การใช้สารก่อผลึกโซเดียมคาร์บอเนตในการปรับปรุงสมบัติเชิงกล ของเพทรีไซเคิลสำหรับการฉีดเข้าแบบ

นางสาว สมรวรรณ ชลประเสริฐ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์และเทคโนโลยีสิ่งทอ ภาควิชาวัสดุศาสตร์
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2542

ISBN 974-334-936-7

SE OF SODIUM CARBONATE NUCLEATING AGENT TO IMPROVE MECHANICAL PROPERTIES OF RECYCLED PET FOR INJECTION MOLDING

Miss Smornwan Cholprasert

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Applied Polymer Science and Textile Technology
Department of Materials Science
Faculty of Science
Chulalongkorn University
Academic Year 1999

ISBN 974-334-936-7

Thesis Title	Use of Sodium Carbonate Nucleating Agent to improve Mechanical Properties of Recycled PET for Injection Molding
By	Miss Smornwan Cholprasert
Department	Department of Materials Science
Thesis Advisor	Associate Professor Saowaroj Chuayjuljit

Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of Faculty of Science

(Associate Professor Wanchai Phothiphichitr, Ph.D.)

THESIS COMMITTEE

.... Chairman

(Associate Professor Khemchai Hemachandra,Ph.D.)

.... Thesis Advisor

(Associate Professor Saowaroj Chuayjuljit)

.... Member

(Associate Professor Paiparn Santisuk)

Onusa Saravari

.... Member

(Associate Professor Onusa Saravari)

บทคัดย่อวิทยานิพนธ์

นางสาวสมรวรรณ ชลประเสริฐ : การใช้สารก่อผลึกโซเดียมคาร์บอเนตในการปรับปรุงสมบัติเชิงกลของเพทรีไซเคิลสำหรับงานฉีด. (USE OF SODIUM CARBONATE NUCLEATING AGENT TO IMPROVE MECHANICAL PROPERTIES OF RECYCLED PET FOR INJECTION MOLDING) อ. ที่ปรึกษา : รศ. เสาวรจน์ ช่วยจุลจิตร์, 96 หน้า. ISBN 974-334-936-7.

ขวดเพทที่ใช้แล้วถูกนำมารีไซเคิลโดยการหลอมรวมกับเม็ดเพทใหม่ ในอัตราส่วนต่าง ๆ และใช้โซเดียมคาร์บอเนตเป็นสารก่อผลึกในปริมาณ 0.1 ถึง 1 phr เพื่อเพิ่มปริมาณและอัตราการเกิดผลึกของพลาสติกสำหรับงานฉีด

จากการศึกษาสมบัติทางความร้อนด้วยเทคนิคดิฟเฟอเรนเชียลสแกนนิงแคลอริเมทรี การทดสอบความทนแรงดึง การวัดความหนืดของสารละลายพอลิเมอร์ และการหดตัวของชิ้นงานภายหลังการแอนนีลเป็นเวลา 40 ชั่วโมง พบว่าชิ้นงานที่ได้จากการผสมขวดเพทกับเม็ดเพทใหม่ในอัตราส่วน 50 ต่อ 50 และใช้สารก่อผลึก 0.3 phr มีความทนแรงดึง และการทนความร้อนใกล้เคียงกับชิ้นงานที่ได้จากการใช้เม็ดเพทใหม่

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต ....

สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์ฯ ลายมือชื่ออาจารย์ที่ปรึกษา ....

ปีการศึกษา 2542

AN ABSTRACT

4072492023 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY

KEY WORD : recycled PET / nucleating agent / sodium carbonate / PET waste bottle

SAMORNWAN CHOLPRASERT : USE OF SODIUM CARBONATE NUCLEATING AGENT TO IMPROVE MECHANICAL PROPERTIES OF RECYCLED PET FOR INJECTION MOLDING. THESIS ADVISOR: ASSOCIATE PROFESSOR SAOWAROJ CHUAYJULJIT. 96 pp. ISBN 974-334-936-7.

PET waste bottles were recycled by melting together with virgin PET in various ratios. Sodium carbonate of 0.1 to 1 phr was used as nucleating agent to increase the amount and rate of crystallization for the use of injection molding.

The following studies were done : thermal properties by DSC, tensile test , solution viscosity measurement and the shrinkage of specimen after annealing for 40 hrs. It was found that the mixture of 50 to 50 of recycled and virgin PET with nucleation agent of 0.3 phr had the similar tensile strength and thermal stability as those of the virgin PET.

ภาควิชาวัสดุศาสตร์ ลายมือชื่อนิสิต..
สาขาวิชาวิทยาศาสตร์พอลิเมอร์ประยุกต์ฯ ลายมือชื่ออาจารย์ที่ปรึกษา.......S. Chuayjuljit
ปีการศึกษา 2542

ACKNOWLEDGEMENTS

The author wishes to express her deep gratitude to Assoc. Prof. Saowaroj Chuayjuljit for her help in various ways, invaluable advice, guidance and encouragement throughout this work. It goes without saying to the thesis committee, Assoc. Prof. Khemchai Hemachandra, Assoc. Prof. Paiparn Santisuk, Assoc. Prof. Onusa Saravari, for reading and criticizing the manuscript.

Thanks are due in particular to East Polymer Co., Ltd., Nippon Trading Co., Ltd., Global Co., Ltd., for their kind supports of the materials.

She also would like to thank National Metal and Materials Technology Center (MTEC), King Mongkut's Institute of Technology North Bangkok, King Mongkut's University of Technology Thonburi, Rachamangala Institute of Technology.

Last but not least, the author would like to express her sincere thanks to her parents, Miss Karuna Nakornchai, Miss Worawan Asawet for their help and encouragement.

Contents

Page

Chapter

Contents (Continued) Page

Contents (Continued) Page

List of Tables

List of Figures

Figures (Continued) Page

Figures (Continued) Page

Chapter I

Introduction

In the rapidly growing business of plastics recycling, profit opportunities vary with the type of plastic. Polyethylene (PE), polystyrene (PS), and Poly (ethylene terephthalate) (PET) are now being recycled in large volumes. PET is best known as plastic used as bottles for beverages (more than 540 million pounds were used in 1999 in the United States alone). It was estimated that PET bottles can be ground, washed and separated from PE base cups and aluminum, dried and pelletized in a 50 million pound-per-year plant for about $0.20 per pound less than the price of virgin PET pellets.

The plastics recycling, which saves energy, recovers valuable materials for reuse, and spares overflowing landfills some of their ever increasing load, includes three parts:

1. The collection, sorting and transportation to processing center
2. The processing itself
3. The development of markets for recycled plastic.

Slow growth in the first area is limiting recycling overall. However, new equipment and techniques are being developed rapidly for processing used plastic.

The commercial PET bottles were first applied to the containers of soya-sauce in 1977. Later, the amount of the production has increased remarkably, and now the application covers broad areas, namely food applications (beverage, liquor), living applications (detergent, shampoo, cosmetics) and medical applications (eye drop, mouthwash).

After PET containers have completed their first life as a container for soft drinks or other consumer products, they are collected for recycling, sorted locally and shipped to processors. The containers are ground, washed and separated by resin to produce clean flakes of PET, which can be recycled into a variety of new products.

Recycling is not only an environmental issue but also an economic development issue. Studies show great economic benefits for communities that can harness local waste streams for new recycling industries. It is easy to see why recovered PET plastic is such a valuable commodity. As a versatile resource, there are abundant markets for recovered PET containers. Moreover, an attractive price structure for clean, post consumer PET gives communities an economic incentive for encouraging PET recycling and product manufacturers an economic incentive for using such recycled materials.

Recycled plastics have nearly all the desirable properties of virgin plastics. They can be blended with virgin plastics or used in composite structure, sandwiched between layers of virgin plastic. Additives and compatibilizers improve the product properties, but contribute significantly to the cost.

Post consumer PET plastic can be turned into a number of different high value recycled products or end-uses beyond food and soda containers. Unlike other plastics, recycled PET is used in everything such as non food contact container, fiber application, carpet, stapping, sheet, film, auto parts, and injection molding; products that generally have high market values.

In fact, well-known companies are stocking their shelves with products made from post consumer PET polyester fiber. Shoes, pullover sweaters and T-shirts made from old soft drink bottles with the warmth and softness of their cotton counterparts are being successfully marketed in the U.S.

Recycled PET has also made inroads into the automobile industry. Chrysler uses the plastic in upholstery and headliner fabrics in its automobiles. Ford has used more than 23 million pounds of recycled PET in bumpers, grilles and luggage racks in its cars and trucks since 1988.

But there is an exception for injection molding. Unreinforced recycled PET is not in great demand because it is slow to crystallize and has a propensity to become brittle when annealed. The development of an injection-molding grade from PET recycled needs to address its slow crystallization at normal mold temperature.

A variety of organic and inorganic substances, known as nucleating agents, are commonly added at small amount to produce high degree of crystallinity and a fine spherulitic structure with concomitant improvements in mechanical properties and a faster overall rate of crystallization. Increased rates resulting from the higher nucleus density yield shorter cycles with corresponding economic advantages.

Inorganic compounds are widely used as nucleating agents for PET. A variety of inorganic oxides and salt, such as antimony oxides, sodium borohydride, sodium nitrite, carbonate, phosphate, sulfate, silicate, and chloride salts and even talc, have been patented as promoters of fast PET crystallization.

The key factors determining the efficiency of nucleating on PET are the alkalinity of the salt, its solubility and ability to disperse in PET, and the purity and thermal stability of the nucleating agent.

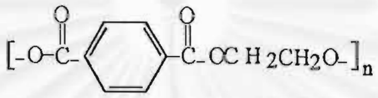
In this study, sodium carbonate was used as nucleating agent for virgin-recycled PET blend to improve the mechanical properties of the products. The overall crystallization rate and the activity of sodium carbonate were examined. In addition, the effects of the carbonate salt on the viscosity and MW of the resin after melt processing were investigated in attempts to determine its overall relative performance as potential nucleating agents during injection molding. To determine the heat stability of sodium carbonate, thermogravimetric analysis was used. The mechanical properties of the resin were examined by tensile testing. The useful parameters obtained from differential thermal analysis used to affirm the crystalline occurred.

Chapter II

Literature Survey

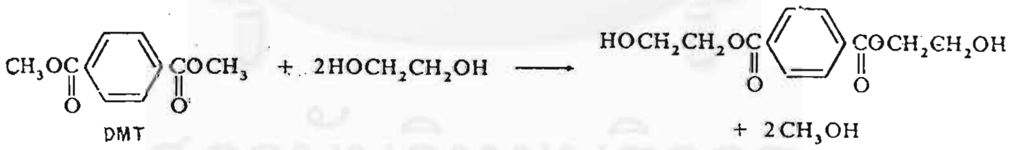
2.1 General Information of Poly (ethylene terephthalate) (PET)

The basic chemical structure is

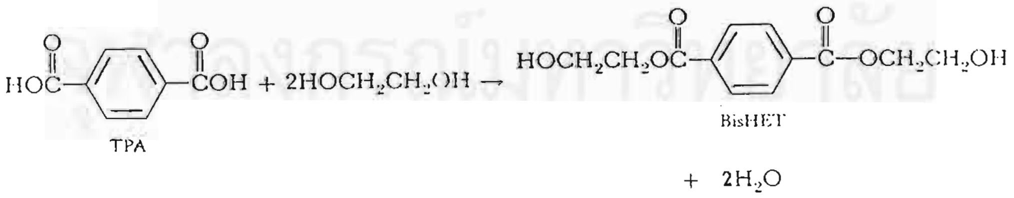


(Eq. 1)

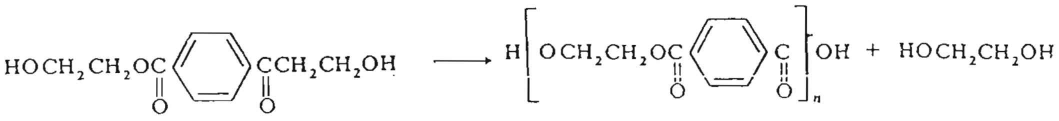
Poly (ethylene terephthalate) (PET) is a polycondensation polymer that is manufactured by two principal routes. The original process, still widely used, employs dimethyl terephthalate (DMT) and ethylene glycol (EG) as raw materials. More recently process using direct esterification of terephthalic acid (PTA) with ethylene glycol. This method has gained increasing acceptance because of the greater availability of highly purified PTA. With either process, the next step is the preparation of the intermediate diester, bishydroxyethyl terephthalate (BHET), which then is further condensed to the polymer [4,9].



(Eq. 2)



(Eq. 3)



(Eq. 4)

Properties: PET is a water-white polymer with excellent resistance to weak acids, bases, and most solvents. PET is also excels in strength, toughness, and clarity. Because of its high crystalline melting point and glass transition temperature, PET retains good mechanical properties at temperature up to 150-175 °C [7]. To develop the maximum properties of PET the resin has to be processed to raise its level of crystallinity and/or to orient the molecules. Orientation increases the tensile strength and reduces permeability. Tensile strength of unoriented materials is 8,000 psi, but this can be increase to over 30000 psi by orientation [2]. Permeability of gases in oriented PET is lower than most other plastics, which make this material suitable for soft drinks, but not for products sensitive to oxygen.

Application: PET can be made into fibers, films, sheets, and blow-molded and thermoformed containers for soft drinks and foods. From its excellent strength and toughness, 2-liters filled bottles dropped on concrete from 6 ft. have a survival rate greater than 97 percent. Shelf life for carbonated beverages in half-liter bottles is 8 weeks, and for 1-liter bottles is about 12 weeks [3].

Other applications include fiber application glass-reinforced PET compounds, which can be injection-molded into parts for automotive, electrical/electronic, and other industrial and consumer products.

2.2 Recycling of Poly (ethylene terephthalate) from Soft-Drink Bottles

In last decade, it has seen dramatic growth in the use of PET, a tend that has only accelerated. Versatile PET plastic comes in a wide variety of shapes and sizes but is best known as the plastic used in soft drink containers. PET resin use for bottles in USA exceeded 1.6 billion pounds in 1994 [5].

With the acceleration of the environmental movement and over diminishing landfill space, increasing attention is being placed on the disposition of plastic waste. The goal of improving the overall environmental efficiency is illustrated in Figure 2.1.

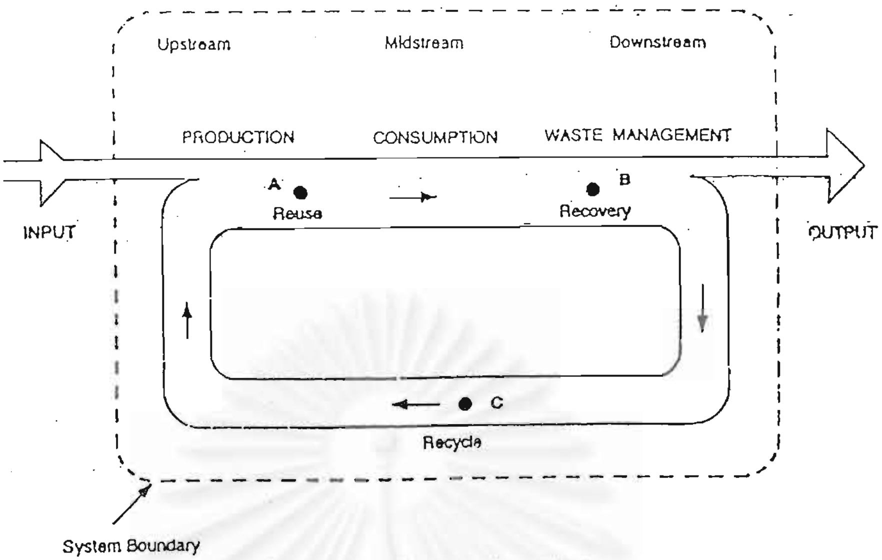


Figure 2.1 Basic model for the “Recycle Society” [1].

Soft-drink-bottle recycling got its start with the introduction of deposit legislation, with resulted in collection of significant volumes of material and recognition of the economic value embedded in them. Recycling rates for soft-drink-bottles have continued to grow, reaching a recycling rate of 48.6 percent in 1994. The recycling rate in deposit state is over 90 percent. The overall recycling rate for PET was estimated to be 34 percent in 1994. Five hundred sixty-five million pounds of PET bottles were collected for recycling. That represents a 200 percent increase since 1987 [5].

It's easy to see why recovered PET Plastic is such a valuable commodity. As a versatile resource, there are abundant markets for recovered PET containers. Moreover, an attractive prince structure for clean, post consumer PET gives communities an economic incentive for encouraging PET recycling and product manufactures an economic incentive for using such recycled materials.

2.3 Type of Recycling Processes

As shown in Figure 2.2, a process of recycling post consumer PET containers starts when bales of PET containers arrive at the processor, where they are fed into a granulator to produce flake.

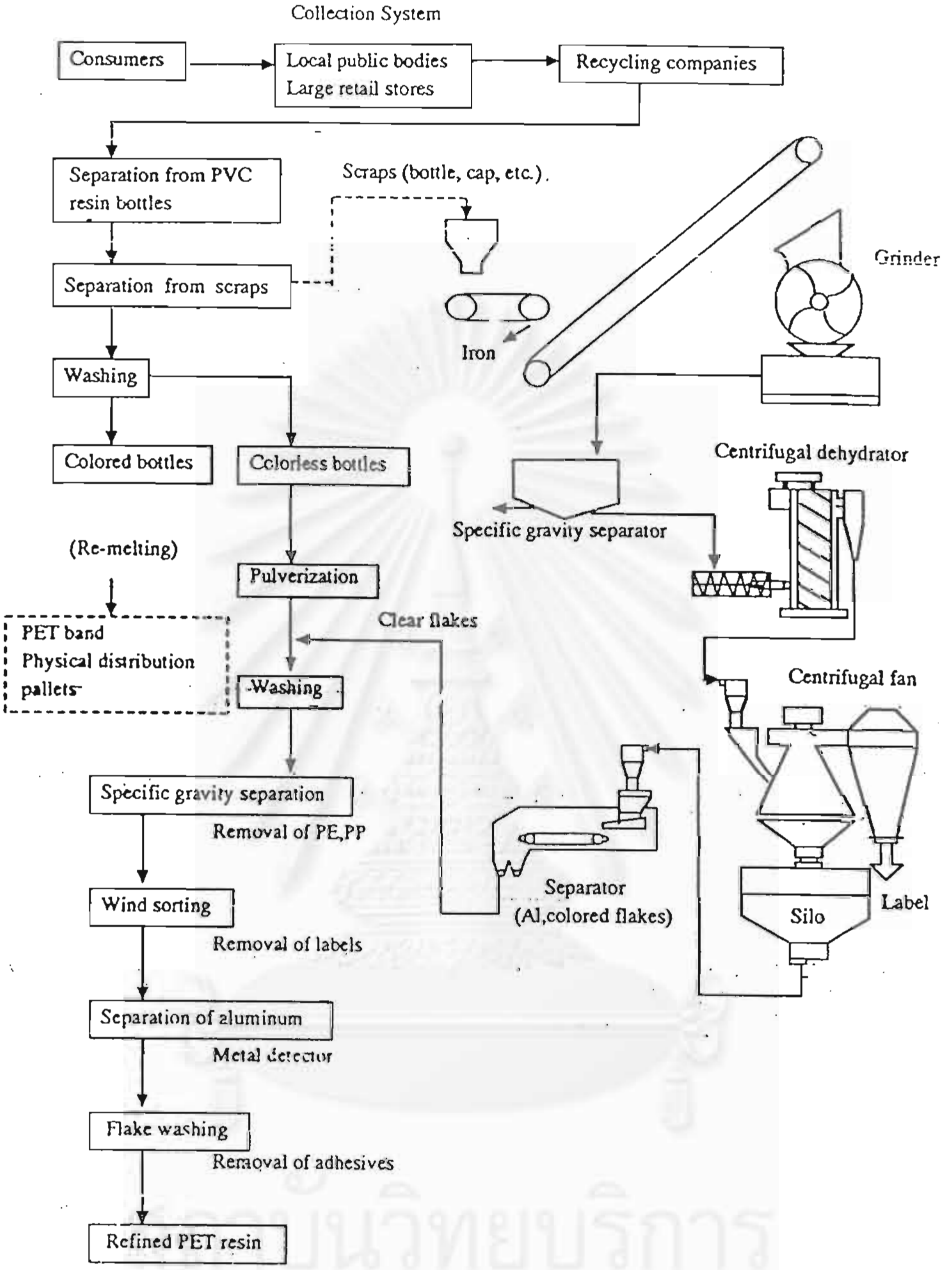


Figure 2.2 A recycled system for beverage PET bottles [1].

The flake mixture then pass through a series of cleaning and sorting steps to separate the PET flakes from contamination such as labels, base cups, dirt and other materials.

First, labels are removed. The flake mixture is then washed in a scrubber. In this step, additional contaminants such as small amounts of food residue, flue and dirt are removed with a variety of industrial strength surfactants and cleaners. Next, the flakes pass through a float/sink classifier. This is a water-based separation method, as the flakes pass through this step, the PET flakes sink while lighter plastic products such as base cups, bottle caps and rings float off. After being dried thoroughly, the PET flakes pass through an electrostatic separator. In this step, an electro-magnetic field separates and removes any remaining aluminum (from thing like bottle caps). Once all these steps are complete, the facility can use the clean flake in several ways.

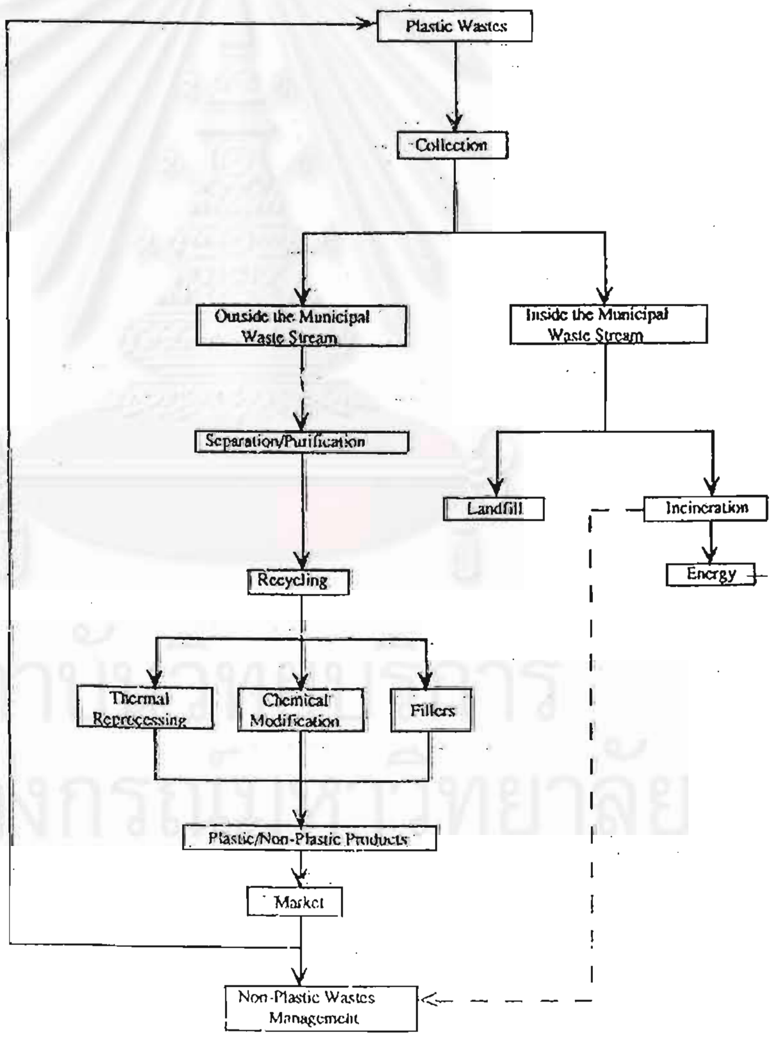


Figure 2.3 Flow chart of a plastic waste management process [15].

While plastics recycling has been practiced for many years, it has been mostly confined to “primary” recycling. The recycling of all post consumer plastic waste, comprised of a variety of plastics and products, is still fairly new. However, the recycling of PET beverage containers has proven to be an exception. The chemical nature of PET permits a broad range of recycling options, from mechanical recycling to a range of chemical recycling process. A flow chart of plastic waste management process is shown in Figure 2.3.

2.3.1 Primary Recycling Process

Primary recycling is defined as applications producing the same or similar products or the reuse of uncontaminated manufacturing scrap (i.e. regrid).

2.3.2 Secondary Recycling Process

Presently, post consumer PET recycling is accomplished via “secondary“ recycling processes; that is, physically converting the bottles into new products. PET flakes can be readily reprocessed into granules by conventional melt extrusion. However, water and trace of acidic impurities induce chain scission processes that lead to a reduction in the molecular weight of the recycled PET resin.

Compared to chemical recycling routes, mechanical recycling of PET by melt reprocessing is relatively simple, requires low investments utilizes established equipment, is flexible in terms of feedstock volume and has little adverse environmental impact.

