กราฟต์โคพอลิเมอไรเซชันของกรดอะคริลิกบนเส้นใยพีอีทีใช้ตัวริเริ่มปฏิกิริยาซีริก(IV)

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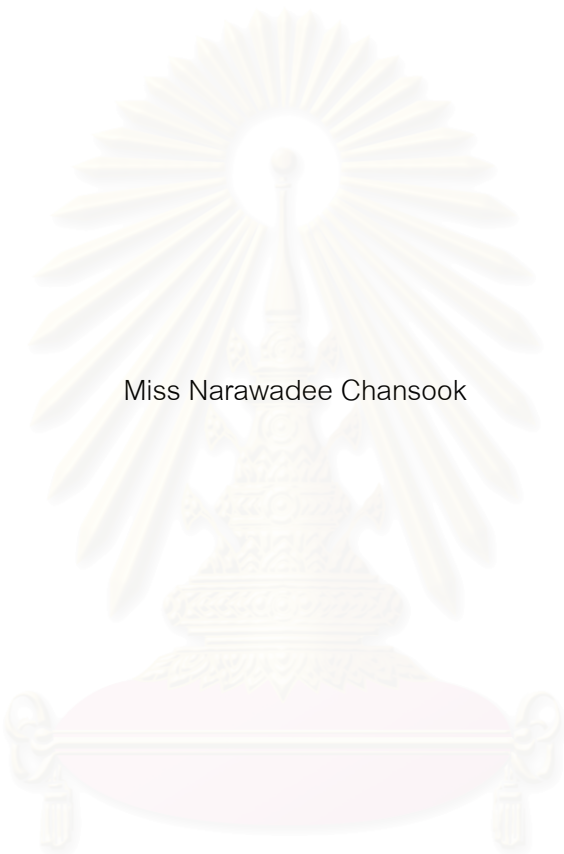
GRAFT COPOLYMERIZATION OF ACRYLIC ACID ONTO PET FIBER USING Ce(IV) INITIATOR

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A Thesis Submitted in Partial Fulfillment of the Requirements

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นราวดี จันทร์สุข : กราฟต์โคพอลีเมอไรซันของกรดอะคริลิกบนเส้นใยพีอีทีใช้ตัวริเริ่มปฏิกิริยา ซีริก (IV). (GRAFT COPOLYMERIZATION OF ACRYLIC ACID ONTO PET FIBER USING Ce(IV) INITIATOR) อ. ที่ปรึกษา : ศ. ดร. สุดา เกียรติกำจรวงศ์,   จำนวนหน้า 112 หน้า. ISBN 974-03-0957-7.

งานวิจัยนี้ทำขึ้นเพื่อปรับปรุงสมบัติด้อยของเส้นใยพีอีที เช่น การดูดซึมน้ำและการย้อมติดสีที่ อุณหภูมิต่ำ เป็นต้น โดยเทคนิคของการกราฟต์ การศึกษาการใช้ซีริกแอมโมเนียมไนเทรตในการริเริ่ม ปฏิกิริยากราฟต์โคพอลิเมอไรเซชันของกรดอะคริลิกบนเส้นใยพีอีทีได้ศึกษาตัวแปรต่างๆของการ กราฟต์ ได้ผลิตภัณฑ์ของการกราฟต์ที่เหมาะสมเป็นร้อยละ 43.6 ณ ภาวะของการทดลองที่เหมาะสม ดังนี้: อุณหภูมิ 323 เคลวิน ใช้เวลา 1 ชั่วโมง ซีริกแอมโมเนียมไนเทรตเข้มข้น 1.82 มิลลิโมล กรด อะคริลิกเข้มข้น 2.19 โมล และกรดไนทริกเข้มข้น 0.80 โมล ขอบเขตของการเกิดโฮโมพอลิเมอไรเซชัน ของกรดอะคริลิกมีผลกระทบต่อประสิทธิภาพระบบการเกิดกราฟต์ของกรดอะคริลิกบนพีอีที ปริมาณ พอลิเมอร์กราฟต์ลดลงเมื่อปริมาณของโฮโมพอลิเมอร์เพิ่มขึ้น แล้วนำพอลิอะคริลิกแอซิดโฮโมพอลิ-เมอร์มาพิสูจน์ลักษณะโดยใช้อินฟราเรดสเปกโทรสโกปี การศึกษาสัณฐานวิทยาของกราฟต์โคพอลิ-เมอร์โดยใช้กล้องจุลทรรศน์อิเล็กตรอนแบบกราด (เอสอีเอ็ม) สามารถสรุปได้ว่า ซีเรียมแอมโมเนียม ไนเทรตในกรดไนทริกเจือจางเป็นตัวริเริ่มปฏิกิริยารีดอกซ์ของระบบการทำกราฟต์โคพอลิเมอไรเซชัน ของกรดอะคริลิกบนพีอีที ผลิตภัณฑ์ของเส้นใยพีอีทีกราฟต์ที่ได้สามารถดูดซึมน้ำได้มากสุดถึงร้อยละ 2.0 ที่ร้อยละ 39.5 ของการกราฟต์ ความสามารถในการย้อมติดสีด้วยสีเบสิก (เมทิลีนบลู) และสี ดิสเพอร์ส (ซีไอ ดิสเพอร์สบลู 79) เพิ่มขึ้นร้อยละ 100 และ 22 ตามลำดับ เนื่องจากการกราฟต์บนเส้น ใยพีอีที ส่วนค่าความเหนียวและค่าการยืดตัวของเส้นใยมีค่าลดลงร้อยละ 51.15 และ 28.9 ตามลำดับ เมื่อปริมาณการกราฟต์สูงขึ้นซึ่งลดอายุการใช้งานของเส้นใย และเส้นโค้งทีจีเอของเส้นใยพีอีทีที่กราฟต์ ด้วยกรดอะคริลิก ชี้ให้เห็นว่าการกราฟต์ไม่ได้เปลี่ยนอุณหภูมิการสลายตัวของเส้นใยพีอีที งานวิจัยนำ เสนอกลไกของการเกิดปฏิกิริยาการกราฟต์เส้นใยพีอีทีกับกรดอะคริลิกด้วยซีริก(IV) ซึ่งเป็นตัวริเริ่ม ปฏิกิริยารีดอกซ์

ภาควิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์   ลายมือชื่อนิสิต ....
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NARAWADEE CHANSOOK : THESIS TITLE. GRAFT COPOLYMERIZATION OF ACRYLIC ACID ON PET FIBER USING CERIC(IV) INITIATOR   THESIS ADVISOR : PROF. SUDA KIATKAMJORNWONG, Ph.D., 112 pp. ISBN 974-03-0957-7.

This thesis deals with the improvement the drawbacks of PET fiber, such as moisture regain and dyeability at low temperature by grafting technique. Ceric ammonium nitrate (CAN) initiated graft copolymerization of acrylic acid onto PET fiber was carried out. The variables affecting the grafted PET were investigated. The optimum condition of graft copolymer to obtain the optimum percentage of graft yield of 43.6% was found as follows: 323 K reaction temperature, 1-h reaction time, 1.82 mmol of CAN, 2.19 mol of acrylic acid, and 0.80 mol of nitric acid. The extent of acrylic acid homopolymerization affected the acrylic acid/PET grafting system. The poly(acrylic acid) homopolymer was characterized by the infrared spectroscopy. The morphology of the graft copolymer was characterized by scanning electron microscope (SEM). Based on the morphology of the PET fiber, it could be concluded that CAN in dilute nitric acid is redox initiator for the graft copolmerization of acrylic acid/PET system. The grafted PET fiber showed an increase in improved moisture regain to reach a maximum of 2.0% for 39.5% graft yield. The dyeability with the basic dye (methylene blue) and disperse dye (CI disperse blue 79) significantly increased by 100% and 22%, respectively, due to the grafting onto PET fiber. Both tenacity and elongation gradually decreased by 51.15% and 28.90%, respectively, with increasing graft yield, which reduced the fiber service lifespan. TGA curves of the acrylic acid grafted PET fiber indicated that the grafting did not change the decomposition temperature of PET fiber. A mechanism for grafting PET with acrylic acid using the ceric(IV) redox initiation was proposed.

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Field of study Petrochemistry and Polymer Science Advisor' signature

Academic year 2001   Co-advisor's signature

ACKNOWLEDGEMENTS

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ABBREVIATIONS

AA	Acrylic acid
Ce^{4+}	cerium (IV) ion
Ce^{3+}	cerium (III) ion
cm^3	cubic centimeter
cm^{-1}	unit of wave number
Co-60	cobalt-60
Cs-137	cesium-137
C=O	carbonyl group
Co^{3+}	cobalt (III) ion
Cr^{6+}	chromium (VI) ion
Cu^{2+}	copper (II) ion
D	denier
DGT	diglycol terephthalate
DMT	dimethyl terephthalate
DTA	Differential thermal analsis
Fe^{2+}	iron (II) ion
Fe^{3+}	iron (III) ion
FT-IR	Fourier Transform Infrared
g	gram
-*g*-	graft
h	hour
[I]	initiator concentration
J	joule
K	degrees Kelvin
k_d	initiator dissociation rate constant
k_p	propagation rate constant
k_t	termination rate constant
kJ	kilojoule
kg	kilogram
l	liquid
m^3	cubic metre

M	molarity
MA	methacrylic acid
MEG	monoethylene glycol
MEHQ	monomethyl ether hydroquinone
ml	milliliter
min	minute
MMA	methyl methacrylic acid
Mn(III)	manganic (III) ion
P	polymer
PAA	poly(acrylic acid)
PET	poly(ethylene terephthalate)
PET-g-PAA	poly(ethylene terephthalate) graft poly(acrylic acid)
POY	partially oriented yarn
PTA	purified terephthalalic acid
ppm	part per million
$R^{\bullet}$	radical
R_p	rate of polymerization
s^{-1}	per second
TGA	Thermal gravimetric Analysis
TMA	Thermal mechanical Analysis
TPA	terephthalic acid
V^{3+}	vanadium (III) ion
V(V)	vanadium (V) ion
w/v	weight by volume
w/w	weight by weight
°C	degrees Celsius
%	percent

CHAPTER I

INTRODUCTION

Introduction

       There is a widespread use of fibers of synthetic origin in the textile industry today. Poly(ethylene terephthalate) (PET) fibers have a prominent place among these synthetic fibers because of its outstanding stabilities and excellent mechanical properties (1). However, in spite of many superior properties of PET fibers, some of their features such as low moisture regain, difficulty of dyeing, and poor antistatic properties limit their fields of usage (2).

       In recent years, the scientific literature has revealed a growing interest in graft copolymerization on textiles as a method for modification of the properties of textile fabrics without changing the manufacturing process. It is generally thought that, as a result of graft copolymerization, the properties of PET backbone are not affected and the fibers acquire new properties, depending upon the monomer grafted (3). This process has concentrated on the addition of carboxylic groups into fibers either to improve their hydrophilic properties or to prepare the fibers for further modification. Many monomers such as acrylic acid, methacrylic acid have been employed in grafting studies.

       Most of the literature reports dealing with grafting on polymer chains come from Japanese and Indian authors in the field of radiation-induced grafting. However, the current method is the graft copolymerization on PET fibers initiated by a chemical method such as a redox initiation. It is generally initiated by transition metal ions of which Fe^{3+}, Cu^{2+}, Co^{3+}, V^{3+}, and Cr^{6+} are the most commonly used initiators.

       It was Mino and Kaiziermann who observed that the oxidation of alcohol by ceric ion proceeds by a single electron transfer (4). The macroradical is generated by ceric ion mainly on the polymerlic backbone; thus the possibility of formation of homopolymer in the graft copolymerization was reduced considerably. Ceric salts in aqueous acidic solution are the well-known initiator of vinyl polymerization and graft copolymerization of vinyl monomers onto various natural and synthetic fibers. A number of studies investigated the graft copolymerization of vinyl monomers such as

methyl methacrylate onto sago starch (5), methyl acrylate onto potato starch (6) acrylic acid and methyl methacrylate onto poly(vinyl alcohol) (7).

In graft copolymerization the investigation of the factors affecting the grafting (such as temperature, monomer, and initiator concentration) is as important as the investigation of the properties of grafted PET fibers. In this study, the effect of the changes of the graft copolymerization conditions upon the graft yield of acrylic acid onto PET fibers using ceric ammonium nitrate in nitric acid mediums has been examined. The changes in the physical properties of PET fibers grafted with acrylic acid such as moisture regain, dye uptake, and thermal stability were also observed.

Objective

The objectives of this research are the following:

1. To prepare the graft copolymerization of acrylic acid onto PET fibers using ceric (IV) as initiator.
2. To determine the optimum conditions of the graft copolymerization of acrylic acid onto PET fibers.
3. To study the effect of reaction conditions on the graft yield.
4. To investigate the properties of PET fibers grafted with acrylic acid.

Scope of investigation

In this research, the plan for graft copolymerization of acrylic acid onto PET fibers using ceric (IV) as an initiator to achieve the improved properties of PET fibers is as follows:

1. Literature survey and in-depth study of this research work.
2. Preparing the chemical reagents and equipment for analysis.
3. Preparing the copolymerization of acrylic acid onto PET fibers using ceric (IV) as initiator, by studying the following parameters so as to select the suitable technique and to attain the appropriate reaction conditions.

    a). The optimum quantity of acrylic acid concentration [M];

    b). The optimum quantity of ceric(IV) concentration [M];

    c). The optimum quantity of nitric acid concentration [M];

    d). The optimum reaction temperature (K);

    e). The optimum reaction time (hour);

4. The graft yields of graft copolymers were calculated.

5. The thermal stability of graft copolymers was determined by TGA.

6. The tensile properties of graft copolymers were determined.

7. The moisture regain of graft copolymers was determined.

8. Dyeability of methylene blue and disperse dye onto the graft copolymers was determined by the spectrophotometric method.

9. The characterization of poly(acrylic acid) homopolymer was done using the FT-IR technique.

CHAPTER II

THEORY and LITERATURE REVIEW

2. Theoretical Background

   2.1 PET

   Polyester fiber is produced from poly(ethylene terephthalate) i.e. PET polymer. The molecular weight of polymer used for the preparation of polyester fiber is in the range of 20,000-40,000. The raw materials for the preparation of polyester are dimethyl ester of terephthalic acid (DMT) or terephthalic acid (TPA) and monoethylene glycol (MEG). Most of the earlier plants were based on DMT as the raw material since high purity TPA required for polymerization was not available. However, methods for preparing purified TPA are now available and TPA is increasingly used as the raw material for the production of polyester (8).

   2.1.1 The Chemical Reaction of PET Preparation

   PET is a condensation polymer and is industrially produced by terephthalic acid with ethylene glycol. A linear polyester, PET is polymerized by a direct esterification (Figure 2.1).

$$HOOC-\!\!\!\!\bigcirc\!\!\!\!-COOH \ + \ HO(CH_2)_2OH$$

$$\downarrow$$

$$HO(H_2C)_2OOC-\!\!\!\!\bigcirc\!\!\!\!-\Big[COO(CH_2)_2OOC-\!\!\!\!\bigcirc\!\!\!\!-\Big]_X COO(CH_2)_2OH \ + \ H_2O$$
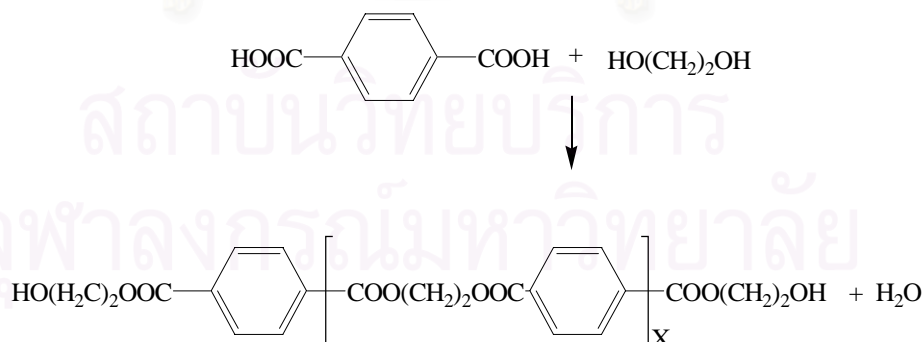
where x = 0 – 4

Figure 2.1 The esterification stage of PET production

The major portion in the esterified product is diglycol terephthalate, DGT in which case x = 0. It has the following structure:

$$HO(H_2C)_2OOC - \text{[benzene ring]} - COO(CH_2)_2OH$$
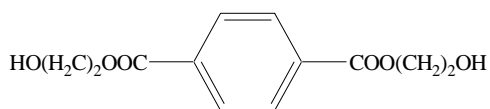
Figure 2.2 Chemical structure of diglycol terephthalate

The second stage of preparation of PET polymer is called a polycondensation process. In the polycondensation process, DGT containing some quantity of dimer, trimer and tetramer is heated at high temperature and under vacuum to get PET with the liberation of H_2O.
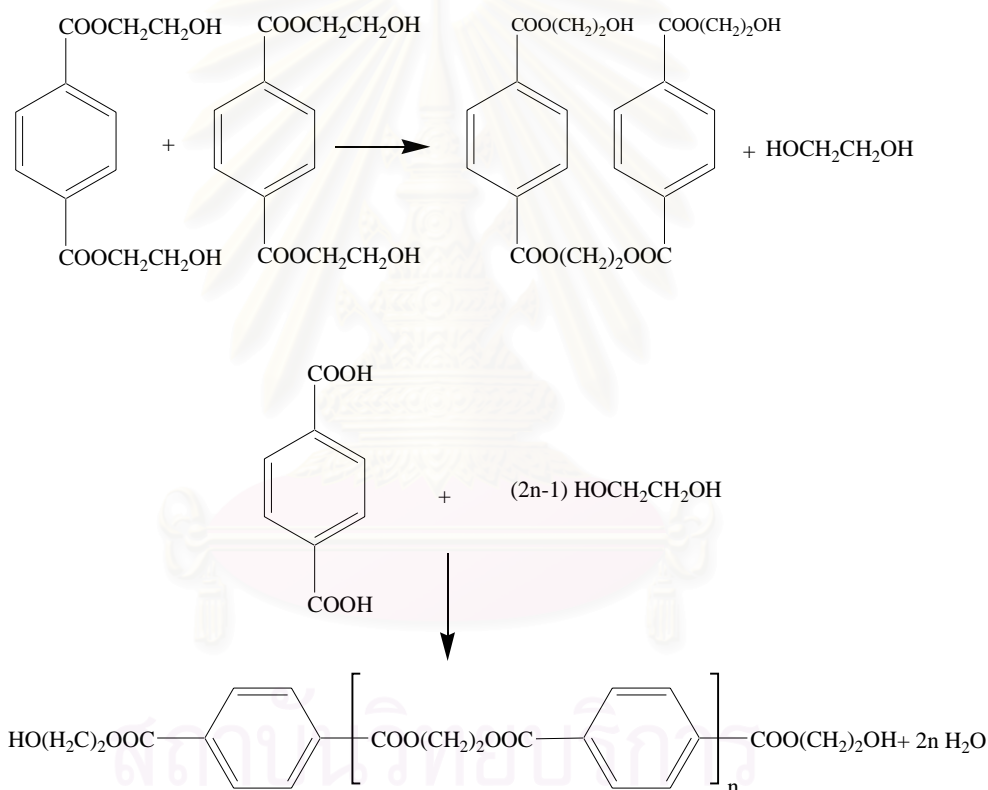
n = 80 – 100

Figure 2.3 The polycondensation stage of PET production

2.1.2 Structural Composition of PET Fiber

One of the distinguishing characteristics of PET is attributed to the benzene rings in the polymer chain. The aromatic character leads to chain stiffness, preventing the deformation of disordered regions, which results in weak van der

Waals interaction forces between chains (9). Due to this, PET is difficult to be crystallized. Polyester fibers may be considered to be composed of crystalline, oriented semicrystalline and noncrystalline (amorphous) regions. This aromatic, carboxyl and aliphatic molecular groups are nearly planar, its configuration exists in a side-by-side arrangement. Stabilization distances between atoms in neighboring molecules are usually van der Waals contact distances, and there is no structural evidence of any abnormally strong forces among the molecules. The unusually high melting point of PET (compared to aliphatic polyester) is not the result of any unusual intermolecular force, but is attributed to ester linkages. The cohesion of PET chains is a result of hydrogen bonds and van der Waals interaction, caused by dipole interaction induction and dispersion forces among the chains. The capacity to form useful fibers and the tendency to crystallize depend on these forces of attraction. The interactive forces create inflexible tight packing among macromolecules, showing high modulus, strength, and resistance to moisture, dyestuffs, and solvent. The limited flexibility in the macromolecules is mainly due to the ethylene group. The extensively quenched fiber does not show any early development of crystallinity; the growth of crystals starts to occur upon drawing.

All polymeric fibers that are useful in textile applications are semicrystalline, irreversibly oriented polymers. Due to the semicrystalline character of the polymer fibers, one is led to the concept of crystallinity. The crystallinity of these fibers could vary over a wide range. Typical values are in the range of 30 to 80% crystallinity.

Amorphous regions having irregular arrangement of chains are not completely structureless. One could visualize a varying degree of order existing in the amorphous region. Many important properties of fibers can be directly related to amorphous regions, such as absorption of dyes and moisture, ability to deform, etc.

Molecular orientation is inherently present in fibers. Crystalline regions have preferred orientation along the fiber axis, which is designated in terms of the average angle between the fiber axis and the chain axis. Chain axis is usually c-axis in the crystal unit cell of polymeric system. Some degree of orientation in the amorphous region is also present which is represented by amorphous orientation function and it is found to correlate with mechanical behavior. Both crystalline and amorphous orientations affect the modulus and strength along the fiber axis.

2.1.3 <u>Properties and Identification of Fiber</u>

2.1.3.1 Physical and Mechanical Properties

The mechanical properties of textile fibers determine their behavior during processing and also during their usages in the form yarns, fabrics, etc. The types of forces to which textiles are subjected may be tensile, compressive, flexural or torsional strength or their combinations (10). In general, PET fiber is characterized by high strength, superior abrasion resistance, very good crease recovery properties, and low density. Many properties such as tenacity, elongation, cross-section and so on can be adjusted to the end-use requirement. Typical physical and mechanical properties of PET fiber are given in Table 2.1 (11).

Table 2.1 Physical Properties of Polyester Fibers

Properties	Unit	Quantity
Density	g/cm^3	1.38
Tenacity	g/denier	3.5-7.0
Elongation	%	12-55
Elastic recovery at 5% elongation	%	75-95
Moisture regain at 293 K and 65% RH	%	0.4
Melting point	K	533

Birefringence measures the orientation in both crystalline and amorphous domains. PET has the highest birefringence ($\Delta_n = 0.175$) (12) when compared with other fibers. Thus, the molecules of PET are highly oriented. Table 2.2 shows optical properties of PET.

Table 2.2 Typical Optical Properties of PET

Fiber	Refractive Indices		Birefringence
	n_s	n_w	$n_s - n_w = \Delta_n$
PET	1.710	1.535	0.175

PET is both hydrophobic and oleophilic. The hydrophobic nature imparts water repellency and rapid drying, because of the oleophilic property and difficult removal of oil stains. Under normal conditions, polyester fiber has a low moisture regain of around 0.4%, which contributes to good electrical insulating properties even at high temperatures.

2.1.3.2 Chemical properties

PET fiber has good resistance to weak mineral acids, even at boiling temperature, and to most strong acids at room temperature, but is dissolved with partial decomposition by concentrated sulfuric acid. PET fiber displays excellent resistance to oxidizing agents, such as conventional textile bleaches, and is resistant to cleaning solvents and surfactants. Also, PET is insoluble in most solvents except for some polyhalogenated acetic acids and phenols. Concentrated solutions of benzoic acid and o-phenylphenol have a swelling effect.

2.1.3.3 Thermal Properties

PET is thermoplastic. One of the most important properties of PET fiber is their thermal behavior. The temperature-dependent properties of fiber undergo major changes at one of two transition points: first-order transition at the crystalline melting point and second-order transition at the glass-transition temperature.

The thermal properties of PET fiber depend on the method of manufacture (13). The DTA (Figure 2.4) and TMA (Figure 2.5) data for fibers spun different speeds show peaks corresponding to glass transition, crystallization, and melting regions.
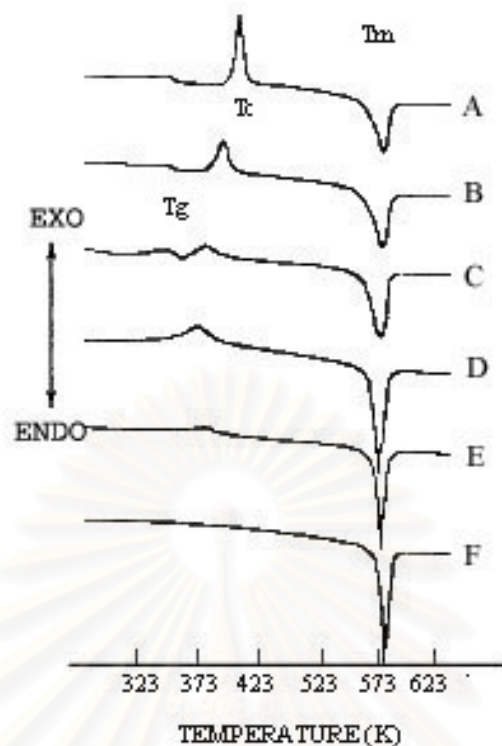
Figure 2.4 TDA curves of PET yarn spun at different spinning speeds, m/min
A: 2,000, B: 3,000, C: 4,000, D: 4,500, E: 5,000, F: 6,000
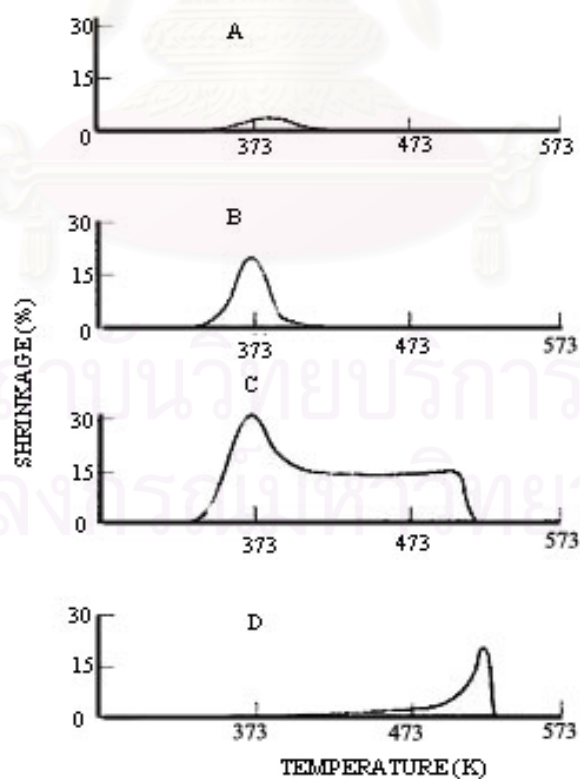
Figure 2.5 TMA curves of PET yarn spun at different spinning speeds, m/min
A: <1,000, B: 1,000-2,000, C: 2,000-5,000, D: >6,000

Their contours depend on the amorphous and crystalline contents. The curves shown for 6,000 m/min and above are characteristics of the drawn fiber. The glass transition temperature is usually at 378 K; crystallization and melting ranges are around 403 K and 533 K, respectively.

2.1.3.4 Dyeing Properties

Because of its rigid structure, well-developed crystallinity and lack of reactive dyeing sites, PET absorbs very little dye in conventional dye systems. This is particularly true for the highly crystalline (highly drawn), high tenacity-high modulus fibers. Polyester fibers are therefore dyed almost exclusively with disperse dyes.

2.1.3.5 Other Properties

PET is used for clothing (62%), home furnishings (17%), and textile cord (10%). For PET fiber, it displays good resistance to sunlight but long-term degradation appears to be initiated by ultraviolet radiation. However, protected from daylight by glass, PET fiber gives excellent performance, when enhanced by an UV stabilizer, used in curtains and automobile interiors. Although PET is flammable, the fabric usually melts and drops away instead of spreading the flame. PET fiber will burn however, in blends with cotton, which supports combustion.

Polyester has good oxidative and thermal resistance. The resistance to both oxidative and thermal degradation may be improved by antioxidants. Finally the resistance of polyester fiber to mildew, and abrasion is of course excellent. Molds, mildew and fungus may grow on some of lubricants or finishes, but do not attack the fiber.

2.1.4 Drawbacks of PET Fiber

PET fiber has become popular because they have certain desirable properties. These properties are high strength, wash and wear property, good dimensional stability, elegant appearance and suitability for blending with cellulosic and protein fibers. However, PET fiber has certain drawbacks, which are inhibiting their rapid growth (15).

(a). The moisture regain of PET fiber is 0.4% (Table 2.1). It is very low. Because of low moisture regain the fabric made from PET fiber is unable to absorb perspiration from the body of the wearer and is therefore uncomfortable to wear, particularly during hot humid days.

(b). Synthetic fibers have tendency to accumulate static electricity. This accumulation of static electricity creates number of problems. For example the garments have also tendency to cling to the body of the wearer or to the inside garments. Due to excessive static accumulation by synthetic fabric, sparks are created, which can produce explosion and fire, if a wearer is working in oil refinery, explosive factory or coal mine.

(c). Dyeing of PET fiber is rather difficult to dye.

(d). PET fiber is easily flammable. A number of fire accidents occur due to flammability of these fibers.

