# A STUDY OF MODIFICATION OF HYDROPHILICITY OF POLYESTER FABRICS

BOONSRI KUSUKTHAM

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
( POLYMER SCIENCE )

ได้รับวิทยานิพนธ์
จาก
.....

IN

FACULTY OF GRADUATE STUDIES
MAHIDOL UNIVERSITY

1996

36556

Copyright by Mahidol University

Thesis
entitled

# A STUDY OF MODIFICATION OF HYDROPHILICITY OF POLYESTER FABRICS

Boonsri Kusuktham
Candidate

Krisda Suchiva, Ph. D.
Major Advisor

Pranee Phinyocheep,
Doctorat de l'Universite du Maine
Co- advisor

Nantaya Yanumet, Ph.D.
Co- advisor

Adulya Viriyavejakul,
M.D., LL.B., F.R.C.P.
Dean
Facuty of Graduate Studies

Pranee Phinyocheep,
Doctorat de l'Universite du Maine
Chairman
Master of Science Program in
Polymer Science
Faculty of Science

Copyright by Mahidol University

Thesis
entitled

A STUDY OF MODIFICATION OF HYDROPHILICITY
OF POLYESTER FABRICS

was submitted to the Faculty of Graduate Studies, Mahidol University
for the degree of Master of Science (Polymer Science)
on
May 27, 1996

Boonsri Kusuktham
Boonsri Kusuktham
Candidate

Krisda Suchiva, Ph. D.
Chairman

Pranee Phinyocheep,
Doctorat de l'Universite du Maine
Member

N. Yanumet.
Nantaya Yanumet, Ph.D.
Member

Adulya Viriyavejakul, M.D., LL.B., F.R.C.P.
Dean
Faculty of Gradute Studies

Pornchai Matangkasombut, M.D., Ph.D.
Dean
Faculty of Science

Copyright by Mahidol University

# BIOGRAPHY

| | |
|---|---|
| **NAME** | Miss Boonsri Kusuktham |
| **DATE OF BIRTH** | 20 July 1964 |
| **PLACE OF BIRTH** | Bangkok |
| **INSTITUTE ATTENDED** | Srinakharinwirot University, 1983-1986 |
| | Bachelor of Education (Science-Chemistry) |
| | Srinakharinwirot University, 1987-1989 |
| | Master of Education (Chemistry) |
| | Mahidol University, 1993-1996 |
| | Master of Science (Polymer Science) |
| **RESEARCH GRANT** | National Science & Technology Development |
| | Agency (NSTDA), 1993-1994 |

**POSITION HELD &OFFICE**

1989-present

Rajamangala Institute of Technology

Bangkok Technical Campus

Textile Chemistry Division

Position : Teacher

Copyright by Mahidol University

# ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my advisor Dr. Krisda Suchiva for his valuable guidance, continuous interest and encouragement throughout this study. Dr. Pranee Phinyocheep and Dr. Nantaya Yanumet for their suggestions and many helpful discussion.

This work was funded by the National Science & Technology Development Agency (NSTDA) and I wish to thank NSTDA for financial support.

I wish to express my appreciation to Dr. Saran Poshyachinda of the National Metal and Materials Technology Centre (MTEC) for his advice on the analysis polyester fabrics with FT-Raman spectroscopy, Mr. Bunpot Maingam, also of MTEC, for his help in using the DMTA. In addition, I wish to thank to staff of the Textile Chemistry Division , Bangkok Technical Campus for useful comments.

Finally, I would like to thank all of my friends for their helps throughout this work.

Boonsri Kusuktham

Copyright by Mahidol University

ชื่อวิทยานิพนธ์ การศึกษาเพื่อปรับปรุงสมบัติในด้านการดูดความชื้นของผ้าโพลีเอสเตอร์

ผู้วิจัย บุญศรี คู่สุขธรรม

ปริญญา วิทยาศาสตรมหาบัณฑิต ( วิทยาศาสตร์พอลิเมอร์)

คณะกรรมการควบคุมวิทยานิพนธ์

กฤษฎา สุชีวะ, Ph.D.

ปราณี ภิญโญชีพ, Doctorat de l'Universite du Maine

นันทยา ยานุเมศ, Ph.D.

วันที่สำเร็จการศึกษา 27 พฤษภาคม พ.ศ. 2539

## บทคัดย่อ

งานวิจัยนี้เป็นการศึกษาวิธีการปรับปรุงผ้าโพลีเอสเตอร์โดยการกราฟท์ด้วยโพลีเมธาไครลิกแอซิด จุดประสงค์ของการศึกษาเพื่อปรับปรุงสมบัติในด้านการดูดความชื้นของผ้าโพลีเอสเตอร์

ผลการศึกษาพบว่าการกราฟท์เมธาไครลิกแอซิดไปบนผ้าโพลีเอสเตอร์ สามารถทำได้โดยปฏิกิริยาลูกโซ่โดยใช้เบนโซอิลเปอร์ออกไซด์เป็นตัวเริ่มปฏิกิริยา การทำให้ผ้าโพลีเอสเตอร์พองตัวด้วยเบนซิลแอลกอฮอล์พบว่ามีความสำคัญต่อการเกิดกราฟท์ ปัจจัยที่มีผลต่อการเกิดปฏิกิริยาคือ ความเข้มข้นของตัวริเริ่ม, อัตราส่วนระหว่างโมโนเมอร์กับผ้า, อุณหภูมิ, และเวลาที่ใช้ในการทำปฏิกริยา

ผ้าโพลีเอสเตอร์ที่ผ่านการปรับปรุงแล้วได้รับการนำมาตรวจสอบการเปลี่ยนแปลง (characterised) โดยวิธีการชั่งน้ำหนักที่เพิ่ม การใช้อินฟราเรดและรามานสเปกโทรสโกปี การใช้เครื่องวิเคราะห์การรับแรงสั่นสะเทือน (Dynamic Mechanical Thermal Analyser : DMTA) และกล้องจุลทรรศน์อิเล็คตรอนแบบส่องกราด (Scanning Electron Microscope : SEM) ผลการศึกษาพบว่า ผ้าโพลีเอสเตอร์ที่ผ่านการปรับปรุงมีร้อยละของการดูดความชื้นเพิ่มขึ้น จาก ร้อยละ 1 เป็น ร้อยละ 4.6 เมื่อปริมาณกราฟท์เพิ่มขึ้นจาก ร้อยละ 5 เป็น ร้อยละ 32 และมีความกระด้างมากกว่าผ้าที่ไม่ได้ผ่านการกราฟท์ แต่พบว่าสามารถปรับให้ผ้านุ่มขึ้นโดยการควบคุมการทำปฏิกิริยากับสารละลายโซเดียมไฮดรอกไซด์ อย่างไรก็ตามพบว่าการทำปฏิกิริยากับสารละลายโซเดียมไฮดรอกไซด์มีผลทำให้ผ้ามีความเสถียรลดลง โดยเฉพาะอย่างยิ่งเมื่อปริมาณกราฟท์เพิ่มขึ้น

Copyright by Mahidol University

( ที่อัตราส่วนระหว่าง โมโนเมอร์กับผ้าสูงๆ) และความเข้มข้นของสารละลายโซเดียมไฮดรอกไซด์เพิ่มขึ้น ดังนั้นในขั้นตอนของการทำปฏิกิริยากับสารละลายโซเดียมไฮดรอกไซด์ จึงต้องควบคุมอย่างระมัดระวัง เพื่อป้องกันการเสื่อมสภาพของผ้าโพลีเอสเตอร์

Copyright by Mahidol University

Thesis Title A Study of Modification of Hydrophilicity of Polyester Fabrics

Name Boonsri Kusuktham

Degree Master of Science (Polymer Science)

Thesis Supervisory Committee

Krisda Suchiva, Ph.D.

Pranee Phinyocheep, Doctorat de l'Universite'du Maine

Nantaya Yanumet, Ph.D.

Date of Graduation 27 May B.E. 2539 (1996)

## ABSTRACT

Modification of polyester (poly(ethylene terephthalate) : PET) fabric by grafting with poly(methacrylic acid) (PMAA) was studied. The objective was to improve the hydrophilicity of PET and, hence, its water uptake.

It was found that grafting of MAA onto polyester fabrics could be effected by radical reaction using benzoyl peroxide (BPO) as radical initiator. Swelling of polyester fabric with benzyl alcohol was also found to be necessary for grafting to occur. The parameters which affected the modification reaction were initiator concentration, monomer to fabric ratio, reaction temperature and reaction time.

The modified polyester fabrics were characterised by gravimetric method, FT-IR and FT-Raman spectroscopies, dynamic mechanical analysis and scanning electron microscopy. It was shown that the percentage uptake of moisture of the modified fabrics (1 to 4.6%) increased with increasing extent of grafting ( 5 to 32%) The modified fabrics tended to be stiffer than

Copyright by Mahidol University

the unmodified fabrics, but they could be softened by controlled treatment with aqueous solution of sodium hydroxide. The stability of the modified polyester fabric, however, was found to decrease with increasing extent of modification ( high monomer to fabric ratio) and increasing concentration of sodium hydroxide solution. Thus, careful control of sodium hydroxide treatment process was necessary to prevent deterioration of the modified polyester fabric.

Copyright by Mahidol University

# TABLE OF CONTENTS


| | PAGE |
|---|---|
| BIOGRAPHY | i |
| ACKNOWLEDGEMENTS | ii |
| ABSTRACT (in Thai ) | iii |
| ABSTRACT ( in English) | v |
| TABLE OF CONTENT | vii |
| LIST OF TABLES | xi |
| LIST OF FIGURES | xiii |
| CHAPTER I INTRODUCTION | 1 |
| 1.1 Polyester Fibres and Fabrics | 1 |
| 1.1.1 Formation of Polyester Fibres and Fabrics | 1 |
| 1.1.2 Properties of Polyester Fibres | 5 |
| 1.1.2.1 Physical Properties | 7 |
| 1.1.2.2 Chemical Properties | 8 |
| 1.1.3 Inadequacy of Polyester Fibres | 8 |
| 1.2 Modification of Polyester Fibres by Grafting | 9 |
| 1.2.1 Initiator Used in Grafting Reactions | 10 |
| 1.2.2 Method of Grafting | 11 |
| 1.2.3 Structure of Grafting polyester | 13 |
| 1.2.4 Problems with Grafting of PET | 14 |
| 1.3 Previous Studies on Graft Modifications of Polyester Fibres | 15 |
| 1.3.1 Studied on Grafting Method | 15 |
| A. Grafting by Using Swelling | 15 |
| B. Grafting by Using No Swelling Agent | 19 |


Copyright by Mahidol University

| | PAGE |
|---|---|
| 1.3.2 Characterisation of Grafted PET | 22 |
| A. Gravimetric Measurement | 23 |
| B. Spectroscopic Technique | 24 |
| C. Thermal Analytical Method | 26 |
| D. Chemical Analysis | 28 |
| 1.3.3 Properties of Grafted Polyesters | 30 |
| A. Moisture Regain | 30 |
| B. Mechanical Properties | 31 |
| 1.4 Scope of The Present Thesis | 33 |
| CHAPTER II EXPERIMENTAL | 35 |
| 2.1 Pretreatment of Polyester Fabrics | 35 |
| 2.2 Reagents | 38 |
| 2.3 Measurements of Swelling of Monomer | 38 |
| and Swelling Agent in Polyester Fabrics | 38 |
| 2.4 Study of Polymerisation Reaction of | |
| Methacrylic Acid by Differential Scanning Calorimetry | 39 |
| 2.5 Modifications of Polyester Fabrics | 40 |
| 2.5.1 Method of Modification of Polyester | 40 |
| A. Study of Effect of Initiator Concentration | 41 |
| B. Study of Effect of Grafting Temperature | 42 |
| C. Study of Effect of Monomer Concentration | 42 |
| 2.6 Characterisation of Modified polyester | 43 |
| 2.6.1 Determination of Percentage Grafting | 43 |
| 2.6.2 Determination of Moisture Regain | 43 |


Copyright by Mahidol University

PAGE

2.6.3 FT-IR and FT-Raman Spectroscopic 44

2.6.3.1 FT-IR Spectroscopy 44

2.6.3.2 FT-Raman Spectroscopy 45

2.6.4 Dynamic Mechanical Analytical Studies of Modified Polyesters 45

2.6.5 Measurement of Tensile Properties of Yarns 46

2.6.6 Measurement of Thickness of Polyester Fabrics 47

2.6.7 Scanning Electron Microscopic Study 48

2.7 Treatment of Modified Polyester with NaOH 48

CHAPTER III RESULTS AND DISCUSSION 50

3.1 Preliminary Studies 50

3.1.1 Determination of Suitable Swelling Agent For Modification of polyester 50

3.1.1.1 Swelling Study of Polyester Fabric in Methacrylic Acid 50

3.1.1.2 Swelling Study of Polyester Fabric in Swelling Agents 51

3.1.2 Study of Estimate Suitable Grafting Condition By Using Differential Scanning Calorimetry (DSC) 53

A. Polymerisation Temperature 53

B. Effect of Swelling Agent on Polymerisation Reaction of MAA 56

3.1.3 Determination of Method For Effecting Modification of Polyester 62

Copyright by Mahidol University

PAGE

3.1.4 Determination of Percentage Grafting by Solvent Extraction 64

3.2 Studies of Modification of Polyesters 67

3.2.1 Effect of Initiator Concentration 67

3.2.2 Effect of Temperature 70

3.2.3 Effect of Monomer to Fabric Ratio 72

3.3 Characterisation of Modified Polyester 74

3.3.1 Moisture Regain 74

3.3.2 FT-IR and FT-Raman Spectroscopies 77

3.3.3 Dynamic Mechanical Analysis (DMA) of Modified Polyesters 85

3.3.4 Tensile Property 96

3.3.5 Measurement of Thickness 98

3.3.6 Treatment of Modified Polyester with NaOH 106

CHAPTER IV CONCLUSION 113

BIBLIOGRAPHY 115

Copyright by Mahidol University

# LIST OF TABLES


| TABLE | PAGE |
|---|---|
| 1.1 Important fiber properties for textile uses | 6 |
| 1.2 Physical properties of polyester fibre | 7 |
| 1.3 Moisture regain and fiber resistivity | 9 |
| 1.4 Solubility parameters of selected organic solvents | 12 |
| 1.5 Effect of percentage pickup of swelling agent on graft yield | 18 |
| 1.6 Percentage of grafting polyester fibre with MMA | 24 |
| 1.7 Effect of PVA graft on melting temperature, heat of fusion, and percentage of crystallinity of the grafted polyester fibre | 27 |
| 2.1 Experimental condition of thermal analytical polymerisation reaction by using DSC | 40 |
| 3.1 Percentage swelling of polyester fabrics in MAA | 51 |
| 3.2 Percentage swelling of polyester fabrics in various swelling agents | 52 |
| 3.3 Percentage swelling of polyester fabrics in benzyl alcohol | 53 |
| 3.4 Time of polymerisation of MAA at various temperatures | 54 |
| 3.5 Time of polymerisation of BPO, MAA and benzyl alcohol at various temperature | 56 |
| 3.6 Reaction system of grafting MAA onto polyester fabrics | 62 |
| 3.7 Percentage graft yield of polyester fabric after grafting by swelling in 2% benzyl alcohol | 63 |
| 3.8 Percentage graft yield of polyester fabric after grafting by swelling in benzyl alcohol | 64 |
| 3.9 % grafting by solvent extraction of modified polyester fabrics | 65 |
| 3.10 Weight of polyester fabric after extraction with methanol | 66 |


Copyright by Mahidol University

| TABLE | PAGE |
|---|---|
| 3.11 Effect of initiator concentration on %graft yield of MAA onto PET | 68 |
| 3.12 Effect of reaction temperature on graft yield (monomer: fabric ratio = 2:1) | 70 |
| 3.13 Effect of monomer to fabric ratio on graft yield | 73 |
| 3.14 Relation between moisture regain and graft yield obtained at various monomer to fabric ratios | 75 |
| 3.15 Glass transition temperatures of modified polyester fabric with various monomer to fabric ratios | 93 |
| 3.16 Tensile property of modified polyester yarns | 97 |
| 3.17 Thickness values of MAA grafted polyester fabrics | 98 |
| 3.18 Percentage weight loss of polyester fabrics after treatment with NaOH solution | 106 |


Copyright by Mahidol University

## LIST OF FIGURES


| FIGURE | | PAGE |
|---|---|---|
| 1.1 | Flow diagram showing process in polyester manufacture | 3 |
| 1.2 | Fabric formation | 4 |
| 1.3 | Diagram of filling and warp yarns in a fabric | 5 |
| 1.4 | Effect of acrylic acid concentration on graft yield. [$H_2O_2$], 100 mequiv/l; reaction time, 4h; temperature,85°C; material : liquor ratio, 1:100 | 16 |
| 1.5 | Rate of grafting of MAA onto PET at different concentrations of MMA. [MMA] (%): (•) 8; (▲) 10; (Θ) 12; (x) 16; (□) 20. [$H_2O_2$] 30 mequiv/l; temperature 85°C;material:liquor ratio 1:100 | 20 |
| 1.6 | Variation of the percent grafting with changing the ratio of acrylic acid and styrene in the comonomer mixtures. Monomer concentration, 20%; [$H_2O_2$],100 mequiv/l; temperature 85°C;reaction time 4h; material : liquor ratio 1:100. | 21 |
| 1.7 | FT-IR spectra of PET fibers: (top) ungrafted; (bottom) 13.1% AA-grafted | 25 |
| 1.8 | DSC thermograms for PET fibre grafted with PVA: (1) PET control, (2) PET (hydrolysed), (3) PVA graft-3%, (4) PVA graft-9.7% (5) PVA graft-15.6%. | 28 |
| 1.9 | Moisture regain values of AA-grafted PET fibers | 31 |
| 1.10 | Effect of graft yield on mechanical properties of polyester fibers | 32 |
| 2.1 | Winch machine | 36 |


Copyright© by Mahidol University

FIGURE PAGE

2.2 Scheamatic diagram showing procedure for modification of polyester fabric 41
2.3 Scheamatic diagram showing tensile head sample arrangement 46
3.1 DSC thermogram of MAA polymerisation; isothermal condition at 70°C, 80°C and 90°C 55
3.2 DSC thermogram of MAA polymerisation in benzyl alcohol ; isothermal condition at 70°C, 80°C and 90°C 57
3.3 Comparison of DSC thermogram of MAA polymerisation; isothermal condition at 70°C, in the absence (a) and presence (b) of benzyl alcohol 58
3.4 Comparison of DSC thermogram of MAA polymerisation; isothermal condition at 80°C, in the absence (a) and presence (b) of benzyl alcohol 59
3.5 Comparison of DSC thermogram of MAA polymerisation; isothermal condition at 90°C, in the absence (a) and presence (b) of benzyl alcohol 60
3.6 Variation of graft yield with initiator concentration 68
3.7 Variation of graft yield with polymerisation temperature 71
3.8 Variation of graft yield with fabric to MAA ratio 73
3.9 Variation of moisture regain with graft yield in polyester fabric grafted with MAA 76
3.10 FT-IR spectrum of ungrafted polyester 78
3.11 FT-IR spectrum of PMAA 79
3.12 FT-IR spectrum of polyester fabric grafted with MAA ( monomer to fabric ratio 0.5: 1) 79