The markets for these recycled products include carpeting, fiberfill, strapping, piping and non-food containers.

2.3.3 Tertiary Recycling Process

Recovered PET can be chemically broken down into small molecular species, purified, and then repolymerized to produce new PET for use in a number of applications. Recycling processes that use the recycled material as a chemical feedstock are generally classified as tertiary recycling. Under this polymerization category there are currently three processes. Figure 2.4 is summarizes the mechanisms of the three recycling processes while Figure 2.5 shows the structures of the major chemical recycling products that can be used as starting materials in the manufacture of new PET.

- Methanolysis (Total depolymerization by methanol) involves the treatment of post consumer PET with methanol to recover dimethyl terephthalate (DMT) and ethylene glycol. The ethylene glycol is further refined for reuse or sale into the antifreeze market. The DMT is further purified through several crystallization and distillation steps to yield a pure DMT monomer used to produce recycled PET resin.

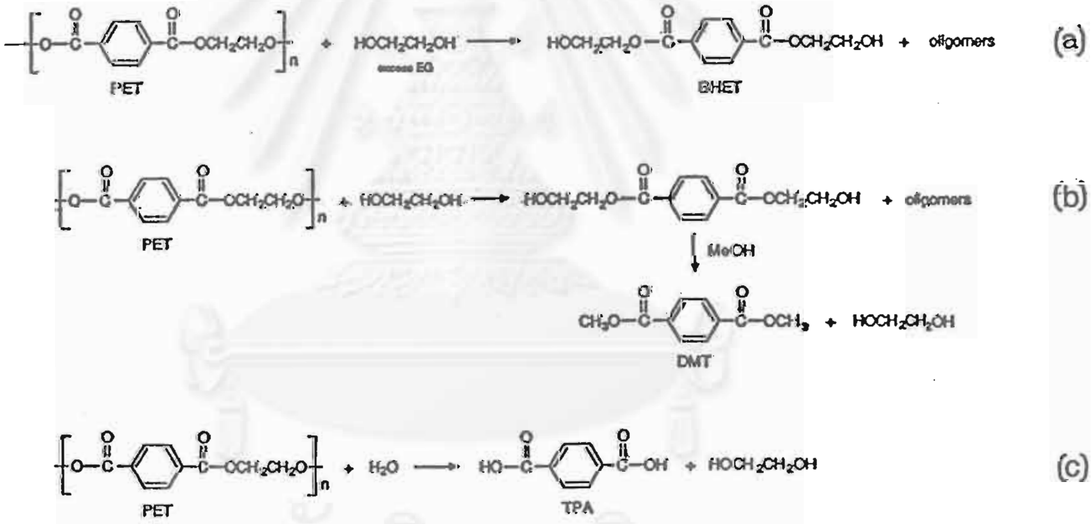


Figure 2.4 Mechanism of chemical recycling of PET; a) glycolysis, b) methanolysis, c) hydrolysis [6].

- Glycolysis (Partial depolymerization by ethylene glycol) breaks down the polymeric chain only partially by heating post-consumer PET with ethylene glycol to form bis-hydroxy ethyl terephthalate (BHET) and oligomers. Glycolysis produces a mixture, which is difficult to totally purify since the resultant products do not undergo simple crystallization and distillation techniques. To further purification, a solvent extraction technique may be used. However this step may lead to questions of the relative toxicity of the particulate solvent and the presence of trace amounts of solvent in the final product. In any event, the resultant glycolysis mixture must be polymerized with "virgin" resin to produce the final recycled resin.

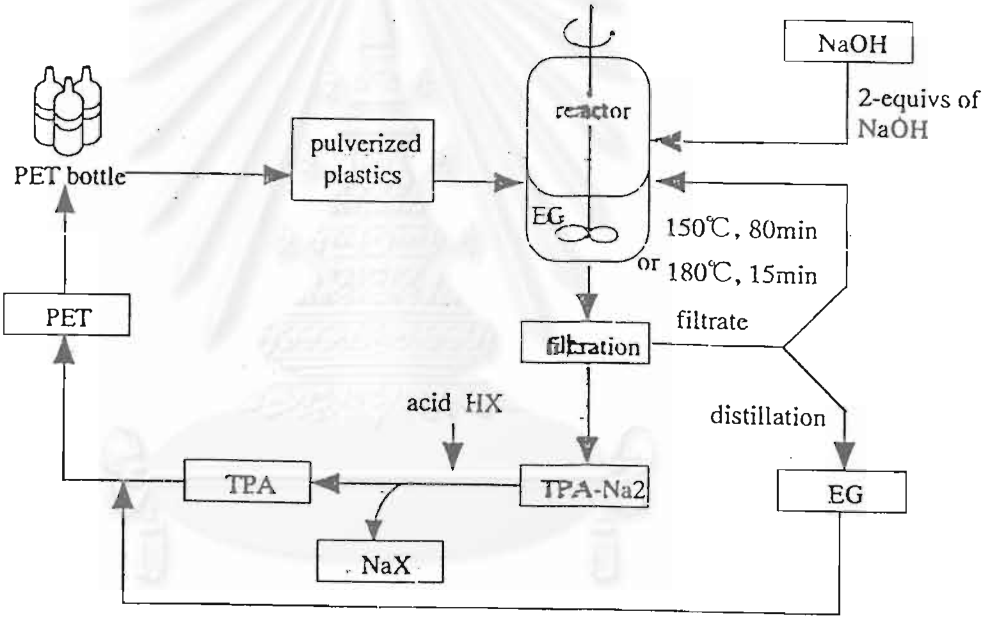


Figure 2.5 Chemical recycle system of PET wastes with NaOH in nonagueous EG [1].

- Hydrolysis (Total depolymerization by water) relates to the breakdown of polymer by water, acids, caustic soda or ammonium hydroxide. Hydrolysis remains and academic interest that may never be commercialized due, among other things, to the inherent difficulty in purifying the resultant terephthalic acid (TPA) from the reaction mixture and the general presence of salt by-products.

Table 2.1 PET recycling: depolymerization process [13].

Properties	Hydrolysis	Glycolysis	Methanolysis
Feed Quality	High	High	Low
Operating Cost	Moderate	Moderate	High
Product Quality	Moderate	Moderate	“Virgin”
Recycle Turnover	To Be Determined	To Be Determined	Infinite

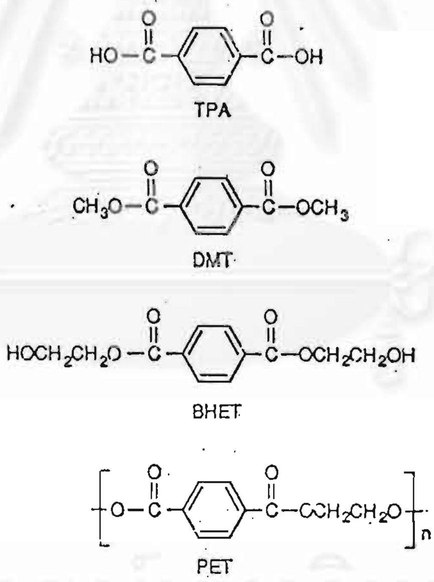


Figure 2.6 structure of compounds obtained by the depolymerization of PET [6].

Glycolysis and methanolysis, Both processes produce PET that is essentially chemically identical to virgin resin and has been approved by the U.S. Food and Drug Administration for food contact applications. At the present time, PET produced by these processes is more costly than virgin resin. Selection of the most appropriate recycling technique is dependent upon the quality of the available feed stock and the type of the end products required.

2.3.4 Thermal Recycling Process

Pyrolysis

An alternative to traditional recycling methods is to convert the polymers, using heat, into small molecules that can then be used as a chemical feedstock or alternatively can be used as liquid or gaseous fuel. These processes are termed pyrolysis [1].

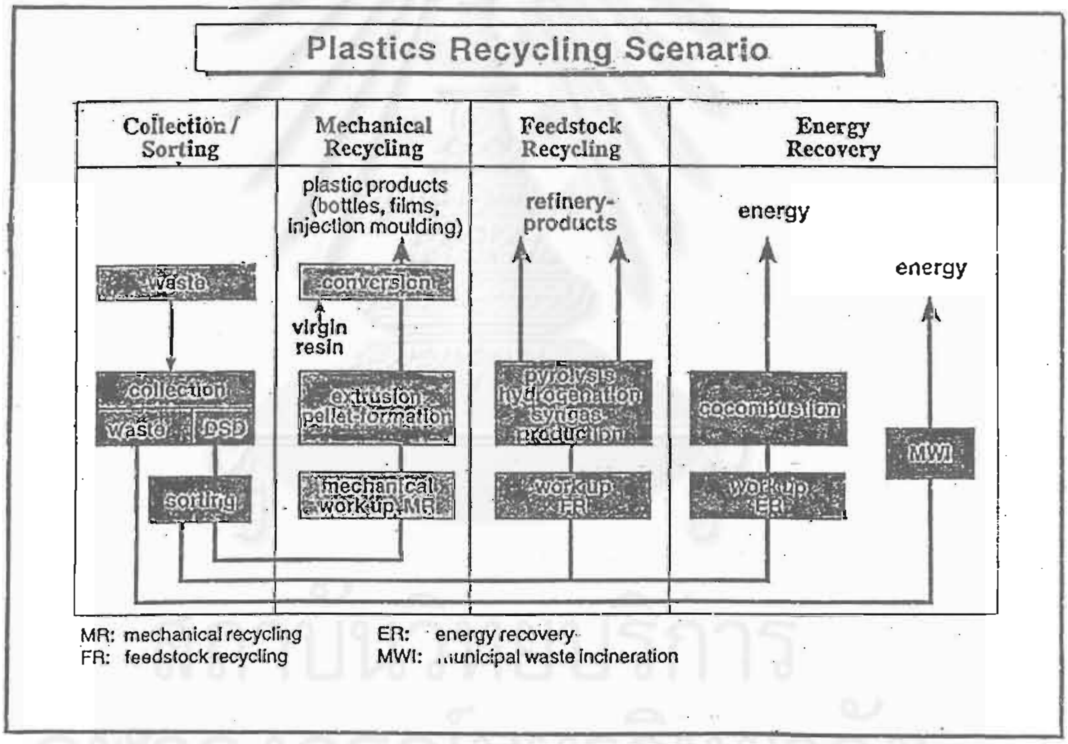


Figure 2.7 Plastic recycling scenario [31].

Other processes

Research on hydrogenation of plastic waste is currently being undertaken in Germany. A slurry-phase hydrogenation is carried out at temperatures up to 500 °C and pressures of 20 Mpa. The products consisted of gases, liquids, and solid residue [5]. Simplified overview of the main recycling process is shown in Figure 2.7 while mechanical recycling process and energy recovery are compared in Figure 2.8.

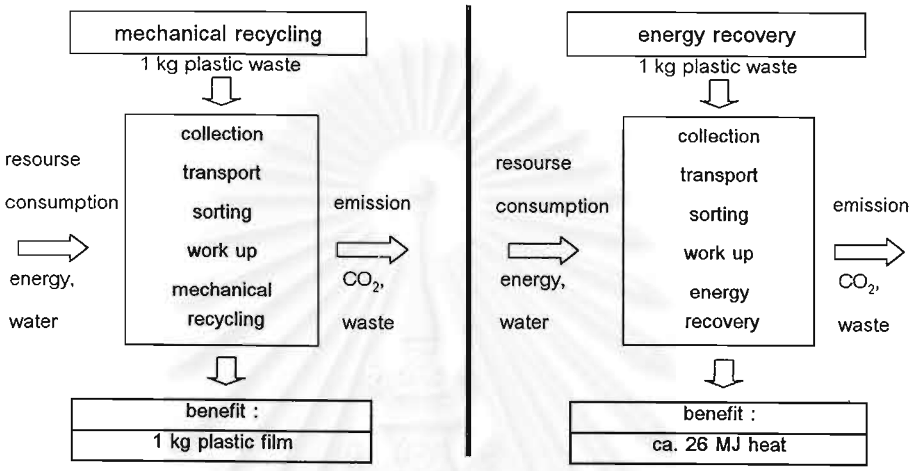


Figure 2.8 Mechanical recycling and energy recovery [31].

2.4 Properties of Recycled PET

Recycled PET by mechanically process general retains very favorable properties. Some reduction in intrinsic viscosity is common, but solid stating can reverse this. PET is very susceptible to damage from contamination with PVC. The density of PET and PVC are overlapping, making them difficult to separate by mechanical means. Under PET processing conditions, PVC decomposes, leaving black fleck in the resin as well as causing the other problems.

Residual adhesives from attachment of labels and base cups are a common contaminant concern in recycled PET. Some of the adhesive residue can become trapped in the PET granules and is not removed by washing. Since these adhesives often contain rosin acids and ethylene vinyl acetate. When the PET is extruded, the rosin acids plus acetic acid from hydrolysis of ethylene vinyl acetate can catalyze the hydrolysis of the PET itself. A similar problem can be caused by residues of caustic soda or alkaline detergents from the washing step. In addition, the adhesive residues tend to darken at PET extrusion temperatures, causing discoloration of the resin [5].

Repolymerized PET, produced by glycolysis, methanosis or hydrolysis, is identical in properties to virgin PET.

2.5 Application of Recycled PET

Post consumer PET can be turned into a number of different high-value recycled products. Unlike other plastics, recycled PET is used in everything from new bottles to carpet and fabric to auto parts-products that generally have high market value.They can be blended with virgin plastics or used in composite structure, sandwiched between layers of virgin plastic. Additives and compatibilizers improve the product properties, but contribute significantly to the cost. The market for recycled PET can be divided as the following. The overall uses of recycled PET is shown in Table 2.2.

2.5.1 Fiber application

The PET fiber industry comprises four major application areas; namely staple, filament, non-woven and fiberfill.

2.5.2 Carpet

A relatively new application for recycled high molecular weight PET is in carpet backing and carpet tiles. The recycled PET is blended in a 1:8 ratio with recycled LDPE and extruded into a monoaxial film, which is then split into narrow strips that can be woven.

2.5.3 Strapping

Strapping is a high-tenacity tape that can be produced from PET with a high intrinsic viscosity and low contamination. It competes with steel and polypropylene material. This application can accept green or colored PET bottles.

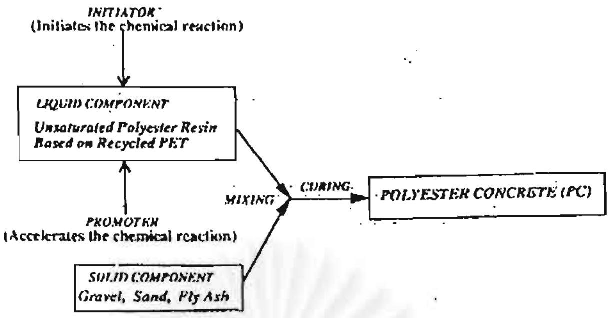


Figure 2.9 production of PC using unsaturated polyester resin based on recycled PET [15].

2.5.4 Composite Material

Polymer concrete (PC) is a relatively new high performance material commercialized. Recycled PET could be used in the production of high performance polymer concrete [15,16]. An example of production PC using unsaturated polyester based on recycled PET is shown in Figure 2.9.

2.5.5 Sheet

Recycled PET from post consumer soft drink bottles has been shown to be suitable for the production of thermoformed packaging trays with good gloss, impact strength and tensile strength.

2.5.6 Film

Film that has a recycled content up to 25% has a FDA (Food and Drug Administration) approval for food contact application [17].

2.5.7 Coextrusion Multilayer Films

Thermoformed food packaging trays with a proportion of recycled PET enclosed within two external layers of virgin PET are now in production on North America and Europe.

Table 2.2 Uses of Recycled PET, 1990 [5].

	Million lbs.
Fiber	165
Extruded strapping	12
Alloys and compounds	11
Extruded Sheet	2
Bottles and containers	1
Chemical conversion	10

2.5.8 Non Food Contact Containers

Single- wall PET bottles are an application that can use 100% post-consumer PET depending on its quality or it can be blended with virgin resin. These are used for detergent of household products and the bottles are sometimes colored. Since PET is competing with PVC and HDPE in this Application, the market is very price sensitive.

2.5.9 Engineering Resins

Post consumer PET can be upgraded with fillers such as glass fiber, and injection molded to produce parts for the automotive, household and computer applications such as fan housings, appliance housings and furniture. High quality flake is generally needed to satisfy this market. Since these applications are often heavily pigmented and filled they can tolerate green-tinted post consumer PET bottles.

2.5.10 Injection Molding

Unreinforced recycled PET is not in great demand an injection molding resin because it is slow to crystallize and has a propensity to become brittle when annealed [18,19].

The development of an injection-molding grade PET from recycled rigid containers needs to address its slow crystallization at normal mold temperature [4]. The crystallization rate can be increased by using high mold temperature (at lease 130 °C) attained by oil or electrical heating longer mold cycled; these techniques present economic disadvantages [5] and often yield finished parts of low crystallinity that are difficult to remove from the mold or brittle products with a coarse spherulitic structure.

2.6 Crystallization of Polymer

Polymer crystallize from a melt under the following conditions [8]:

- The molecular structure of the polymer must permit crystalline ordering: insufficient mobility of the main chain, irregularly sited side groups, and branching or bulky side chains can prevent crystallization.
- The crystallization temperature must be below the melting point, but not too close to the glass point, so that the molecule chains have the mobility necessary to crystallization.
- Nuclei must be present to initiate the crystallization, from which crystallites are then formed, the latter arranging themselves into a superstructure, the spherulites.
- The rate of crystallization must be sufficiently high.

The overall rate of crystallization can be determined from the nucleus density and the growth rate of the spherulites.

Polymer with a medium crystal growth rate, such as polyethylene terephthalate, can be more strongly supercooled than the rapidly crystallizing polyethylene, and for this reason respond very well to heterogeneous and athermal nucleation with the aid of foreign substances – nucleating agents. The number and size of spherulites formed are determined by whether the nucleus formation is homogeneous or heterogeneous. The mechanism of heterogeneous nucleation is not well understood. It is believed, though, that nucleation occurs more easily in the presence of foreign particles, which reduce the free-energy barrier that needs to be overcome in order to form nuclei having the required critical size. In general, the decrease in size and increase in number of spherulites can qualitatively judge the nucleating effect of an additive.

Since very many more nuclei are formed in the presence of a nucleating agent, under the same cooling conditions the resulting spherulites will be considerably smaller than in a material to which no nucleating agents have been added. Nucleated polymers therefore have finer grain structures than unnucleated ones, and this is reflected in their physicochemical characteristics; thus, coarse-spherulitic plastics are more brittle and less transparent or translucent than ones with the same crystalline fraction but a fine-spherulitic structure. The more precise details relating to the connections between the type of the polymer and chemical and physical character of the nucleating agent and its action have not yet been completely clarified. However, in the case of organically based nucleating agents a few general observations can be made on what makes a substance capable of nucleation [8]:

- The nucleating agents should be wetted or adsorbed by the polymer;
- It should be insoluble in the polymer;
- Its melting point should be higher than that of the polymer; it should be homogeneously dispersable in the polymer melt in as fine a form as possible (1 to 10 μm).

Nucleating agents can be roughly classified as follows:

- Inorganic additives such as talc, silica, kaolin;
- Organic compounds such as salts of mono- or polycarboxylic acids, certain pigments;
- Polymers such as ethylene/acrylic ester copolymers.

In practice, concentration up to 0.5% are used. Concentrations higher than that do not, as a rule, produce any further enhancement of the nucleation effect. The nucleating agents are incorporated as powder/powder mixtures, as suspensions or solutions, or in the form of a master batch. Whichever method is used, good predispersion of the nucleating agent is necessary if an optimal effect is to be achieved.

2.7 Influence of nucleating agents on characteristics of polymer

Most industrial nucleating agents produce high degree of crystallinity resulting in increased hardness, elasticity modulus, tensile strength, and yield point compared with the unnucleated material. In addition, the fine-grain spherulite structure of nucleated polymers improves optical properties such as transparent or translucency, the elongation at break, and the impact strength, since as a result of this structure more uniform stress distribution is produced on mechanical stressing.

Shortening of cycle time in the injection molding of nucleated molding compounds is of economical importance. The shortening is caused by higher crystallization temperatures and faster overall rates of crystallization resulting from the higher nuclear density. Thus, the crystallization process is initiated with less supercooling and is completed after shorter cooling times.

2.8 Nucleating agents in poly (ethylene terephalate) (PET)

The low crystallization rate and the slow nucleus formation of PET are particularly advantageous for the manufacture of highly transparent, partly crystalline PET, but they constitute a serious handicap in the injection molding of PET. Injection into heated molds (e.g. to about 150 °C), to accelerate crystallization and to shorten cycle times, yields finished articles of low crystallinity that are difficult if not impossible to remove from the mold; if very long and uneconomical cycle times are used the resultant articles are too brittle (large spherulites). These problems can be avoided by the use of nucleating agents, and good material properties are then obtained (many small spherulites) with economically acceptable cycle times.

2.9 Modification of PET Crystallization Characteristics by Using Nucleating Agent

PET synthesis requires the presence of a catalyst commonly based on Mn, Zn, Pb, Cd, Mg, Ca, Ce, Co, Li, Na, and Sb. Catalyst remnants, which are impurities in the

PET resin, can act as nucleating agent for PET crystallization [21, 22]. Inorganic compounds are widely used as nucleating agents for PET. A variety of inorganic oxides and salts, such as antimony oxide, sodium borohydride, sodium nitrite, carbonate, phosphate, sulfate, silicate, and chloride salts and even talc, have been patented as promoters of fast PET crystallization.

Aharoni [23] used hydroxides of aluminum, copper (II), nickel (II), indium, barium, magnesium, cobalt (II), and lanthanum as nucleating agents for PET. The conclusion from these studies was that nonalkali metal hydroxides capable of releasing water within the range of PET processing temperatures are effective nucleating agents. Aharoni argued that the increased crystallization rates can be attributed to either a localized severe hydrolysis or a localized supercooling of PET In the vicinity of the hydroxide particles. In either case, the effect is from the water released from the hydroxide. In these studies, alkali metal hydroxides were not considered, since they may have induced severe hydrolytic degradation of the polyester.

Use of nucleating agents at high concentrations may decrease rather than increase the PET crystallization rate. This was the case in a study reported by Szekeley-pecsi et al. [24] where high MgO concentrations yielded a large number of hydroxocarboxylate complexes which reduced the mobility of polyester chains.

Organic salts is another large category of additive used as nucleating agents for PET in industrial application. This category includes salts of hydrocarbon and polymeric carboxylic acids, alkali metal salts of benzoic acid, [23, 24] and amine carboxylate, which has been reported to act not only as a nucleant, but also as a plasticizer as well. Sodium carboxylates based on pyrrole carboxylic acids were found to be effective nucleants without causing reduction of the resin molecular weight [25].

Legras et al. [26, 27] studies the crystallization of PET in the presence of additives such as sodium *o*-chlorobenzoate, sodium *p*-chlorobenzoate, sodium benzoate, sodium p-hydroxybenzoate, and disodium terephthalate and suggested that a reaction occurs between the salt and molten polyester. This reaction produces species having ionic end groups, which are the actual nucleating agents for PET-more specifically, the sodium-PET salt. More soluble additives lead to an increased probability for reaction and, thus, formation of the actual nucleant.

If chemical reaction is involved, one should be thinking along the lines of homogeneous rather than heterogeneous nucleation. Further confirmation of the homogeneous nature of PET nucleation with sodium-organic acid salts was given by Garcia [28] who concluded that the key factors determining the efficiency of an additive for PET nucleation are the alkalinity of the salt, its finally, the purity and thermal stability of the additive. Other substances that have been tried as nucleating agents for PET include some sodium-type ionomers (high and MW) and various polymers [29]. Recently, Reinsch and Rebenfeld [30] demonstrated that crystallization half-times of PET in composites depend on the type of fibrous reinforcement (Kevlar, glass) and its sizing. However, the degree of crystallinity is largely unaffected by the crystallization temperature and the presence of PET additives reinforcing fibers.

Xanthos et. al. [20] studies the crystallization kinetics of the carbonate salts as a nucleating agent in recycled PET. It is shown that sodium carbonate is the most effective nucleating agent for recycled PET with relative small reduction in molecular weight.

2.10 Sodium carbonate

The common name of sodium carbonate, Na_2CO_3, is soda ash, which is the most important industrial alkali. It is a grayish-white lumpy material, odorless, small crystal or crystalline powder. Sodium carbonate is a hygroscopic material and soluble in water. Its decomposition temperature is about 851 °C.

For household use in hydrous crystallized form, $Na_2CO_3 \cdot 10H_2O$. Another grade, with one molecule of water, $Na_2CO_3 \cdot H_2O$, is the standard product for scouring solutions. Commercial high-quality sodium carbonate contains 99% minimum Na_2CO_3. It varies in size of particle and in bulk density, being marketed as extra-light, and dense. The custom grade has a density of 40 lb. per cu ft, the extra-light is 23 lb. per cu ft, and the dense is 63 lb. per cu ft [10].

