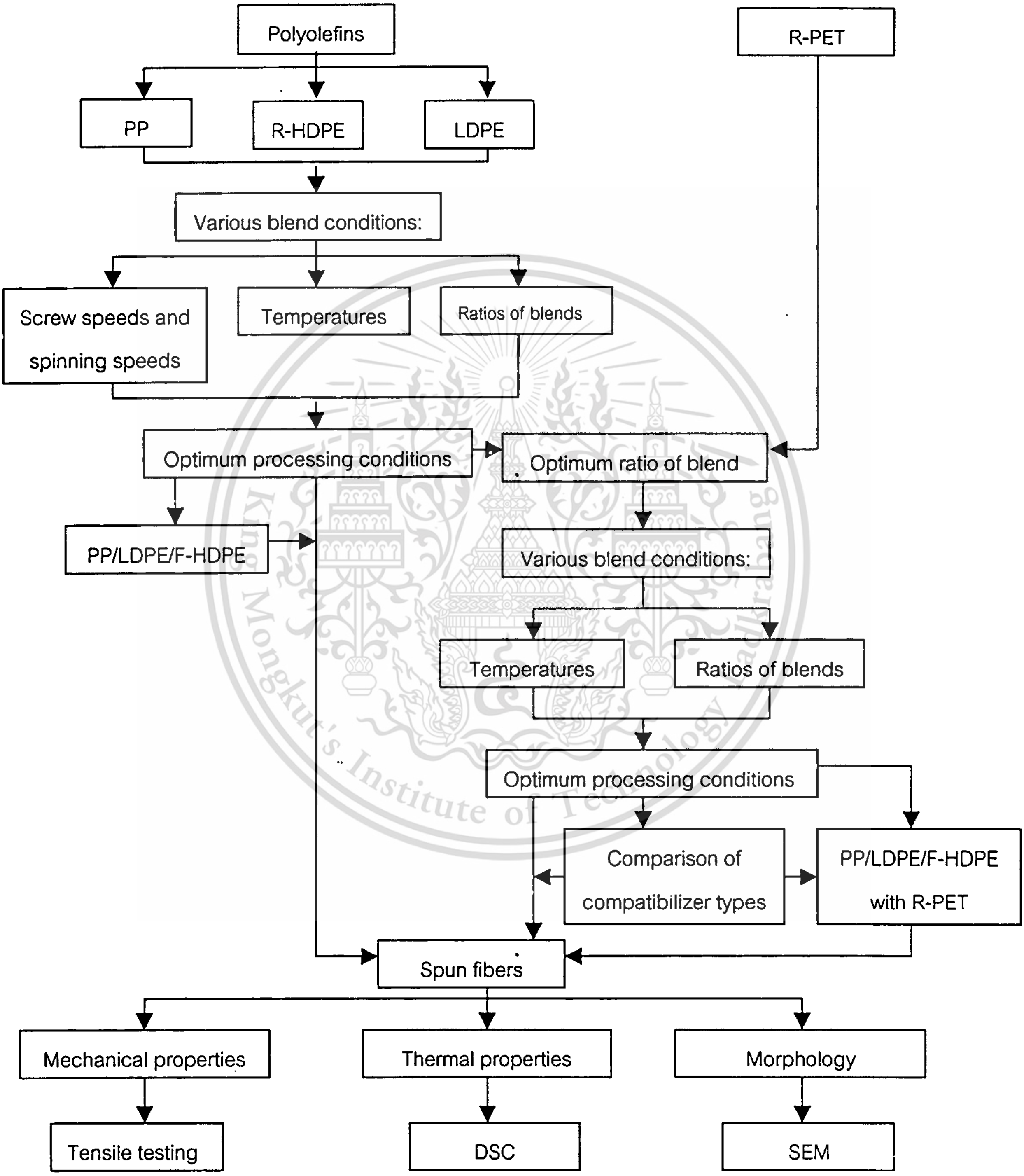


Figure 3.1 Flow chart of the experiment.

3.3.1 Preparation of materials before blending

The flow chart of preparation of recycled high-density polyethylene bottle (R-HDPE) and recycled poly(ethylene terephthalate) bottles are shown in Figure 3.2.

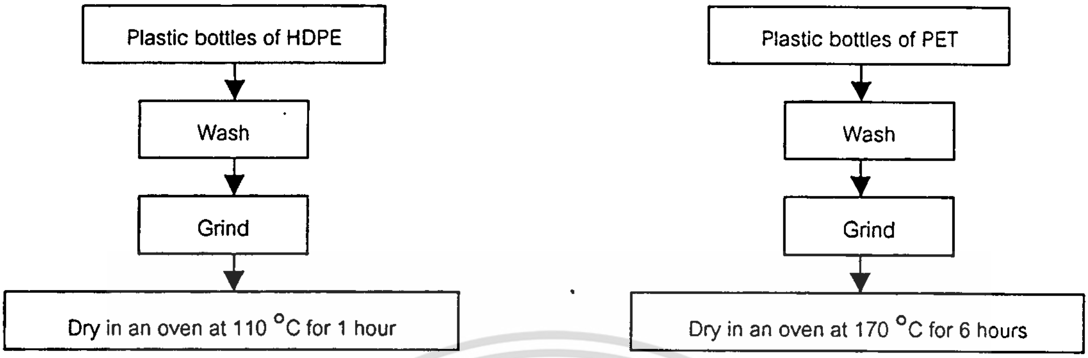


Figure 3.2 Flow chart of preparation R-HDPE and R-PET from plastic bottles.

3.3.2 Preparation of polyolefins blend as spun fibers

The spun fibers of recycled polyolefins blend were prepared by melt spinning process with 14-hole spinneret of single-screw extruder, which has shown in Figure 3.3.

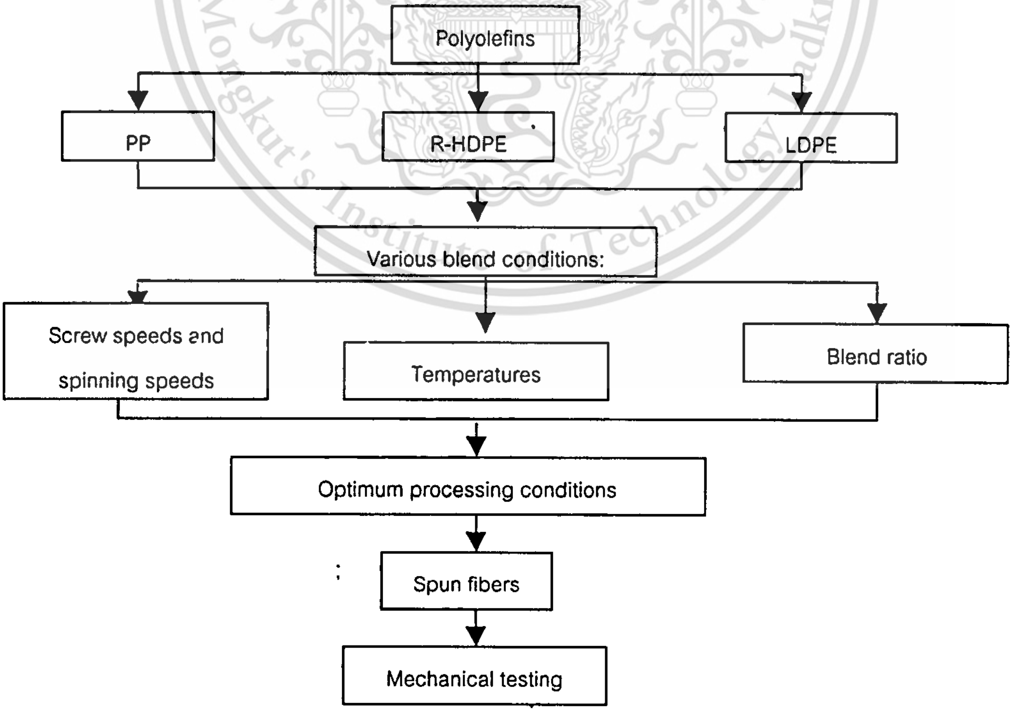


Figure 3.3 Flow chart of polyolefins blend on spun fibers.

3.3.3 Preparation of polyolefins with R-PET blend on spun fibers

The same process, the spun fibers were prepared with recycled polyolefins and R-PET blend as shown in Figure 3.4.

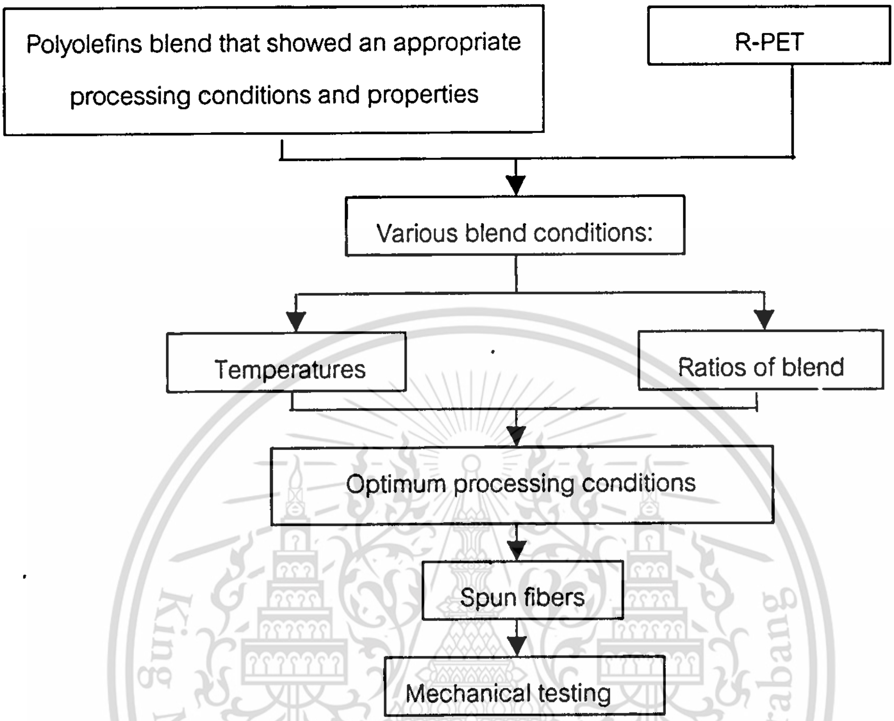


Figure 3.4 Flow chart of polyolefins with recycled poly(ethylene terephthalate) blend on spun fibers.

3.3.4 Appropriate processing conditions of polyolefins blends as spun fibers

3.3.4.1 The appropriate screw speed and spinning speed of polyolefins blends with a fixed ratio of blend (PP/R-HDPE/LDPE) as 25/50/25 and temperature as 230 °C were determined and tested by Universal Testing Machine (Table 3.4).

Table 3.4 Spun fibers of polyolefins blend with various screw speeds and spinning speeds

Screw speed (rpm)	Spinning speed (m/min)				
20	-	-	8.82	10.30	11.90
30	4.57	7.19	8.82	10.30	11.90
40	4.57	7.19	8.82	10.30	11.90
50	-	-	8.82	10.30	11.90

3.3.4.2 The appropriate temperature was investigated in range of temperature of 210 to 270 °C with the fixed ratio of blend PP/R-HDPE/ LDPE as 25/50/25 by using screw speeds and spinning speeds from the result of 3.3.4.1.

3.3.4.3 The appropriate ratio of PP/R-HDPE/LDPE/ blends was investigated by using appropriate screw speed and spinning speed from the result of 3.3.4.1 and appropriate temperature from the results of 3.3.4.2 as shown in Table 3.5.

Table 3.5 Spun fibers of polyolefins blend with various ratios of blend

Compositions	Ratios of blends								
	1	2	3	4	5	6	7	8	9
1. PP	100	0	0	50	50	0	25	25	25
2. R-HDPE	0	100	0	0	50	50	50	37.5	25
3 LDPE	0	0	100	50	0	50	25	37.5	50

3.3.5 Appropriate processing conditions of polyolefins with R-PET blends as spun fibers.

The appropriate temperature and appropriate ratio of polyolefins with R-PET blends were investigated by using screw speed and spinning speed from the result of 3.3.4.1, and appropriate ratio of PP/R-HDPE/LDPE blend from the results of 3.3.4.3 were investigated. The temperature and ratios of blend are shown in Table 3.6.

Table 3.6 Spun fibers of polyolefins with R-PET blend with various ratios of blend and temperatures

Temperature	Ratio of polyolefins/ R-PET blends				
260 °C	100/0	75/25	50/50	25/75	100/0
270 °C	100/0	75/25	50/50	25/75	100/0

3.3.6 Comparison of compatibilizer types

This step polypropylene grafted maleic anhydride (PP-g-MA), polypropylene grafted acrylic acid (PP-g-AA) and high-density polyethylene grafted acrylic acid (HDPE-g-AA) were used as compatibilizers for improvement the mechanical properties. The compatibilizers were added in fibers that indicated the best mechanical properties for both in polyolefins and polyolefins with R-PET blends by various ratios as shown in Table 3.7.

Table 3.7 Filled compatibilizers in polyolefins and polyolefins with R-PET blends shaped into fibers form.

Types of compatibilizer	Amount of compatibilizers (% by weight)		
PP-g-MA	1	3	5
PP-g-AA	1	3	5
HDPE-g-AA	1	3	5

3.3.7 Comparison of fiber properties from high-density polyethylene fiber grade (F-HDPE) and high-density polyethylene recycled grade (R-HDPE) in the components of blends.

In this step, F-HDPE was used instead of R-HDPE in the components of polyolefins and polyolefins with R-PET blends (selected from the step of 3.3.4 and 3.3.5) which indicated the best mechanical properties. Then the results were compared between the components of R-HDPE and F-HDPE.

3.3.8 Characterization of polymer blends as fibers form

3.3.8.1 Tensile testing

The mechanical properties; linear density (g/9000 m), tensile strength at break (MPa) or tenacity (g/denier), elongation at break (%), breaking load (N), and modulus of elasticity (MPa) were tested by Universal Testing Machine (ASTM D3822-91). By using 10 spun fibers in test and followed the following conditions:

Load cell	1	kN
Test speed	240	mm/min
Gauge length	100	mm

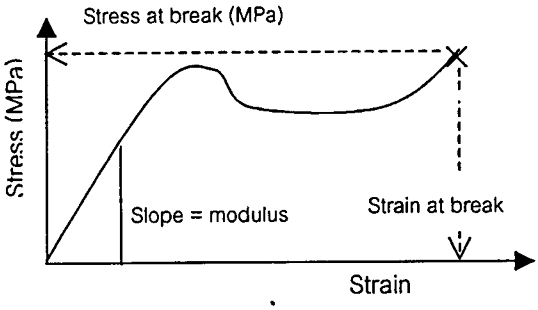


Figure 3.5 Relationship of stress-strain curve [30].

3.3.8.1.1 Tensile strength

From tensile testing, tensile strength was calculated by the equation (3.1).

$$\sigma = F/A \tag{3.1}$$

where σ = tensile strength (MPa or N/mm^2)

F = force at break (N)

A = initial cross-section area of the test specimen (mm^2)

3.3.8.1.2 Initial modulus at 1 % strain

Modulus at 1 % strain could be calculated by the equation (3.2)

$$E = (\delta/\varepsilon)/(1/100) \tag{3.2}$$

where E = modulus at 1 % strain (MPa)

δ = stress at 1 % strain (MPa)

ε = strain at 1 %

3.3.8.1.3 Elongation at break

The elongation at break (EB) was obtained from the equation (3.3)

$$EB = (L-L_0)/L_0 * 100 \tag{3.3}$$

where EB = elongation at break (%)

L = the distance between gauge marks at break (mm)

L_0 = the initial gauge length, which set at 100 mm (mm)

The standard deviation (sd) and mean value ($\overline{x}$) were calculated from equations (3.4 and 3.5),

$$\overline{x} = \sum x_i/n \tag{3.4}$$

and

$$sd = \sqrt{\sum (x_i - \overline{x})^2/n} \tag{3.5}$$

where x_i = values of properties of each sample

n = number of observation

3.3.8.2 Differential scanning calorimeter (DSC)

DSC is used to study the melting and crystallization behaviors of the blends. It directly measures the heat flow of a sample as a function of temperature. A typical sample consists of 5-10 mg of the fiber and it scans from 25 °C to 280 °C at a rate of 20 °C /min. Degree of crystallinity could be calculated by the equation (3.6),

$$\text{Degree of crystallinity (\%)} = (\Delta H_{100\%\text{polymer}}/\Delta H_{100\%\text{ crystal polymer}})*100$$

$$\text{or } = (\Delta H_f/\Delta H_{f^\circ})*100 \tag{3.6}$$

where ΔH_{f° PE = 293 J/g

ΔH_{f° PP = 165 J/g

ΔH_{f° PET = 140 J/g

For the close peaks of melting peaks (for examples C.20) can be calculated heats of fusion by fixing at bottom of another peak for a base line and then calculated for each peak.

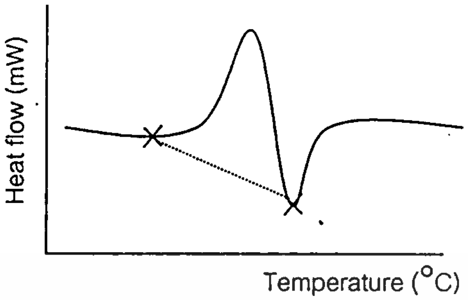


Figure 3.6 DSC thermogram of polyolefins with recycled poly(ethylene terephthalate) blends

3.3.8.3 Scanning electron microscope (SEM)

A scanning electron microscope was used to study the morphology of the blends. The test samples were obtained from fracturing surface specimen under tension by using a constant speed (240 mm/min). The samples were coated with a thin film of gold by using a sputter coater. The coated samples were then examined under a scanning electron microscope (JEOL JSM- 6400).

3.3.8.4 Density

The density of the spun fibers was measured using a density gradient column. The temperature of the column was held at a constant temperature of 25 °C. Carbon tetrachloride (ρ = 1.59 g/cc) and xylene (ρ = 0.87 g/cc) were used to construct a gradient column of the density range (0.90 -1.40). The density reported is an average of three density measurement.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 An appropriate spinneret with single-screw extruder

The spun fibers of recycled polyolefins and polyolefins with recycled poly (ethylene terephthalate) blends were prepared by melt spinning process with 14-hole spinneret (die), circular holes and 1mm in diameter which fed from a single-screw extruder. The spinneret (die) is shown in Figure 4.1. The extruded fibers were spun out in horizontal line and cooled by an air, and then solidified. They were wound up at various spinning speeds subsequently. The process is shown in Figure 4.2.

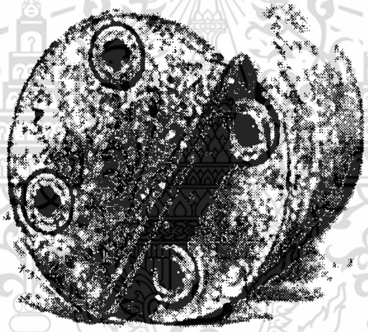


Figure 4.1 Spinneret

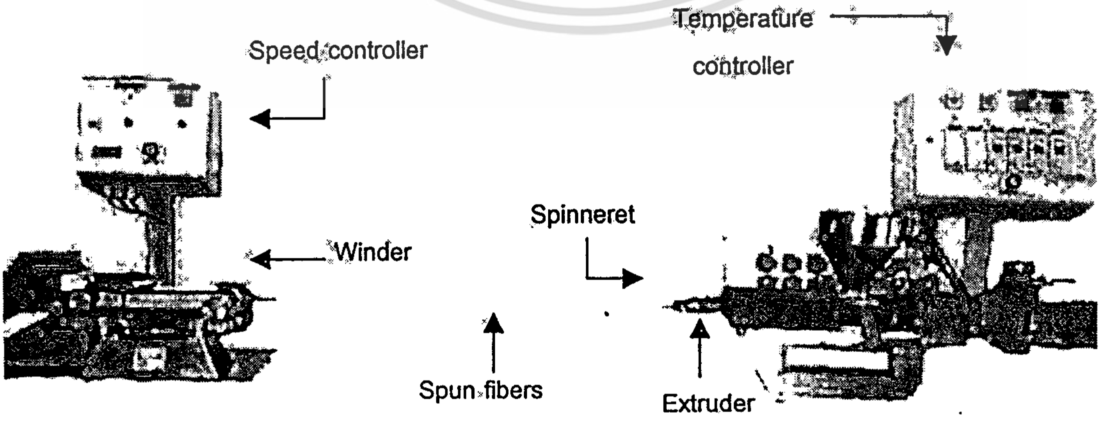


Figure 4.2 Fibers extruded by melt spinning process

4.2 Appropriate processing conditions of polyolefins blend on spun fibers

4.2.1 Mechanical properties

4.2.1.1 Screw speed and spinning speed

Screw speeds and spinning speeds of polyolefins blend with the ratio of blend (PP/R-HDPE/LDPE) as 25/50/25 and temperature as 230 °C were varied in the range of 20 to 50 rpm and 4.57, 7.19, 8.82, 10.30 and 11.90 m/min, respectively. The mechanical properties are shown in Figures 4.3 to 4.6. The relationship of spinning speed and mechanical properties indicated that at high spinning speed as the mechanical properties were improved due to increasing spinning speed, the molecular orientation development were high enough to induce crystallization on the spinning line (6). At the same screw speed, the tensile strength at break and modulus of elasticity (Figures 4.3 to 4.5) increased with increasing spinning speed but decreased with increasing screw speed (at the same spinning speed). The results were opposite to elongation at break (Figure 4.6). The influence of screw speed was also investigated. With increasing screw speed, the spun fibers could not be wound (the limit of speed controller is only 11.90 m/min which is not high enough to wind the spun fibers at high screw speed), it was slack and the diameter was bigger than that at lower screw speed. The diameter was related to tenacity; the higher the diameter, the lower the tenacity [8]. Thus, increasing screw speeds gave decreasing in mechanical properties.

The results indicated that the screw speed of 20 rpm and spinning speed of 11.90 m/min were the appropriate conditions because better mechanical properties could be achieved. The screw speed of 20 rpm and spinning speed of 11.90 m/min showed linear density of 226 denier/filament, tensile strength at break of 53 MPa or tenacity of 0.6 g/denier, modulus of elasticity of 45 MPa and elongation at break of 233%. This condition was corresponding to fiber forming requirements because the fibers should contain high tensile strengths and moduli of elasticity.