2.2 Graft Copolymer and Copolymerization

Polymers are classified according to their chemical structures into homopolymer, copolymers, block copolymer, and graft copolymer. A graft copolymer comprises a backbone species and a side-chain species. The side chains comprise units of mer that differ from those comprising the backbone chain (16). A graft copolymer can be represented as follows.

```
~~~ A A A A A A A A ~~~
    |    |    |    |
    B    B    B    B
    |    |    |    |
    B    B    B    B
    |    |    |    |
    B    B    B    B
```

Figure 2.6 Graft Copolymer

Where A and B are two different monomers. The properties of graft copolymer differ from those of either a random copolymer ABABBAB or a physical mixture consisting of two homopolymers from $(A)_n$ and $(B)_n$.

Graft copolymer is of great interest in the field of developing new materials capable of competing with nature polymers and processing new characteristics. However, modification of polymers using graft copolymerization created increasing interest due to the varieties of both monomer and substrates participating in such a process. In addition, the wide field of applications makes such a modification method important for industrial and biomedical applications.

Graft copolymerization is affected, generally, through an initiation reaction involving an attack by a macroradical on the monomer to be grafted (17). The generation of the macroradical is accomplished by different means such as: (a) decompositions of weak bonds or the liberation of the unstable groups present in side groups in the chemical structure of the polymer, (b) chain-transfer reactions, (c) redox initiation, (d) photochemical initiation, and (e) gamma radiation-induced copolymerization.

2.2.1 Method of Graft Copolymerization

In this thesis, the backbone polymer for grafting is PET fiber. The grafted side chains can be hydrophilic in nature, cationic, anionic and nonionic. This can be prepared by a direct grafting such as acrylic acid monomer.

In principles, there are two general methods for the synthesis of a graft copolymer.

- The side chain polymer could be linked directly by a suitable chemical reaction to the backbone.

- The backbone polymer could have active sites such as free radicals or ions formed upon it. These can then be used to polymerize a suitable monomer to produce the side chain of polymer.

2.2.1.1 Free Radical Initiation

Radicals can be produced by a variety of redox, thermal, photochemical, and irradical methods. In order to function as a useful source of radicals, an initiator system should be readily available and stable under ambient to refrigerated conditions, which proceeding at a practical rate of radical generation at proceed temperatures, which are not excessively high (18).

(a) Redox Initiation

The redox systems are particularly convenient for the preparation of graft copolymer. An excellent technique based on direct peroxidation of various polymers was developed by Mesrobian and Mark (19). This reaction produces radicals that can be used to initiate polymerization.

A prime advantage of redox initiation is that radical production occurs at reasonable rates over a very wide range of temperatures, depending on the particular redox system including the initiation of the moderate temperature of 273-323 K and even lower (18).

A wide range of redox reactions, including both inorganic and organic components, either wholly or in part, may be employed for this purpose. Some redox systems involve a direct electron transfer between a reductant and an oxidant, while others involve the intermediate formation of reductant-oxidant complex; the latter are charge-transfer complexes in some case. The types of redox initiations are in widespread use of graft copolymerization such as (9):

- Ceric Ion Initiation

The ceric(IV) ion has been used for the oxidation of many organic compounds, in the form of ceric(IV) ammonium nitrate, ceric(IV) ammonium sulfate. Ceric(IV) ion forms complexes with anions such as nitrate, sulfate, and hydroxyl in aqueous solution whose relative concentrations have been found to be the function of hydrogen ion, respective anion concentration and ionic strength (20). The formation of an intermediate complex between the substrate and ceric ion, which subsequently is disproportionated to a free radical species. Using alcohol as a reductant, the reaction can be written as follows (17):

$$Ce^{4+} + RCH_2OH \longrightarrow [ceric – alc. complex] \qquad (2.1)$$
$$Ce^{3+} + H^+ + R—CH—OH \text{ or } [R—CH_2O^\bullet]$$
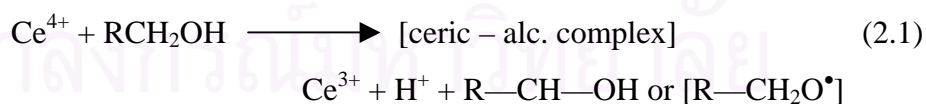
If poly(vinyl alcohol) is used as the reducing agent and the oxidation is conducted in the presence of vinyl monomer, grafting occurs. This method of grafting yields substantially pure graft copolymers, since the free radicals are formed exclusively on the polymer backbone.

- V(V) Systems

Oxidation of organic substances such as alcohols, acids, aldehydes, sugar, and mercaptans by vanadium, V(V), is able to initiate graft copolymerization. Most such reactions are found to proceed through a free radical path that effectively initiates vinyl polymerization. Macromolecules containing pendent groups, such as OH, COH, NH_2, SH, and –OOH interact with V(V) to form free radicals on the backbone. The macroradicals attack monomers in the intermediate vicinity, resulting in a formation of graft copolymer.

- Mn(III) initiating System

Mn(III) is able to oxidize many organic substrates via the free radical mechanism. The free radical species, generated during oxidation smoothly initiate vinyl polymerization. Mn(III) interacts also with polymeric substrates to form effective systems leading to the formation of radicals. These radicals are able to initiate vinyl polymerization and, consequently, grafting in the presence of vinyl monomers.

- Co(III) Initiating System

As in the case of ceric and vanadium ions, the reaction of organic compounds with Co(III) proceeds via formation of an intermediate complex. Such a complex decomposes and produces free radicals capable of initiating vinyl polymerization.

(b) Persulphate Systems

In aqueous solutions, the persulphate ion is known as a strong oxidizing agent, either alone or with activators. Thus it has been extensively used as the initiator of vinyl polymerization. The reaction proceeds by a free radical mechanism. The mechanism involves the decomposition of persulphate ions to sulphate radical ions either when heated alone or in the presence of a reducing agent as described below:

$$1) \ S_2O_8^{2-} \quad \rightleftharpoons \quad 2^-SO_4^{\bullet} \tag{2.2}$$

$$2) \ S_2O_8^{2-} + Fe(II) \quad \rightleftharpoons \quad Fe(III) + {}^-SO_4^{\bullet} + {}^-SO_4^{\bullet} \tag{2.3}$$

$$^-SO_4^{\bullet} + H_2O \quad \rightleftharpoons \quad {}^{\bullet}OH + HSO_4^- \tag{2.4}$$
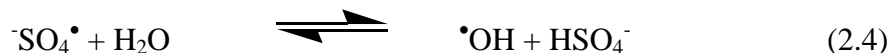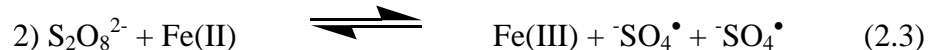
(c) Fenton's Reagent (Fe(II)/H_2O_2) System

Fenton's reagent (H_2O_2) as an effective system is used for grafting vinyl monomers. The reaction of hydrogen peroxide and Fe^{2+} is a typical redox reaction.

$$HO-OH + Fe(II) \quad \longrightarrow \quad Fe(III) + {}^{\bullet}OH + {}^-OH \tag{2.5}$$

The OH radicals may initiate grafting reaction via an abstraction of the hydrogen atom from a polymer chain or may also initiate homopolymerization.

(d) Hydrogenperoxide Systems

Peroxide, in combination with a reducing agent, is a common source of radicals, for example,

$$H_2O_2 + Fe^{2+} \quad \rightleftharpoons \quad OH^- + HO^{\bullet} \ Fe^{3+} \tag{2.6}$$

$$HO^{\bullet} + Fe^{3+} \quad \rightleftharpoons \quad OH^- + Fe^{2+} \tag{2.7}$$

The $HO^{\bullet}$ radical further decomposes the H_2O_2 molecules.

$$HO^{\bullet} + H_2O_2 \quad \rightleftharpoons \quad HO_2^{\bullet} + H_2O \tag{2.8}$$

$$HO_2^{\bullet} + H_2O_2 \quad \rightleftharpoons \quad HO^{\bullet} + H_2O + O_2 \tag{2.9}$$

However, decomposition of H_2O_2 by $HO^{\bullet}$ radicals takes place to an appreciable extent only if H_2O_2 is present in large excess over Fe^{2+} ions.

(e) Thermal decomposition of initiators

The thermal, homolytic dissociation of initiators is the most widely used mode of generating radicals to initiate a polymerization. The number of different types of compounds that can be used as thermal initiators is rather limited. One is usually limited to compounds with bound dissociation energies in the range of 100-170 kJ/mole. Compounds with higher or lower dissociation energies will dissociate too slowly or too rapidly. Only a few classes of compound, involving those with O-O, S-S, N-O bonds, proceed the desired range of dissociation energies. However, it is only the peroxides, which find extensive use as radical sources. The other classes of compounds are usually either not readily available or not stable enough. Several different types of peroxide compounds are widely used. These are acryl peroxides, such as, acetyl and benzoyl peroxides.

(f) Radiation

Grafting by irradiation of certain polymers either in the presence or absence of a vinyl monomer has been one of the most successful methods and has been applied to an enormous number of polymer-monomer systems.

The irradiation of organic macromolecules leads predominantly to the formation of free radicals. If the irradiation is carried out in air, and an effective free radical scavenger, peroxides and hydrogen peroxides, are thus formed within the polymer. If, however, the polymeric substrate is highly crystalline, and in particular, if the irradiation is carried out at low temperature and in the complete absence of air, the free radicals can be trapped in the system and can remain active for a considerable time. The free radical, peroxide and hydrogenperoxide formed or trapped in polymeric substrate, upon irradiation, can be used quite conveniently to initiate block and graft copolymerization.

The two common γ sources available are the Co-60 and Cs-137, though the Co-60 is the one commonly use in radiation plants. The Co-60 source is relatively cheap, and has a useful half life of 5.25 years, the source itself is unaffected by high energy radiations from external sources, and may be used up to a temperature of 1300 K.

Radiation is a very convenient source for graft initiation as it allows a considerable degree of control to be exercised over structural

factors, such as, the number and length of the grafted chains by a careful selection of the dose and dose rate. Preirradition and mutual irradiation are two different techniques used for radiation grafting (21).

(g) Chain Transfer and Copolymerization

An active site capable of initiating a graft copolymerization may be formed on a polymer via a chain transfer reaction in vinyl addition polymerization. For an initiation by chain transfer, the efficiency of the grafting reaction is dependent on the tendency of a propagating radical to transfer to a polymer (22).

In this method, radicals are created on the PET fiber backbone by the following reactions:

$$R^\bullet + PET\ (P) \rightleftharpoons P^\bullet + RH \qquad (2.10)$$

$$P^\bullet + Monomer^\bullet \rightleftharpoons Graft\ copolymer \qquad (2.11)$$
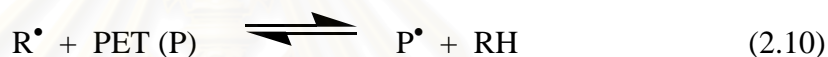
$R^\bullet$ can be the growing chains of polymer formed by the polymerization with a radical initiator in the presence of the PET, or by the primary radical from the initiator itself. The efficiency of this type of grafting reaction is also greatly improved by increasing the ratio of PET to monomers, such as by using a simple swollen system or with the correct choice of swollen agents. With the primary radical approach, the initiator can be absorbed first into the PET.

2.2.2 Characterization of Graft Copolymer

The graft products are usually characterized by different methods. The gravimetric method is the calculation of graft parameters known as the graft yield (%G), grafting efficiency (GE), weight conversion percentage (WC) and graft ratio (GR) (17).

- Percent graft yield

It is referred to as the weight percent of synthetic polymer in the graft copolymer and is determined as follows:

$$\%G = \frac{\text{Weight of polymer grafted x 100}}{\text{Weight of the grafted copolymer}} \qquad (2.12)$$

- Graft efficiency

It is a term often used to describe graft copolymerization reactions and is defined as the percentage of the total synthetic polymer formed that has been grafted to PET. High grafting efficiencies are desirable since a polymerization of the low grafting efficiency would afford mainly a physical mixture PET and homopolymer. It can be then calculated as follows:

$$\%GE = \frac{\text{Weight of polymer grafted x 100}}{\text{Weight of polymer grafted + Weight of homopolymer}} \qquad (2.13)$$

- Percentage weight conversion

It is used to describe the degree of polymerization of the monomer, which gives graft copolymer and homopolymer. It can be evaluated by the following expression.

$$\%WC = \frac{\text{Weight of polymer formed x 100}}{\text{Weight of monomer charged}} \qquad (2.14)$$

- Graft ratio

It is term used to describe a graft copolymerization, which is defined as the percentage ratio of the polymer grafted PET with respect to the PET, and can be calculated by the following expression.

$$\%GR = \frac{\text{Weight of polymer grafted x 100}}{\text{Weight of PET}} \qquad (2.15)$$

Other characterization methods are usually used to detect the changes in physical properties, which usually result from the change in morphology and structures of the grafted substrates.

2.2.3 Applications of Graft Copolymerization

Since the changes in physical properties are often the impetus for grafting. In this thesis, a number of general reviews on grafting have also included, some discussions are given on the changes in physical properties that usually determine the field of applications. Grafting has often been used to change the moisture regain of PET when hydrophilic monomers, such as acrylamide, acrylic acid, and methacrylic acid, were grafted.

In this thesis, grafting of acrylic acid onto PET can impart water absorbing property for use in textile. The dyeability of PET was found to be affected by such a grafting, which has been examined by the dyeability with a cationic dye and a disperse dye.

2.2.4 Tensile Testing

The tenacity (stress at break) and the breaking elongation are both large strain mechanical properties and it is well-known that they show maximum scattering values. The tenacity and the breaking elongations represent limiting properties and the defects in fiber therefore play a predominant role. Many techniques can be used to determine the tensile properties, in this study, Lenzing Vibrodyn 400 and Vibroskop 400 were chosen.

Vibrodyn 400 is an automatic instrument for the tensile test on a single fiber and monofilament. The test is performed with a constant rate of elongation (CRE-principle) according to DIN 53816 and ASTM D3822. CRE is the constant rate of extension. In this instrument of CRE type, the application of load is made in such a way that the rate of elongation of the specimen is kept constant.