Safety profile: poison by intraperitoneal route. Moderate toxic by inhalation and subcutaneous routes. Mildly toxic by ingestion. Experimental reproductive effects. Skin and eye irritant. It migrates to feed from packaging materials [12].

2.11 Characterization of the activity of nucleating agents

Differential thermal analysis (DTA, DSC) is used most frequently to study the crystallization behavior of a polymer melt and to determine the activity of a nucleating agent.

2.11.1 The glass transition temperature

When the melt of a non-crystallizable polymer is cooled, it becomes more viscous and flows less readily. If the temperature is reduced low enough it becomes rubbery and then as the temperature is reduced further it becomes a relatively hard and elastic polymer glass. The temperature at which the polymer undergoes the transformation from a rubber to a glass is known as the glass transition temperature, Tg. The ability to form glasses is not confined to non-crystallizable polymers. Any material, which can be cooled sufficiently below its melting temperature without crystallizing, will undergo a glass transition.

The Tg is normally taken as the point at which the extrapolations of the two lines meet. Another characteristic of the Tg is that the exact temperature depends upon the rate at which the temperature is changed. It is found that the lower the cooling rate the lower the value of Tg that is obtained. It is still a matter of some debate as to whether a limiting value of Tg would eventually be reached if the cooling rate were low enough. It is also possible to detect a glass transition in a semi-crystalline polymer, but the change in properties at Tg is usually less marked than for a fully amorphous polymer.

The value of Tg will depend upon the physical and chemical nature of the polymer molecules. The most important factor effects Tg is chain flexibility. A small number of branches on a polymer chain are found to reduce the value of Tg. The value of the Tg is found to increase as the molar mass of the polymer is increased. Tg is most effected by molecular mobility, should decreased in the direction of molecular mobility increase with increasing the rate of crystal growth.

The crystallization temperature

The crystallization of the melt is followed at a constant rate of cooling and the temperature at which the crystallizing rate reaches its maximum is determined. This temperature, at which the heat released by the crystallizing melt climbs to a peak at a constant rate of cooling, is generally known as the crystallization temperature. Crystallization temperature is highly affects to lamella thickness and growth rate of polymer crystal.

The melting temperature

The melting if polymer crystal us essentially the reverse if crystallization. There are several characteristics of the melting behavior of polymers, which distinguishes them from other materials. They can be summarized as follows.

- It is not possible to define a single melting temperature for a polymer sample as the melting generally takes place over a range of temperature.
- The melting behavior depends upon the specimen history and in particular upon the temperature of crystallization.
- The melting behavior also depends upon the rate at which the specimen is heated.

The melting process can be shown by the Gibb's free energy theory [11].

$$\Delta G = \Delta H - T\Delta S \qquad \text{(Eq. 5)}$$

Where ΔH is the enthalpy change and ΔS is the change in entropy. At the melting process, where a steady equilibrium is reached, $\Delta G = 0$ and

$$Tm = \Delta H / \Delta S \qquad \text{(Eq. 6)}$$

As the crystalline structure becomes more orderly, the entropy, ΔS, the measurement of the disorderliness, is decreased the Tm is therefore increased.

Concerning to crystallite size, a qualitative analysis can be approached according to Hoffman's nucleation theory, where

$$Tm = Tm^{\circ} [1 - (2\delta e / \Delta H_v \times l)] \quad \text{(Eq. 7)}$$

Tm° is the equilibrium melting point, δe is the basal interfacial energy, ΔH_v is the heat of fusion of a unit volume of crystal, and l is a thin dimension of crystal.

Percents crystallinity

Most of crystalline polymers are Semicrystalline, that is, a certain fraction of the polymer is amorphous, while the remainder is crystalline. The reason why polymers fail to attain 100% crystallinity is kinetic, resulting from the inability of the polymer chains to completely disentangle and line up properly in a finite periods of cooling or annealing.

Degree of crystallinity has an important effect upon the physical properties of a polymer. One of the several methods for determining the percent crystallinity in such polymers is Differential scanning calorimetric analysis (DSC) which involves the determining of the heat of fusion. Then the percent crystallinity is given by

$$\% \text{ Crystallinity} = (\Delta Hm - \Delta Hc) / \Delta H^{\circ} \times 100\% \quad \text{(Eq. 8)}$$

where ΔHm = heat of fusion of the melting peak

ΔHc = heat of fusion of the crystallization peak

ΔH° = heat of fusion of the polymer from handbook.

Chapter III

Experimental

3.1 Raw Materials

Injection grade polyethylene terephthalate (PET) was obtained from Global Connection Co., Ltd. The specifications of the PET chips are shown in Table 3. Laboratory grade sodium carbonate powder used as nucleating agent was obtained from AJAX Chemicals. Thermal stability of the nucleating agent was characterized by using Thermogravimetric Analysis (TGA).

Table 3.1 Characteristics of PET used in this experiment

Properties	Typical Value
Glass transition temperature (T_g)	81 °C
Inherent Viscosity	0.75
Specific Gravity	1.27

3.2 Sample Preparation

3.2.1 Extrusion Procedure

Post-consumer PET bottles were collected, removed cap and label and washed to remove dirt. Cleaned bottles were then fed into a granulator to crush into flake. Flake was first mixed with sodium carbonate to prepare masterbatch. Prior to mixing, materials were predried under vacuum (PET at 80 °C for 4 hour and sodium carbonate at 80 °C for 12 hour). Masterbatch was prepared by Brabender plasticorder at 260 °C and 40 rpm. First, flake was melt and after about 5 min sodium carbonate was added and continued mixing for several minutes. Masterbatch and PET flake were dry blend and then pelletized by a twin-screw extruder. The compositions of the PET specimens used for this study are described in Table 3.2.

Table 3.2 Composition of the PET specimens.

Sample code	Virgin PET %	Recycled PET %	Nucleating agent (phr)
001	0	100	0
101			0.1
301			0.3
501			0.5
701			0.7
1001			1.0
028	20	80	0
128			0.1
328			0.3
528			0.5
728			0.7
1028			1.0
055	50	50	0
155			0.1
355			0.3
555			0.5
755			0.7
1055			1.0
082	80	20	0
182			0.1
382			0.3
582			0.5
782			0.7
1082			1.0

Table 3.1 (Continued)

Sample code	Virgin PET %	Recycled PET %	Nucleating agent %
010	100	0	0
110			0.1
310			0.3
510			0.5
710			0.7
1010			1.0

3.2.2 Injection molding Procedure

The extruded chips were predried under vacuum at 80 °C for 4 hours before injection molded into tensile bar as ASTM D638. The condition of injection molding process is shown in Table 5. The tensile bars were then used for mechanical testing, differential thermal analysis, shrinkage and intrinsic viscosity study.

Table 3.3 Process Condition of Injection Molding

Sample Drying (°C)	80
Drying (h)	4
Cylinder setting temperature (°C)	240-260
Mold control temperature (°C)	50
Injection-maintain pressure	
Gauge (bar)	30-40
Back (bar)	10
Time (s)	1
Product cooling time (s)	50-60
Nozzle type	open
Screw diameter (m/m)	30

Figure 3.1 Injection Molding Machine.

3.3 Characterization

3.3.1 Thermogravimetric Analysis

A Perkin-Elmer Thermogravimetric analyzer (TGA-7) was used to determine the thermal stability of the sodium carbonate to ensure that it has heat stability above the estimated maximum process temperature of PET (300 °C) attained in this study, without decomposition. The heat scans were performed under nitrogen atmosphere at a heating scan rate of 20 $^{\circ}C \cdot min^{-1}$, from 60 to 300 °C. Data were recorded continuously and analyzed by TGA analysis program.

3.3.2 Tensile Testing

Tensile testing is a widely used method to provide basic design information on the strength of materials and a guide to how a polymer will behave in a finish product by determining the stress-strain curve in tension mode. Tensile testing involve pulling or stretching a test specimen and measuring the corresponding load applied. Normally, the experimental data are plotted in the form of a nominal stress - nominal strain plots. If the cross-sectional area is monitored one can plot the data in the form of true stress versus true strain curves.

The nominal stress, σ, is given by

$$\sigma = P / A_o$$

Where P is the applied load and A_o is the original cross-section area.

The elongation, e, is given by

$$e = L - L_o$$

Where L is refers to the instantaneous length of the gauge section at any moment and L_o refers to the original length.

The uniaxial tensile strain, ε, is defined as the elongation per unit of length, and hence

$$\varepsilon = L - L_o / L_o$$

Over some finite range of strain the polymer exhibits Hookean behavior; that is, the stress- strain relation is essentially linear. Hence over this range we may write

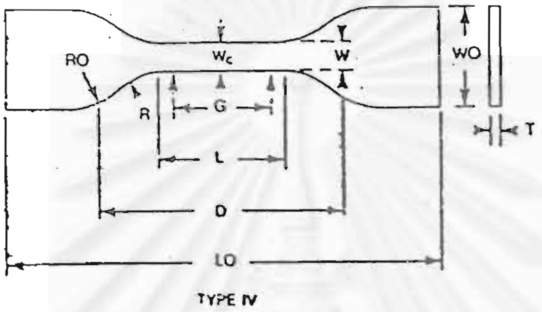
$$\sigma = E\varepsilon$$

Where E is so called Young's modulus of elasticity, is given by the slope of the initial portion of the stress-strain curve.

Generally, plastic does not shows a simple linear stress-strain relationship, it will produced a curved line. Polymers' properties are time dependent because of the viscoelastic nature so the shape of the observed curve will also depend on the strain rate and temperature. In order to compare the result of each sample, testing should be done at the same condition. The generalized stress-strain curve for the plastic serves to define many useful quantities, including modulus or stiffness (the slope of the curve), yield stress, strength and elongation at break.

The tensile specimens were prepared from injection molding, in according to ASTM D638 as shown in Figure 3.2.

Tensile test was performed in a Universal Testing Machine (LLoyd, model), using 100 kN load cell, at a crosshead speed of 1 mm·min^{-1} (Figure 3.2). The testing was performed at room temperature. The system used was controlled via a computerized.



Symbol	Description	Dimension in millimeters
W	Width of narrow section	6
L	Length of narrow section	33
WO	Width overall	19
LO	Length overall	115
G	Gage length	25
D	Distance between Grips	65
RO	Outer radius	25
R	Radius of fillet	65
RO	Outer radius	25

Figure 3.2 Dimension of tensile test specimens.

The specimens were mounted between the face of grips, they were held firmly to minimized slippage without crushing the ends. During this test, the test specimen is extended along its major longitudinal axis at constant speed until the specimen fractures. The mean value of five measurements was taken. Finally, the values of stress, strain and % elongation were calculated.

Figure 3.3 Tensile Testing Machine.

3.3.3 Differential Scanning Calorimetry (DSC)

Thermal and crystallization behavior of the specimens was investigated by Differential Scanning Calorimeter (Perkin-Elmer DSC 7). All measurements were conducted on predried samples under nitrogen atmosphere to minimize the possibility of moisture regain and consequent hydrolytic degradation. The samples underwent two heating/cooling cycles as follows:

- First heating from 60 to 280°C at 20°C·min^{-1}; keep for at least 5 min to eliminate effects of past thermal/mechanical history.
- First cooling by quenching to 60°C at 320 °C·min^{-1}
- Second heating from 60 to 280°C at 20°C·min^{-1}
- Second cooling at 20°C·min^{-1} to 60°C

The following data in °C, usually referring to first heating or second heating / cooling, are reported:

T_g glass transition temperature of polymer

T_{ch} temperature at which the maximum of the crystallization exotherm peak occurs in heating scan (cold crystallization)

T_{cc} temperature at which the maximum of the crystallization exotherm peak occurs in a cooling scan

Figure 3.4 Differential Scanning Calorimeter (DSC7)

T_m temperature at which the minimum of the melting endotherm peak occurs in heating scan

$\triangle T_c$ temperature spans between T_{cc} and T_{ch}

3.3.4 Intrinsic Viscosity Measurement

The determination of dilute solution viscosity provides one item of information toward to the molecular characterization of polymers. It is related to the composition and molecular weight of a polymer. Basically a measure of molecular size and not molecular weight, the dilute solution viscosity can be correlated appropriately with molecular weight or chain length only if there is a unique relationship between the mass and the size of the dissolved polymer molecules. For polymers meeting the restriction, empirical relationships can be developed between the dilute solution of a polymer and its hydrodynamic volume or average chain dimension.

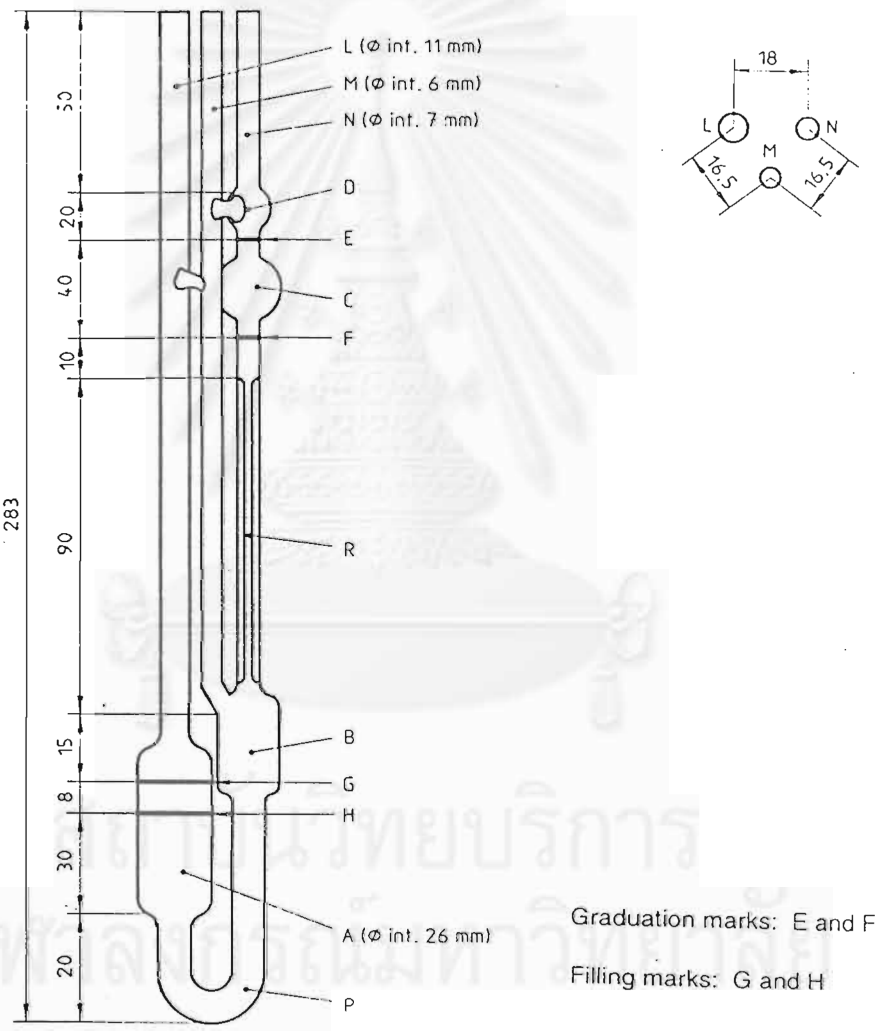
The intrinsic viscosity is determined by measuring the flow time of a solution (η_p) of known polymer concentration (C) and the flow time of the pure solvent (η_s) in a capillary viscometer at a fixed temperature. The intrinsic viscosity value (IV; $[\eta]$) derived from the average of the two intercepts by using the following standard equations:

$$\eta_{sp}/C = [\eta] + K'[\eta]^2 C \qquad \text{(Huggins equation)}$$

$$\ln \eta_r/C = [\eta] - K''[\eta]^2 C \qquad \text{(Kramer equation)}$$

Where $\eta_r = \eta_p / \eta_s$; $\eta_{sp} = \eta_r - 1$.

The measurement was performing according to ASTM D2857 and D4603-96. A mixture of phenol (60-wt%) and 1,1,2,2 tetrachloroethane (40-wt%) was used as a solvent to dissolve PET. The predried samples were accurately weighted, dissolved at concentrations, C, up to 1 g/dl, at temperature 80 °C for 30 minute while stirred. The solution was placed in a constant temperature bath preset at 30 °C for 10 minute when the samples have completely dissolved. The solution was poured into a clean, dry, Cannon ubbelohde viscometer through a funnel and filtered into the top of the larger viscometer tube. Suction was used to draw the solution through the capillary to a level above the top calibration mark. The flow time required for the liquid to fall back from the



Graduation marks: E and F

Filling marks: G and H

Figure 3.5 Ubbelohde viscometer.

higher calibration mark to lower calibration mark above the capillary was recorded. The measurement was repeated three more times and the results were averaged.

3.3.5 Shrinkage

Linear shrinkage was measured on injection-molded bars after annealing in a vacuum oven at 130 °C for 48 hours.

Chapter IV

Results and Discussion

4.1 Thermogravimetric Analysis of the Nucleating Agent

The TGA thermogram of sodium carbonate under nitrogen within the 60-300 °C temperature range is shown in Figure 4.1. Weight loss at 300 °C is only 0.05%. The result indicates that sodium carbonate has an excellent thermal stability above the estimated maximum processing temperature of PET attained in this study, without decomposition.

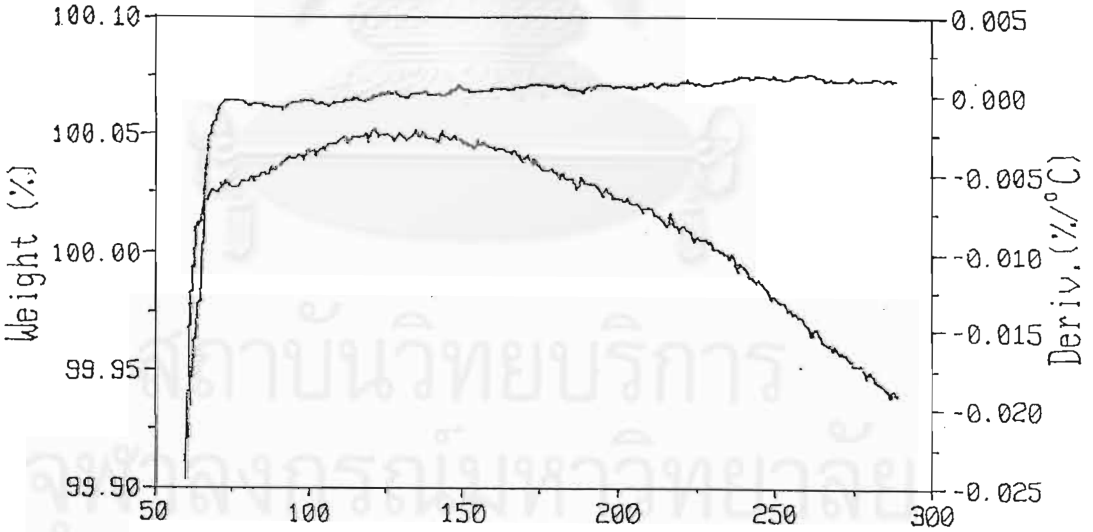


Figure 4.1 TGA study of sodium carbonate.

4.2 Tensile Testing

Tensile testing was performed on injection molded tensile bar. Tensile strength and % elongation at break were collected. Sample code used in this study is described in Table 3.2.

4.2.1 Tensile strength

Tensile strength obtained from the tensile testing is summarized in Table 4.2. According to Figure 4.2, the graph shows tensile strength of the PET blends without nucleating agent. Increasing of recycled PET performs the decrease of tensile strength.

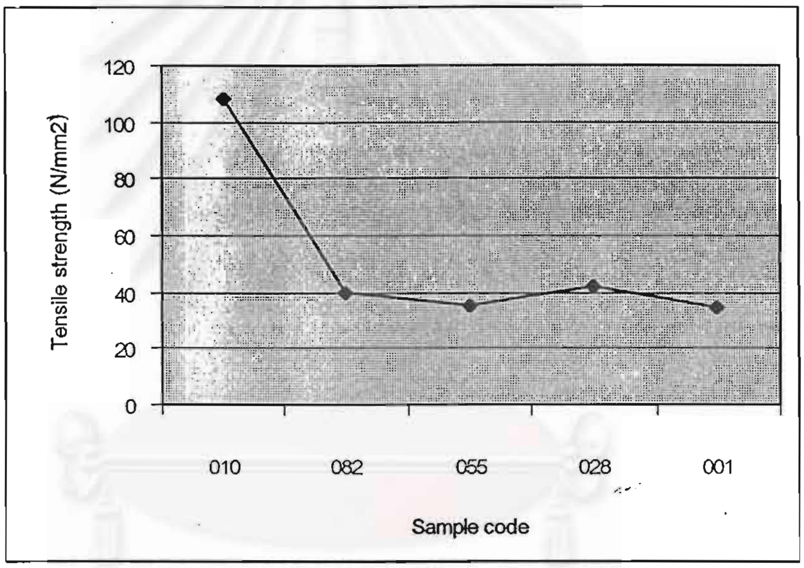


Figure 4.2 Tensile strength of the virgin and recycled PET blends without nucleating agent.

Figure 4.3 shows the tensile strength of virgin PET at various concentrations of nucleating agent. Tensile strength shows the decreasing trend in the direction of increasing concentration of nucleating agent. Since virgin PET used is PETG, which incorporated with co-monomers other than ethylene glycol (EG) and terephthalic acid (TPA) that disrupts the regularity of the PET chains, and changes crystallization behavior. Therefore, nucleating agent intervenes between molecular chain of PET and causes the decrement of tensile strength. In the 80:20 ratio of virgin and recycled PET

Table 4.1 Mechanical properties of the test specimens.

Mechanical properties of the test specimens		
Sample code	Tensile strength (N/mm^2)	Elongation at break (%)
010	107.66	40.976
110	46.29	13.286
310	26.186	7.6858
510	26.478	5.6594
710	20.286	5.0688
1010	21.334	4.3344
082	39.81	7.8136
182	30.516	9.4176
382	91.922	28.512
582	97.534	10.2112
782	45.874	8.592
1082	38.77	10.0322
055	35.406	7.0488
155	34.346	5.6024
355	101.12	23.456
555	105.5	23.244
755	29.23	7.9876
1055	18.678	7.6316
028	41.828	7.9526
128	36.246	8.4224
328	26.044	8.1982
528	44.458	12.064
728	32.434	11.8258
1028	21.556	5.636
001	34.452	9.2446
101	28.238	9.227
301	28.996	9.588
501	35.986	11.372
701	21.458	5.9532
1001	21.334	5.6328

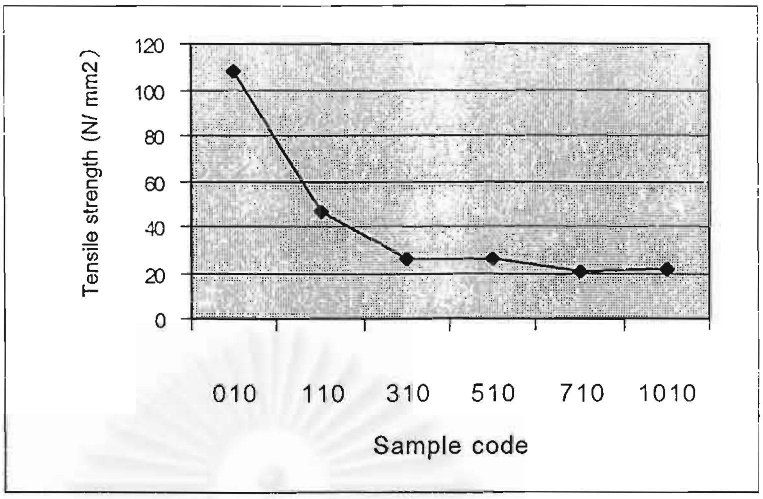


Figure 4.3 Tensile strength of virgin PET at various concentrations of nucleating agent.

blends (Figure 4.4), nucleating agent nucleates crystallite and causes the increment in the direction of increase in nucleating agent concentration up to 0.5 phr. In the samples with nucleating agent dope more than 0.5 phr, the excessed nucleating agent acts as defect in the structure of the resin so that tensile strength is decreased. The same trend can be seen in the ratio of 50:50 (Figure 4.5), 20:80 (Figure 4.6), and 0:100 (Figure 4.7) of virgin and recycled PET.