Copyright by Mahidol University

**FIGURE** **PAGE**

3.13 FT-IR spectrum of polyester fabric grafted with MAA (monomer to fabric ratio 1: 1) 80
3.14 FT-IR spectrum of polyester fabric grafted with MAA (monomer to fabric ratio 1.5 : 1) 80
3.15 FT-IR spectrum of polyester fabric grafted with MAA (monomer to fabric ratio 2:1) 81
3.16 FT-IR spectrum of polyester fabric grafted with MAA (monomer to fabric ratio 2.5: 1) 81
3.17 FT-IR spectrum of polyester fabric grafted with MAA (monomer to fabric ratio 3: 1) 82
3.18 FT-Raman spectrum of PVA 82
3.19 FT-Raman spectrum of PMAA 83
3.20 FT-Raman spectrum of poly (acrylic acid) 83
3.21 FT-Raman spectrum of ungrafted polyester 84
3.22 FT-Raman spectrum of of polyester fabric grafted with MAA at monomer to fabric ratio 3: 1 84
3.23 Log $E'$ and tan $\delta$ versus temperature curve for filling yarn of polyester fabric 86
3.24 Log $E'$ and tan $\delta$ versus temperature curve for warp yarn of polyester fabric 86
3.25 Show the DMTA curves of grafted polyester at monomer to fabric ratio 0.5: 1 (filling yarn) 88
3.26 Show the DMTA curves of grafted polyester at monomer to fabric ratio 0.5: 1 (warp yarn) 88

Copyright by Mahidol University

| FIGURE | PAGE |
|---|---|
| 3.27 Show the DMTA curves of grafted polyester at monomer to fabric ratio 1: 1 (filling yarn) | 89 |
| 3.28 Show the DMTA curves of grafted polyester at monomer to fabric ratio 1:1 (warp yarn) | 89 |
| 3.29 Show the DMTA curves of grafted polyester at monomer to fabric ratio 1.5: 1 (filling yarn) | 90 |
| 3.30 Show the DMTA curves of grafted polyester at monomer to fabric ratio 1.5: 1 (warp yarn) | 90 |
| 3.31 Show the DMTA curves of grafted polyester at monomer to fabric ratio 2: 1 (filling yarn) | 91 |
| 3.32 Show the DMTA curves of grafted polyester at monomer to fabric ratio 2: 1 (warp yarn) | 91 |
| 3.33 Show the DMTA curves of grafted polyester at monomer to fabric ratio 2.5: 1 (filling yarn) | 92 |
| 3.34 Show the DMTA curves of grafted polyester at monomer to fabric ratio 2.5: 1 (warp yarn) | 92 |
| 3.35 Chemical structure of poly(ethylene terephthalate) | 94 |
| 3.36 Gauche and Trans-form for the -O-$CH_2$-$CH_2$-O- group in PET | 96 |
| 3.37 Effect of graft yield on tensile property of polyester yarn | 97 |
| 3.38 Relation between percent graft yield and thickness of polyester fabrics | 99 |
| 3.39 SEM micrographs of an ungrafted polyester a. magnification 80 x b. magnification 500 x | 101 |


Copyright by Mahidol University

**FIGURE** **PAGE**

3.40 SEM micrographs of polyester fabric grafted with MAA at monomer to fabric ratio 1:1 a. magnification 80 x b. magnification 300 x c. magnification 300 x d. magnification 300 x e. magnification 500 x 102

3.41 SEM micrographs of polyester fabric grafted with MAA at monomer to fabric ratio 2.5:1 a. magnification 80 x b. magnification 300 x 105

3.42 SEM micrographs of hydrolysis polyester fabric in 4% NaOH a.magnification 50 x b. magnification 500 x 110

3.43 SEM micrographs of hydrolysis polyester fabric grafted with MAA at monomer to fabric ratio 1:1 and in 4% NaOH a. magnification 80 x b. magnification 500 x 111

3.44 SEM micrographs of hydrolysis polyester fabric grafted with MAA at monomer to fabric ratio 2.5:1 and in 0.1% NaOH a. magnification 80 x b. magnification 500 x 112

Copyright by Mahidol University

# CHAPTER I

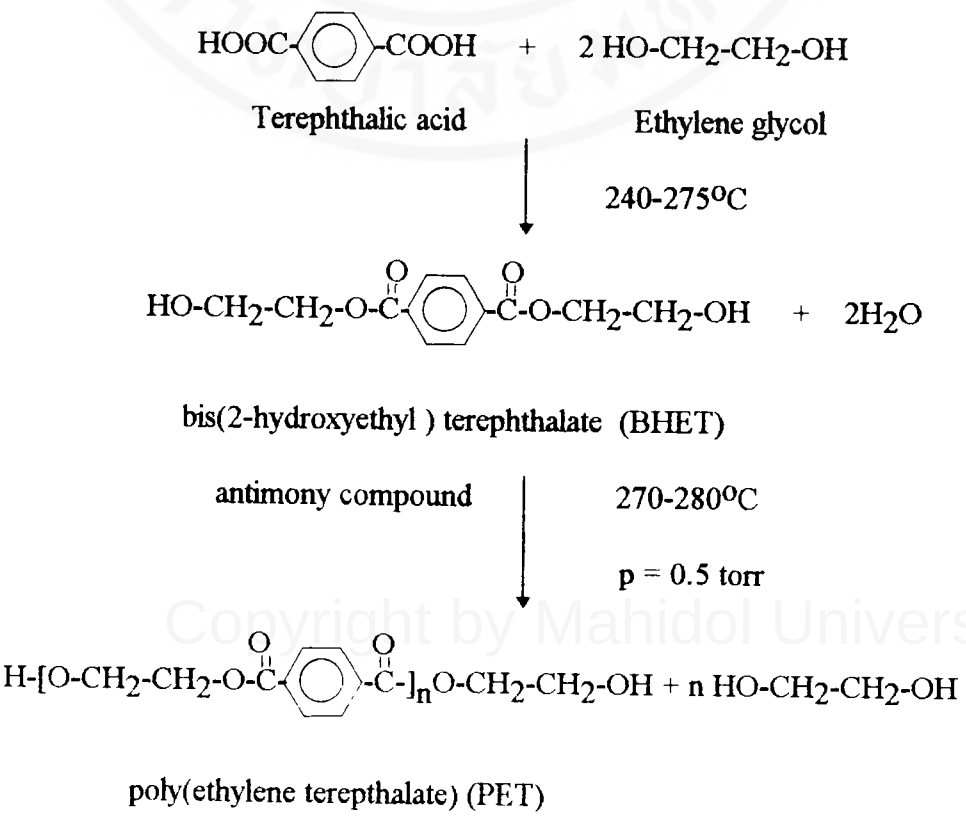
# INTRODUCTION

## 1.1 POLYESTER FIBRES AND FABRICS

### 1.1.1 Formation of Polyester Fibres and Fabrics (1)

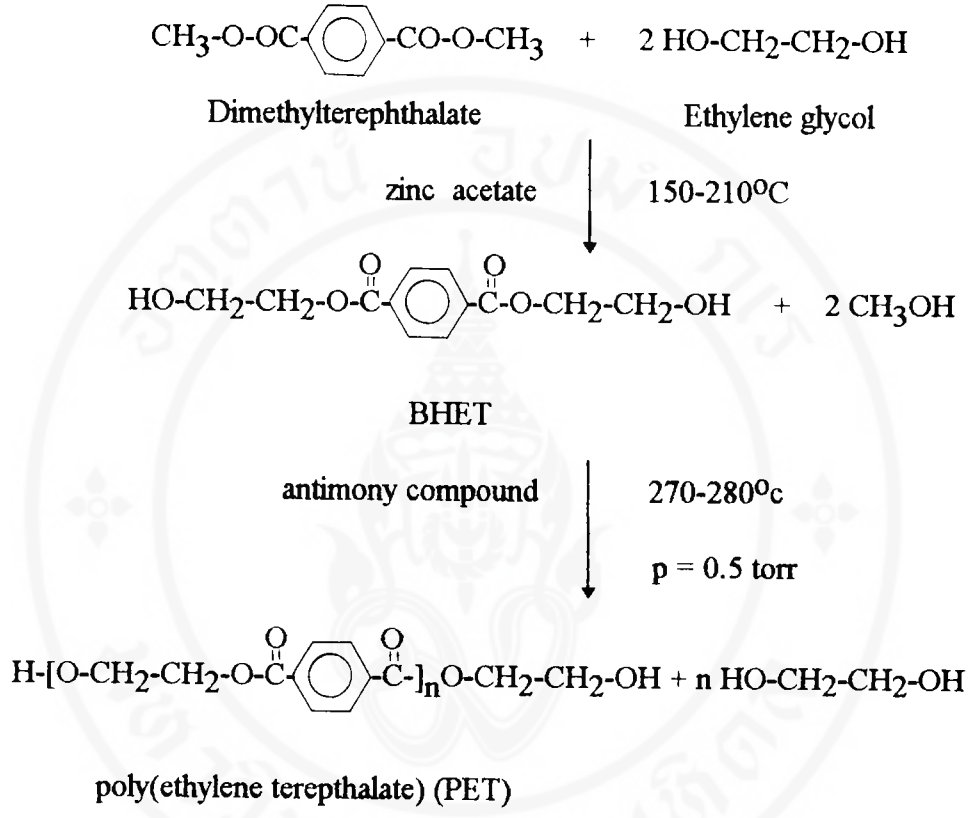
Polyester fibres commonly used in the textile industry are long-chain polymers, derived from the condensation reaction between terephthalic acid or dimethyl terephthalate and ethylene glycol. The schematic reactions of the formation of polyester are shown below.

**Direct Esterification**




Copyright by Mahidol University

**Ester Interchange**




Dimethyl terephthalate is more frequently used than terephthalic acid because it is more easily obtained in pure form. Also, the ester interchange reaction, typically using a dimethylester, is usually a faster reaction than esterification of the diacid.

The processes in polyester manufacture are shown in Figure1.1

Copyright by Mahidol University

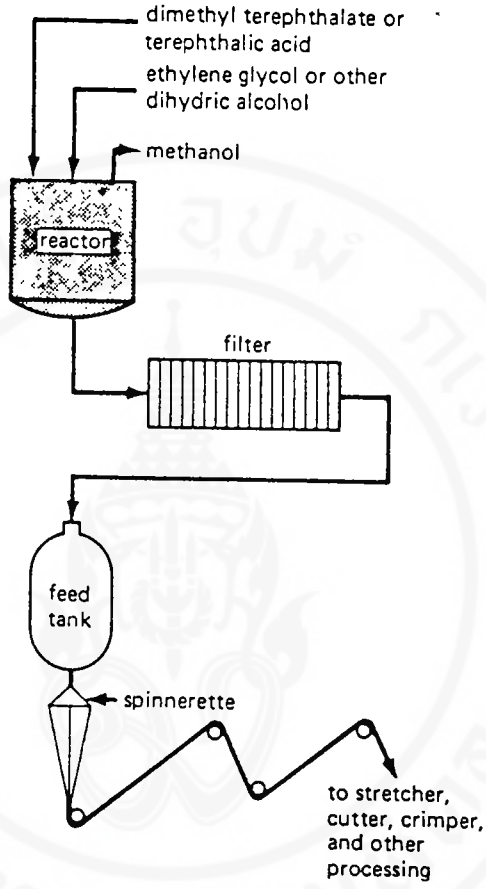



**Figure 1.1** Flow diagram showing processes in polyester manufacture

The starting products are polymerised at high temperature and then filtered to remove any impurities. The molten polymer may be spun directly, or it may be extruded, cooled, and cut into small pellets or chips, which can be stored for later extrusion.

During the extrusion step, the molten polymer (or remelted chips) is metered through a spinnerette. Polyester fibres are melt-spun, normally

Copyright by Mahidol University

through circular spinnerette holes, although a variety of profiled fibres can be produced by specially designed spinnerette orifices. The molten polymer jets solidify almost immediately after extrusion. The filaments are drawn to develop orientation and crystallinity and wound for direct use as continuous multifilament yarn. Alternatively, the continuous filaments can be crimped after drawing and cut into desired lengths for use as staple fibres(2).

Usually the fibres are converted first into yarns. The yarns are then made into fabrics by one of the various methods used for fabric construction (see Figure 1.2)

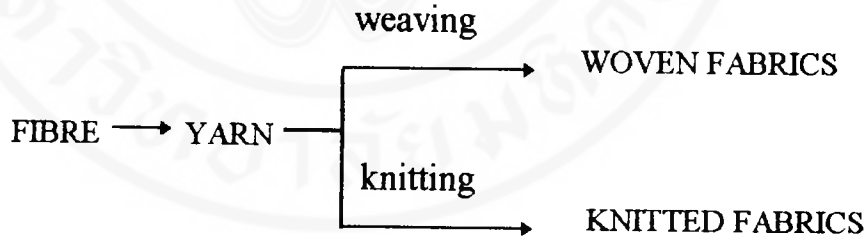



**Figure 1.2** Fabrics formation (3)

Woven fabric consists of sets of yarns interlaced at right angles in an established sequence, or pattern. The yarns parallel to the lengthwise direction of a woven fabric are called warp, those across the fabric, are called filling yarns. Warp yarns usually are stronger than filling yarns.

Copyright by Mahidol University

The two edges of the fabric that run its length are called selvages (3)(see Figure 1.3 ).

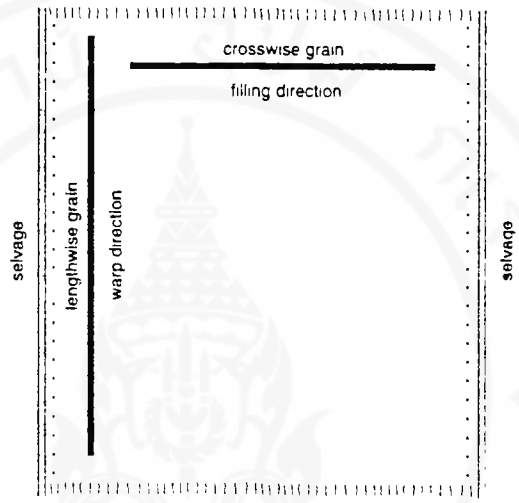



**Figure 1.3** Diagram of filling and warp yarns in a fabric

### 1.1.2 Properties of Polyester Fibres

Fibre properties are governed by the inherent characteristics of the base polymer and such geometric features as fibre length, cross-section shape,area and stiffness. Fabric properties are the results of fibre and yarn characteristics (1). In order to qualify as a suitable substance for used as a textile fibre a polymer must possess certain essential properties or characteristics. Table 1.1 shows fibre properties important in textile uses.

Copyright by Mahidol University

**Table 1.1** Important fibre properties for textile uses (4)

| Chemical properties | Physical properties | Biological properties | Fabric properties |
|---|---|---|---|
| 1. Stability towards<br>Acids<br>Bases<br>Bleaches<br>Solvents<br>Sunlight<br>Aging<br>2. Flammability<br>3. Dyeability | 1. Mechanical properties<br>Elongation<br>Stiffness<br>Flex life<br>Abrasion resistance<br>Work recovery<br>Tensile recovery<br>2. Thermal properties<br>Melting point<br>Softening point<br>Glass transition - temperature<br>Decomposition temperature<br>3. Electrical properties<br>Surface resistivity | 1. Toxicity<br>2. Resistance to<br>Bacteria<br>Molds<br>Insects | 1. Appearance<br>Feel<br>Luster<br>2. Comfort<br>Warmth<br>Moisture - retention<br>Wicking<br>3. Stability<br>Shape<br>Shrinkage<br>Felting<br>Pilling<br>Crease - resistance |

Polyester, one of the most successful man made fibre, constituted 52% of total synthetic production in 1992 and world production was 9765 million tons (compose of filament 4572 million tons and staple 5193 million tons)(5). The properties of polyester fibres may be conveniently divided into two categories: physical and chemical properties

Copyright© by Chiang Mai University

### 1.1.2.1 Physical Properties (2)

Polyester fibres have a number of desirable physical properties, which depend on the method of manufacture and the molecular weight of the polymer.

Polyester fibre may be classified as relatively strong fibre. Fabrics of regular tenacity polyester filament yarns are very strong and durable.In general, polyester fibre is characterised as having a high degree of stretch resistance, which means that polyester fabrics are not likely to stretch out of shape too easily. It recovers well from stretch because of high initial modulus. Typical physical properties of PET fibre are given in Table 1.2.

**Table 1.2** Physical properties of polyester fibre (2)

| Properties | Filament yarn (regular tenacity)* |
|---|---|
| Breaking tenacity** (N/tex) | 0.35-0.5 |
| Breaking elongation(%) | 24-25 |
| Elastic recovery at 5% elongation(%) | 88-93 |
| Initial modulus (N/tex) | 6.6-8.8 |
| Melting temperature (°C) | 258-263 |

Copyright by Mahidol University

* Textile filament yarns for woven and knit fabrics

** Standard measurements are conducted in air at 65% RH and 22°C

### 1.1.2.2 Chemical Properties

Polyester fibres show outstanding resistance to damage by most common chemicals under ordinary conditions of exposure and a wide range of substances have little or no effect on their strength(6). Fabrics of polyester have good resistance to deterioration by household bleaches(7). Phenol and its homologues act as solvent or swelling media for polyester fibres (8). It has no significant loss of strength from continued contact with either acid or alkaline perspiration(7).

### 1.1.3 Inadequacy of Polyester Fibres

Polyester fibres are highly crystalline and hydrophobic in nature. For these reasons, polyester fibres are not easily penetrated by dyes of large molecular dimensions and cannot combine with anionic or cationic dyes (9). They have a very low moisture regain (moisture uptake) of 0.4 % at standard condition (at a relative humidity of 65+2% and at temperature 21+1 °C (70+2°F). Even at 95 to 100 percent relative humidity, the moisture content is only 0.6 to 0.8 %(1). The moisture regain of the fibre plays an important role in static dissipation, as is seen from the inverse relationship of moisture regain(%) with the log specific area resistivity (log SAR) (10) (see Table 1.3).

Copyright by Mahidol University

**Table 1.3** Moisture regain and fibre resistivity(10)

| Fibre | Moisture regain(%) | log SAR |
|---|---|---|
| Viscose rayon | 12.0 | 7 |
| Cotton | 8.0 | 7 |
| Cellulose acetate | 6.5 | 12 |
| Polyamide | 4.0 | 12 |
| Polyacrylic | 1.5 | 14 |
| Polyester | 0.4 | 14 |
| Poly (vinyl acetate) | 0 | 15 |

The higher the moisture regain, the lower is the log SAR and the lower is the static charge accumulated. Because of low moisture regain, polyester fabric is uncomfortable to wear in hot climate since the fabric is unable to absorb perspiration from the body of the wearer and the fibre has a tendency to accumulate static electricity, which creates a number of problem. For instance, yarns may balloon during winding processes as a result of the individual fibres repelling each other.

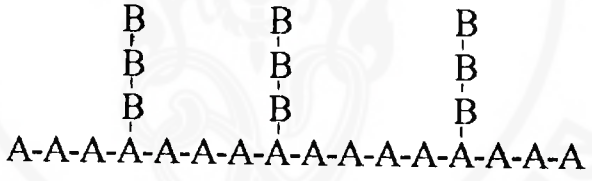
## 1.2 MODIFICATION OF POLYESTER FIBRES BY GRAFTING

Copyright by Mahidol University

The grafting technique has been successfully used for modifying the physical and chemical properties of various polymers. The main purposes of grafting various vinyl monomers onto polyester fabrics are to improve

their inferior properties (low moisture regain and poor antistatic properties) and to furnish them with new properties (hydrophilicity to polyester, improvement in dyeability, and improved tensile strength).