The fiber sample, shown in Figure 2.7, is gripped by two clamps operated by electromagnetic force. The specimens were tested at the rate of elongation of 100 mm/min with a gauge length of 10 mm. The top clamp is connected with the force measuring device and the bottom clamp is the moving device. Tension

is measured using an electronic force-measuring device. After testing, the stress-strain curve was plotted as shown in Figure 2.8.

(a)   (b)
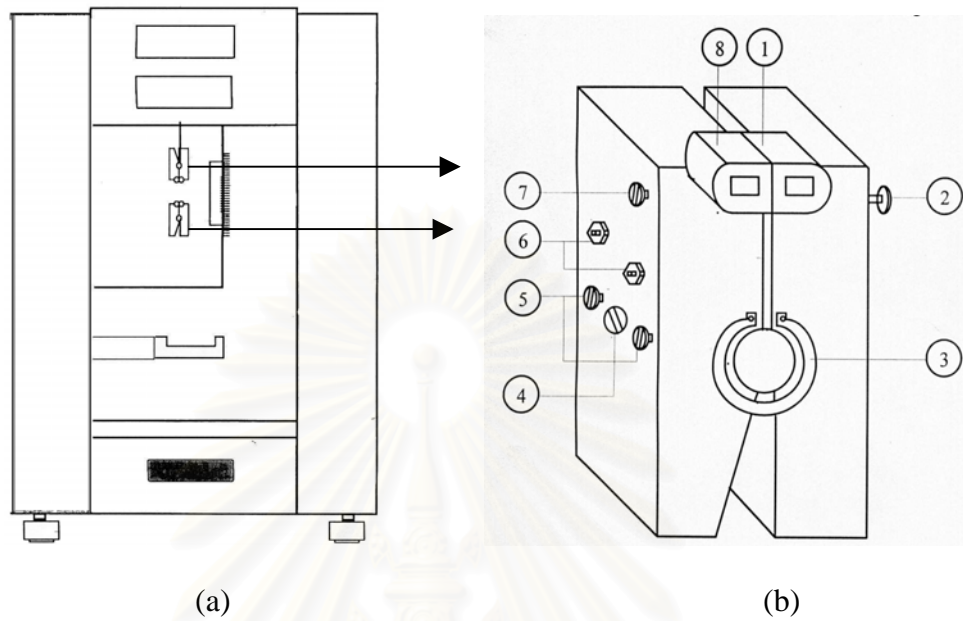
1. Clamp jaw   5. Adjust screw
2. Screw   6. Nuts
3. Tension spring   7. Screw
4. Screw   8. Clamp jaw

Figure 2.7 Lenzing Vibrodyn 400
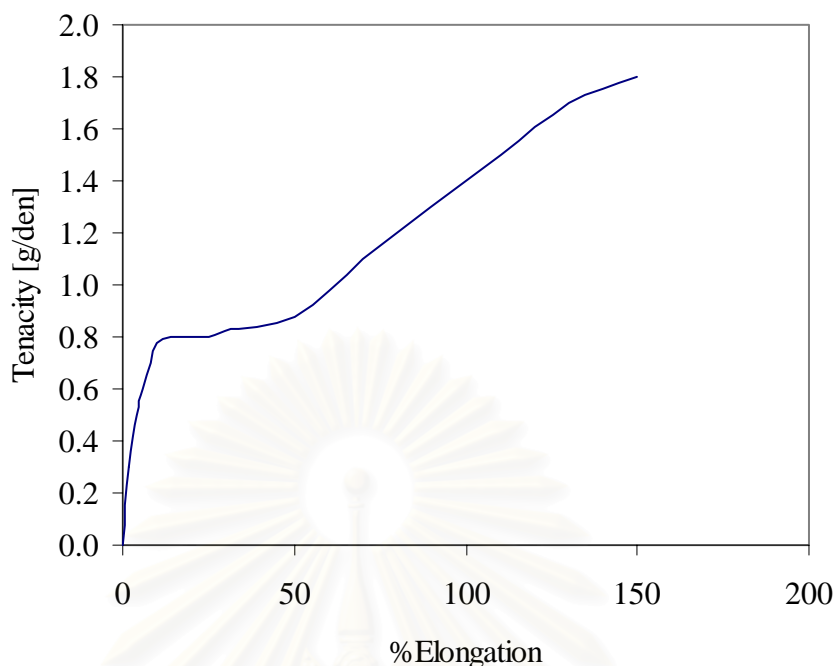
Figure 2.8 The Stress-Strain Curve from Vibrodyn 400 Testing

- Tenacity

Tenacity is the tensile stress at rupture expressed in gram force per denier. The higher number indicates that more load is needed to break the fiber.

- Elongation

Elongation is the increase in length of a sample at the breaking point. Elongation is associated with the uncoiling state of polymer molecules and their movement relative to other molecules. Elongation can vary widely among polymers and is usually taken as a percent of the original length of the sample (12).

Elongation at break (EB) is a measure of the yarn's ability to resist "shock" loads. It is obtained from the following expression:

$$\%EB = \left(\frac{1 - l_0}{l_0} \right) \times 100 \tag{2.16}$$

l = the distance between gauge marks at break in mm

l_0 = the initial distance between gauge length set at 10 mm

Vibroskop (Figure 2.9) 400 is an instrument for measuring the titer (denier) of individual fiber. Denier is the weight in grams of 9,000 meters of a yarn. It operates according to the vibration method (DIN 53812 and ASTM D1577). As shown in Figure 2.10, the sample fiber under tension is induced to perform transverse vibrations at constant length by an electronic impulse. The specimens were tested at the tension weight of 300 mg using a fiber length of 24 mm. The natural frequency is scanned via an opto-electronic device. The titer is derived from the fiber's vibration frequency. It is then calculated for the tension weight in use.
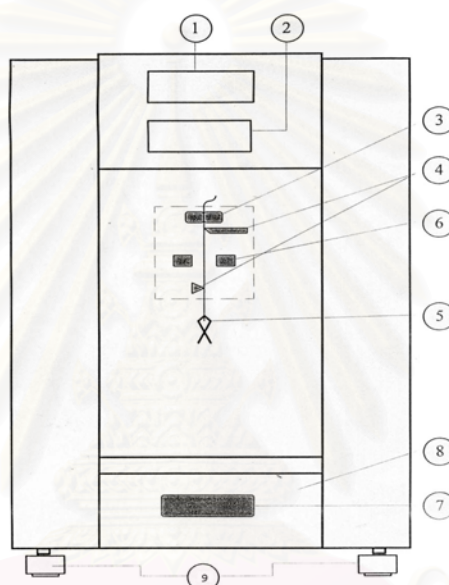
1. Digital test-display of denier
2. Digital test-display of tension weight
3. Top clamp
4. Top fiber supporting
5. Bottom fiber supporting
6. the tension weight 300 mg (Vibroclip)
7. Push button to make all automatic test
8. Drawer for keyboard and data display
9. Adjustable studs

Figure 2.9 Linzing Vibroskop 400

2.2.5 Thermal Gravimetric Analysis

Thermogravimetry (TG) plays an increasingly important role in the polymer industry. The thermogravimetry is measurement presents limiting properties and the defects in fiber therefore play a predominant role. This technique can be used to determine the thermal stability of ungrafted and grafted PET. In this study, Netzsch thermo-microbalance TG 409 was chosen as shown in Figure 2.10.
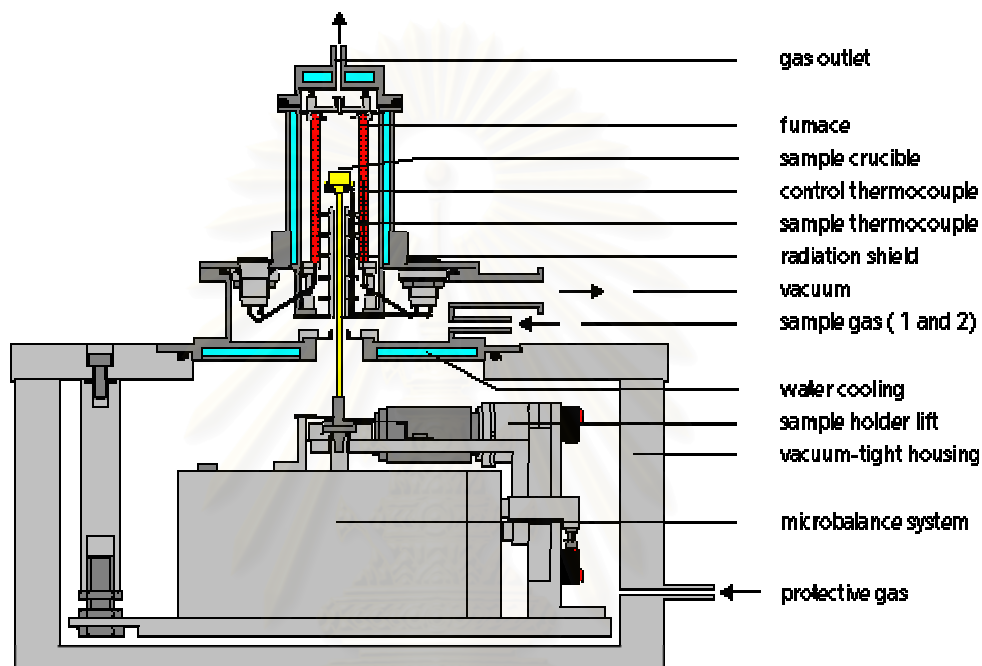
Figure 2.10 Netzsch Thermo-Microbalance TG 409

In a thermogravimetric analysis, the percentage weight loss of a test sample is recorded while the sample is being heated at a uniform rate in an appropriate environment. The loss in weight over a specific temperature range provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The temperature of the sample is recorded as the X-axis. A plot of mass or mass percent versus time or temperature is called a thermogram or thermal decomposition curve.

Literature Review

In recent years the scientific literature has revealed a growing interest in graft copolymerization on textile as a method for allowing modification of the properties of textile fabrics without changing the manufacturing process. Grafting is a well-established technique used to cause more or less extensive modification of properties and textile performance of PET fiber, as well as other synthetic and natural fibers. Although a lot of work has been done on graft copolymerization of vinyl monomers onto cellulosic and other textile fibers, much less has been reported on grafting of vinyl monomers onto PET fiber.

The graft copolymerization of fiber with various monomers such as methyl methacrylate (MMA) (25, 26), methyl acrylate (MA) (27), ethyl acrylate (EA) (28), acrylonitrile (AN) (29, 30) using various initiator systems has gained considerable importance in recent years. Saçak et. al. (2) investigated graft copolymerization of MA onto PET fibers using benzoyl peroxide. The graft yield increased up to 358 K, and then decreased with the further increase in temperature. The maximum graft yield was obtained at benzoyl peroxide concentration of 4.0×10^{-3} M. The increase in the concentration of monomer was found to increase the graft yield. The change in the graft yield was followed by the experiments carried out using different water/solvent mixture. Also, the changes in the properties of PET fibers grafted with methacrylic acid such as moisture regain, density, and diameter were investigated. The density decreased while moisture regain, diameter, and dye uptake of grafted fiber increased with the graft yield. Karakişla and Saçak (31) reported the graft copolymerization of EA onto monofilament poly(ethylene terephthalate) fiber using benzoyl peroxide as a chemical initiator. Breaking tenacity and densities of grafted fiber decreased while breaking elongation increased with the graft yield. Scanning electron micrographs showed that the fiber geometry and its diameter were not affected by grafting.

There are also studies concerned with the grafting of acrylic acid (AA) onto PET fiber in the literature. The grafting of acrylic acid onto backbone polymer either by various chemical initiators or by radiation such as glow-dischardge, ultraviolet (UV), γ-ray, is very interesting for enhanced ion exchange and water sorbency properties. Unfortunately, it is difficult to realize such a grafting due to their sensitivity, which leads to homopolymerization and irreproducibility. In view of the wide application of acrylic acid grafted fibers, ceric ion-initiated grafting of acrylic

acid onto PET fiber has been reported by Osipenko and Martinovicz (32). They studied the effect of solvent nature; concentrations of monomer, initiator, and homopolymerization inhibitors of AA grafted PET fiber and film. The AA grafting was initiated by radicals formed from thermal decomposition of benzoyl peroxide. It has been established that preswelling of PET in dichloroethane leads to change in its sorption-diffusion properties. Addition of the Fe(II), Ni(II), and Cu(II) salts to AA solution decreased homopolymer yield. The so studied process of grafting can be described by reactions of diffusion kinetics. Distribution of the poly(acrylic acid) (PAA) over the cross section of samples and a number of physical and chemical properties depend also on conditions of performing the graft copolymer. Okoniewski and Sojka-Ledakowicz (33) studied the kinetic of grafting of PET fabrics initiated by benzoyl peroxide. Extent of grafting depended upon time, concentration of the initiator and the monomer, as well as the presence of the activator used. From the temperature dependence of the initial rate of the grafting, the overall activation energy for grafting was found to be 90 kJ/mol. The results of the monomer and temperature dependence are consistent with the rate expression derived from a normal kinetic scheme for grafting. Bucheñska (34) investigated the grafting of AA on PET using benzoyl peroxide. The influence of the parameters of grafting, the effect of additives on the degree of grafting, and the amount of homopolymer formed during the process have been determined. Furthermore, the apparent activation energy has been calculated. The influences of the degree of grafting on the moisture sorption and swelling of modified fiber have also determined. An additional treatment of the grafted fiber with antibiotics from fiber into solutions has been examined and mathematically described. Yuhai et al (35) studied AA grafted onto the surface of PET fabric after having a short-time corona-discharge treatment (CDT) the presence of an initiator. The effects of N,N-dimethylformamide (DMF) pretreatment time, CDT time, graft copolymerization time and temperature, concentration of AA and the content of initiator on graft yield of PET fabric were discussed. The results indicate that for the graft of AA onto PET fabric by CDT, the graft yield increases in the presence of the ammonium persulfate (APS) initiator. The graft yield is improved with a short-time CDT, but drops with an increase of the time. Gupta et al (36) studied the graft copolymerization of AA onto PET films that had been pretreated with argon plasma and subsequently exposed to oxygen to create peroxides. The influences of

synthesis conditions such as plasma treatment time, plasma power, monomer concentration temperature, and the presence of Mohr's salt, on the degree of grafting were investigated. The observed initial increase in grafting the monomer concentration accelerated at about the monomer concentration 20%. The grafting reached a maximum at 40% monomer concentration and subsequently decreased with further increases in monomer concentration. The reaction temperature had a pronounced effect on the degree of grafting. The reaction temperature had also a profound effect on the degree of grafting. The initial rate of grafting increased with increasing temperature, but the degree of grafting showed a maximum at 50°C. The activation energy of the grafting obtained from an Arrhenius' plot was 29.1 kJ/mol. The addition of Mohr's salt to the reaction medium not only led to a homopolymer-free grafting reaction but also diminished the degree of grafting. The degree of grafting increased with increasing plasma power treatment time.

Ceric(IV) salts are also well known initiators for graft copolymerization of vinyl monomers such as acrylonitrile (37, 38), methyl acrylate (39), and methyl methacrylate (40). The grafting studies carried out using ceric ion also have a prominent place in the literature. Mino and Kaizermann have graft copolymerized a number of vinyl monomers by employing the ceric ion technique (17). They achieved that certain ceric salts, such as the nitrate and sulphate formed very effective redox systems in presence of organic reducing agents such as alcohols, thiols, glycols, aldehyde, and amines. Duck et. at. suggested the formation of an intermediate complex between the substrate and ceric ion, which was subsequently disproportionated to a free radical species (17). Evidence of a complex formation between Ce(IV) and cellulose has been found by several investigators. Using alcohol , the reaction can be written as mentioned in reaction number (2.1).

Lui et al (6) studied ceric ammonium nitrate (CAN) initiated graft copolymerization of methyl acrylate (MA) onto potato starch. The variables affecting the graft were investigated. They found the optimal reaction conditions as follows the concentrations of MA, CAN, and nitric acid (HNO_3) are 1.08, 5.0 x 10^{-3}, and 0.081 mol/L, respectively. Fakhrul-razi et al. (5) studied the graft copolymerization of methyl methacrylate (MMA) onto sago starch in aqueous media by different initiators of CAN and potassium persulfate (KPS) under a nitrogen gas atmosphere. Using CAN as an initiator, the maximum percentage of graft yield (%G) was 246% at the

following optimum condition: 343 K reaction temperature, 2 h reaction period, 2.0 mmol of CAN, 0.4 mmol of nitric acid, and 141 mmol of MMA. The maximum %G achieved with KPS as the initiator was 90%. The optimum conditions were 50°C reaction temperature, 1.5 h reaction period, 47 mmol of MMA, and 1.82 mmol of KPS. Chowdhury and Banerjee [41] reported the graft copolymerization of methyl methacrylate (MMA) onto poly(vinyl alcohol) (PVA) using ceric ammonium sulfate (CAS) as initiator in aqueous medium. The grafting efficiency of MMA was studied as a function of monomer and initiator concentration, time, pH, and temperature. The optimum grafting efficiency was found at a particular level of CAS condition (3.16 x 10^{-3} mol/L), PVA (1.0 g/L), MMA (0.469 mol/L), sulfuric acid (0.188 mol/L), temperature (318 K), and time (4 h).

CHAPTER III

EXPERIMENTAL

Chemicals, Equipment and Glassware

3.1   Chemicals

The PET filament yarn (250 denier, 48 filaments) was provided by Oriental Fiber Co., Ltd., Thailand. The PET fiber is partially oriented yarn (POY). This yarn does not contain TiO_2 as the delustering agent (superbright grade).

Acrylic acid was obtained from Siam Industry Co., Ltd., Thailand. Acrylic acid is a clear, colorless liquid. The molecular weight is 72.06. The freezing and boiling points are 286.5 K and 414 K, respectively. The heat of vaporization is 435 J g^{-1} and the heat of polymerization is 76.99 kJ mol^{-1}; the density at 298 K is 1045 (kg m^{-3}) (42). The monomethyl ether hydroquinone (MEHQ) is frequently used as an inhibitor of acrylic acid. The inhibitor of acrylic acid monomer is particularly suitable for the manufacture of its polymer without pretreatment. Acrylic acid polymerizes very easily. The polymerization is catalyzed by heat, light and peroxides to produce an insoluble polymer. The highly exothermic, spontaneous polymerization of acrylic acid is extremely violent. Poly(acrylic acid) is soluble at the extent of at least 1-2 pph (wv^{-1}) in water, dioxane, ethanol and methanol (43). The solubility of poly(acrylic acid) depends on concentration, temperature, molecular weight, and extent of neutralization.

Ceric(IV) ammonium nitrate ($H_8CeN_8O_{18}$), analytical grade, was obtained from Fluka. It is an orange powder. The molecular weight is 548.23. The melting is 453 K. The bulk density of ceric(IV) ammonium nitrate is 1200 (kg m^{-3}).

Methanol (CH_3OH), analytical grade, was obtained from Merck. Methanol is a clear, colorless liquid. The molecular weight is 32.04. The freezing and boiling points are 175 K and 337.5 K, respectively. The density of methanol at 293 K is 790 (kg m^{-3}).

Nitric acid (HNO_3) 70% (ww^{-1}), analytical grade, was obtained from Ajax. Nitric acid is a clear liquid. The color is 10 APHA. The molecular weight is 63.01.

The freezing and boiling points are 232 K and 395 K, respectively. The density of nitric acid at 293 K is 1420 (kg m^{-3}).

Methylene blue ($C_{16}H_{18}ClN_3S \cdot 2H_2O$) analytical grade, was obtained from Merck. Methylene blue is a dark green powder. The molecular weight is 319.86. The melting point is 93 K. The bulk density of Methylene blue is ~400-600 (kg m^{-3}).

Hicron navy blue GRL-SF 200% or CI disperse blue 79 ($C_{20}H_{21}O_3N_6Br$) was obtained from Kangwal Polyester co., ltd. This dye is a navy blue powder. The molecular weight is 473.

3.2 Equipment

FT-IR spectra were recorded on a Perkin Elmer Spectrophotometer (Model 1760x), USA. TGA were carried using a NETZSCH thermo-microbalance TG 409 analyzer, Germany. The tensile properties were measured with Lenzing technik Vibrodyn 400 and Vibroskop 400, Austria. SEM was recorded using a JEOL JSM-5800LV scanning microscope, Japan. The moisture regain was carried using a temperature & humidity chamber, Korea and a Satorius drying oven, Germany. The dyeability measurement was carried using a Spectrometer Unicam 5625 UV/VIS, England and a Phisit Dyeing apparatus, Thailand. The other general laboratory equipment were used in the experimental such as a heating mantle, a waterbath circulator, and an analytical balance.