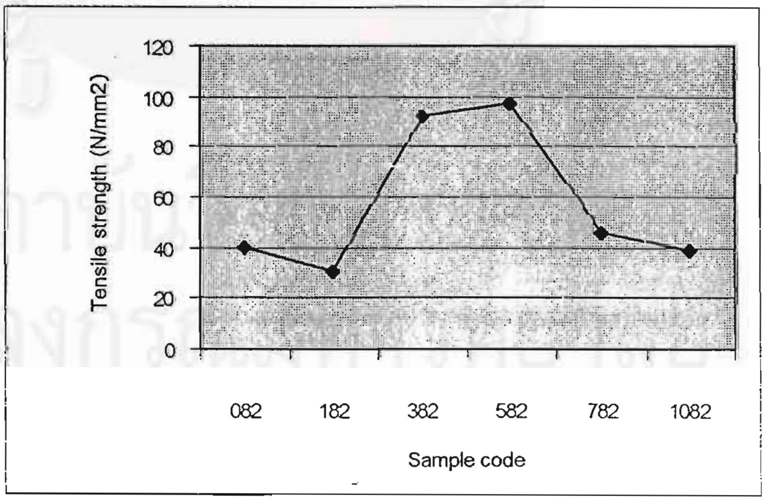


Figure 4.4 Tensile strength of 80:20 virgin and recycled PET blends at various concentrations of nucleating agent.

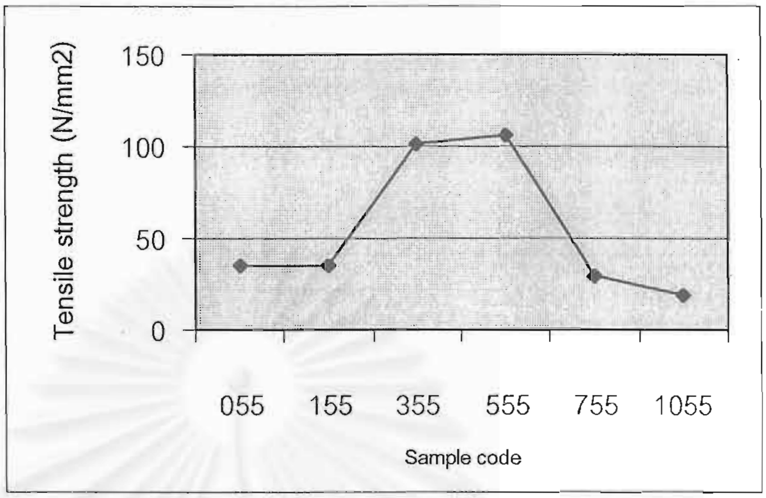


Figure 4.5 Tensile strength of 50:50 virgin and recycled PET blends at various concentrations of nucleating agent.

From Table 4.1, the PET blends of virgin and recycled in the ratio of 80:20 and 50:50 with 0.3 phr and 0.5 phr nucleating agent show insignificant different values of tensile strength (91.922, 97.534, 101.12, and 105.5, respectively) comparing to the virgin PET without nucleating agent (107.66). It means that, the component of recycled

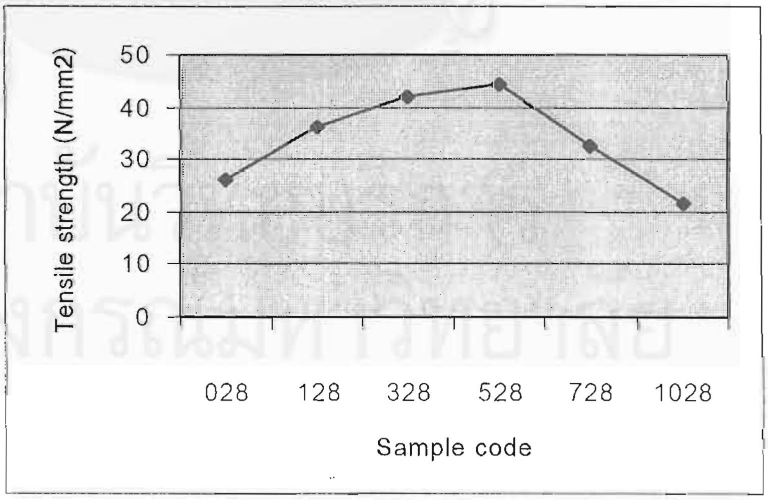


Figure 4.6 Tensile strength of 20:80 virgin and recycled PET blends at various concentrations of nucleating agent.

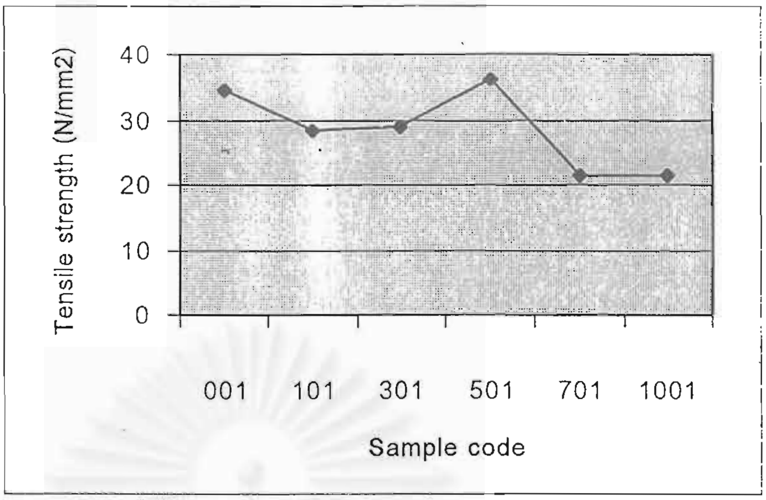


Figure 4.7 Tensile strength of recycled PET at various concentrations of nucleating agent.

PET up to 0.5 phr, nucleating agent can improve tensile strength properties to the value near as of virgin PET. This is dues to crystalline morphology and gradient of morphology, which was induced by nucleating agent.

% Elongation at break

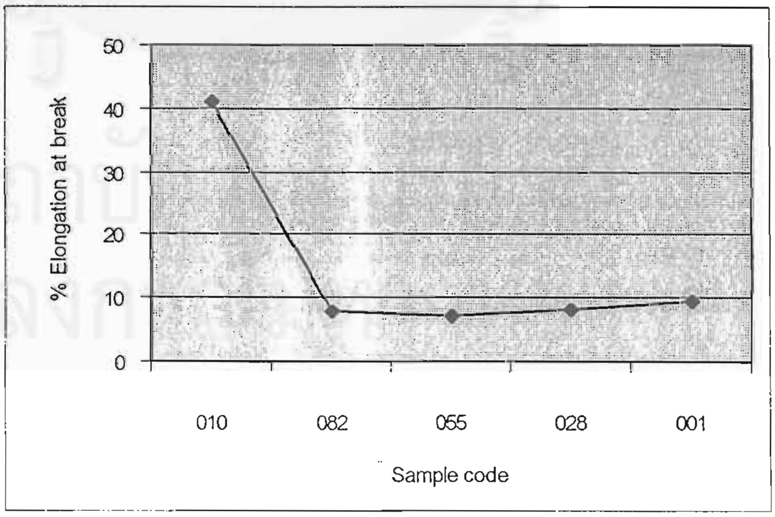


Figure 4.8 % Elongation at break of virgin and recycled PET blends without nucleating agent.

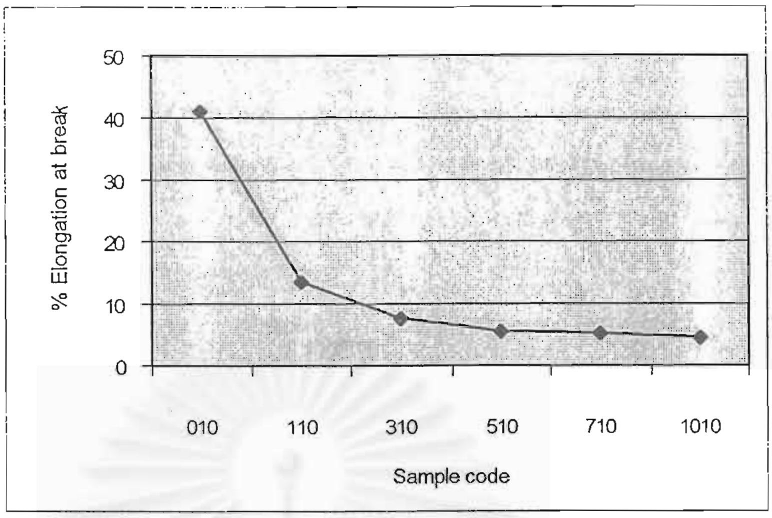


Figure 4.9 %Elongation of virgin PET at various concentrations of nucleating agent.

% Elongation at break measured from tensile testing is summarized in Table 4.2 According to Figure 4.8, the graph shows %elongation at break of the PET blends without nucleating agent. Increasing of recycled PET performs the decrease %elongation at break.

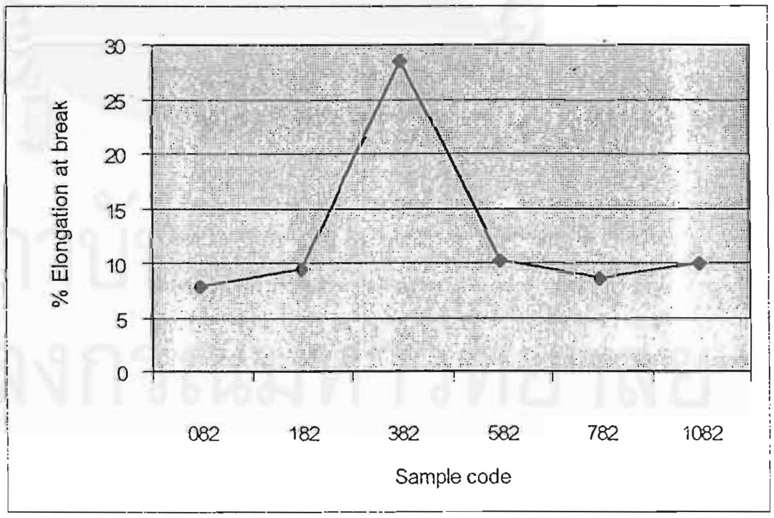


Figure 4.10 %Elongation at break of 80:20 virgin and recycled PET blends at various concentrations of nucleating agent.

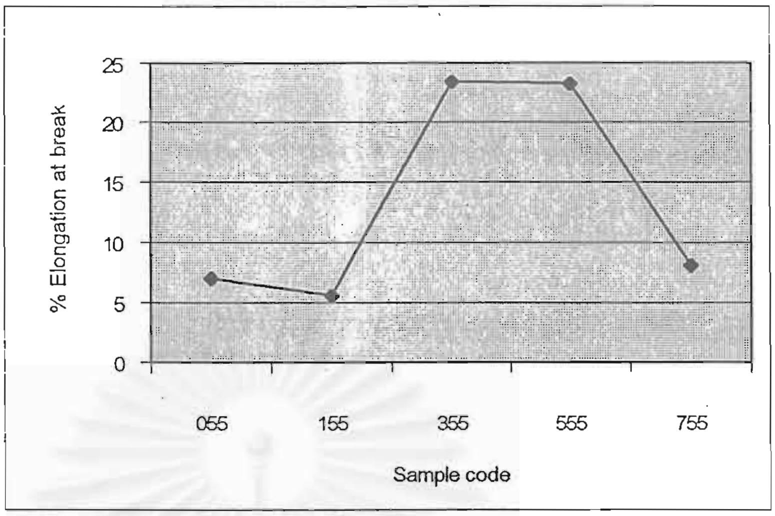


Figure 4.11 %Elongation at break of 50:50 virgin and recycled PET blends at various concentrations of nucleating agent.

Figure 4.9 shows %elongation at break of virgin at various concentration of nucleating agent. %elongation at break shows the decreasing trends in the direction of increasing concentration of nucleating agent . In the 80:20 ratio of virgin and recycled PET blend (Figure 4.10), nucleating agent nucleates crystallite and causes the

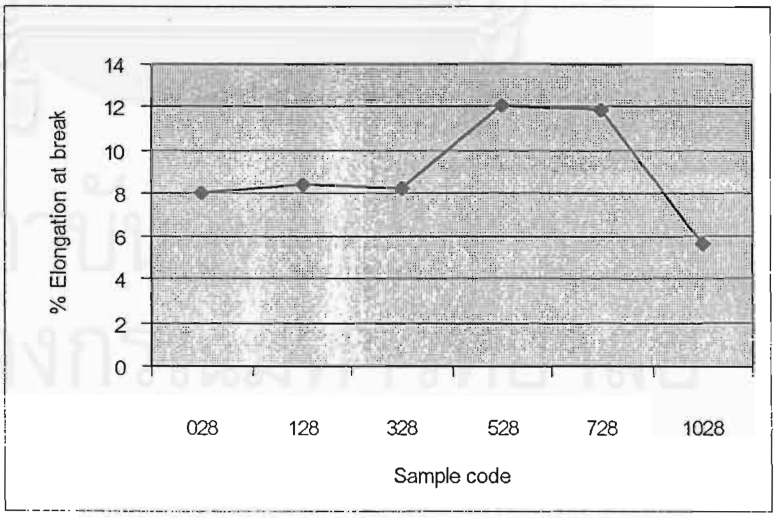


Figure 4.12 %Elongation at break of 20:80 virgin and recycled PET blends at various concentrations of nucleating agent.

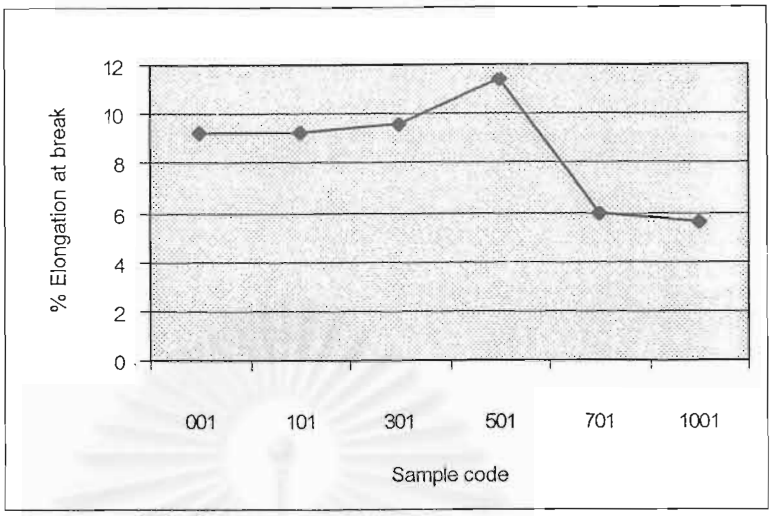


Figure 4.13 %Elongation at break of recycled PET at various concentrations of nucleating agent.

increment in the direction of increased nucleating agent concentration up to 0.3 phr. In the samples with nucleating agent concentration more than 0.3 phr, the excessed nucleating agent acts as defect in the structure of the resin so that %elongation at break is decreased. In the 50:50 ratio of virgin and recycled PET blend (Figure 4.11) the increment of %elongation at break appears up to 0.5 phr of nucleating agent concentration. In the sample with nucleating agent concentration more than 0.5 phr, %elongation at break decrease with increased nucleating agent concentration. The same trends also occur in the 20:80 and 0:100 ratio of virgin and recycled PET blend (Figure 4.12 – 4.13).

The PET blends of virgin and recycled PET in the ratio of 80:20 with 0.3 phr of nucleating agent concentration, and the ratio of 50:50 with 0.3 and 0.5 phr of nucleating agent concentration show the high values of %elongation at break (28.512, 23.456, and 23.244, respectively) as shown in Table 4.2.

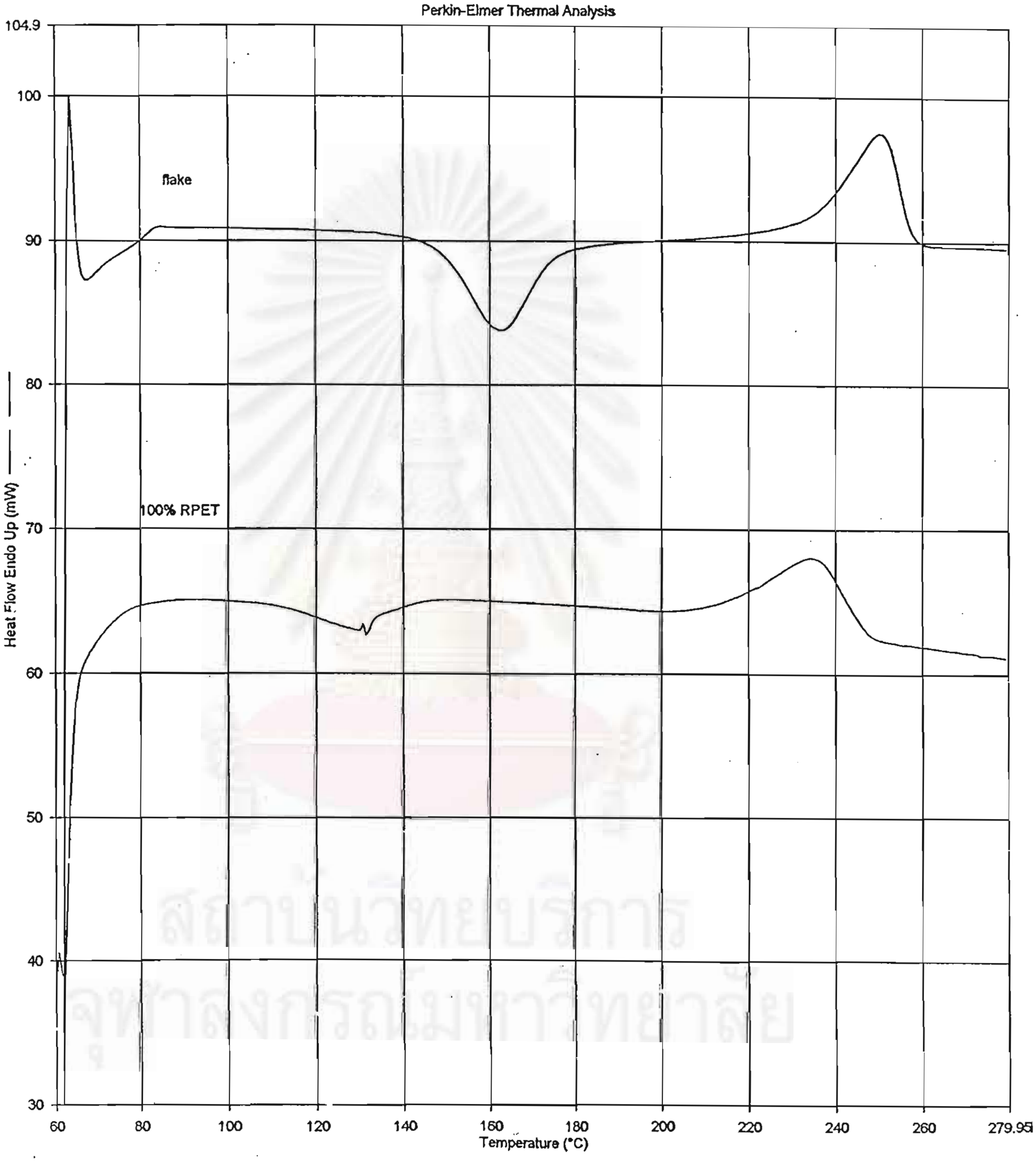


Figure 4.14 DSC heating scan curves of flake and injection molded recycled PET.

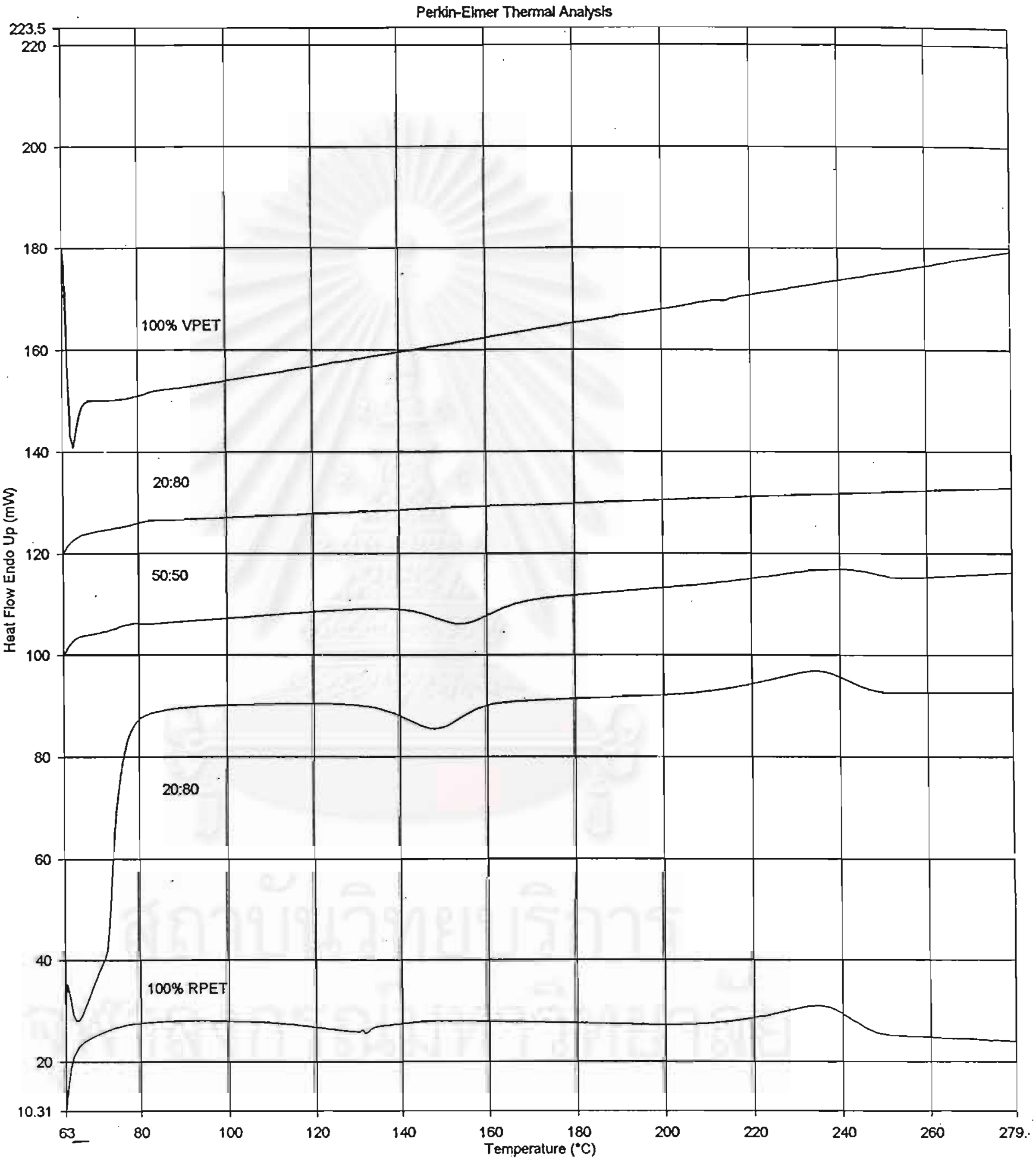


Figure 4.15 DSC heating scan curves of virgin and recycled PET blends without nucleating agent.

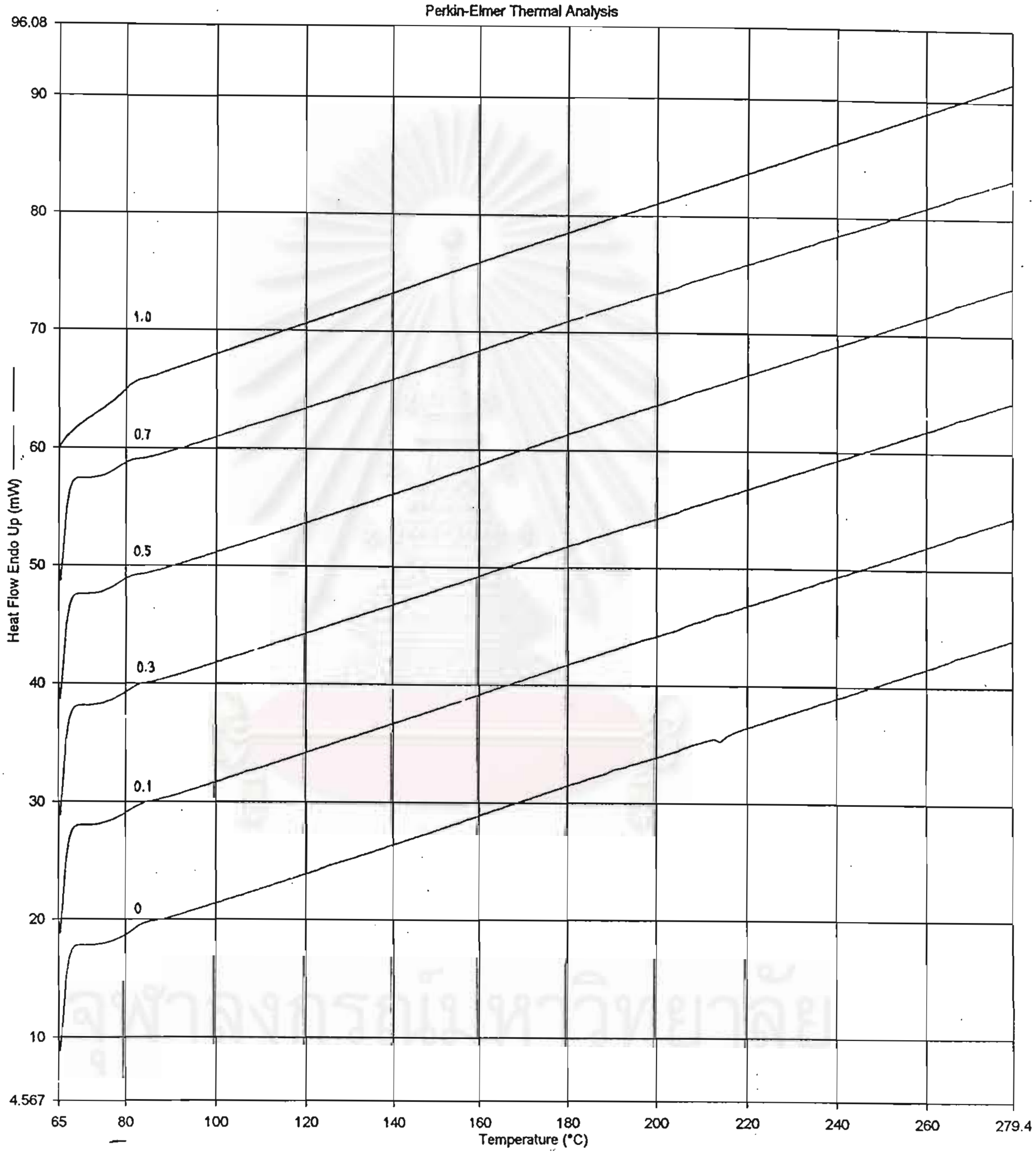


Figure 4.16 DSC heating scan curves of virgin PET at various concentrations of nucleating agent.