Grafting reaction takes place when a preformed polymer provides initiation sites for the growth of branches formed from a new monomer. Thus, a graft copolymer can be represented by the following structure(11).



-A- = Host polymer

-B- = Grafted chains

### 1.2.1 Initiator Used in Grafting Reactions

Vinyl graft polymerisation onto polyester can be initiated by high-energy radiation using γ-rays from $Co^{60}$ or by chemical means using different initiators such as benzoyl peroxide, hydrogen peroxide, persulfate, or azobisisobutyronitrile (9). With high-energy radiation, it is generally known that the bulk properties of the host polymer are affected as a result of

Copyright by Mahidol University

degradation. But chemical methods are more advantageous as regards the degradation of the main polymer.

An organic peroxide is thermally unstable. At elevated temperature, the oxygen-oxygen bond of the peroxide is homolytically cleaved to form radicals. The radicals formed may abstract hydrogen atoms from the polymer, and macroradicals are thereby formed. These macroradicals may act as grafting sites for vinyl monomers(12).

One advantage with peroxide-initiated grafting is that no special equipment is needed. Only heating is necessary to facilitate the grafting reaction (12).

### 1.2.2 Methods of Grafting

Three components are necessary for grafting to occur : polymer(PET), vinyl monomer and initiator. The function of the initiator is to react with original polymer to form free radicals on the polymer backbone, which initiate polymerisation of the monomer. When using low monomer concentration, small amount of homopolymer is formed (12). Therefore, vinyl monomer ought to be diluted in the grafting reaction system. When water is used as a reaction medium (good heat transfer) and a water-soluble monomer and a water-insoluble initiator are used, grafting will be limited to

Copyright by Mahidol University

the outermost surface of the PET due to the hydrophobic nature of the PET. Since vinyl monomers suitable for modification of hydrophilicity of PET are insoluble PET, the reactions have to be conducted in heterogeneous system.

In a heterogeneous polymer-monomer reaction system, diffusion controls chain growth and chain termination in the internal structure of the polymer. One way of facilitating diffusion is to open up the physical structure of the polymer by swelling to allow the monomer to enter in sufficient quantities(13).

The solubility parameter values of PET is 10.5 (14). Selected organic solvents, whose solubility parameters are close to those of PET can be used as swelling agents to promote diffusion and incorporation of monomer (see Table 1.4).

**Table 1.4** Solubility parameters of selected organic solvents

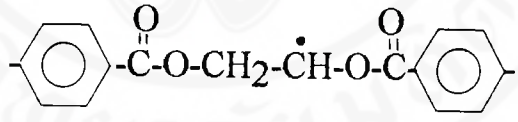
| Organic solvents | Solubility parameter(δ) |
|---|---|
| Benzyl alcohol | 12.10 |
| Dimethyl formamide | 12.14 |
| Dimethyl sulfoxide | 12.93 |
| 1,2 -dichloroethane | 9.00 |
| Pyridine | 10.61 |
| Tetrachloroethane | 9.85 |

Copyright by Mahidol University

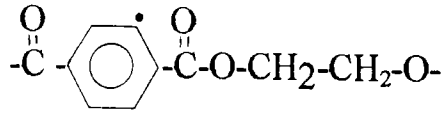
Kildal et.al.,(11) suggested that if the interaction between the solvent and the polymer is small, grafting would preferentially occur on the surface. If the interaction between the solvent and the polymer is strong, grafting will preferentially occur below the surface.

### 1.2.3 Structures of Grafted Polyester

Electron spin resonance (ESR) spectroscopic study shows that the radical sites for grafting of PET are as shown (15):

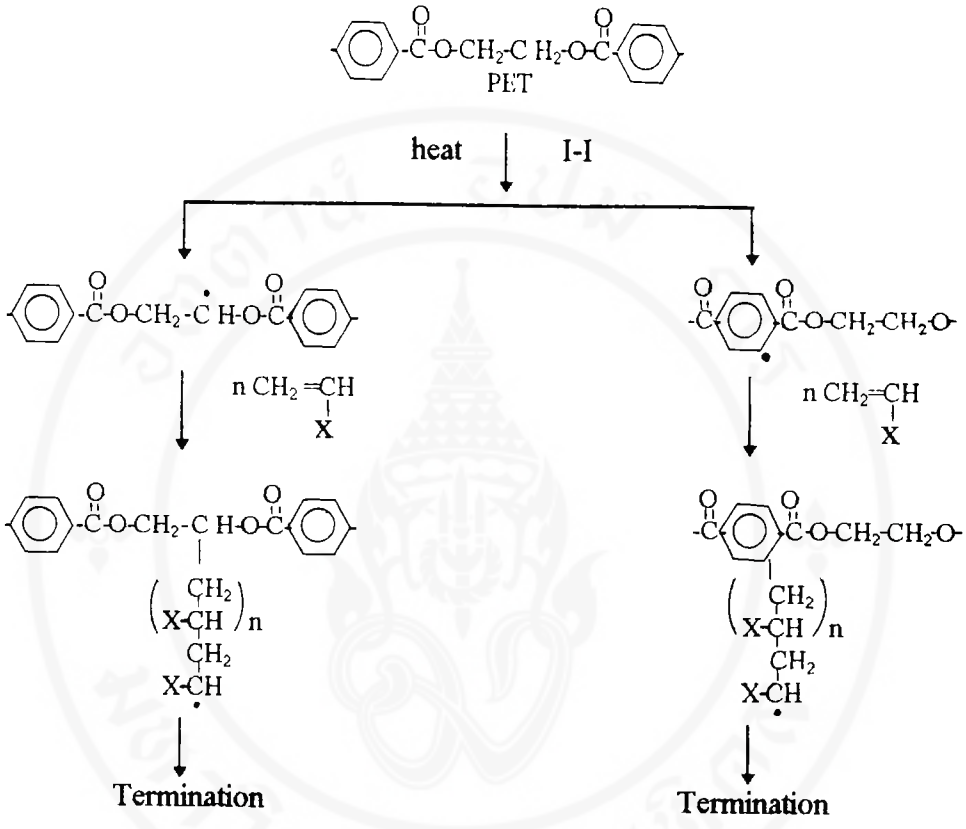


or



Grafting then occurs according to the following mechanisms proposed by Adwait (16) for grafting of vinyl monomer.

Copyright by Mahidol University




### 1.2.4 Problems with Grafting of PET (14, 17)

1. The chemical nature of PET does not allow formation on its macrochain appreciable quantity of radicals that can initiate grafting reaction. This is because -$CH_2$-$CH_2$- groups are situated between two carboxyl groups (electron-releasing groups) which makes the C-H bond stable.

Copyright by Mahidol University

2. The high crystallinity of PET and highly ordered macromolecules in amorphous regions hinder monomer diffusion inside the materials and limit grafting zones to subsurface regions.

3. Homopolymerisation of monomer to be grafted tends to compete with the grafting reaction, thus lessen the probability of grafting occurring.

## 1.3 PREVIOUS STUDIES ON GRAFT MODIFICATIONS OF POLYESTER FIBRES

Previous studies deal with grafting of PET by using different initiators and monomers, despite the fact that PET is one of the most difficult polymer to be grafted (14).

### 1.3.1 Studies on Grafting Method

Two methods have been studies for grafting of PET,grafting by using swelling agent and grafting without using swelling agent.

#### A.Grafting by Using Swelling Agent

The composition of graft copolymerisation medium plays an important role in the grafting of vinyl monomers onto PET fibres(18). Hebeish et.al.,(9) reported that grafting acrylic acid (AA) to PET fibres using $H_2O_2$ as the initiator in aqueous medium resulted in very little or practically no grafting. This necessitated the use of organic swelling agent. Benzyl alcohol was used as a medium for grafting AA to PET fibres. PET

Copyright by Mahidol University

fibres were immersed in benzyl alcohol containing AA (10%) and $H_2O_2$ (100 mequiv/l) using a material-to-liquor ratio of 1:100. The reaction was carried out at 85°C for 4h. The degree of grafting obtained was 4.5% (9).

The effect of AA concentration on percentage grafting is shown in Figure1.4

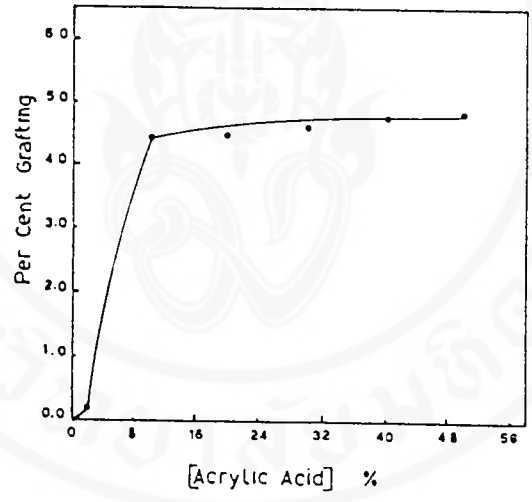



**Figure 1.4** Effect of acrylic acid concentration on grafting of PET (9).

As is evident, the percentage grafting increases by increasing the AA concentration up to 10%. Thereafter, no significant improvement in the percentage grafting was observed upon further increases of the monomer concentration.

Copyright by Mahidol University

Lokhande and Teli (19) studied graft copolymerisation of AA onto polyester fibres using BPO as initiator.The polyester was first swollen at 95°C for 3 h in a solvent/nonsolvent consisting of 1,2- dichloroethane/water (20/80,v/v). Dichloroethane was then removed from the fibre by treatment with boiling water, This fibre was then used for grafting.

In this experiment, BPO(0.125g) was dissolved in benzene(10ml) and distilled water (90ml) was added to it. Then the addition of AA was made. The grafting was carried out at the temperature of 81°C. The graft add-on increased from 0% to 12.24% when the concentration of the monomer was varied from 0% to 5%(w/w).

Hebeish et.al.(20) reported that 1,1,2,2-tetrachloroethane is a good swelling agent for PET fibre. After swelling PET fibres in 1,1,2,2-tetrachloroethane, the sample was introduced into a polymerisation solution containing MMA (10%) and $H_2O_2$ (30 mequiv /l). A material-to-liquor ratio of 1:100 was used. The polymerisation was allowed to proceed for 240 minutes at 85°C. The results obtained are shown in Table 1.5.

Copyright by Mahidol University

**Table 1.5** Effect of percentage pickup of swelling agent on graft yield

| Swelling agent uptake (%) | Graft yield (%) |
|---|---|
| 419 | 1.0 |
| 236 | 22.0 |
| 220 | 48.6 |
| 196 | 5.1 |
| 174 | 3.8 |
| 147 | 3.2 |
| 57 | 0 |

It was apparent that an uptake of swelling agent by the fibres of 220% constitutes the optimum amount of tetrachloroethane to enhance the fibre toward grafting. A graft yield of 48.6 % could be achieved at this uptake. The explanation given was that the presence of excess tetrachloroethane within the fibres impedes diffusion of monomer and initiator by forming a barrier thereby decreasing grafting. At low uptake, the amount of tetrachloroethane is probably not high enough to keep the PET structure swollen (20).

Copyright by Mahidol University

**B. Grafting by Using No Swelling Agent**

By using no swelling agent, the initiator and the monomer will be localised only in the outermost surface layer of the polymer so that grafting occurs only in those regions.

The grafting of 2-dimethylaminoethyl methacrylate onto polyester fabric using BPO as initiator was carried out in water containing a few drop of benzene. The grafting of polyester fabrics was enhanced by increasing the BPO concentration up to 0.36% where a grafting of 11.2% was obtained at a constant monomer concentration of 1% (21).

Hebeish et.al., (20) studied graft polymerisation of methymethacrylate (MMA) on PET fibre using $H_2O_2$ as the initiator. PET fibre (0.5g) was introduced into a 50 ml aqueous solution containing the monomer. The initiator was then added at the required temperature. Figure 1.5 shows the effect of MMA concentration on the rate of grafting. Evidently, the rate of grafting increases as the MMA concentration was increased.

Copyright by Mahidol University

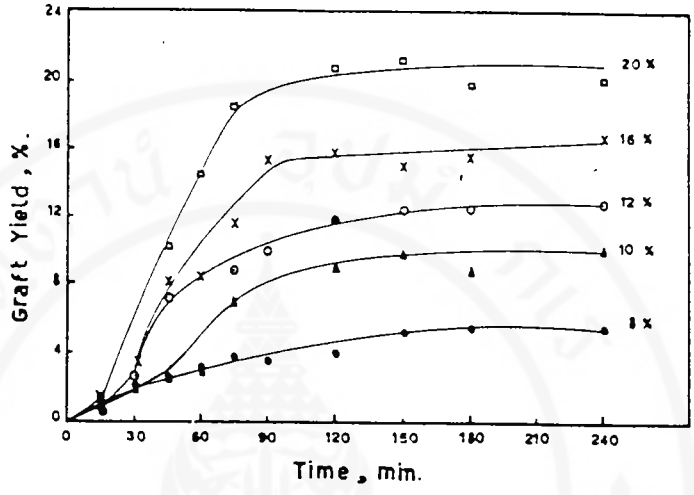



**Figure 1.5** Rate of grafting of MMA onto PET at different concentrations of MMA . [MMA] (%) : (•) 8; (▲)10; (Θ) 12; (x)16; (□)20. [$H_2O_2$] 30 mequiv/l; temperature 85°C; material: liquor ratio 1: 100

Graft polymerisation of acrylic/styrene mixture on PET fibres using $H_2O_2$ as initiator was investigated under different acrylic acid/styrene ratio. PET fibre (0.5g) was introduced into 50 ml aqueous solution containing monomer at temperature of 85°C. The initiator was then added. After 4h the contents were filtered, washed with water, and washed several times with benzene and with a mixture of benzene and methyl alcohol (50:50) and boiled with water three times. The sample was then Soxhlet extracted with (1:1) mixture of benzene: methyl alcohol and dried. Variation of the

Copyright by Mahidol University

percentage grafting with changing the ratio of each monomer in the comonomer mixture is shown in Figure 1.6.

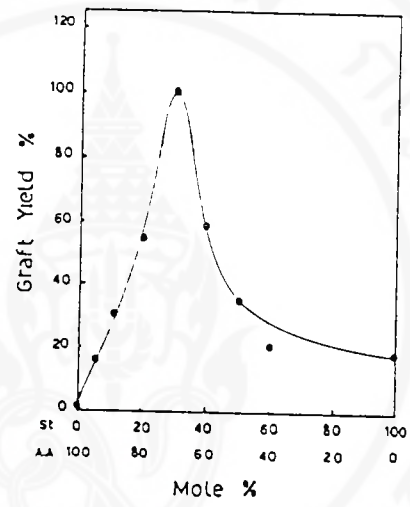



**Figure 1.6** Variation of the percent grafting with changing the ratio of acrylic and styrene in the comonomer mixtures. Monomer concentration, 20%; [$H_2O_2$], 100 mequiv/l; temperature 85°C; reaction time 4h; material:liquor ratio = 1:100

Results of Figure 1.6 show a synergistic effect when mixtures of styrene and acrylic acid were used for grafting of PET fibres (22).

Copyright by Mahidol University

Sacak et.al., (14) studied grafting of MMA onto PET fibers using AIBN as initiator. The polymerisation vessel containing the PET fibre (0.3 g), monomer, and 45 ml. deionised water was placed in a water bath

adjusted to the polymerisation temperature and kept there for 5 minutes and then 5 ml acetone containing AIBN was added. The fibres taken from the polymerisation system following the grafting procedure were roughly washed with acetone. They were then Soxhlet extracted with benzene for 8h and with acetone for 6h. The maximum graft yield was 14.5% for a MMA concentration of 0.15 mol/l and AIBN $0.9x10^{-2}$ mol/l at 90°C for 90 minutes.

The grafting of AA onto PET fibres subjected to no swelling treatment using BPO as initiator was investigated. The mixture containing the fibre (0.3 g), AA (0.875 mol/l), BPO ($4x10^{-3}$ mol/l) in 5 ml acetone was made up to 50 ml with deionised water. After the polymerisation procedure,PET fibre was roughly washed with water. Then, it was washed in boiling water for 4h by changing the washing water at least three times. It was finally Soxhlet extracted with methanol and dried. The graft yield found to increase from 2.5% at 65°C to 13.1% at 90°C (23).

### 1.3.2 Characterisation of Grafted PET

Copyright by Mahidol University

The following methods have been used for characterisation of grafted PET fibres; gravimetric measurement, spectroscopic technique, thermal characterisation, and chemical analysis.

**A. Gravimetric Measurement**

Several studies reported the determination of % grafting of modified PET fibers by weighing method (9, 13, 19, 22, 24). In this method the homopolymer must first be removed by solvent extraction. The increase in weight of the sample divided by its original dry weight and multiplied by 100 will be referred to as percentage grafting

$$\%\text{grafting} = \frac{W - W_O}{W_O} \times 100$$

$W_O$ = dry weight of original sample

$W$ = dry weight of grafted sample

Copyright by Mahidol University

Table 1.6 shows percentage of graft yield (by weighing method) of PET fiber grafted with MAA by using AIBN as initiator.

**Table 1.6** Percentage of grafting polyester fibre with MAA (13)

| Time (min) | Graft yield (%) |
|---|---|
| 5 | 2.2 |
| 10 | 5.7 |
| 15 | 6.7 |
| 20 | 8.5 |
| 30 | 12.0 |
| 45 | 14.7 |
| 60 | 14.4 |
| 75 | 15.8 |
| 90 | 14.3 |

Conditions : [MAA] = 0.15 mol/l

[AIBN] = $0.9 \times 10^{-2}$ mol/l

reaction temperature 90°C

**B. Spectroscopic Technique**

Spectroscopic techniques are of great importance in polymer characterisation. The technique most commonly used to observe vibrational spectra is infrared spectroscopy. With the advent of Fourier-transform (FT)

Copyright by Mahidol University

spectrometer, the spectrum can be quickly acquired and sophisticated data manipulation is possible (25).

Oflaz (23) studied grafting of AA onto PET fibres by using BPO as initiator. Figure 1.7 shows the FT-IR spectra of ungrafted and 13.1% AA-grafted PET fibres. When these spectra are examined, a strong band is seen due to the stretching of OH groups from AA at 3440 $cm^{-1}$.