3.3 Glassware

3-necked round bottom flask, beaker, Soxhlet extractor, funnel, Erlenmeyer flask, volumetric flask and other general laboratory glassware.

Procedure

3.4 PET fiber preparation

The fabric was extracted with methanol to remove any material adhering to the surface, such as oil or spin finish, by Soxhlet at 338 K for 6 hours. After washing with methanol, the sample was dried at 383 K for 4 hours and kept in a desiccator.

3.5 Preparation of the Solutions

3.5.1 Nitric acid 50% (ww^{-1}) Solution

Nitric acid (70% (ww^{-1})) 100 g was weight in a 200-ml glass beaker and 40 g of distilled water were then added.

3.5.2 9.1 x 10^{-4} M Ceric Ammonium Nitrate Solution

Ceric ammonium nitrate 0.5 g was dissolved in distilled water. This solution was transferred into a 100-ml volumetric flask and filled up to volume with distilled water.

3.5.3 6.25 x 10^{-4} M Methylene Blue Solution

Methylene blue 0.2 g was dissolved in distilled water, and was transferred into a 1000-ml volumetric flask and the volume was filled up with distilled water.

3.5.4 4.23 x 10^{-4} M Hicron Navy Blue GRL-SF 200% Solution

Hicron navy blue GRL-SF 200% 0.2 g was dissolved in distilled water, and was transferred into a 1000-ml volumetric flask and the volume was filled up with distilled water.

3.6 Grafting of Acrylic Acid onto PET Fiber

Graft copolymerization reaction was carried out in 100 cm^3 3-necked round bottom flask. PET filament yarn 1.0 g was impregnated with 15 cm^3 acrylic acid for about 20 min, and 8 cm^3 nitric acid 50% (ww^{-1}) was then added. After adding nitric acid for 20 min, 2 cm^3 ceric (IV) ammonium nitrate solution was added into the reaction mixture and the time was noted. The grafting reaction was carried out in a nitrogen atmosphere under heating within the temperature range of 323 ± 1K for one hour. Then, the reaction was stopped by quenching the vessel with ice water (13).

3.7 Influential Parameters on Grafting Copolymerization

To obtain a good copolymer with an appropriate percent grafting, moisture regain and dyeability with methylene blue, important effects on graft copolymerization were carried out as follows:

3.7.1 Effect of Monomer Concentration

All other variables were fixed except that acrylic acid monomer was varied. Various amounts of acrylic acid of 8, 10, 12, 15, and 18 cm^3 (1.17, 1.46, 1.75, 2.19, and 2.62 M) were added to each of PET samples.

The acrylic acid concentration at which the highest percent grafting would be used for the subsequent experiment.

3.7.2 Effect of Initiator Concentration

All other variables were fixed except that ceric (IV) ammonium nitrate solution was varied. Various amounts of ceric (IV) ammonium nitrate solution of 0.5, 1.0, 1.5, 2.0, and 2.5 cm^3 (0.46, 0.91, 1.37, 1.82, and 2.28 mmole) were added to each of PET samples.

The ceric (IV) concentration at which the highest percent grafting would be used for the subsequent experiment.

3.7.3 Effect of Nitric Acid Concentration

All other variables were fixed except nitric acid was varied. Various amounts of nitric acid 50% (ww^{-1}) of 5, 6, 7, 8, 9, and 10 cm^3 (0.50, 0.60, 0.70, 0.80, 0.91, and 1.01 M) were added to each of PET fiber samples.

The nitric acid concentration at which the highest percent grafting would be used for the subsequent experiment.

3.7.4 Effect of Reaction Temperature

In this experiment, the temperature of the grafting reaction was taken as a variable. Various levels of temperature for the graft copolymerization were 313, 318, 323, 328, and 333 K.

The reaction temperature which gave the highest percent grafting would be used for the subsequent experiment.

3.7.5 Effect of Reaction Time

In this experiment, the time of the grafting reaction was taken as a variable. Various levels of time for the graft copolymerization were 45, 60, 75, and 90 minutes.

The reaction time which gave the highest percent grafting would be used for the subsequent experiment.

3.8   Homopolymer

3.8.1   Homopolymer Extraction by Methanol

The product derived from Section 3.6, was isolated for graft copolymer and homopolymer by adding methanol into the reaction medium. The solution was filtered and the precipitated product was washed with methanol, then dried at 383 K. Dried homopolymer and graft copolymer mixtures were subjected to an extraction with methanol in a Soxhlet apparatus at 338 K for 48 hours to remove the homopolymer, and precipitated copolymer was filtered.

3.8.2   Homopolymer Characterization

The infrared spectrum of poly(acrylic acid) homopolymer was investigated on a FT-IR Spectrophotometer (Perkin Elmer Model 1760x) using a KBr pellet technique.

3.9   Graft Copolymer Characterization

3.9.1   Fiber/ Grafted Morphology by Microscopy

The surfaces of 40% graft yield of the AA-grafted PET filament and the ungrafted PET fiber were coated with thin layer of gold to provide electric conductivity. A JEOL JSM-5800LV scanning microscope was used for surface morphology characterization at 15 keV acceleration voltage. The micrographs were taken at different angle of view with different magnifications.

3.9.2   Tensile Properties

3.9.2.1 Denier

The ungrafted and the grafted samples (0, 10, 20, 30, 40% grafting) were tested on Lenzing Vibroskop 400. The specimens were tested at tension weight of 300 mg with a fiber length of 24 mm.

3.9.2.2 Tenacity, Elongation and Force

The ungrafted and the grafted samples (0, 10, 20, 30, 40% grafting) were tested on Lenzing Vibrodyn 400. The specimens were tested at the testing speed of 100 mm min^{-1} using a gauge length of 10 mm.

3.9.3 Thermal Stability

The ungrafted and the grafted samples of weighting 0.30 mg of several grafting levels (0, 10, 20, 30, 40% grafting) were investigated by TGA and DTG techniques, on the NETZSCH thermo-microbalance TG 409 analyzer within a temperature range of 273-923 K and a heating rate of 10 K per minute in nitrogen atmosphere.

3.9.4 Moisture Regain (ASTM D 1909)

The moisture regain of the ungrafted and grafted samples (0, 10, 20, 30, 40% grafting) was determined by exposing the fibric (1.0 g) to 65% relative humidity at 293 K in a humidity-temperature chamber for 5 days. The sample were weighed in the conditioned state, then dried at 383 K for 12 hours in an oven and weighed again. Each sample was repeated for three replications based on ASTM D 1909.

3.9.5 Dyeability of Methylene Blue

3.9.5.1 Calibration Curve

a) Cationic dye (Methylene Blue)

Methylene blue stock solution was prepared by dissolving 0.2 g methylene blue in distilled water and diluted to the volume in a 1000-cm^3 volumetric flask. This solution (25 cm^3) was pipetted into a 100-cm^3 volumetric flask and it was diluted with distilled water. Thus 1 cm^3 of this solution contains 5×10^{-5} g methylene blue.

The stock solutions of 1, 2, 4, 6, 8, 10, and 12 cm^3 (5×10^{-5}, 1×10^{-4}, 2×10^{-4}, 3×10^{-4}, 4×10^{-4}, 5×10^{-4}, and 6×10^{-4} g) were each filled in a 100-cm^3 volumetric flask and diluted to the volume with distilled water. The calibration curve was constructed by measuring their absorbance of solutions at 663

nm wavelength in Unicam 5625 UV/VIS Spectrometer. Distilled water and a quartz cell of 1.0 cm path length were used for the measurement. Calibration curve was plotted between the absorbance values and the concentrations of the solution.

b) Disperse Dye (Hicron Navy Blue GRL-SF 200%)

Hicron navy blue GRL-SF 200% (CI disperse blue 79) stock solution was prepared by dissolving 0.2 g Hicron navy blue GRL-SF in distilled water and diluted to the volume in a 1000-cm^3. Thus 1 cm^3 of this solution contains 2×10^{-4} g Hicron Navy Blue GRL-SF 200%.

The stock solutions of 5, 10, 15, 20, 25, and 30 cm^3 (1×10^{-3}, 2×10^{-3}, 3×10^{-3}, 4×10^{-3}, 5×10^{-3}, and 6×10^{-3} g) were each filled in a 100-cm^3 volumetric flask and diluted to the volume with distilled water. The calibration curve was constructed by measuring their absorbance of solutions at 545 nm wavelength in Unicam 5625 UV/VIS Spectrometer. Distilled water and a quartz cell of 1.0 cm path length were used for the measurement. Calibration curve was plotted between the absorbance values and the concentrations of the solution.

3.9.5.2 Dyeing

a) Cationic dye (Methylene Blue)

The ungrafted and grafted (0, 10, 20, 30, 40% grafting) samples were dyed with 6.25×10^{-4} M methylene blue (0.2 g/l) by Phisit dyeing apparatus. The sample fiber weighing 0.2 g was placed into an aqueouse solution of the dye (100 cm^3) in a pot, allowed to stand for 2 hours at 373 K. The material/liquor ratio is 0.2/100. The dye remaining on the filament sample and in the pot were washed with distilled water, diluted them to the volume in a 1000-cm^3 volumetric flask with distilled water. This solution 25 cm^3, was filled into a 100-cm^3 volumetric flask and diluted with distilled water again. This solution was measured for the absorbance at 663 nm wavelength versus distilled water as a blank on Unicam 5625 UV/VIS Spectrometer, in a quartz cell of 1.0 cm path length. The concentration of the methylene blue dye remaining was determined from the calibration curve and the concentration of the dye on the fiber was calculated.

b) Disperse Dye (Hicron Navy Blue GRL-SF 200%)

The ungrafted and grafted (0, 10, 20, 30, 40% grafting) samples were dyed with 4.23 x 10^{-4} M Hicron Navy Blue GRL-SF 200% (0.2 g/l) by Phisit dyeing apparatus. The sample filament weighing 0.2 g was placed into an aqueouse solution of the dye (100 cm^3) in a pot, allowed to stand for 2 hours at 403 K. The material/liquor ratio is 0.2/100. The dye remaining on the fiber sample and in the pot were washed with distilled water, diluted them to the volume in a 1000-cm^3 volumetric flask with distilled water. This solution 25 cm^3, was filled into a 100-cm^3 volumetric flask and diluted with distilled water again. This solution was measured for the absorbance at 545 nm wavelength versus distilled water as a blank on Unicam 5625 UV/VIS Spectrometer, in a quartz cell of 1.0 cm path length. The concentration of the Hicron Navy Blue GRL-SF 200% dye remaining was determined from the calibration curve and the concentration of the dye on the fiber was calculated.

CHAPTER IV

RESULTS and DISCUSSION

4.1 Graft Copolymerization of Acrylic Acid onto PET Fiber

The grafting of acrylic acid onto PET fiber was conducted to develop the material properties that accommodated a high density surface of carboxyl groups. The overall process involved the treatment of PET fiber with acrylic acid in ceric aqueous acid medium. This led to the formation of graft copolymer. A schematic presentation of the modification of PET backbone is depicted in Figure 4.1.
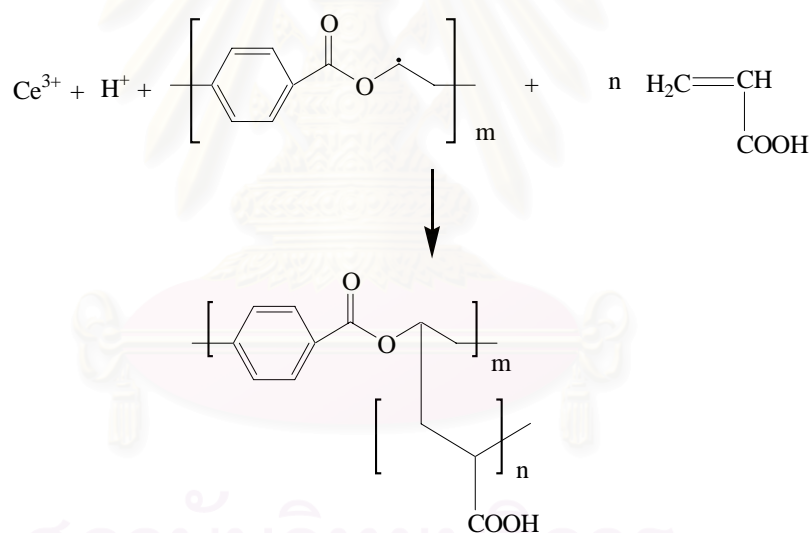
Figure 4.1 Schematic representation of the surface modification of PET fiber.

These graft copolymerizations use a redox initiation method. The ceric ion produces PET macroradicals via direct abstraction of hydrogen atoms from PET molecules. This reaction may be represented as follows:

$$P\text{-}H + Ce^{4+} \rightleftharpoons complex \longrightarrow P^\bullet + Ce^{3+} + H^+$$

where P-H represents the PET molecule.

In the presence of a vinyl monomer, the double bond of the vinyl monomer is added to the PET macroradical, resulting in the covalent bond between the monomer and PET with creation of a free radical on the monomer, i.e., a chain is initiated. Subsequent addition of monomer molecules to the initiated chain propagates the grafting reaction onto PET as follows:
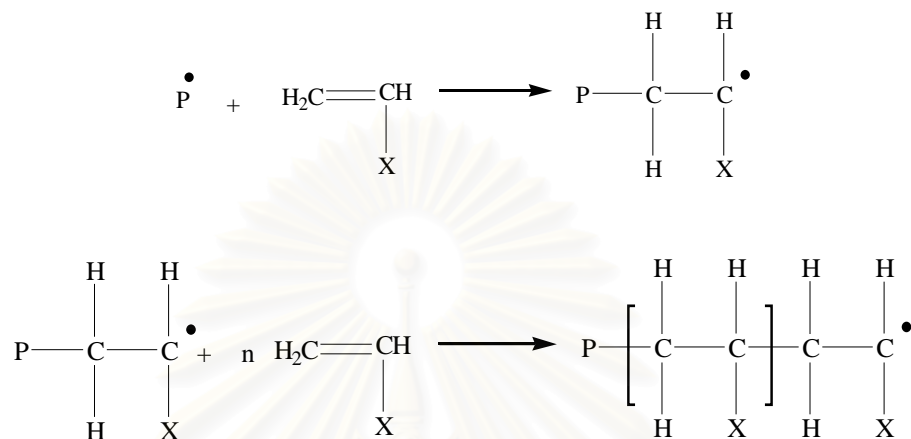
Finally, termination of the growing grafted chain may occur via reaction with disproportionation, coupling, or chain transfer, as follows:
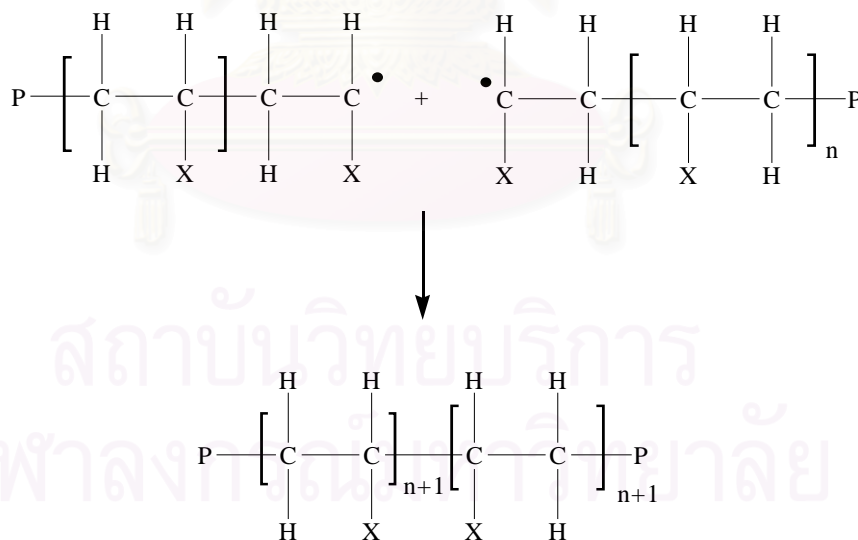
(Graft termination by coupling or combination)

(Graft termination by disproportionation)
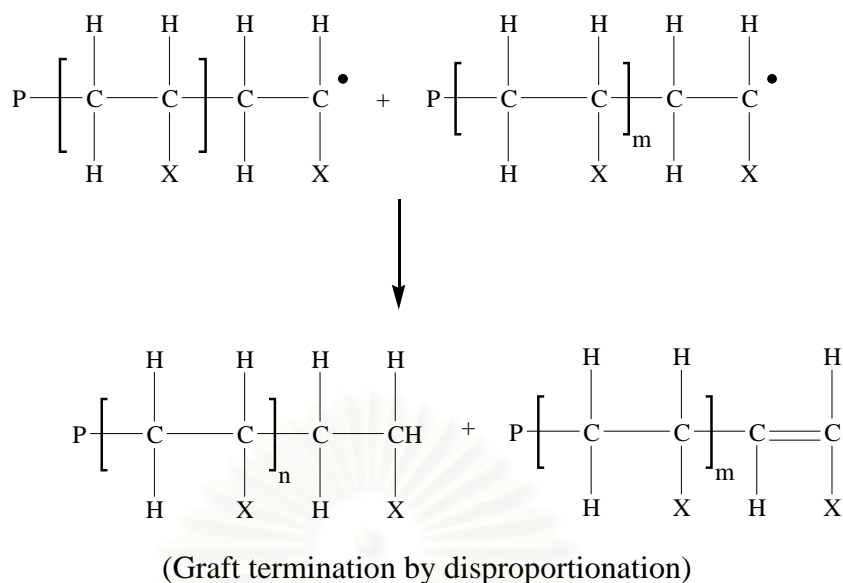
The yield of poly(acrylic acid) grafted PET was considerably influenced by the functions of monomer, initiator, and acid concentration, and reaction conditions. The influences of this parameter on the graft yield are discussed below.

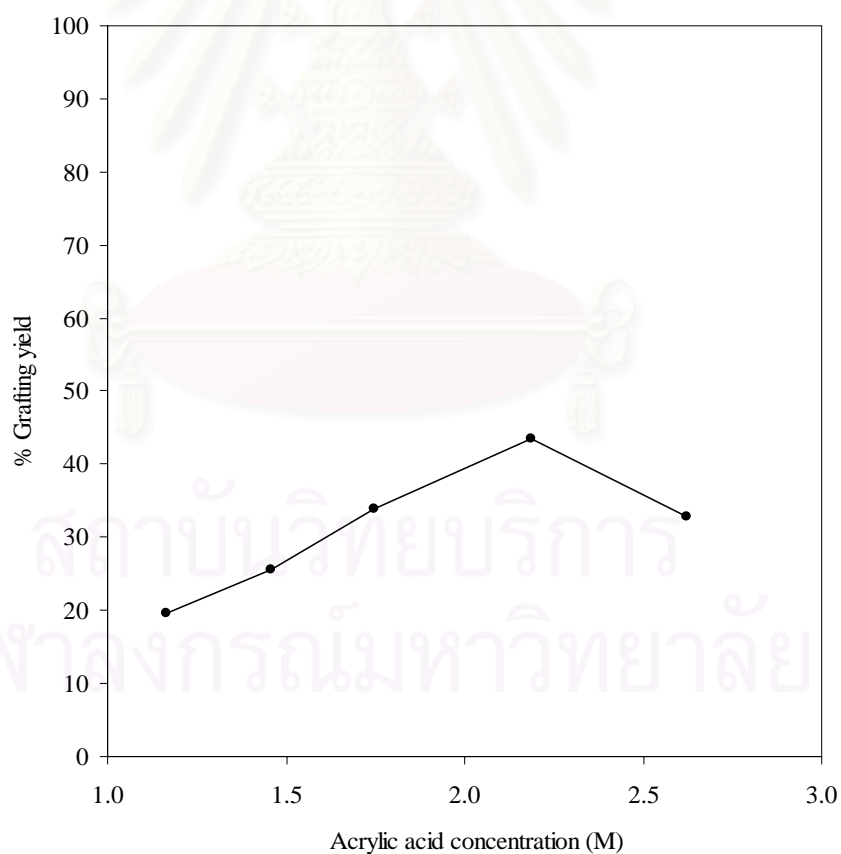### 4.1.1 Effect of Monomer Concentration

The relation between the graft yield and the monomer concentration was investigated by the experiments carried out at five different acrylic acid concentrations from 1.17 M to 2.62 M. The results of graft yield for various monomers are tabulated in Table 4.1 and shown in Figure 4.2.

Table 4.1 Effect of acrylic acid monomer on graft yield

Acrylic acid concentration[a] (M)	Graft yield (% by weight)
1.17	19.6 $\pm$ 0.59
1.46	25.5 $\pm$ 0.43
1.75	34.0 $\pm$ 0.49
2.19	43.6 $\pm$ 0.26
2.62	32.8 $\pm$ 0.77

[a]Data were obtained under the following condition: PET fiber 1g; $[HNO_3]$ = 0.80 M; $[Ce(IV)]$ = 1.82 x 10^{-3} M, the reaction time = 60 min, and the reaction temperature 323 K, number of replication is three.

Figure 4.2 Effect of acrylic acid concentration on graft yield

It is seen that the graft yield increases steadily with the increasing monomer concentration from 1.17 M to 2.19 M, and then decreases with further increases in acrylic acid monomer concentration. The increase in the concentration of acrylic acid content diffuses into the PET fiber and the excess amount presence in the outer solution. This increases chances for the PET macroradicals and growing grafted side chains to encounter more monomer units to add and increase the graft yield. However, the decreasing trend of the graft yield was found when further increase in the concentration of acrylic acid had been added. The more the monomer concentration in the aqueous phase, the more the homopolymer due to the competition between the homopolymerization and graft copolymerization, where the former prevails over the latter at higher acrylic acid concentration and at the expense of the latter (28). The poly(acrylic acid) homopolymer accumulated increases the medium viscosity, which inhibits the acrylic acid diffusion to the active site leading to the decrease in graft yield.
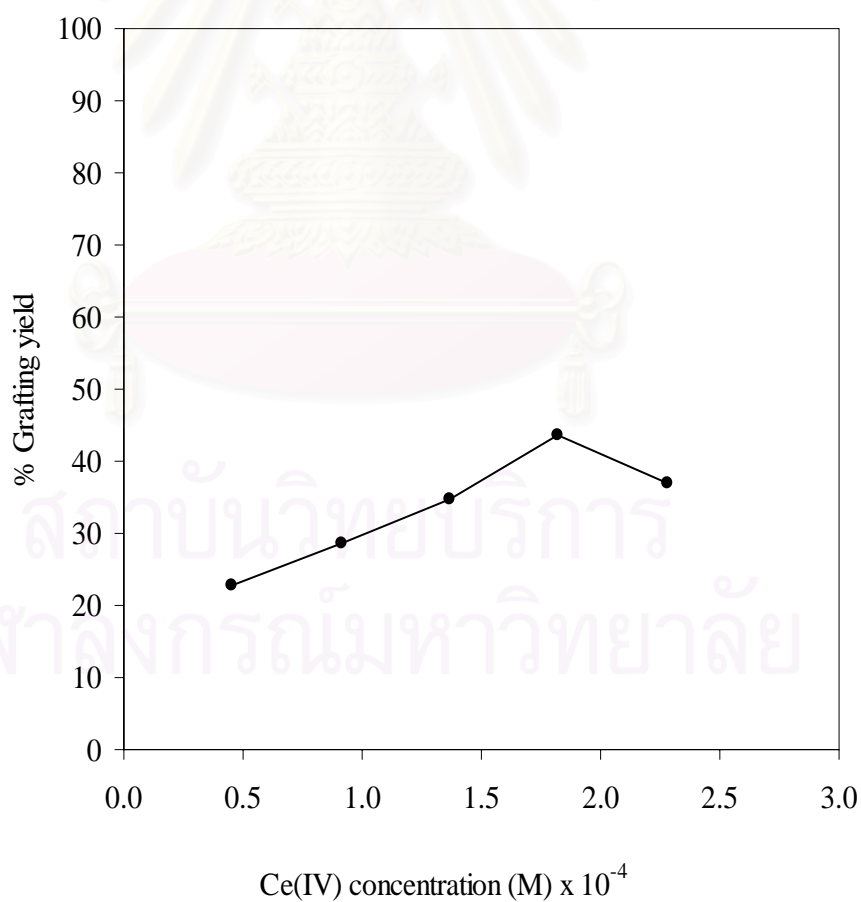
4.1.2 <u>Effect of initiation concentration</u>

The relation between the graft yield and the initiator concentration was investigated by the experiments carried out at five different Ce(IV) ion concentrations from 0.49×10^{-3} M to 2.28×10^{-3} M. The effect of variation of Ce(IV) ion concentration on the graft yield has been tabulated in Table 4.2 and shown in Figure 4.3.

Table 4.2 Effect of initiation concentration on graft yield and homopolymer

Ce(IV) ion $\times 10^{-3}$ concentration[a] (M)	Graft yield (% by weight)	Homopolymer (% by weight)
0.49	22.8 ± 0.35	83 ± 2.52
0.91	28.6 ± 0.21	78 ± 2.65
1.37	34.6 ± 0.46	75 ± 2.08
1.82	43.6 ± 0.26	69 ± 1.53
2.28	36.9 ± 0.55	75 ± 1.15

[a]Data were obtained under the following condition: PET fiber 1 g, [AA] = 2.19 M, [HNO$_3$] = 0.80 M, the reaction time = 60 min, and the reaction temperature 323 K, number of replication is three.
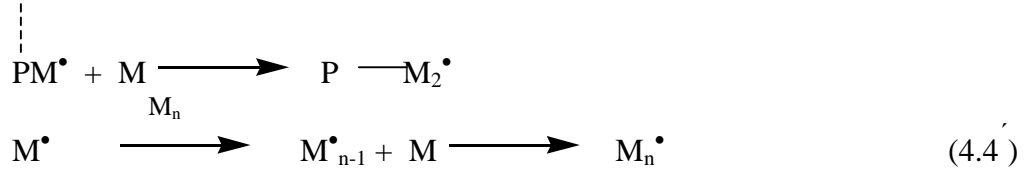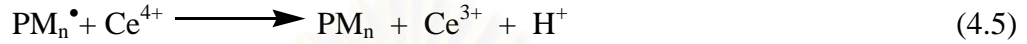