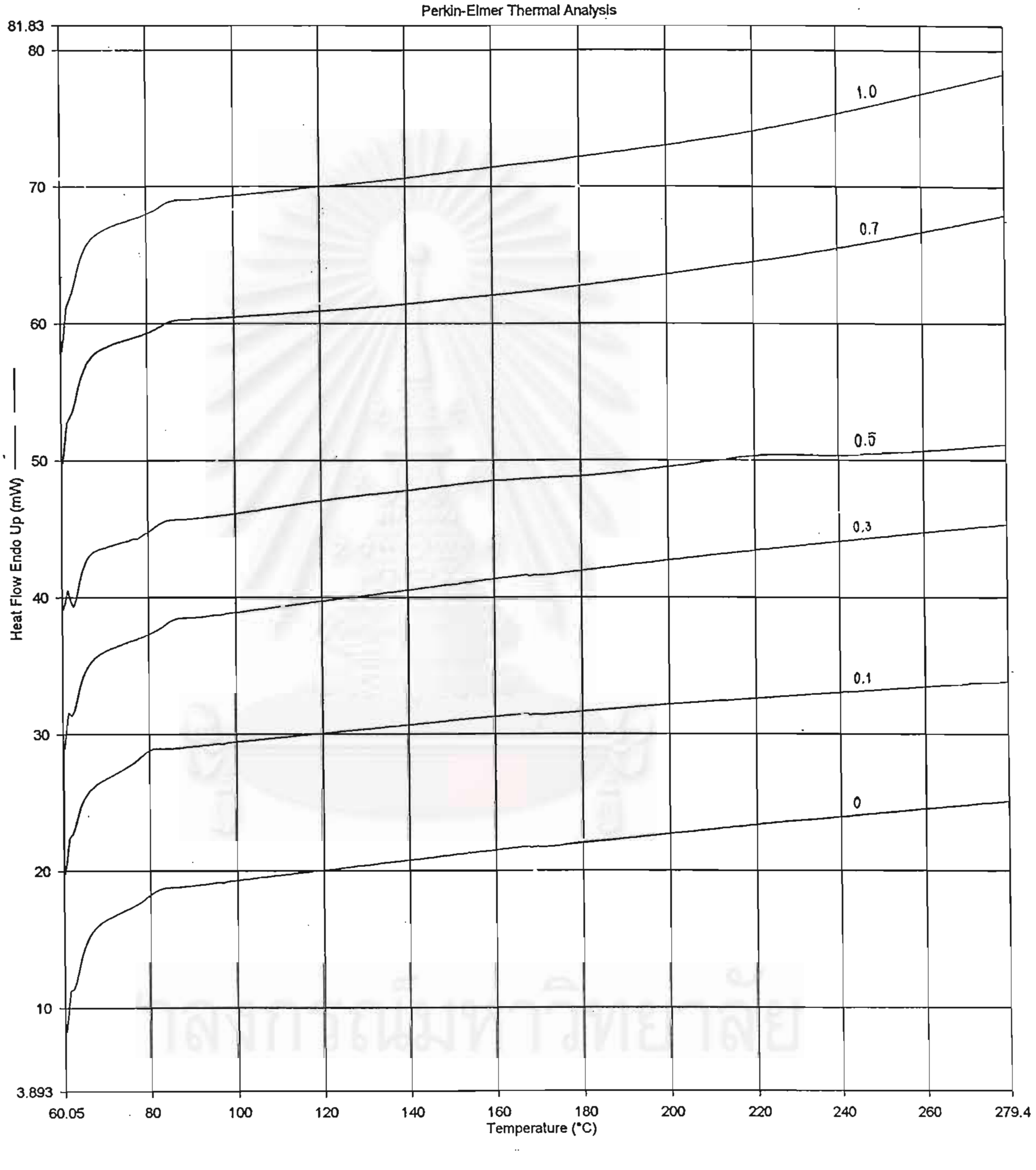


Figure 4.17 DSC heating scan curves of 80:20 virgin and recycled PET blends at various concentrations of nucleating agent.

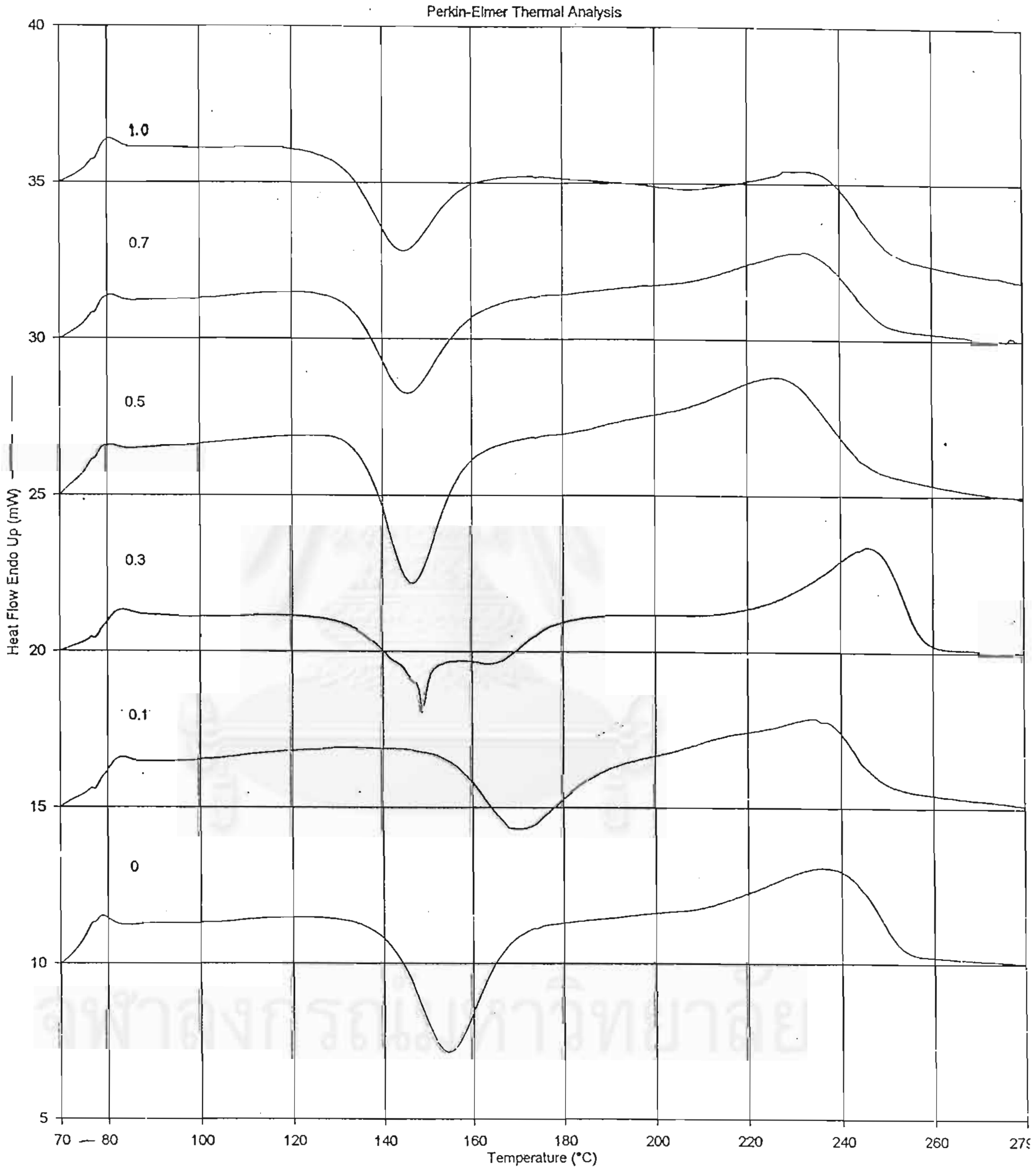


Figure 4.18 DSC heating scan curves of 50:50 virgin and recycled PET blends at various concentrations of nucleating agent.

1028

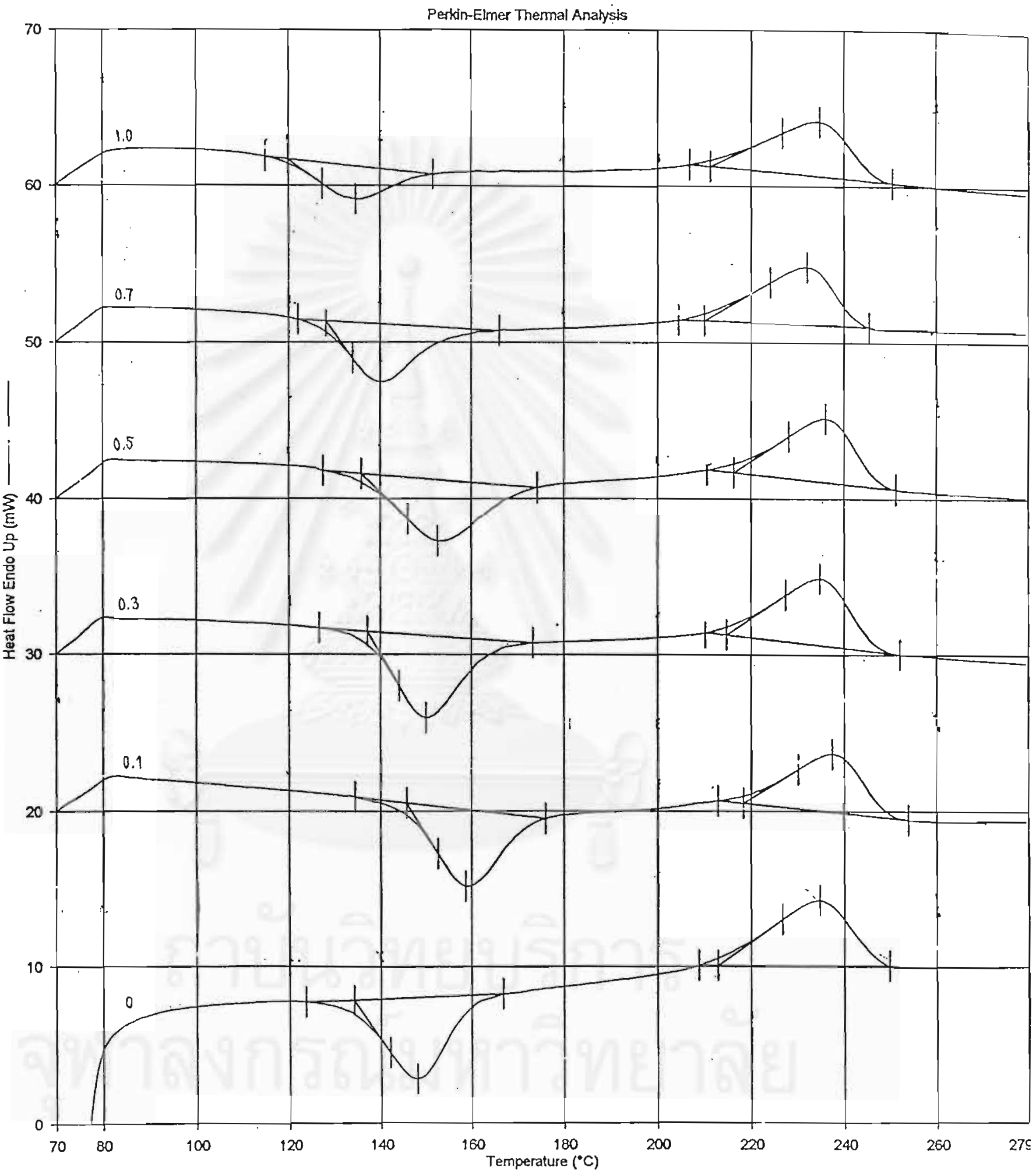


Figure 4.19 DSC heating scan curves of 20:80 virgin and recycled PET blends at various concentrations of nucleating agent.

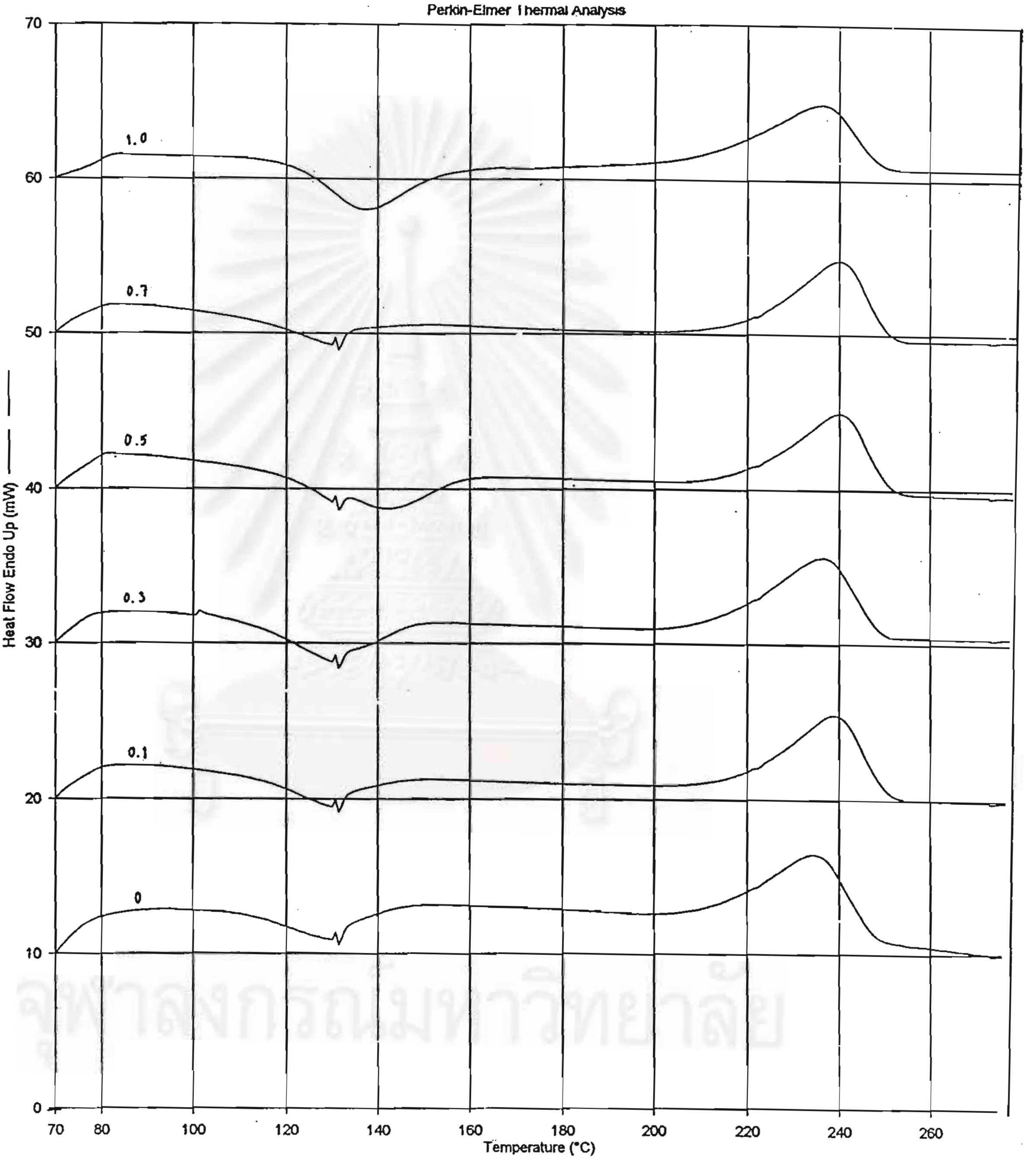


Figure 4.20 DSC heating scan curves of recycled PET at various concentrations of nucleating agent.

Table 4.2 Non-isothermal DSC transitions of the test specimens.

Sample	Tg	Tch	Tcc	ΔTc	Tm	Hm	Hc	%crystallinity
As received virgin PET	85.374							
Flake	81.485	162.716	163.283	0.567	234.282	27.847	-27.767	46.345
001	63.387	131.383	177.950	46.567	214.579	28.150	-28.842	47.493
101	63.889	131.383	181.950	50.567	218.944	26.953	-28.071	45.853
301	63.214	131.383	179.283	47.900	214.750	31.722	-30.175	51.581
501	64.287	131.383	177.283	45.900	219.386	27.944	-27.864	46.507
701	64.663	131.383	183.283	51.900	219.718	24.418	-24.682	40.917
1001	65.243	137.383	175.283	37.900	213.187	22.285	-19.316	34.668
028	73.846	148.050	173.950	25.900	212.842	22.546	-22.633	37.649
128	73.259	158.716	168.616	9.900	218.284	17.318	-20.667	31.654
328	76.074	150.050	162.616	12.566	214.726	21.144	-23.709	37.378
528	77.903	152.716	165.283	12.567	216.302	18.744	-19.817	32.134
728	75.967	140.050	161.950	21.900	209.935	19.982	-17.920	31.585
1028	72.813	134.716	169.283	34.567	211.203	19.512	-9.929	24.534
055	76.631	154.716	160.616	5.900	212.772	12.742	-18.898	26.367
155	81.005	170.716	149.950	-20.766	200.882	-15.395	-6.465	-7.442
355	80.607	148.716	165.283	16.567	225.338	15.239	-16.375	26.345
555	78.136	146.716	154.616	7.900	203.051	13.809	-18.674	27.069
755	78.436	145.383	159.950	14.567	206.350	13.660	-17.545	26.004
1055	78.274	144.716	161.950	17.234	216.466	12.669	-11.479	20.123
082	81.070							
182	79.022							
382	84.872							
582	78.339							
782	84.258							
1082	83.999							
010	81.533							
110	79.234							
310	80.976							
510	78.752							
710	78.470							
1010	72.885							

4.3 Differential Scanning Calorimetric Analysis

Table 4.3 summarizes the information obtained from non-isothermal DSC scans on quenched samples during the first cooling with the various PET materials. The materials are virgin PET, flake (crushed PET bottles), recycled PET and the blends with and without nucleating agent. Figure 4.14 - 4.20 show the DSC thermograms of heating scan. Figure 4.26-4.30 shows the DSC thermograms of cooling scan. The Figures perform the concentrations of nucleating agent increase from bottom to top of the diagram. In virgin PET with various concentrations of nucleating agent, and virgin and recycled 80:20 blend ratio, the DSC thermograms are not shown crystallization peak and melting peak. That is because PETG is used. PETG is totally amorphous; therefore, it is not shows characteristics of crystalline phase, Tc and Tm.

4.2.1 heating Scan

Glass transition temperature (Tg) of PETs

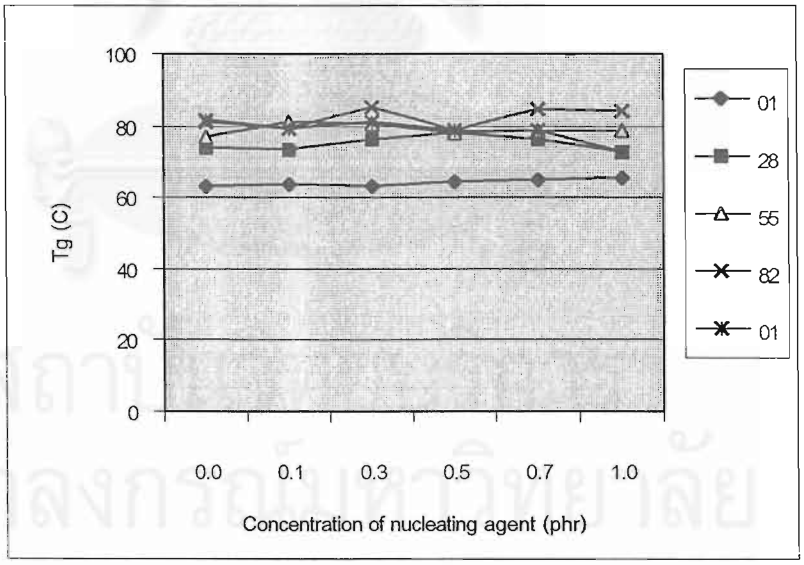


Figure 4.21 The glass transition temperatures of the test specimens

From Figure 4.14, injection molded recycled PET shows lower Tg than flake because recycled PET are subjected to more thermal treatments. This is understandable because the more thermal cycles that the sample endured presumably causes the more reduction in MW. That results in higher mobility of the PET segments. From Figure 4.21, the specimens of PET blends with no nucleating agent show lower Tg with percents of recycled increased, as expected.

The PET with nucleating agent shows lower Tg than the PET without nucleating agent.

The crystallization temperature (T_{ch}) of PETs

The DSC heating thermogram study indicates the lowering of temperature at which crystallization begins to appear. As shown in Table 4.3, Tch value was 162 °C for recycled PET flake decreased to 131 °C for injection molded recycled PET sample. This is quit related to the thermal cycles that the samples endured, means that the recycled PET can crystallize more readily than the less thermal cycles samples. In the virgin and recycled PET blends, the decreasing trend is also observed, as shown in Figure 4.22. The recycled PET and its blends begin to crystallize easier in the lower temperature in the heating cycles.

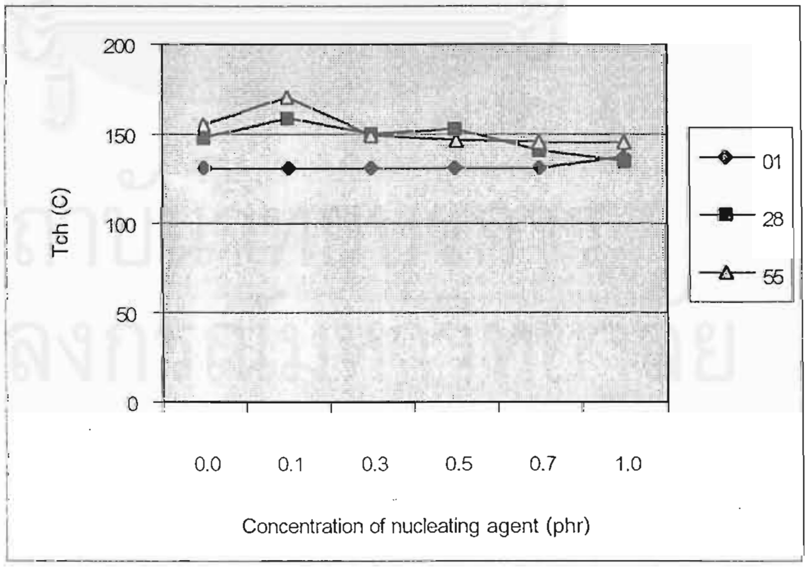


Figure 4.22 The crystallization temperature of the test specimens; heating scans

According to the previous text, decrease of Tch is not due to severe incision of the molecular chain present in the materials. The molecule threads protruding from entanglements are attacked first and break off during the thermal recycling process. This thermal cycling process releases the entanglement and increases the crystallinity. With this mild thermal degradation, recycled PET is in better condition for the crystallization and the less amorphous segment is retained.

In the samples with nucleating agent, the decreasing trends with increase concentration of nucleating agent are observed. This is caused by nucleating agent nucleates crystallite that eases the crystallization process.