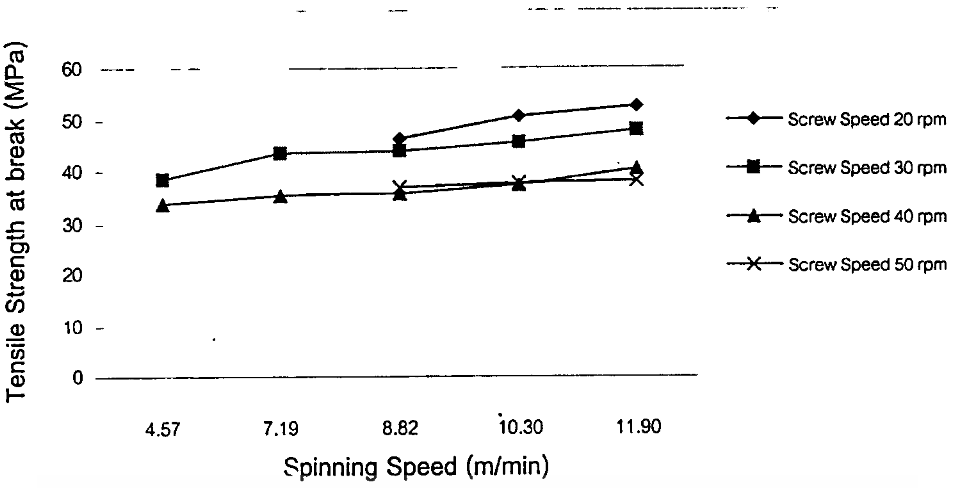


Figure 4.3 Tensile strength at break of polyolefins blend by using screw speeds of 20, 30, 40 and 50 rpm and spinning speeds of 4.57, 7.19, 8.82, 10.30 and 11.90 m/min.

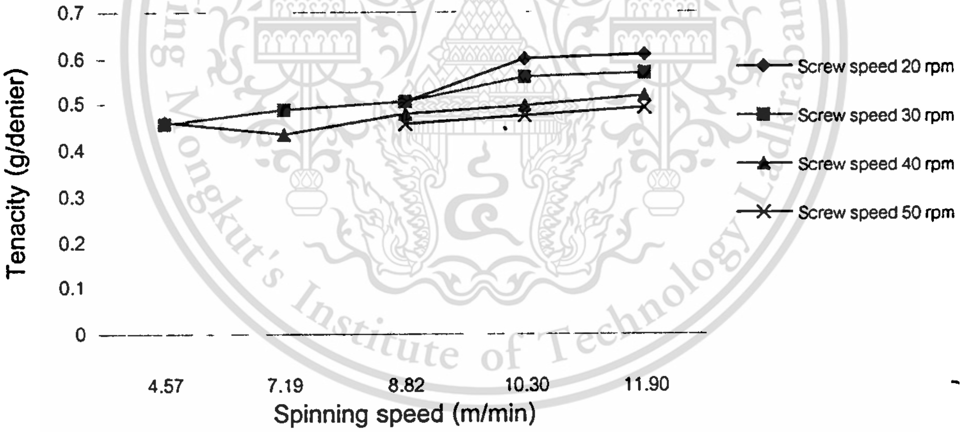


Figure 4.4 Tenacity of polyolefins blend by using screw speeds of 20, 30, 40 and 50 rpm and spinning speeds of 4.57, 7.19, 8.82, 10.30 and 11.90 m/min.

Notes: 1) at the beginning of the experiment, screw speed 50 rpm was studied. The extruded fibers at this screw speed could not be collected at low spinning speeds of 4.57 and 7.19 m/min. Therefore, there was no data at the spinning speeds of 4.57 and 7.19 m/min.

2) At the screw speeds of 40 and 30 rpm, it was found that the higher the spinning speeds, the better the mechanical properties. Thus, the lower spinning speeds (4.57 and 7.19 m/min) with screw speed 20 rpm did not involve in the results.

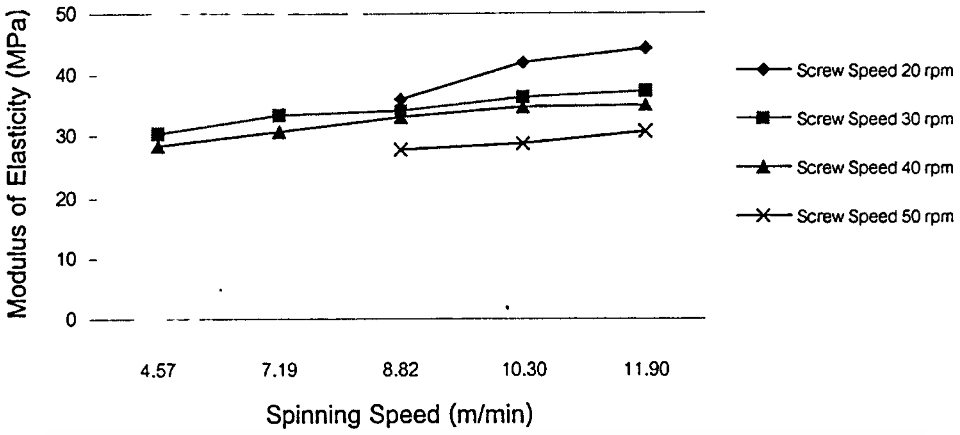


Figure 4.5 Modulus of elasticity of polyolefins blend by using screw speeds of 20, 30, 40 and 50 rpm and spinning speeds of 4.57, 7.19, 8.82, 10.30 and 11.90 m/min.

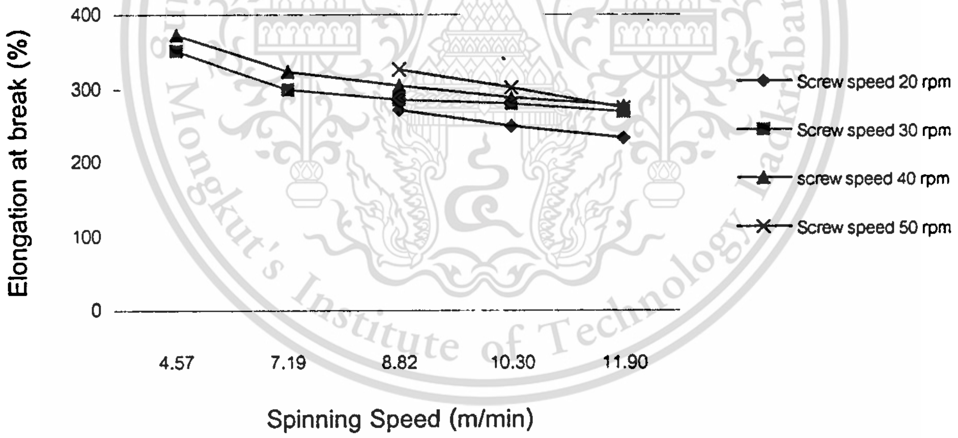


Figure 4.6 Elongation at break of polyolefins blend by using screw speeds of 20, 30, 40 and 50 rpm and spinning speeds of 4.57, 7.19, 8.82, 10.30 and 11.90 m/min.

4.2.1.2 Temperature

Mixing temperatures of polyolefins blend were varied in the range of 210 to 270 °C by using the ratio of blend (PP/R-HDPE/LDPE) as 25/50/25 and the screw speed and spinning speed as 20 rpm and 11.90 m/min, respectively. The results are shown in Figures 4.7 to 4.9. Tensile strength at break or tenacity and modulus of elasticity (Figures 4.7 and 4.8) increased with mixing temperature. Higher temperatures would also permit better mixing of polyolefins blend but at the temperature higher than 230 °C, the mechanical properties decreased. The decreasing of mechanical properties may be attributed to using mixing temperatures greater than processing temperature of LDPE, 250 to 450 °F or 121 to 232 °C (30) and so, the chain mobility of LDPE could slide over each other easily, which caused viscosity of LDPE too low to be processed. Thus, mechanical properties of polyolefins blend fibers were not good at temperatures higher than 230 °C.

Figures 4.7 to 4.9 indicated that 230 °C was the appropriate processing temperature for polyolefins blend because it had the better mechanical properties average than other conditions. Mixing temperature of 230 °C had linear density of 226 denier/filament, tensile strength at break of 53 MPa or tenacity of 0.6 g/denier, elongation at break of 233% and modulus of elasticity of 45 MPa.

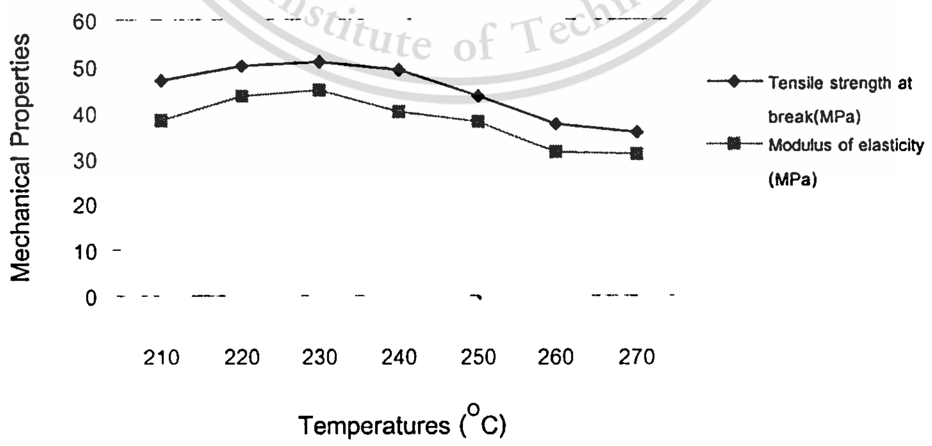


Figure 4.7 Tensile strength at break and modulus of elasticity of polyolefins blend at various temperatures.

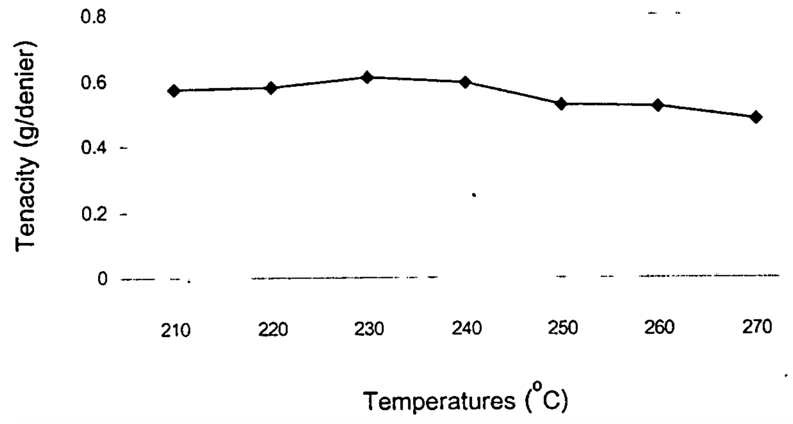


Figure 4.8 Tenacity of polyolefins blend at various temperatures.

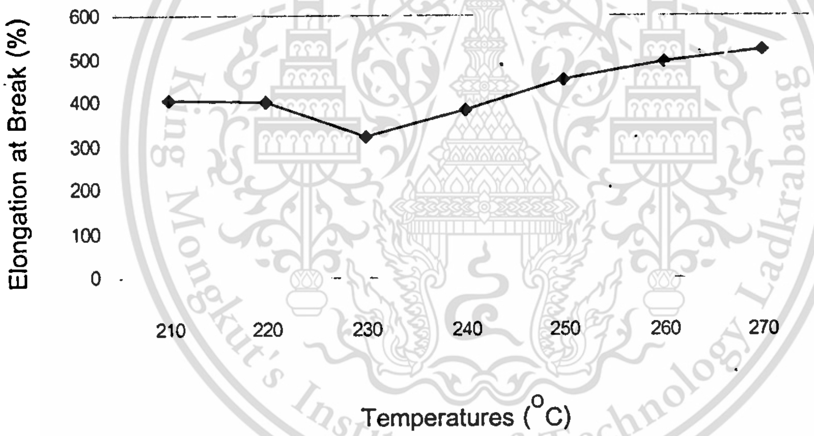


Figure 4.9 Elongation at break of polyolefins blend at various temperatures.

4.2.1.3 Blend ratio of polyolefins blend

Blend ratios of polyolefins (PP/R-HDPE/LDPE) were varied by using a screw speed of 20 rpm, a spinning speed of 11.90 m/min and a mixing temperature of 230 °C. The results are shown in Figures 4.10 to 4.12.

PP had higher tensile strength and modulus of elasticity than HDPE and LDPE. Thus, the blends that had amount of PP or HDPE greater than LDPE should indicate better mechanical properties. In systems of polyolefins blend that had PP, R-HDPE and LDPE as 25/50/25, 25/37.5/37.5 and 25/25/50, the results showed that the polyolefins blend at the ratio of 25/50/25 had greater mechanical properties than those of 25/37.5/37.5 and 25/25/50, respectively because R-HDPE enhanced the higher tensile strength at break and modulus of elasticity to the blends.

Among all the conditions studied, the results at the ratio of polyolefins blend (PP/R-HDPE/LDPE) as 25/50/25 was the appropriate blend ratio as the blend linear density of 226 denier/filament, tensile strength at break of 53 MPa or tenacity of 0.6 g/denier, elongation at break of 233 and modulus of elasticity of 45 MPa.

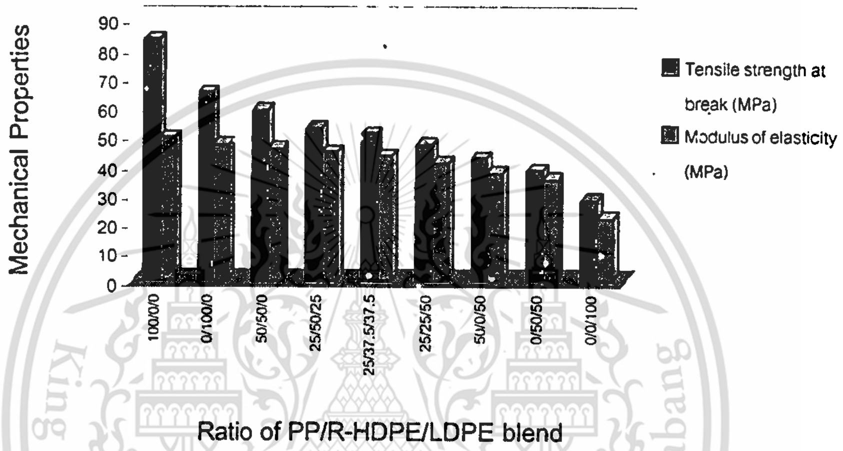


Figure 4.10 Tensile strength at break and modulus of elasticity of polyolefins blend at various blend ratios.

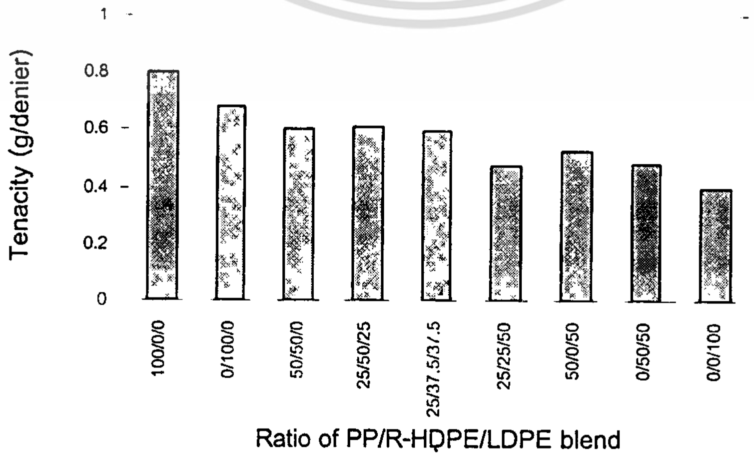


Figure 4.11 Tenacity of polyolefins blend at various blend ratios.

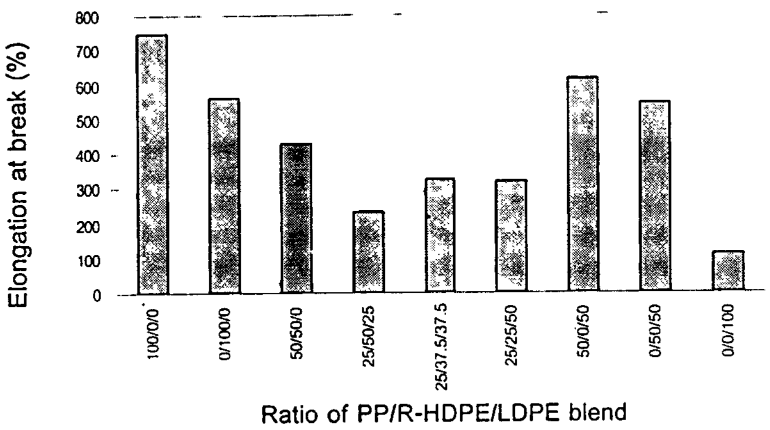


Figure 4.12 Elongation at break of polyolefins blend at various blend ratios.

4.2.2 Thermal properties

Differential scanning calorimetry (DSC) was the method that used to study the thermal behavior of polyolefins blends. The melting temperature (T_m) and degree of crystallinity are meaningful for thermal behavior. The typical DSC thermograms of polyolefins blends are shown in Appendix C.

4.2.2.1 Screw speed and spinning speed

The melting temperatures and degrees of crystallinity of polyolefins blends with various screw speeds (20 and 50 rpm) and spinning speeds (8.82 and 11.90 m/min) are shown in Table 4.1. It was found that the melting temperatures of all polymers were not changed at different screw speeds and spinning speeds. The degree of crystallinity of PP increased with spinning speed but decreased with increasing screw speed.

Table 4.1 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins blend with various screw speeds and spinning speeds.

Screw speed (rpm)	Spinning speed (m/min)	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity$_2$ (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity$_3$ (%)
50	8.82	132	47.29	32	164	10.27	25
	11.9	132	48.23	33	164	11.15	27
20	8.82	133	64.38	44	165	13.52	33
	11.9	133	64.48	44	165	16.21	39

Notices: 1) T_{m1} and ΔH_{f1} :T_m and ΔH of LDPE, the value is too low so, could not be measured

2) T_{m2}: T_m of R-HDPE, T_{m3} : T_m of PP

3) ΔH_{f2} : ΔH of R-HDPE, ΔH_{f3} : ΔH of PP

4) Degree of crystallinity$_2$: Degree of crystallinity of R-HDPE

5) Degree of crystallinity$_3$: Degree of crystallinity of PP

At the same screw speed, increasing spinning speed had a little effect to degree of crystallinity of PP, the higher spinning speed (11.90 m/min) had higher degree of crystallinity than the lower spinning speed (8.82 m/min) of both screw speeds (20 rpm and 50 rpm). The molecules, because of their improved alignment, are able to pack themselves in a more orderly manner, so that the fibers becomes more crystalline. When increased spinning speed, the molecules turn into the direction of stretched and were oriented parallel to the fiber axis, causing increased the crystallinity of PP. Therefore, the screw speed of 20 rpm and spinning speed of 11.90 m/min were considered to be the appropriate screw speed and spinning speed for producing fibers with higher degree of crystallinity. The thermal behaviors were corresponding to the results of mechanical properties.

4.2.2 2 Temperature

A DSC technique was used to evaluate the melting temperatures and degrees of crystallinity of PP/R-HDPE/LDPE blend with various temperatures. They are shown in Table 4.2. The results indicated that the melting temperatures appeared to be independent for the processing conditions. The melting temperatures of all materials were observed in temperatures range of ± 1 °C but for the degrees of crystallinity both of R-HDPE and PP increased with mixing temperature (up to 230°C). But at processing temperatures greater than 230 °C the crystallinity was higher than those at other conditions. The reasons were that: at this condition the molecule of polymer chains can slide over each other easily causing better mixing of the blends [34] and heat of fusion is related to degrees of crystallinity; the higher heat of fusion and the higher degree of crystallinity.

Table 4.2 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins blend with various temperatures.

Temperatures (°C)	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity$_2$ (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity$_3$ (%)
210	132	40.62	28	165	14.28	35
220	133	58.46	40	165	14.00	34
230	133	64.48	44	165	16.21	39
240	133	50.01	34	165	17.00	40
250	132	49.00	36	165	16.97	40
260	132	47.20	32	165	13.15	32
270	132	36.45	25	165	13.45	33

Notices: 1) T_{m1} and ΔH_{f1} :T_m and ΔH of LDPE, the value is too low so, could not be measured

2) T_{m2}: T_m of R-HDPE, T_{m3} : T_m of PP

3) ΔH_{f2} : ΔH of R-HDPE, ΔH_{f3} : ΔH of PP

4) Degree of crystallinity$_2$(%) : Degree of crystallinity of R-HDPE

5) Degree of crystallinity$_3$(%) : Degree of crystallinity of PP

4.2.2.3 Blend ratio of polyolefins

The melting temperatures and degrees of crystallinity of PP/R-HDPE/LDPE blend with various ratios of blend are shown in Table 4.3. In general, increasing amount of LDPE leads to lower degree of crystallinity. It was due to higher degree of branching that would affect the packing ability of the polymer chain [31]. Thus, the ratio of PP/R-HDPE/LDPE blend as 25/50/25, R-HDPE showed highest degree of crystallinity. From the previous Tables 4.1 to 4.3 it can be concluded that appropriate conditions were at the ratio of PP/R-HDPE/LDPE blend of 25/50/25, screw speed of 20 rpm, spinning speed of 11.90 m/min, and mixing temperature of 230 °C that gave highest degree of crystallinity. This result was consistent to the results of mechanical properties.

Table 4.3 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins blend with various blend ratios.