Figure 4.3 Effect of ceric initiator concentration on graft yield

It is observed that increasing the initiator concentration from 0.49×10^{-3} M to 1.82×10^{-3} M, the graft yield increases, and thereafter the graft yield decreases considerably. The variation of ceric ammonium nitrate produces a considerable change in the number of free radicals generated (4). The increase in the ceric ion concentration increases more decomposition of the complex of Ce^{4+}. Nitric acid also catalyzes the oxidation of Ce^{4+}. These primary free radicals abstract hydrogen from the active centers on PET and produce PET macroradicals which lead to the formation of graft copolymer and increase the graft yield. However, further increase in initiator concentration (higher than 1.82×10^{-3} M) brings in the following effects (41, 44): (a) For the abundant free radicals in the aqueous phase, acrylic homopolymer could be particularly formed in the solution, which might terminate the growing chains; (b) free radicals formed on the main chain of PET filament could be oxidized, and thus terminate the reactive sites; (c) the graft copolymerization and homopolymerization of acrylic acid are competing with each other in the system, depending on the direct attack of free radicals to either the PET filament or to the monomer. The net result is that, a higher concentration of initiator results in the production of more free radicals, therefore, reduces the graft yield due to efficiency of Ce^{4+} to take part in termination of growing graft chain.

A mechanism for the grafting of acrylic acid onto PET filament was postulated by assuming a prior complex formation between PET (PH) and ceric ion. The complex then decomposes to generate the PET macroradicals ($P^\bullet$). They can also react with the monomer to form a growing monomeric radical, which is able to convey its radical character to the PET chain, and to induce acrylic acid graft copolymerization as well as homopolymerization. The reaction then proceeds through the following steps (4.1) – (4.6), for grafting of acrylic acid onto PET filament:

Initiation

$$PH + Ce^{4+} \underset{\longleftarrow}{\overset{K}{\longrightarrow}} complex \xrightarrow{k_d} P^\bullet + Ce^{3+} + H^+ \qquad (4.1)$$

$$P^\bullet + M \xrightarrow{k_i} PM^\bullet \qquad (4.2)$$

$$Ce^{4+} + M \longrightarrow M^\bullet + Ce^3 + H^+ \qquad (4.3)$$

Propagation

$$PM^\bullet + M \xrightarrow{k_p} P\!-\!\!M_2^\bullet \tag{4.4}$$

$$PM^\bullet + M \xrightarrow{} P\!-\!\!M_2^\bullet$$

$$M^\bullet \xrightarrow{M_n} M^\bullet_{n-1} + M \xrightarrow{} M_n^\bullet \tag{4.4'}$$

Termination

$$PM_n^\bullet + Ce^{4+} \xrightarrow{} PM_n + Ce^{3+} + H^+ \tag{4.5}$$

$$M_n^\bullet + Ce^{4+} \xrightarrow{-k_t'} M_n + Ce^{3+}\ H^+ \tag{4.5'}$$

Oxidation

$$P^\bullet + Ce^{4+} \xrightarrow{k_o} \text{oxidation product} + Ce^{3+} + H^+ \tag{4.6}$$
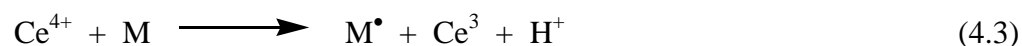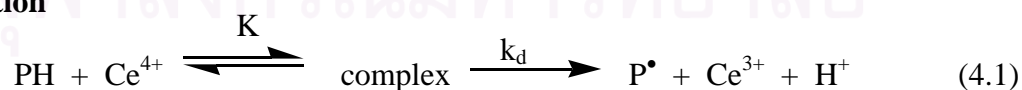
where Ce(IV), PH, $P^\bullet$, M, K, k_d, k_i, k_p, k_t and k_o are ceric ion, PET molecule, PET macroradical, monomer, rate constants, rate constants for decomposition, rate constants for initiation, rate constants for propagation, rate constants for termination, and rate constants for oxidation, respectively.

The most probable explanation for this type of behavior can be obtained by considering the above mentioned reaction schemes (4.1) – (4.6). Taking into account of the above reaction schemes and applying the steady-state principle (49) to all kinds of radicals involved; the following expression for the rate of grafting (R_g) could be:

$$\frac{d[P^\bullet]}{dt} = K\,k_d[Ce^{4+}][PH] - k_i[P^\bullet][M] - k_o[P^\bullet][Ce^{4+}] = 0$$

$$K\,k_d\,[Ce^{4+}][PH] = k_i\,[P^\bullet][M] + k_o[P^\bullet][Ce^{4+}]$$

$$K\,k_d\,[Ce^{4+}][PH] = [P^\bullet]\,(k_i\,[M] + k_o[Ce^{4+}])$$

$$[P^\bullet] = \frac{K\,k_d\,[Ce^{4+}][PH]}{(k_i\,[M] + k_o[Ce^{4+}])} \tag{4.7}$$

$$\frac{d[PM^\bullet]}{dt} = k_i[P^\bullet][M] - k_t[PM_n^\bullet][Ce^{4+}] = 0$$

$$k_i[P^\bullet][M] \qquad = k_t[PM_n^\bullet][Ce^{4+}]$$

$$[PM_n^\bullet] \qquad = \frac{k_i[P^\bullet][M]}{k_t[Ce^{4+}]} \qquad (4.8)$$

Replacing the value of $[P^\bullet]$ from eq. (4.7), to give a general R_g (the rate of grafting) equation in eq. (4.9)

$$[PM_n^\bullet] \qquad = \frac{k_i}{k_t[Ce^{4+}]} \frac{K k_d [Ce^{4+}][PH][M]}{(k_i[M] + k_o[Ce^{4+}])}$$

$$R_g \qquad = k_p[PM_n^\bullet][M]$$

$$R_g \qquad = \frac{k_p k_i}{k_t[Ce^{4+}]} \frac{K k_d [Ce^{4+}][PH][M][M]}{(k_i[M] + k_o[Ce^{4+}])}$$

$$R_g \qquad = \frac{k_p k_i [M]^2}{k_t[Ce^{4+}]}\left(\frac{K k_d [Ce^{4+}][PH]}{(k_i[M] + k_o[Ce^{4+}])}\right) \qquad (4.9)$$

At low ceric ion concentration,

$$R_g \qquad = k_p k_i [M]^2\left(\frac{K k_d [Ce^{4+}][PH]}{k_i[M]}\right) \qquad (4.10)$$

which shows that, with an increase in ceric ion concentration, R_g should increase, which is found to be true.

But at higher concentration of Ce^{4+} and when $k_t \gg k_p$ and k_i

$$R_g \qquad = \frac{k_p k_i [M]^2}{k_t[Ce^{4+}]}\left(\frac{K k_d [Ce^{4+}][PH]}{(k_i[M] + k_o[Ce^{4+}])}\right) \qquad (4.11)$$

Since eq. (4.9) equals to eq. (4.11) resulting from the moderate and high concentration og Ce^{4+}. Eq. (4.11) requires that increases in Ce^{4+} ion concentration increase the magnitude of the denominator, which results in decreasing the value of R_g. A maximum value of the graft yield is obtained in an optimum concentration of Ce^{4+} ion, beyond which the graft yield decreases.

As mentioned above, homopolymer formation takes place simultaneously with graft copolymerization. To attain a good property of graft copolymer, the homopolymer should be removed. The most commonly employed

method for the removal of this homopolymer from the grafted fiber is extraction in a good solvent for the homopolymer while the graft copolymer remains unaffected. Many work used THF (45), acetone (46) or methanol (47) as a solvent in the removal of poly(acrylic acid) from the grafted fiber. In this thesis, methanol was employed for the extraction of homopolymer by Soxhlet extraction method. The extraction time was determined based on the extraction time at which the fiber weight remained unchanged.

The relation between homopolymer content and the graft yield was determined at four levels of graft yield from 22.6% to 41.6%. The effect of homopolymer content on grafting of acrylic acid onto PET fiber has been tabulated in Table 4.2 and shown in Figure 4.4.
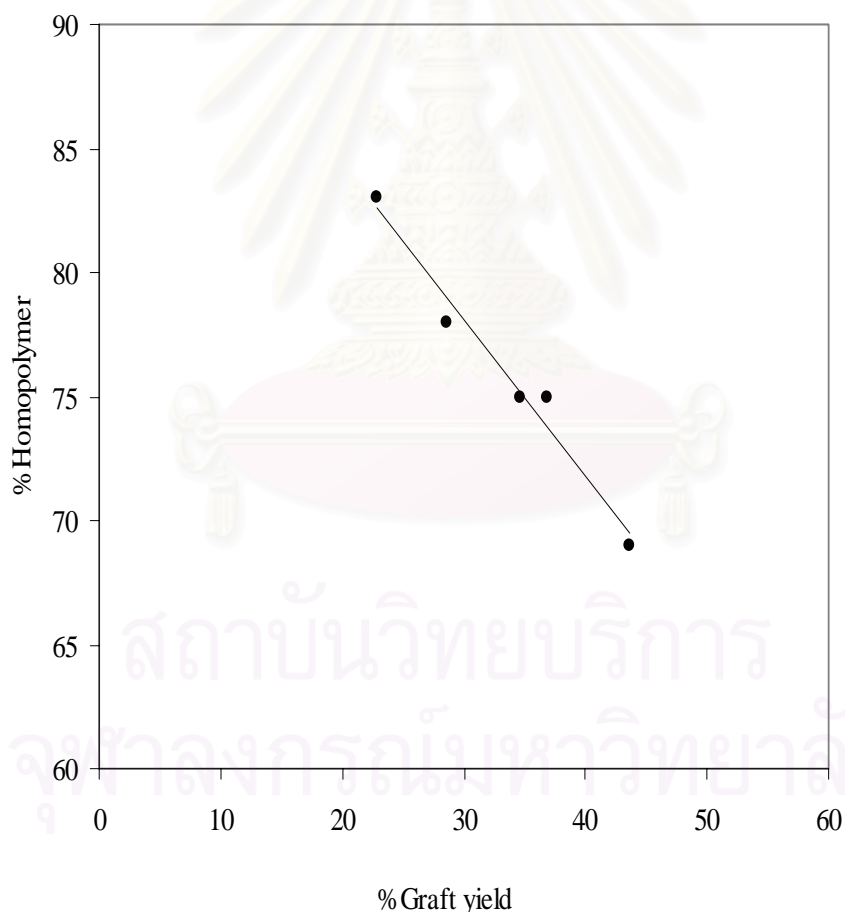
Figure 4.4 Effect of homopolymer content on graft yield

Figure 4.4 shows the grafting yields versus homopolymer percentage. The graft yield decreases when the homopolymer content increases. The homopolymer content in the reaction bath brings about an increase in its viscosity and introduces diffusion difficulty of free vinyl monomer into the fiber, which decreases both the grafting degree on fiber and its utilization in the process.

4.1.3 Effect of nitric acid concentration

The relation between the graft yield and the nitric acid concentration was investigated by the experiments carried out at four different nitric acid concentrations from 0.50 M to 1.01 M. The effect of variation of nitric acid concentration on grafting of acrylic acid onto PET fiber has been tabulated in Table 4.3 and shown in Figure 4.5.

Table 4.3 Effect of nitric acid concentration on graft yield

Nitric acid concentration[a] (M)	Graft yield (% by weight)
0.50	28.2 ± 0.64
0.60	30.1 ± 0.52
0.70	35.5 ± 0.13
0.80	43.6 ± 0.26
0.91	33.8 ± 0.37
1.01	32.2 ± 0.49

[a]Data were obtained under the following condition : PET fiber 1 g, [AA] = 2.19 M, [Ce(IV)] = 1.82 x 10^{-3} M, the reaction time = 60 min, and the reaction temperature 323 K, number of replication is three.
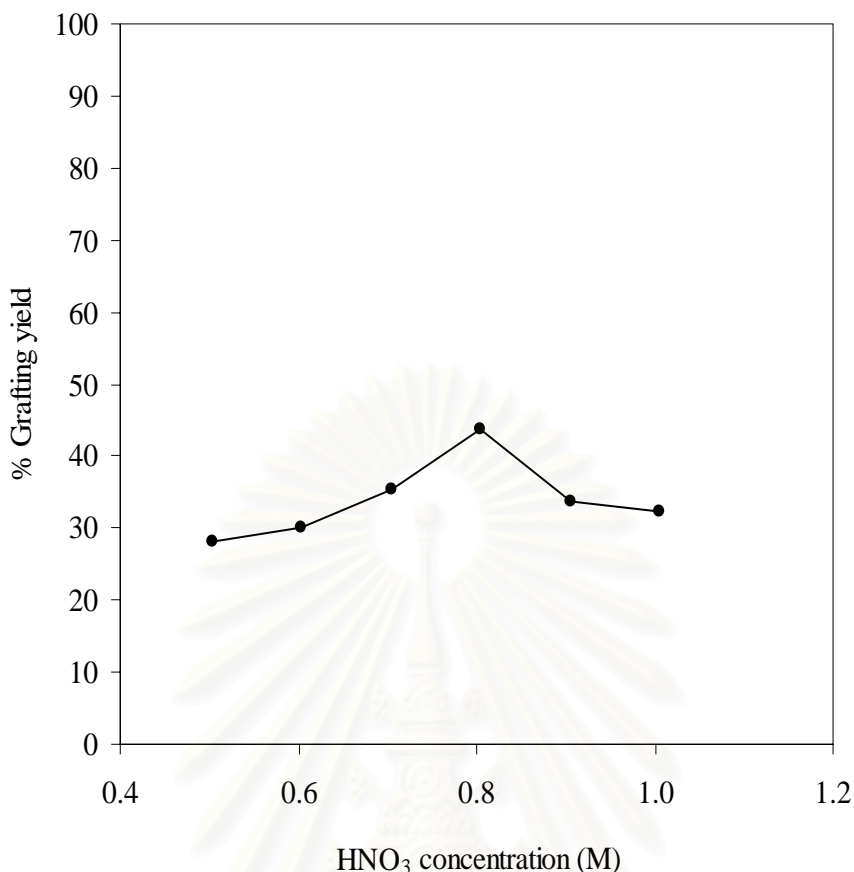
Figure 4.5 Effect of the nitric concentration on graft yield

From Table 4.3, it is observed that the increases of acid concentration in the reaction mixture enhance the percent graft yield. This may be attributed to increase in the oxidation potential of ceric ion resulting in the production of more active Ce^{4+} species and/or $Ce(OH)_3^{3+}$. These ceric species have been proved to be potential oxidizers of a large number of organic substrates, the oxidation of which proceeds through a free radical path. In this case, the ceric species probably attacks PET backbone at a faster rate resulted in the system of a large number of the grafting sites to which monomer addition takes place (47). Nitric acid also acted as a catalyst in the reaction. This is explained by the fact that ceric ion in water is believed to react in the following manner (4, 6):

$$Ce^{4+} \; + \; 3H_2O \; \rightleftharpoons \; [Ce(OH)_3]^{3+} \tag{4.12}$$

$$2[Ce(OH)_3]^{3+} \; \rightleftharpoons \; [Ce\text{-}O\text{-}Ce]^{6+} \; + \; H_2O \tag{4.13}$$
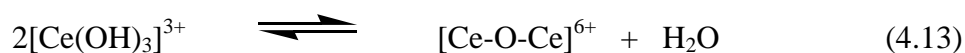
Thus, ceric ions exist as Ce^{4+}, $[Ce(OH)_3]^{3+}$, and $[Ce-O-Ce]^{6+}$ in water solution. The observed zero grafting at zero nitric acid concentration indicates the inability of $[Ce-O-Ce]^{6+}$ to form a complex with PET (PH). With increase in nitric acid concentration to 0.80 M, the reactions (4.12) and (4.13) shift toward the left to give more and more Ce^{4+} and $[Ce(OH)_3]^{3+}$, which is in favor of graft copolymerization. These species at higher concentration affect grafting efficiency adversely.

Mechanistically, the acid enhancement effect in grafting, based on considerable work (48), has attributed to a partitioning phenomenon. In terms of this concept, increased partitioning of monomers occurs in the graft region of the backbone polymer when acid is dissolved in the bulk grafting solution, thus permitting higher concentration of the monomer to be available for grafting at a particular site. These mechanisms of an acid effect in grafting initiated by ceric ions cause an increase in the grafting yield. Inclusion of acid accelerates homopolymerization and a reduction in grafts. Generally, the extent of this improved monomer partitioning depends upon the polarity of monomer, the substrate and the concentration of the nitric acid present. The positive effect of acid enhancement as that both a partitioning phenomenon and ceric ion initiation acted in concert to optimize the graft yield.

At a higher concentration of acid, the effect of acid hydrolysis on the PET backbones as another possible cause for the lowering in graft yield could be observed.

4.1.4   Effect of the reaction temperature on graft yield

The grafting reaction was carried out at five different temperatures, between 313 K to 333 K; and the results are tabulated in Table 4.4 and shown in Figure 4.6. The graft yield reaches a maximum at 323 K, using the various experimental temperatures. The graft yield was seen to decrease when the temperature increases to 328 K.

Table 4.4 Effect of the reaction temperature on graft yield

Temprature[a] (K)	Graft yield (% by weight)
313	20.3 ± 0.52
318	26.6 ± 0.61
323	43.6 ± 0.26
328	35.7 ± 0.39
333	33.2 ± 0.46

[a]Data were obtained under the following condition : PET fiber 1g; [AA] = 2.19 M, [HNO$_3$] = 0.80 M; [Ce(IV)] = 1.82 x 10^{-3} M, and the reaction time 60 min, number of replication is three.
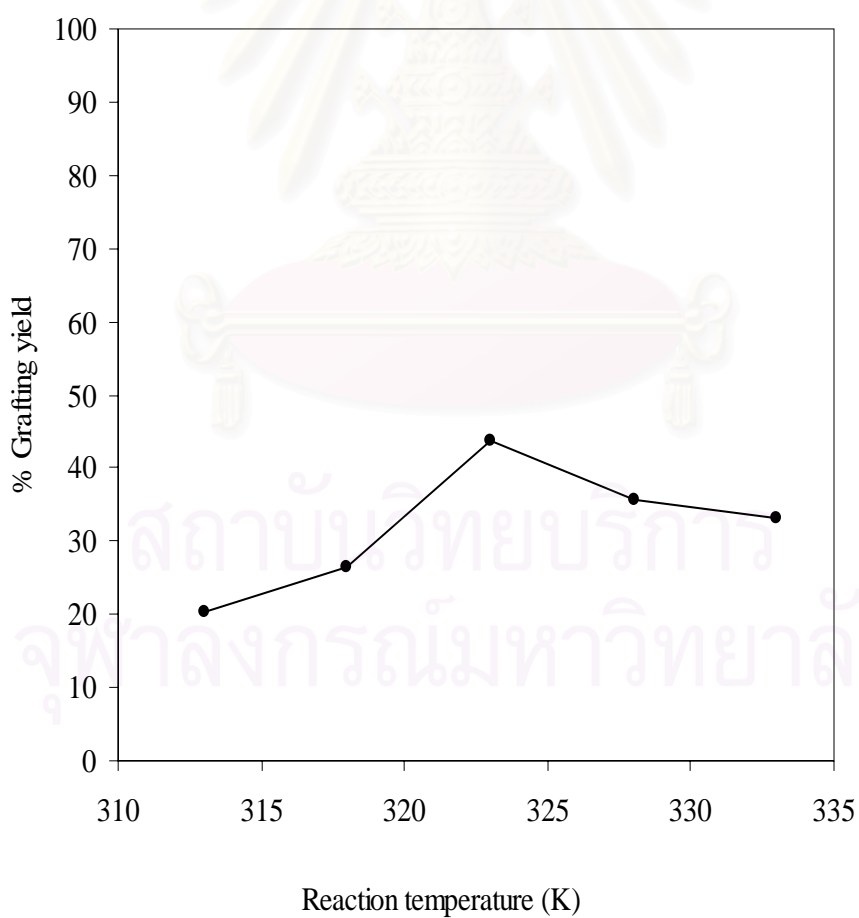
Figure 4.6 Effect of the reaction temperature on graft yield

It is proposed that in the early stages of the reaction, homopolymer formation was very limited and the concentration of acrylic acid monomer around the growing chain was maintained. This causes a fast chain initiation and propagation, leading to a high graft yield. The favorable effect of temperature on grafting (41, 49) could be ascribed to: (a) enhanced diffusion of the acrylic acid monomer and Ce^{4+} molecules onto the PET structure; (b) improving the swellability of PET fiber and eases the diffusion into it; (c) facilitated the radical reactions as a result of the increased mobility of monomer molecules and their collision with macroradicals; and (d) increased propagation of the grafted PET fiber.

Further increase in temperature decreased the graft yield. This indicated that at higher temperature, the collision between monomer free radicals also increased, where in the homopolymer formation becomes predominant. The graft copolymerization occurs with poor selectivity and various hydrogen abstractions. It is possible that chain termination and chain transfer reactions given by the reactions (4.5) and (4.5$^{'}$) might be accelerated, thereby decreasing the graft yield.

4.1.5   Effect of the reaction time on graft yield

The effect of the reaction time on grafted PET fiber was investigated at five different reaction times from 30, 45, 60, 75, and 90 minutes, and the results are tabulated in Table 4.5 and shown in Figure 4.7. It is observed that increasing the reaction time from 30 to 60 minutes the graft yield increases, and thereafter the graft yield decreases considerably.

Table 4.5 Effect of the reaction time on graft yield

Time[a] (min)	Graft yield (% by weight)
30	14.7 ± 0.67
45	29.5 ± 0.43
60	43.6 ± 0.26
75	36.9 ± 0.62
90	32.8 ± 0.77

[a]Data were obtained under the following condition : PET fiber 1g; [AA] = 2.19 M, [HNO$_3$] = 0.80 M; [Ce(IV)] = 1.82 x 10^{-3} M, and the reaction temperature 323 K, number of replication is three.
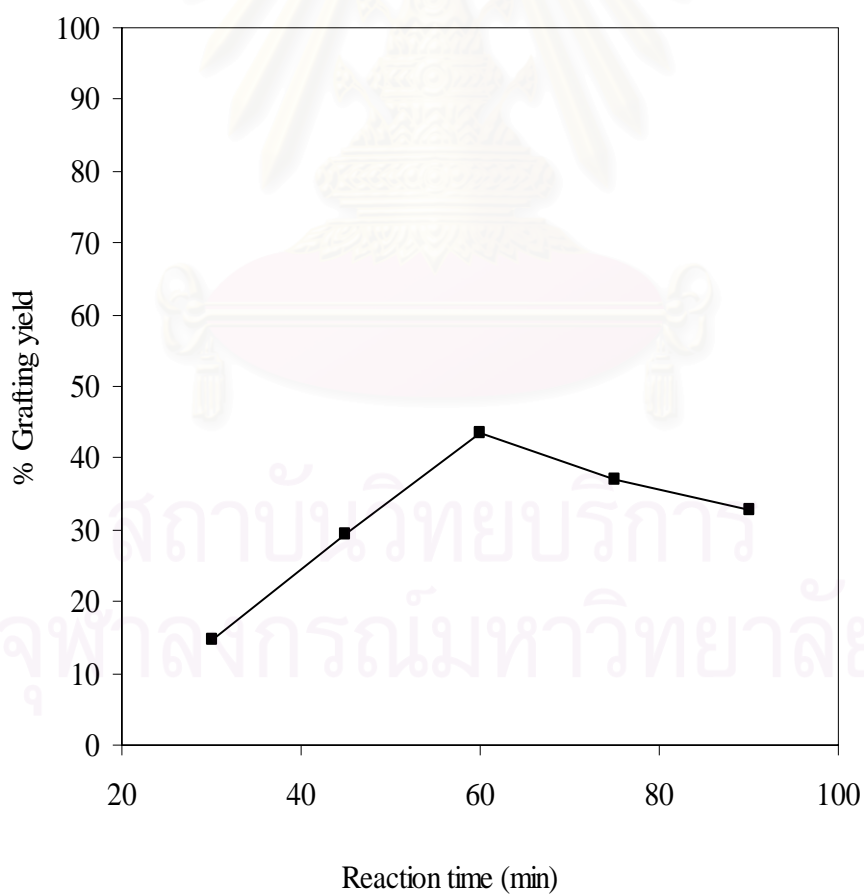
Figure 4.7 Effect of the reaction time on graft yield

In the beginning, the rate of grafting increases and reaches a maximum when the reaction time was 60 minutes. This increase can be explained as follows (50): (a) the higher the contact time of monomer molecules with the PET macroradical sites; (b) an increase in the length of poly(acrylic acid) grafted chain; (c) an increase in the number of grafted chains. These three hypotheses could possibly explain the reasons for the product so obtained for 60 minutes of copolymerization. When the time of reaction proceeds beyond 60 minutes, the graft yield decreased gradually. Similar observations have also been reported earlier (30, 51). The reducing reactive sites were exposed to the acrylic acid as the result of the increase in the viscosity of the solution. This situation induced difficulties for acrylic acid to react with the reducing reactive sites, which was very difficult for acrylic acid to react with these sites. However, the monomer and PET copolymerization takes place during the first 60 minutes when the rate of grafting increases.

4.2 Poly(acrylic acid) homopolymer

Infrared spectra of poly(acrylic acid) homopolymer in a form of KBr pellet are presented in Figure 4.8.

The FT-IR spectrum of poly(acrylic acid) in Figure 4.8 give absorption bands of O-H stretching at 3490 cm^{-1}, broad, weak, the C=O stretching at 1734 cm^{-1}, strong, sharp, and the C=O and C-O asymmetry and symmetry stretching of carboxylate anion at 1559 cm^{-1}, sharp, weak, and 1267 cm^{-1}, broad, weak, respectively. Besides that, IR spectrum shows a weak peak around at 2394 cm^{-1}. It is possible that a nitrile C≡N stretching from nitration. The FT-IR spectrum of poly(acrylic acid) homopolymer in Figure 4.8 shows the following peaks in Table 4.6.
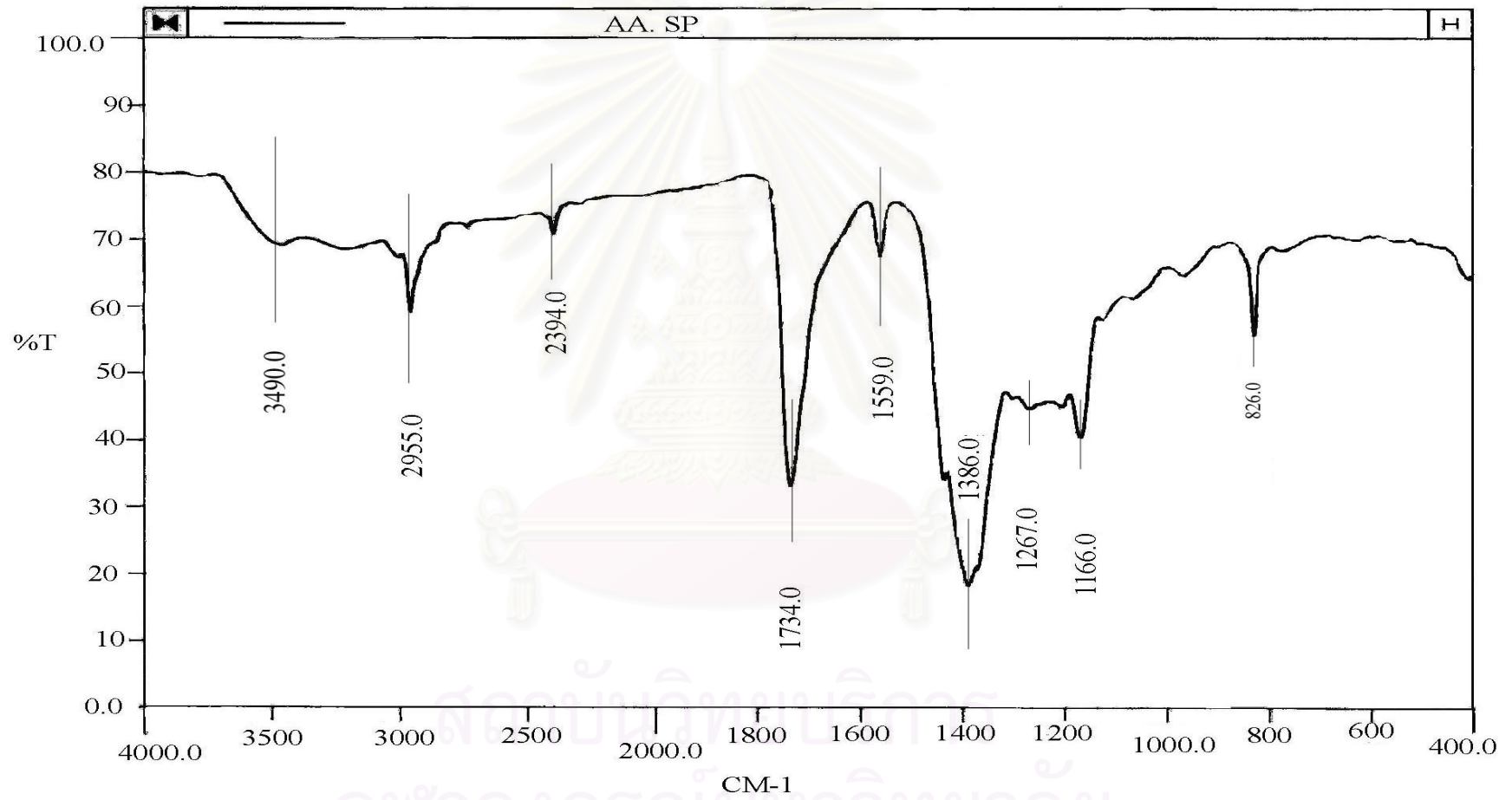
Figure 4.8 Infrared spectrum of poly(acrylic acid)