The melting temperature (Tm) of PETs

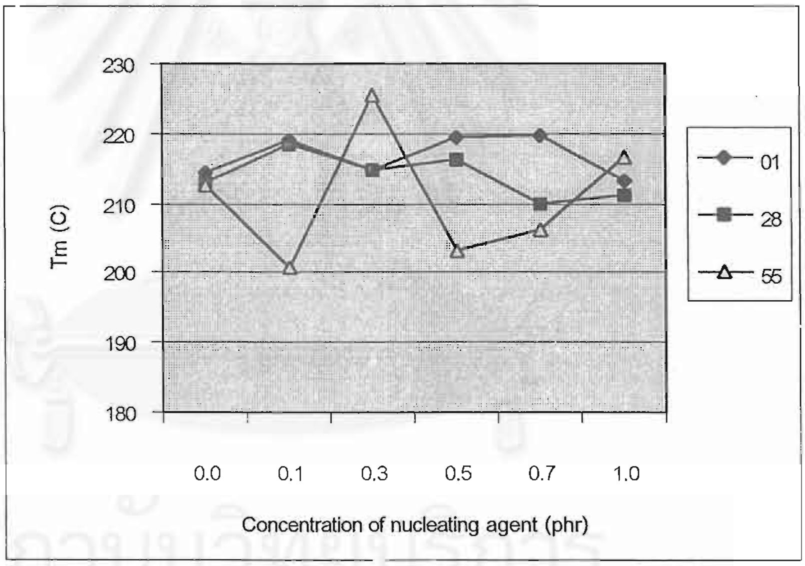


Figure 4.23 The melting temperature of the test specimens.

Figure 4.23 shows the melting temperature of various PET specimens. Tm decreases in the direction of the ratio of recycled PET increased. In the samples with nucleating agent, it can be seen that nucleating agent effects to increase Tm compared to the samples without nucleating agent. In the other words, nucleating agent help the polymer to improve its heat stability. Virgin and recycled PET blend at the ratio of 50:50 with 0.3% nucleating agent shows the highest Tm as shown in Figure 4.23.

The increment of Tm can be described by Equation 7. The recycled PET was through the recycling process and has the lower Tc threshold temperature, the interfacial free energy of the recycled could be decrease and the crystalline thickness (l) may be increased as the term of ($2\delta e / \Delta H_v \times l$) becomes smaller. The overall effects may lead the crystalline structure to become thicker with less interfacial free energy. As a result of the thickening effect on the increasing of the crystalline size formation, a more orderly structure and a higher Tm occurs.

4.3.2 The cooling scan

The crystallization temperature (Tcc)

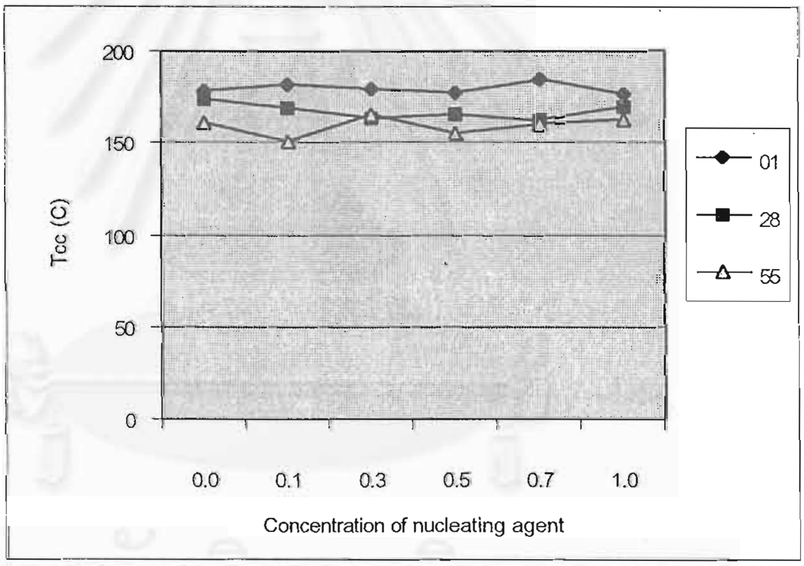


Figure 4.24 The crystallization temperature of the test specimens; cooling scan.

DSC curves obtained form the cooling cycled of the PET specimens were shown in Figure 4.23 The crystallization temperature from the cooling scan (Tcc) is mostly affected by molecular mobility. In the other words, Tcc increase with crystallization rate increase. As shown in Figure 4.24, Tcc of the blends increases when recycled PET component increased. In all samples with nucleating agent, the highest value of Tcc appears at 0.3 phr of nucleating agent.

Temperature spans between crystallization temperature in heating and cooling scan

In general, the crystallization rate should be improved with additive, which increase value of Tcc or lower the value of Tch. So for the most effective nucleating agent, ΔTc should be the largest as possible. In all blend ratios, 100% recycled PET shows the highest ΔTc values, which decrease with recycled PET component decreased (Figure 4.25).

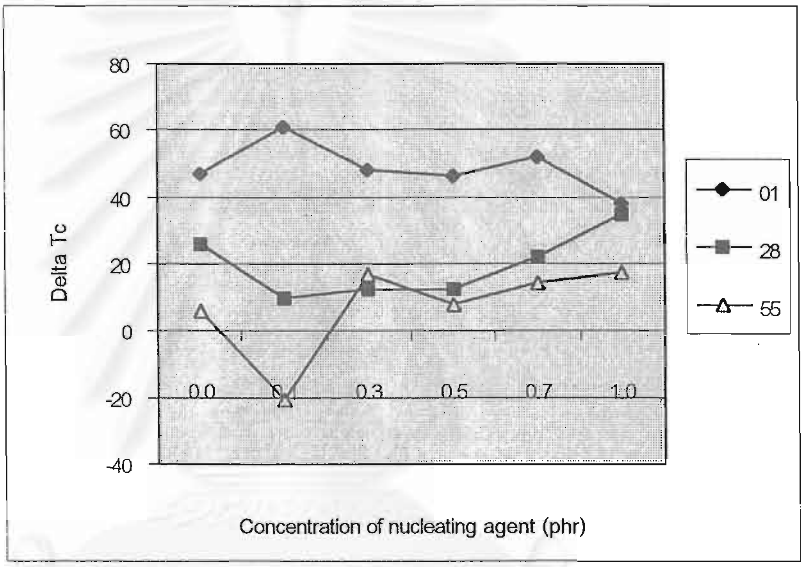


Figure 4.25 The temperature spans between the crystallization temperature of heating and cooling scan.

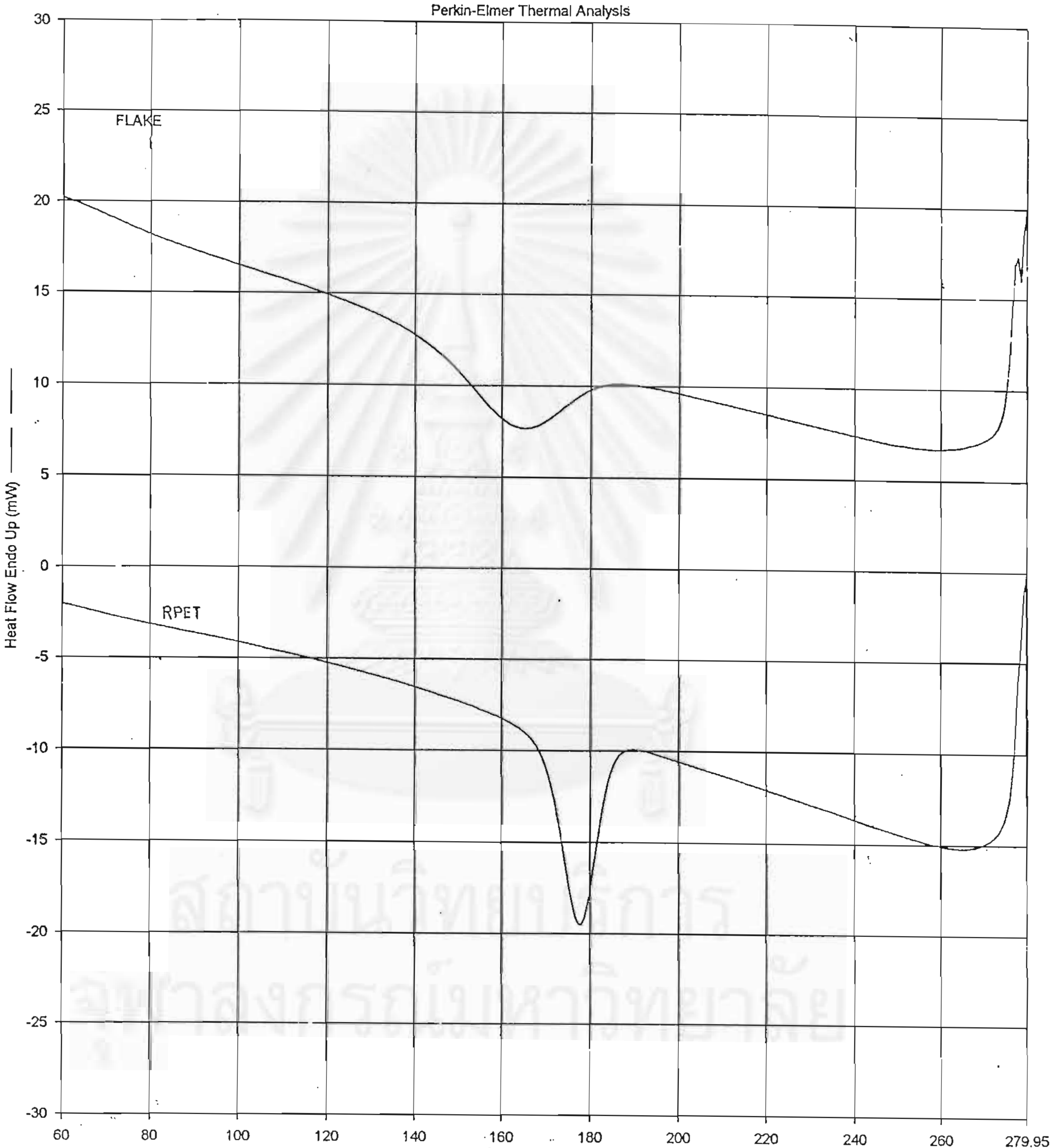


Figure 4.26 DSC cooling scan curves of flake and injection molded recycled PET .

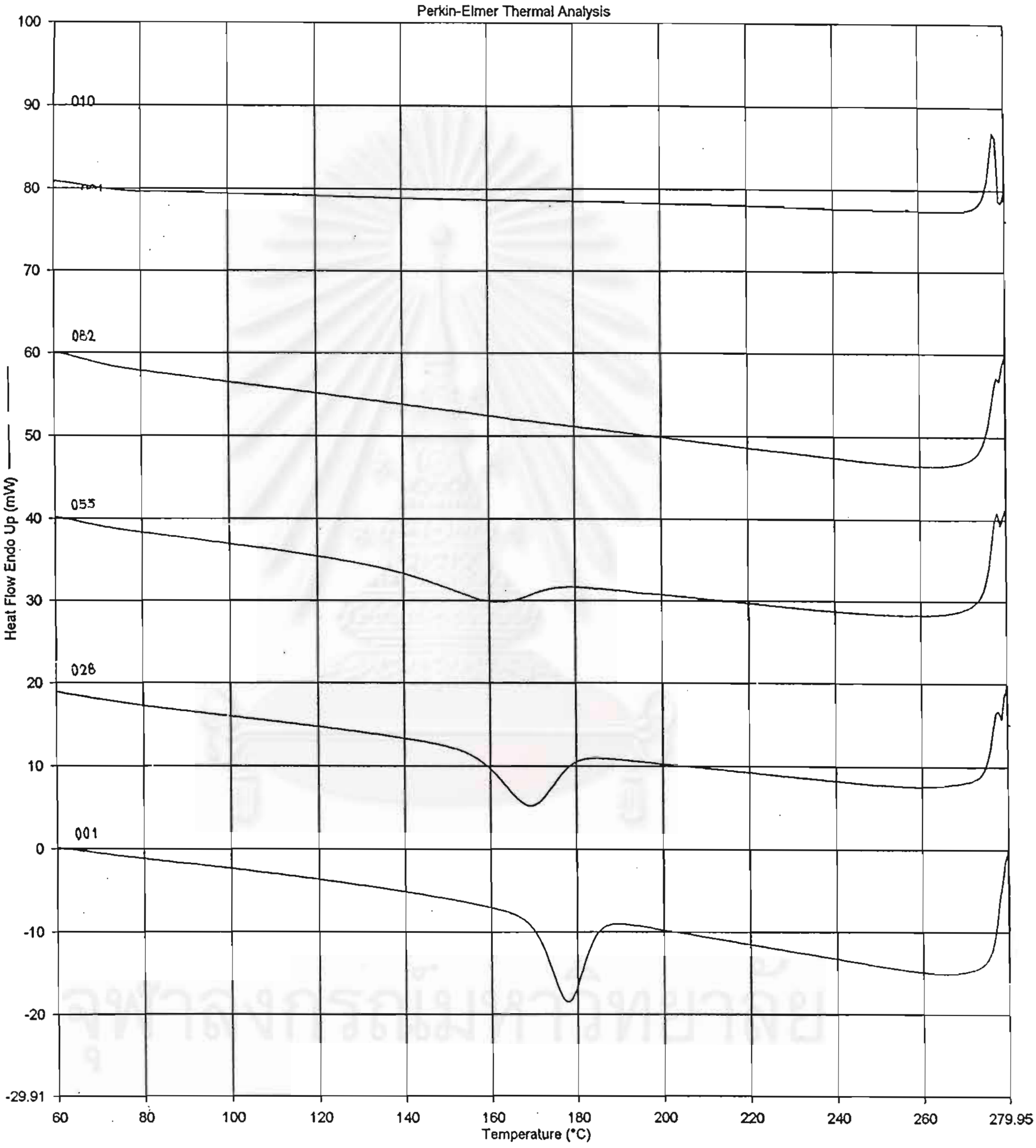


Figure 4.27 DSC cooling scan curves of virgin and recycled PET blends without nucleating agent.

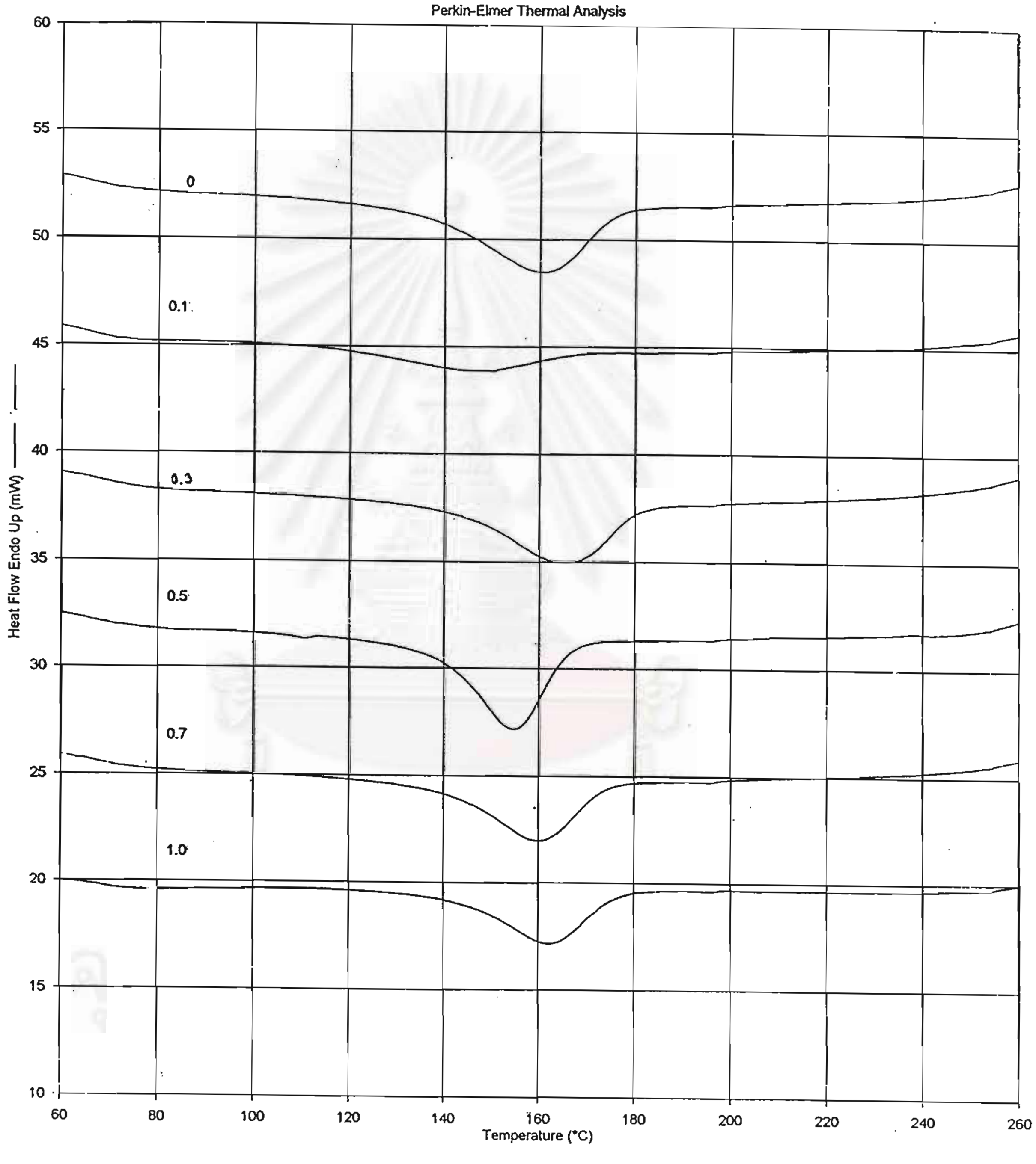


Figure 4.28 DSC cooling scan curves of 50:50 virgin and recycled PET blends at various concentrations of nucleating agent

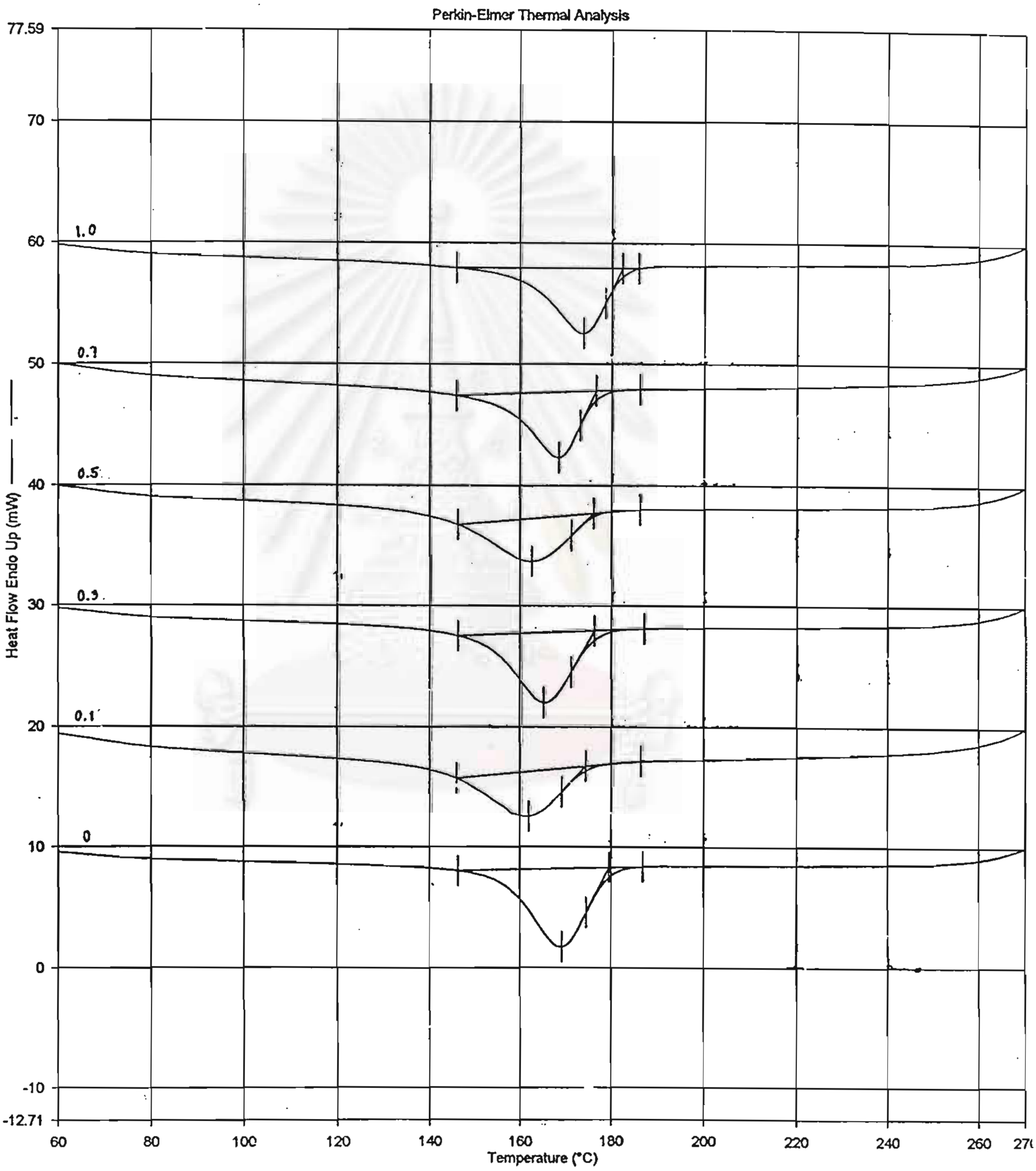


Figure 4.29 DSC cooling scan curves of 20:80 virgin and recycled PET blends at various concentrations of nucleating agent

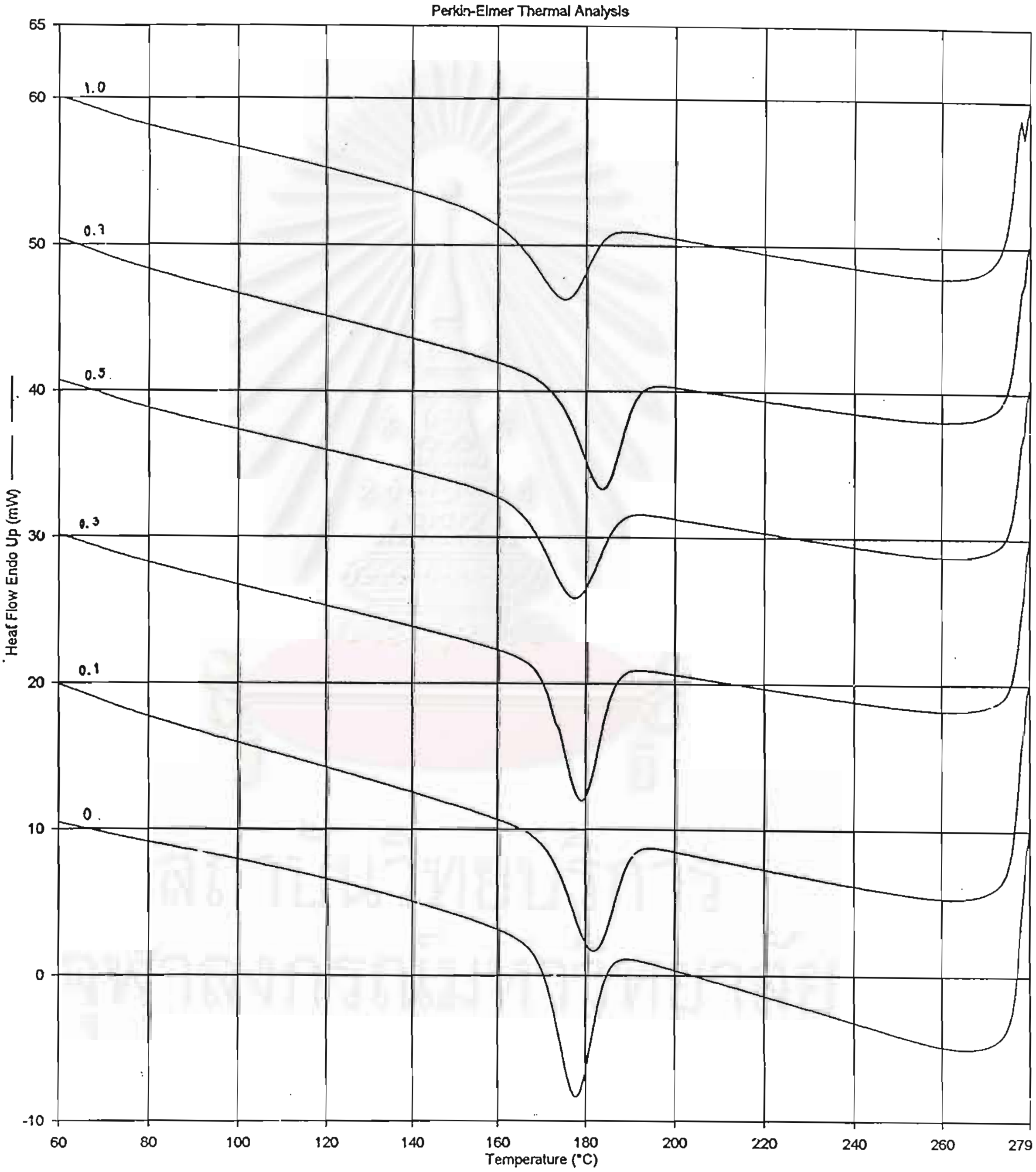


Figure 4.30 DSC cooling scan curves of recycled PET at various concentrations of nucleating agent

4.3.3 Percents crystallinity of the PETs

As shown in Figure 31, 100% recycled PET shows the highest % crystallinity compared to that of the other blended samples.