Ratio of PP/R-HDPE/ LDPE blend	T_{m1} (°C)	ΔH_{f1} (J/g)	Degree of crystallinity$_1$ (%)	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity$_2$ (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity$_3$ (%)
100/0/0	-	-	-	-	-	-	168	66.70	40
0/100/0	-	-	-	136	156.12	53	-	-	-
50/50/0	-	-	-	135	32.61	43	166	26.61	32
25/50/25	-	-	-	133	64.48	44	165	16.21	39
25/37.5/37.5	-	-	-	132	23.00	29	165	11.15	27
25/25/50	-	-	-	131	47.20	31	165	13.15	32
50/0/50	111	16.56	11	-	-	-	166	25.00	30
0/50/50	111	3.72	2	135	92.68	63	-	-	-
0/0/100	111	52.50	18	-	-	-	-	-	-

Notices: 1) For T_{m1} and ΔH_{m1}, the value is too low so, could not be measured

2) T_{m1}: T_m of LDPE, T_{m2}: T_m of R-HDPE, T_{m3} : T_m of PP

3) ΔH_{f1} : ΔH of LDPE, ΔH_{f2} : ΔH of R-HDPE, ΔH_{f3} : ΔH of PP

4) Degree of crystallinity$_1$: Degree of crystallinity of LDPE

5) Degree of crystallinity$_2$: Degree of crystallinity of R-HDPE

6) Degree of crystallinity$_3$: Degree of crystallinity of PP

4.2.3 Morphological properties

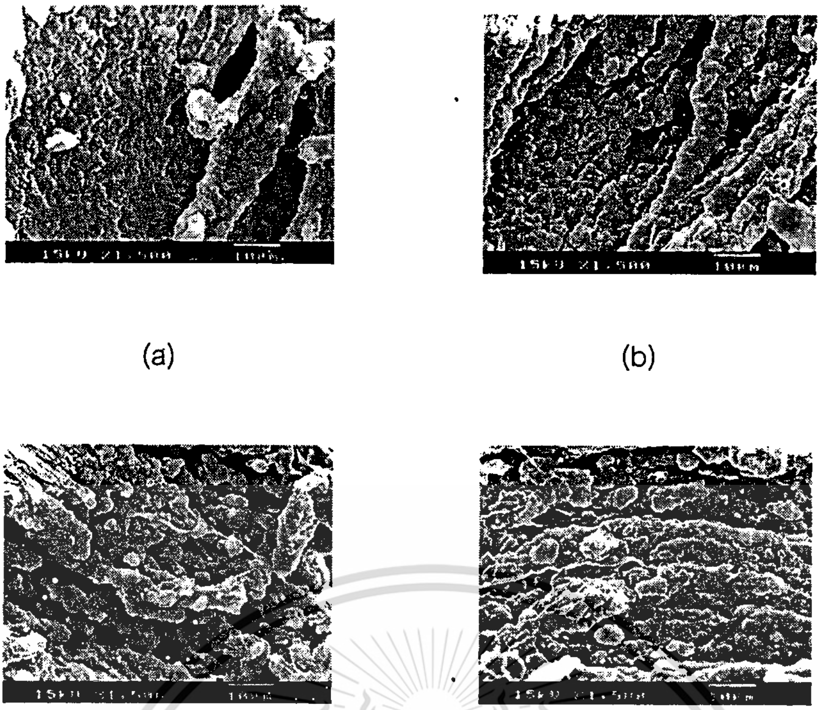
In general, the morphologies of polymer blends depend on shear history in the mixer, viscosity ratio and the interfacial tension between matrix and minor components. In particular, the interfacial tension between polymers is very important for phase morphology. The interfacial tension between polyolefins and polyolefins with recycled poly(ethylene terephthalate) blend were investigated by scanning electron microscope (SEM) in order to observe the effect of screw speed, spinning speed, temperature and blend ratio with and without compatibilizers into spun fibers. The SEM micrographs of fracture surface in transverse section of blends are shown in Figures 4.13 to 4.23.

4.2.3.1 Screw speed and spinning speed

SEM micrographs of polyolefins blend with various screw speeds and spinning speeds (at high and low screw speeds of 50 and 20 rpm and spinning speeds of 11.90 and 8.82 m/min, respectively) are shown in Figure 4.13. It could not indicate the different of phase morphology of polyolefins at different screw speeds and spinning speeds, because the difference of spinning speed in this research is very low (only 11.90 m/min) due to limitation of speed controller.

4.2.3.2 Temperature

Comparison of phase morphology of polyolefins blend to spun fibers that had the highest and the lowest mechanical properties, especially at processing temperature of 230 °C and 270 °C. The SEM micrographs are shown in Figure 4.14.



(a) (b)

(c) (d)

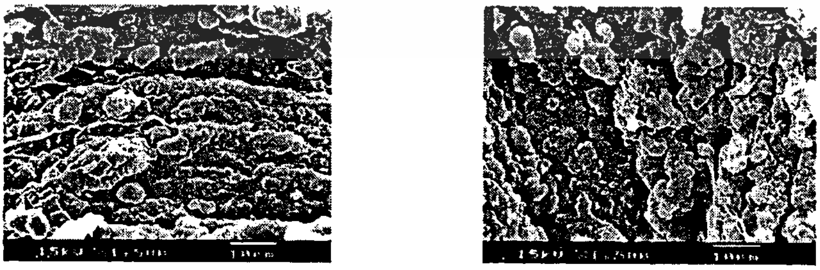
Figures 4.13 SEM micrographs of fracture surfaces under tension of polyolefins blends to spun fibers with various screw speeds and spinning speeds

a) screw speed of 50 rpm and spinning speed of 8.82 m/min

b) screw speed of 50 rpm and spinning speed of 11.9 m/min

c) screw speed of 20 rpm and spinning speed of 8.82 m/min

d) screw speed of 20 rpm and spinning speed of 11.9 m/min

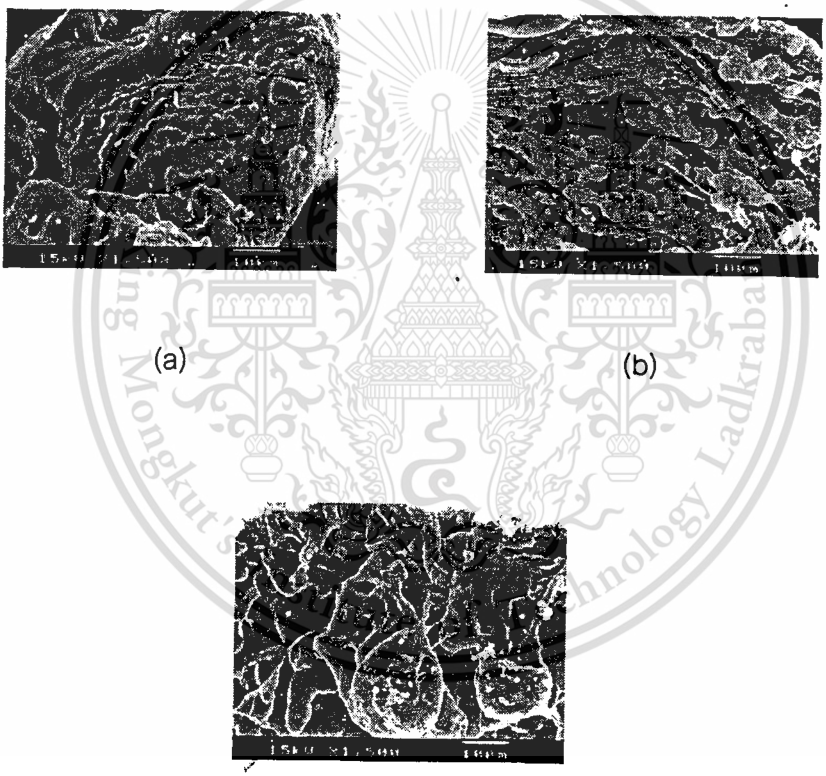


(a) (b)

Figure 4.14 SEM micrographs of fractured surfaces under tension of polyolefins blend to spun fibers with various temperatures; a) 230 °C and b) 270 °C

4.2.3.3 Blend ratio of polyolefins blend

Figures 4.15 and 4.16 showed the phase morphologies of polyolefins blend (PP/R-HDPE/LDPE) with various ratios of blend. The SEM micrographs of neat materials are shown in Figure 4.15. From Figure 4.16, the ratios of polyolefins blend were important to phase morphology of blends. The phase morphology would indicate the similarly morphology with material that had the highest amount in those conditions. Thus, the phase morphology between virgin materials and the blends that indicated the similar phase could be compared as following; Figure 4.15 (a) with Figure 4.16 (a), Figure 4.15 (b) with Figure 4.16 (c), (d) and (e) and Figure 4.15 (c) with Figure 4.16 (b) and (f.16 d)



(a) (b)

(c)

Figure 4.15 SEM micrographs of fractured surfaces under tension of virgin materials to spun fibers

a) PP 100%

b) R-HDPE 100%

c) LDPE 100%

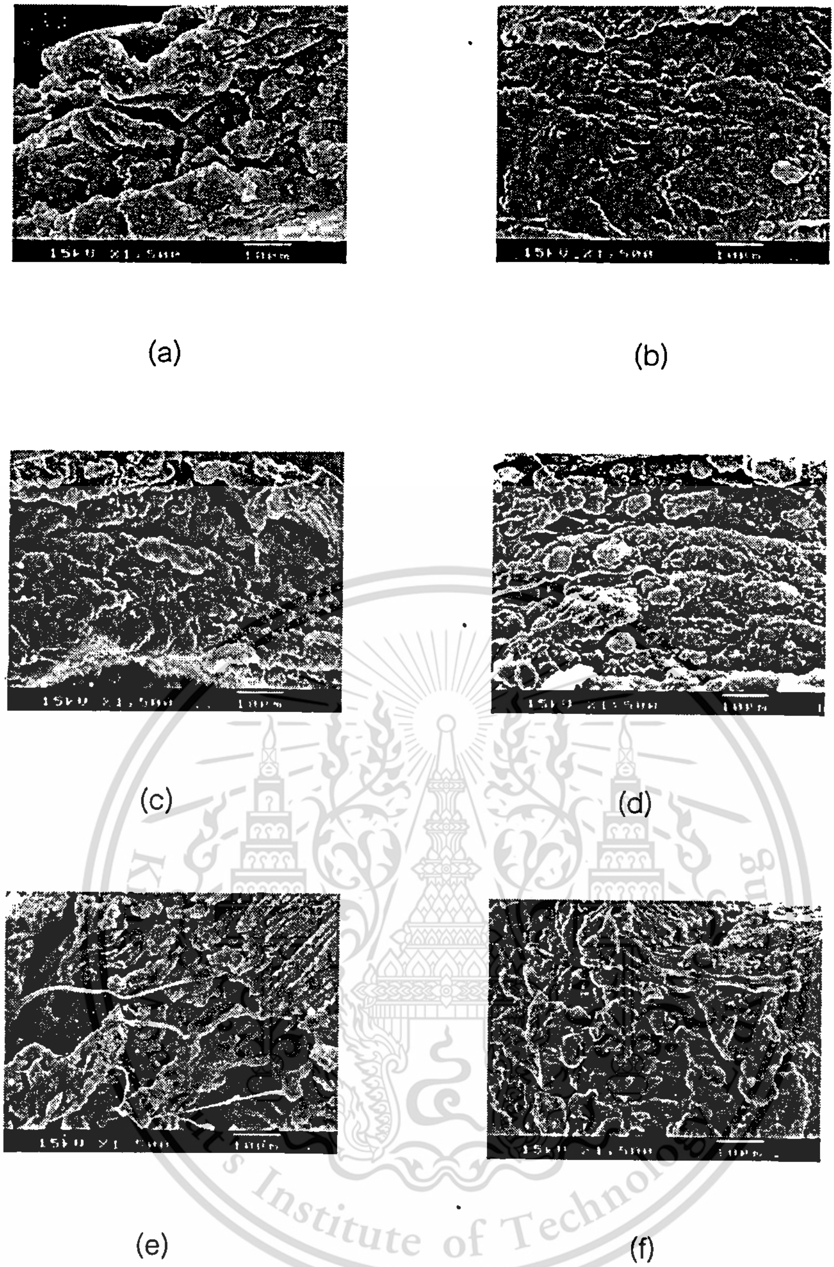


Figure 4.16 SEM micrographs of fractured surfaces under tension of polyolefins blend (PP/R-HDPE/LDPE) to spun fibers with various ratios of blend

a) PP/R-HDPE (50/50)

b) PP/LDPE (50/50)

c) R-HDPE/LDPE (50/50)

d) PP/R-HDPE/LDPE (25/50/25)

e) PP/R-HDPE/LDPE (25/37.5/37.5)

f) PP/R-HDPE/LDPE (25/25/50)

4.3 Appropriate processing conditions of polyolefins with recycled poly (ethylene terephthalate) blend (without-compatibilizer).

4.3.1 Mechanical properties

The effect of mixing temperature and the blends ratio between polyolefins and recycled poly(ethylene terephthalate) were investigated using tensile test. Figures 4.17 to 4.20 showed the mechanical properties of recycled polyolefins (PP/R-HDPE/LDPE) and recycled poly(ethylene terephthalate) blends, by using appropriate ratio of PP/LDPE/R-HDPE blend, screw speed and spinning speed as 25/50/25, 20 rpm and 11.90 m/min, respectively (from the results of polyolefins blend).

It was found that the tensile strength at break and modulus of elasticity increased when the PET composition increased from 25 to 75% by weight comparing to R-PET because R-PET had higher tensile strength at break and modulus of elasticity than polyolefins. Increased ratios of R-PET in blends gave increasing in mechanical properties. The effect of temperature was also investigated and it was found that the tensile strength at break and modulus of elasticity were increased as the temperature increased from 260 to 270 °C. For neat R-PET, the tensile strength and modulus of elasticity were also higher as temperature increased. This was because increasing temperatures favored a better mixing but R-PET did not fully melt at 260 °C (T_m of R-PET as 253 °C). Comparing to polyolefins, the tensile strength at break and modulus of elasticity were decreased with increasing temperature according to viscosity of material was too low to be processed at higher temperatures.

From the results (Figures 4.17 to 4.20) showed that the blend ratio of polyolefins and recycled poly(ethylene terephthalate) blend of 25/75 and mixing temperature of 270 °C were the appropriate blend ratio and temperature for this system because these conditions indicated the better mechanical properties than other conditions. This system had linear density of 684 denier/filament, tensile strength of 60 MPa or tenacity of 0.6 g/denier, elongation at break of 39% and modulus of elasticity of 68 MPa.

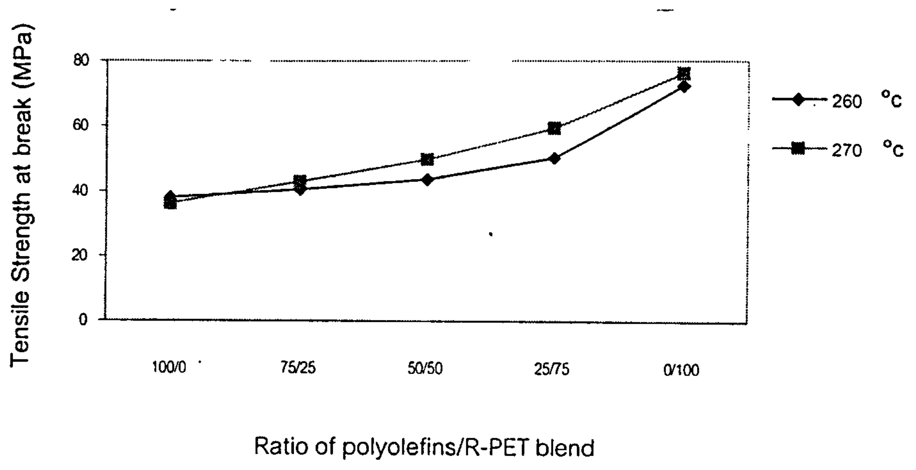


Figure 4.17 Tensile strength at break of polyolefins with recycled poly(ethylene terephthalate) blend at various ratios of blend by using temperatures at 260 °C and 270 °C.

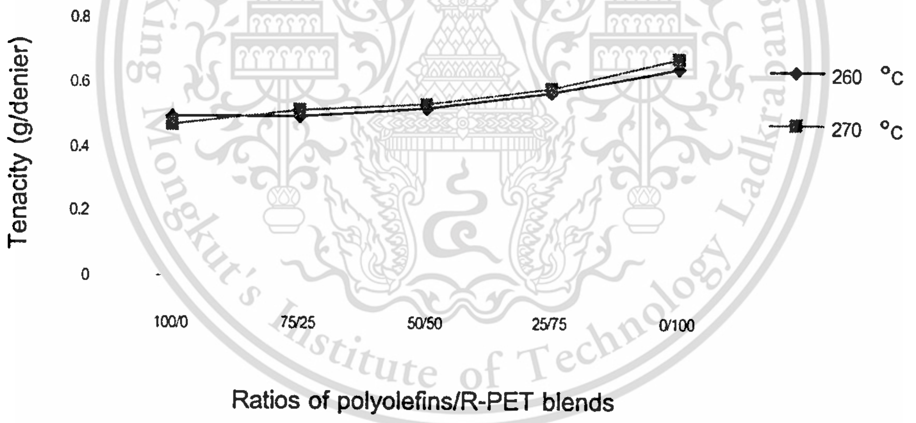


Figure 4.18 Tenacity of polyolefins with recycled poly(ethylene terephthalate) blend at various ratios of blend by using temperatures at 260 °C and 270 °C .

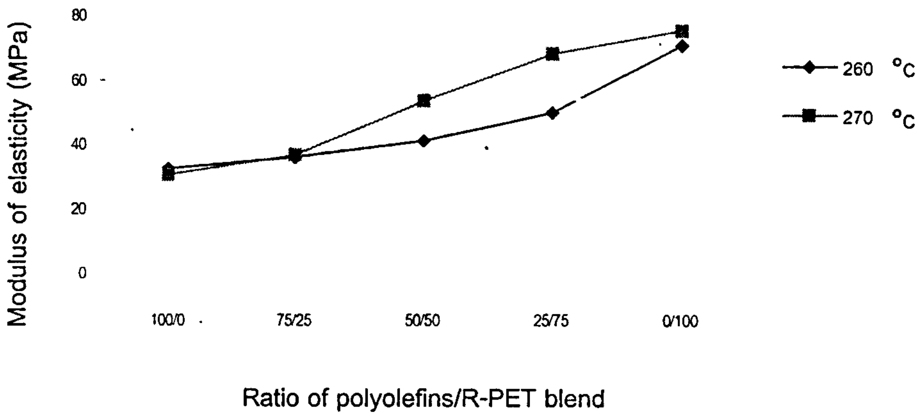


Figure 4.19 Modulus of elasticity of polyolefins with recycled poly(ethylene terephthalate) blend at various ratios of blend by using temperatures at 260 °C and 270 °C.

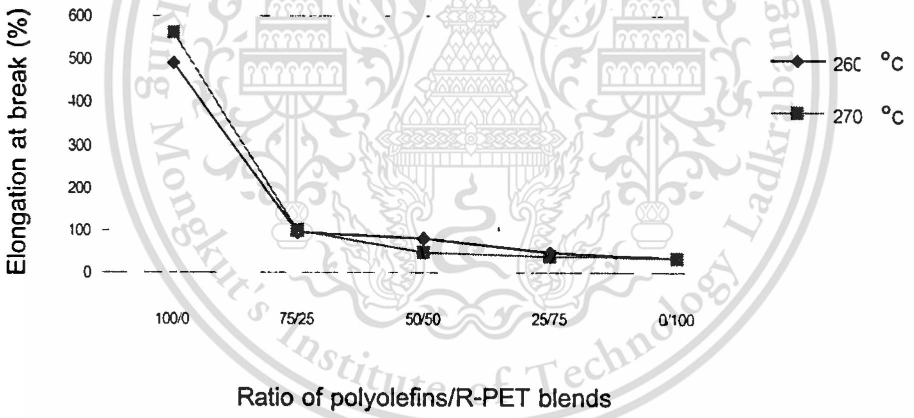


Figure 4.20 Elongation at break of polyolefins with recycled poly(ethylene terephthalate) blend at various ratios of blend by using temperatures at 260 °C and 270 °C.

4.3.2 Thermal properties

The melting temperatures and degrees of crystallinity of polyolefins and recycled poly(ethylene terephthalate) blend with various ratios between PP/R-HDPE/LDPE with R-PET blend by using appropriate ratio of PP/R-HDPE/LDPE blend of 25/50/25 and temperature as 270 °C are shown in Table 4.4. The melting temperatures appeared to be independent for the processing conditions. The melting temperatures of materials were observed in temperatures range of ± 1-2 °C and degree of crystallinity of materials (R-HDPE, PP and R-PET) were decreased when the R-PET composition was increased from 25 to 75% by weight. Thus, neat R-PET showed lower crystallinity than those of blends. For R-PET, polyolefins should be a nucleating agent which induced the crystallization of R-PET but R-PET would disturb the crystallization both of R-HDPE and PP. Thus, increasing ratio of polyolefins from 25 to 75 % by weight caused increasing in degree of crystallinity of R-HDPE, PP and R-PET.

Table 4.4 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins/R-PET blend at 270 °C with various ratio of PP/R-HDPE/LDPE with R-PET blends

Blend ratios of polyolefins/ R-PET	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity_2 (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity_3 (%)	T_{m4} (°C)	ΔH_{f4} (J/g)	Degree of crystallinity_4 (%)
100/0	132	36.45	25	165	13.75	33	-	-	-
75/25	132	29.14	27	165	13.02	42	251	14.29	41
50/50	131	18.03	25	165	7.97	39	252	13.70	20
25/75	131	8.42	23	165	2.76	27	253	17.27	16
0/100	-	-	-	-	-	-	253	11.58	8

Notices: 1) T_{m1} and ΔH_{f1} : T_m ΔH_f of LDPE, the value is too low so, could not be measured

2) T_{m2}: T_m of R-HDPE, T_{m3}: T_m of PP and T_{m4}: T_m of R-PET

3) ΔH_{f2}: ΔH_m of R-HDPE, ΔH_{f3}: ΔH_m of PP and ΔH_{f4}: ΔH_m of R-PET

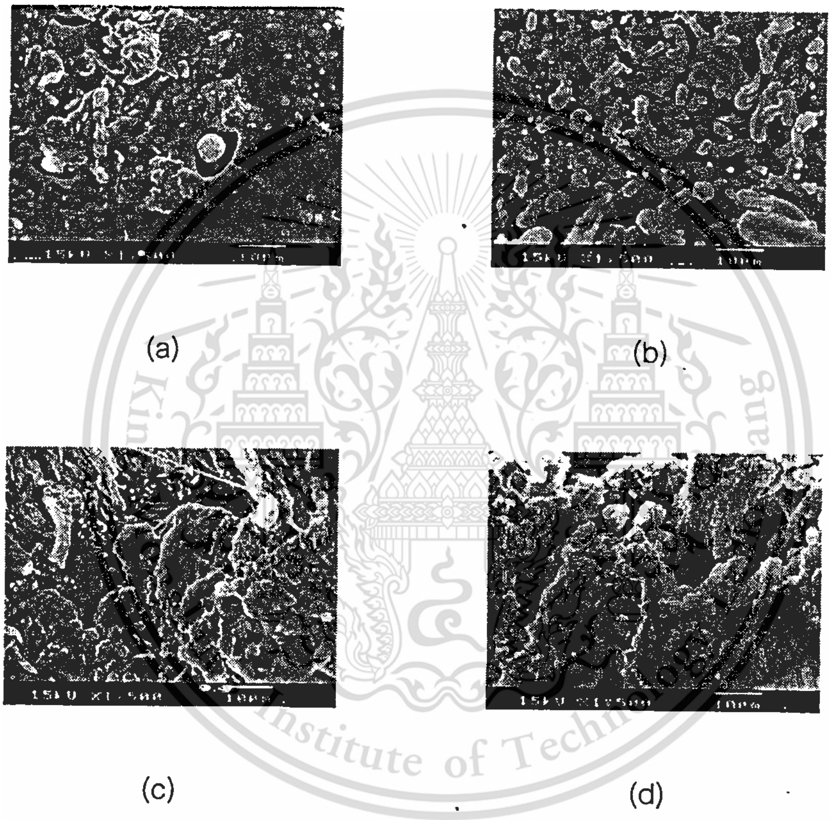
4) Degree of crystallinity_2 : Degree of crystallinity of R-HDPE

5) Degree of crystallinity_3 : Degree of crystallinity of PP

6) Degree of crystallinity_4 : Degree of crystallinity of R-PET

4.3.3 Morphological properties

Figure 4.21 is the SEM micrographs of spun fibers of polyolefins blend and recycled poly(ethylene terephthalate) with various ratios of blend by using appropriate ratio of PP/LDPE/R-HDPE blend of 25/50/25, screw speed of 20 rpm and spinning speed of 11.90 m/min, respectively (from the results of polyolefins blend) and mixing temperature of 270 °C (from the result of mechanical properties, at 270 °C indicated the higher properties than 260 °C).