Table 4.6 The infrared absorption of functional groups in poly(acrylic acid) homopolymer

Wave number, cm^{-1}	Assignment
3490	O-H stretching
2955	C-H stretching of CH$_2$
2394	C$\equiv$N stretching of nitrile group
1734	C=O stretching
1559	C=O and C-O asymmetrical stretching of the carboxylate anion
1386	C-H scissors bending
1267	C=O and C-O asymmetrical stretching of the carboxylate anion
1166	C-O-C stretching

4.3 Properties of acrylic acid grafted PET fiber

4.3.1 Fiber/ grafted morphology by microscopy

The morphological structure of PAA-g-PET fiber initiated by ceric (IV) was investigated by scanning electron microscopy. Figure 4.9 (a) - (d) show the scanning electron micrographs of PET fiber and grafted fiber at 350 and 2000 magnifications, respectively. Drastic change after AA grafting is observed.

(a)   (b)

(c)   (d)
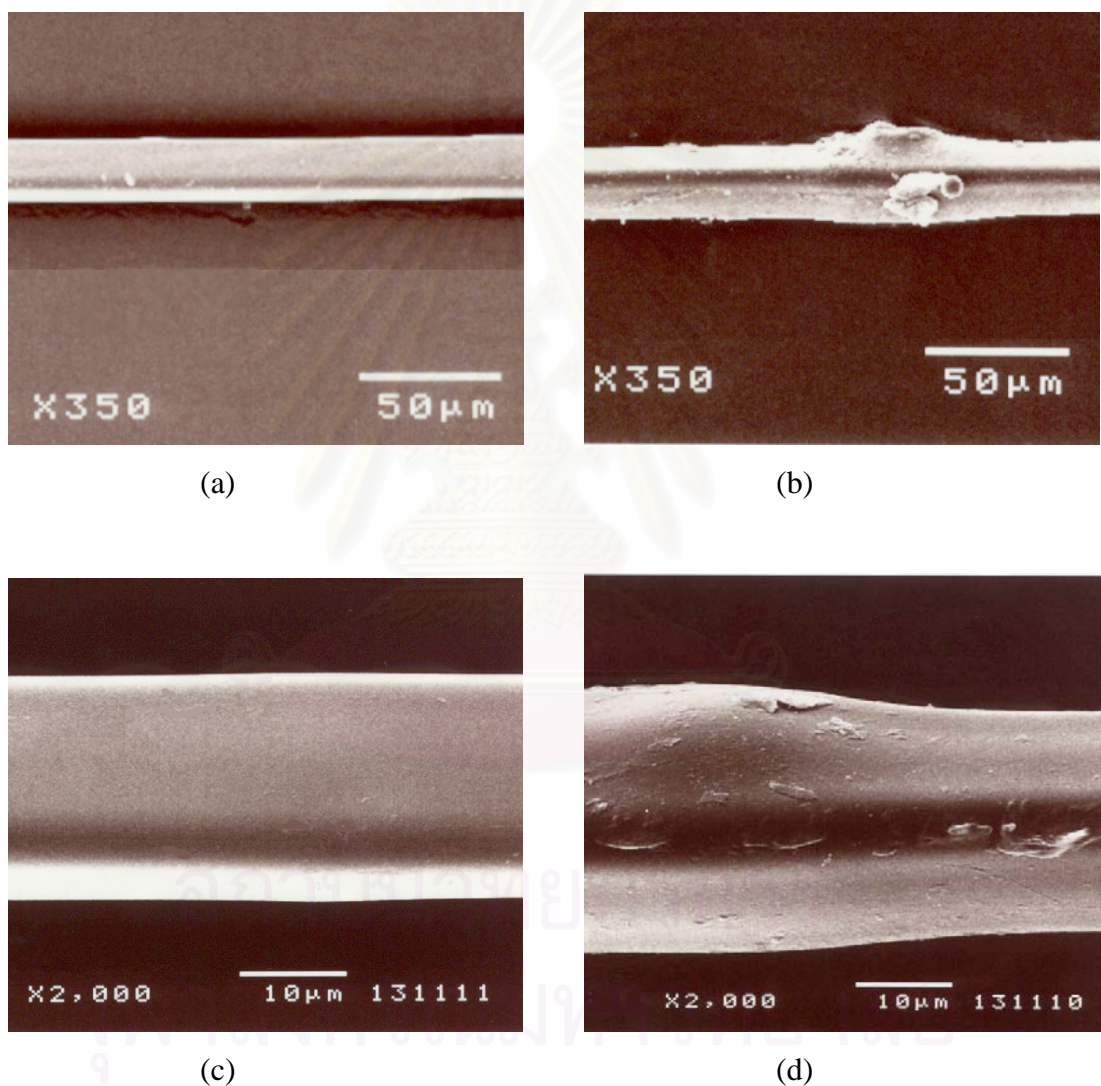
Figure 4.9 Scanning electron micrographs of AA-grafted PET fiber. Graft yield: (a) 0%; (b) 43.6%, (c) 0%; (d) 43.6%.

The surface of the ungrafted PET [Figure 4.9 (a) and (c)] was smooth, showing the typical features of the control PET fiber. However, electron

photomicrographs illustrate a coating of the AA-grafted PET fiber [Figure 4.9 (b) and (d)]. A thin and uneven layer of poly(acrylic acid) is deposited. Additionally, the dimension of the treated fiber is changed. The treated one becomes thicker and less shinny.

4.3.2 <u>Tensile properties</u>

The effects of acrylic acid grafting on the tenacity, the breaking elongation and breaking load of PET fiber are tabulated in Table 4.7.

Table 4.7 Effect of acrylic acid grafting on tensile properties of the PET fiber

Graft yield (%)	Denier	Breaking load (g force)	Decrease in breaking load (%)	Breaking tenacity (g/den)	Decrease in breaking tenacity (%)	%Breaking elongation	Decrease in breaking elongation (%)
0.0	5.03 ± 0.21	13.17 ± 0.65	0.00	2.62 ± 0.11	0.00	164.9 ± 10.6	0.0
9.7	5.62 ± 0.22	11.04 ± 0.58	16.17 ± 5.21	1.97 ± 0.11	24.81 ± 5.45	150.2 ± 18.7	8.9 ± 12.4
19.3	6.15 ± 0.19	11.17 ± 0.47	15.19 ± 4.16	1.82 ± 0.08	30.53 ± 4.14	145.5 ± 8.2	11.8 ± 5.61
29.4	6.58 ± 0.24	10.94 ± 0.44	16.93 ± 3.98	1.66 ± 0.08	36.64 ± 4.49	133.3 ± 12.5	19.2 ± 9.39
40.0	6.73 ± 0.28	8.62 ± 0.32	34.55 ± 3.75	1.28 ± 0.04	51.15 ± 2.42	117.3 ± 5.6	28.9 ± 5.0

Number of repeats is 20.

Table 4.7 shows the change in denier of fiber with grafting. The graft yield was observed to increase the fiber denier. The fiber denier increased from its untreated status of 5.03 to 6.73 at the highest graft yield of 40.0%. Breaking tenacity, breaking load and breaking elongation of PAA-grafted PET fiber decreased with increasing graft yield (Figures 4.10 to 4.13).
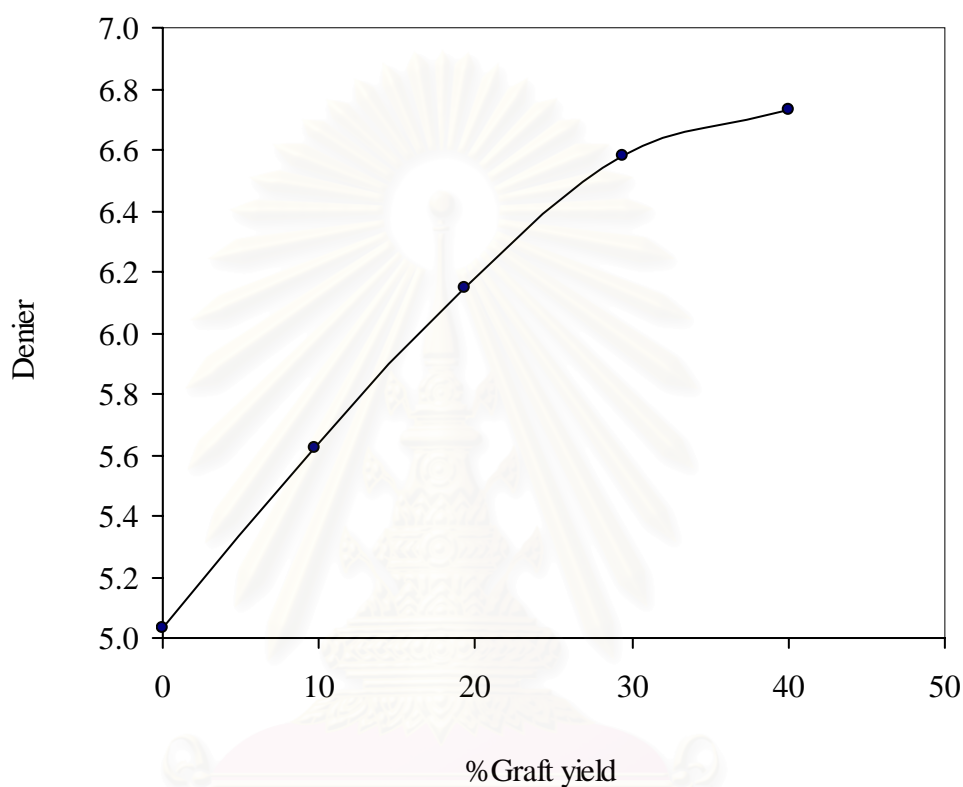
Figure 4.10 Effect of acrylic acid grafting on denier of the PET fiber
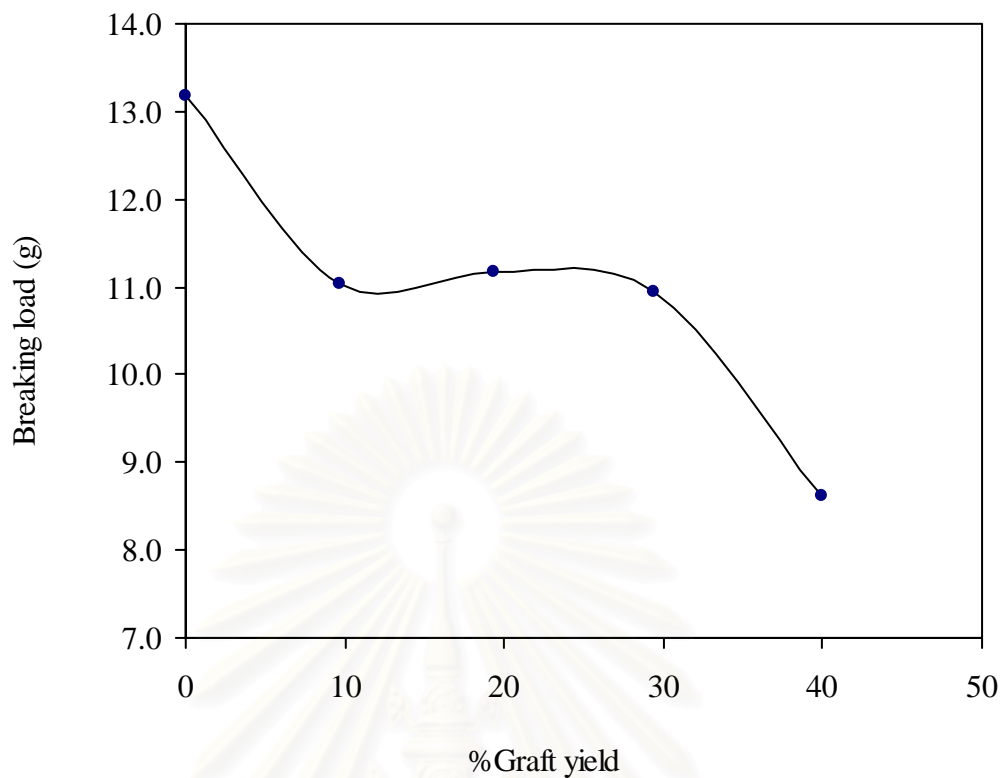
Figure 4.11 Effect of acrylic acid grafting on breaking load of the PET fiber
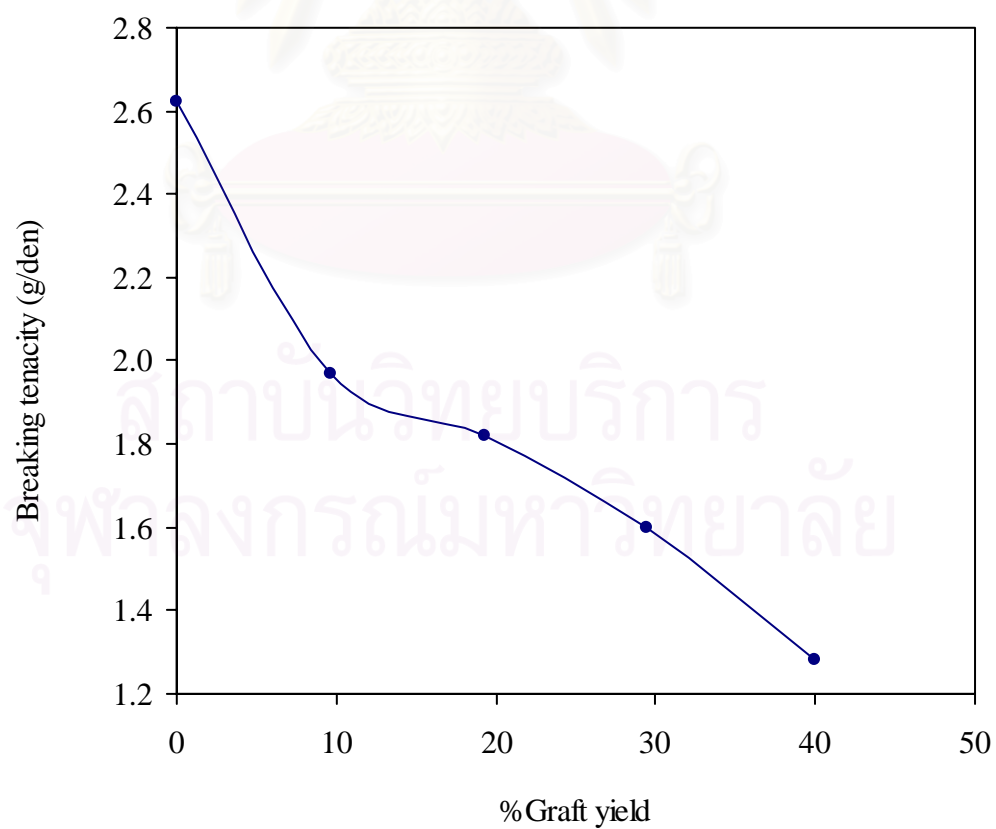
Figure 4.12 Effect of acrylic acid grafting on breaking tenacity of the PET fiber
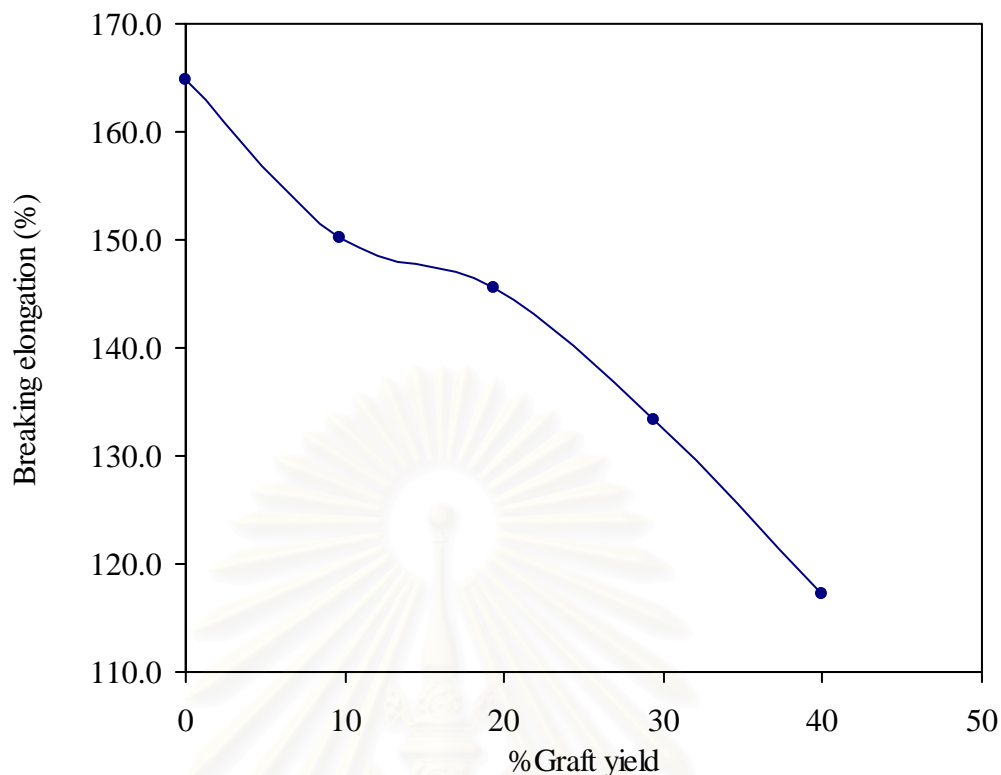
Figure 4.13 Effect of acrylic acid grafting on elongation of the PET fiber

Grafting on the PET fiber resulted in a general loss of tensile performance of the PET fiber, in good agreement with previously reported result (52). The intrinsic physicochemical characteristics of the grafted polymer are known to exert only a marginal effect on the tensile properties of grafted PET fiber. The segments in the amorphous regions of PET fiber may be disoriented as a result of grafting. The decrease in orientation, which is one of the most important fiber characteristics responsible for good mechanical behavior, decreases the fiber breaking tenacity. The reorientation of these disoriented regions under the influence of stretching force decreases the breaking elongation of the fiber, as seen in Table 4.7. At 40% grafting, the breaking tenacity of PET fiber drops 51% from 2.62 g/den to 1.28 g/den and breaking load drops 34.55% from 13.17 g to 8.62 g. The breaking elongation value of ungrafted PET is 164.9%, which decrease to 117.3% at 40.0% grafting. It was decreased by 29% elongation.

The drastic changes in fiber properties, as well as other factors, such as disordering of chain arrangement, steric hindrance as a consequence of polymer loading, and the presence of newly established boundary interactions

between PET fiber chains and grafted polymer, must be considered mainly responsible for the observed drop of fiber strength, extensibility, and toughness induced by grafting.

4.3.3 Thermal properties

The thermal properties of PET fiber and acrylic acid–grafted PET fiber are examined through TGA and DTG curves, which were recorded on the NETZSCH thermo-microbalance TG 409 analyzer within a temperature range 273-923 K with a heating rate of 10 K per minute in an atmosphere of nitrogen. The thermal properties of the PET fiber are shown in Figures 4.14 to 4.16.
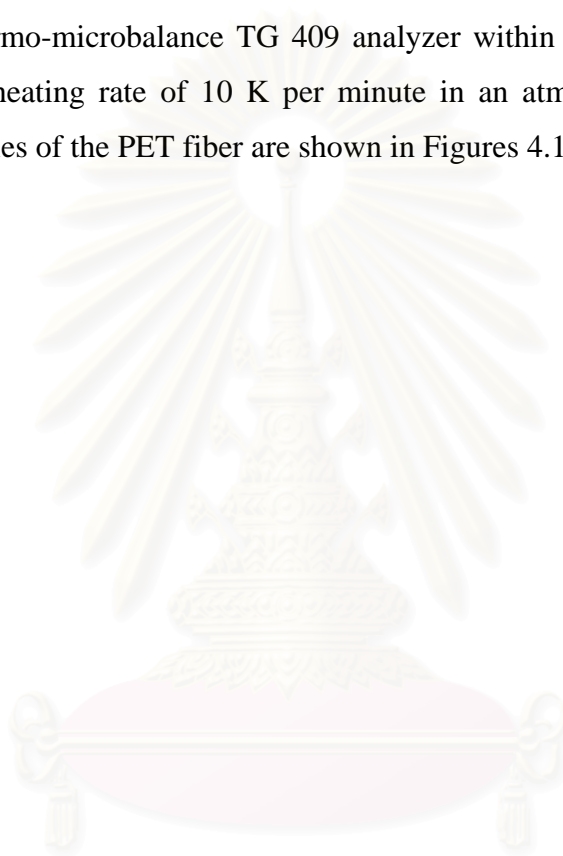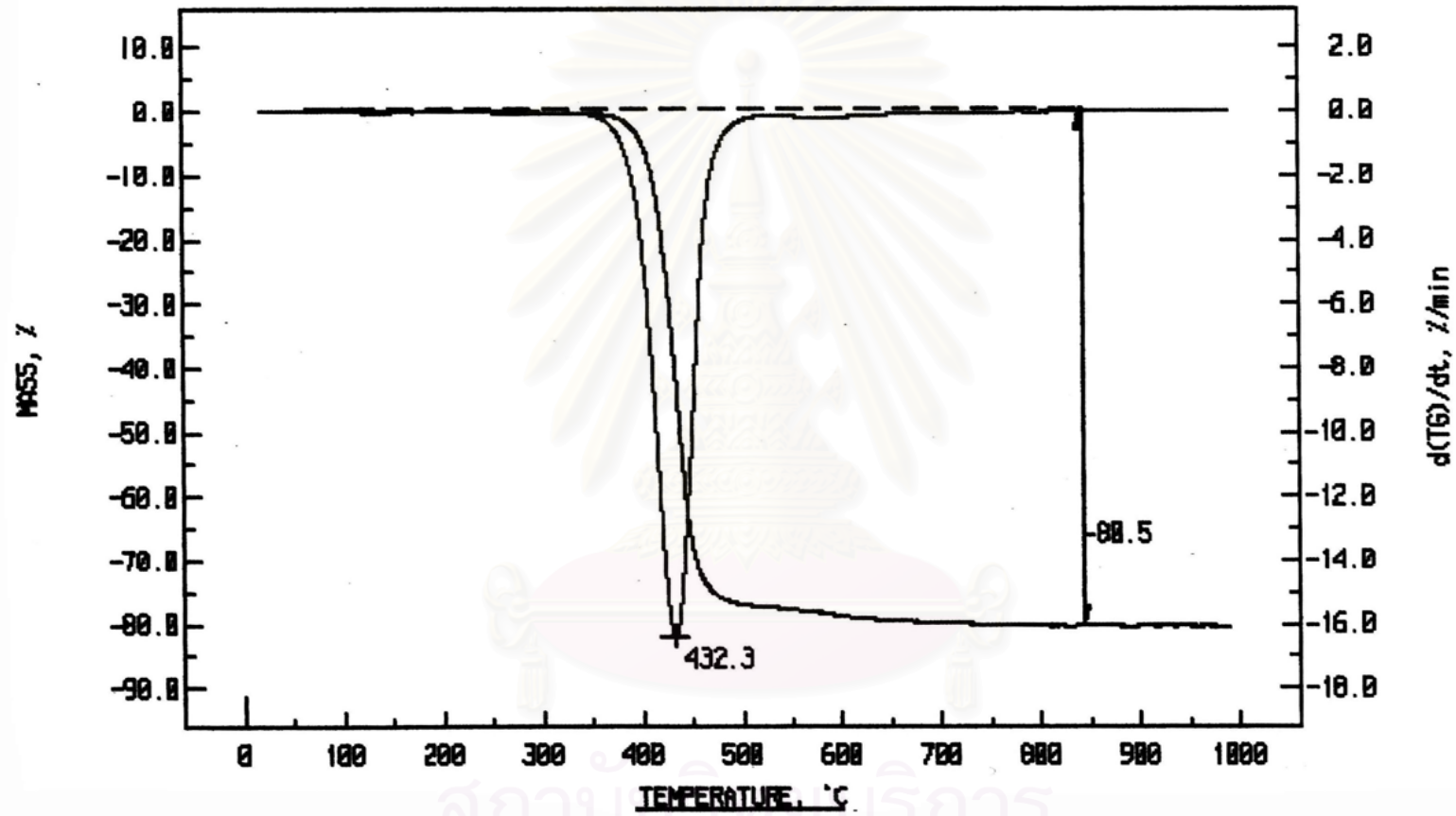
Figure 4.14 TGA and DTG of ungrafted PET
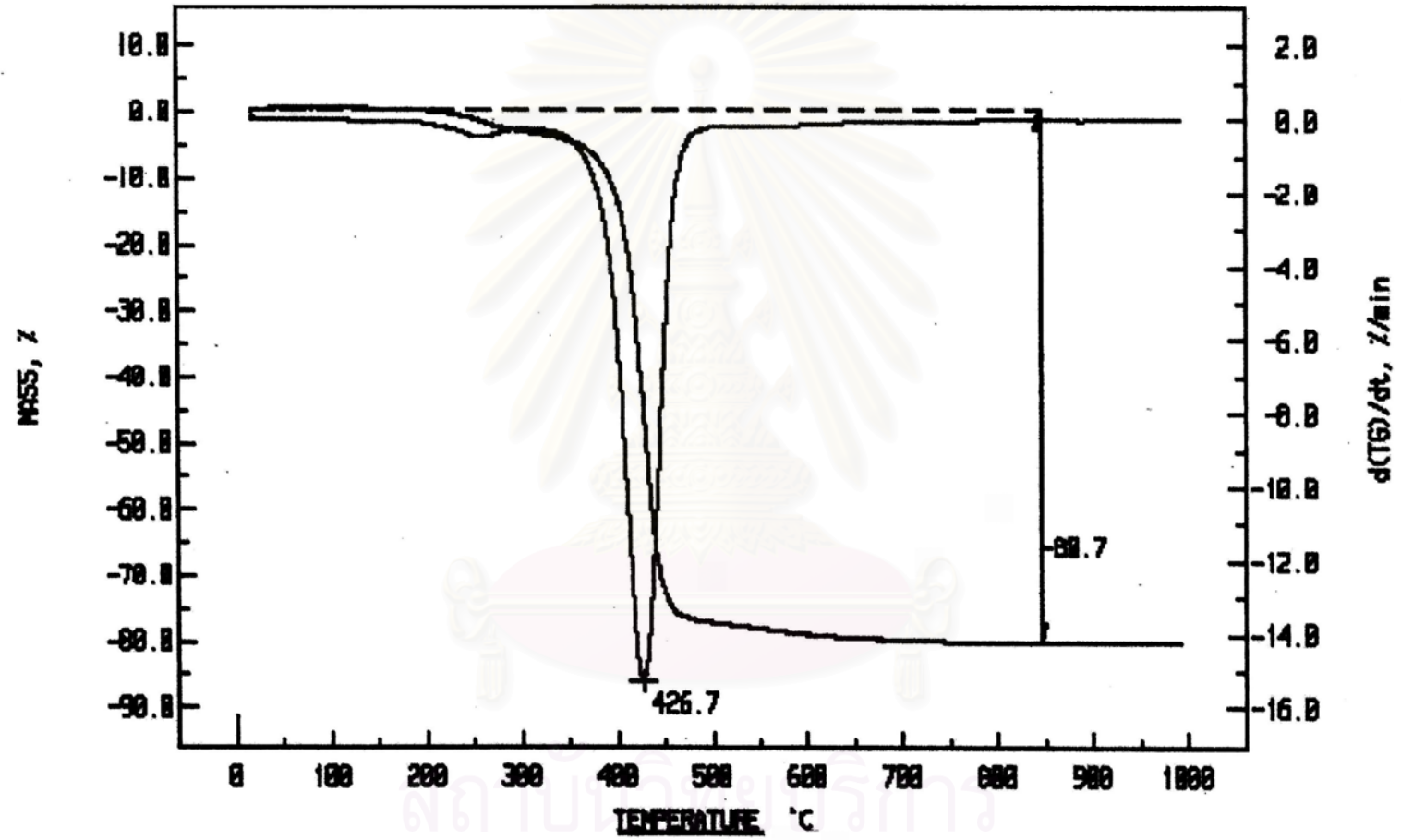
Figure 4.15 TGA and DTG of PAA-*g*-PET (Graft yield = 20%)
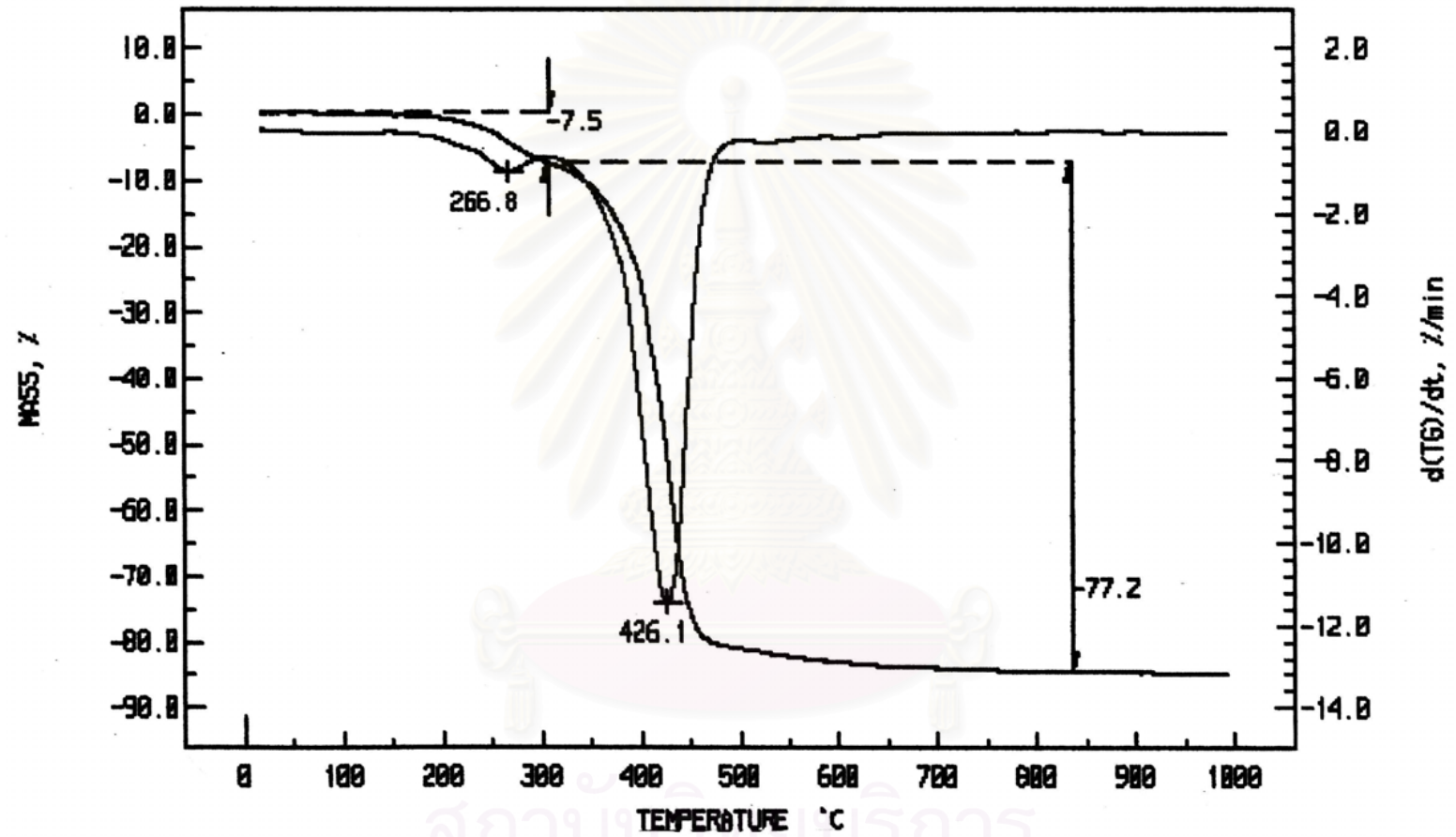
Figure 4.16 TGA and DTG of PAA-*g*-PET (Graft yield = 40%)

Table 4.8 Weight Loss for Ungrafted and Grafted PET Fiber at Heating Rate 283 K min^{-1} by thermal analysis

%Graft Yield	Properties	Stage of decomposition		
		I	II	III
O	%weight loss	-	80.5	19.3
	temperature (K)	-	623-723	>723
20	%weight loss	4	76.7	19.3
	temperature (K)	493-573	573-723	>723
40	%weight loss	7.5	77.2	15.3
	temperature (K)	463-573	573-723	>723

I, II, and III: Pre, second, and third stages

Figure 4.14 shows the continuous weight loss curve for thermal degradation of the ungrafted PET fiber. Thermal decomposition of the sample took place of two distinct stages in the temperature range 273 to 1276 K. The temperature ranges from 623-723 K for most of the decomposition of PET took place at about 80.5% weight loss. For the next, temperature higher than 723 K, the undecomposed PET and other impurities, which are amounted to about 19.5% of the total weight are lost.

Figures 4.15 and 4.16 present the thermal degradation of 20% and 40% graft yield of acrylic acid grafted PET fiber, respectively. The initial weight loss by decomposition around start at 493 K amounting to 4% and 7.5% of the weight loss. This decomposition was attributed to removal of the absorbed water. In the second stage for a major weight loss, about 76.7% and 77.2% weight occurred between 573 to 723 K. In the third step, the rest of the decomposition took place at the temperature higher than 723 K. At 973 K, only 19.3% and 15.3% char yield was obtained. Nearly 80.7% to 84.7% of the PAA-g-PET degraded at 733 K. The weight loss of the lower temperature range, i.e., 463-573 K, is due to the formation of anhydride with elimination of one water molecule from the two neighboring carboxylic groups of grafted chains as shown in Figure 4.17 (53). The second T_{max} is attributed to the pyrolysis of PET.
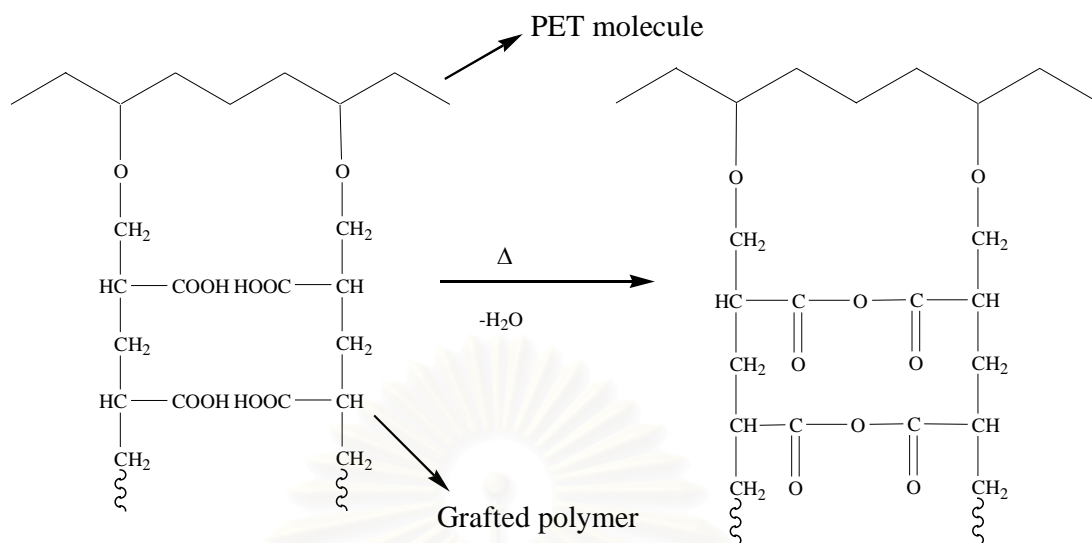
Figure 4.17 The dehydration of PAA-*g*-PET

Figure 4.18 shows the thermogravimetric analysis of AA-grafted PET fiber with different graft yields. The increase of graft yield exhibited by the AA-grafted PET fiber confirmed Figure 4.18 observations of a decreased thermal stability by fiber after grafting. The grafting decreases the decomposition temperature and heat resistance of PET fiber. The poly(acrylic acid) grafting chain yield onto PET, have a low decomposition temperature, but they do not contribute to thermal stability of the grafted polymer.
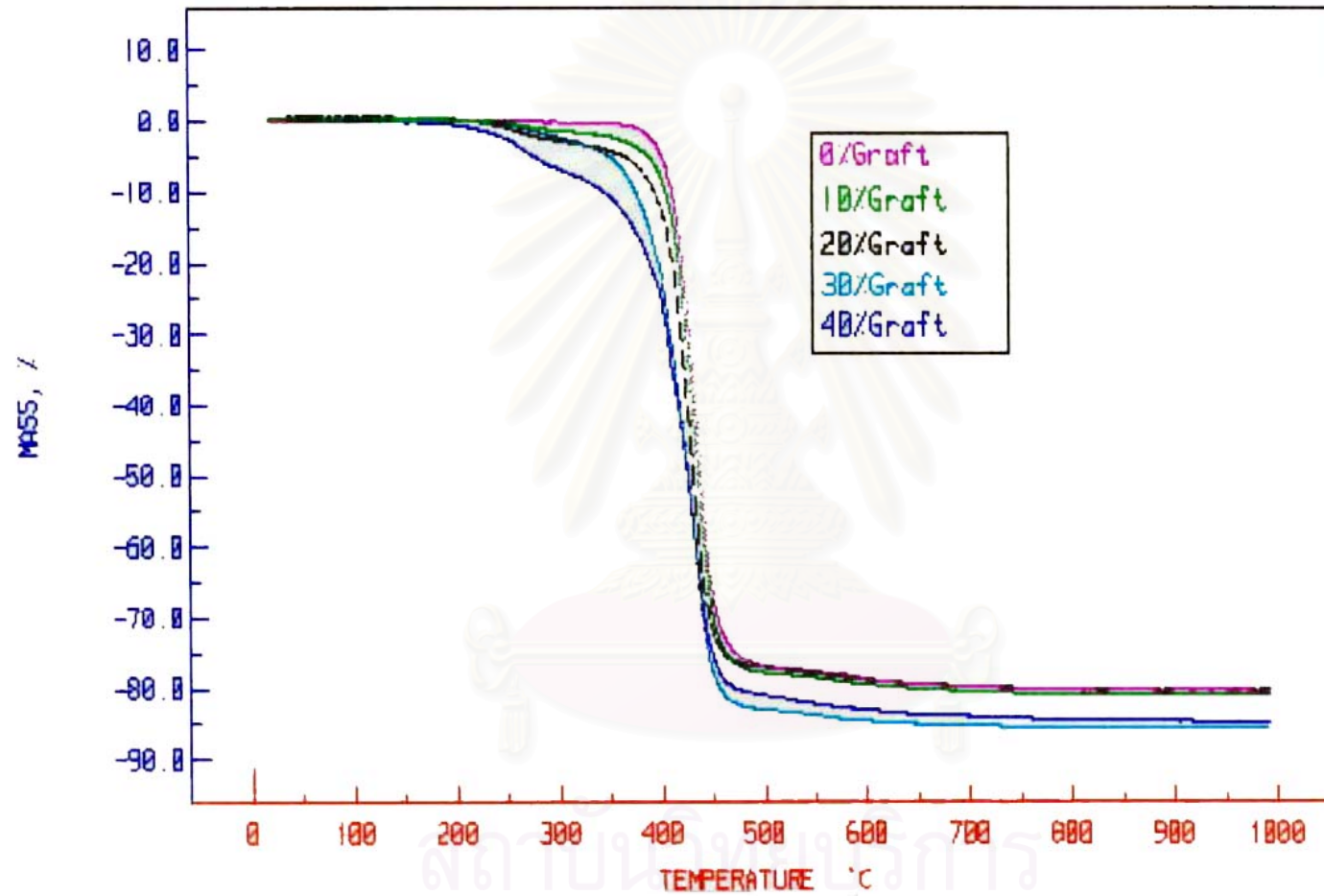
Figure 4.18 TGA curves of the AA-grafted PET fiber. Graft yield (%): 0, 10, 20, 30, and 40.

4.3.4 <u>Moisture regain</u>

      The moisture regain of the ungrafted and acrylic acid-grafted PET was investigated and the results are tabulated in Table 4.9 and shown in Figure 4.19.

Table 4.9 Moisture regain values of AA-grafted PET fiber

Graft yield (%)	Moisture regain (%)
0.0	0.2
9.0	0.6
20.1	0.8
31.1	1.0
39.5	2.0
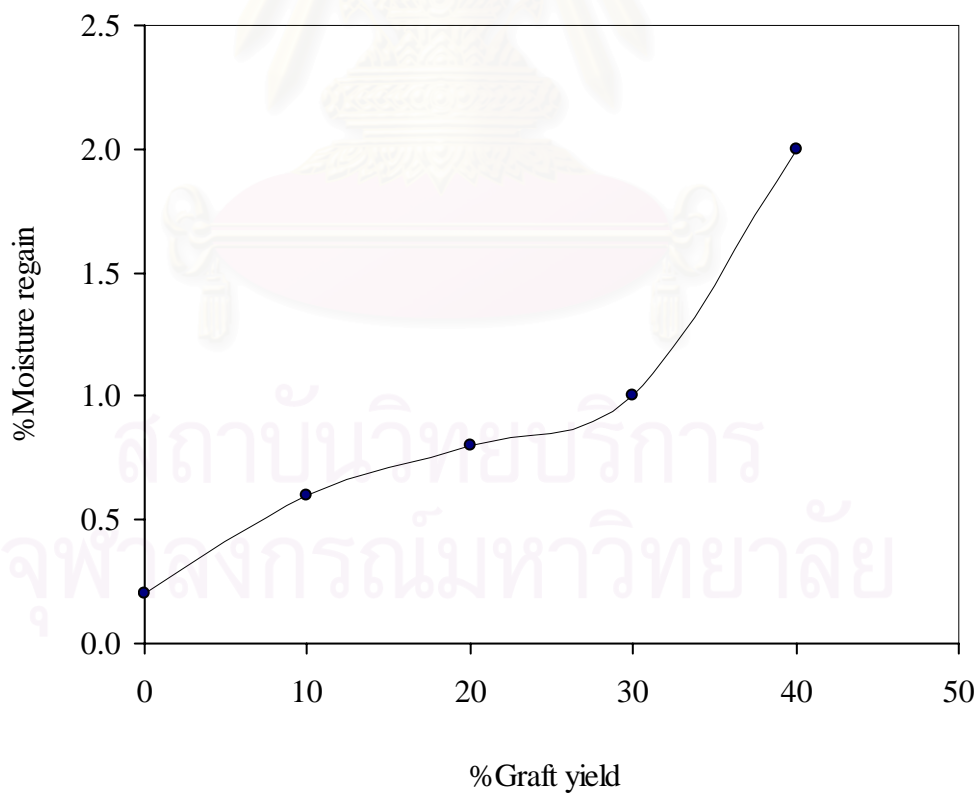
Figure 4.19 Moisture regain of AA-grafted PET fiber

The moisture regain value of the hydrophobic ungrafted PET fiber is 0.2%, which increases to 2.0% at 39.5% graft yield. It was increased by 900% moisture regain. This is essentially due to the hydrophilic nature of the acrylic acid monomer used for grafting, which increases the hydrophilic characteristics of the fiber by the insertion of some polar carboxylic groups (-COOH) into PET fiber and increase in the moisture regain character of fiber (2). It can also be claimed that the AA grafted PET fiber structure has an influence in the increase in the moisture regain value of the fiber.

4.3.5 Dyeability

Two types of dye chemistry are used for dyeability study as follows:

a) Methylene blue

The dyeability of the ungrafted and the acrylic acid-grafted PET fiber with various graft levels is presented in tabulated in Table 4.10 and shown in Figure 4.20. The dye uptake of ungrafted PET fiber is 0.001 g dye/g fiber while the dye uptake of PET fiber grafted with 43.5% acrylic acid increases up to 0.724 g dye/g fiber. It was increased by 100% dyeability.

Table 4.10 Dyeability of the AA-grafted PET fiber with methylene blue

Graft yield (%)	Dye uptake $\times 10^{-3}$ (g dye/ g fiber)
0.0	1
16.3	315
22.0	446
31.7	529
39.0	647
43.5	724

Table 4.10 shows that the higher the graft yield, the greater the dye uptake. Therefore, for dyeing purpose, grafting of hydrophilic monomer on PET can enhance the dyeing ability of the cationic dye.
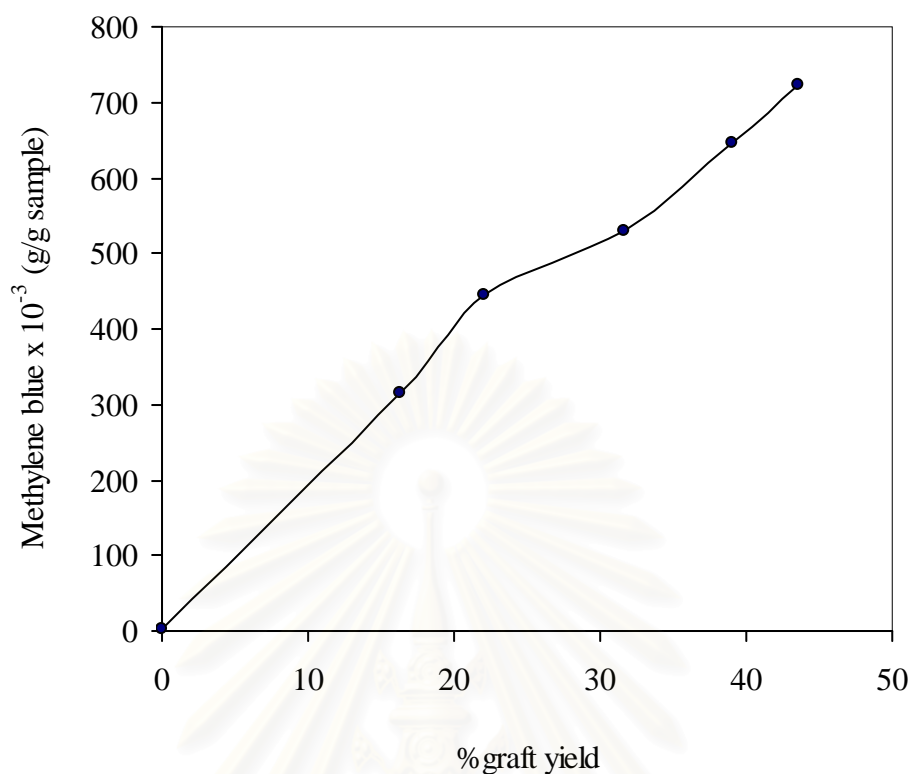
Figure 4.20 Effect of %graft yield on dyeability of methylene blue

The dyeability of PET fiber can be increased by introducing suitable functional groups in the fiber structure, so that they become the centers of adsorption or reaction with the appropriate class of dye molecule.
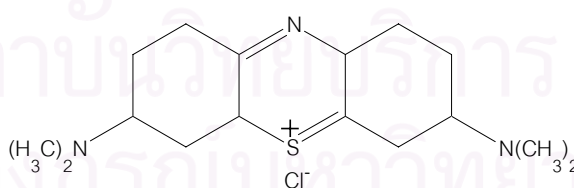
Figure 4.21 Structure of Methylene Blue

Methylene blue is a basic dye or cationic dye. This dye dissolves in water yielding a blue colorant having a cationic characteristic. A chemical structure of methylene blue is shown in Figure 4.21. The process of dyeing in an ionic system can be derived into three steps (54): (1) adsorption of a dye on a

fiber, (2) diffusion of the dye from the surface into the fiber, and (3) interaction of the dye with the dyeing sites in the fiber. The uptake of cationic dye on the treated fiber occurs by means of ion-ion interaction operating between the cationic dye and the anionic group within the fiber.

In the dyeing of PET-g-PAA fiber, the basic dye reacted with the carboxylic groups present in the grafted chains and chain ends of the polymer. Interaction force such as ion-dipole, dipole-dipole and dipole-induce dipole can be considered to contribute to the dye-fiber adsorption (55). As seen from the results of dyeing experiments of the grafted PET fiber using methylene blue, the dye uptake increases with graft yield. This must be due to the increase in the number of –COOH groups, which provides the higher dyeability. The fiber structure as a result of grafting will undoubtedly contribute to improving the dye uptake of the fiber.

b) Hicron Navy Blue GRL-SF (CI disperse blue 79)

The dyeability of the ungrafted and various graft levels of the acrylic acid-grafted PET fiber with Hicron navy blue GRL-SF is presented in Table 4.11 and shown in Figure 4.22. The dye uptake at the dyeing temperature of 403 K for the ungrafted PET fiber is 0.077 g dye/g fiber, while the dye uptake of PET fiber grafted with 43.2% acrylic acid increases up to 0.094 g dye/g fiber. It was increased by 22% dyeability.

Table 4.11 Dyeability of AA-grafted PET fiber with disperse dye (Hicron navy blue GRL-SF 200%)

Graft yield (%)	Dye uptake x 10^{-3} (g dye/ g fiber)
0.0	77
16.9	87
19.2	88
30.4	93
43.2	94
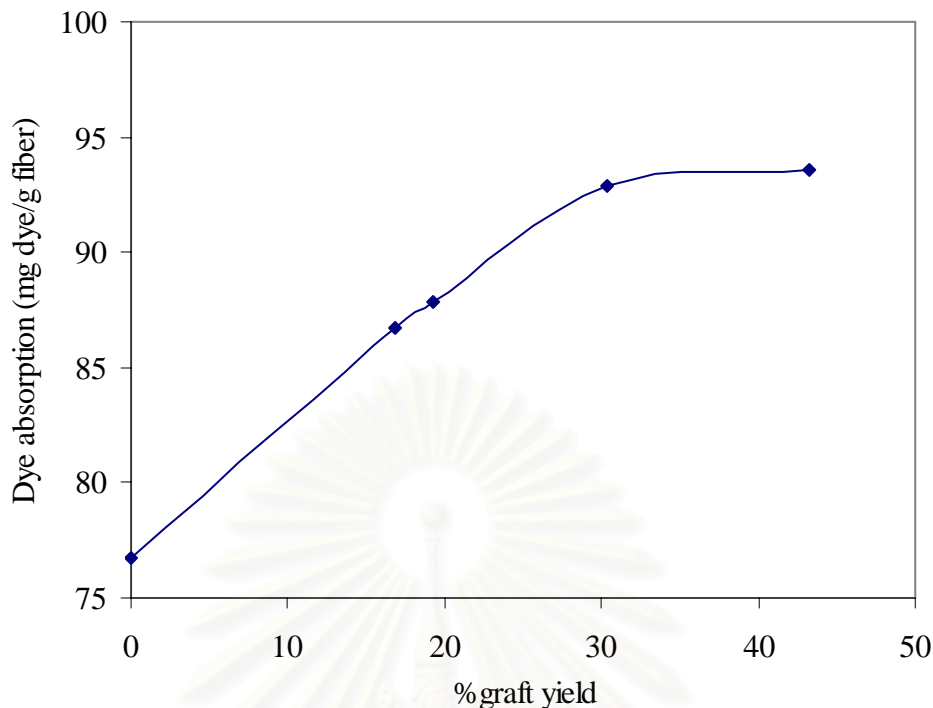
Figure 4.22   Effect of %graft yield on dyeability of Hicron navy blue GRL-SF 200%
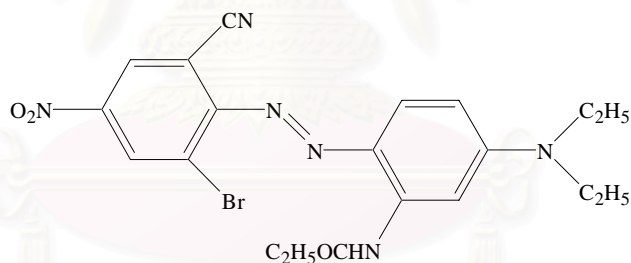
N-[2-(2-Bromo-6-cyano-4-nitro-phenylazo)-5-diethylamino-phenyl]-propionamide

Figure 4.23 Chemical structure of Hicron navy blue GRL-SF 200% (CI disperse blue 79)

The dyeability of PET fiber with Hicron navy blue GRL-SF 200% (CI disperse blue 79) can be increased by acrylic acid grafted PET. Figure 4.23 shows a chemical structure of Hicron navy blue GRL-SF 200%. The grafting changed in voids and structural parameter of the fibers. These changes had their own contributions to increasing in dyeability of the disperse dye. The nature of the interaction between the disperse dye and PET-*g*-PAA fiber is, in contrast to that of

methylene blue (cationic dye) and the fiber, as that the disperse dye is essentially nonionic, there are not any ion-ion interaction between the dye and the treated fiber. The disperse dye can directly take either a colloid or an adsorption at mechanistic sites on the polymer segments, which are in the mobile phase due to the thermal motion. Thus, the dye molecules penetrated through the disoriented regions of the fiber. The graft copolymerization of acrylic acid proceeds with the incorporation of amorphous poly(acrylic acid) chains in the noncrystalline region of fiber. With the increase in amorphous domain due to the grafting, the disperse dye molecules can easily approach the reactive sites in the disordered regions.

CHAPTER V

CONCLUSION and SUGGESTION

5.1 Conclusion

Graft copolymerization of acrylic acid onto PET filament using ceric ammonium nitrate as an initiator was carried out with the satisfactory result. The reaction variables such as monomer, initiator, and acid concentration, temperature and time considerably affect the graft yield. Several attempts were carried out to pursue the possible technique to acquire the suitable graft yield of the graft copolymer through the adjustment of moisture regain, dyeability, thermal stability, and tensile properties. The following conclusions were drawn from studies on the reaction conditions and the application of the acrylic acid grafted PET for textile dyeing:

(1)   PET filament could be grafted with acrylic acid using Ce^{4+} as redox initiator. The optimum condition that gave the 43.6% graft yield with 1.00 g of PET filament was as follows: a 323 K reaction temperature, a 60 min reaction time, 2.91 M of acrylic acid, 1.82×10^{-3} M of Ce^{4+}, and 0.80 M of nitric aid.

(2)   Graft copolymerization may be assumed that the reactivity of primary radicals is an important factor in graft initiation; it is, at last, the viscosity of the grafting medium that dominates the reaction at higher temperatures, larger times, and higher concentration of monomer, initiator, and acid. The termination of growing poly(acrylic acid) grafts may follow various routes, as summarized in Figure 5.1:
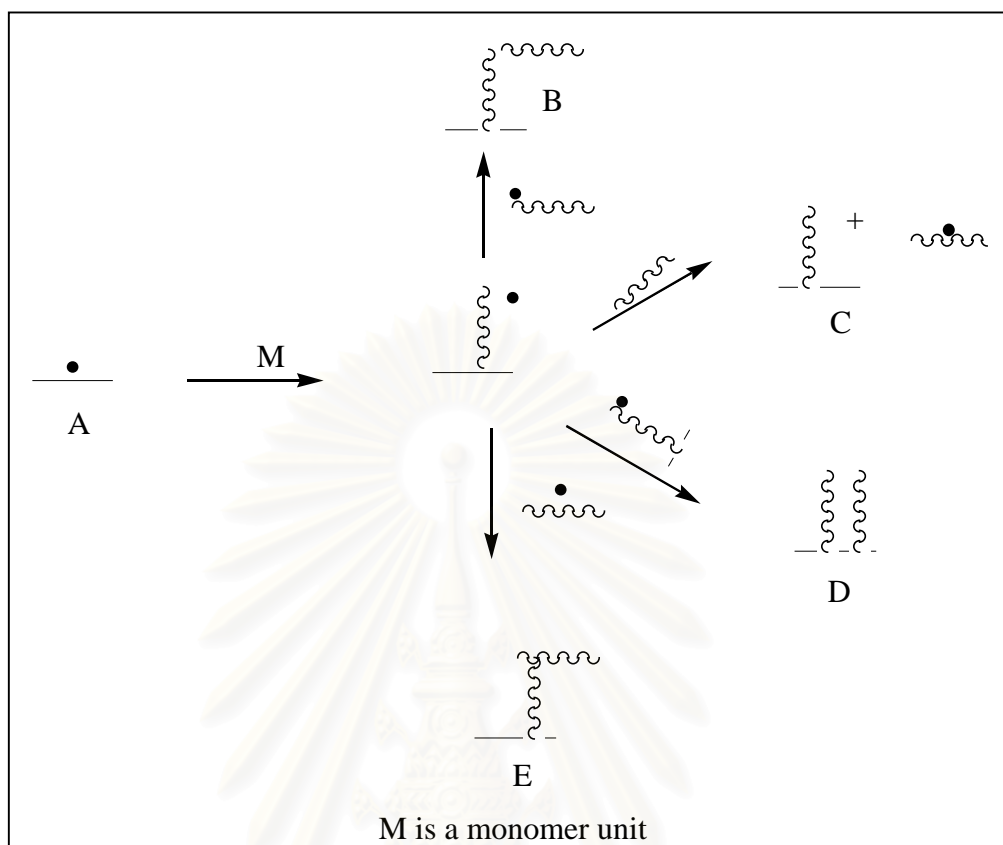
Figure 5.1 Schematic representation of the termination of growing poly(acrylic acid) graft chains.

These routes include the deactivation of primary radicals, bimolecular growing chain termination, and chain transfer to the homopolymer or to an inactive species.