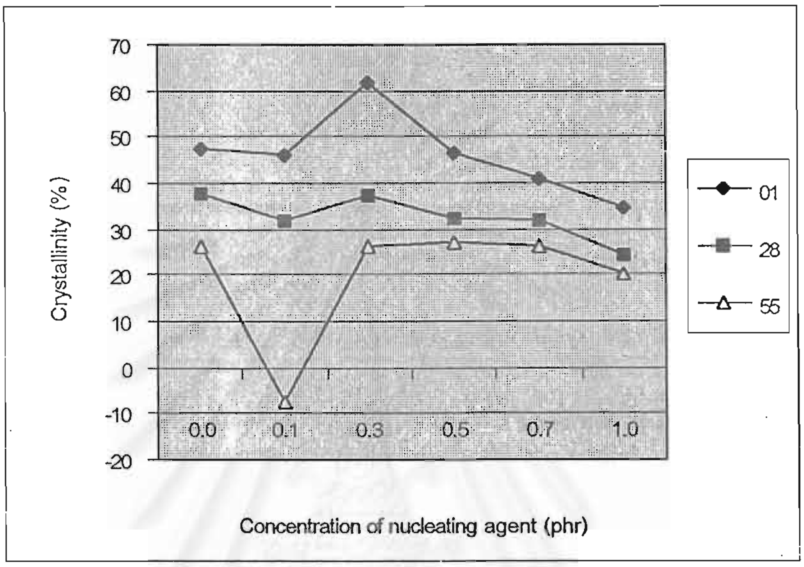


Figure 4.31 % Crystallinity of the test specimens.

In the samples with nucleating agent, the highest % crystallinity appears at 0.3 phr nucleating agent in all blend ratios. These mean that 0.3% of nucleating agent is the most efficiency concentration to induce the crystallization which results in the improvement of properties of recycled PET blends.

4.4 Shrinkage

Dimensional shrinkage of the test specimens in the direction of parallel to the flow

Table 4.5 summarizes dimensional shrinkage of the test specimens in the direction of the flow. In the samples without nucleating agent, %shrinkage increase when recycled PET component increased. While annealing, recycled PET, which can be readily crystallizes, recrystallizes to perform a better spherulite. Thus recycled PET causes more shrinkage compared to virgin PET. Dimensional shrinkage of injection

Table 4.3 % Shrinkage of the test specimens.

% Shrinkage		
Sample code	Parallel direction	Perpendicular direction
010	7.446	0.007
110	5.988	3.539
310	0.765	2.703
510	1.461	0.607
710	0.476	3.496
1010	0.451	2.102
082	3.29	3.685
182	2.644	5.268
382	2.648	3.525
582	1.565	3.401
782	0.619	3.751
1082	2.371	3.484
055	3.071	5.156
155	2.581	1.28
355	3.778	2.231
555	3.366	2.52
755	2.210	1.277
1055	5.729	2.001
028	2.343	2.777
128	3.034	1.452
328	1.592	1.463
528	2.995	1.775
728	3.588	2.26
1028	2.850	1.433
001	6.383	2.862
101	2.292	2.279
301	2.141	2.445
501	1.925	1.164
701	0.833	2.73
1001	4.416	2.681

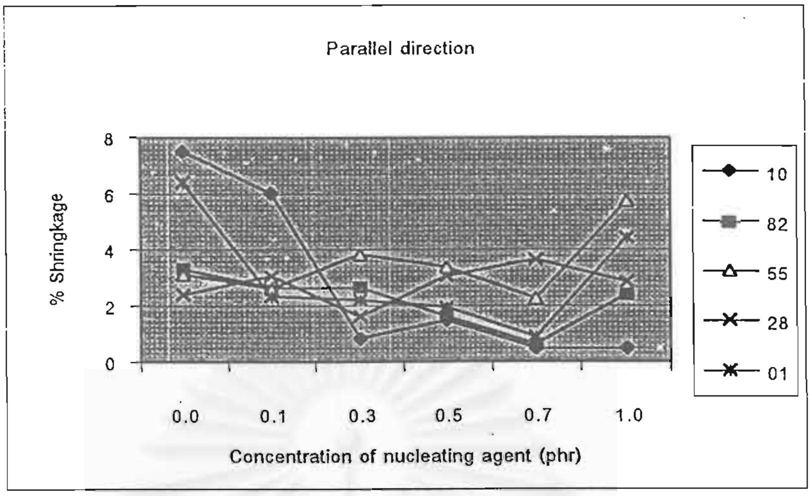


Figure 4.32 %shrinkage in the direction of parallel to the flow.

molded recycled PET bar containing nucleating agent appeared to lower than that of recycled PET bar without nucleating agent. These can be correlated to the increased crystallinity, which was induced by nucleating agent.

Dimensional shrinkage of the test specimens in the direction perpendicular to the flow

Dimensional shrinkage of the test specimens in the direction perpendicular to the flow is summarized in Table 4.6. The samples with nucleating agent show lower percents of shrinkage than the sample without nucleating agent.

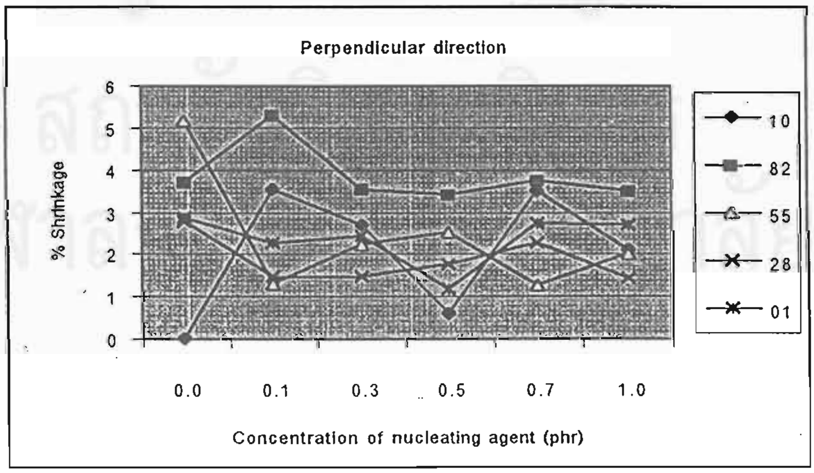


Figure 4.33 %shrinkage in the direction of perpendicular to the flow.

4.5 Intrinsic viscosity

Values for the intrinsic viscosity (IV) of virgin PET, recycled PET, and the blends are shown in Table 4.4. Increasing Sodium carbonate concentration is shown to result in lower IV values with the highest reduction at 0.5 phr of sodium carbonate in the ratio of 50:50 virgin and recycled PET blend.

Table 4.4 Intrinsic viscosity of the injection-molded specimens.

Formula	010	382	582	355	555	001
η	0.6359	0.5490	0.5328	0.5241	0.4690	0.2779

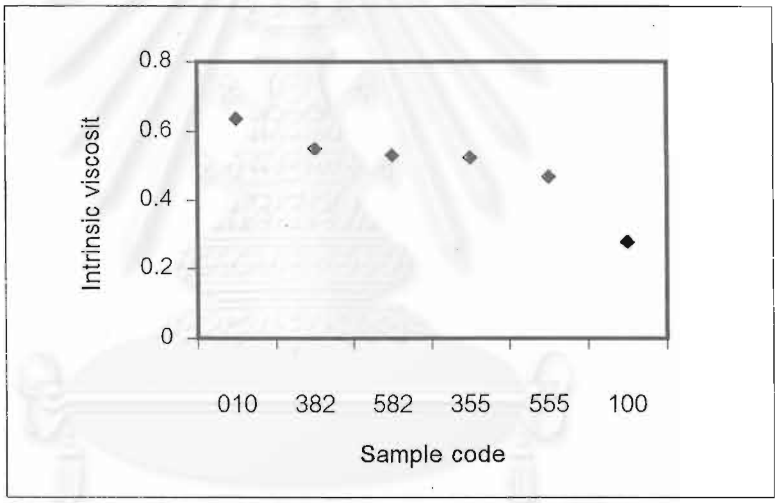


Figure 4.34 Intrinsic viscosity of the injection-molded specimens.

Chapter V

Conclusions

1. Virgin and recycled PET blends in the ratio of 80:20 and 50:50 with concentrations of nucleating agent 0.3 and 0.5 phr show good tensile strength, which is comparable to the virgin PET.
2. Virgin and recycled PET blends in the ratio of 80:20 and 50:50 with concentrations of nucleating agent 0.3 and 0.5 phr show high % elongation at break, which is comparable to virgin PET.
3. In theory, efficient nucleating agent would result in a high value of the crystallization temperature (in the cooling scan) as close as possible to the melting temperature. From DSC study, it was found that sodium carbonate shows the great efficiency at a concentration of 0.3 phr in 50:50 virgin and recycled PET blend.
4. Sodium carbonate causes the decrease in intrinsic viscosity. The highest decrement appears at the concentration of 0.3 phr in 50:50 virgin and recycled PET blend.
5. Nucleating agent has an effect to lower the % shrinkage. With the addition of the nucleating agent, the % shrinkage appears in the range of 1-2 %.
6. According to above results, 0.3 phr of sodium carbonate in 50:50 virgin and recycled PET blend is the appropriate formula for improving the mechanical properties of recycled PET for injection molding.

Chapter VI

Recommendation

1. Results indicate that nucleating agent can improve the crystallinity of PET blends, it will be useful to study the morphology of crystallite induced.
2. Virgin PET used in this study was PETG, which is 100% amorphous. If PETA is used to blend with recycled PET, crystallization behavior may be changed.

References

1. Prasad, P.N. Science and Technology of Polymers and Advanced Materials. New York : Plenum Press, 1988.
2. Berins, M.L. Plastics Engineering Handbook of the Society of the Plastics Industry Inc. SPi. 5 ed. New York : Chapman&Hall, 1974.
3. Hanlon, J.F. Handbook of Package Engineering. 2 ed. New York : McGraw-Hill, 1984.
4. Dux, J.P. Polyester Fibers. Chemical and Process Technology Encyclopedia. New York : Plenum Press, 1998.
5. Harper, C.A. ed. In chief. Handbook of Plastics, Elastomers, and Composites. 3 ed. New York : McGraw-Hill, 1996.
6. Seheirs, J. Polymer Recycling Science, Technology and Application. London : John Wiley&Sons, 1998.
7. Sauer, J.A., and Pae, K.D. Introduction to Polymer Science and Technology . New York : John Wiley&Sons, 1977.
8. Gauchter, R., and Muller, H. Plastics Additives Handbook. 4 ed. Munich : Hanser Publisher, 1993.
9. Saunder, J.H. Encyclopedia of Materials Science and Engineering. Vol. 5. New York : Pergamon Press, 1986.
10. Brandy, G.S., and Clauser, H.R. Materials Handbook. 11 ed. New York : McGraw-Hill, 1977.
11. Young, R.J., and Lovell, P.A. Introduction to Polymers. 2 ed. London : Chapman&Hall, 1991.
12. Lewis, R.J. Hazardous Chemical. 3 ed. New York : Van Nostrand Reinhold, 1993.
13. Barham, V.F. Closing the PET Loop for Soft Drink Containers. RecyclingPlas VI-Conference : Plastics Recycling as a Future Business Oppotunity. Pp.55-57. Mayflower Hotel, Washington DC, May 22-23, 1991. Pensylvania : technomic, 1991.
14. Li, Y., White, D.J., and Lee, P.R. Composite Material form Fly Ash and Post-Consumer PET. Resource, Conservation and Recycling 24(1998) : 87-182.

15. Rebeiuz, K.S., and Craft, A.P. Plastic Waste Management in Construction: Technological and Institutional Issue. Resource, Conservation and Recycling 15 (1995) : 145-272.

16. Rebeiuz, K.S. Strength Properties of Unreinforced and Reinforced Polymer Concrete Using Recycled PET. Polymer Recycling 2(1996) : 133-139.

17. Vergnaud, J.M. recycled Plastic Reused as Food Packaging. Interest of a Functional Barrier. Resource, Conservation and Recycling 24(1998) : 87-182.

18. Fann, D.M., Huang, S.K., and Lee, J.Y. Kinetics and Thermal Crystallinity of the Injection Molded Recycled PET: I. Dynamic Cooling Crystallization Studies on Blends Recycled with Engineering PET. Journal of Applied Polymer Science 61 (1996) : 1375-1385.

19. Fann, D.M., Huang, S.K., and Lee, J.Y. Kinetics and Thermal Crystallinity of the Injection Molded Recycled PET: II. Topographic Study on Thermal Crystallinity of the Injection Molded Recycled PET. Journal of Applied Polymer Science 61 (1996) : 261-271.

20. Xanthos, M., Baltzis, B.C., and Hsu, P.P. Effects of Carbonate Salts on Crystallization Kinetics and Properties of Recycled PET. Journal of Applied Polymer Science 64(1997) : 1423-1435.

21. Fiore, C.D., Leone, B., Rosa, C.D., Guerra, G., and Petraccone, V. Influence of the Antimony Catalyst Remnants on the Melt Crystallization of PET. Journal of Applied Polymer Science 48(1993) : 1997-2001.

22. Lawton, E.L. Nucleation of Crystallization of Polyester by Catalyst Remnants-A Review. Polymer Engineering and Science 25(1985) : 348-354.

23. Aharoni, S.M. Nucleation of PET Crystallization by Metal Hydroxides. Journal of Applied Polymer Science 29(1984) : 853-865.

24. Szekei-Pecsi, Z., Vansco-Szmercsanyi, I., and Cser, F. Metal-Containing Coordination Polymers. XI. Crystallization and Melting Behavior of a Semicrystalline Polyester and Its Mg (II) Complexes. Journal of Polymer Science: Polymer Physics Edition 19(1981) : 703-717.

25. Gilmer, J.W., Neu, R.P., Liu, Y.J., and Jen, A.K.Y. The Use of Sodium Salts as Nucleation Agents for Polyethylene Terephthalate with Minimal Molecular Weight Reduction. Polymer Engineering and Science 35(1995) : 1407-1412.

26. Legras, R., and Mercier, J.P. Polymer Crystallization by Chemical Nucleation. Nature 304(1983) : 432-434.

27. Legras, R., Mercier, J.P., Dekoninck, J.M., and Vanzieleghem, A. Crystallization of Poly (ethylene terephthalate) Induced by Organic Salts: Model compound Study of the Mechanism of Action of the Nucleating Agent. Polymer 27(1986) : 106-117.

28. Garcia, D. Heterogeneous Nucleation of Poly (ethylene terephthalate). Journal of Polymer Science: Polymer Physics Edition 22(1984) : 2063-2072.

29. Misra, A., and Garg, S.N. Block Copolymers of Poly (ethylene terephthalate-Polybutylene terephthalate). I. Preparation and Crystallization behavior. Journal of Polymer Science: Part B: Polymer Physics 24(1986) : 983-997.

30. Reinsch, V.E., and Rebenfeld, L. Crystallization Process in Poly (ethylene terephthalate) as Modified by Polymer Additives and Fiber Reinforcement. Journal of Applied Polymer Science 52(1994) : 649-662.

31. Brandrup, J. Plastic Waste Issues in Germany. Polymer Recycling 2(1996) : 95-108.

Appendix

Appendix A : Mechanical Properties

Table A1 Tensile strength (N/mm^2) of PETs.

Tensile strength							
Sample code	Trial No.					Mean	SD
	1	2	3	4	5		
010	107.500	107.300	107.700	107.900	107.900	107.660	0.261
110	47.640	47.640	42.150	48.230	45.790	46.290	2.490
310	25.850	26.690	25.190	26.480	26.720	26.186	0.658
510	24.020	30.250	23.260	25.790	29.070	26.478	3.075
710	20.080	20.570	19.040	20.600	21.140	20.286	0.791
1010	21.850	23.070	23.720	17.410	20.620	21.334	2.494
082	54.710	38.710	37.360	38.500	29.770	39.810	9.107
182	30.520	30.390	31.330	31.320	29.020	30.516	0.944
382	90.130	90.270	92.900	93.190	93.120	91.922	1.576
582	97.340	97.760	96.770	97.770	98.030	97.534	0.493
782	44.180	47.380	42.200	53.410	42.200	45.874	4.715
1082	43.070	41.010	33.040	31.480	45.250	38.770	6.154
055	38.190	34.300	32.680	36.630	35.230	35.406	2.117
155	37.930	32.050	33.470	30.600	37.680	34.346	3.318
355	101.200	101.500	101.100	100.900	100.900	101.120	0.249
555	104.600	107.000	106.100	104.600	105.200	105.500	1.039
755	28.590	30.720	26.530	29.690	30.620	29.230	1.737
1055	19.060	21.160	19.880	17.880	15.410	18.678	2.183
028	32.670	49.550	39.920	48.830	38.170	41.828	7.238
128	20.640	33.640	31.860	58.440	36.650	36.246	13.805
328	26.570	24.100	26.160	27.560	25.830	26.044	1.266
528	54.910	51.470	33.260	33.530	49.120	44.458	10.307
728	32.420	30.120	35.550	31.390	32.690	32.434	2.014
1028	22.120	21.540	20.470	23.280	20.370	21.556	1.212
001	37.680	28.700	39.530	31.540	34.810	34.452	4.413
101	26.260	32.560	31.010	25.260	26.100	28.238	3.306
301	30.100	27.820	28.200	29.090	29.770	28.996	0.980
501	37.170	35.470	35.060	38.330	33.900	35.986	1.759
701	21.220	21.810	18.820	24.630	20.810	21.458	2.099
1001	21.850	23.070	23.720	17.410	20.620	21.334	2.494

Table A2 Elongation at break (%) of PETs.

%Elongation at break							
Sample code	Trial No.					Mean	SD
	1	2	3	4	5		
010	40.19	40.08	43.66	40.87	40.08	40.976	1.536
110	12.87	12.87	13.57	12.35	14.77	13.286	0.936
310	7.707	7.649	6.188	7.211	9.854	7.6858	1.338
510	6.747	6.874	4.549	4.993	5.134	5.6594	1.074
710	5.551	4.22	4.876	4.22	6.477	5.0688	0.961
1010	2.296	4.348	4.795	3.34	3.893	4.3344	0.968
082	8.709	8.352	7.001	8.616	6.39	7.8136	1.051
182	8.896	10.19	6.854	12.45	8.698	9.4176	2.071
382	26.53	28.5	31.54	27.85	28.06	28.512	1.853
582	9.868	11.13	9.328	10.8	9.93	10.2112	0.736
782	8.951	10.4	9.455	7.063	7.091	8.592	1.478
1082	10.23	9.811	8.857	11.29	9.973	10.0322	0.874
055	5.396	9.506	7.816	6.161	6.365	7.0488	1.629
155	5.694	5.808	5.682	5.632	5.226	5.6024	0.223
355	25.4	22.22	20.7	25.03	23.88	23.456	1.972
555	24.29	21.4	24.56	21.51	24.46	23.244	1.636
755	8.879	8.672	8.42	7.232	6.735	7.9876	0.947
1055	7.147	8.544	6.031	7.506	8.93	7.6316	1.154
028	8.612	7.732	7.837	7.207	8.375	7.9526	0.555
128	7.032	8.009	6.251	11.17	9.65	8.4224	1.992
328	7.79	8.474	8.512	7.678	8..537	8.1982	0.441
528	10.55	13.48	12.91	10.73	12.65	12.064	1.336
728	11	12.36	12.39	9.429	12.45	11.8258	1.320
1028	4.981	6.635	4.593	5.814	6.157	5.636	0.839
001	9.559	9.754	8.626	8.453	9.832	9.2446	0.654
101	11.72	8.492	10.71	8.048	7.165	9.227	1.910
301	10.81	6.154	9.475	9.491	12.01	9.588	2.189
501	5.531	13.71	11.21	10.37	11.14	11.372	2.994
701	4.42	7.97	5.151	4.792	7.433	5.9532	1.628
1001	4.299	5.971	6.507	4.497	4.89	5.6328	0.962

Appendix B : Shrinkage

Table B1 Shrinkage in the direction of parallel to the flow of virgin PET.

010	(Lo-L)/Lo				
Lo	12.135	12.135	12.125		
L	11.235	11.230	11.220		
(Lo-L)	0.900	0.905	0.905	Mean	SD
(Lo-L)/Lo	0.074	0.075	0.075	0.074	0.000

Table B2 Shrinkage in the direction of parallel to the flow of virgin PET at 0.1 phr of nucleating agent.

110	(Lo-L)/Lo				
Lo	12.130	12.140	12.135		
L	11.430	11.410	11.385		
(Lo-L)	0.700	0.730	0.750	Mean	SD
(Lo-L)/Lo	0.058	0.060	0.062	5.988	0.002

Table B3 Shrinkage in the direction of parallel to the flow of virgin PET at 0.3 phr of nucleating agent.

310	(Lo-L)/Lo				
Lo	12.220	12.205	12.195		
L	12.115	12.100	12.125		
(Lo-L)	0.105	0.105	0.070	Mean	SD
(Lo-L)/Lo	0.009	0.009	0.006	0.008	0.002

Table B4 Shrinkage in the direction of parallel to the flow of virgin PET at 0.5 phr of nucleating agent.

510	(Lo-L)/Lo				
Lo	12.195	12.195	12.225		
L	11.990	12.050	12.040		
(Lo-L)	0.205	0 145	0.185	Mean	SD
(Lo-L)/Lo	0.017	0.012	0.015	0.015	0.003

Table B5 Shrinkage in the direction of parallel to the flow of virgin PET with 0.7 phr of nucleating agent.

710	(Lo-L)/Lo				
Lo	12.185	12.305	12.190		
L	12.120	12.205	12.180		
(Lo-L)	0.065	0.100	0.010	Mean	SD
(Lo-L)/Lo	0.005	0.008	0.001	0.005	0.004

Table B6 Shrinkage in the direction of parallel to the flow of virgin PET at 1.0 phr of nucleating agent.

1010	(Lo-L)/Lo				
Lo	12.215	12.195	12.195		
L	12.155	12.155	12.130		
(Lo-L)	0.060	0.040	0.065	Mean	SD
(Lo-L)/Lo	0.005	0.003	0.005	0.004	0.001

Table B7 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend.

082	(Lo-L)/Lo				
Lo	12.125	12.140	12.155		
L	11.612	11.845	11.765		
(Lo-L)	0.513	0.295	0.390	Mean	SD
(Lo-L)/Lo	0.042	0.024	0.032	0.032	0.009

Table B8 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend at 0.1 phr of nucleating agent.

182	(Lo-L)/Lo				
Lo	12.505	12.525	12.380		
L	12.125	12.150	12.145		
(Lo-L)	0.380	0.375	0.235	Mean	SD
(Lo-L)/Lo	0.030	0.030	0.019	0.026	0.006

Table B9 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend at 0.3 phr of nucleating agent.

382	(Lo-L)/Lo				
Lo	12.145	12.160	12.140		
L	11.715	11.905	11.860		
(Lo-L)	0.430	0.255	0.280	Mean	SD
(Lo-L)/Lo	0.035	0.021	0.023	0.026	0.008

Table B10 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend at 0.5 phr of nucleating agent.

582	(Lo-L)/Lo				
Lo	12.130	12.145	12.145		
L	11.940	11.990	11.920		
(Lo-L)	0.190	0.155	0.225	Mean	SD
(Lo-L)/Lo	0.016	0.013	0.019	0.016	0.003

Table B11 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend at 0.7 phr of nucleating agent.

782	(Lo-L)/Lo				
Lo	12.100	12.125	12.120		
L	12.025	12.055	12.040		
(Lo-L)	0.075	0.070	0.080	Mean	SD
(Lo-L)/Lo	0.006	0.006	0.007	0.006	0.000

Table B12 Shrinkage in the direction of parallel to the flow of 80:20 virgin and recycled PET blend at 1.0phr of nucleating agent.

1082	(Lo-L)/Lo				
Lo	12.455	12.575	12.470		
L	12.210	12.200	12.200		
(Lo-L)	0.245	0.375	0.270	Mean	SD
(Lo-L)/Lo	0.020	0.030	0.022	2.371	0.005

Table B13 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend.

055	(Lo-L)/Lo				
Lo	12.095	12.145	12.130		
L	11.746	11.665	11.842		
(Lo-L)	0.349	0.480	0.288	Mean	SD
(Lo-L)/Lo	0.029	0.040	0.024	0.031	2.288

Table B14 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 0.1phr of nucleating agent.