(a) (b)

(c) (d)

Figure 4.21 SEM micrographs of fractured surfaces under tension of polyolefins with R-PET blend of spun fibers at 270 °C with various ratios of blend

a) PET 100%

b) polyolefins/R-PET (25/75)

c) polyolefins/R-PET (50/50)

d) polyolefins/R-PET (75/25)

Glass transition temperatures (T_g) of polypropylene, polyethylenes and poly (ethylene terephthalate) were –20 °C, –120 °C and 65 °C ,respectively (30). At prepared conditions for SEM test (25 °C room temperature and constant velocity), polyolefins were rubbery state but poly(ethylene terephthalate) was glassy state. Thus, polyolefins were elongated when applied stress to fibers.

This step focused on the ratio of blend that showed the better mechanical properties than others. Thus, interest only Figure 4.21 (b). It was found that the fine fibrils of polyolefins dispersed in a matrix of R-PET throughly. The fibrils are random in size and locations of the fibrils were aligned in the axial direction. Adhesion is not essential to fiber integrity because of finer dispersion and high interfacial area.

Polyolefins with R-PET blend 25/75 (Figure 4.21 b) could be seen dispersed phase clearly. In this condition, the distribution of dispersed phase was penetrated in matrix (R-PET) thoroughly. In other conditions, polyolefins/R-PET 75/25 (d) and 50/50 (c), could not be seen phase difference between dispersed and matrix phase clearly because of excess amount of polyolefins.

4.4 Comparison of compatibilizer types

4.4.1 Mechanical properties

The appropriate operating conditions of recycled polyolefins and recycled poly (ethylene terephthalate) blend, with the blend ratio as 25/75 (by weight) and temperature of 270 °C were further studied by adding compatibilizers; polypropylene grafted maleic anhydride (PP-g-MA), polypropylene grafted acrylic acid (PP-g-AA) or high-density polyethylene grafted acrylic acid (HDPE-g-AA). Figures 4.22 to 4.25 show the effect of compatibilizers on mechanical properties of blend.

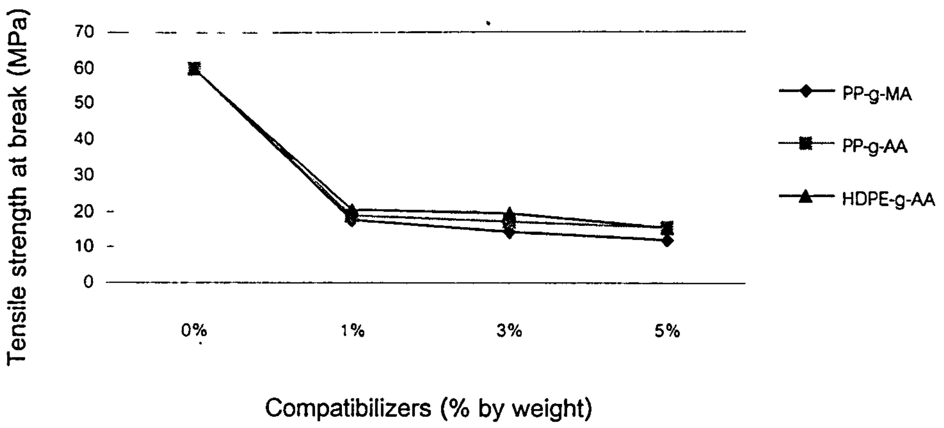


Figure 4.22 Tensile strength at break of polyolefins with recycled poly(ethylene terephthalate) blend that were filled with various compatibilizers by using processing temperature of 270 °C.

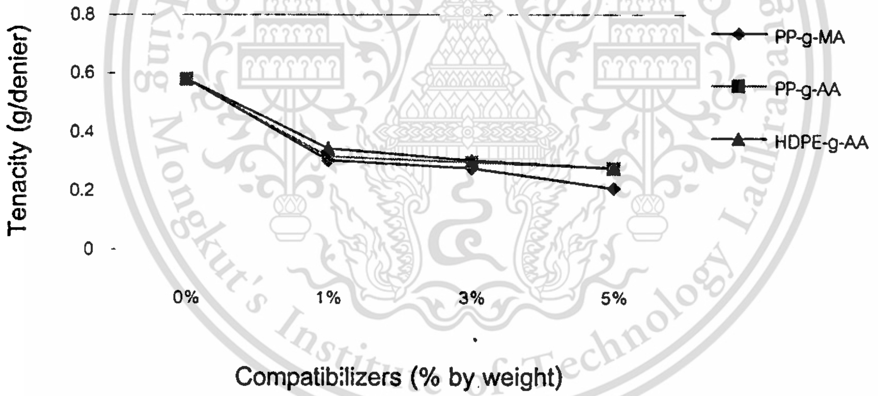


Figure 4.23 Tenacity of polyolefins with recycled poly(ethylene terephthalate) blend that were filled with various compatibilizers by using processing temperature of 270 °C.

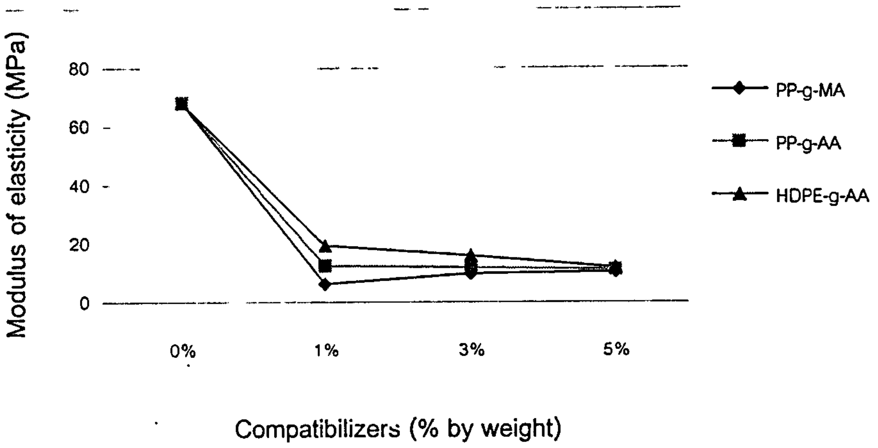


Figure 4.24 Modulus of elasticity of polyolefins with recycled poly(ethylene terephthalate) blend that were filled with various compatibilizers by using processing temperature of 270 °C.

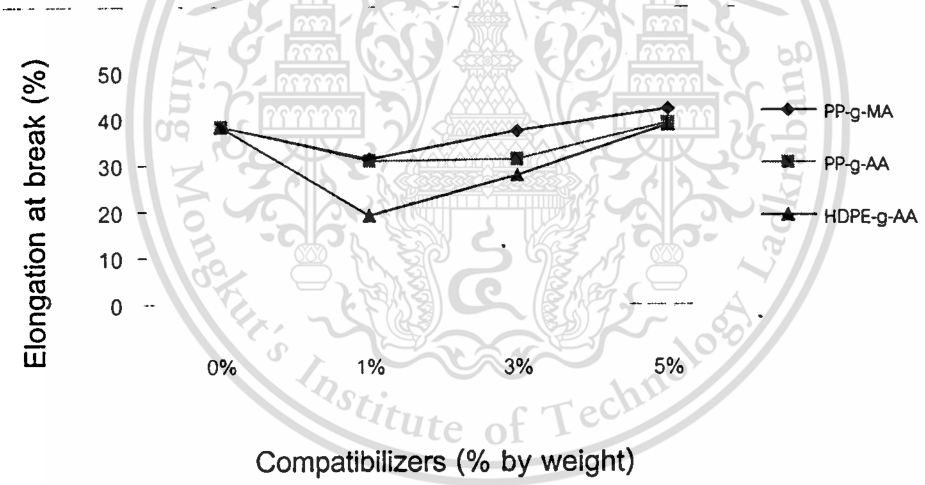


Figure 4.25 Elongation at break of polyolefins with recycled poly(ethylene terephthalate) blend that were filled with various compatibilizers by using temperature of 270 °C.

The results showed that adding any increased amount of compatibilizers in blend gave the significantly decreased in mechanical properties. When compatibilizers were added, the segments of compatibilizers that had polar groups (acrylic acid or maleic anhydried) expected to react with the polar groups of recycled poly(ethylene terephthalate) and led to form chemical bonding at processing temperature which acted as a true compatibilizer and had parts at the interface which they were entangled to both phases [15]. When compatibilizers were added, the viscosity of systems increased (from the result of DSC, crystallization temperature (T_c) of blends increased when adding any amount of compatibilizers). The T_c was related to the viscosity, the higher T_c, the viscosity of systems increased [34]. When the viscosity increased causing lower mixing of blends. This may be a reason for decreasing on mechanical properties. With the results indicated that the compatibilizers should not be added into this system.

4.4.2 Thermal properties

The melting temperatures and degrees of crystallinity of polyolefins/recycled poly(ethylene terephthalate) blend at the blend ratio of 25/75 and temperature 270 °C by using HDPE-g-AA as a compatibilizer with various amount of compatibilizers are shown in Table 4.5. The melting temperatures appear to be independent for the processing conditions. The melting temperatures of all materials were observed in temperatures range of ± 1 °C. The degree of crystallinity of R-HDPE was increased but the degrees of crystallinity of PP and R-PET were decreased when increased amount of compatibilizers in blend. This may be attributed to molecules of compatibilizer should be a heterogeneous nucleation which induced the crystallization of R-HDPE but disturbed the crystallization both of PP and R-PET. This caused reduction of heat of fusion and the degree of crystallinity of systems were decreased when the compatibilizers were added.

Table 4.5 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins/recycled poly(ethylene terephthalate) blend that used HDPE-g-AA as compatibilizers with various amount of compatibilizers

% by weight	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity$_2$ (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity$_3$ (%)	T_{m4} (°C)	ΔH_{f4} (J/g)	Degree of crystallinity$_4$ (%)
0	131	8.42	23	165	2.76	27	253	17.27	16
1	131	12.36	34	165	2.72	26	252	9.37	12
3	130	13.75	38	165	2.67	19	252	9.26	9
5	130	14.52	40	165	1.12	11	252	8.91	6

Notices: 1) T_{m1} and ΔH_{f1} : T_m ΔH_f of LDPE, the value is too low so, could not be measured

2) T_{m2}: T_m of R-HDPE. T_{m3}: T_m of PP and T_{m4}: T_m of R-PET

3) ΔH_{f2}: ΔH_m of R-HDPE, ΔH_{f3}: ΔH_m of PP and ΔH_{f4}: ΔH_m of R-PET

4) Degree of crystallinity$_2$: Degree of crystallinity of R-HDPE

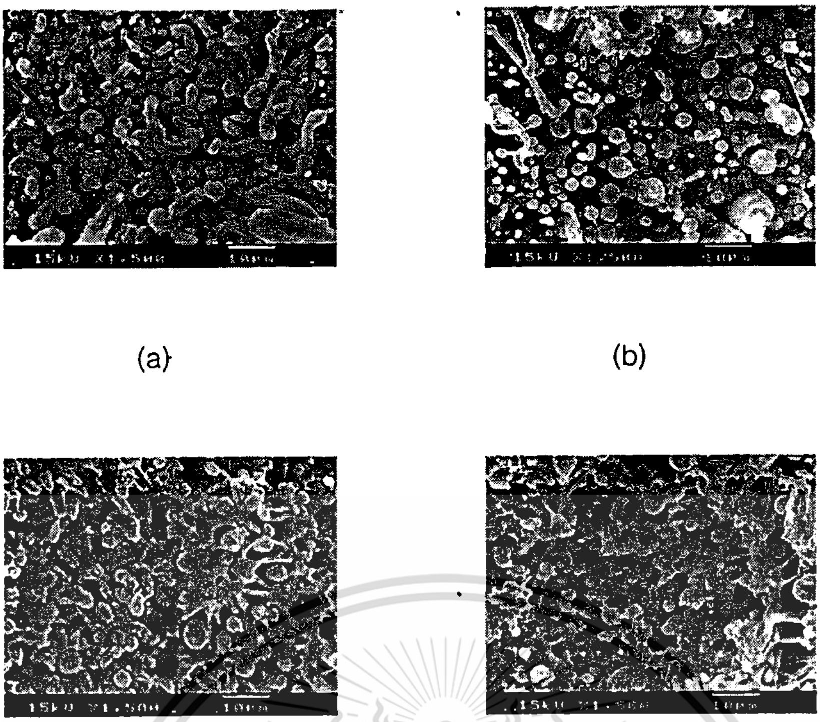
5) Degree of crystallinity$_3$: Degree of crystallinity of PP

6) Degree of crystallinity$_4$: Degree of crystallinity of R-PET

4.4.3 Morphological properties

The phase morphologies of compatibilized blend between polyolefins and recycled poly(ethylene terephthalate) are shown in Figure 4.22.

The phase arrangements of polyolefins with R-PET blend with and without compatibilizers were matrix-fibril, the fibrils of polyolefins were dispersed in a matrix of R-PET. The fibrils were aligned in the axial direction. The differences of phase morphologies were difficult to analyze because they were the complex system.



(a) (b)

(c) (d)

Figure 4.26 SEM micrographs of fractured surfaces under tension of polyolefins with R-PET with various amount of compatibilizer, HDPE-g-AA, blend to spun fibers at 270 °C

a) polyolefins/R-PET (25/75)

b) polyolefins/R-PET (25/75) with 1% HDPE-g-AA

c) polyolefins/R-PET (25/75) with 3% HDPE-g-AA

d) polyolefins/R-PET (25/75) with 5% HDPE-g-AA

4.5 Comparison high-density polyethylene fiber grade (F-HDPE) and high-density polyethylene recycled grade (R-HDPE) in the components of blends.

4.5.1 Mechanical properties

This step used F-HDPE instead of R-HDPE in the components of polyolefins with R-PET blends and polyolefins/R-PET with compatibilizers by using screw speed of 20 rpm, spinning speed of 11.9 m/min and mixing temperature of 230 °C for polyolefins blend and 270 °C for polyolefins with R-PET blends and the system that added compatibilizers, which indicated the appropriate mechanical properties. The comparison of mechanical properties of R-HDPE and F-HDPE is shown in Table 4.6. The results showed that the tensile strength at break and modulus of elasticity of R-HDPE were higher than those of F-HDPE and those of blends. In the opposite way, the systems that used F-HDPE in the compositions had higher elongation at break than those that used R-HDPE in all compositions of both compatibilized and non-compatibilized blends. In general, bottle grade high-density polyethylene had melt flow index (MFI) of about 0.3-0.4 (35) and this is lower than F-HDPE which had MFI of 0.8. The MFI was related to molecular weights (M_w) as the lower the MFI, the higher the M_w. The M_w was also related to the bottle strengths; high M_w gives high strengths which is required for industrial bottles needs.

Table 4.6 Mechanical properties of polyolefins, polyolefins with R-PET and polyolefins/ R-PET blends with compatibilizers that used F-HDPE instead of R-HDPE in the components

Types	Tensile strength at break (MPa)	Tenacity (g/denier)	Modulus of elasticity (MPa)	Elongation at break (%)
R-HDPE	65	0.4	47	564
F-HDPE	54	0.3	34	743
PP/R-HDPE/LDPE	53	0.6	45	233
PP/F-HDPE/LDPE	42	0.5	23	723
PP/R-HDPE/LDPE/PET	56	0.7	68	39
PP/F-HDPE/LDPE/PET	28	0.6	15	47
PP/R-HDPE/LDPE/PET + 1% PP-g-MA	18	0.3	12	31
PP/F-HDPE/LDPE/PET+ 1% PP-g-MA	17	0.3	12	37
PP/R-HDPE/LDPE/PET + 1% PP-g-AA	19	0.3	13	31
PP/F-HDPE/LDPE/PET + 1% PP-g-AA	18	0.7	13	35
PP/R-HDPE/LDPE/PET + 1% HDPE- g-AA	21	0.4	20	19
PP/F-HDPE/LDPE/PET + 1% HDPE-g-AA	20	0.3	20	28

4.5.2 Thermal properties

The melting temperatures and degrees of crystallinity of DSC on fibers presented in Table 4.7. It showed that neat spun fibers of F-HDPE had lower melting temperature and degree of crystallinity than R-HDPE due to lower lamella thickness [4] and conditions with incorporating of R-HDPE component had higher thermal properties than spun fibers of F-HDPE. Bottle grade of high-density polyethylene had MFI lower than F-HDPE. The MFI was related to M_w as the higher the MFI, the lower the M_w. The M_w was related to chain ends of polymers also; the lower the M_w, the higher chain ends. Chain ends of polymers impede the orderly arrangement of the molecules caused to decreasing on melting temperatures [34].

4.5.3 Morphological properties

SEM micrographs of recycled polyolefins, non-compatibilized and compatibilized blend between recycled polyolefins/R-PET with HDPE-g-AA as compatibilizer, comparing to F-HDPE material to R-HDPE components of all conditions were shown in Figure 4.23. The spun fiber phase morphology of virgin R-HDPE (a) had similar morphology with F-HDPE (b). The morphology of polyolefins blend that used F-HDPE material (d) had similar morphology with R-HDPE (c) which showed the similar phase to the highest amount in ratios of blend, R-HDPE. For non-compatibilized (e and f) and compatibilized blend of polyolefins and R-PET with HDPE-g-AA (g and h), the phase arrangement of both R-HDPE and F-HDPE were matrix-fibrils which fine fibrils of polyolefins were dispersed in a matrix of R-PET.

Table 4.7 Melting temperatures (T_m), heats of fusion (ΔH_f) and degrees of crystallinity of polyolefins, polyolefins with R-PET blends and polyolefins/R-PET blends with compatibilizers that used F-HDPE instead of R-HDPE in the components

Types	T_{m2} (°C)	ΔH_{f2} (J/g)	Degree of crystallinity$_2$ (%)	T_{m3} (°C)	ΔH_{f3} (J/g)	Degree of crystallinity$_3$ (%)	T_{m4} (°C)	ΔH_{f4} (J/g)	Degree of crystallinity$_4$ (%)
R-HDPE	136	156.12	53	-	-	-	-	-	-
F-HDPE	134	130.62	45	-	-	-	-	-	-
PP/R-HDPE/LDPE	133	64.48	44	165	18.21	44	-	-	
PP/F-HDPE/LDPE	131	51.25	35	165	14.59	35	-	-	-
P/R-HDPE/ LDPE/ PET	131	8.42	18	165	2.67	26	253	14.19	13
P/F-HDPE/LDPE /PET	129	8.19	16	166	2.51	24	251	13.86	11
/R-HDPE/LDPE /PET + 1% PP-g-MA	131	2.35	16	166	5.27	51	251	13.18	10
/F-HDPE/LDPE /PET + 1% PP-g-MA	129	7.57	14	165	4.29	42	251	12.44	10
/R-HDPE/LDPE /PET + 1% PP-g-AA	131	9.74	27	166	3.98	39	251	12.75	10
/F-HDPE/LDPE /PET + 1% PP-g-AA	129	9.02	25	165	1.78	17	251	9.48	8
/R-HDPE/LDPE /PET + 1% HDPE- g-AA	131	12.36	29	165	2.72	26	252	12.94	11
/F-HDPE/LDPE /PET + 1% HDPE-g-AA	129	10.10	27	165	2.20	19	252	8.08	7

Notices: 1) T_{m1} and ΔH_{f1} : T_m ΔH_f of LDPE, the value is too low so, could not be measured

2) T_{m2}: T_m of R-HDPE, T_{m3}: T_m of PP and T_{m4}: T_m of R-PET

3) ΔH_{f2}: ΔH_m of R-HDPE, ΔH_{f3}: ΔH_m of PP and ΔH_{f4}: ΔH_m of R-PET

4) Degree of crystallinity$_2$: Degree of crystallinity of R-HDPE

5) Degree of crystallinity$_3$: Degree of crystallinity of PP

6) Degree of crystallinity$_4$: Degree of crystallinity of R-PET

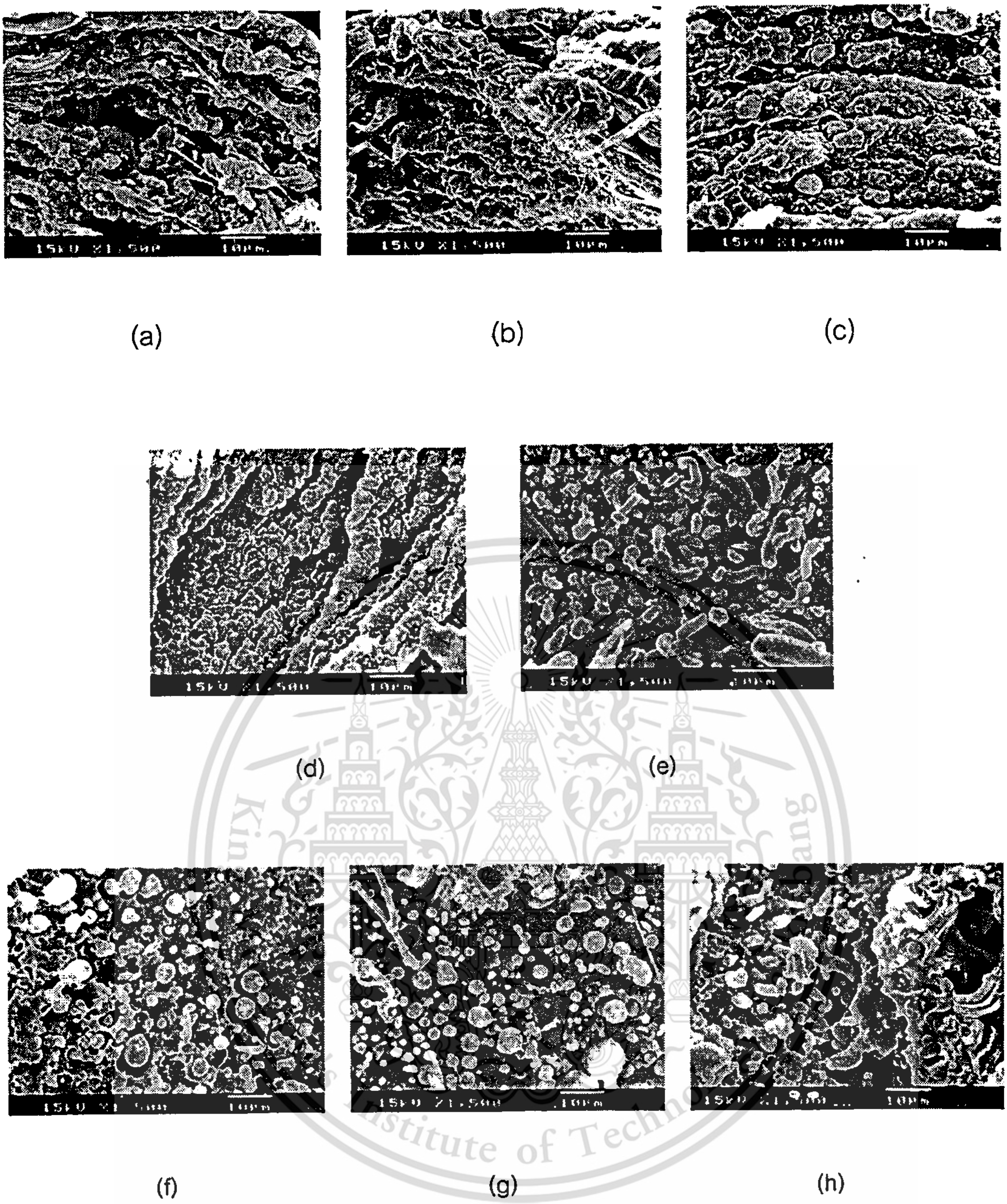


Figure 4.27 SEM micrographs of fractured surfaces under tension of polyolefins, polyolefins with R-PET and polyolefins with R-PET and compatibilizer, by using F-HDPE instead of R-HDPE in the components: (a) HDPE 100% (b) F-HDPE 100% (c) PP/R-HDPE/LDPE (25/50/25) (d) PP/F-HDPE/LDPE (25/50/25) (e) PP/R-HDPE/LDPE with R-PET (25/75) (f) PP/F-HDPE/LDPE with R-PET (25/75) (g) PP/R-HDPE/LDPE with R-PET and 1% HDPE-g-AA (h) PP/F-HDPE/LDPE with R-PET and 1% HDPE-g-AA.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS

This research focused on processing conditions and properties of recycled polyolefins, polyolefins and recycled poly(ethylene terephthalate) with and without compatibilizers for producing fibers.