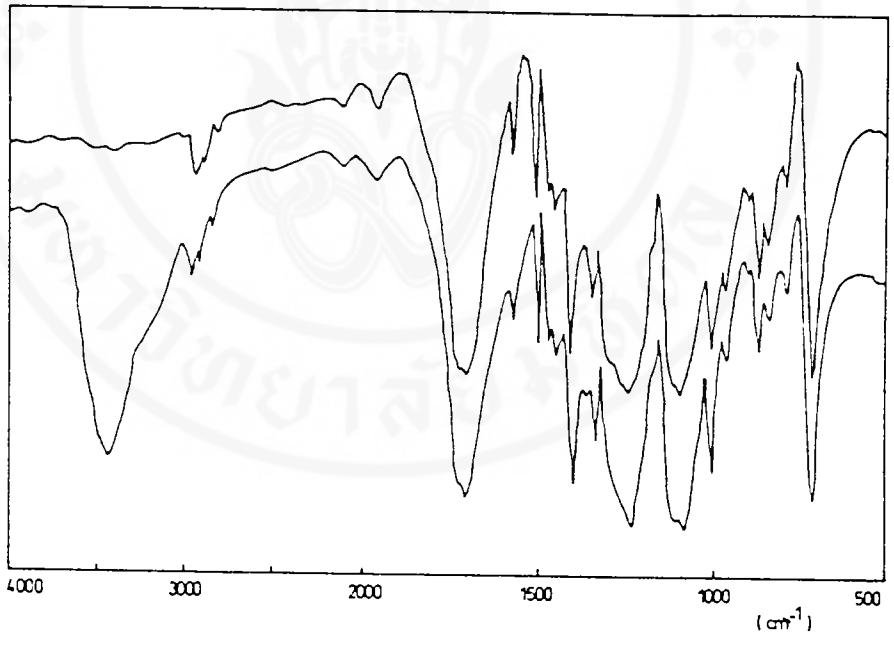



**Figure 1.7** FT-IR spectra of PET fibres: (top) ungrafted; (bottom) 13.1% AA-grafted

Copyright by Mahidol University

However,IR technique is not sufficient to evaluate the points of the side chains binding to the main polymer backbone(26).

**C. Thermal Analytical Method (27)**

Polyester fibres were modified by grafting with poly(vinyl alcohol) (PVA) using the irradiation process. Initially, polyester fibres were grafted with poly(vinyl acetate) using γ-radiation from $Co^{60}$ and then hydrolysed to get polyester-graft-PVA by using 10% HCl at 100°C for determined period.

Thermal characterisation of polyester fibre grafted with PVA was investigated by differential scanning colorimemetry (DSC). The percentage of crystallinity of polyester fibres grafted with PVA was calculated by

$$\beta = \frac{\Delta H}{\Delta H_f} \times 100$$

$\beta$ = percentage of crystallinity

$\Delta H$ = heat of fusion of the fibre

$\Delta H_f$ = heat of fusion of completely crystalline PET

$\Delta H_f$ was taken as 28.1 cal/g. Melting temperature (Tm), heat of fusion, and percentage of crystallinity of polyester fibres grafted with PVA at different percentage levels are shown in Table 1.7 and DSC thermograms are shown in Figure 1.8

Copyright by Mahidol University

**Table 1.7** Effect of PVA graft on melting temperature, heat of fusion, and percentage of crystallinity of the grafted polyester fibre

| % PVA grafted | Tm (°C) | Heat of fusion (cal/g) | Crystallinity ( %) |
|---|---|---|---|
| PET (control) | 252 | 11.62 | 41.3 |
| PET (acid treated) | 254 | 13.20 | 47.0 |
| 3.0 | 257 | 12.46 | 44.5 |
| 5.8 | 257 | 13.40 | 47.7 |
| 7.5 | 255 | 12.44 | 44.3 |
| 9.7 | 255 | 12.35 | 44.0 |
| 13.0 | 254 | 12.40 | 44.0 |
| 15.6 | 254 | 12.89 | 45.9 |

Copyright by Mahidol University

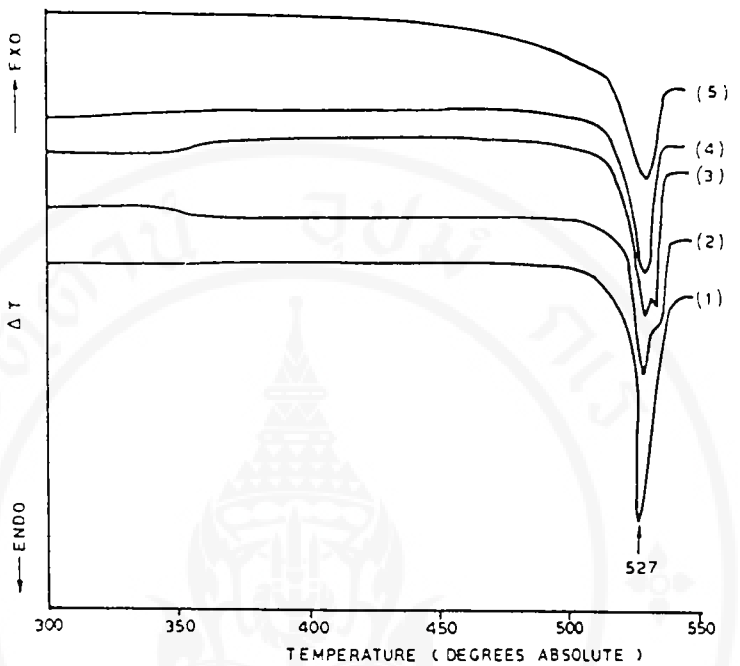



**Figure 1.8** DSC thermograms for PET grafted with PVA: (1) PET (control), (2) PET (hydrolysed), (3) PVA graft-3% (4) PVA graft-9.7% (5) PVA graft-15.6%

In this case, it is evident that grafted PVA did not affect the heat of fusion, melting temperature and percentage of crystallinity of the polyester fibres. It could be concluded that grafting take place predominately in amorphous region without influencing the crystalline nature of the fibres.

Copyright by Mahidol University

**D. Chemical Analysis**

Chemical analysis method has been used to measure the amount of grafted polyacryamide and poly(acrylic acid) on PET fibres. The acrylamide

content in the copolymer was calculated from nitrogen percentage in the fibres which was estimated using semimicro Kjehldal's method (19, 28).

Lokhande and Teli (19) grafted PET fibre with acryamide (5% w/w) by using BPO (0.125g) as initiator and the reaction temperature of 81°C. The Kjehldal's method for N-estimation was employ to determine acrylamide. The total graft add on was 13.5%.

The determination of the amount of poly (acrylic acid) grafted to PET was monitored by analysis of the carboxyl content. The sample was dissolved in 100 ml phenol/tetrachloroethane mixture (50:50) followed by potentiometric titration against 0.05 N NaOH till pH = 7. A blank experiment was carried out in which pure PET dissolved in 100 ml of the phenol/tetrachloroethane mixture was similarly titrated against 0.05 N NaOH(22). The carboxyl content was calculated from the following formula,

$$\text{Carboxyl content} = \frac{(V-V') \times N \times 0.045 \times 100}{W}$$

V = amount of NaOH in presence of grafted fibre (ml)

V' = amount of NaOH in presence of ungrafted fibre (ml)

N = Normality of NaOH

W = weight of the fibre used (g)

Copyright by Mahidol University

Hebeish et.al.(22) studied graft polymerisation of acrylic acid/ styrene mixture (95:5) on PET fibres using $H_2O_2$ (100 mequiv/l) as initiator.The reaction was carried out in water medium using the monomer concentration of 20% by weight of water, the reaction temperature of 80°C and reaction time of 4h. It was found that the content of AA in poly (acrylic acid )/ polystyrene grafted to PET fibres composed of AA 24.3% weight and styrene 75.7% weight.

### 1.3.3 PROPERTIES OF GRAFTED POLYESTERS

#### A. Moisture Regain

Moisture regain indicates the hydrophilicity of the bulk of the substrate. The moisture content of the substrate is dependent mainly upon the monomer type (29). Grafting of acidic group to polyester increases the moisture regain as well as the dye uptake(30). Sacak and Oflaz (25) grafted AA onto PET fibre using BPO as initiator. The relation between moisture regain and percentage graft is represented in Figure 1.9

Copyright by Mahidol University

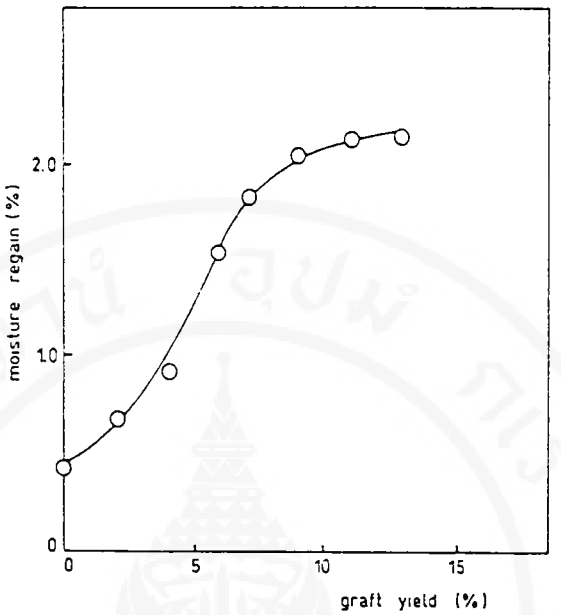



**Figure 1. 9** Moisture regain values of AA-grafted PET fibres

The increase in moisture regain value as a result of AA grafting,shows a rapid increase up to graft value of 9.1%. The rate of increase slows down at higher grafting values.

### B. Mechanical Properties

The effect of grafting yield on tensile strength of polyester fibres was evaluated and is represented in Figure 1.10 (24).

Copyright by Mahidol University

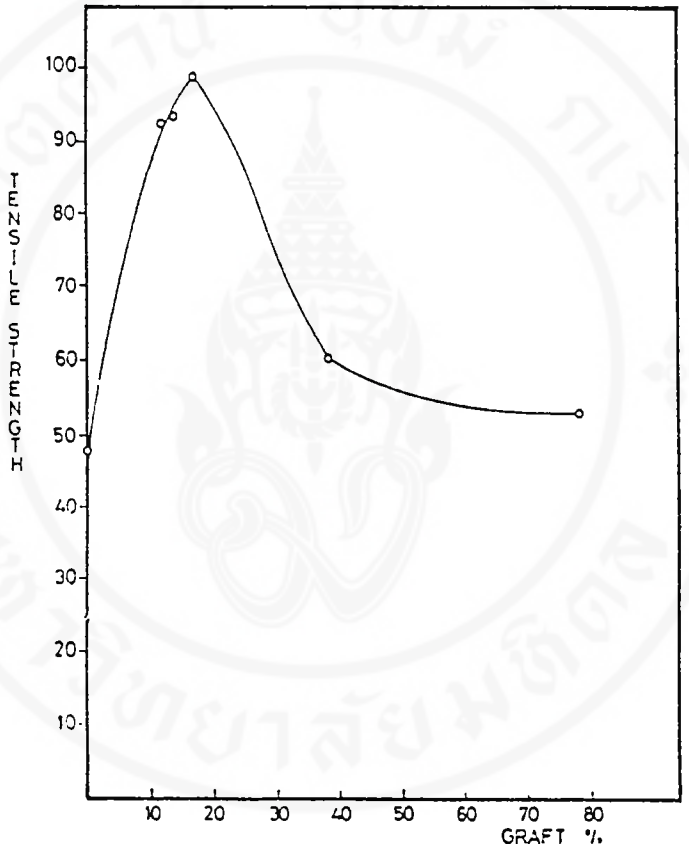



**Figure 1.10** Effect of graft yield on mechanical properties of polyester fibres

It is shown that tensile strength value increases with increasing grafting yield up to 17% grafting. Beyond 17% grafting, there is decrease in tensile strength(24).

Copyright by Mahidol University

MAHIDOL UNIVERSITY



## 1.4 SCOPE OF THE PRESENT THESIS

The present thesis is concerned with the study to improve the hydrophilicity of polyester fabric by grafting with methacrylic acid (MAA).

The followings are the scope of work,

1. Determination of suitable grafting method

1.1 One-step swelling of polyester fabric in 2% aqueous solution of benzyl alcohol containing monomer and initiator.

1.2 Two-step swelling of polyester fabric first in benzyl alcohol and then in solution containing monomer and initiator.

2. Conditions affecting the grafting reactions, in order to establish the optimum operating conditions:

-Effect of initiator concentration

-Effect of monomer concentration

-Effect of reaction temperature

-Effect of reaction time

3. Characterisation of grafted polyester fabrics

Grafted polyester fabrics were characterised by using gravimetric method, spectroscopic method (FT-IR and FT-Raman Spectroscopy), scanning electron microscope (SEM)and thermal analysis (DSC,DMTA).

Copyright by Mahidol University

36556

Moisture regain of the modified polyester fabrics, their tensile properties and changes in dimensions of the yarns were also measured.

4. Treatment of modified polyester with NaOH

The modified polyester fabrics were treated with NaOH in order to observe any changes in feel characteristics of the modified fabrics.

Copyright by Mahidol University

# CHAPTER II

# EXPERIMENTAL

## 2.1 PRETREATMENT OF POLYESTER FABRICS

### Specification of Polyester Fabric

1. Number of yarns / inch (warp yarn x filling yarn); 146 x 52

2. Size of yarns ;

$$\frac{\text{warp yarn x filling yarn}}{\text{number of warp yarn x number of filling yarn}}$$

$$\frac{\text{3.75d / 40 filament x 3.75d / 40 filament}}{\text{146 x 52}}$$

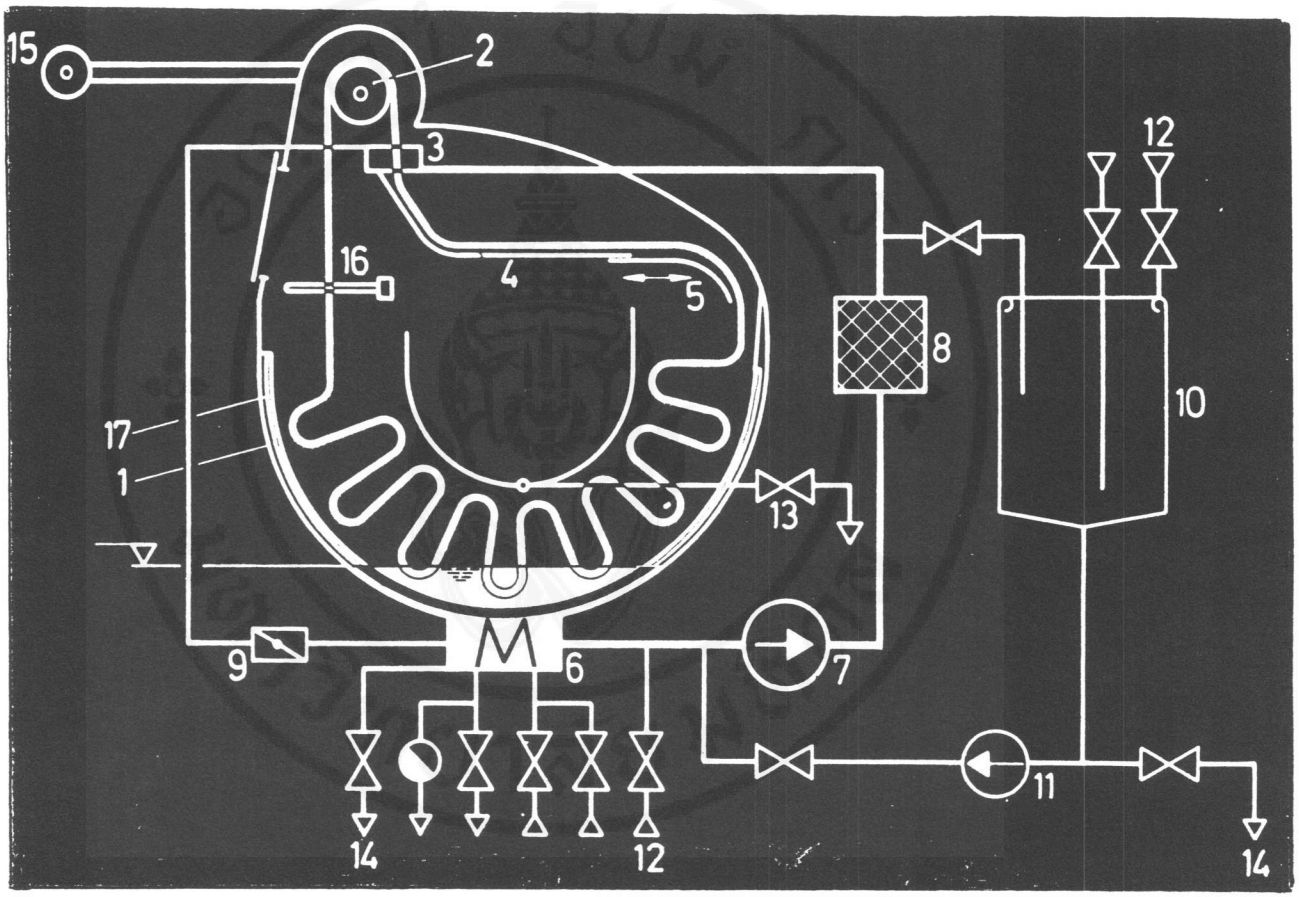
3. Weight of fabric in grams / squar meter ; 161.7 g / $m^2$

In the production of woven fabrics, warp yarns are sized with a protective coating (sizing agent, such as starch, poly(vinyl alcohol), poly (acrylic acid) ) to improve weaving efficiency. Therefore,before the polyester fabrics are modified, the sizing agent has to be removed in order to avoid interference with the modification reaction. This is the pretreatment step of polyester fabrics.

Copyright by Mahidol University

## A. Apparatus :

- Winch machine




1.fabric store room 2. winch 3.immersion 4. transport section 5. plating-down device 6. heating and cooling unit 7.bath pump 8.filter 9.bypass 10. preparation tank 11. add pump 12.water feed 13.overflow rinse 14.drain 15 . take-off roller 16. distribution rake 17. special slide bottom

**Figure 2.1** Winch machine

Copyright by Mahidol University

**B. Procedure :**

The polyester fabrics were washed in water containing aqueous nonionic detergent (Lavoral WS ; Ethoxylated adduct, Stockhausen product). The conditions are shown below,

| | |
|---|---|
| concentration of detergent | 0.5 g/l |
| time | 30 minutes |
| temperature | 70 $^{o}$C |
| material-to-liquor ratio (M:L) | 1: 28 |

They were then rinsed with hot and cold water (three times), and dried at room temperature.

**C. Testing :**

The polyester fabric was spotted with iodine solution and observed the colour change. If poly (vinyl alcohol) was present, pale blue/green colour would be observed.

The iodine solution is prepared from the following agents,

| | |
|---|---|
| $I_2$ | 0.25 g |
| KI | 100 ml |
| HCl (conc.) | 0.5 ml |
| borax | 0.5 g |

Copyright by Mahidol University

## 2.2 REAGENTS

All the following reagents were used as purchased

**A. Initiator**

- Benzoyl peroxide (BPO) (Fluka product, purum > 97%)

**B. Monomers**

- Methacrylic acid (MAA) ; bp. 163°C( Sigma product)

**C. Swelling Agents**

- Benzoic acid (BDH product, Laboratory grade)
- Benzyl alcohol (Fluka product , purum > 98%)
- m- Cresol (Merck product , Laboratory grade)
- Phenol (Merck product , Analar)

## 2.3 MEASUREMENTS OF SWELLING OF MONOMER AND SWELLING AGENTS IN POLYESTER FABRICS

The swelling measurements were made by immersing the fabric in either the monomer or swelling agent for various time between 30 and 180 minutes. The fabric was taken out from the solution and quickly

Copyright by Chulalongkorn University

calculated as the percentage increase in weight of the fabric as a function of time of immersion.

$$\text{Percent swelling} = \frac{W-Wo}{Wo} \times 100$$

W = weight after swelling

Wo = weight before swelling

## 2.4 STUDY OF POLYMERISATION REACTION OF METHACRYLIC ACID BY DIFFERENTIAL SCANNING CALORIMETRY

### A. Apparatus :

- Differential scanning calorimeter (Perkin Elmer DSC 7)

### B. Condition :

Polymerisation of MAA was studied under isothermal condition at 70°C, 80°C, and 90°C under nitrogen atmosphere.