155	(Lo-L)/Lo				
Lo	12.145	12.135	12.140		
L	11.845	11.835	11.800		
(Lo-L)	0.300	0.300	0.340	Mean	SD
(Lo-L)/Lo	0.025	0.025	0.028	0.026	0.563

Table B15 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 0.3 phr of nucleating agent.

355	(Lo-L)/Lo				
Lo	12.230	12.220	12.215		
L	11.795	11.785	11.700		
(Lo-L)	0.435	0.435	0.515	Mean	SD
(Lo-L)/Lo	0.036	0.036	0.042	0.038	0.984

Table B16 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 0.5 phr of nucleating agent.

555	(Lo-L)/Lo				
Lo	12.140	12.140	12.115		
L	11.755	11.725	11.690		
(Lo-L)	0.385	0.415	0.425	Mean	SD
(Lo-L)/Lo	0.032	0.034	0.035	0.034	1.114

Table B17 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 0.7 phr of nucleating agent.

755	(Lo-L)/Lo				
Lo	12.150	12.155	12.120		
L	11.855	11.895	11.870		
(Lo-L)	0.295	0.260	0.250	Mean	SD
(Lo-L)/Lo	0.024	0.021	0.021	0.022	0.315

Table B18 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 1.0 phr of nucleating agent.

1055	(Lo-L)/Lo				
Lo	12.140	12.145	12.120		
L	11.610	11.585	11.125		
(Lo-L)	0.530	0.560	0.995	Mean	SD
(Lo-L)/Lo	0.044	0.046	0.082	0.057	0.874

Table B19 Shrinkage in the direction of parallel to the flow of 20:80 virgin and recycled PET blend.

028	(Lo-L)/Lo				
Lo	12.255	12.220	12.235		
L	11.935	11.945	11.970		
(Lo-L)	0.320	0.275	0.265	Mean	SD
(Lo-L)/Lo	0.026	0.023	0.022	0.023	0.002

Table B20 Shrinkage in the direction of parallel to the flow of 20:80 virgin and recycled PET blend at 0.1 phr of nucleating agent.

128	(Lo-L)/Lo				
Lo	12.145	12.140	12.135		
L	11.775	11.780	11.760		
(Lo-L)	0.370	0.360	0.375	Mean	SD
(Lo-L)/Lo	0.030	0.030	0.031	0.030	0.007

Table B21 Shrinkage in the direction of parallel to the flow of 20:80 virgin and recycled PET blend at 0.3 phr of nucleating agent.

328	(Lo-L)/Lo				
Lo	12.140	12.150	12.140		
L	11.960	11.960	11.930		
(Lo-L)	0.180	0.190	0.210	Mean	SD
(Lo-L)/Lo	0.015	0.016	0.017	0.016	0.002

Table B22 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 0.5 phr of nucleating agent.

528	(Lo-L)/Lo				
Lo	12.105	12.145	12.145		
L	11.755	11.775	11.775		
(Lo-L)	0.350	0.370	0.370	Mean	SD
(Lo-L)/Lo	0.029	0.030	0.030	0.030	0.014

Table B23 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 1.0 phr of nucleating agent.

728	(Lo-L)/Lo				
Lo	12.240	12.225	12.000		
L	11.720	11.735	11.710		
(Lo-L)	0.520	0.490	0.290	Mean	SD
(Lo-L)/Lo	0.042	0.040	0.024	0.036	0.014

Table B24 Shrinkage in the direction of parallel to the flow of 50:50 virgin and recycled PET blend at 1.0 phr of nucleating agent.

1028	(Lo-L)/Lo				
Lo	12.240	12.220	12.210		
L	11.890	11.875	11.860		
(Lo-L)	0.350	0.345	0.350	Mean	SD
(Lo-L)/Lo	0.029	0.028	0.029	0.028	0.009

Table B25 Shrinkage in the direction of parallel to the flow of recycled PET.

001	(Lo-L)/Lo				
Lo	12.120	12.155	12.150		
L	11.300	11.405	11.395		
(Lo-L)	0.820	0.750	0.755	Mean	SD
(Lo-L)/Lo	0.068	0.062	0.062	0.064	1.256

Table B26 Shrinkage in the direction of parallel to the flow of recycled PET at 0.1 phr of nucleating agent.

101	(Lo-L)/Lo				
Lo	12.125	12.155	12.150		
L	11.875	11.87	11.85		
(Lo-L)	0.250	0.285	0.300	Mean	SD
(Lo-L)/Lo	0.020619	0.023447	0.024691	0.023	1.011

Table B27 Shrinkage in the direction of parallel to the flow of recycled PET at 0.3 phr of nucleating agent.

301	(Lo-L)/Lo				
Lo	12.155	12.145	12.140		
L	11.900	11.890	11.870		
(Lo-L)	0.255	0.255	0.270	Mean	SD
(Lo-L)/Lo	0.021	0.021	0.022	0.021	1.085

Table B28 Shrinkage in the direction of parallel to the flow of recycled PET at 0.5 phr of nucleating agent.

501	(Lo-L)/Lo				
Lo	12.225	12.205	12.195		
L	11.980	11.990	11.950		
(Lo-L)	0.245	0.215	0.245	Mean	SD
(Lo-L)/Lo	0.020	0.018	0.020	0.019	0.960

Table B29 Shrinkage in the direction of parallel to the flow of recycled PET at 0.7 phr of nucleating agent.

701	(Lo-L)/Lo				
Lo	12.225	12.205	12.195		
L	12.090	12.115	12.115		
(Lo-L)	0.135	0.090	0.080	Mean	SD
(Lo-L)/Lo	0.011	0.007	0.007	0.008	1.216

Table B30 Shrinkage in the direction of parallel to the flow of recycled PET at 0.3 phr of nucleating agent.

1001	(Lo-L)/Lo				
Lo	12.145	12.160	12.155		
L	11.610	11.630	11.610		
(Lo-L)	0.535	0.530	0.545	Mean	SD
(Lo-L)/Lo	0.044	0.044	0.045	0.044	1.182

Table B31 Shrinkage in the direction of perpendicular to the flow of the virgin PET.

010	(Lo-L)/Lo								
Lo	2.580	2.585	0.640	0.635	0.635	2.590	2.590		
L	2.355	2.545	0.680	0.665	0.640	2.570	2.570		
(Lo-L)	0.225	0.040	-0.040	-0.030	-0.005	0.020	0.020	Mean	SD
(Lo-L)/Lo	0.087	0.015	-0.063	-0.047	-0.008	0.008	0.008	0.000	0.049

Table B32 Shrinkage in the direction of perpendicular to the flow of the virgin PET with 0.1 phr of nucleating agent.

110	(Lo-L)/Lo								
Lo	2.600	2.600	0.670	0.695	0.660	2.580	2.580		
L	2.450	2.570	0.650	0.630	0.630	2.565	2.570		
(Lo-L)	0.150	0.030	0.020	0.065	0.030	0.015	0.010	Mean	SD
(Lo-L)/Lo	0.058	0.012	0.030	0.094	0.045	0.006	0.004	0.035	0.033

Table B33 Shrinkage in the direction of perpendicular to the flow of the virgin PET with 0.3 phr of nucleating agent.

310	(Lo-L)/Lo								
Lo	2.625	2.625	0.690	0.685	0.695	2.635	2.695		
L	2.530	2.615	0.660	0.645	0.675	2.635	2.645		
(Lo-L)	0.095	0.010	0.030	0.040	0.020	0.000	0.050	Mean	SD
(Lo-L)/Lo	0.036	0.004	0.043	0.058	0.029	0.000	0.019	0.027	0.021

Table B34 Shrinkage in the direction of perpendicular to the flow of the virgin PET with 0.5 phr of nucleating agent.

510	(Lo-L)/Lo								
Lo	2.660	2.690	0.685	0.670	0.690	2.650	2.620		
L	2.695	2.645	0.685	0.660	0.680	2.645	2.600		
(Lo-L)	-0.035	0.045	0.000	0.010	0.010	0.005	0.020	Mean	SD
(Lo-L)/Lo	-0.013	0.017	0.000	0.015	0.014	0.002	0.008	0.006	0.011

Table B35 Shrinkage in the direction of perpendicular to the flow of the virgin PET with 0.7 phr of nucleating agent.

710	(Lo-L)/Lo								
Lo	2.655	2.685	0.710	0.695	0.725	2.740	2.795		
L	2.695	2.635	0.685	0.665	0.675	2.625	2.650		
(Lo-L)	-0.040	0.050	0.025	0.030	0.050	0.115	0.145	Mean	SD
(Lo-L)/Lo	-0.015	0.019	0.035	0.043	0.069	0.042	0.052	0.035	0.027

Table B36 Shrinkage in the direction of perpendicular to the flow of the virgin PET with 1.0 phr of nucleating agent.

1010	(Lo-L)/Lo								
Lo	2.730	2.665	0.670	0.695	0.690	2.730	2.635		
L	2.640	2.635	0.680	0.660	0.670	2.630	2.630		
(Lo-L)	0.090	0.030	-0.010	0.035	0.020	0.100	0.005	Mean	SD
(Lo-L)/Lo	0.033	0.011	-0.015	0.050	0.029	0.037	0.002	0.021	0.023

Table B37 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend.

082	(Lo-L)/Lo								
Lo	2.670	2.680	0.770	0.635	0.640	2.655	2.665		
L	2.590	2.625	0.645	0.635	0.640	2.600	2.600		
(Lo-L)	0.080	0.055	0.125	0.000	0.000	0.055	0.065	Mean	SD
(Lo-L)/Lo	0.030	0.021	0.162	0.000	0.000	0.021	0.024	0.037	0.057

Table B38 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend with 0.1 phr of nucleating agent.

182	(Lo-L)/Lo								
Lo	2.900	2.895	0.800	0.780	0.835	2.940	2.920		
L	2.895	2.700	0.740	0.630	0.835	2.880	2.885		
(Lo-L)	0.005	0.195	0.060	0.150	0.000	0.060	0.035	Mean	SD
(Lo-L)/Lo	0.002	0.067	0.075	0.192	0.000	0.020	0.012	0.053	0.069

Table B39 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend with 0.3 phr of nucleating agent.

382	(Lo-L)/Lo								
Lo	2.615	2.675	0.815	0.785	0.770	2.840	2.790		
L	2.596	2.575	0.755	0.730	0.740	2.790	2.785		
(Lo-L)	0.019	0.100	0.060	0.055	0.030	0.050	0.005	Mean	SD
(Lo-L)/Lo	0.007	0.037	0.074	0.070	0.039	0.018	0.002	0.035	0.029

Table B40 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend with 0.5 phr of nucleating agent.

582	(Lo-L)/Lo								
Lo	2.785	2.870	0.720	0.745	0.750	2.820	2.790		
L	2.680	2.800	0.640	0.725	0.755	2.785	2.700		
(Lo-L)	0.105	0.070	0.080	0.020	-0.005	0.035	0.090	Mean	SD
(Lo-L)/Lo	0.038	0.024	0.111	0.027	-0.007	0.012	0.032	0.034	0.037

Table B41 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend with 0.7 phr of nucleating agent.

782	(Lo-L)/Lo								
Lo	2.740	2.765	0.765	0.760	0.805	2.760	2.605		
L	2.690	2.685	0.740	0.730	0.730	2.680	2.550		
(Lo-L)	0.050	0.080	0.025	0.030	0.075	0.080	0.055	Mean	SD
(Lo-L)/Lo	0.018	0.029	0.033	0.039	0.093	0.029	0.021	0.038	0.026

Table B42 Shrinkage in the direction of perpendicular to the flow of the 80:20 virgin and recycled PET blend with 1.0 phr of nucleating agent.

1082	(Lo-L)/Lo								
Lo	2.940	3.025	0.880	0.815	0.830	3.020	2.960		
L	2.945	2.940	0.875	0.770	0.750	2.930	2.870		
(Lo-L)	-0.005	0.085	0.005	0.045	0.080	0.090	0.090	Mean	SD
(Lo-L)/Lo	-0.002	0.028	0.006	0.055	0.096	0.030	0.030	0.035	0.033

Table B43 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend.

055	(Lo-L)/Lo								
Lo	2.585	2.570	0.625	0.615	0.620	2.565	2.570		
L	2.545	2.534	0.575	0.602	0.615	2.510	2.054		
(Lo-L)	0.040	0.036	0.050	0.013	0.005	0.055	0.516	Mean	SD
(Lo-L)/Lo	0.015	0.014	0.080	0.021	0.008	0.021	0.201	0.051	0.070

Table B44 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend with 0.1 phr of nucleating agent.

155	(Lo-L)/Lo								
Lo	2.645	2.575	0.660	0.630	0.650	2.590	2.590		
L	2.565	2.565	0.645	0.630	0.640	2.575	2.560		
(Lo-L)	0.080	0.010	0.015	0.000	0.010	0.015	0.030	Mean	SD
(Lo-L)/Lo	0.030	0.004	0.023	0.000	0.015	0.006	0.012	0.012	0.011

Table B45 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend with 0.3 phr of nucleating agent.

355	(Lo-L)/Lo								
Lo	2.675	2.635	0.685	0.670	0.690	2.660	2.655		
L	2.540	2.595	0.670	0.660	0.675	2.625	2.605		
(Lo-L)	0.135	0.040	0.015	0.010	0.015	0.035	0.050	Mean	SD
(Lo-L)/Lo	0.050	0.015	0.022	0.015	0.022	0.013	0.019	0.022	0.013

Table B46 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend with 0.5 phr of nucleating agent.

555	(Lo-L)/Lo								
Lo	2.620	2.585	0.655	0.655	0.645	2.595	2.575		
L	2.465	2.510	0.645	0.630	0.640	2.545	2.555		
(Lo-L)	0.155	0.075	0.010	0.025	0.005	0.050	0.020	Mean	SD
(Lo-L)/Lo	0.059	0.029	0.015	0.038	0.008	0.019	0.008	0.025	0.019

Table B47 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend with 0.7 phr of nucleating agent.

755	(Lo-L)/Lo								
Lo	2.585	2.575	0.640	0.630	0.640	2.585	2.585		
L	2.565	2.610	0.630	0.625	0.640	2.535	2.550		
(Lo-L)	0.020	-0.035	0.010	0.005	0.000	0.050	0.035	Mean	SD
(Lo-L)/Lo	0.008	-0.014	0.016	0.008	0.000	0.019	0.014	0.007	0.011

Table B48 Shrinkage in the direction of perpendicular to the flow of the 50:50 virgin and recycled PET blend with 1.0 phr of nucleating agent.

1055	(Lo-L)/Lo								
Lo	2.565	2.575	0.660	0.635	0.660	2.585	2.615		
L	2.460	2.575	0.640	0.625	0.630	2.585	2.595		
(Lo-L)	0.105	0.000	0.020	0.010	0.030	0.000	0.020	Mean	SD
(Lo-L)/Lo	0.041	0.000	0.030	0.016	0.045	0.000	0.008	0.020	0.019

Table B49 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend.

028	(Lo-L)/Lo								
Lo	2.670	2.650	0.675	0.665	0.670	2.880	2.625		
L	2.615	2.615	0.660	0.655	0.665	2.645	2.535		
(Lo-L)	0.055	0.035	0.015	0.010	0.005	0.235	0.090	Mean	SD
(Lo-L)/Lo	0.021	0.013	0.022	0.015	0.007	0.082	0.034	0.028	0.025

Table B50 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend with 0.1 phr of nucleating agent.

128	(Lo-L)/Lo								
Lo	2.620	2.580	0.645	0.640	0.665	2.595	2.595		
L	2.595	2.525	0.635	0.625	0.640	2.635	2.570		
(Lo-L)	0.025	0.055	0.010	0.015	0.025	-0.040	0.025	Mean	SD
(Lo-L)/Lo	0.010	0.021	0.016	0.023	0.038	-0.015	0.010	0.014	0.016

Table B51 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend with 0.3 phr of nucleating agent.

328	(Lo-L)/Lo								
Lo	2.605	2.565	0.650	0.635	0.630	2.685	2.620		
L	2.600	2.550	0.650	0.625	0.630	2.550	2.545		
(Lo-L)	0.005	0.015	0.000	0.010	0.000	0.135	0.075	Mean	SD
(Lo-L)/Lo	0.002	0.006	0.000	0.016	0.000	0.050	0.029	0.015	0.019

Table B52 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend with 0.5 phr of nucleating agent.

528	(Lo-L)/Lo								
Lo	2.580	2.575	0.660	0.615	0.650	2.580	2.590		
L	2.530	2.535	0.650	0.605	0.640	2.525	2.535		
(Lo-L)	0.050	0.040	0.010	0.010	0.010	0.055	0.055	Mean	SD
(Lo-L)/Lo	0.019	0.016	0.015	0.016	0.015	0.021	0.021	0.018	0.003

Table B53 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend with 0.7 phr of nucleating agent.

728	(Lo-L)/Lo								
Lo	2.605	2.630	0.695	0.685	0.700	2.625	2.640		
L	2.540	2.600	0.675	0.660	0.675	2.605	2.605		
(Lo-L)	0.065	0.030	0.020	0.025	0.025	0.020	0.035	Mean	SD
(Lo-L)/Lo	0.025	0.011	0.029	0.036	0.036	0.008	0.013	0.023	0.012

Table B54 Shrinkage in the direction of perpendicular to the flow of the 20:80 virgin and recycled PET blend with 1.0 phr of nucleating agent.

1028	(Lo-L)/Lo								
Lo	2.625	2.630	0.665	0.660	0.675	2.640	2.635		
L	2.560	2.560	0.665	0.660	0.665	2.595	2.590		
(Lo-L)	0.065	0.070	0.000	0.000	0.010	0.045	0.045	Mean	SD
(Lo-L)/Lo	0.025	0.027	0.000	0.000	0.015	0.017	0.017	0.014	0.011

Table B55 Shrinkage in the direction of perpendicular to the flow of the recycled PET blend.

001	(Lo-L)/Lo								
Lo	2.595	2.590	0.645	0.650	0.670	2.585	2.615		
L	2.575	2.560	0.640	0.635	0.640	2.525	2.400		
(Lo-L)	0.020	0.030	0.005	0.015	0.030	0.060	0.215	Mean	SD
(Lo-L)/Lo	0.008	0.012	0.008	0.023	0.045	0.023	0.082	0.029	0.027

Table B56 Shrinkage in the direction of perpendicular to the flow of the and recycled PET blend with 0.1 phr of nucleating agent.

101	(Lo-L)/Lo								
Lo	2.575	2.575	0.650	0.635	0.635	2.585	2.585		
L	2.49	2.515	0.64	0.61	0.63	2.535	2.53		
(Lo-L)	0.085	0.060	0.010	0.025	0.005	0.050	0.055	Mean	SD
(Lo-L)/Lo	0.03301	0.0233	0.01538	0.0394	0.00787	0.01934	0.0213	0.023	0.011

Table B57 Shrinkage in the direction of perpendicular to the flow of the recycled PET blend with 0.3 phr of nucleating agent.

301	(Lo-L)/Lo								
Lo	2.635	2.590	0.655	0.635	0.635	2.605	2.595		
L	2.560	2.520	0.635	0.625	0.630	2.515	2.525		
(Lo-L)	0.075	0.070	0.020	0.010	0.005	0.090	0.070	Mean	SD
(Lo-L)/Lo	0.028	0.027	0.031	0.016	0.008	0.035	0.027	0.024	0.009

Table B58 Shrinkage in the direction of perpendicular to the flow of the recycled PET blend with 0.5 phr of nucleating agent.

501	(Lo-L)/Lo								
Lo	2.610	2.625	0.680	0.650	0.660	2.650	2.655		
L	2.500	2.525	0.665	0.645	0.655	2.585	2.630		
(Lo-L)	0.110	0.100	0.015	0.005	0.005	0.065	0.025	Mean	SD
(Lo-L)/Lo	0.042	0.038	0.022	0.008	0.008	0.025	0.009	0.022	0.014

Table B59 Shrinkage in the direction of perpendicular to the flow of the recycled PET blend with 0.7 phr of nucleating agent.

701	(Lo-L)/Lo								
Lo	2.595	2.615	0.680	0.650	0.660	2.650	2.655		
L	2.500	2.525	0.660	0.650	0.640	2.495	2.650		
(Lo-L)	0.095	0.090	0.020	0.000	0.020	0.155	0.005	Mean	SD
(Lo-L)/Lo	0.037	0.034	0.029	0.000	0.030	0.058	0.002	2.730	0.020

Table B60 Shrinkage in the direction of perpendicular to the flow of the recycled PET blend with 1.0 phr of nucleating agent.

1001	(Lo-L)/Lo								
Lo	2.630	2.585	0.685	0.645	0.650	2.600	2.555		
L	2.510	2.530	0.650	0.635	0.645	2.525	2.510		
(Lo-L)	0.120	0.055	0.035	0.010	0.005	0.075	0.045	Mean	SD
(Lo-L)/Lo	0.046	0.021	0.051	0.016	0.008	0.029	0.018	0.027	0.016

Appendix C : Intrinsic viscosity

Table C3 Intrinsic viscosity of the 80:20 vi7rgin and recycled PET blend at 0.5 phr of nucleating agent.

582	C5	C4	C3	C2	C1
conc	0.5561	0.6257	0.715	0.8342	1.001
flow time	66.13	67.67	69.54	71.83	74.56
Nr=t/to	1.275656	1.305363	1.341435	1.38561	1.438272
Nsp=Nr-1	0.275656	0.305363	0.341435	0.38561	0.438272
Nsp/C	0.495695	0.488034	0.477532	0.462251	0.437834
(lnNr)/C	0.4378	0.425892	0.410825	0.390962	0.363079

Table C2 Intrinsic viscosity of the 80:20 virgin and recycled PET blend at 0.3 phr of nucleating agent.

382	C5	C4	C3	C2	C1
Conc	0.5561	0.6257	0.715	0.8342	1.001
Flow time	68.46	70.51	73.42	77.18	82.46
Nr=t/to	1.320602	1.360147	1.416281	1.488812	1.590664
Nsp=Nr-1	0.320602	0.360147	0.416281	0.488812	0.590664
Nsp/C	0.576518	0.57559	0.582211	0.585965	0.590074
(lnNr)/C	0.500068	0.491597	0.486761	0.477078	0.463688

Table C1 Intrinsic viscosity of virgin PET.

010	C5	C4	C3	C2	C1
conc	0.5566	0.6261	0.7156	0.8348	1.0018
flow time	71.35	73.89	77.2	81.56	87.65
Nr=t/to	1.37635	1.425347	1.489198	1.573302	1.690779
Nsp=Nr-1	0.37635	0.425347	0.489198	0.573302	0.690779
Nsp/C	0.676159	0.67936	0.683619	0.686754	0.689538
(lnNr)/C	0.573905	0.566068	0.556508	0.542857	0.524246

Table C6 Intrinsic viscosity of recycled PET.

001	C5	C4	C3	C2	C1
conc	0.5567	0.6262	0.7157	0.835	1.002
flow time	59.77	60.74	61.97	63.59	65.8
Nr=t/to	1.152971	1.171682	1.195409	1.226659	1.26929
Nsp=Nr-1	0.152971	0.171682	0.195409	0.226659	0.26929
Nsp/C	0.274781	0.274165	0.273032	0.271448	0.268753
(lnNr)/C	0.255689	0.253019	0.24939	0.244664	0.237982

Table C5 Intrinsic viscosity of 50:50 virgin and recycled PET blend
at 0.5 phr of nucleating agent.

555	C5	C4	C3	C2	C1
conc	0.5568	0.6264	0.7158	0.8352	1.0022
flow time	65.83	67.66	69.95	73.04	77.27
Nr=t/to	1.269869	1.30517	1.349344	1.408951	1.490548
Nsp=Nr-1	0.269869	0.30517	0.349344	0.408951	0.490548
Nsp/C	0.484678	0.48718	0.488047	0.489644	0.489471
(lnNr)/C	0.429083	0.425181	0.418579	0.410495	0.398268

Table C4 Intrinsic viscosity of 50:50 virgin and recycled PET blend
at 0.3 phr of nucleating agent.

355	C5	C4	C3	C2	C1
conc	0.5563	0.6259	0.7153	0.8345	1.0014
flow time	68.4	70.68	73.67	77.77	83.72
Nr=t/to	1.319444	1.363426	1.421103	1.500193	1.614969
Nsp=Nr-1	0.319444	0.363426	0.421103	0.500193	0.614969
Nsp/C	0.574231	0.580645	0.588709	0.599392	0.614109
(lnNr)/C	0.498312	0.495288	0.491309	0.486032	0.478646

CURRICULUM VITAE

Miss Smornwan Cholprasert was born in May 13, 1976 in Bangkok. She received her Bachelor degree in Science majoring in Industrial Chemistry from the Faculty of Science, King Mongkut's Institute of Technology Ladkrabang in the academic year 1996. She began her Master Degree study in November 1997 and completed the programme in April 2000.