(3) As a general rule of graft copolymerization, homopolymer formation usually accompanies grafting reaction at the expense of the graft copolymer. The graft yield was decreased when the homopolymer content was increased

(4) Poly(acrylic acid) homopolymer was confirmed by FT-IR spectroscopy. Poly(acrylic acid) is indicated by the spectrum,

(IR, KBr pellet): v(O-H) 3490 cm^{-1}, broad, weak, v(C=O) 1734 cm^{-1}, strong, sharp, v(C=O)-C) asym. 1559 cm^{-1} sharp, weak, and v(C=O)-C) sym. 1267 cm^{-1}, broad, weak.

The latter four peaks indicate the presence of poly(acrylic acid) homopolymer in the grafting medium.

(5)   The breaking tenacity and elongation of grafted PET fiber decrease, while denier increased with the graft yield.

(6)   Poly(acrylic acid) grafted PET fiber, has a low decomposition temperature, but it does not contribute to thermal stability of the grafted polymer.

(7)   The hydrophilic nature of the acrylic acid monomer used for grafting increases the hydrophilicity of the fiber and the moisture regain character of the fiber. The moisture regain value of hydrophobic PET fiber is 0.2%. The moisture regain value increases to 2.0% at the graft yield of 40%. It was increased by 900% moisture regain.

(8)   The dyeability of the AA grafted PET using methylene blue increased 100% with 43.5% graft yield and also increases dyeability using disperse dye 22% with 43.2% graft yield.

(9)   The application of acrylic acid grafted PET is to modify the properties of textile fabrics, such as improve their hydrophilic properties and dye uptake whereas thermal stability of the grafted PET does not change. In addition, moisture regain is another fabric property for excellent wear comfort and better performance.

(10) For manufacturing the acrylic acid grafted PET copolymer, the grafting may be more effective in the PET melting stage rather than the solid-stage like fiber. Because the tensile properties of the AA grafted PET melt can be easily controlled in the spinning and draw processes of the fiber. Through the melting stage grafting, good properties of the moisture regain and other could be optimized.

5.2 <u>Suggestion and Future Work</u>

There are many techniques to synthesize a graft copolymerization of a vinyl monomer onto PET. In this work, a ceric(IV) initiation method is used. To further develop the properties of textile, more investigations should be carried out as follows:

1. The PET melting or PET chips can be used in the place of PET fiber in order to develop or maintain the desirable tensile strength.

2. Use the staple fiber as the backbone PET polymer for grafting to improve the properties in non-woven fiber application.

3. Use other chemical initiator such as potassium permanganate, potassium persulfate to develop a technique of graft copolymerization.

4. Instead of using acrylic acid as a grafting monomer, methacrylic acid, vinyl acrylic acid and/or other unsaturated organic acids with an inherently stable structure and better thermal properties should also be tried.

5. Other suitable methods to determine the dyeability on the grafted substrate, such as the extraction of the dye uptake on the graft copolymer, using a suitable solvent and the dye content can be determined either by titration or spectrophotometry method.

REFERENCES

1. Karayannidis, G. P., Sideridou, I. D., Zamboulis, D. N., Bikiaris, D. N., and Sakalis, A. J. Thermal Behavior and Tensile Properties of Poly(ethylene terephthalate-co-ethylene isophthalate). J. Appl. Polym. Sci. 78(2000): 200-207.

2. Saçak, M., Sertkaya, F., and Talu, M. Grafting of Poly(ethylene terephthalate) Fibers with Methacrylic Acid using Benzoyl Peroxide. J. Appl. Polym. Sci. 44(1992): 1737-1742.

3. Karakisla, M., and Sacak, M. Grafting of Ethyl Acrylate onto Monofilament Polyester Fibers using Benzoyl Peroxide. J. Appl. Polym. Sci. 70(1998): 1701- 1708.

4. Shukla, J. S., and Sharma, G. K. Graft Copolymerization of Methyl Methacrylate onto Wool Initiated By Ceric Ammonium Nitrate-Thioglycolic Acid Redox Couple in the Presence of Air. J. Polym. Sci. 25(1987): 595-605.

5. Fakhrul-Razi, A., Qudsieh, I. Y. M., Yunus, W. M. Z. W. and Ahmad, M. B. Graft Copolymerization of Methyl Methacrylate onto Sago Starch using Ceric Ammonium Nitrate and Potassium Persulfate as Reox Initiator System. J. Appl. Polym. Sci. 82(2001): 1375-1381.

6. Lui, M., Cheng, R., Wu, J., and Ma, C. Graft Copolymerization of Methyl Acrylate onto Potato Starch Initiated By Ceric Ammonium Nitrate. J. Polym. Sci. 31(1993): 3181-3186.

7. Misher, S., Panda, A., and Singh, B. C. Characterization of Poly(vinyl alcohol) Grafted with Acrylic Acid and Methyl Methacrylate using a Ce (IV) Glucose Redox System. J Appl. Polym. Sci. 73(1999): 677-683.

8. Vaidya, A. A. Production of Synthetic Fibres. New Delhi: Prentice-Hall, 1988. pp. 33-35.

9. Gupta, V. B., and Kothari, V. K. Man-Made Fibres Production, Processing, Structure, Properties and Application. 1st ed. New Delhi: Quality Improvement and Continuing Education Programmes of Indian Institute of Technology, pp. 56-58.

10. Ibid, pp. 53-54.

11. Vaidya, A. A. Production of Synthetic Fibres. New Delhi: Prentice-Hall, 1988. p. 217.

12. Ibid, pp. 218-220.

13. Ibid, p. 205.

14. Ibid, p. 280.

15. Ibid, p. 279.

16. Sperling, L. H. Introduction to Physical Polymer Science. 2nd ed. New York: John Willey & Sons, 1992. pp. 45-46.

17. Odian, G. Principles of Polymerization. 2nd ed. New York: McGraw Hill, 1991. pp. 715-720.

18. Ibid, pp. 212-213.

19. Burke J. J., Weiss V. <u>Block and Graft Copolymers</u>. 1st ed. New York: Vail-Ballou Press, 1973. p. 11.

20. Allcock, H. R., and Lampe, F. W. <u>Contemporary polymer chemistry</u>. New Jersey: Prentice-Hall, 1981. pp. 103-107.

21. Sarac, A. S., Redox Polymerization. <u>Prog. Polym. Sci</u>. 24(1999): 1149-1205.

22. Lenz, R. W. <u>Organic Chemistry of Synthesis High Polymers</u>.. New York: Interscience Publishers, A Division of John Willey & Sons, 1967. p. 142

23. Burkinshaw, S. M. <u>Chemical Principles of Synthetic Fibre dyeing.</u> 1st ed. Glasgow: Chapman & Hall, 1995. pp. 2-3.

24. Burke J. J., Weiss V. <u>Block and Graft Copolymers</u>. 1st ed. New York: Vail-Ballou Press, 1973. p. 228.

25. Mohanty, E., Singh, B. C. Graft Copolymerization of Methyl Methacrylate onto Jute Fiber Initiated by Cerium (IV)-DMSO Redox Initiator System. <u>J. Appl. Polym. Sci.</u> 69(1998): 2569-2576.

26. Das, A., Saikia, C. N., and Hussain, S. Grafting of Methyl Methacrylate onto Antheraea Assama Silk Fiber. <u>J. Appl. Polym. Sci.</u> 81(2001): 2633-2641.

27. Liu, Y., Li, W., Deng, K. and Zhang, J. Graft copolymerization of Methyl Acrylate onto Nylon1010 Initiated by Potassium Diperiodatonickelate. <u>J. Appl. Polym. Sci.</u> 82(2001): 2636-2640.

28. Misra, B. N., Mehta, I. K., and Dogra, R. Grafting onto wool. VII. Ceric-initiated Graft Copolymerization of Vinyl Monomers. Comparison of Monomer Reactivities. <u>J. Appl. Polym. Sci.</u> 25(1980): 235

29. Nayak, N. C., Das, H. K., and Singh, B. C. Influence of Glycine on The Kinetics of The Graft Copolymerization of Acrylonitrile onto Jute Fibers Initiated by Ceric Ion. J. Appl. Polym. Sci. 42(1991): 2391-2396.

30. Mohanty, A. K., Parija, S., and Misra, M. Ce(IV)-N-Acetylglycine Initiated Graft Copolymerization of Acrylonitrile onto Chemically Modified Pineapple Leaf Fibers. J. Appl. Polym. Sci. 60(1996): 931-937.

31. Karakişla, M. and Saçak, M. Grafting of Ethyl Acrylate onto Monofilament Polyester Fibers onto Benzoyl Peroxide. J. Appl. Polym. Sci. 70(1998): 1701-1705.

32. Osipenko, I. F. and Martinovicz, V. I. Grafting of The Acrylic Acid on Poly(ethylene terephthalate). J. Appl. Polym. Sci. 39(1990): 935-942.

33. Okoniewski, M., and Sojka-Ledakowicz, J. Chemically Induced Graft Polymerization of Acrylic Acid onto Polyester Fabrics. I. Kinetic Investigation of Grafting. J. Appl. Polym. Sci. 35 (1988): 1241-1249.

34. Bucheñska, J. Modification of Polyester Fiber by Grafting with Poly(acrylic acid). J. Appl. Polym. Sci. 65 (1997): 967-977.

35. Yuhai, G., Jianchun, Z., and Meiwu, S. Surface Graft Polymerization of Acrylic Acid onto Corona-Treated Poly(ethylene terephthalate) Fabric. J. Appl. Polym. Sci. 73 (1999): 1161-1164.

36. Gupta, B., Hilborn, J. G., Bisson, I., and Frey, P. Plasma-Induced Graft Polymerization of Acrylic Acid onto Poly(ethylene terephthalate) Film. J. Appl. Polym. Sci. 81 (2001): 2993-3001.

37. Eromosele, I. C., Agbo, A. Grafting Acrylonitrile on Kenaf Fibers using Ceric Ion-*p*-Xylene Redox Pair. J. Appl. Polym. Sci. 73(1999): 1751-1755.

38. Eromosele, I. C., Bayero, S. S. Graft Copolymerization of Acrylonitrile on Kenaf Fibers by Ceric Ion in the Presence of Allyl Compounds. J. Appl. Polym. Sci. 73(1999): 1757-1761.

39. Trimnell, D., Fanta, G. F., and Salch, J. H. Graft Polymerization of Methyl Acrylate onto Granular Starch: Composition of the Fe^{2+}/H_2O_2 and Ceric Initiating System. J. Appl. Polym. Sci. 60(1996): 285-292.

40. Padhi, N. P., Tripathy, S. S., Jena, S., and Singh, B. C. Graft Copolymerization of Methyl Methacrylate onto Silk Fibers with Ce(VI)-Sucrose Redox System. J. Appl. Polym. Sci. 28(1983): 1811-1813.

41. Chowdhury, P. and Banerjee, M. Graft Polymerization of Methyl Methacrylate onto Poly(vinyl alcohol) using Ce(IV) Initiator. J. Appl. Polym. Sci. 70(1998): 523-527.

42. Nemce, J. W., and Bauer, W. Jr. Acrylic Acid and Methacrylic Acid Polymer. In Mark, H. F., Bikales, N. M., Overberger, C. G., and Manges, G.(eds.), Encyclopedia of Polymer science and Technology. Vol 1. New York: John Wiley, 1978. pp. 211-234.

43. Specht, E. H., Palolla, E. A., Kelvic, A.L. and Schetty, G. O. (eds), Acrylic Acid and Derivatives. Kirk-Othmer Encyclopedia of Chemical Technology. Vol. 1. New York: John Wiley, 1963. pp 285-286.

44. Mostafa, K. M. Graft Polymerization of Acrylic Acid onto Starch using Potassium Permanganate Acid (Redox system). J. Appl. Polym. Sci. 56(1995): 263-269.

45. Vazquez, M. B., Goni I., Gurruchaga, M., Valero, M., and Guzman G. M. Graft Copolymerization of AA Monomer onto Starch Fraction: IV. Effect of Reaction Time on the Grafting of Butyl Acetate onto Amylose. J. Polym. Sci. A. 25 (1987): 719-725.

46. Gürdağ, G., Güclü, G., and Özgümüş, S. Graft Copolymerization of AA onto Cellulose: Effect of Pretreatments and Crossinking Agent, J. Appl. Polym. Sci. 80(2001): 2267-2272.

47. Samal, K., Dash S., and Sahu A. K. Graft Copolymerization of Acrylic acid onto Jute Fibers Initiated by Quinquivalent Vanadium, J. Appl. Polym. Sci. 41 (1990): 195-203.

48. Kiatkamjornwong, S., and Nispa, M. Enhancement of the Grafting Performance and The Water Absorption of Cassava Starch Graft Copolymer by Gamma Radiation, Radiat, Phys. Chem. 49(1997): 689-696.

49. Chowdhury, P. and Samui, S. Graft Copolymerization of Methyl Methacrylate onto Guar Gum with Ceric Ammonium Sulfate/ Dextrose Redox Pair. J. Appl. Polym. Sci. 82 (2001): 3520-3525.

50. Goni, I., Gurruchaga, M., Valero, M., and Guzman, G. M. Graft Copolymerization of Acrylic acid onto Starch Fractions. I. Effect of Reaction Time and Grafting of Methyl Methacrylate onto amylase. J. Polym. Sci. A. Polym. Chem. Ed. 21 (1983): 2573-2580.

51. Lee, M. H., Yoon, K. J., and Ko. S. Grafting onto Cotton Fiber with Acrylamidomethylate β-Cyclodextrin and Its Application. J. Appl. Polym. Sci. 78 (2000): 1986-1991.

52. Tsukada, M., Arai, T., Freddi, G., Imai, T., and Kasai, N. Grafting Vinyl Monomers onto Silk (Bombyx Mori Mori) using Different Initiator: Properties of Grafted Silk. J. Appl. Polym. Sci. 81 (2001): 1401-1409.

53. Taunk, K. and Behari, K. Graft Copolymerization of Acrylic acid onto Guar Gum. J. Appl. Polym. Sci. 77 (2000): 39-44.

54. Mukherjee, A. K., and Gupta, B. D., Radiation-induced Graft Copolymerization of Methacrylic Acid onto Polypropylene Fiber: VI. Dyeing Behavior. J. Appl. Polym. Sci. 30 (2001): 4455-4466.

55. Burkinshaw, S. M. Chemical Principles of Synthetic Fibre Dyeing. 1st end. Glasgow: Chapman & Hall, 1995. p. 162.

APPENDICES

Appendix A

Graft copolymerization of acrylic acid onto PET fiber

1. Effect of Monomer Concentration

When all other variables were fixed except acrylic acid, various amounts of acrylic acid of 1.17, 1.46, 1.75, 2.19, and 2.62 M were added to each of PET fiber samples. The result of the monomer effect is shown in Table A-1.

PET fiber 1g; $[HNO_3]$ = 0.80 M; $[Ce(IV)]$ = 1.82 x 10^{-3} M, the reaction time = 1h, and the reaction temperature 323 K

Table A-1 Graft yield at different acrylic acid concentrations.

[AA] No. of test	%Graft yield				
	1.17M	1.46M	1.75M	2.19M	2.62M
1	19.1	26.0	33.7	43.3	32.0
2	19.0	25.4	33.4	43.9	33.5
3	20.1	25.8	34.5	43.6	31.9
4	20.0	25.0	34.2	43.5	33.0
Average	19.5	25.5	34.0	43.6	32.8
SD	0.59	0.43	0.49	0.26	0.77

2. Effect of Initiator Concentration

When all other variables were fixed except ceric (IV) ammonium nitrate solution, various amounts of ceric (IV) ammonium nitrate solution of 0.46, 0.91, 1.37, 1.82, and 2.28 mmole were added to each of PET fiber samples. The result of the initiator effect is shown in Table A-2.

PET fiber 1g, $[AA]$ = 2.19 M, $[HNO_3]$ = 0.80 M, the reaction time = 1h, and the reaction temperature 323 K

Table A-2 Graft yield at different ceric(IV) ion concentrations.

$[Ce^{4+}]$ x 10^{-3} No. of test	%Graft yield				
	0.46M	0.91M	1.37M	1.82M	2.28M
1	22.5	28.7	34.0	43.3	37.6
2	22.7	28.9	34.8	43.9	36.9
3	22.9	28.4	34.7	43.6	36.5
4	23.3	28.6	35.0	43.5	36.4
Average	22.8	28.6	34.6	43.6	36.9
SD	0.35	0.21	0.46	0.26	0.55

3. Effect of Nitric Acid Concentration

When all other variables were fixed except nitric acid, various amounts of nitric acid 50% (w/w) of 5, 6, 7, 8, 9, and 10 cm^3 (0.50, 0.60, 0.70, 0.80, 0.91, and 1.01 M) were added to each of PET fiber samples. The result of the acid effect is shown in Table A-3.

PET fiber 1g, [AA] = 2.19M, [Ce(IV)] = 1.8 x 10^{-3}M, the reaction time = 1h, and the reaction temperature 323 k

Table A-3 Graft yield at different nitric acid concentrations.

[HNO$_3$]	%Graft yield					
No. of test	0.50M	0.60M	0.70M	0.80M	0.91M	1.01M
1	28.4	29.7	35.6	34.0	34.2	32.4
2	27.5	29.5	35.5	34.8	34.0	32.8
3	29.0	30.6	35.6	34.7	33.4	32.0
4	28.0	30.4	35.3	35.0	33.5	31.7
Average	28.2	30.1	35.5	34.6	33.8	32.2
SD	0.64	0.52	0.13	0.46	0.37	0.49

4. Effect of Reaction Temperature

In this experiment, the temperature of the grafting reaction was taken as a variable, various levels of temperature for the graft copolymerization were 313, 318, 323, 328, and 333 K. The result of reaction temperature effect is shown in Table A-4.

PET fiber 1g; [AA] = 2.19 M, [HNO$_3$] = 0.80 M; [Ce(IV)] = 1.8 x 10^{-3} M, and the reaction time 1h.

Table A-4 Graft yield at different reaction temperature.

Temperature	%Graft yield				
No. of test	313 K	318 K	323 K	328 K	333 K
1	20.7	27.0	43.3	35.3	32.7
2	19.7	27.3	43.9	35.4	33.7
3	20.7	26.0	43.6	35.8	33.0
4	19.9	26.2	43.5	36.1	33.5
Average	20.3	26.6	43.6	35.7	33.2
SD	0.52	0.61	0.26	0.39	0.46

5. Effect of Reaction Time

In this experiment, the time of the grafting reaction was taken as a variable, various levels of time for the graft copolymerization were 45, 60, 75, and 90 minutes. The result of reaction Time effect is shown in Table A-5.