The experimental conditions are summarised in Table 2.1

Copyright by Mahidol University

**Table 2.1** Experimental conditions used in the study of polymerisation reaction of MAA by using DSC

| Reaction mixture | Conditions |
|---|---|
| MAA + BPO* | isothermal at 70°C, 80°C and 90°C |
| MAA+benzyl alcohol**+BPO* | isothermal at 70°C, 80°C and 90°C |

* BPO concentration ; 2% by weight of MAA

** MAA : benzyl alcohol ; 1: 0.5 (by weight)

## 2.5 MODIFICATIONS OF POLYESTER FABRICS

### 2.5.1 Method of Modification of Polyester

The polyester fabric was first swollen in benzyl alcohol in a 250 ml. flask at room temperature for 40 minutes. It was then transferred to a 250 ml. flask containing the required amount of monomer (MAA) and initiator (BPO) and left swelling for 5 minutes. The modification reaction was effected in 250ml. flask using water as the heating medium (material : water = 1: 50). The schematic diagram showing the procedure for modification of polyester fabric is shown in Figure 2.2.

Copyright by Mahidol University

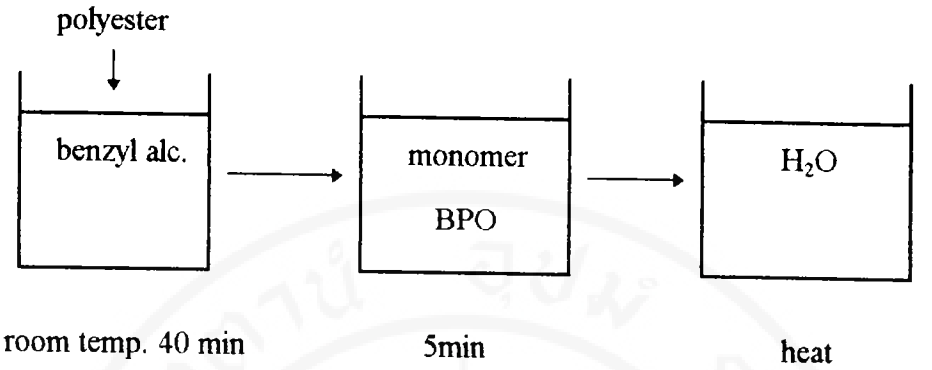



**Figure 2.2** Schematic diagram showing procedure for modification of polyester fabric

The experimental conditions were varied as shown below.

**A. Study of Effect of Initiator Concentration**

**Conditions :**

| | |
|---|---|
| - monomer : fabric | 2 : 1 (by weight) |
| - initiator concentration | 1%, 2% and 3% by weight of monomer |
| - polymerisation temperature | 90°C |
| - reaction time | 30-180 minutes |

Copyright by Mahidol University

**B. Study of Effect of Grafting Temperature**

**Conditions :**

| | |
|---|---|
| - monomer : fabric | 2 : 1 (by weight) |
| - initiator concentration | 2% by weight of monomer |
| - polymerisation temperature | 70°C, 80°C, and 90°C |
| - reaction time | 30-180 minutes |

**C. Study of Effect of Monomer Concentration**

**Conditions :**

| | |
|---|---|
| - monomer : fabric | 0.5 : 1 ( by weight) |
| | 1 : 1 |
| | 1.5 : 1 |
| | 2 : 1 |
| | 2.5 : 1 |
| - initiator concentration | 2% by weight of monomer |
| - polymerisation temperature | 90°C |
| - reaction time | 10-180 minutes |

Copyright by Mahidol University

## 2.6 CHARACTERISATION OF MODIFIED POLYESTER

### 2.6.1 Determination of Percentage Grafting

The percentage grafting of modified polyester was determined by weighing method. The modified polyesters were weighed after extraction (using Soxhlet apparatus) with water or methanol to constant weight (4 hours). The percentage of graft yield was calculated from

$$\% \text{ Grafting} = \frac{W-Wo}{Wo} \times 100$$

Wo = dry weight of initially sample

W = dry weight of modified sample after extraction

### 2.6.2 Determination of Moisture Regain

The moisture regains of modified polyester samples were determined according to ASTM D2654-899 method.

**A.Procedure :**

1. The specimen (size 10x14 cm) was dried at 105°C for 4h cooled and weighed. It was then transferred to the conditioning room and conditioned overnight at the standard atmosphere, 27± 2°C and 65 ± 2% relative humidity. The specimen was reweighed.

Copyright by Mahidol University

**B. Calculation :**

Calculate the moisture regain using the formula

$$\text{moisture regain (\%)} = \frac{W-Wo}{Wo} \times 100$$

W = weight of sample after conditioning

Wo = weight of initially dried sample

### 2.6.3 FT-IR and FT-Raman Spectroscopic Measurements

#### 2.6.3.1 FT-IR Spectroscopy

The FT-IR spectra of unmodified and MAA-modified polyester fabrics were recorded using Perkin-Elmer FT-IR Spectrometer System 2000 between 4000 and 370 $cm^{-1}$.

Copyright by Mahidol University

**Specimen Preparation**

The specimen was cut into pieces less than 1mm long (1-3mg), mixed with KBr (200mg) and pressed under pressure ( 8MPa) for 5 minutes.

### 2.6.3.2 FT-Raman Spectroscopy

The Raman spectra of unmodified and modified polyester fabrics were recorded using Perkin-Elmer FT-Raman Spectrometer System 2000. Samples were in the form of fabric, having the size 10x14 cm. The fabric sample was folded to the final size of approximately 2x3 cm and clamped to the sample platform over the laser beam path.

### 2.6.4 Dynamic Mechanical Analytical Studies of Modified Polyesters

The dynamic mechanical properties of modified polyester fabrics were measured by using dynamic mechanical thermal analyser (Polymer Laboratories DMTA MK II). The tensile head was used for this measurement. The distance between the sample clamps was 1 cm.

Copyright by Mahidol University

Measurements were made over the temperature range of -100°C to 200°C.

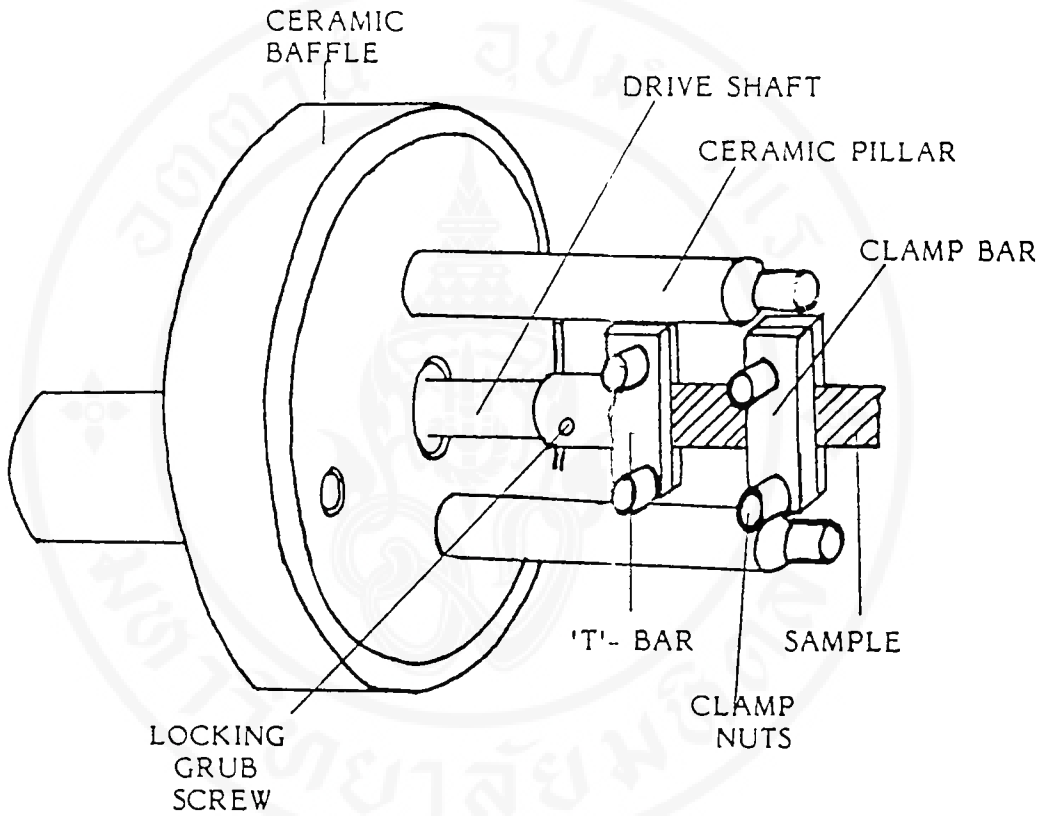



**Figure 2.3** Schematic diagram showing tensile head sample arrangement

### 2.6.5 Measurement of Tensile Properties of Yarns

The tensile properties of polyester yarns were determine by using tensile testing machine (Instron model 4301). The cross head speed used

Copyright by Mahidol University

was 150 mm/minute. 20 samples (filling and warp yarns ) were used for each measurement; using the gauge length 100 mm.

Tensile strengths of the polyester samples were determined in terms of the breaking tenacity, according to the following formulation,

$$B = \frac{F}{T}$$

B = breaking tenacity in mN per denier

F = breaking force in mN

T = linear density in denier

linear density = mass per unit length

Denier = mass in grams of 9,000 metre of materials

### 2.6.6 Measurement of Thickness of Polyester Fabrics

The thicknesses of the polyester fabrics were measured by using micrometer. Measurements were made from twenty-five different regions for each sample, having the size 10x14 cm.

Copyright by Mahidol University

### 2.6.7 Scanning Electron Microscopic Study

**A. Apparatus:**

- Scanning Electron Microscope (Hitachi 2500)
- Coating Unit (Hitachi E 102 ion sputter)

**B. Procedure**

The specimen was coated with platinum-paladium in the Hitachi E102 ion sputter and examined under the Hitachi 2500 Scanning Electron Microscope using the accelerating voltage of 30 kV.

## 2.7 Treatment of Modified Polyester with NaOH

**A. Condition :**

| | |
|---|---|
| material to liquor ratio | 1 : 30 |
| temperature | 95°C |

Copyright by Mahidol University

**B. Procedure :**

1. Polyester fabric (size 5x7 cm) was treated in NaOH solution (vary from 0.1-4% w/v) in a 125 ml. flask at 95°C for 5,10 and 60 minutes with agitation during treatment.

2. At the end of the designated time, the fabric was removed from the reaction vessel and rinsed thoroughly in distilled water at room temperature and dried.

3.The percent weight loss of polyester fabric due to hydrolysis was calculated.

Copyright by Mahidol University

# CHAPTER III

# RESULTS AND DISCUSSION

## 3.1 PRELIMINARY STUDIES

Preliminary studies were undertaken in order to establish the followings,

1. Suitable method for efficient modification of polyester fabrics.
2. Method of characterisation of the modified polyester fabrics.

### 3.1.1 Determination of Suitable Swelling Agent For Modification of Polyester

#### 3.1.1.1 Swelling Study of Polyester Fabrics in Methacrylic Acid

The swelling behaviour of polyester fabrics in methacrylic acid (MAA) is shown in Table 3.1

Copyright by Mahidol University

**Table 3.1** Percentage swelling of polyester fabrics in MAA

| Time (min) | Percentage swelling in MAA |
|---|---|
| 30 | 1.0 |
| 60 | 1.1 |
| 90 | 1.1 |
| 120 | 1.3 |
| 150 | 1.1 |
| 180 | 1.0 |

The results obtained showed that MAA almost did not swell polyester fabrics. Therefore, modification by grafting MAA onto polyester fabrics would require promotion by using swelling organic solvent.

### 3.1.1.2 Swelling Study of Polyester Fabrics in Swelling Agents

In order to select suitable swelling agent, swelling of several swelling agents were studied, viz. benzoic acid, benzyl alcohol, m-cresol and phenol. The results obtained are given in Table 3.2.

Copyright by Mahidol University

**Table 3.2** Percentage swelling of polyester fabrics in various swelling agents

| Solvent | Percentage swelling |
|---|---|
| 2% benzoic acid in water/methanol mixture (1.5:1)* | 9 |
| benzyl alcohol | 115 |
| 2% m-cresol ( in methanol) | 97 |
| 2% phenol (in water) | 12 |

* by volume

Condition : room temperature swelling for 2 hours

The solvents used had various effect on swelling of PET. The swelling of polyester fabric by m-cresol was not used because it occurred yellowing of polyester fabric. Therefore, it used in dilute solution (2% m-cresol). The best swelling was shown to be benzyl alcohol. The solubility parameter(δ)values of water, methanol, benzyl alcohol and m-cresol are 23.4,14.5, 12.1 and 10.2 respectively. It will be seen that the solubility parameter of benzyl alcohol is close to PET (δ=10.5). Therefore, benzyl alcohol gave the highest percentage swelling compared with other solvents.

Copyright by Mahidol University

Thus, swelling by benzyl alcohol was studied at different time. Table 3.3 shows change of percentage swelling of polyester fabrics in benzyl alcohol.

**Table 3.3** Percentage swelling of polyester fabrics in benzyl alcohol

| Time (min) | Percentage swelling |
|---|---|
| 20 | 127 |
| 40 | 137 |
| 60 | 132 |
| 80 | 130 |
| 100 | 127 |
| 120 | 128 |
| 180 | 127 |

Results of this experiment revealed that the maximum percentage swelling of polyester fabrics in benzyl alcohol was obtained in 40 minutes.

### 3.1.2 Study to Estimate Suitable Grafting Conditions By Using Differential Scanning Calorimetry (DSC)

#### A. Polymerisation Temperature

In isothermal condition, polymerisation of MAA using BPO as initiator was studied at 70°C, 80°C, and 90°C. The results are shown in Table 3.4 and Figure 3.1.

Copyright by Mahidol University

It will be seen that increases in temperature increase the decomposition of BPO leading to decrease initial time ($t_i$) and time at peak ($t_p$) of polymerisation of MAA.

**Table 3.4** Time of polymerisation of MAA at various temperatures

| Temperature(°C) | Time of polymerisation (min) | |
|---|---|---|
| | $t_i$ | $t_p$ |
| 70 | 11.6 | 19.2 |
| 80 | 1.4 | 7.5 |
| 90 | 0.1 | 2.8 |

$t_i$ = time at polymerisation started

$t_p$ = time at polymerisation rate reached peak

Copyright by Mahidol University

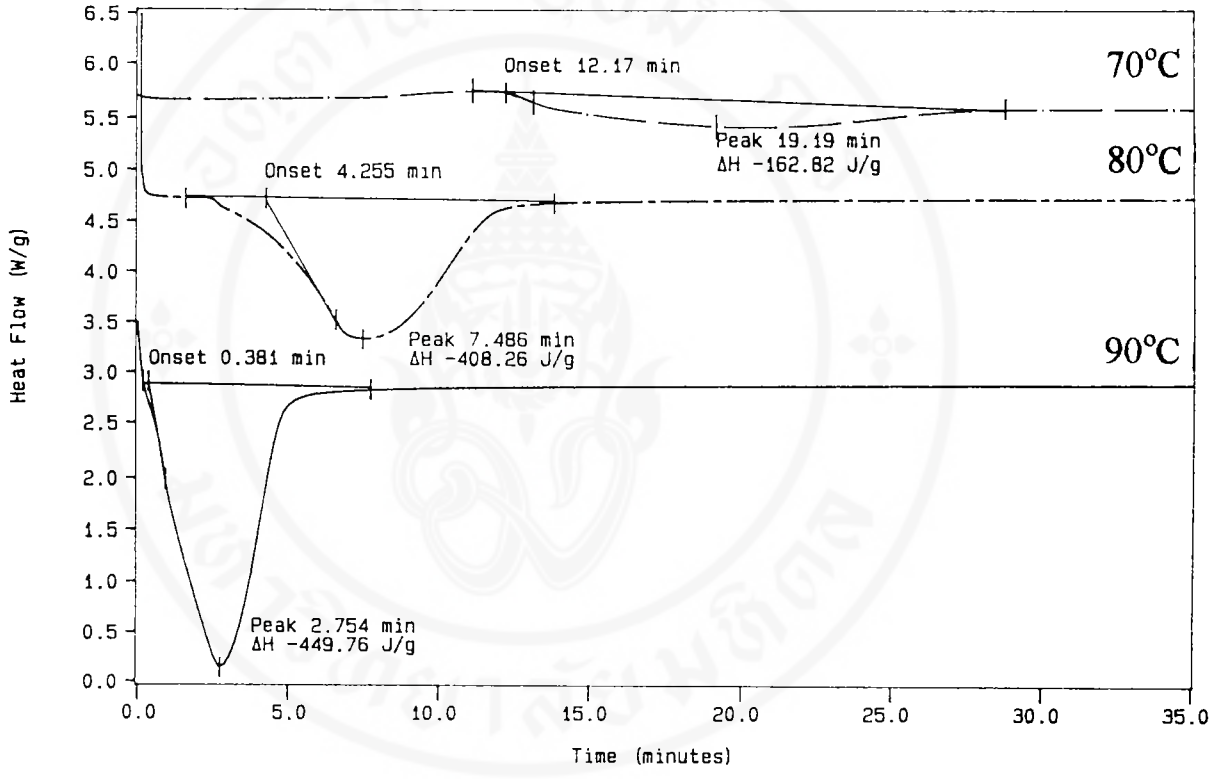



**Figure 3.1** DSC thermogram of MAA polymerisation ; isothermal condition at 70°C, 80°C and 90°C

Copyright by Mahidol University

**B. Effect of Swelling Agent on Polymerisation Reaction of MAA**

The swelling solvent added to the polymerisation medium may have effect upon the grafting reaction. The effect of benzyl alcohol on polymerisation reaction was studied at 70°C,80°C, and 90°C by DSC. The results obtained are shown in Table 3.5 and Figures 3.2-3.5.