PART I : Appropriate processing conditions of polyolefins blend on spun fibers

In this study, it was attempted to indicate the appropriate processing conditions such as screw speed, spinning speed, temperature, and blend ratio of polyolefins for producing fibers.

Screw speed of 20 rpm, spinning speed of 11.90 m/min, temperature of 230 °C and blend ratio of PP/R-HDPE/LDPE at 25/50/25 were chosen as the appropriate processing conditions because the results obtained from these conditions indicated optimum mechanical and thermal properties. The reasons may be attributed to:

1. With increasing spinning speed, tensile strength at break or tenacity and modulus of elasticity were generally increased because the molecules turn into the direction of fiber axis brought to the increased crystallinity of fibers.

2. Higher mixing temperature (240 to 270 °C) would permit better mixing of polyolefins than lower temperature (210 to 230 °C) but it caused viscosity of LDPE too low to be processed.

3. Increasing amount of R-HDPE to PP/R-HDPE/LDPE blend as 25/25/50, 25/37.5/37.5 to 25/50/25 indicated better mechanical and thermal properties of blend.

PART II : Appropriate processing conditions of polyolefins with recycled poly(ethylene terephthalate) blend (without-compatibilizer)

In this study, the effect of mixing temperature and blend ratio between polyolefins and recycled poly(ethylene terephthalate) were investigated. The following conclusions could be drawn:

1. The tensile strength at break or tenacity and modulus of elasticity of blend were increased when the R-PET composition was increased from 25 to 75 wt% and the temperature was increased from 260 to 270 °C.

2. The degree of crystallinity were decreased when the R-PET composition was increased from 25 to 75 wt% because neat R-PET had lower degree of crystallinity than those of blends.

3. At blend ratio 25/75 of polyolefins/R-PET, it could be seen that the distribution of dispersed phase of polyolefins (fibrils) were penetrated in matrix (R-PET) thoroughly.

PART III : Comparison of compatibilizer types

In this study, the effect of amount of compatibilizers and compatibilizer types were studied in the blends of polyolefins and recycled poly(ethylene terephthalate) for finding better mechanical properties of fibers. The following conclusions could be drawn:

1. Adding any amount of compatibilizers in blend gave the significantly decreasing in mechanical properties because the viscosity of systems increased causing lower mixing of blends. Thus, this system should not add compatibilizers to blends because PP-g-MA, PP-g-AA and HDPE-g-AA were not the appropriate compatibilizers for system of polyolefins and R-PET blend.

2. Compatibilizers should be a heterogeneous nucleation for R-HDPE because the degree of crystallinity of R-HDPE was increased. But molecules of compatibilizers could disturb the crystallization both of PP and R-PET causing a decreased in degrees of crystallinity.

PART IV : Comparison of high-density polyethylene fiber grade (F-HDPE) and high-density polyethylene recycled grade (R-HDPE) in the components of blends.

This step was studied comparison of the properties of fibers from F-HDPE and R-HDPE fibers. It could conclude as:

1. The fibers made from R-HDPE had better mechanical properties than the systems that used F-HDPE in all compositions.

2. The neat spun fibers of F-HDPE had lower melting temperature and degree of crystallinity than R-HDPE due to lower in molecular weights.

Suggestions for further work

1. The influence of drawing ratio and temperature to properties of fibers from polyolefins and recycled poly(ethylene terephthalate) blend for enchancing mechanical properties.
2. Adding Flame retardant to polyolefins and poly(ethylene terephthalate) blend for other interesting field.
3. Using higher spinning speeds for improvement properties of spun fibers.
4. To find appropriate compatibilizer for polyolefins and recycled poly(ethylene terephthalate) blend.

REFERENCES

[1] Gerald L. S. **Exploring the World of Plastics.** 5th Ed. Bloomington, IL : Mc Knight. 1997.

[2] Charles H. A., Editor. **Handbook of Plastics, Elastomer, and Composites.** 3rd Ed. Maryland : McGraw-Hill. 1996.

[3] รังสรรค์ ปิ่นทอง. " โครงการพลาสติกไทยรีไซเคิล." [on line]. เข้าถึงได้จาก : http: www.thaienvironment.net/thai pollution.

[4] Daw F. M., Chun C. H., Steve H. K., and Jiunn L. Y. " Study on the Processibility of Recycled PET Fibers." Text. Res. J., 67, 1997, pp. 891-895.

[5] Vallilatos G,, Knok B. H. and Frankfurt H. R., **High Speed Fiber Spinning**, New York : John Wily & Sons.1985.

[6] Ravi S. K., Prashant D., and Abhiraman A. S. " Melt Spinning of Syndiotactic Polypropylene: Structure Development and Implications for Oriented Crystallization." J. Polym. Sci., Part B: Polym. Phys. Ed., 1989. pp. 2469-2472.

[7] Rakesh G. K., and Kim A. F. " Crystallization in Polymer Melt Spinning." J. Appl. Polym. Sci., 32, 1986, pp. 4989-5006.

[8] Napolitano M. J., and Moet A. "The Effect of Processing Conditions on Structural Evolution in Melt spun Poly(ethylene Terephthalate)." J. Appl. Polym. Sci. 1986, pp. 2469-2484.

[9] Edgar T. R, Chaturong B., And Sati B. N. "Processing of Blends of Poly(ethylene terephthalate) and High-Density Polyethylene." ANTEC. Conf. Proc. 1995, pp.3189-3193.

[10] Krasnikova N. P. "The Influence of Viscosity and Dispersion of Incompatible polymer on Fibre Formation in Their Blends." ANTEC. Conf. Proc. 1995, pp.1423-1432.

[11] Bo-run I., James L. W., Joseph E.S. "Polypropylene/Nylon 6 Blends: Phase Distribution Morphology, Rhelogical Measurements and Structure Development in Melt Spinning." J. Appl. Polym. Sci. 1983, pp. 2011-2032.

[12] Shimizu J., Okui N. and Kikutani T. "Fine Structure and Physical Properties of Fibers Melt-Spun At High Speeds from various Polymers." **High-Speed Fiber Spinning-Science and Engineering aspects.** New York : Wiley and Sons. 1985.

[13] Abhiraman S. A. "Melt Spinning of Polymers I. An Elementary Framework for Analysing the Development of Orientation." J. Appl. Polym. Sci. 1987, pp. 809-823.

[14] Traugott D. T., Barlow W. J. and Paul R. D. "Mechanical Compatibilization of Immiscible Blends." J. Appl. Polym. Sci. 1983, pp. 2947.

[15] Somsak W., Nuttion., Wipa. "Processing of Recycled Polyolefins and Poly(ethylene terephthalate) Blends." J. Burapa University. 2000, pp40-52.

[16] Nicholas C.P. **Handbook of Polymer Science and Technology.** Vol 4. New York : Marcel Dekker, Inc. 1989.

[17] Gabriel S. O., George S. P., Editors. **Polymer Blends and Alloys.** United States : Marcel Dekker, Inc. 1999.

[18] Mark A. **Polymer Science Dictionary.** 2thEd. London : Chapman & Hall. 1997.

[19] Utracki L. A. **Polymer Alloys and Blends.** Newyork : Hanser.1989.

[20] Krosehwitz J. **High Performance Polymer and Composites.** New York : Wiley-Interscience. 1987.

[21] Flokes M.J., Hope P.S., Editors. **Polymer Blends and Alloys.** 1st Ed. United States: Chapman & Hall. 1993.

[22] Ashok A.M. "Polyacrylic Acid-Grafted Polypropylene as a Compatibilizer for Polymer Alloys." International Plastics and Rubber Planning Conference. Dusseldorf, 31 October- 1 November 1989.

[23] Richard G. G. **Polymer Processing Engineering.** United States : Chapman & Hall. 1995.

[24] Paul D.R. and Seymour N. **Polymer Blends.** Vol. 2. Acadamic Press, Inc. 1978.

[25] Vesely D. "Microstructural Characterization of Polymer Blends". J. Polm. Eng. Sci. 1996. pp.1586-593.

[26] Hunt B.J., James M. I. **Polymer Characterization.** Glasgow : Blackie Acadamic & Professional. 1993.

[27] Michael B. L. SPI Plastics Engineering Handbook. New York : Van Nostrand Reinfold. 1991.

[28] Howard N. L. Textile Fibers, Dyes, Finishes, and Process A Concise Guide. New Jersey : Noyes Publications. 1986.

[29] Charles Z., Carroll P. Manual of Man-Made Fibers. Guildford : Astex Publishing Company. 1960.

[30] Charles H. A. Handbook of plastics, Elastomers, and Composites. 3rd Ed. Maryland : McGraw-HILL. 1960.

[31] Steven W. N. Fiber Science. New Jersey : Prentice-Hall, Inc. 1995.

[32] Moncrieff W.R Man-Made Fibres. 5th Ed. London : Butterworth & Co Ltd. 1970.

[33] Malinee Chaisupakitsil. Polymer Chemistry. 3th Ed. King Mongkut's Institute of Technology Ladkrabang. Bangkok. 2540.

[34] Itlipol Jengchud. Complementary Documentation for Polymer Physics. Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang Bangkok. 2543.

[35] Data sheet of EL-LENE High-Density Polyethylene from Siam Chemical Trade. 2001.

APPENDICES

APPENDIX A

Appendix A The mechanical properties of polyolefins and polyolefins with recycled poly(ethylene terephthalate) blends

Table A.1 The mechanical properties of polyolefins blend with various screw speeds and spinning speeds and fixed ratio of blend (PP/HDPE/LDPE) of 25/50/25 and temperature of 230°C.

Screw Speed (rpm)	Spinning Speed (m/min)	Tensile Strength at break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
20	8.82	46	2.71	271	86.10	36	5.60	313	5.93	0.5
	10.30	51	6.20	251	58.00	42	6.86	246	5.58	0.6
	11.90	53	8.18	233	117.60	45	9.64	226	3.65	0.6
30	4.57	38	3.35	253	146.40	30	2.48	592	7.58	0.5
	7.19	44	8.10	299	135.70	34	7.25	510	6.11	0.5
	8.82	44	6.35	286	145.60	34	3.45	387	4.86	0.5
	10.30	46	5.72	280	153.00	36	3.82	284	4.54	0.6
	11.90	48	5.28	267	107.30	38	7.32	213	5.58	0.6

Table A.1 (continued)

Screw Speed (rpm)	Spinning Speed (m/min)	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
40	4.57	34	3.30	373	65.80	28	1.87	799	8.53	0.4
	7.19	35	4.88	322	136.90	31	4.71	583	9.39	0.4
	8.82	36	3.13	305	3.13	33	95.10	336	8.63	0.5
	10.30	37	7.42	288	7.42	35	86.80	310	9.85	0.5
	11.90	42	7.41	277	7.41	35	144.40	398	7.25	0.5
50	8.82	37	5.55	326	5.55	28	114.80	802	10.74	0.4
	10.30	38	6.58	300	6.58	29	188.40	639	7.64	0.4
	11.90	38	6.25	275	6.25	31	96.10	591	7.63	0.4

Table A.2 The mechanical properties of polyolefins blend with various temperatures and fixed ratio of blend (PP/HDPE/LDPE/) as 25/50/25 by using screw speed of 20 rpm and spinning speed of 11.90 m/min.

Temperature (°C)	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
210	47	10.94	406	64.30	39	9.61	239	3.87	0.5
220	50	4.42	398	241.90	44	9.62	308	4.53	0.6
230	53	8.18	233	117.60	45	9.64	226	3.65	0.6
240	50	4.69	383	175.20	41	10.55	283	4.85	0.6
250	42	4.47	520	166.80	38	6.66	250	5.87	0.5
260	38	5.68	493	111.30	32	4.58	254	7.59	0.5
270	36	3.98	563	115.80	31	44.72	248	7.25	0.5

Table A.3 The mechanical properties of polyolefins blend with various ratios of polyolefins blend by using screw speed of 20 rpm, spinning speed of 11.90 m/min and temperature of 230°C.

Ratio of PP/R-HDPE/ LDPE blend	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
100/0/0	83	8.46	720	81.80	50	2.39	279	3.95	0.8
0/100/0	65	2.39	564	20.40	47	7.63	226	3.23	0.7
50/50/0	60	4.38	431	74.90	56	6.30	292	4.87	0.6
25/50/25	53	7.36	233	189.20	45	5.47	387	4.38	0.6
25/37.5/37.5	51	5.64	328	146.60	43	3.64	338	5.94	0.6
25/25/50	47	6.70	316	90.80	41	5.45	397	7.53	0.5
50/0/50	43	8.18	616	117.60	37	9.64	226	3.65	0.5
0/50/50	38	7.27	548	131.80	35	8.30	371	6.82	0.5
0/0/100	28	9.82	108	115.0	22	6.49	353	5.75	0.4

Table A.4 The mechanical properties of polyolefins with R-PET blend with various ratios of PP/R-HDPE/LDPE with R-PET blend and temperatures by using screw speed of 20 rpm, spinning speed of 11.90 m/min and ratio of PP/R-HDPE/LDPE blend as 25/50/25.

Temperature (°C)	Ratio of polyolefins/ R-PET blend	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
260	100/0	38	5.68	493	115.80	32	4.58	282	3.95	0.5
	75/25	40	5.71	93	96.20	37	11.42	644	5.94	0.5
	50/50	43	5.79	80	186.10	41	20.79	455	7.27	0.5
	25/75	50	5.90	48	197.60	50	26.34	652	5.59	0.5
	0/100	72	10.93	33	101.90	71	21.01	579	8.53	0.6
270	100/0	36	3.98	563	115.80	31	14.72	256	3.51	0.5
	75/25	43	4.23	98	159.20	37	13.12	509	7.11	0.5
	50/50	50	8.23	46	84.70	54	20.39	457	6.73	0.5
	25/75	60	6.32	39	98.80	68	13.18	684	7.73	0.6
	0/100	76	8.09	31	75.10	75	11.60	603	9.98	0.7

Table A.4 The mechanical properties of polyolefins with R-PET blend with various ratios of PP/R-HDPE/LDPE with R-PET blend and temperatures by using screw speed of 20 rpm, spinning speed of 11.90 m/min and ratio of PP/R-HDPE/LDPE blend as 25/50/25.

Temperature (°C)	Ratio of polyolefins/ R-PET blend	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
		Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
260	100/0	38	5.68	493	115.80	32	4.58	282	3.95	0.5
	75/25	40	5.71	93	96.20	37	11.42	644	5.94	0.5
	50/50	43	5.79	80	186.10	41	20.79	455	7.27	0.5
	25/75	50	5.90	48	197.60	50	26.34	652	5.59	0.5
	0/100	72	10.93	33	101.90	71	21.01	579	8.53	0.6
270	100/0	36	3.98	563	115.80	31	14.72	256	3.51	0.5
	75/25	43	4.23	98	159.20	37	13.12	509	7.11	0.5
	50/50	50	8.23	46	84.70	54	20.39	457	6.73	0.5
	25/75	60	6.32	39	98.80	68	13.18	684	7.73	0.6
	0/100	76	8.09	31	75.10	75	11.60	603	9.98	0.7

Table A.6 The mechanical properties of polyolefins, polyolefins/R-PET and polyolefins/R-PET blends with compatibilizers that used F-HDPE instead of R-HDPE in the components various amount of compatibilizers by using screw speed of 20 rpm, spinning speed of 11.90 m/min,

Types	Tensile Strength at Break (MPa)		Elongation at Break (%)		Modulus of Elasticity (MPa)		Denier (g/9000 m)		Tenacity (g/denier)
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean
R-HDPE	65	2.39	564	20.40	47	7.63	226	3.23	0.4
F-HDPE	54	7.41	743	7.56	34	5.95	585	10.72	0.3
PP/R-HDPE/LDPE	53	7.36	233	117.60	45	5.47	387	4.38	0.6
PP/F-HDPE/LDPE	42	5.60	723	26.90	23	7.65	570	15.41	0.5
PP/R-HDPE/LDPE/PET	56	7.36	39	98.80	68	13.18	684	7.73	0.7
PP/F-HDPE/LDPE/PET	38	2.95	47	37.20	15	7.52	579	9.40	0.6
PP/R-HDPE/LDPE/PET + 1% PP-g-MA	18	7.65	31	22.17	12	14.72	590	11.91	0.3
PP/F-HDPE/LDPE/PET + 1% PP-g-MA	17	4.01	37	35.76	12	12.87	586	10.42	0.3
PP/R-HDPE/LDPE/PET + 1% PP-g-AA	19	7.42	31	17.02	13	20.14	564	15.73	0.3
PP/F-HDPE/LDPE/PET + 1% PP-g-AA	18	5.33	35	20.62	12	18.95	615	7.51	0.3
PP/R-HDPE/LDPE/PET + 1% HDPE-g-AA	21	5.99	19	18.65	20	12.64	496	18.17	0.4
PP/F-HDPE/LDPE/PET + 1% HDPE-g-AA	20	2.73	28	28.59	20	12.04	492	15.63	0.3

Appendix B

Table B.1 Densities of fibers from polyolefins and polyolefins with recycled poly (ethylene terephthalate) blend

Fibers	Densities (g/cm^3)*
PP	0.90
LDPE	0.92
R-HDPE	0.94
R-PET	1.37
PP/LDPE (50/50)	0.91
PP/R-HDPE (50/50)	0.92
LDPE/R-HDPE (50/50)	0.93
PP/LDPE/R-HDPE (25/50/25)	0.93
PP/LDPE/R-HDPE (25/25/50)	0.94
PP/LDPE/R-HDPE (25/37.5/37.5)	0.92
Polyolefins/PET (25/75)	1.23
Polyolefins/PET (50/50)	1.16
Polyolefins/PET (75/25)	1.03

* Measurement by Gradient Column Density method

APPENDIX C

Calculation of degree of crystallinity

Example of calculation :

ΔH_{f° PE = 293 J/g

ΔH_{f° PP = 165 J/g

ΔH_{f° PET = 140 J/g

At the ratio of PP/R-HDPE/LDPE blend as 25/50/25

PP 25% crystal had ΔH_f of 18.21 J/g (obtained from DSC trace)

PP 100% crystal had ΔH_f of (16.21*100)/25 = 72.84 J/g

From equation 3.1: Degree of crystallinity (%) $= (\Delta H_f/\Delta H_{f^\circ})*100$

$= (64.8/165)*100$

$= 39$

R-HDPE 50% crystal had ΔH_f of 64.48 J/g (obtained from DSC trace)

R-HDPE % crystal had ΔH_f of (64.48*100)/50 =128.96 J/g

Degree of crystallinity (%) $= (\Delta H_f/\Delta H_{f^\circ})*100$

$= (128.96/293)*100$

$= 44$

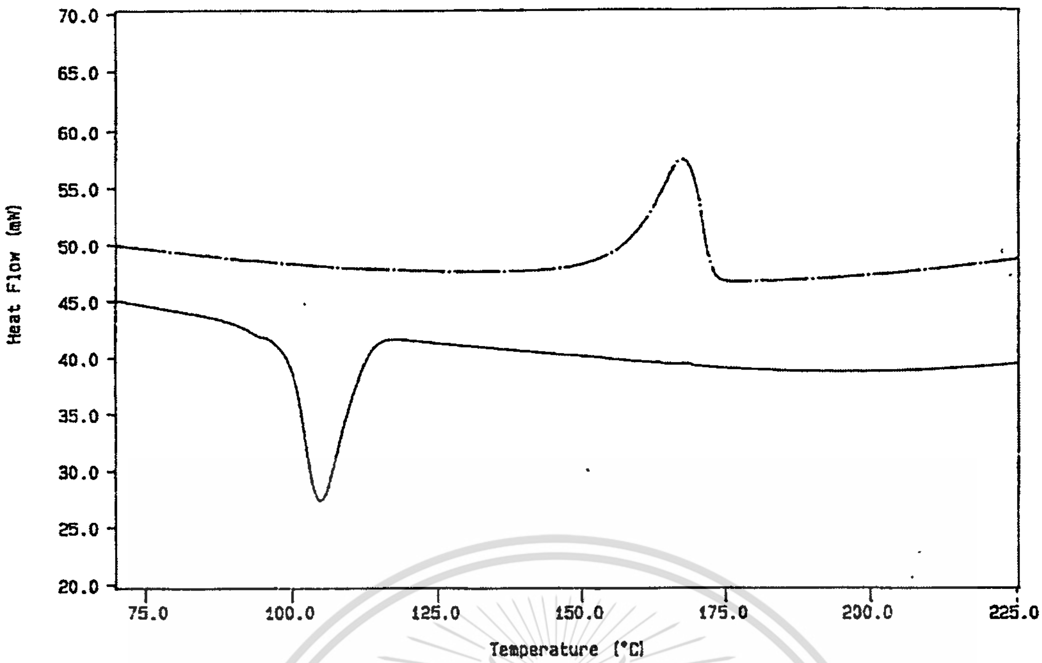


Figure C.1 DSC thermogram of PP processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