PET fiber 1g; [AA] = 2.19 M, [HNO$_3$] = 0.80 M; [Ce(IV)] = 1.8 x 10^{-3} M, and the reaction temperature 323 K.

Table A-5 Graft yield at different reaction time.

Time No. of test	%Graft yield				
	30 min	45 min	60 min	75 min	90 min
1	15.2	29.2	43.3	36.3	33.2
2	15.4	30.0	43.9	36.4	33.7
3	14.1	29.1	43.6	37.2	32.1
4	14.2	29.7	43.5	37.5	32.3
Average	14.7	29.5	43.6	36.9	32.8
SD	0.67	0.43	0.26	0.62	0.77

Appendix B

The tensile properties of PET and AA-grafted PET fiber

The tenacity and the breaking elongations represent limiting properties and the defects in fiber therefore they play a predominant role. As mentioned in Section 4.3.2, many techniques can be used to determine the tensile properties, in this study, Lenzing Vibrodyn 400 and Vibroskop 400 were chosen.

Figure B-1 The tensile properties of PET fiber
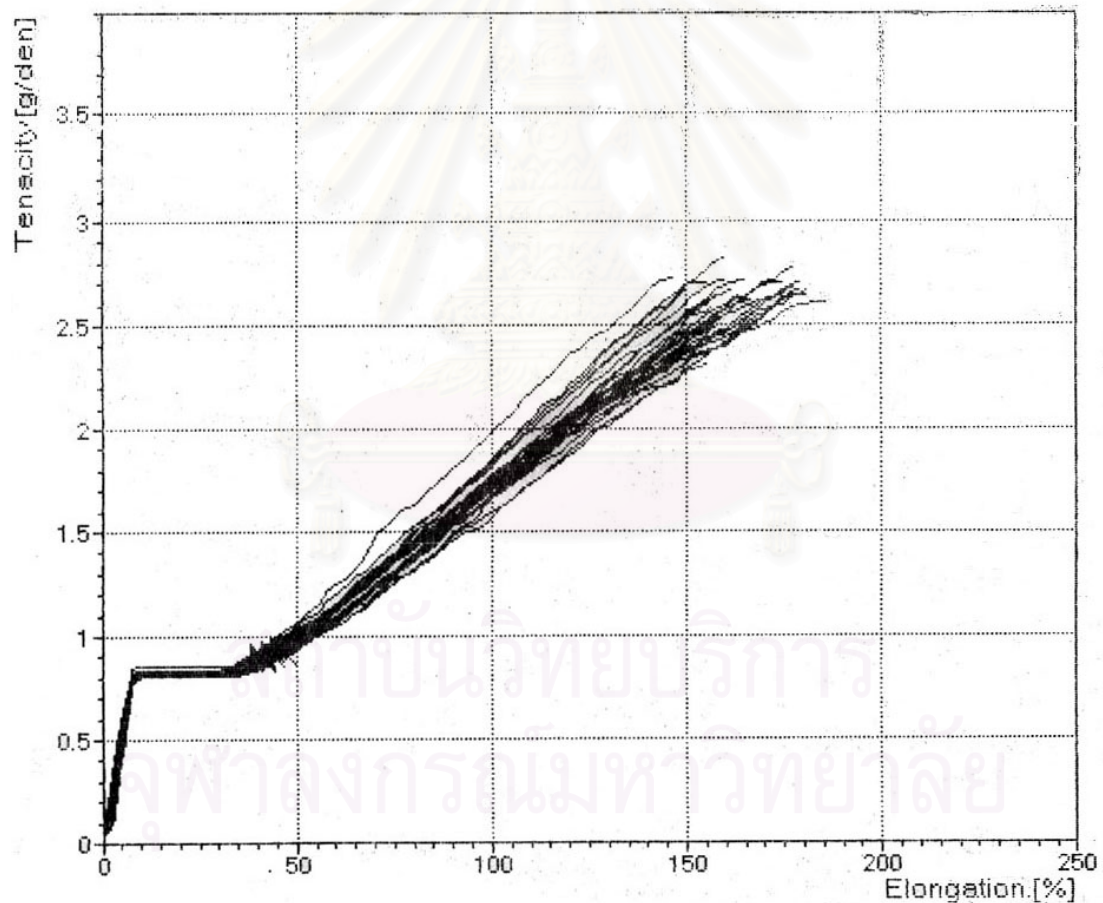
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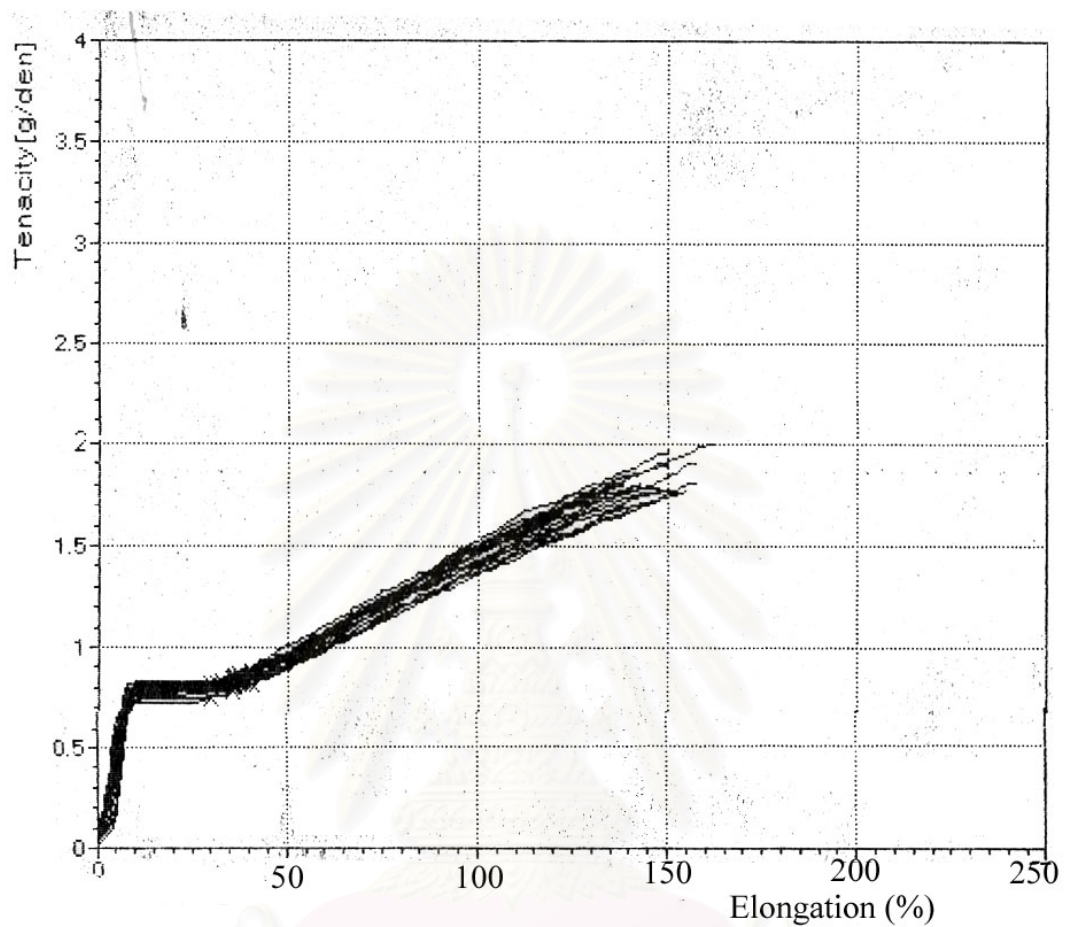
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Comment   : 0%GRAFTED PET
Longterm Code : ST
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Tension Weight [mg] :   300
Testing Speed [mm/min]: 100
calibrated at :

	Titer [den]	Titer [dtex]	Tenacity [g/den]	Tenacity [cN/tex]	Elong. [%]	Force [g]	NDR
001	4.73	5.26	2.82	24.9	159.7	13.36	1.42
002	5.26	5.84	2.66	23.5	161.4	14.00	1.42
003	5.35	5.95	2.64	23.3	163.0	14.14	1.42
004	5.10	5.67	2.72	24.0	164.6	13.88	1.45
005	5.20	5.78	2.49	22.0	156.5	12.97	1.42
006	4.81	5.35	2.70	23.8	179.1	12.99	1.40
007	4.81	5.35	2.61	23.0	185.6	12.55	1.40
008	5.16	5.73	2.45	21.6	159.7	12.62	1.42
009	4.92	5.47	2.66	23.5	179.1	13.11	1.40
010	4.81	5.35	2.66	23.5	180.8	12.82	1.40
011	5.27	5.86	2.52	22.2	153.3	13.27	1.45
012	5.16	5.73	2.71	23.9	154.9	13.97	1.42
013	4.81	5.34	2.70	23.8	174.3	12.96	1.45
014	4.90	5.45	2.47	21.8	154.9	12.12	1.40
015	4.93	5.48	2.71	23.9	172.7	13.36	1.40
016	4.86	5.40	2.64	23.3	180.8	12.83	1.40
017	5.15	5.72	2.64	23.3	158.1	13.59	1.45
018	4.56	5.07	2.67	23.6	177.5	12.21	1.42
019	5.34	5.93	2.53	22.3	169.4	13.49	1.42
020	5.27	5.86	2.44	21.5	154.9	12.85	1.45
021	4.94	5.49	2.64	23.3	174.3	13.05	1.42
022	5.16	5.73	2.72	24.0	159.7	14.03	1.40
023	4.72	5.25	2.73	24.1	146.8	12.91	1.40
024	4.99	5.54	2.31	20.4	154.9	11.53	1.45
025	5.10	5.67	2.71	23.9	153.3	13.82	1.45
026	5.24	5.82	2.53	22.3	158.1	13.24	1.42
027	5.15	5.72	2.78	24.5	177.5	14.29	1.42
028	4.81	5.34	2.58	22.8	156.5	12.42	1.40
029	5.33	5.92	2.50	22.1	158.1	13.35	1.48
030	5.09	5.65	2.62	23.1	166.2	13.31	1.42
Minimum	4.56	5.07	2.31	20.4	146.8	11.53	1.40
Maximum	5.35	5.95	2.82	24.9	185.6	14.29	1.48
Spanw.	0.79	0.88	0.51	4.5	38.8	2.77	0.08
Mean	5.03	5.59	2.62	23.1	164.9	13.17	1.42
Std.dev	0.21	0.24	0.11	1.0	10.6	0.65	0.02
Cv [%]	4.3	4.3	4.4	4.4	6.5	4.9	1.5
Confid.	4.95	5.50	2.58	22.7	160.9	12.93	1.42
Interv.	5.11	5.68	2.66	23.5	168.8	13.41	1.43

Figure B-2 The tensile properties of 9.7% grafted PET fiber
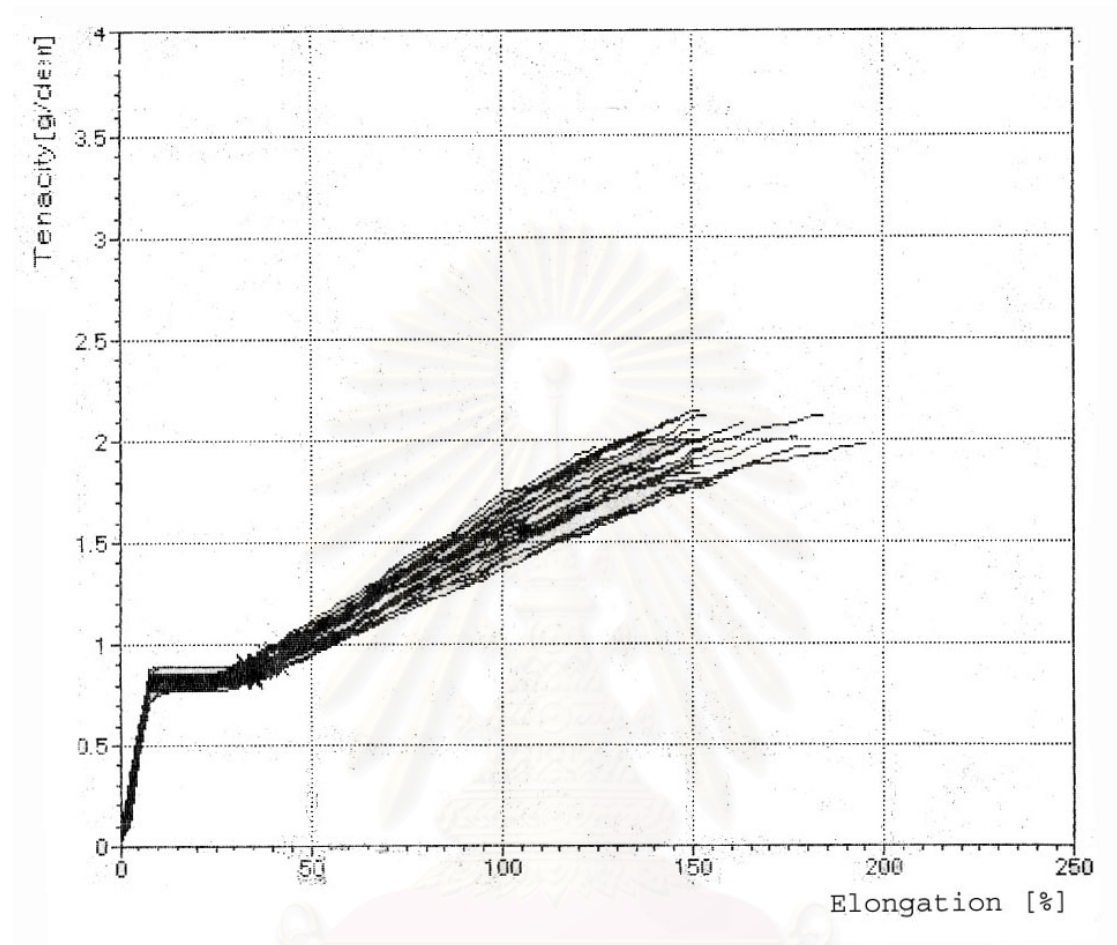
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Tension Weight [mg]   :   300
Testing Speed [mm/min]: 100
calibrated at :

	Titer [den]	Titer [dtex]	Tenacity [g/den]	Tenacity [cN/tex]	Elong. [%]	Force [g]	NDR
001	5.35	5.95	1.98	17.5	132.3	10.62	1.38
002	5.81	6.46	1.84	16.2	143.6	10.68	1.42
003	5.71	6.34	1.84	16.2	151.7	10.48	1.35
004	5.65	6.28	1.86	16.4	142.0	10.51	1.35
005	5.65	6.28	1.96	17.3	124.2	11.08	1.33
006	5.63	6.25	1.79	15.8	156.5	10.07	1.35
007	5.65	6.28	1.98	17.5	133.9	11.21	1.38
008	5.77	6.41	1.97	17.4	195.3	11.38	1.40
009	5.79	6.43	1.89	16.7	167.8	10.95	1.35
010	5.31	5.90	2.01	17.7	133.9	10.65	1.35
011	5.40	6.00	2.01	17.7	135.5	10.83	1.35
012	5.59	6.21	2.12	18.7	153.3	11.85	1.35
013	5.06	5.62	2.10	18.5	146.8	10.61	1.35
014	5.78	6.42	1.94	17.1	145.2	11.20	1.33
015	5.85	6.50	1.95	17.2	153.3	11.40	1.35
016	5.84	6.49	1.96	17.3	180.8	11.45	1.38
017	5.65	6.28	2.02	17.8	177.5	11.40	1.38
018	5.65	6.28	2.12	18.7	184.0	11.98	1.35
019	5.65	6.28	2.06	18.2	142.0	11.66	1.35
020	5.15	5.72	1.99	17.6	153.3	10.27	1.38
021	5.63	6.25	2.01	17.7	148.4	11.28	1.40
022	5.91	6.57	1.88	16.6	135.5	11.12	1.38
023	5.20	5.78	2.08	18.4	163.0	10.85	1.35
024	5.63	6.25	1.96	17.3	161.4	11.03	1.40
025	5.93	6.59	1.86	16.4	163.0	11.02	1.35
026	5.65	6.28	1.99	17.6	138.7	11.27	1.33
027	5.65	6.28	1.97	17.4	132.3	11.15	1.38
028	5.65	6.28	1.67	14.7	108.0	9.42	1.33
029	5.65	6.28	2.14	18.9	151.7	12.11	1.40
030	5.65	6.28	2.05	18.1	151.7	11.59	1.40
Minimum	5.06	5.62	1.67	14.7	108.0	9.42	1.33
Maximum	5.93	6.59	2.14	18.9	195.3	12.11	1.42
Spanw.	0.87	0.97	0.48	4.2	87.3	2.69	0.10
Mean	5.62	6.24	1.97	17.4	150.2	11.04	1.36
Std.dev	0.22	0.24	0.11	0.9	18.7	0.58	0.03
Cv [%]	3.8	3.8	5.4	5.4	12.4	5.2	1.9
Confid.	5.54	6.15	1.93	17.0	143.3	10.82	1.35
Interv.	5.70	6.33	2.01	17.7	157.2	11.25	1.37

Figure B-3 The tensile properties of 19.3% grafted PET fiber

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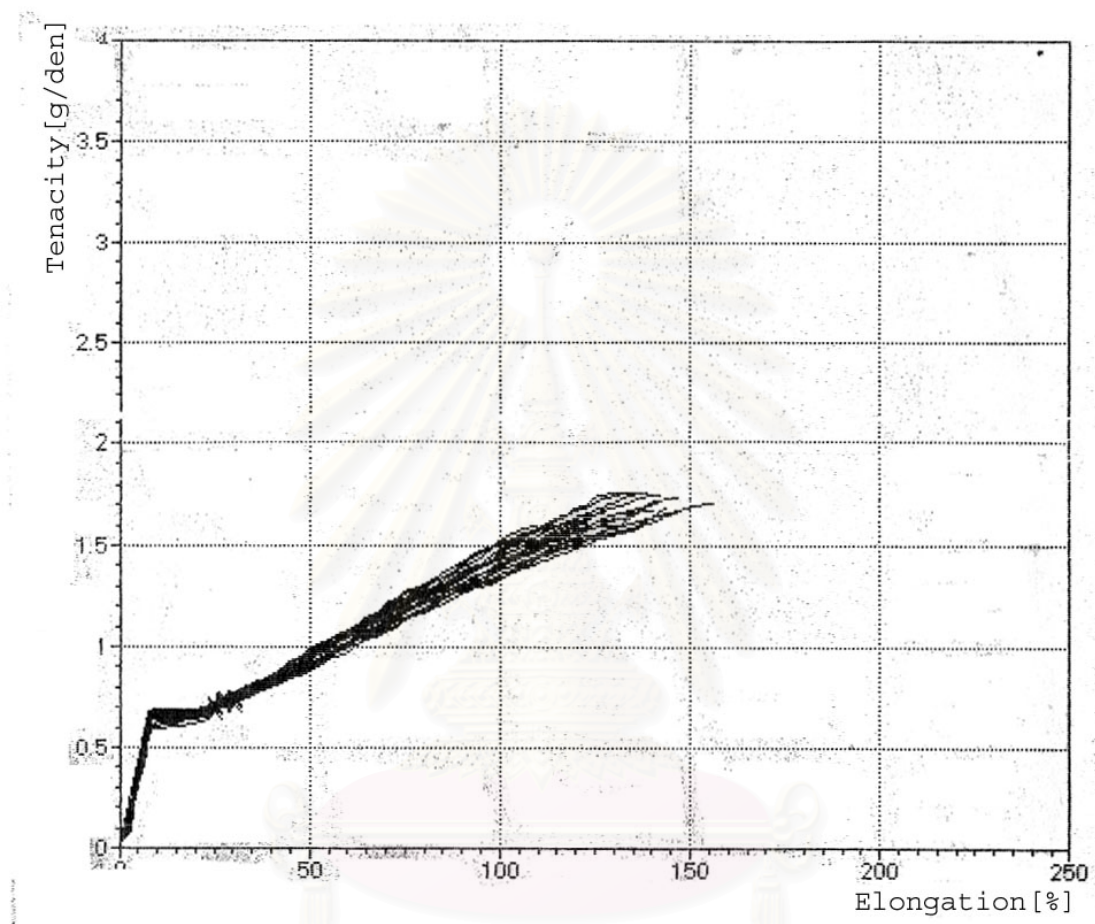
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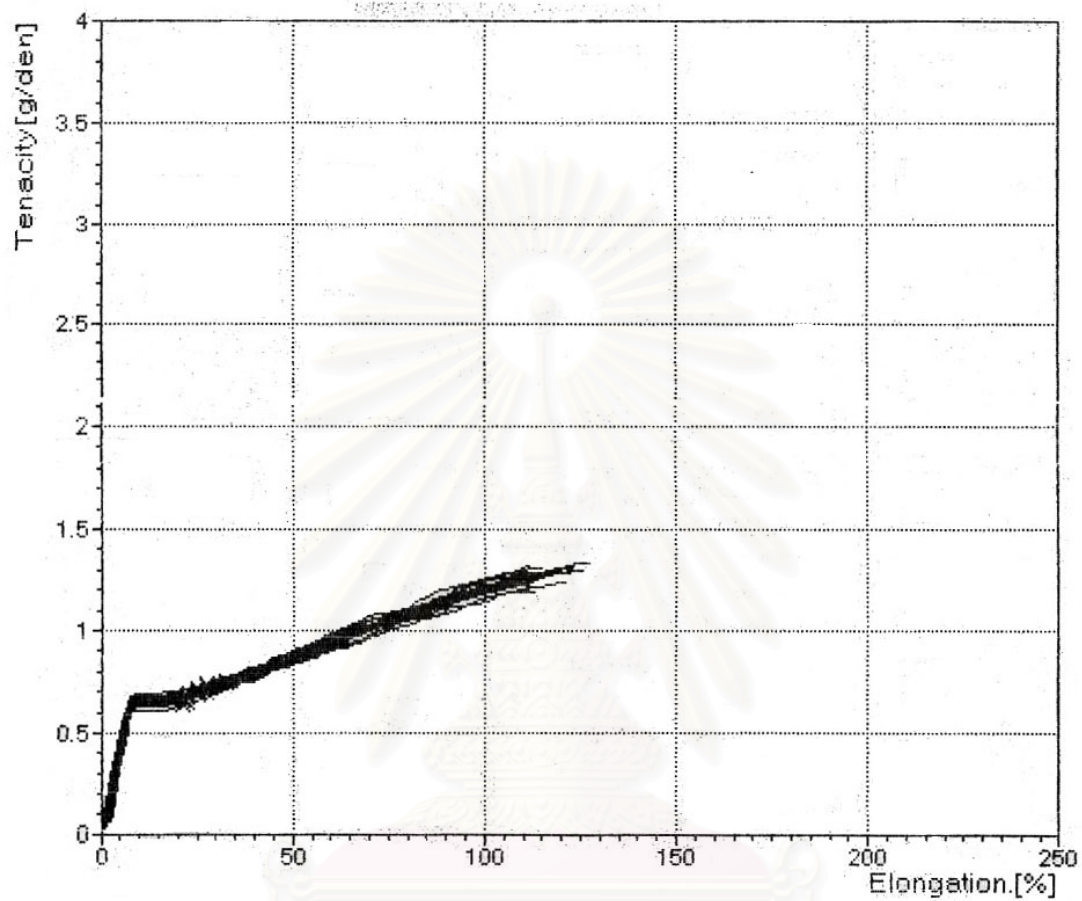
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calibrated at :

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001	6.03	6.70	1.81	16.0	157.2	10.94	1.37
002	6.10	6.78	1.81	16.0	137.8	11.07	1.36
003	6.33	7.03	1.79	15.8	140.2	11.33	1.38
004	6.24	6.93	1.77	15.6	135.3	11.03	1.38
005	5.96	6.62	1.81	16.0	142.6	10.80	1.37
006	6.34	7.05	1.74	15.4	152.3	11.07	1.38
007	6.27	6.97	1.86	16.4	142.6	11.66	1.30
008	6.11	6.79	1.86	16.4	142.6	11.36	1.36
009	6.06	6.73	1.80	15.9	137.8	10.92	1.32
010	6.11	6.79	1.70	15.0	145.0	10.39	1.30
011	5.98	6.64	1.99	17.6	162.0	11.92	1.35
012	5.83	6.48	1.71	15.1	137.8	9.98	1.35
013	6.30	7.00	1.77	15.6	135.3	11.14	1.38
014	5.93	6.59	1.89	16.7	149.9	11.23	1.36
015	6.63	7.37	1.78	15.7	154.7	11.80	1.35
016	6.20	6.89	1.77	15.6	147.5	10.96	1.40
017	6.04	6.71	1.90	16.8	157.2	11.50	1.32
018	6.23	6.92	1.79	15.8	147.5	11.15	1.40
019	5.96	6.62	1.96	17.3	149.9	11.68	1.36
020	6.31	7.01	1.82	16.1	135.3	11.51	1.37
Minimum	5.83	6.48	1.70	15.0	135.3	9.98	1.30
Maximum	6.63	7.37	1.99	17.6	162.0	11.92	1.40
Spanw.	0.80	0.89	0.29	2.6	26.7	1.94	0.11
Mean	6.15	6.83	1.82	16.0	145.5	11.17	1.36
Std.dev	0.19	0.21	0.08	0.7	8.2	0.47	0.03
Cv [%]	3.1	3.1	4.2	4.2	5.6	4.2	2.2
Confid.	6.06	6.73	1.78	15.7	141.7	10.95	1.34
Interv.	6.24	6.93	1.85	16.4	149.3	11.39	1.37

Figure B-4 The tensile properties of 29.4% grafted PET fiber

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Comment   : 29.4%GRAFT
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Testing Speed [mm/min]: 100
calibrated at :

	Titer [den]	Titer [dtex]	Tenacity [g/den]	Tenacity [cN/tex]	Elong. [%]	Force [g]	NDR
001	6.35	7.06	1.67	14.7	138.7	10.59	1.25
002	6.34	7.04	1.73	15.3	146.8	10.99	1.30
003	6.35	7.06	1.67	14.7	140.3	10.59	1.25
004	7.04	7.82	1.50	13.2	117.7	10.53	1.25
005	6.76	7.51	1.68	14.8	148.4	11.34	1.30
006	6.43	7.15	1.77	15.6	137.1	11.38	1.27
007	6.69	7.43	1.62	14.3	120.9	10.84	1.25
008	6.08	6.76	1.68	14.8	127.4	10.21	1.27
009	6.41	7.12	1.77	15.6	133.9	11.33	1.27
010	6.60	7.33	1.74	15.4	142.0	11.51	1.27
011	6.35	7.06	1.77	15.6	138.7	11.23	1.27
012	7.06	7.84	1.70	15.0	156.5	12.00	1.30
013	6.64	7.38	1.59	14.0	130.6	10.54	1.25
014	6.47	7.19	1.71	15.1	142.0	11.07	1.25
015	6.68	7.42	1.63	14.4	130.6	10.90	1.27
016	6.70	7.44	1.60	14.1	109.6	10.70	1.27
017	6.85	7.61	1.54	13.6	111.2	10.56	1.30
018	6.52	7.25	1.61	14.2	122.6	10.50	1.27
019	6.61	7.35	1.68	14.8	143.6	11.10	1.30
020	6.59	7.32	1.65	14.6	127.4	10.90	1.27
Minimum	6.08	6.76	1.50	13.2	109.6	10.21	1.25
Maximum	7.06	7.84	1.77	15.6	156.5	12.00	1.30
Spanw.	0.97	1.08	0.27	2.4	46.9	1.79	0.05
Mean	6.58	7.31	1.66	14.7	133.3	10.94	1.27
Std.dev	0.24	0.27	0.08	0.7	12.5	0.44	0.02
Cv [%]	3.7	3.7	4.5	4.5	9.4	4.0	1.5
Confid.	6.46	7.18	1.63	14.4	127.4	10.74	1.26
Interv.	6.69	7.43	1.70	15.0	179.2	11.14	1.28

Figure B-5 The tensile properties of 40.0% grafted PET fiber

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Identifica.: PET2
Article   : AREA 71
Comment   : 40% GRAFTED PET
Longterm Code : ST
Gauge Length [mm]   : 10
Tension Weight [mg] :   300
Testing Speed [mm/min]: 100
calibrated at :

	Titer [den]	Titer [dtex]	Tenacity [g/den]	Tenacity [cN/tex]	Elong. [%]	Force [g]	NDR
001	7.06	7.84	1.24	10.9	120.9	8.72	1.25
002	6.62	7.36	1.28	11.3	117.7	8.48	1.21
003	6.64	7.38	1.34	11.8	124.2	8.88	1.27
004	6.44	7.16	1.31	11.6	114.5	8.47	1.27
005	7.06	7.84	1.24	10.9	111.2	8.72	1.25
006	6.34	7.04	1.34	11.8	127.4	8.47	1.25
007	5.99	6.66	1.28	11.3	114.5	7.68	1.25
008	6.49	7.21	1.33	11.7	111.2	8.61	1.25
009	7.03	7.81	1.29	11.4	112.9	9.08	1.25
010	6.91	7.68	1.26	11.1	112.9	8.70	1.33
011	6.73	7.48	1.29	11.4	119.3	8.70	1.27
012	7.06	7.85	1.29	11.4	120.9	9.13	1.25
013	6.97	7.75	1.20	10.6	111.2	8.38	1.25
014	6.64	7.38	1.31	11.6	111.2	8.73	1.23
015	6.70	7.44	1.22	10.8	111.2	8.20	1.22
016	6.76	7.51	1.28	11.3	119.3	8.66	1.25
017	6.87	7.63	1.31	11.6	122.6	9.03	1.25
018	6.64	7.38	1.30	11.5	124.2	8.66	1.22
019	6.66	7.40	1.30	11.5	125.8	8.68	1.27
020	7.07	7.86	1.19	10.5	112.9	8.42	1.21

???

	Titer [den]	Titer [dtex]	Tenacity [g/den]	Tenacity [cN/tex]	Elong. [%]	Force [g]	NDR
Minimum	5.99	6.66	1.19	10.5	111.2	7.68	1.21
Maximum	7.07	7.86	1.34	11.8	127.4	9.13	1.33
Spanw.	1.08	1.20	0.15	1.3	16.2	1.45	0.12
Mean	6.73	7.48	1.28	11.3	117.3	8.62	1.25
Std.dev	0.28	0.31	0.04	0.4	5.6	0.32	0.03
Cv [%]	4.2	4.2	3.4	3.4	4.8	3.8	2.1
Confid.	6.60	7.34	1.26	11.1	114.7	8.47	1.24
Interv.	6.87	7.63	1.30	11.5	119.9	8.77	1.26

Appendix C

The thermogravimetry analysis
of PET fiber and AA-grafted PET fiber

NETZSCH thermo-microbalance TG 409 analyzer was used for the thermal stability of PET fiber and AA-grafted PET fiber. The temperature range 273-923 K and with a heating rate 283 K per minute in an atmosphere of nitrogen were studied.

The loss in weight over specific temperature ranges provides an indication of the composition of the sample, including volatiles and inert filler, as well as indications of thermal stability. The temperature of the sample is recorded as the X-axis. A plot of mass or mass percent versus time or temperature is called a thermogram or thermal decomposition curve. The TGA curves of PET fiber and AA-grafted PET fiber were shown in Figures C-1 to C-5.
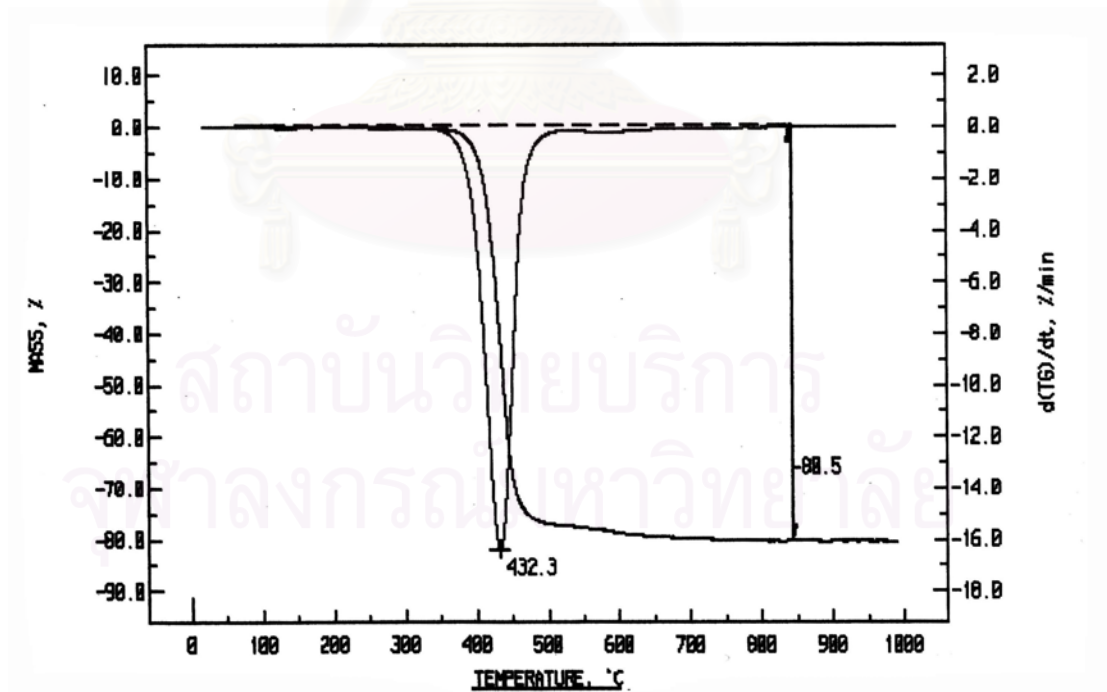
Figure C-1 TGA and DGT of PET fiber
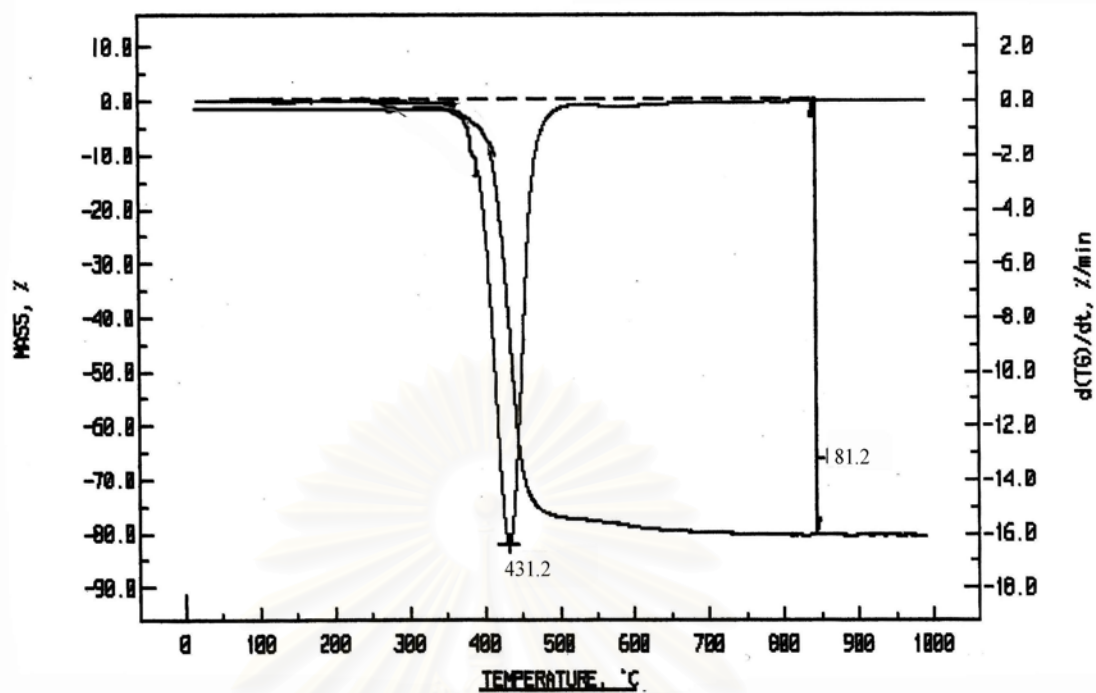
Figure C-2 TGA and DGT of 10% AA-grafted PET fiber
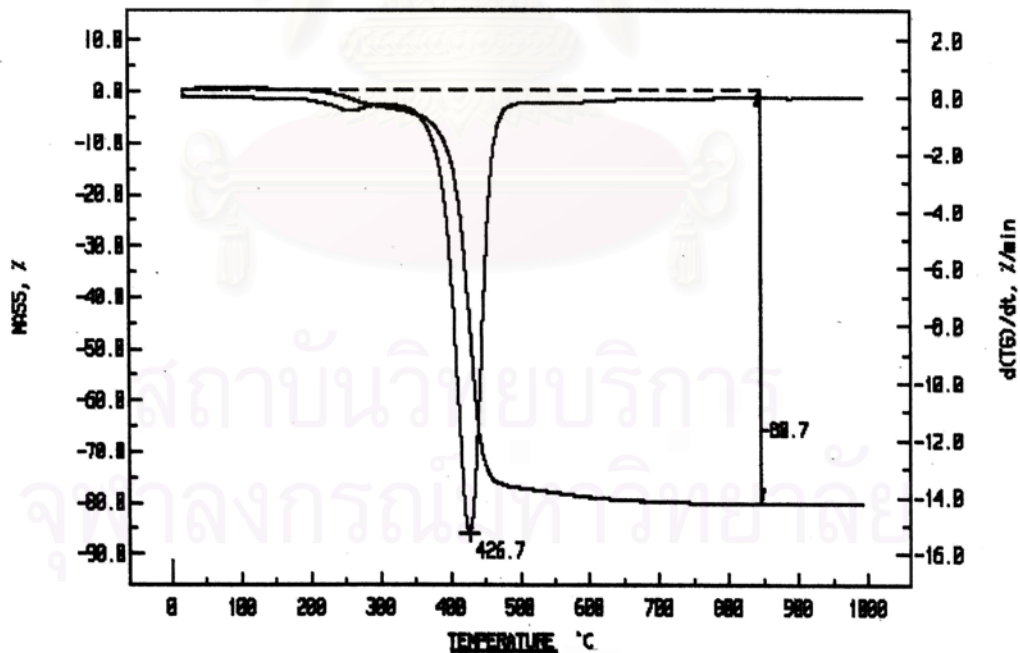
Figure C-3 TGA and DGT of 20% AA-grafted PET fiber
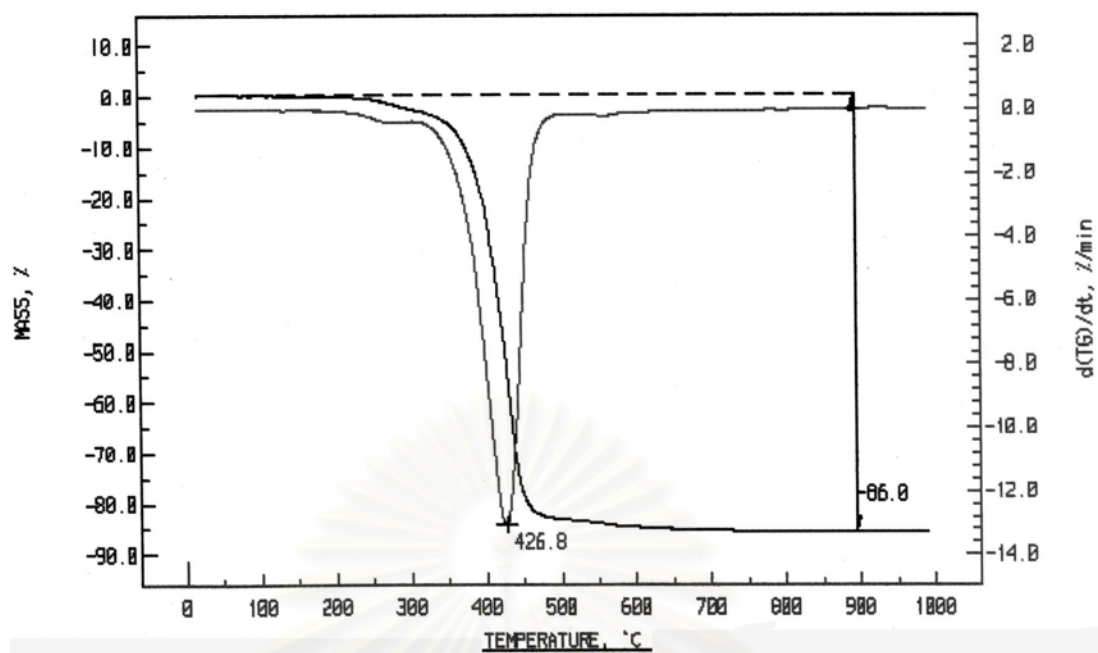
Figure C-4 TGA and DGT of 30% AA-grafted PET fiber
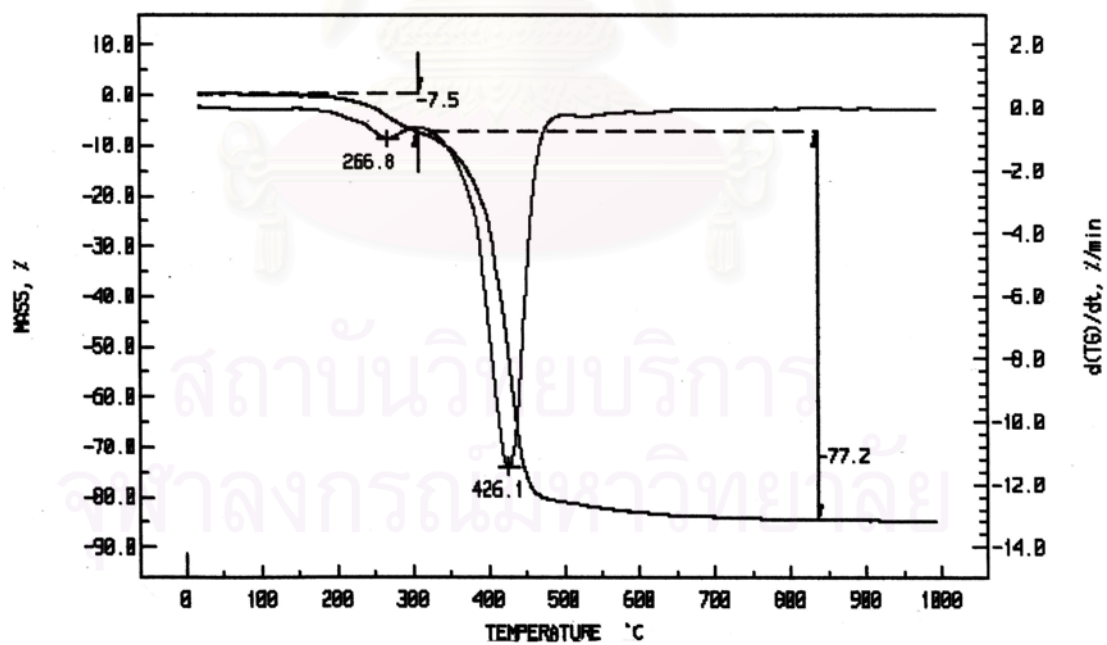
Figure C-5 TGA and DGT of 40% AA-grafted PET fiber

Appendix D

The moisture regain of PET and AA-grafted PET fiber

        The fiber samples were conditioned at 65% relative humidity and $20^{o}C$ in a humidity & temperature chamber for 5 days (ASTM 1909). The sample were weighed in the conditioned state, then dried at $110^{o}C$ for 12 hours in an oven and weighed again. The determination was repeated for 3 times/sample. The result was in Table D-1.

        The result was calculated from the difference in the weight of the conditioned fiber and the dry weight of the original fiber as follows:

$$\%\,moisture\ regain = (A-B) \times 100 / B$$

    A = the weight of the fiber after conditioning at 65% relative humidity and $20^{o}C$ in the humidity & temperature chamber for 5 days in gram

    B = the weight (in gram) of fiber after drying at $110^{o}C$ for 12 hours

Table D-1 Moisture regain of the PET fiber and AA-grafted PET fiber

%Graft yield	No.	A (g)	B (g)	Moisture regain (%)	Average (g)
O	1	1.0001	1.0021	0.200	
	2	1.0026	1.0045	0.190	0.200
	3	1.0017	1.0038	0.210	
10	1	1.0006	1.0066	0.600	
	2	1.0018	1.0078	0.599	0.596
	3	1.0005	1.0064	0.590	
20	1	1.0007	1.0086	0.789	
	2	1.0012	1.0092	0.799	0.799
	3	1.0004	1.0085	0.810	
30	1	1.0003	1.0102	0.990	
	2	1.0001	1.0103	1.018	1.002
	3	1.0008	1.0108	0.999	
40	1	1.0001	1.0202	2.007	
	2	1.0008	1.0209	2.008	2.001
	3	1.0007	1.0206	1.989	

Appendix E

The dyeability of PET and AA-grafted PET fiber

The dyeability of the fiber samples was calculated from the weight of the dye remaining in the dye-bath and predetermined calibration curve. The amount of the dye remaining in the dye-bath was determined by UV-Visible spectrophotometry at the λ_{max} of the dye.

1. Dyeability with methylene blue

    1.1 λ_{max} of Methylene blue

Table E-1 %Absorbance of Methylene blue at 640 – 680 nm

Wavelength (nm)	%Absorbance	Wavelength (nm)	%Absorbance
640	2.825	661	2.916
652	2.910	662	2.916
654	2.911	663	2.918
655	2.913	664	2.915
656	2.915	666	2.913
658	2.917	668	2.910
659	2.917	670	2.908
660	2.916	680	2.869
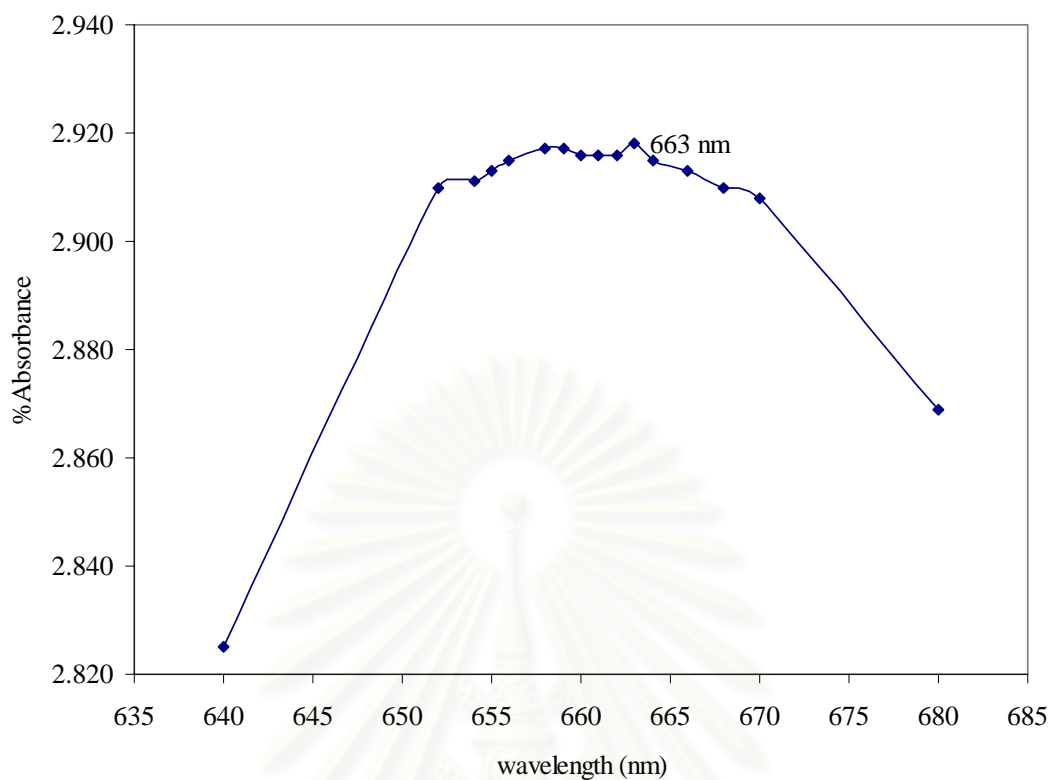
Figure E-1 %Absorbance of Methylene blue at various wavelength

1.2 Calibration curve of Methylene blue

Table E-2 Data of Methylene blue calibration curve at 663 nm

Methylene blue concentration x 10^{-3} (g/l)	0.5	1.0	2.0	3.0	4.0	5.0	6.0
%Absorbance	0.098	0.185	0.388	0.567	0.775	0.960	1.132
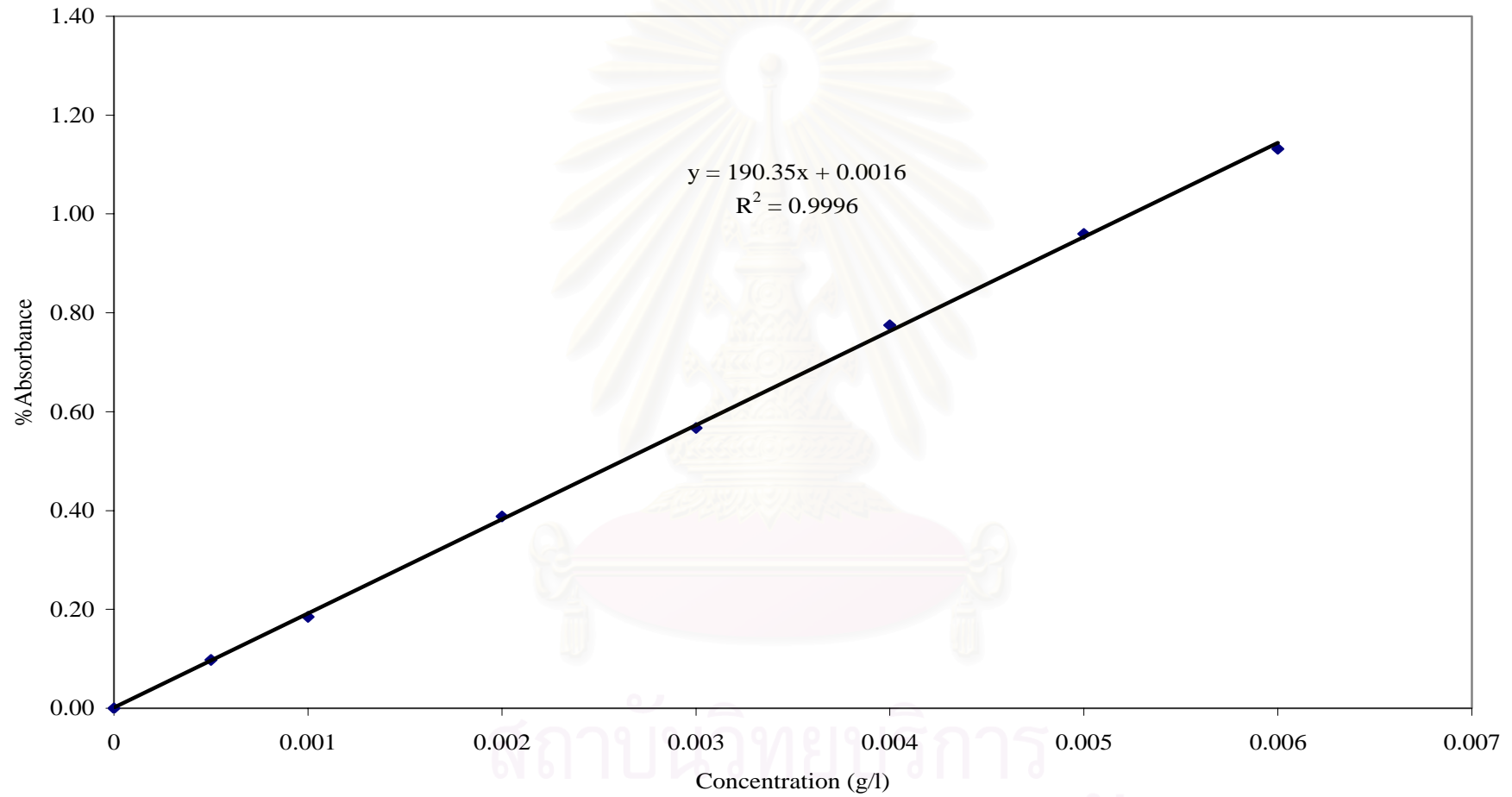
Figure E-2 Calibration curve of Methylene blue at 663 mm

1.3 Dyeability of PET fiber and AA-grafted PET fiber with methylene blue

Table E-3 Dyeability of PET fiber and AA-grafted PET fiber with Methylene blue.

%Graft yield	%Abs	Conc. From curve (g/l) $\times 10^{-3}$	Methylene blue conc. In dye-bath (g/l)	Methylene blue	
				Absorption (g)	g dye/ g sample
0.0	0.952	4.993	0.1997	0.0003	1.42
16.3	0.654	3.427	0.1371	0.0629	314.53
22.0	0.529	2.771	0.1108	0.0892	445.86
31.7	0.450	2.356	0.0942	0.1058	528.87
39.0	0.338	1.767	0.0707	0.1293	646.55
43.5	0.264	1.379	0.0551	0.1449	724.30

2. Dyeability with disperse dye

2.1 λ_{max} of disperse dye

Table E-4 %Absorbance of disperse dye at 510 – 630 nm

| Wavelength (nm)	%Absorbance	Wavelength (nm)	%Absorbance
510	1.273	548	1.373
520	1.302	550	1.367
530	1.349	555	1.362
540	1.365	560	1.349
542	1.370	570	1.329
543	1.374	575	1.316
544	1.374	580	1.309
545	1.376	585	1.311
546	1.370	590	1.293
547	1.373	630	1.115
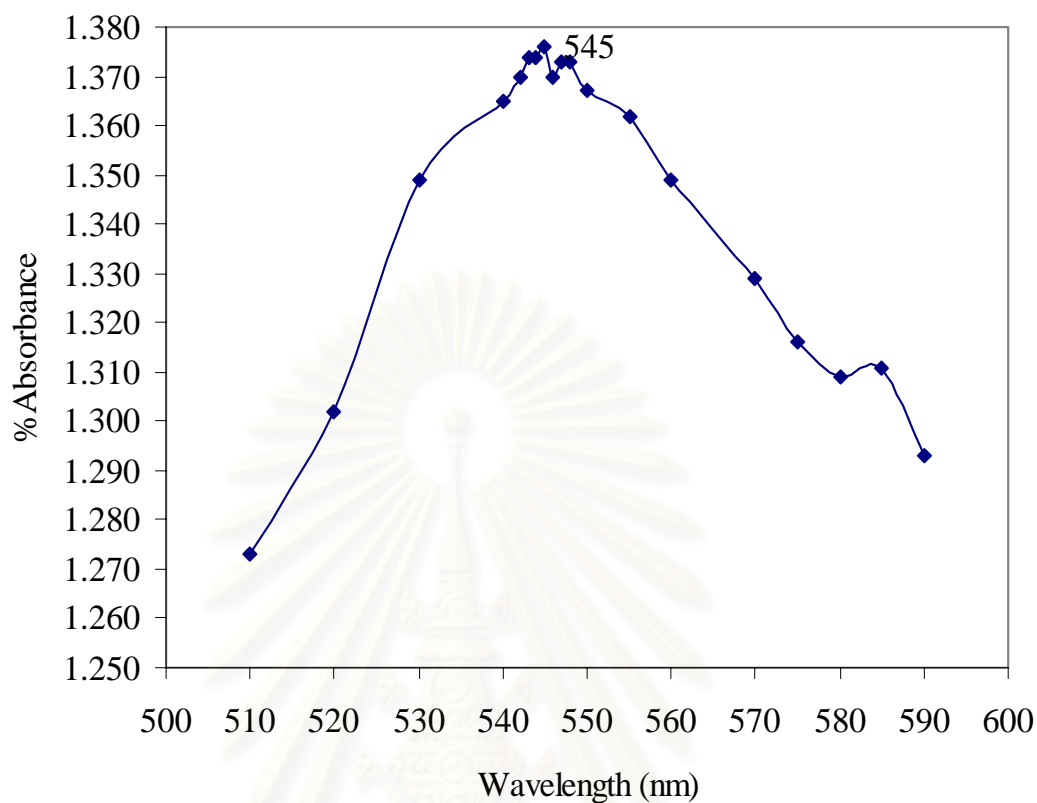
Figure E-3 %Absorbance of disperse dye at various wavelength

2.2 Calibration curve of Methylene blue

Table E-5 Data of disperse dye calibration curve

Methylene blue concentration x 10^{-3} (g/l)	1.0	2.0	4.0	6.0	8.0	10.0
%Absorbance	0.011	0.022	0.045	0.067	0.090	0.114

$y = 0.0113x$

$R^2 = 0.9998$

% Absorbance

Hicron navy blue GRL-SF 200% x 10^{-3} (g/l)
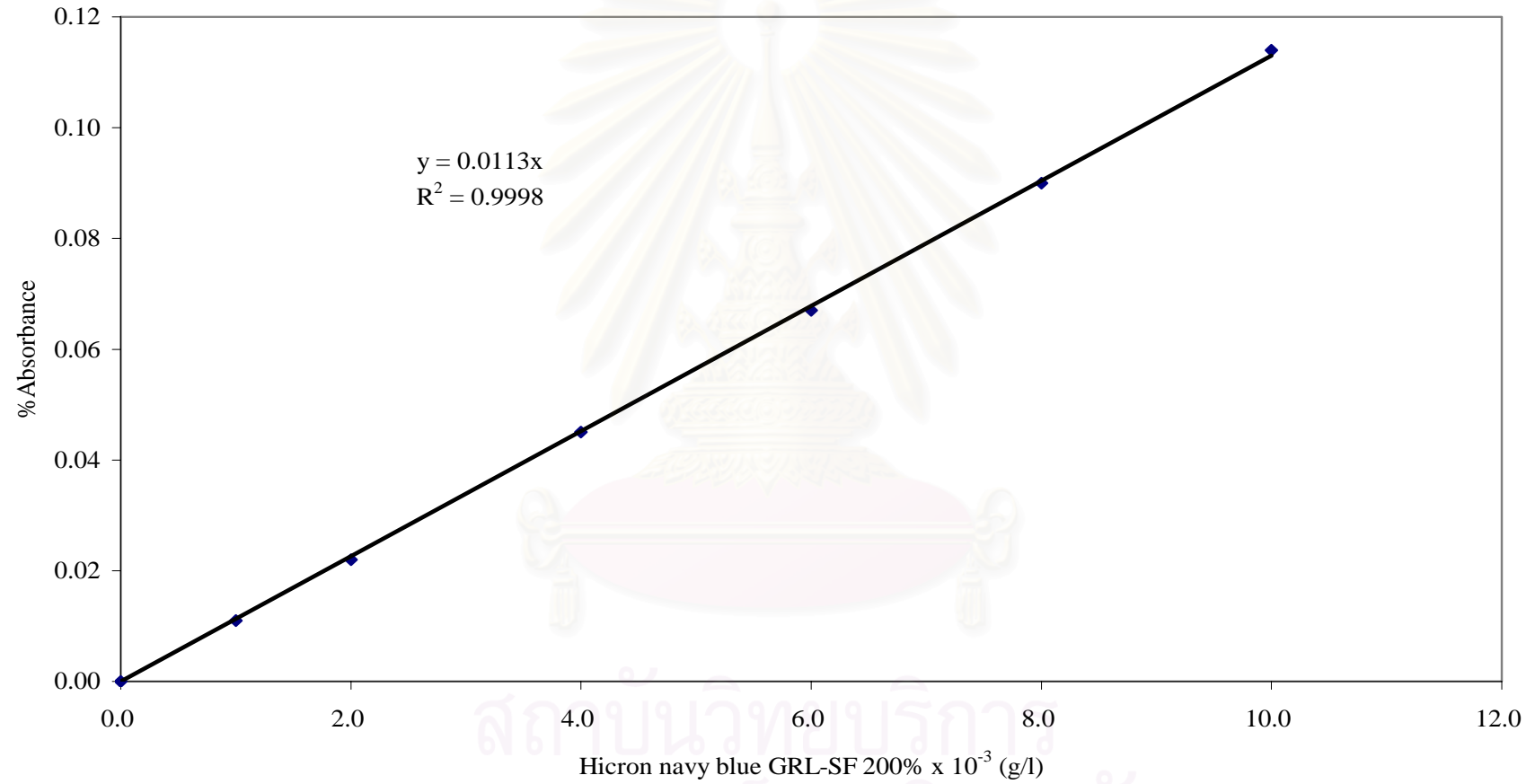
Figure E-4 Calibration curve of Hicron navy blue GRL-SF 200% at 545 nm

2.3 Dyeability of PET fiber and AA-grafted PET fiber with disperse dye

Table E-6 Dyeability of PET fiber and AA-grafted PET fiber with disperse dye (Hicron navy blue GRL-SF 200%.)

%Graft yield	%Abs	Conc. From curve (mg/l)	Disperse dye conc. In dye-bath (mg/l)	Disperse dye	
				Absorption (mg)	mg dye/ g sample
0.0	0.105	9.29	46.46	15.35	76.77
16.9	0.060	5.31	26.58	17.35	86.73
19.2	0.055	4.87	24.34	17.57	87.83
30.4	0.032	2.83	14.16	18.58	92.92
43.8	0.029	2.57	12.83	18.72	93.58

VITA

Miss Narawadee Chansook was born on October 8, 1975, in Prachubkeereekhun. She received her B.Sc. in Chemistry from Faculty of Science, Chulalongkorn University in 1997. Since then she has joined the quality assurance section, Kangwal Polyester co., ltd. She began her master's degree study in Petrochemistry and Polymer Science, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University in 2000.