**Table 3.5** Time of polymerisation of BPO, MAA and benzyl alcohol mixture at various temperature

| Temperature (°C) | Time of polymerisation (min) | |
|---|---|---|
| | $t_i$ | $t_p$ |
| 70 | 65.4 | 79.9 |
| 80 | 31.2 | 40.8 |
| 90 | 0 | 3.9 |

Copyright by Mahidol University

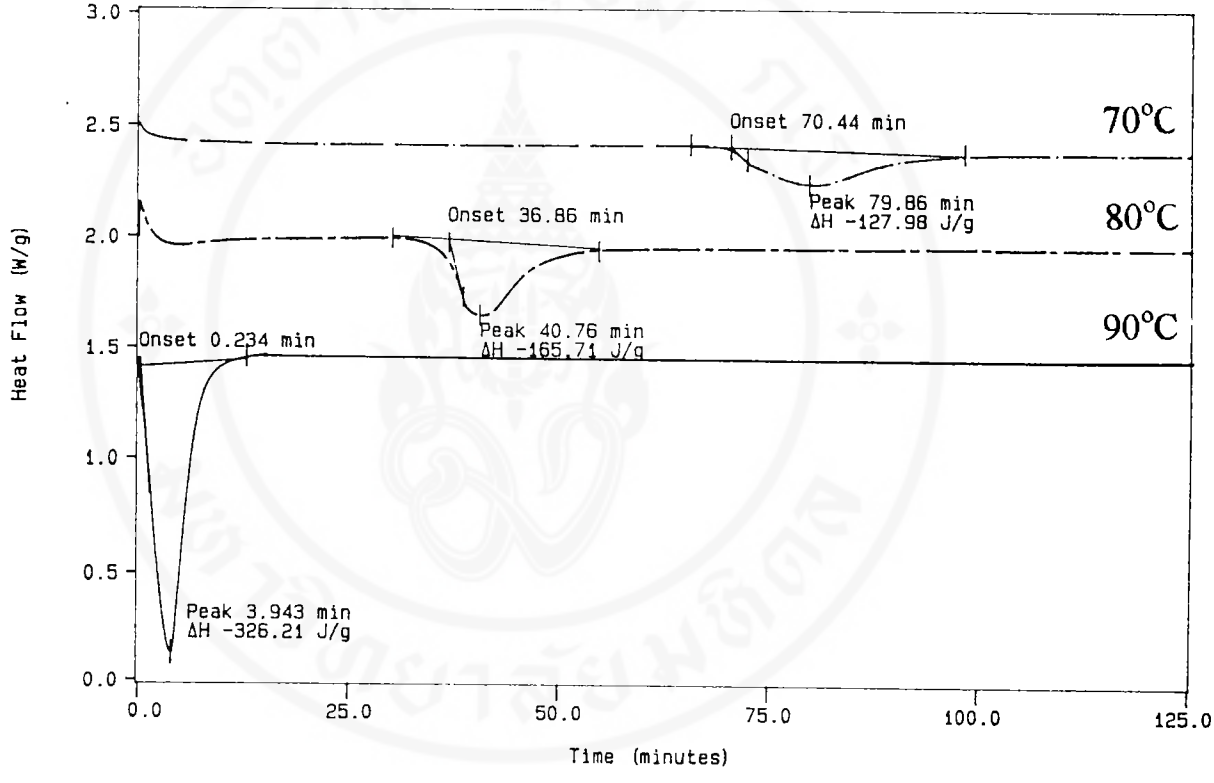



**Figure 3.2** DSC thermogrm of MAA polymerisation in benzyl alcohol; isothermal condition at 70°C, 80°C and 90°C

Copyright by Mahidol University

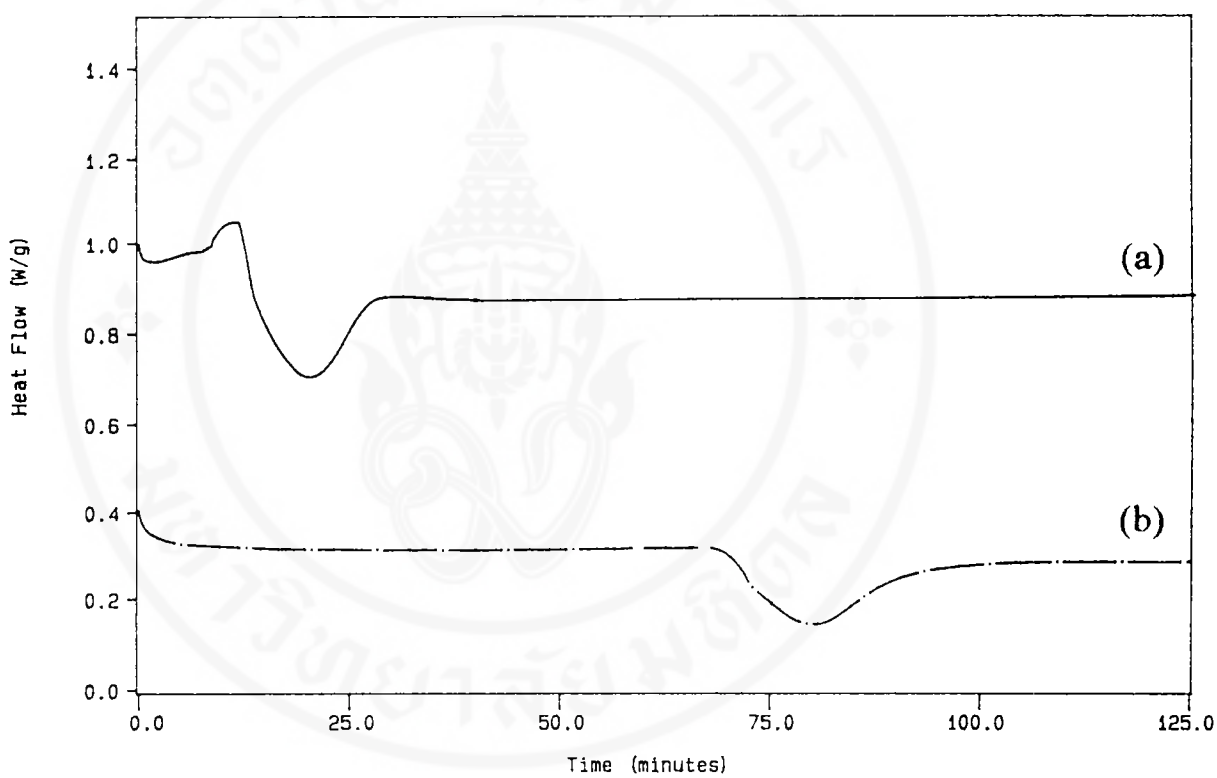



**Figure 3.3** Comparison of DSC thermograms of MAA polymerisation; isothermal condition at 70°C, in the absence (a) and presence (b) of benzyl alcohol

Copyright by Mahidol University

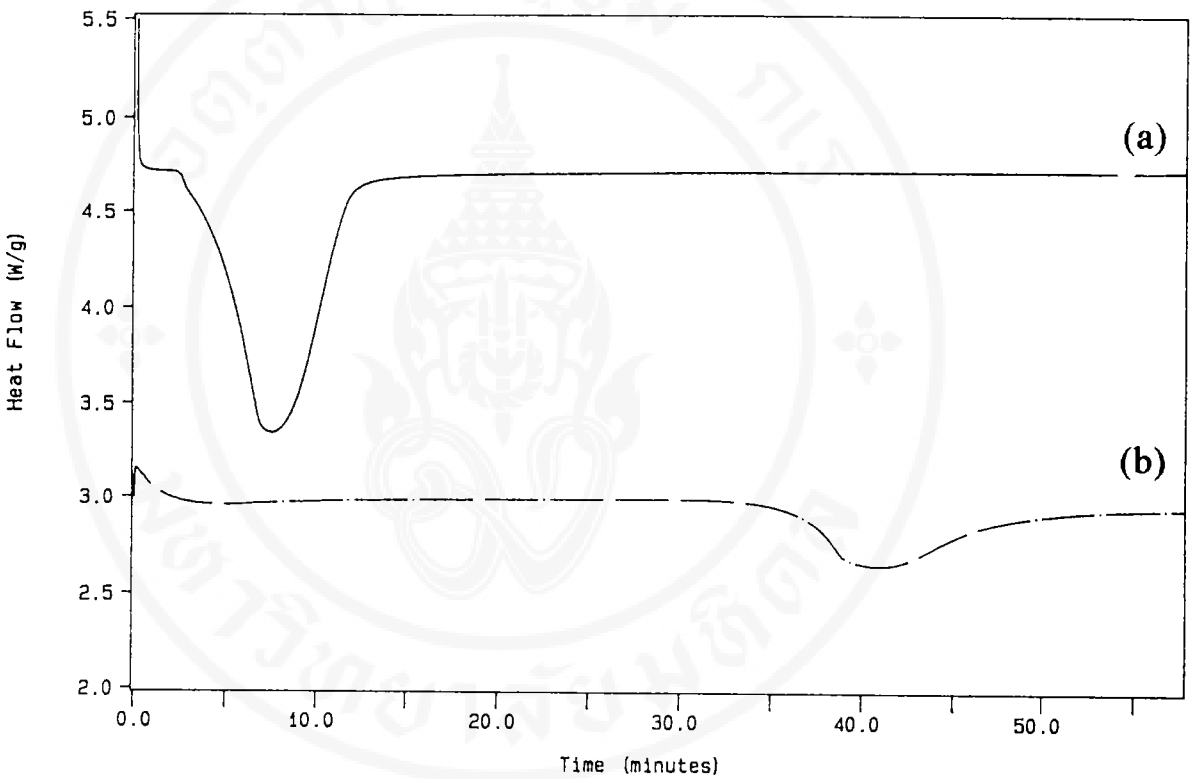



**Figure 3.4** Comparison of DSC thermograms of MAA polymerisation; isothermal condition at 80°C, in the absence (a) and presence (b) of benzyl alcohol

Copyright by Mahidol University

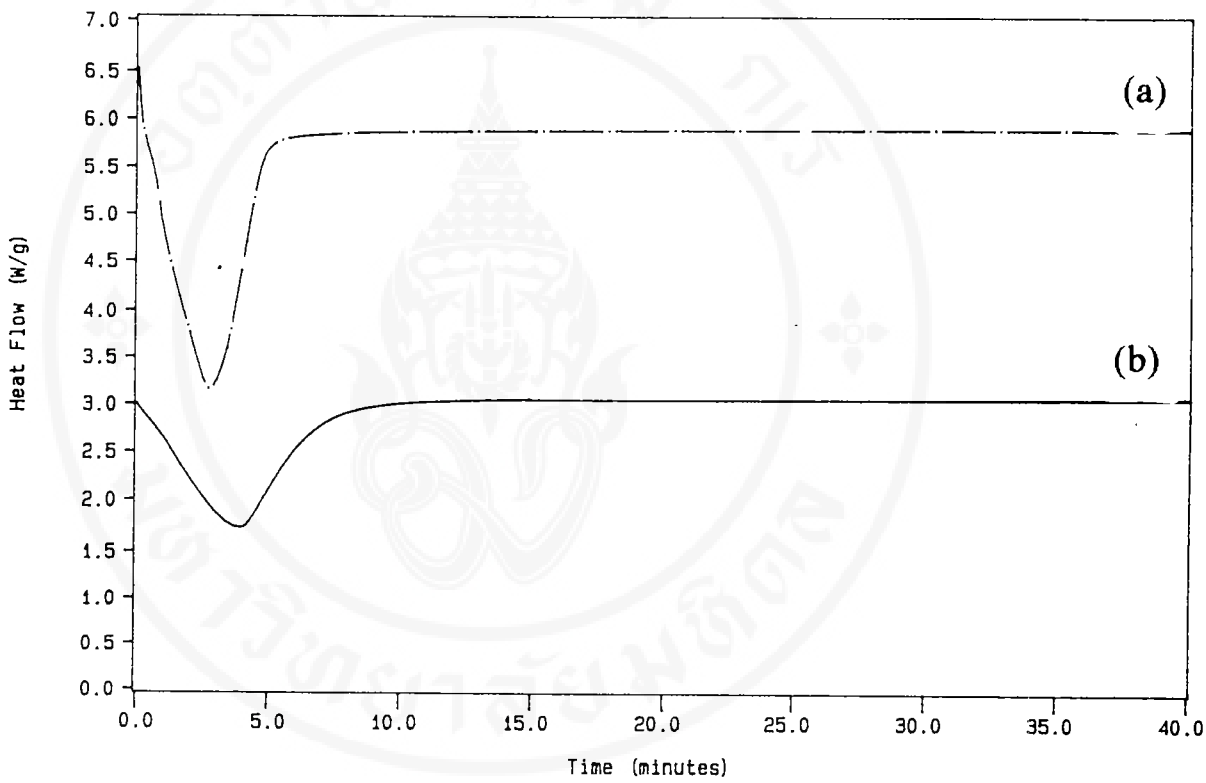



**Figure 3.5** Comparison of DSC thermograms of MAA polymerisation; isothermal condition at 90°C, in the absence (a) and presence (b) of benzyl alcohol

Copyright by Mahidol University

It will be seen that the polymerisation times increased when benzyl alcohol was added to the reaction medium. The initial polymerisation times increased to 65 and 31 minutes for the polymerisation temperature of 70°C and 80°C, respectively, compared with the initial polymerisation times without benzyl alcohol of 12 and 1 minutes (see Tables 3.4-3.5 and Figures 3.3-3.5). At 90°C, the polymerisation reaction occurred immediately, so that the initial polymerisation time could not be measured. The increase in polymerisation rate with increasing polymerisation temperature was well established.

In conclusion, the polymerisation of MAA could occur in the presence of benzyl alcohol but inhibition period was observed for the polymerisation temperatures of 70°C and 80°C. Since the reaction in the presence of benzyl alcohol was not inhibited at the polymerisation of 90°C, this temperature was selected for subsequent experimental study.

From Figures 3.1and 3.2, it was apparent that the homopolymer was formed at the temperature between 70 and 90°C, even in the presence of benzyl alcohol in the polymerisation medium. This implied that the homopolymer formation was likely to occur during grafting under the condition used.

Copyright by Mahidol University

### 3.1.3 Determination of Method For Effecting Modification of Polyester

Preliminary experiments for grafting MAA onto polyester fabrics was carried out by varying the swelling agent for swelling polyester. The swelling agents used are shown in Table 3.6.

**Table 3.6** Reaction system of grafting MAA onto polyester fabrics

| Swelling agents | Dispersing agent for BPO |
|---|---|
| 2%aq. solution of benzyl alcohol | acetone or toluene |
| benzyl alcohol | - |

At first, the fabric (size 6x6 cm, weight 0.63 g) was swollen in 2% aqueous solution of benzyl alcohol containing MAA ( monomer to fabric ratio 3:1), BPO (2% by weight of monomer) and a few drops of dispersing agent (acetone or toluene) at room temperature for 90 minutes. Grafting of polyester fabric was carried out in water contained in a 250ml flask, with stirring, at 90°C. The reaction time was 2 h. The modified fabric was extracted with boiling water for 4h and dried. The percentage graft yield was calculated. The result obtained is shown in Table 3.7, where it will be seen that no grafting could be effected by using 2% aqueous solution of benzyl alcohol as the swelling agent.

Copyright by Mahidol University

MAHIDOL UNIVERSITY



**Table 3.7** Percentage graft yield of polyester fabric after grafting

| Original wt. of PET (g) | Wt. of PET after grafting (g) | % Graft yield |
|---|---|---|
| 0.63 | 0.63 | 0 |

The reason might be that BPO, although dissolved in organic solvent (acetone or toluene), was insoluble in 2% aqueous solution of benzyl alcohol. Since toluene also was not soluble in 2% aqueous solution of benzyl alcohol, its BPO solution could not enter the swollen polyester fabric. Therefore, no reaction could take place.

Therefore, the use of benzyl alcohol as swelling agent for the grafting reaction was studied. The polyester fabric was first swollen in benzyl alcohol in a 250 ml. flask at room temperature for 40 minutes. It was then transferred to 250 ml. flask containing the required amount of MAA (monomer to fabric ratio 1:1 and 2:1) and BPO (2% by weight of monomer) and left swelling for 5 minutes. Grafting of polyester fabric was carried out in water contained in a 250ml flask, with stirring, at 90°C. The reaction time was 2 h. The modified fabric was extracted with boiling water for 4h and dried. The percentage graft yield was calculated. The result obtained is shown in Table 3.8.

Copyright© by Mahidol University

36556

**Table 3.8** Percentage graft yield of polyester fabric after grafting

| Monomer: Fabric | $W_o$ (g) | W (g) | %Graft yield |
|---|---|---|---|
| 1:1 | 1.45 | 1.53 | 5.5 |
| 2:1 | 1.48 | 1.86 | 25.6 |

$W_o$ = Original weight of polyester fabric

W = Weight of polyester fabric after grafting

It will be seen that the weight of the polyester fabrics increased after grafting. The % graft yield increased with increases of monomer to fabric ratio from 1:1 to 2:1. When using benzyl alcohol as swelling agent, the polyester fabric was swollen in the first step. At the second step, MAA and BPO could diffuse into the polyester fabric. Furthermore, MAA and BPO are soluble in benzyl alcohol. Thus, grafting could occur. Therefore, benzyl alcohol was used as the swelling agent for modification of polyester fabrics.

### 3.1.4 Determination of Percentage Grafting by Solvent Extraction

Copyright by Mahidol University

During the grafting reaction of monomer onto the polyester fabrics homopolymerisation is also expected to occur. In order to

determine the % grafting , any homopolymer formed would have to be removed.

Preliminary experiment was, therefore, undertaken to determine suitable solvent for extraction of the poly (methacrylic acid) and hence the method for determination of the % grafting.

Because PMAA is soluble in water and methanol, study was made to extract the modified polyester fabric with water or methanol. The results obtained are given in Table 3.9.

**Table 3.9** % grafting by solvent extraction of modified polyester fabrics

| Monomer : Fabric | Extraction with $H_2O$ | | | | Extraction with Methanol | | | |
|---|---|---|---|---|---|---|---|---|
| | Time (h) | Wo (g) | W (g) | Graft yield (%) | Time (h) | Wo (g) | W (g) | Graft yield (%) |
| 0.5:1 | 11 | 1.84 | 1.85 | 0.5 | 3 | 1.90 | 1.91 | 0.5 |
| 1:1 | 11 | 1.87 | 1.98 | 6.0 | 3 | 1.57 | 1.63 | 3.8 |
| 2:1 | 15 | 1.95 | 2.43 | 24.6 | 3 | 1.92 | 2.30 | 20.0 |
| 3:1 | 30 | 1.95 | 2.81 | 44.1 | 4 | 1.69 | 2.29 | 35.5 |

Conditions : initiator concentration 2% by weight of monomer

reaction temperature 90°C, reaction time 2 hours

$W_o$ = Original weight of polyester fabric

W = Weight of polyester fabric after extraction

Copyright by Mahidol University

From Table 3.9 it will be seen that the homopolymer could be removed from the modified fabric by extraction with water or methanol. However, extraction with water required much longer time than using methanol to effect constant weight extract. Methanol also appeared to be more efficient extracting solvent as could be seen by amounts of extractable PMAA.

Methanol was, therefore, used as extracting solvent for determination of % graft yield.

In order to prove that the increase in weight of modified polyester fabric after extraction with methanol was PMAA covalently linked to the polyester fabric. A separate experiment was carried out to show that if PMAA was physical attached to polyester fabric, sample was coated with a known weight of PMAA by dipping the fabric into the aqueous solution of PMAA. The coated fabric was then extracted with methanol. The results obtained are shown in Table 3.10.

**Table 3.10** Weight of polyester fabric after extraction with methanol

| Original wt. of polyester fabric (g) | Wt. after treatment with PMAA (g) | Wt. after extraction with methanol (g) |
|---|---|---|
| 1.48 | 2.10 | 1.48 |

Copyright by Mahidol University

It could be concluded, therefore, that the increase in weight of modified polyester fabric after extraction with methanol was due to the formation of PMAA grafted or chemically linked to polyester fabric.

## 3.2 STUDIES OF MODIFICATION OF POLYESTERS

Modifications of polyester fabrics were effected by using the method established from preliminary study (see 3.1.3).

Several parameters were available for controlling the modification process of polyester fabrics , including initiator concentration, monomer to fabric ratio, reaction temperature and reaction time. The effects of these parameters were studied. The results obtained are reported below.