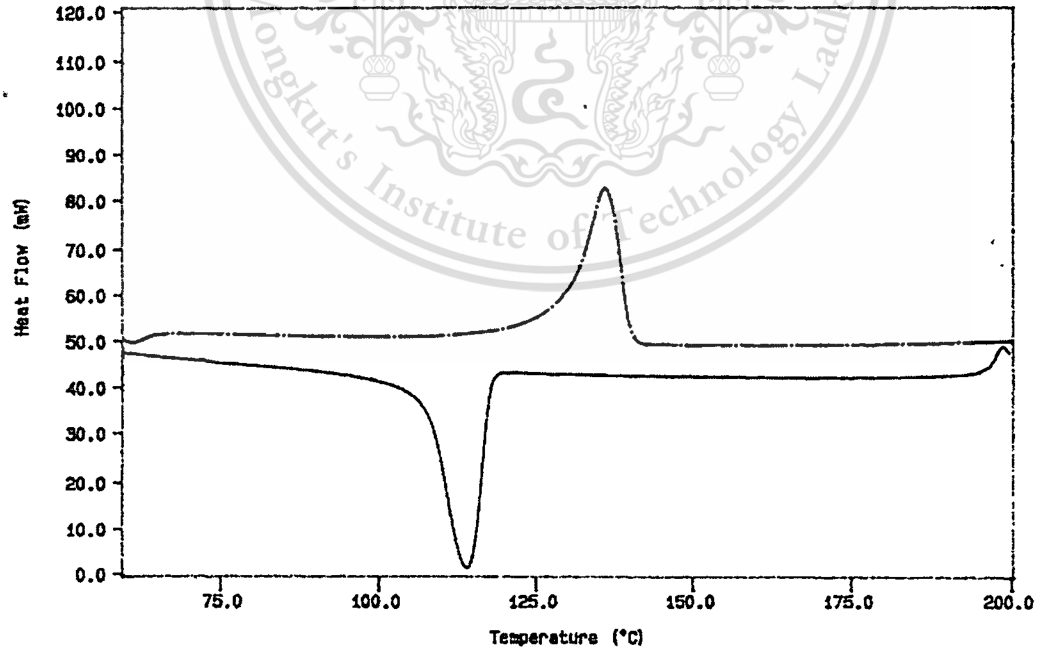


Figure C.2 DSC thermogram of R-HDPE processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

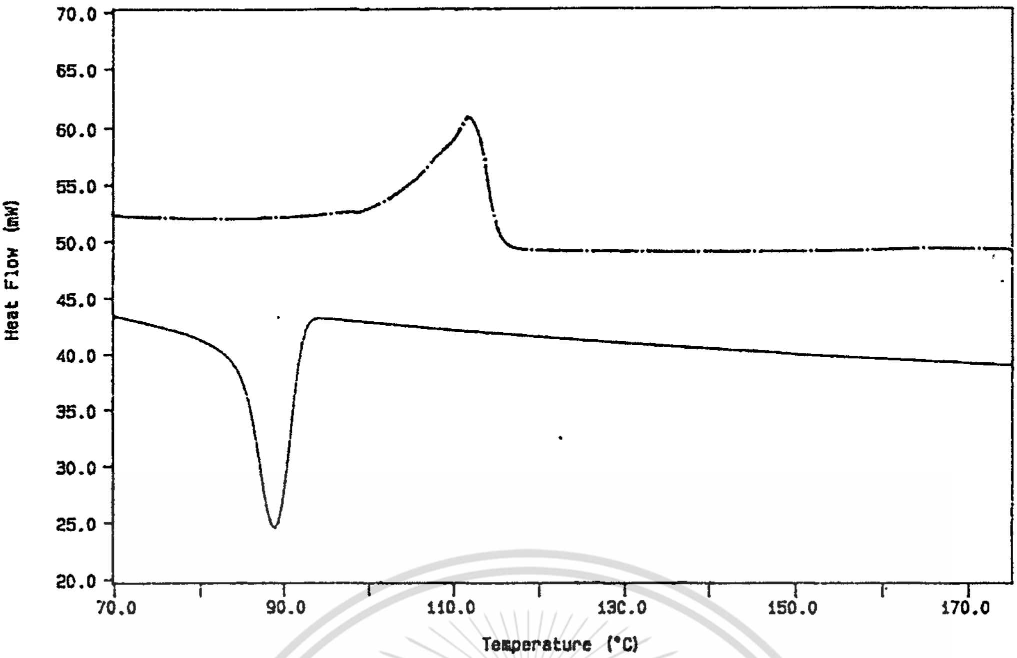


Figure C.3 DSC thermogram of LDPE processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

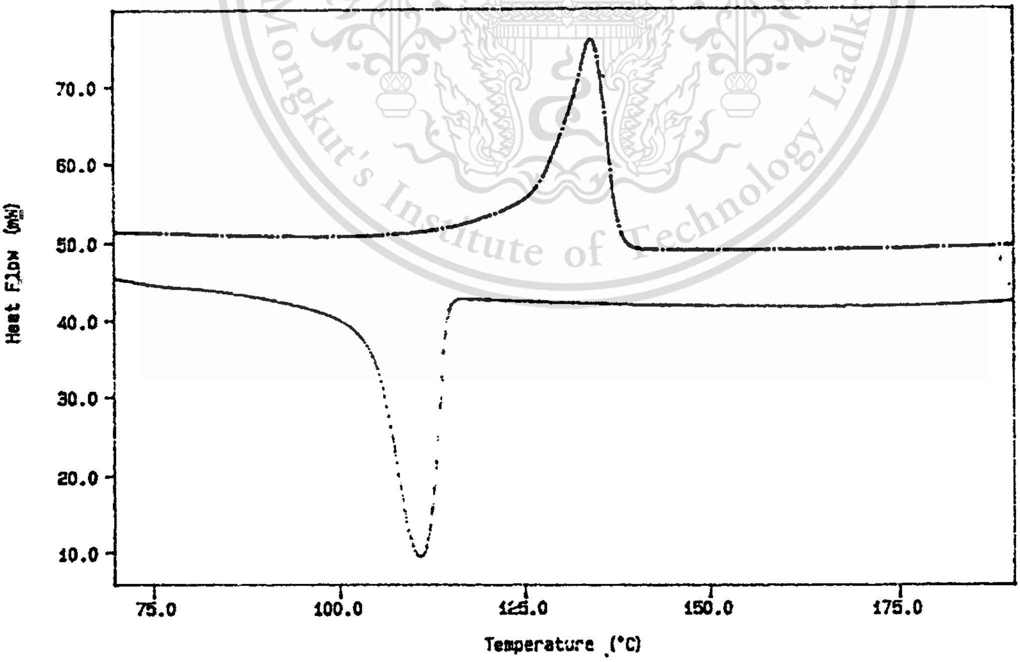


Figure C.4 DSC thermogram of F-HDPE processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

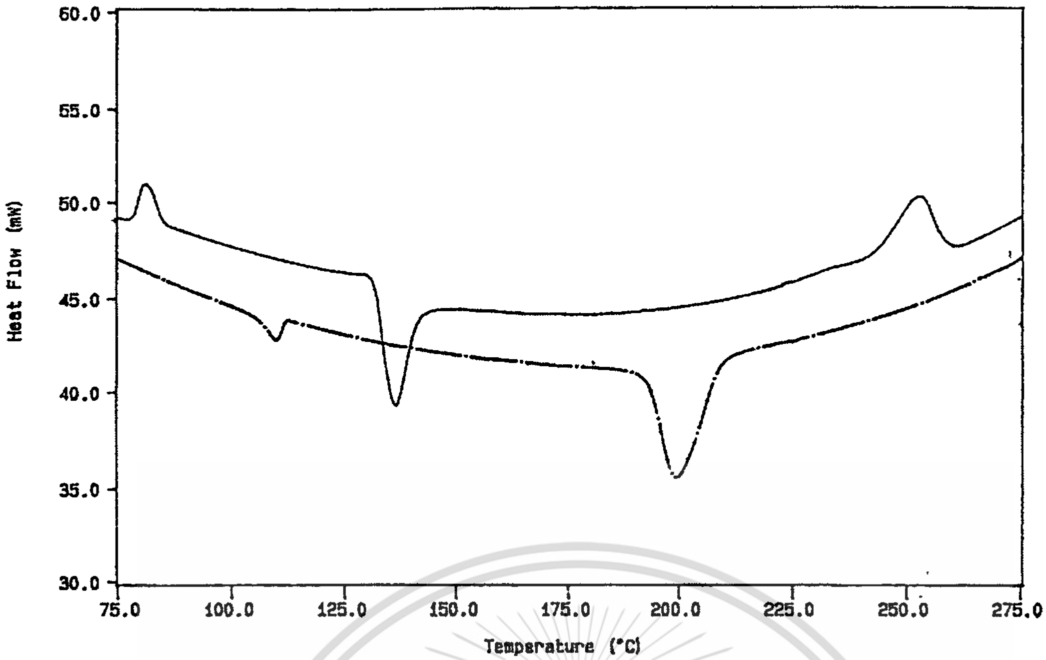


Figure C.5 DSC thermogram of R-PET processed at mixing temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

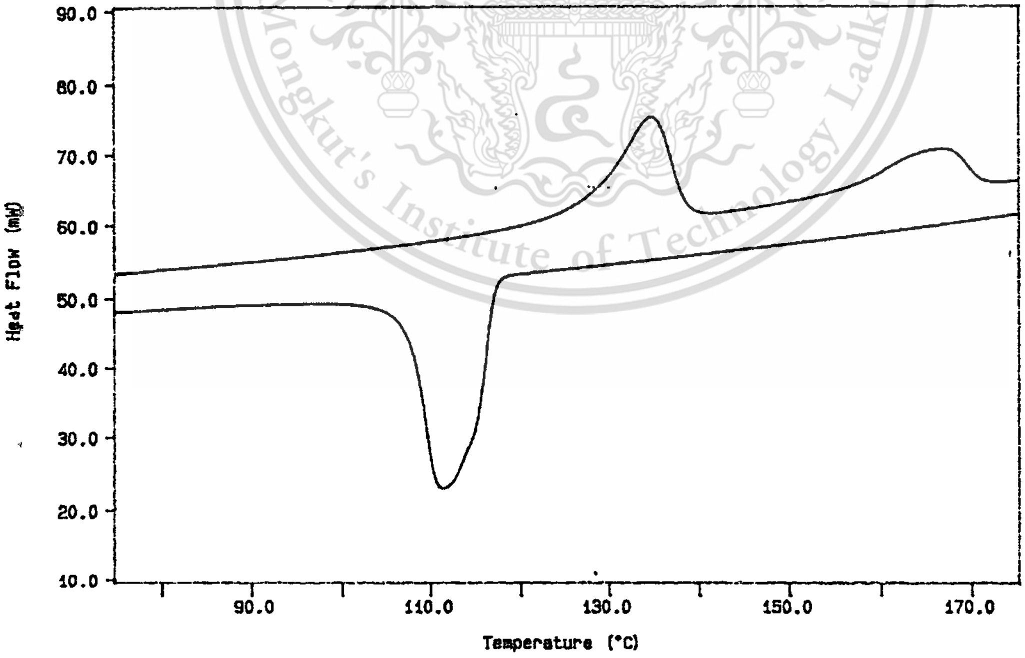


Figure C.6 DSC thermogram of PP and R-HDPE blend (50/50) processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

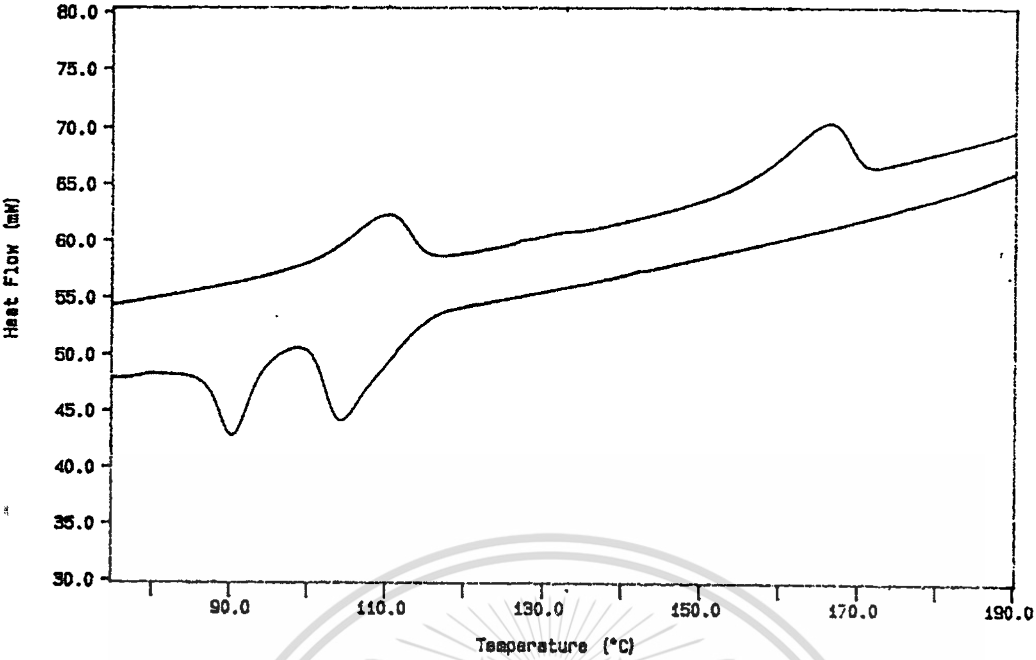


Figure C.7 DSC thermogram of PP and LDPE blend (50/50) processed at temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

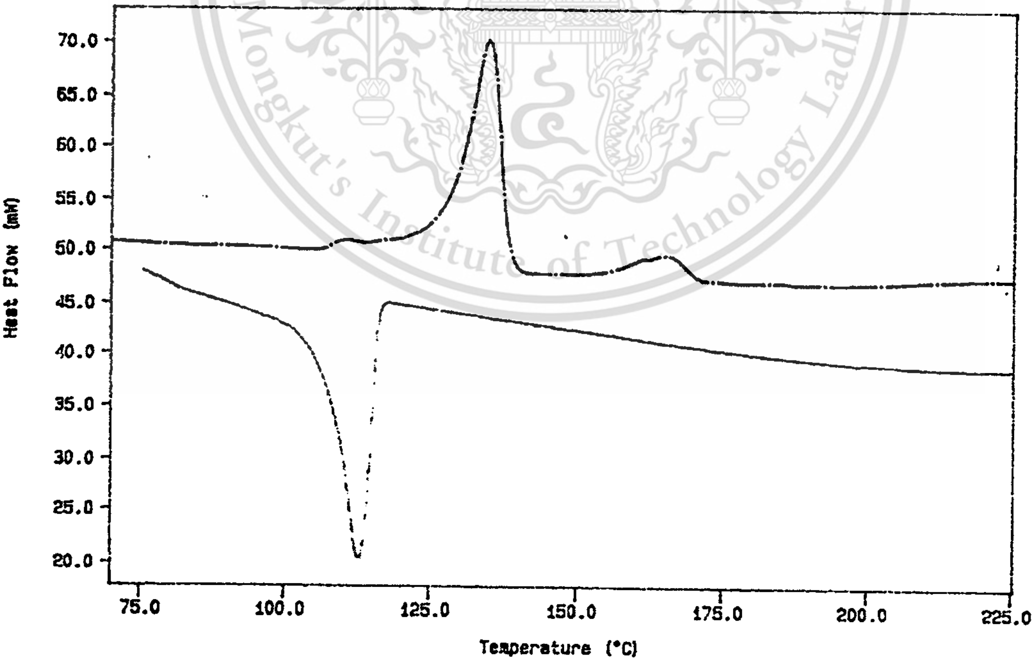


Figure C.8 DSC thermogram of R-HDPE and LDPE blend (50/50) processed at mixing temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

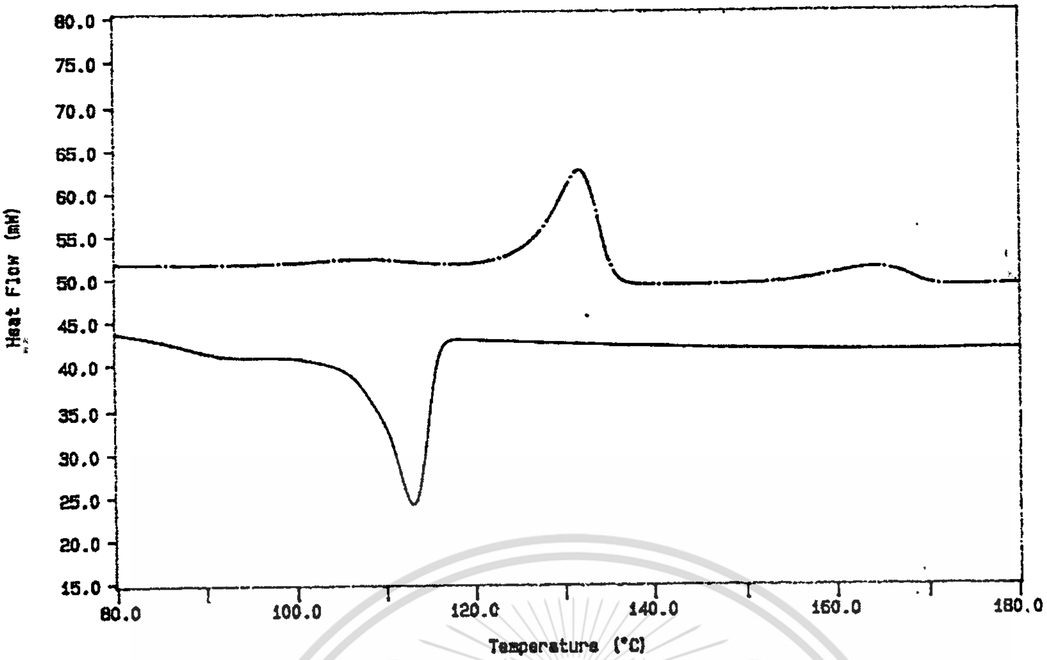


Figure C.9 thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

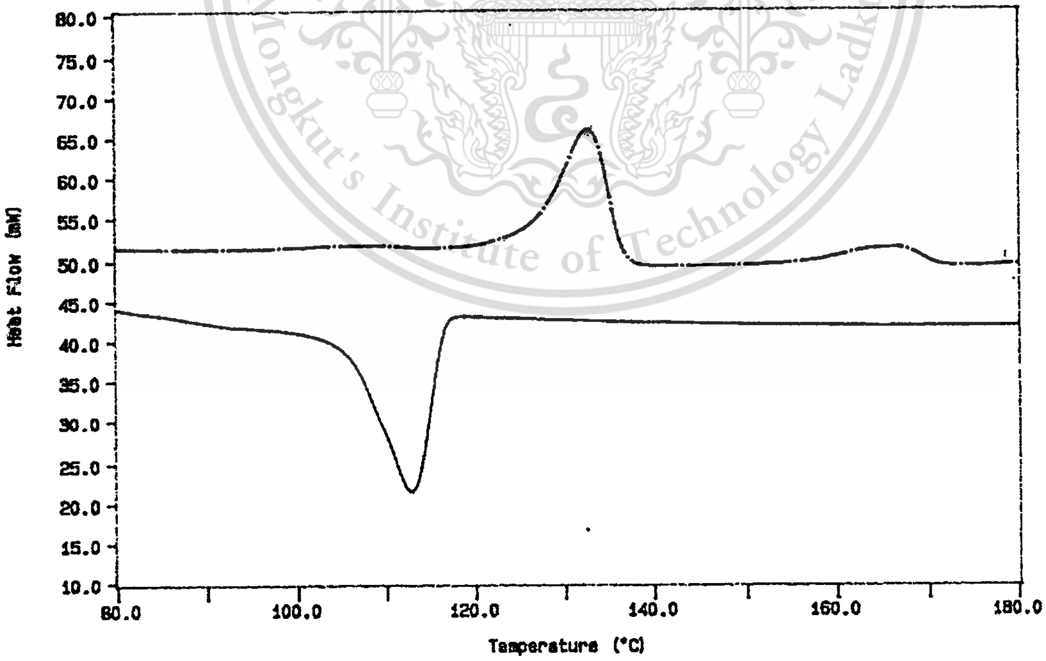


Figure C.10 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 230 °C, screw speed of 20 rpm and spinning speed of 8.82 m/min.

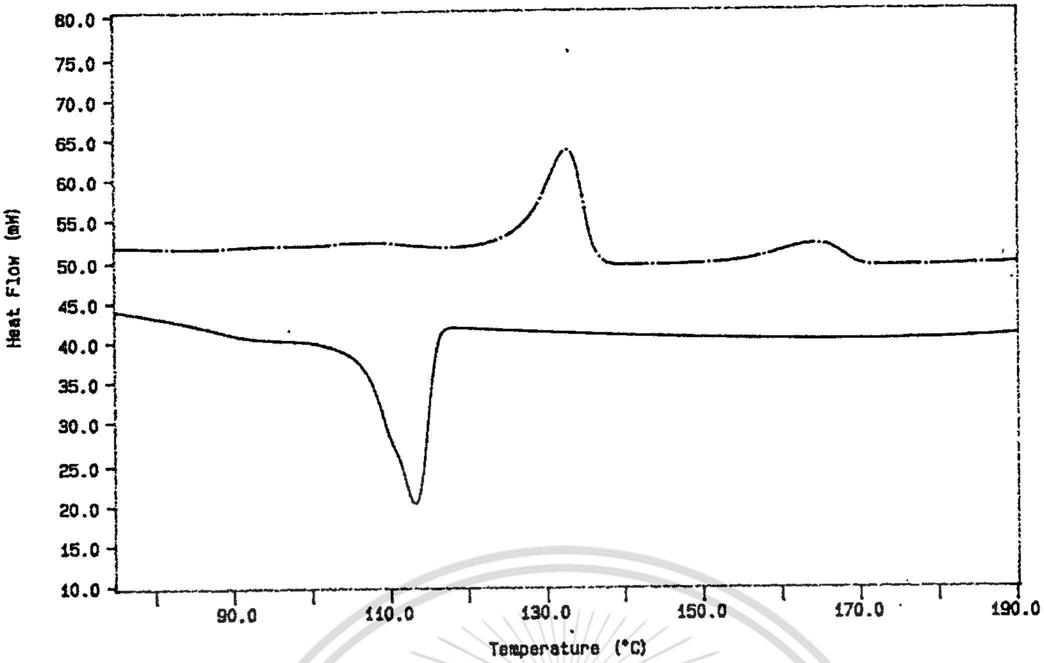


Figure C.11 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 230 °C, screw speed of 50 rpm and spinning speed of 11.90 m/min.