### 3.2.1 Effect of Initiator Concentration

To study the effect of BPO concentration on the extent of grafting of MAA to PET ,the BPO concentration was varied from 1% to 2% and to 3% by weight of the monomer. The experimental results obtained are shown in Table 3.11 and also in Figure 3.6.

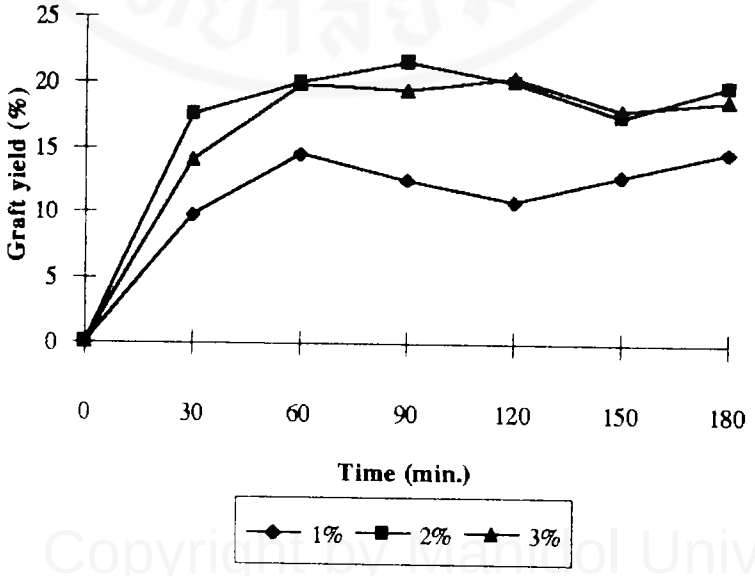
Copyright by Mahidol University

**Table 3.11** Effect of initiator concentration on % graft yield of MAA onto PET

| Time (min) | Graft yield (%) | | |
|---|---|---|---|
| | Initiator concentration (w/w of MAA) | | |
| | 1% | 2% | 3% |
| 30 | 9.7 | 17.6 | 14.1 |
| 60 | 14.5 | 20.1 | 19.8 |
| 90 | 12.6 | 21.6 | 19.5 |
| 120 | 10.8 | 20.0 | 20.3 |
| 150 | 12.8 | 17.5 | 17.8 |
| 180 | 14.6 | 19.7 | 18.7 |

Conditions : fabric : monomer ratio = 1: 2

temperature 90°C




Copyright© by Mahidol University

**Figure 3.6** Variations of graft yield with initiator concentration

It is seen that graftings were characterised by initial fast rates, followed by slower changes for all initiator concentrations used. Furthermore, the percentage graft yields showed increases with increasing BPO concentration. For 1% BPO, the % graft obtained were 12-14%. For 2% and 3% BPO, the % graft obtained were at the same level of 19-20%. It appeared, therefore, that there is no advantage in using BPO greater than 2% as the % graft derived seemed to have reached the maximum level obtainable.

The increases in % graft of MAA onto PET as the concentration of BPO was increased were to be expected since increasing the amount of BPO would result in the increase in the quantity of free radicals. As the result, the probability of hydrogen abstraction from the polyester main chains would increase, leading eventually to increase of the extent of grafting.

Above 2% BPO concentration , there will be abundance of free radicals. As a result, combination of free radicals (of BPO) would be favoured over graft initiation and no increase in graft yield was observed. Similar observation has been reported by Abdel-Bary et. al. (24) in the case of grafting of 2-hydroxyethyl methacrylate onto polyester fibres using BPO as the initiator. Thus, it may be concluded from the results obtained that the optimum initiator concentration existed for grafting of

Copyright by Mahidol University

polyester with MAA. For the experimental conditions used, the optimum initiator concentration was 2%.

### 3.2.2 Effect of Temperature

In thermal reaction, the temperature is expected to play important role. Therefore, it is necessary to study the effect of temperature on grafting reaction . For the present study, the reaction temperature was varied between 70°C and 90°C. Table 3.12 and Figure 3.7 show results of the effects of reaction temperature on the graft yield obtained.

**Table 3.12** Effect of reaction temperature on graft yield (monomer: fabric ratio = 2: 1)

| Time (min) | Graft yield (%) at various temperatures | | |
|---|---|---|---|
| | 70°C | 80°C | 90°C |
| 30 | 0 | 2.1 | 17.6 |
| 60 | 0 | 5.6 | 20.1 |
| 90 | 0 | 8.1 | 21.6 |
| 120 | 0 | 10.5 | 20.0 |
| 150 | 0 | 17.1 | 17.5 |
| 180 | - | - | 19.7 |
| 210 | - | - | 15.6 |

Copyright by Mahidol University

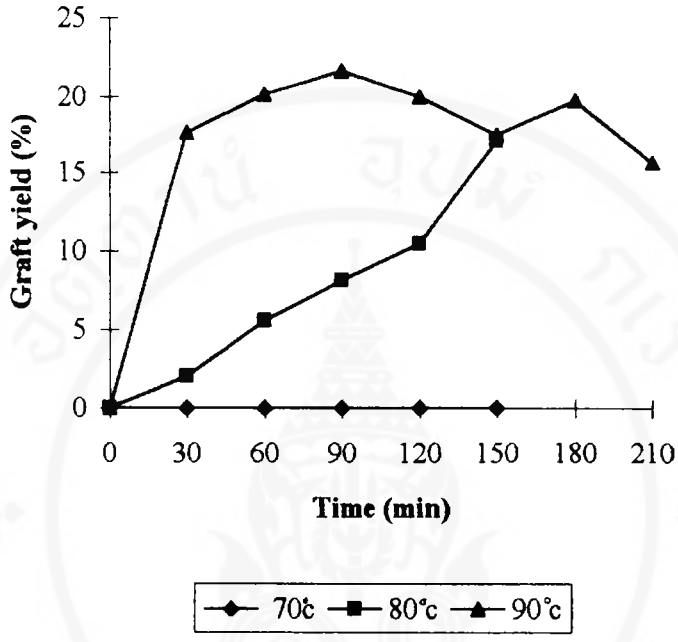



**Figure 3.7** Variations of graft yield with reaction temperatures

It was clear from the results obtained that no grafting occurred at the reaction temperature of 70°C. At 80°C and 90°C, grafting of MAA onto PET could take place. The % graft showed increases with increasing reaction time and increasing reaction temperatures. The % graft increase was more rapid at the reaction temperature of 90°C, compared with 80°C, reaching the maximum level of 20-21% after 60 minutes of reaction time. At extended grafting reaction time, the % graft appeared to decrease somewhat. Hebeish A. et. al. reported similar observation (22). The results could be explained as follows.

Copyright by Mahidol University

The increase in temperature increases the initiation and propagation of the grafting reaction, together with the decomposition of the initiator leading to more free radicals. The diffusion of monomer and initiator from the solution phase to the fabric phase becomes much easier at temperature near the glass transition temperature of polyester fabric (ca. 80°C) since the mobilities of polyester segments increase near this temperature. The results of the present study may be explained in a similar fashion (see Figure 3.7).

It was observed that at longer time of grafting (above 90 minutes) lower graft yields were obtained. This may be because the chain termination began to predominate.

From the results obtained, the reaction temperature of 90°C was chosen as suitable grafting temperature.

### 3.2.3 Effect of Monomer to fabric ratio

The graftings of MAA onto polyester fabrics were also studied at different monomer to fabric ratio,using a fixed concentration of initiator. The results obtained are shown in Table 3.13 and Figure 3.8.

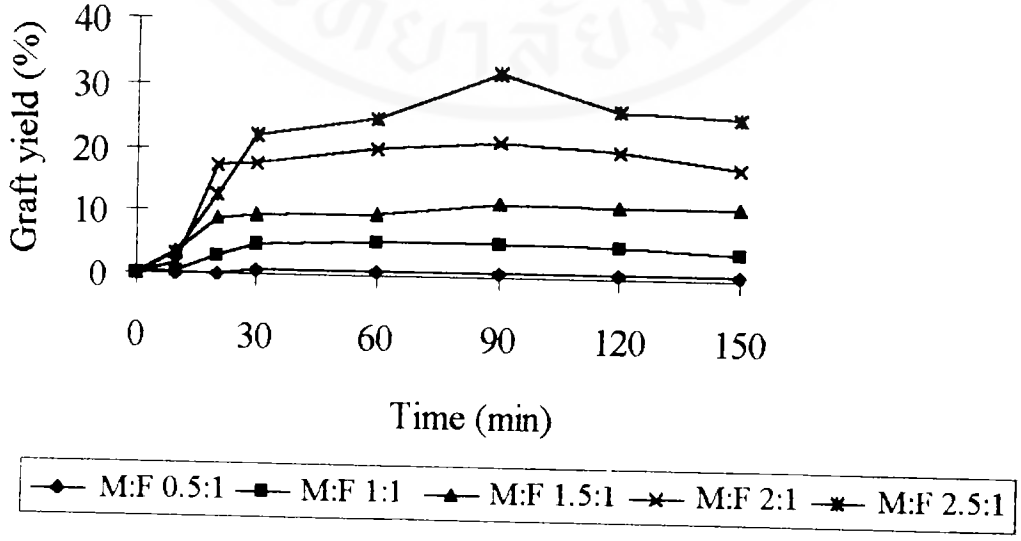
Copyright by Mahidol University

**Table 3.13** Effect of MAA to fabric ratio on graft yield

| Time (min) | Graft yield(%) at various MAA : fabric | | | | |
|---|---|---|---|---|---|
| | 0.5 : 1 | 1 : 1 | 1.5 : 1 | 2 : 1 | 2.5 : 1 |
| 10 | 0 | 0.4 | 3.6 | 1.5 | 3.8 |
| 20 | 0 | 3.0 | 9.0 | 17.2 | 12.5 |
| 30 | 0.6 | 4.6 | 9.4 | 17.6 | 22.0 |
| 60 | 0.6 | 5.4 | 9.8 | 20.1 | 25.0 |
| 90 | 0.7 | 5.3 | 11.5 | 21.6 | 32.2 |
| 120 | 0.6 | 5.1 | 11.4 | 20.0 | 26.6 |
| 150 | 0.6 | 4.0 | 11.2 | 17.5 | 25.5 |

Conditions : initiator concentration 2% by weight of monomer

reaction temperature 90°C




Copyright by Mahidol University

**Figure 3.8** Variation of graft yield with MAA to fabric ratio

As is evident from Table 3.13 and Figure 3.8, the % graft yield increased progressively with increases of MAA to fabric ratio from 0.5 : 1 to 2.5 : 1. This may be attributed to the concentration effect of monomer during grafting reactions. At higher concentration of the monomer, a greater number of monomer molecules are available for combination with the free radicals on the backbone of the polyester chains.

The fact that the graft yields did not increase very much with increases of reaction time after 90 minutes may be explained by the enhancement of homopolymer formation after this period. The homopolymer accumulated increases the reaction medium viscosity, which inhibits MAA diffusion toward grafting polymer chains.

## 3.3 CHARACTERISATION OF MODIFIED POLYESTERS

### 3.3.1 Moisture Regain

The relations between moisture regain and percentage graft yield, obtained by varying the MAA to fabric ratio, are shown in Table 3.14 and Figure 3.9.

Copyright by Mahidol University

**Table 3.14** Relations between moisture regain and graft yield obtained at various MAA to fabric ratios

| Graft yield (%) | Moisture regain (%) |
|---|---|
| 0 | 0.38 |
| 5.6 | 1.09 |
| 8.1 | 1.39 |
| 10.5 | 1.68 |
| 12.8 | 1.92 |
| 17.6 | 2.11 |
| 20.1 | 2.43 |
| 22.0 | 2.88 |
| 25.0 | 3.08 |
| 32.2 | 4.59 |

Copyright by Mahidol University

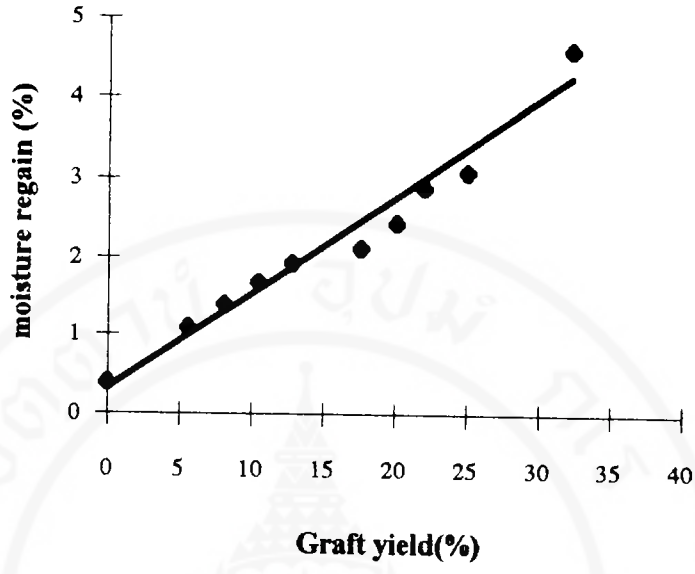



**Figure 3.9** Variation of moisture regain with graft yield in polyester fabrics grafted with MAA

Ungrafted polyester has a moisture regain value of 0.38. The moisture regain increased linearly with increasing the percentage grafts in the polyester. This is essentially due to hydrophilic nature of the grafted polyester as the result of the incorporation of the polar carboxyl groups to the fibre matrix.

Copyright by Mahidol University

### 3.3.2 FT-IR and FT-Raman Spectroscopies

The FT-IR spectra of MAA grafted polyesters were identified by comparing with the spectrum of the ungrafted polyester fabrics taken under the same conditions and the spectrum of PMAA (see Figures 3.10-3.11). The spectra of the polyesters grafted with MAA at different concentration ratios are shown in Figures 3.12-3.17. There are seen the band of OH group coming from MAA can be seen in the range 3300-3400 $cm^{-1}$

In order to prove that Raman spectroscopic method could be used to detected the OH group, the polymer with a great number of OH groups was characterised. Therefore,PMAA, PVA and poly(acrylic acid) were used as standard polymers. Figures 3.18-3.20 show the Raman spectra of PMAA, PVA and poly(acrylic acid). It will be seen that the band of OH group (at 3420 $cm^{-1}$) of PVA was very clear and the band of OH group of PMAA and poly(acrylic acid) (not very clear) at about 3300 and 3355$cm^{-1}$ respectively.

Figures 3.21 and 3.22 show the Raman spectra of ungrafted polyester fabric and MAA grafted polyester fabrics respectively. When the spectrum of the grafted polyester (at monomer: fabric ratio 3:1) was examined the band of OH group at about 3300 $cm^{-1}$ did not appear. The

Copyright by Mahidol University

The observations made with IR and Raman spectroscopic studies were understandable since, with IR, the intense IR bands usually arise from polar bonds such as O-H. With Raman spectroscopy strong bands are observed for bonds having nearly symmetrical charge distribution, such as C-C. Thus, the polar OH group could not be seen clearly by Raman spectroscopic method.