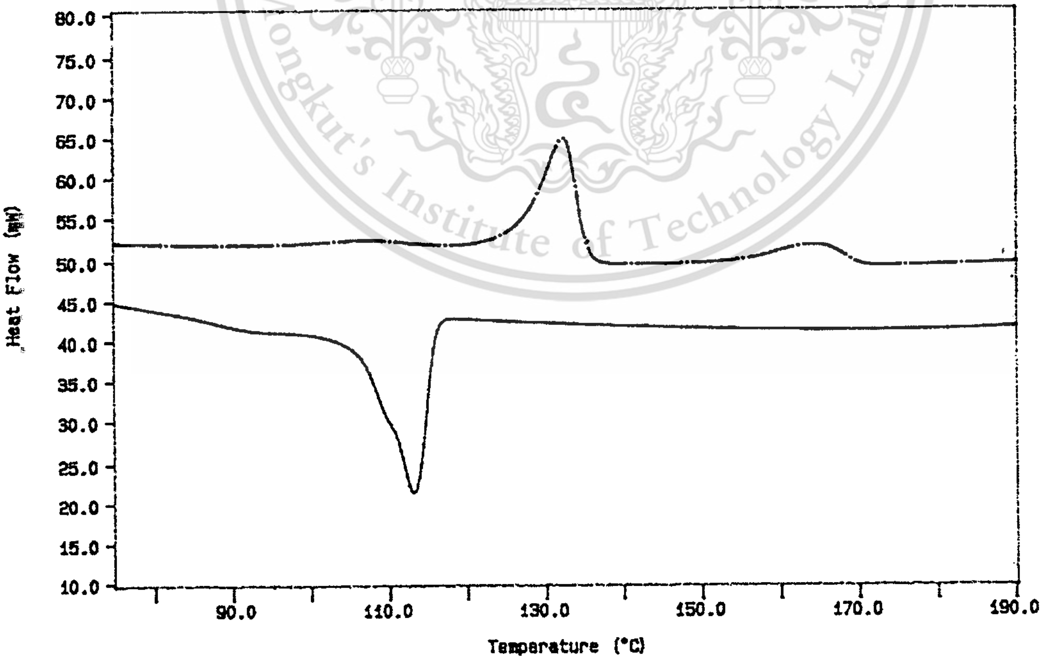


Figure C.12 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 230 °C, screw speed of 50 rpm and spinning speed of 8.82 m/min.

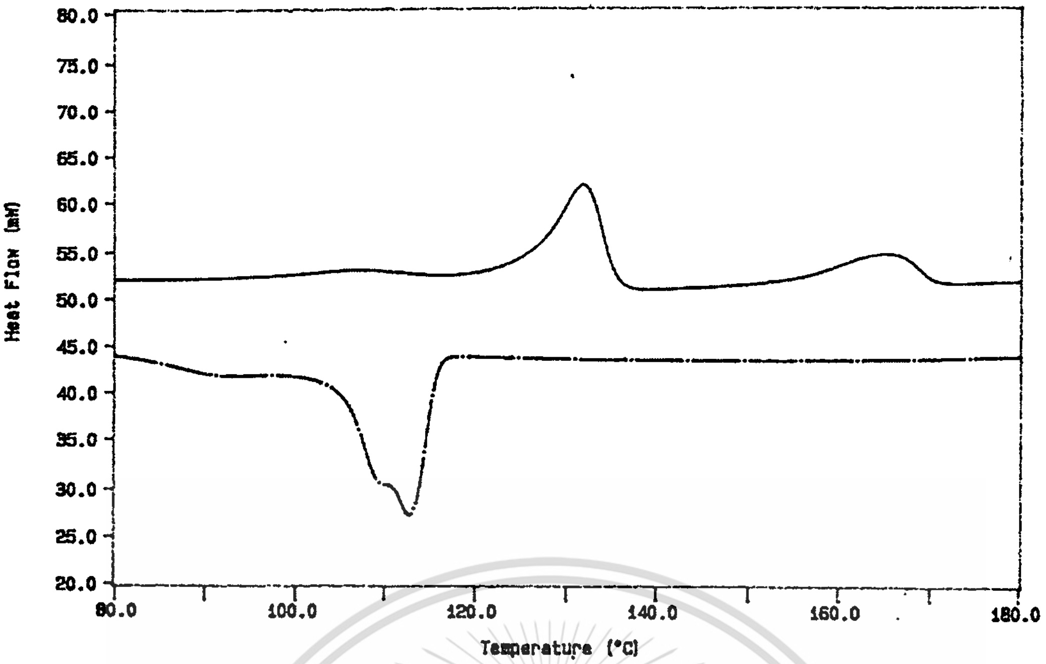


Figure C.13 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 210 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

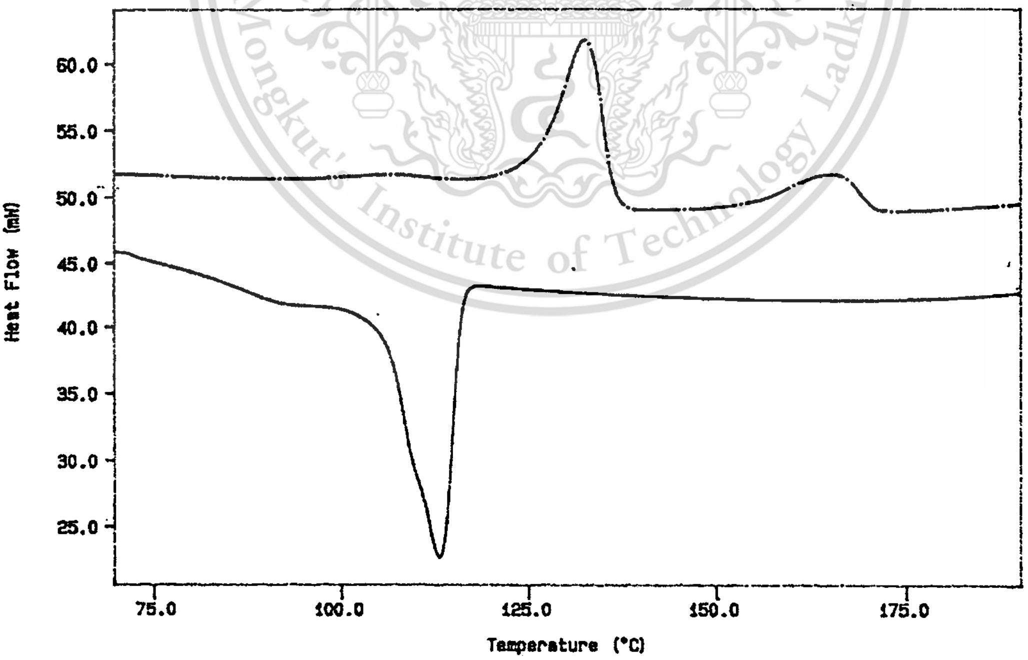


Figure C.14 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 220 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

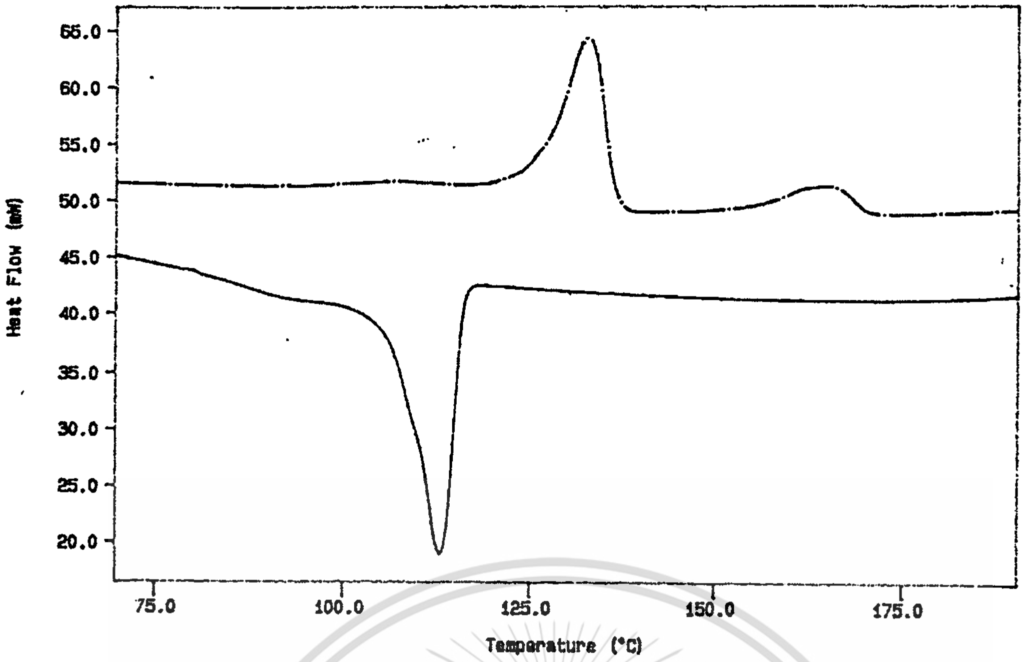


Figure C.15 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 240 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

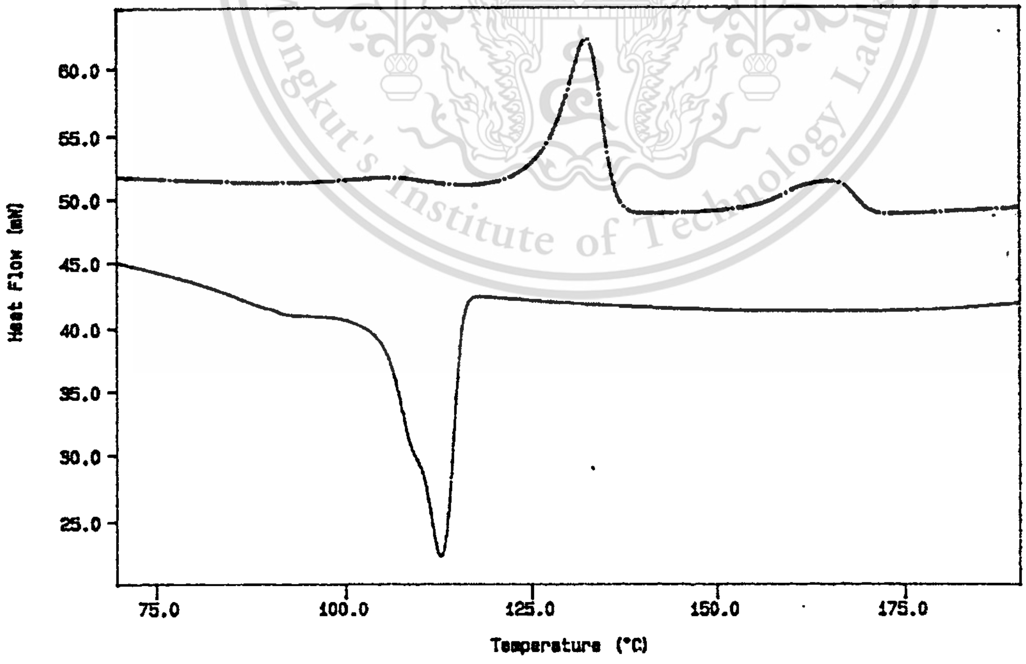


Figure C.16 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature 250 °C, screw speed 20 rpm and spinning speed 11.90 m/min.

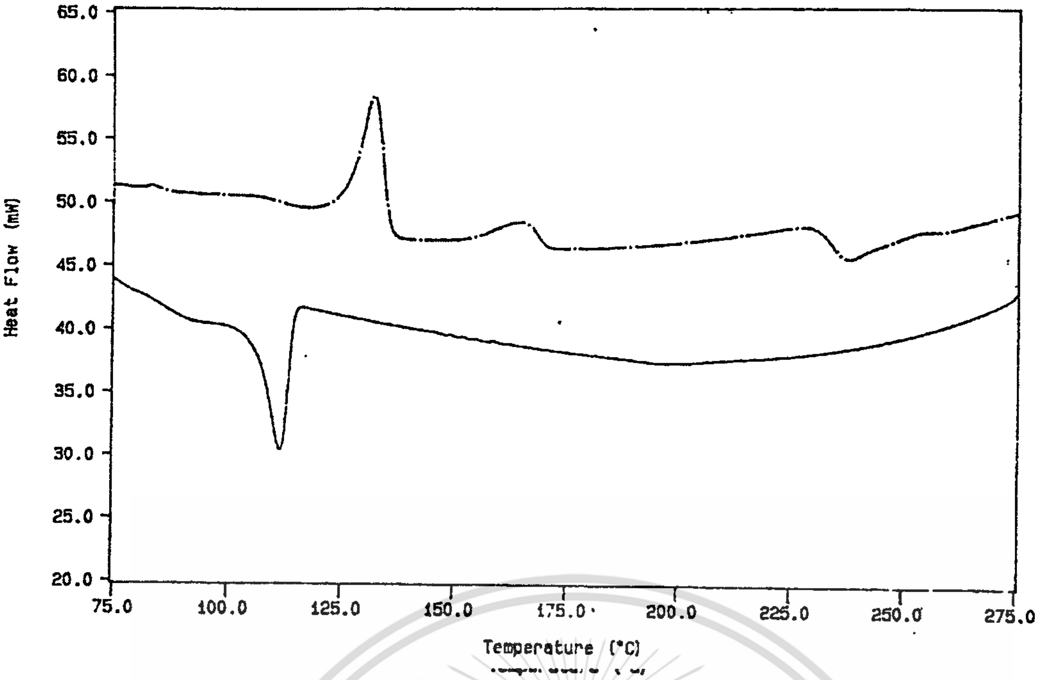


Figure C.17 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 260 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

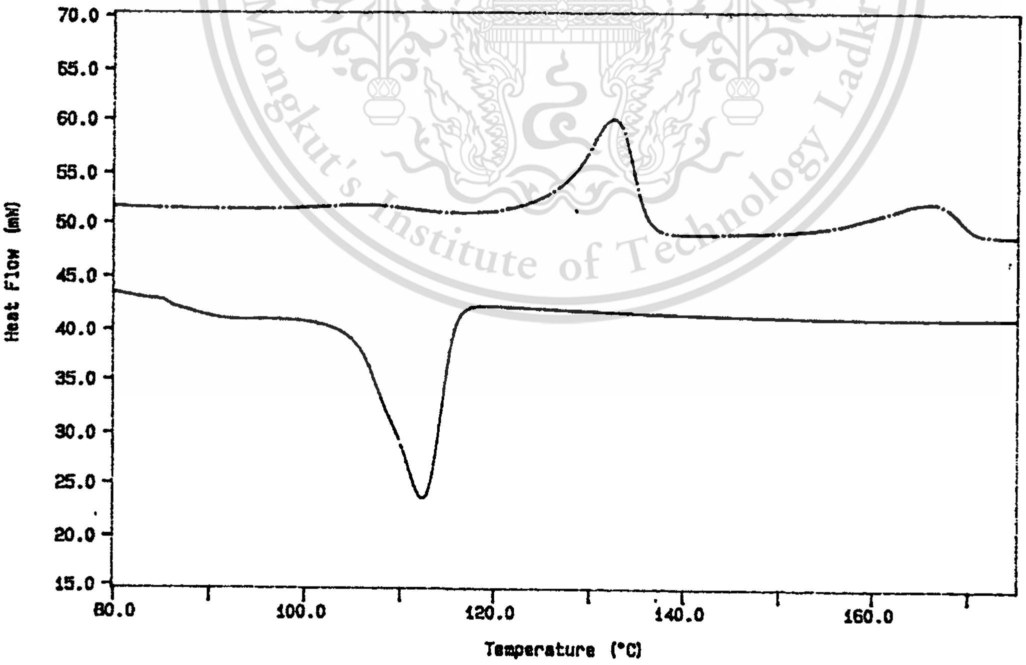


Figure C.18 DSC thermogram of PP/R-HDPE/LDPE blend (25/50/25) processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

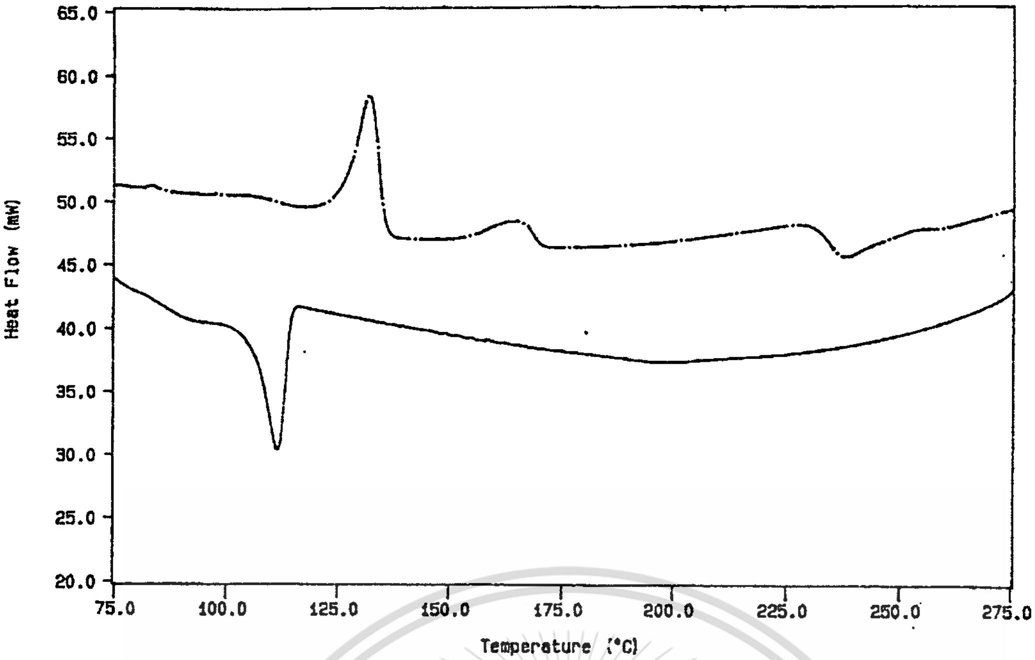


Figure C.19 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend (75/25) processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

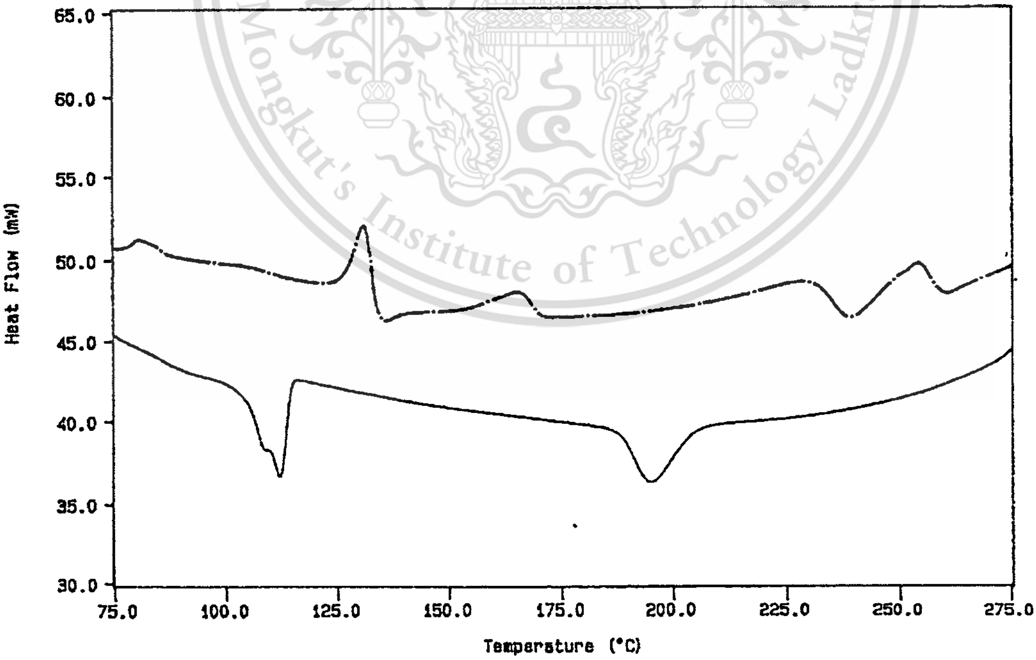


Figure C.20 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend (50/50) processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

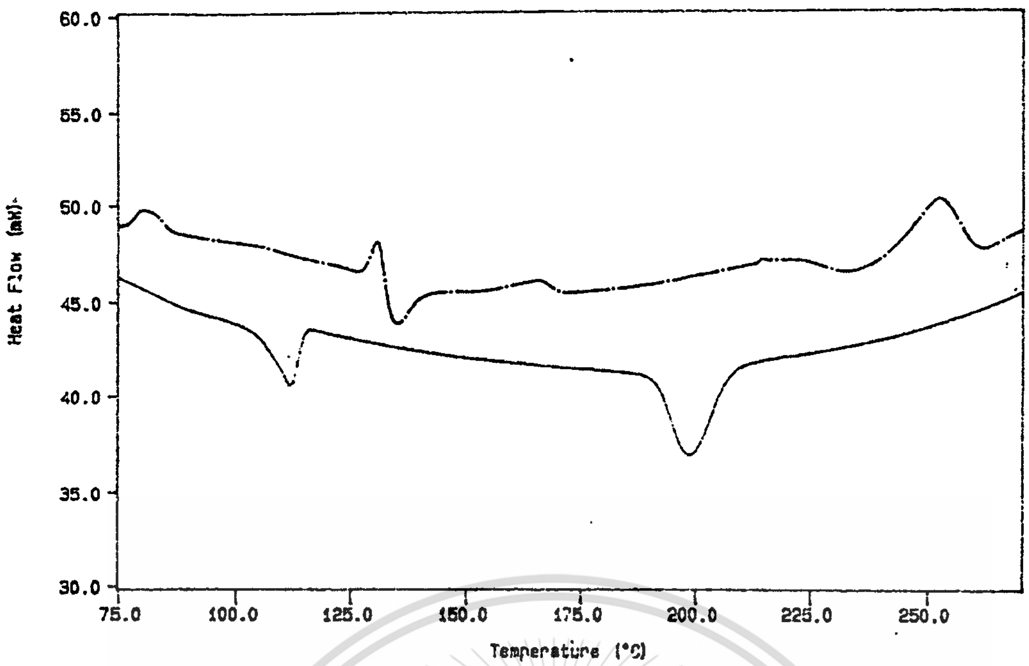


Figure C.21 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend (25/75) processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

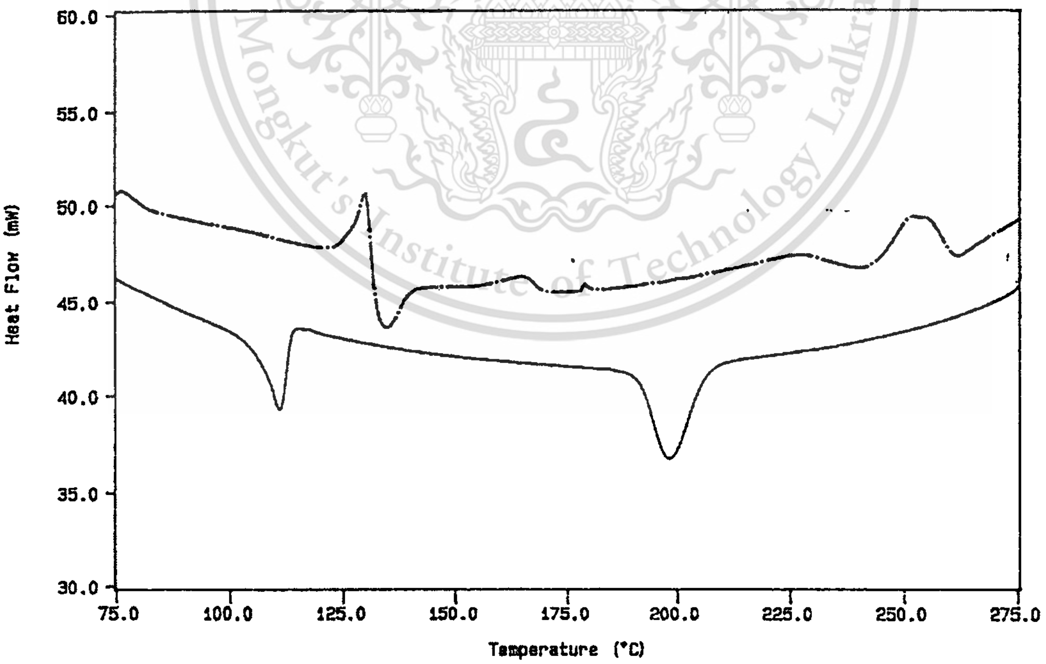


Figure C.22 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend with 1% HDPE-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

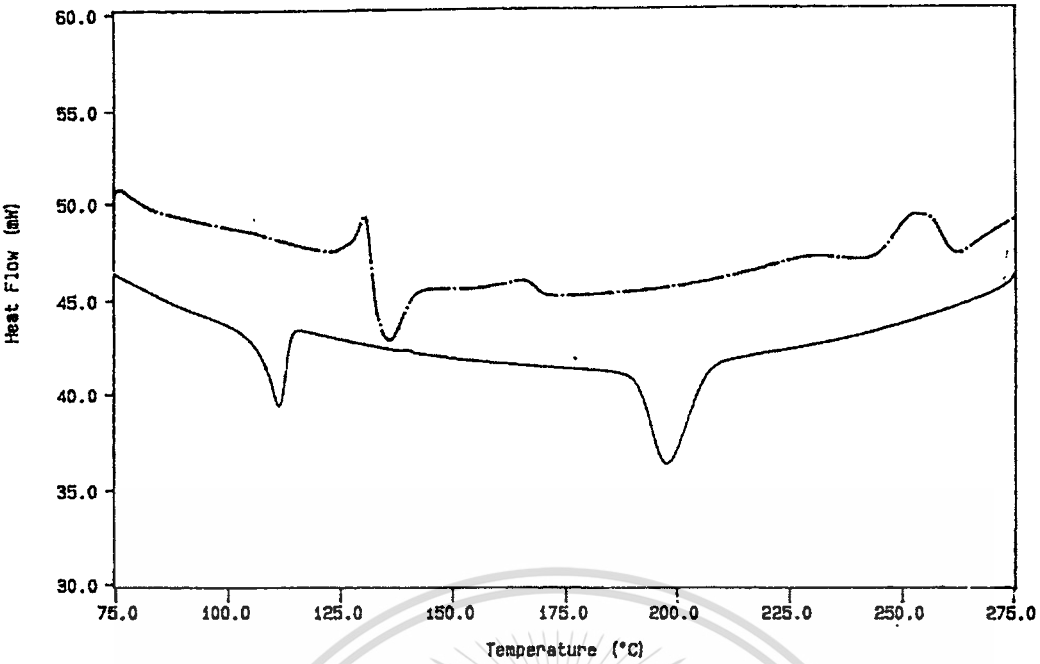


Figure C.23 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend with 3% HDPE-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

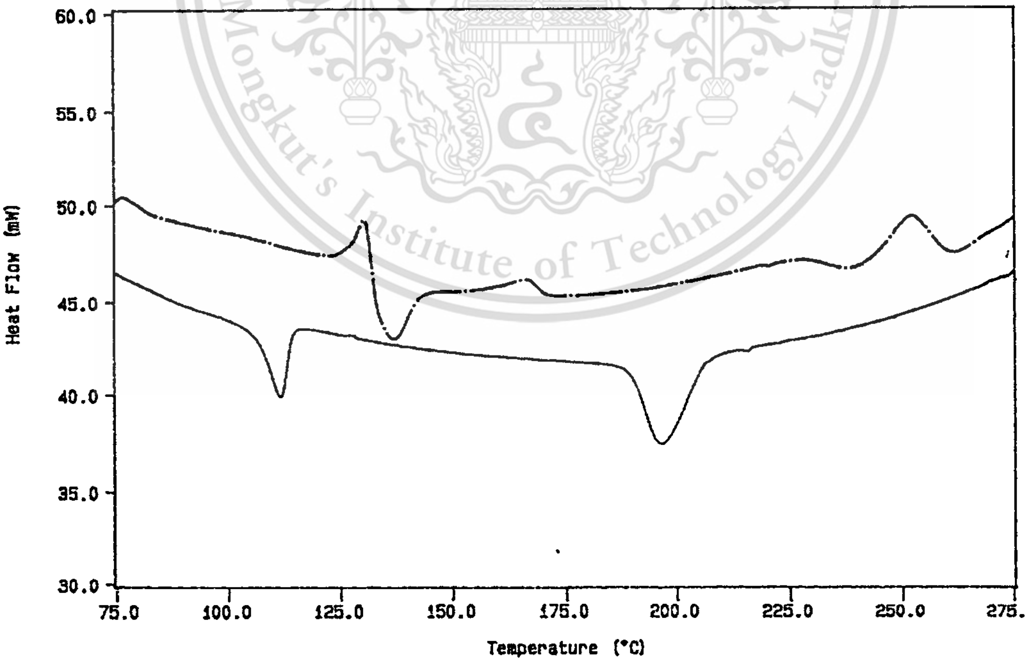


Figure C.24 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend with 5% HDPE-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

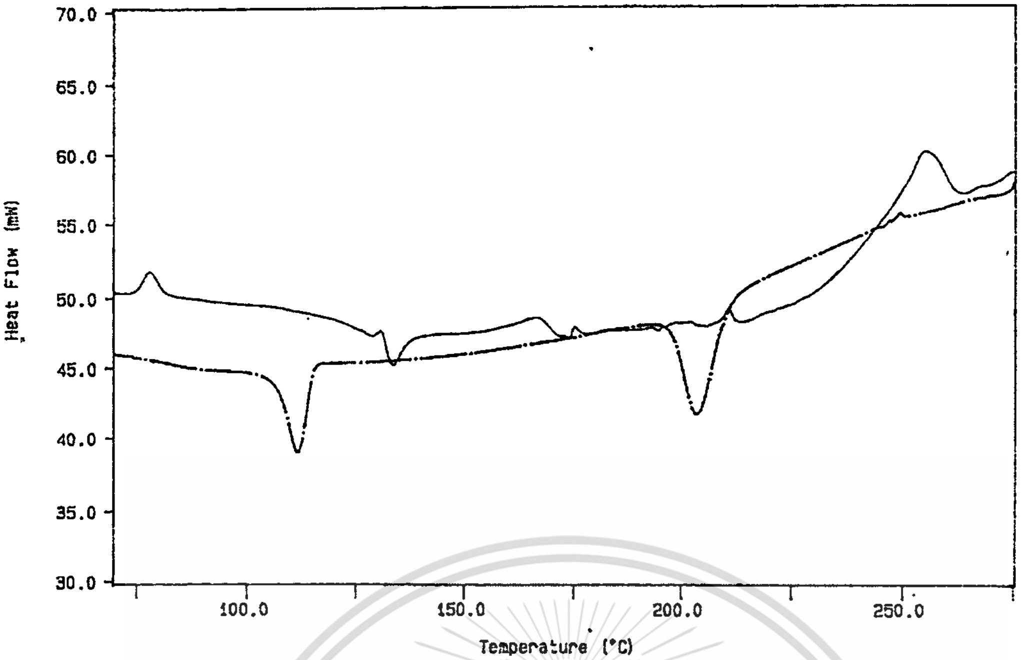


Figure C.25 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend with 1% PP-g-MA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

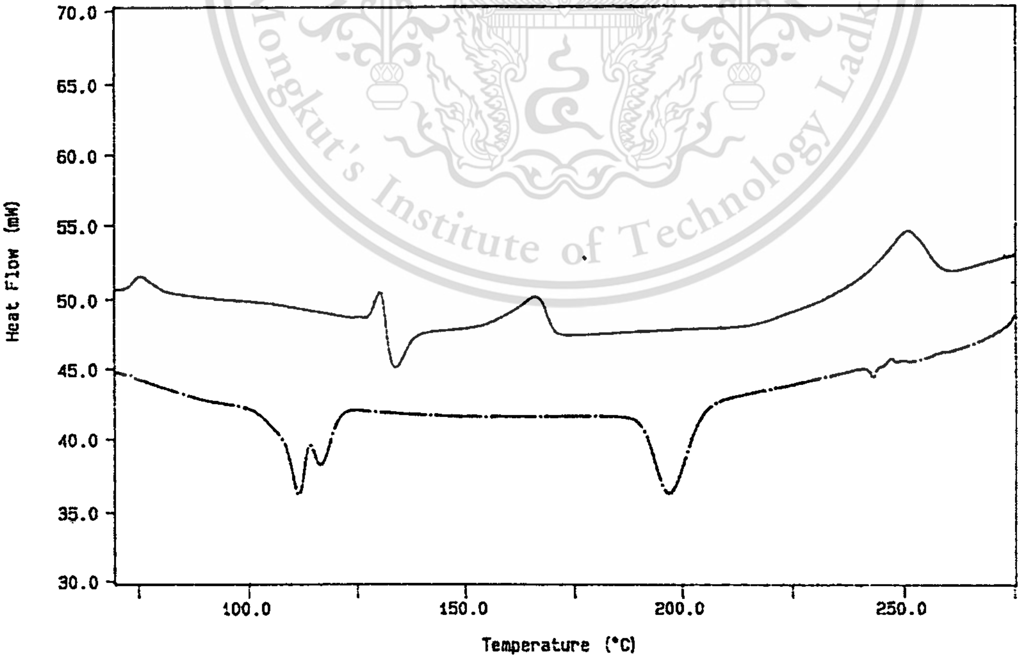


Figure C.26 DSC thermogram of PP/R-HDPE/LDPE and R-PET blend with 1% PP-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

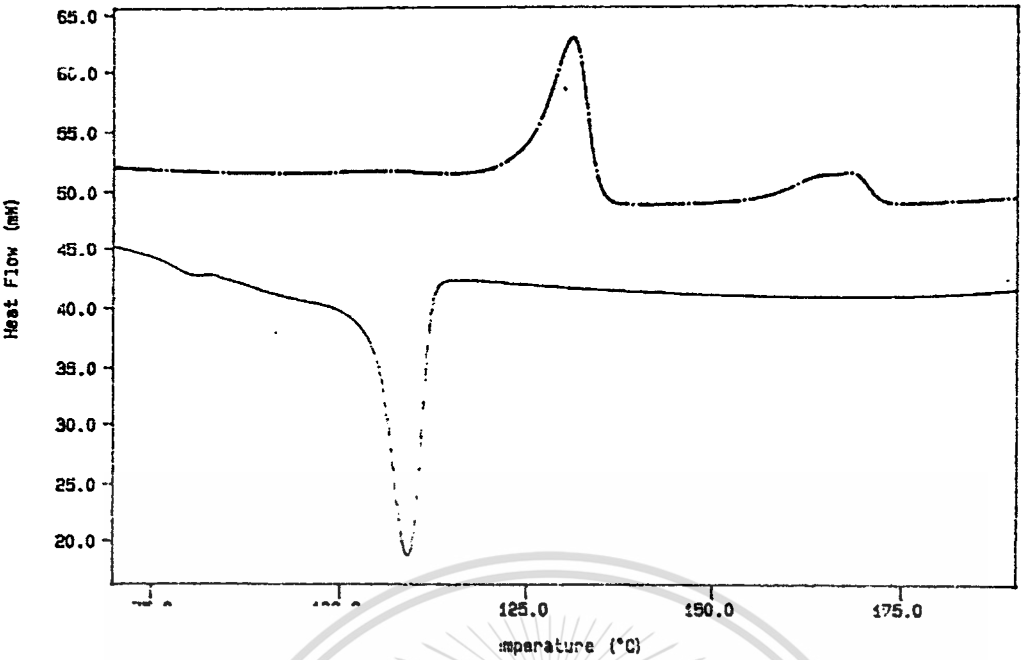


Figure C.27 DSC thermogram of PP/F-HDPE/LDPE blend (25/50/25) processed at temperature of 230 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

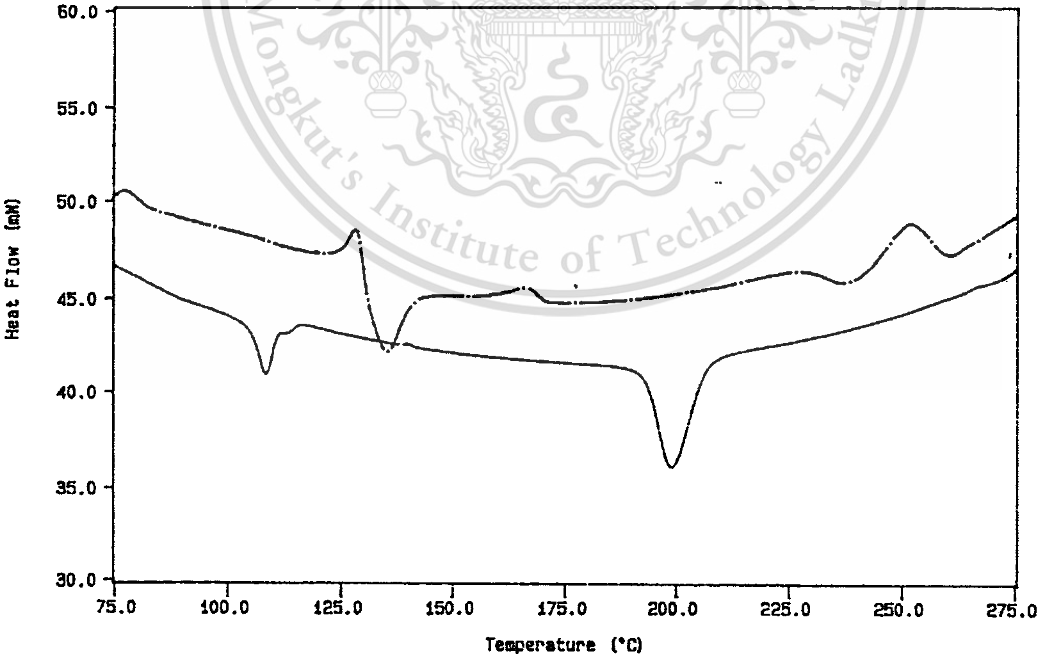


Figure C.28 DSC thermogram of PP/F-HDPE/LDPE and R-PET blend (25/75) processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

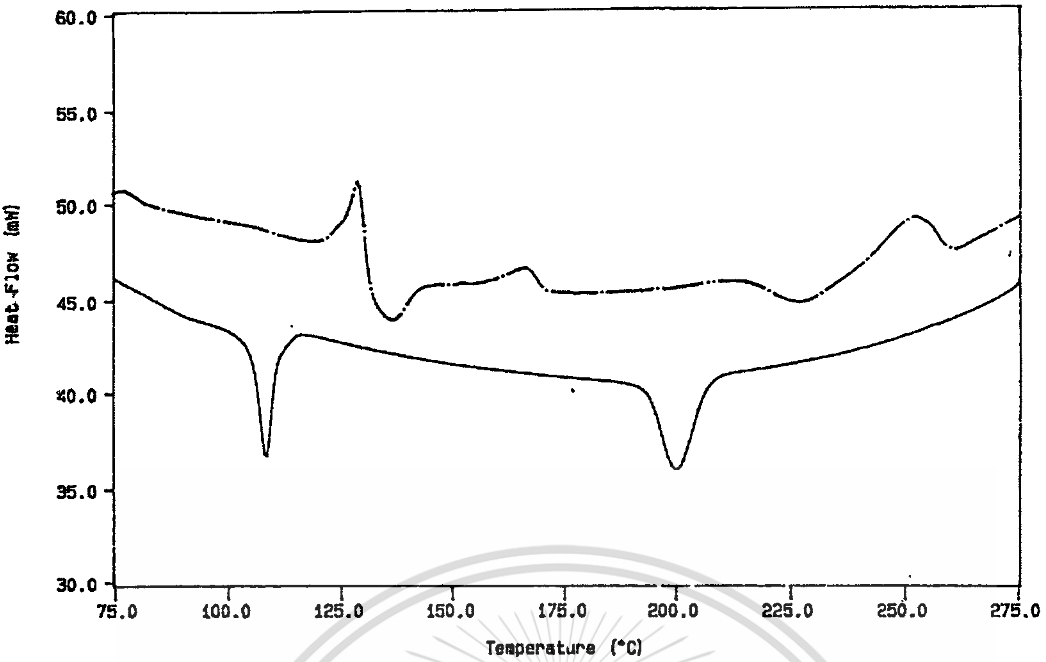


Figure C.29 DSC thermogram of PP/F-HDPE/LDPE and R-PET blend (25/75) with 1% PP-g-MA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

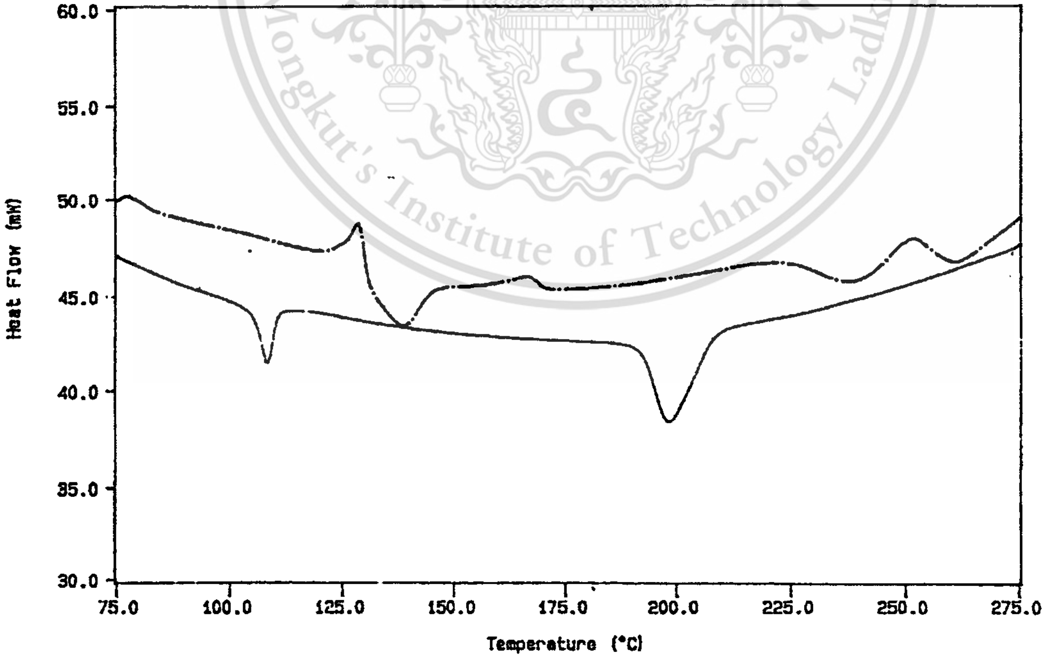


Figure C.30 DSC thermogram of PP/F-HDPE/LDPE and R-PET blend (25/75) with 1% PP-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

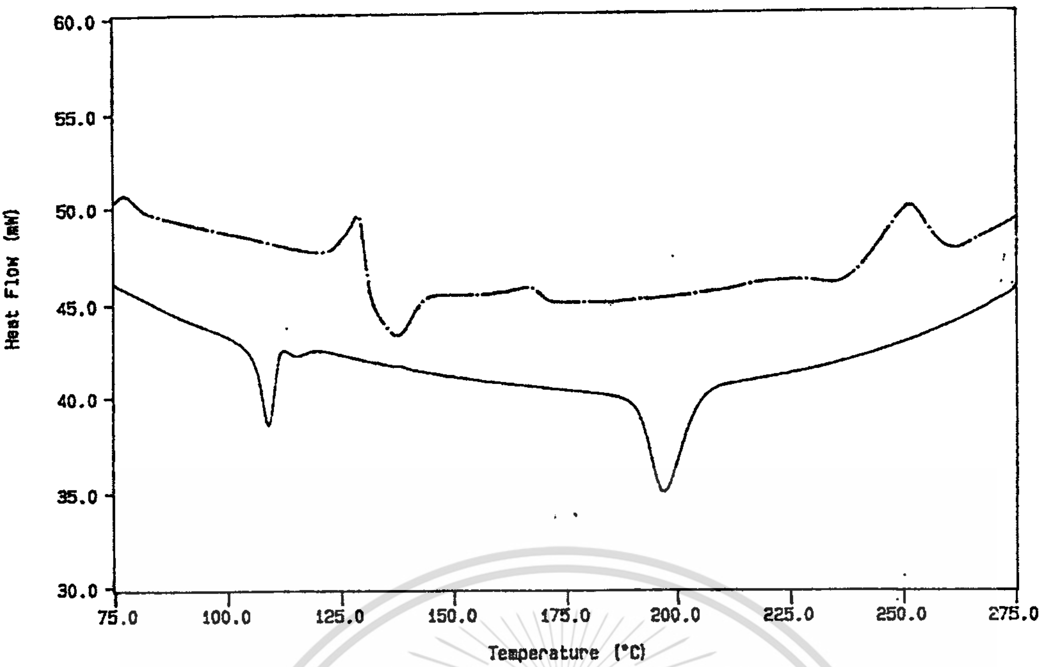


Figure C.31 DSC thermogram of PP/F-HDPE/LDPE and R-PET blend (25/75) with 1% HDPE-g-AA processed at temperature of 270 °C, screw speed of 20 rpm and spinning speed of 11.90 m/min.

AUTHOR BIOGRAPHY

The author was born on July 16, 1976, in Bangkok, Thailand. She graduated with a Bachelor of Science in chemistry at Naresuan University in 1997. She entered into King Mongkut's Institute of Technology Ladkrabang in 1997.