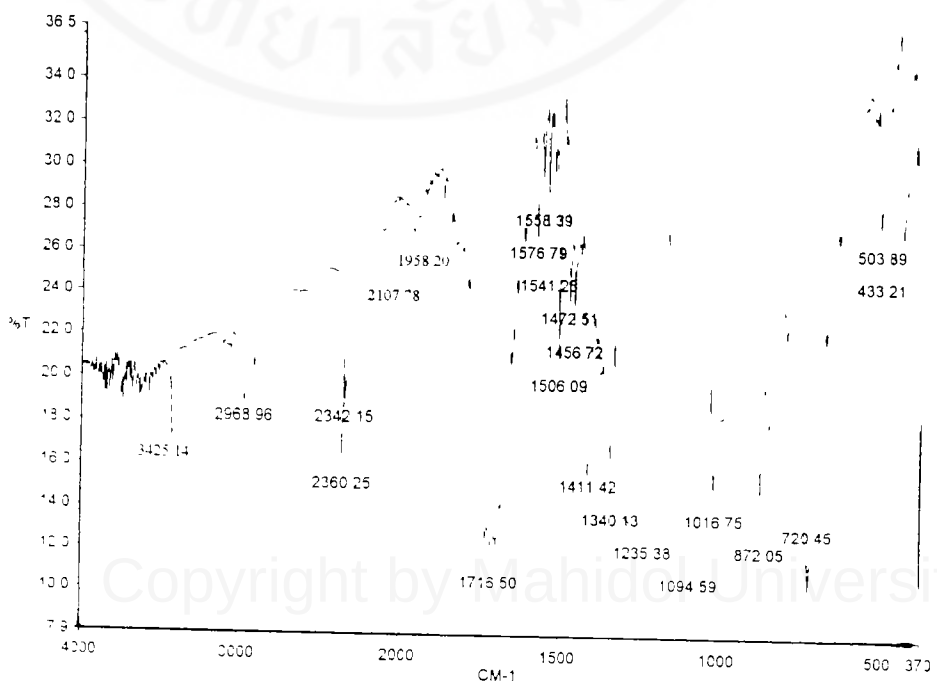



**Figure 3.10** FT-IR spectrum of ungrafted polyester

Copyright by Mahidol University

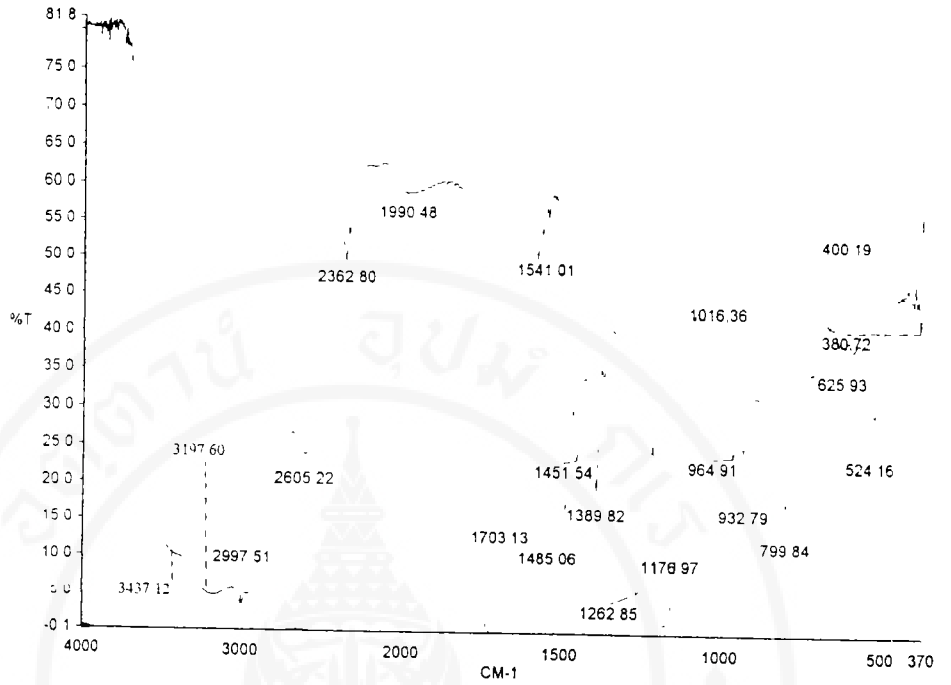



**Figure 3.11** FT-IR spectrum of PMAA

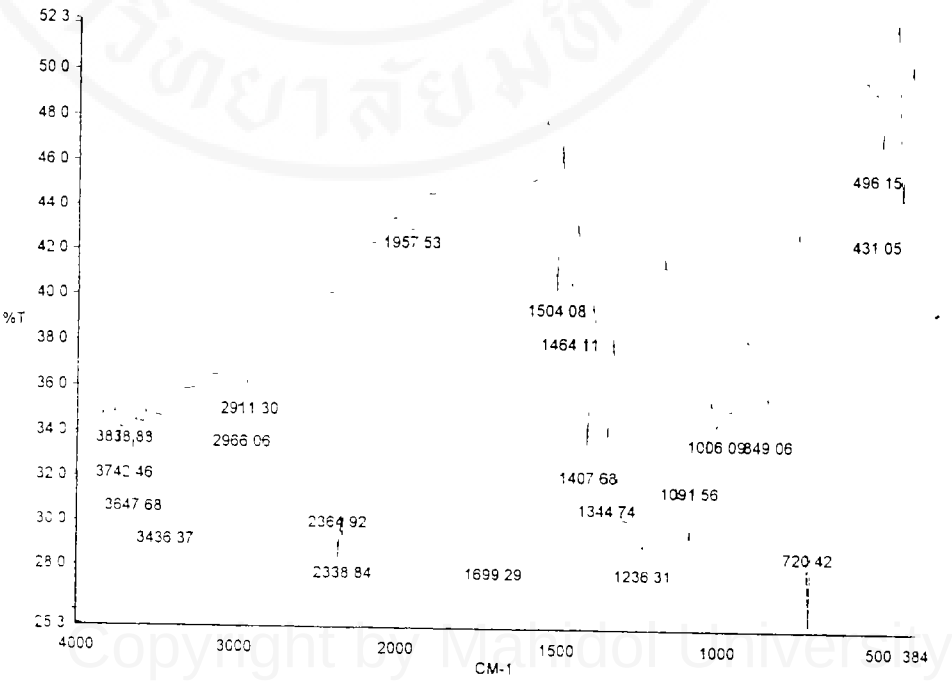



**Figure 3.12** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 0.5:1)

Copyright by Mahidol University

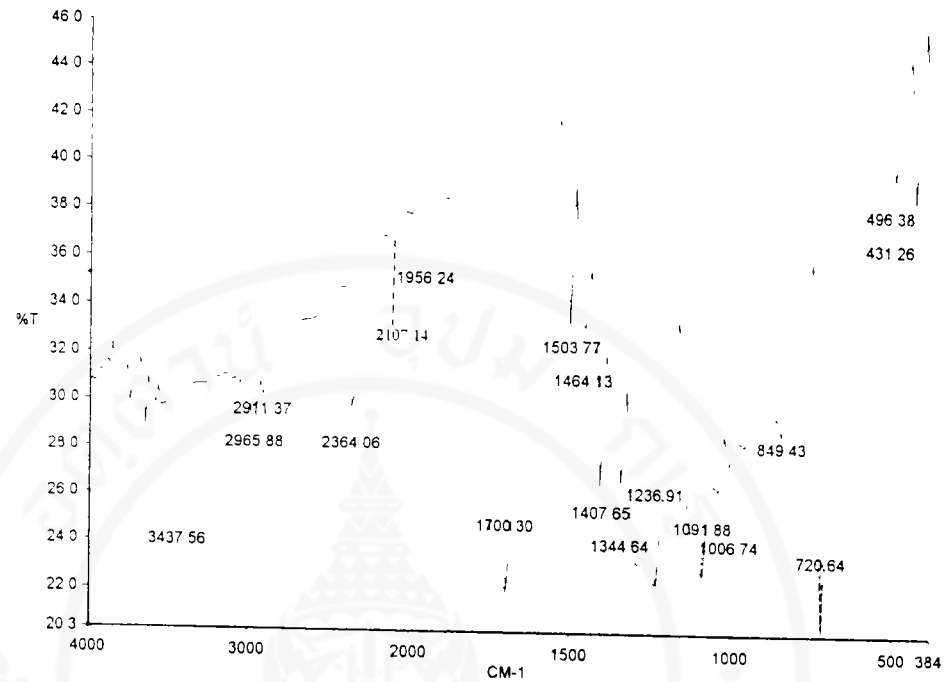



**Figure 3.13** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 1:1)

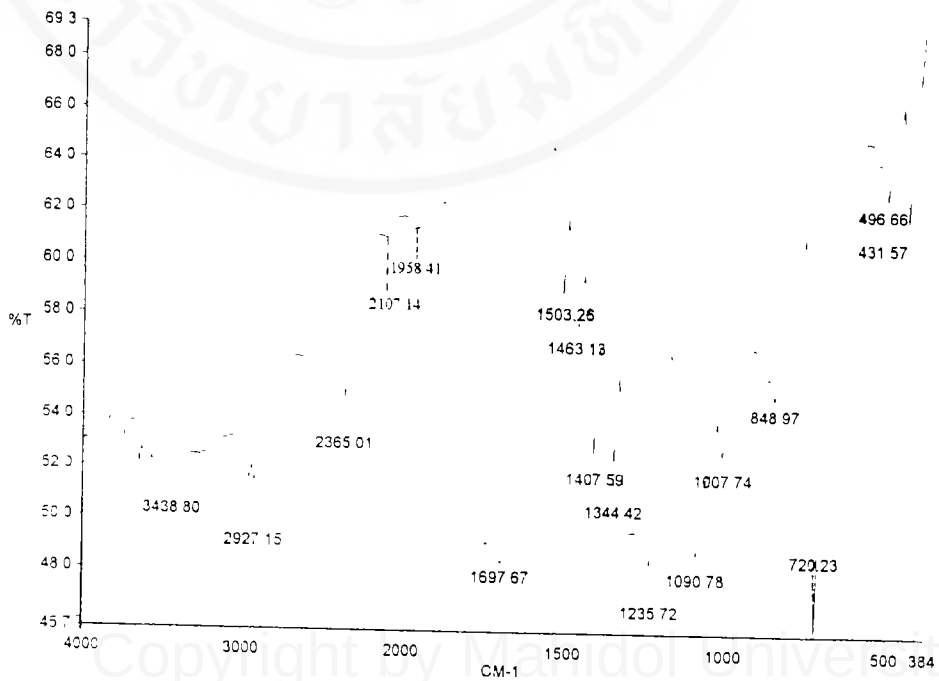



**Figure 3.14** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 1.5:1)

Copyright by Mahidol University

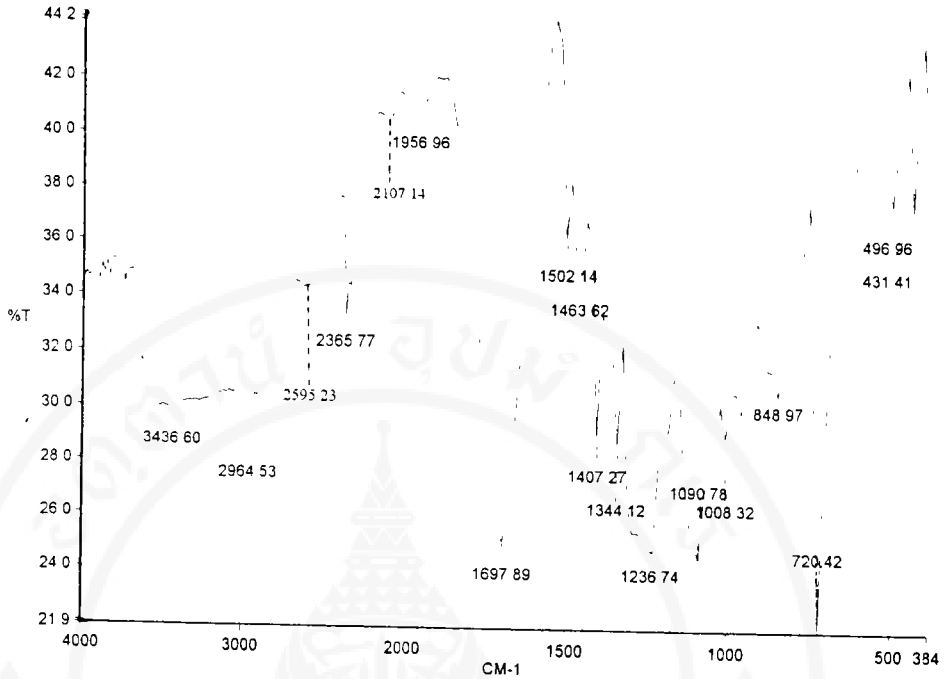
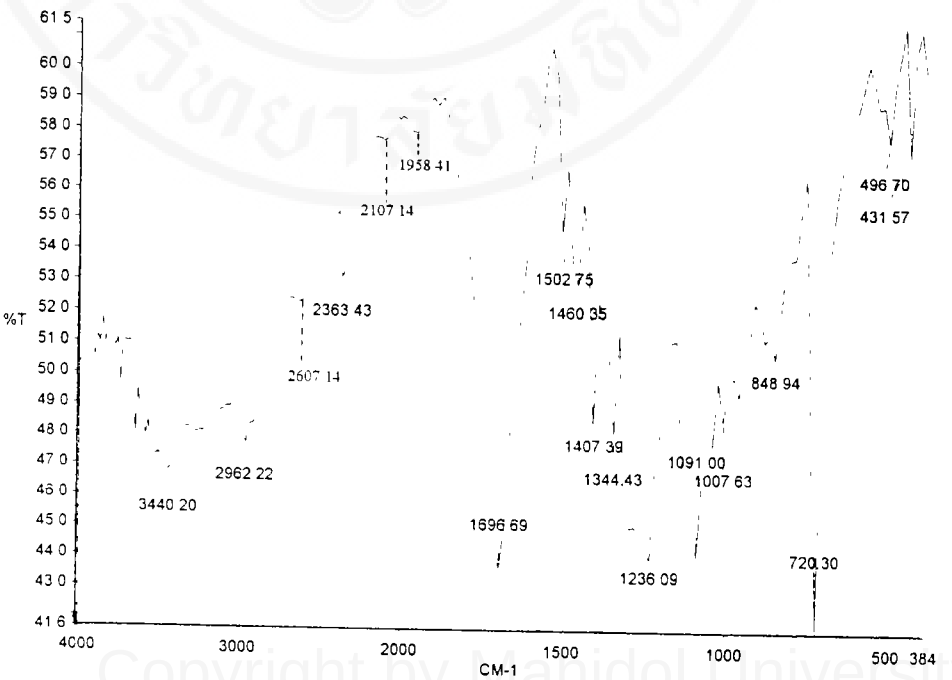



**Figure 3.15** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 2:1)




Copyright by Mahidol University

**Figure 3.16** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 2.5:1)

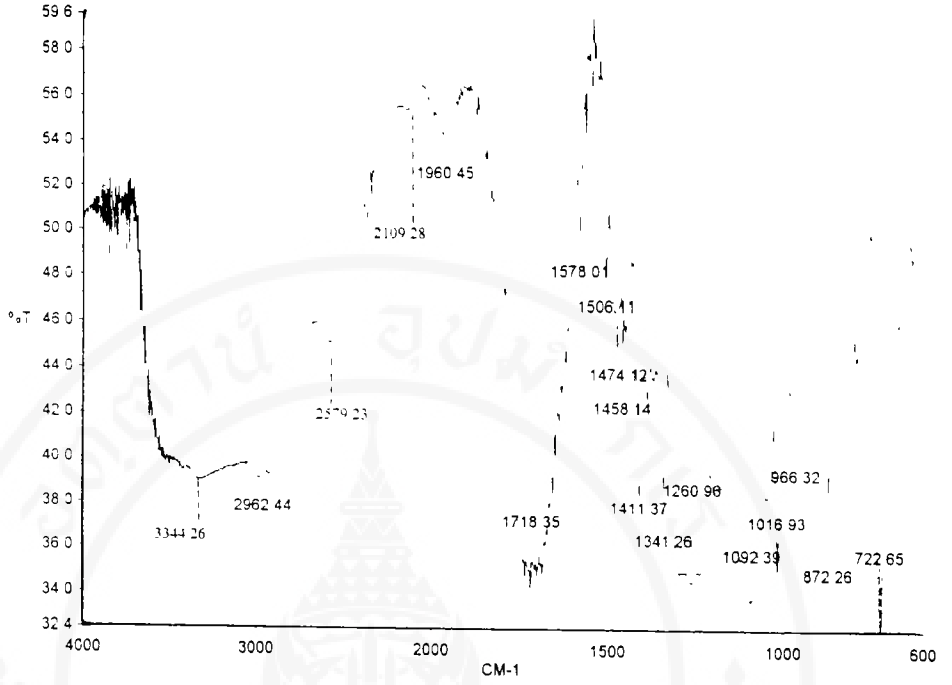
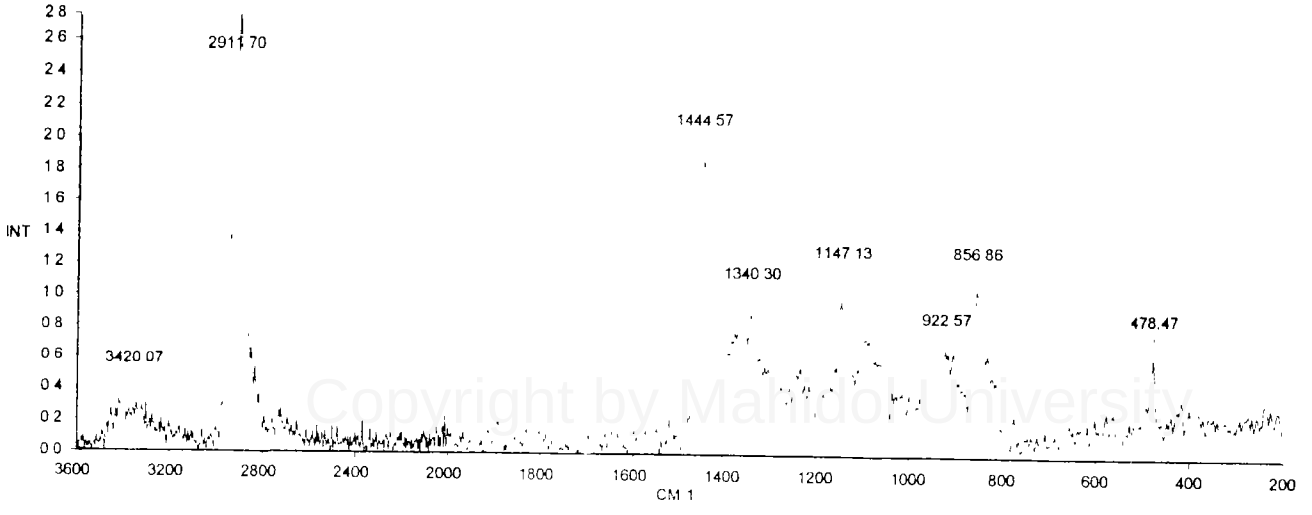



**Figure 3.17** FT-IR spectrum of polyester fabric grafted with MAA (monomer : fabric ratio 3:1)




Copyright by Mahidol University

**Figure 3.18** FT-Raman spectrum of PVA

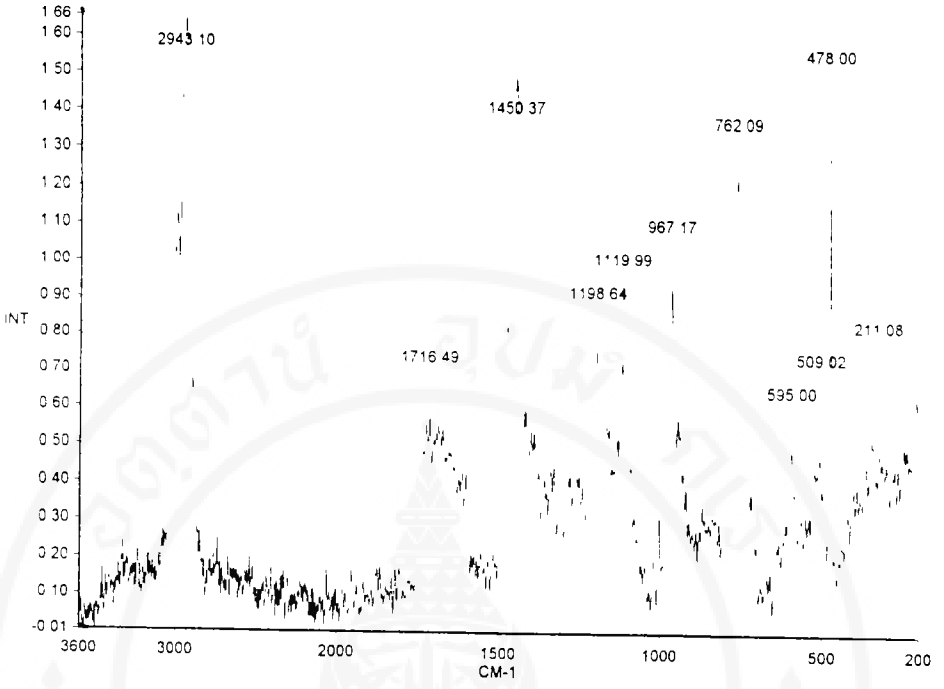



**Figure 3.19** FT-Raman spectrum of PMAA

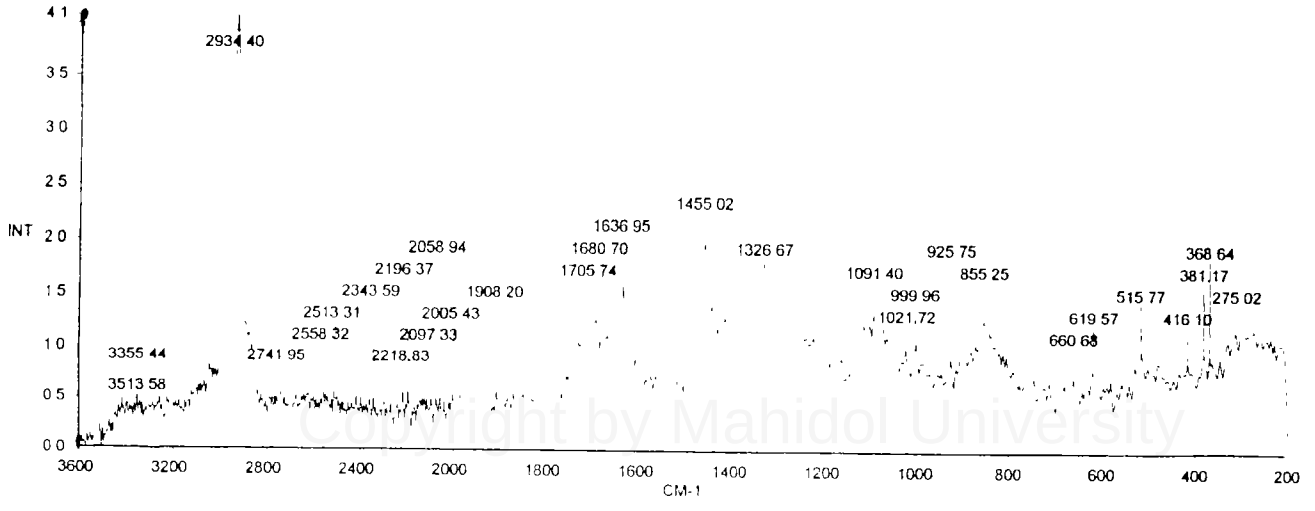



**Figure 3.20** FT-Raman spectrum of poly(acrylic acid)

Copyright by Mahidol University

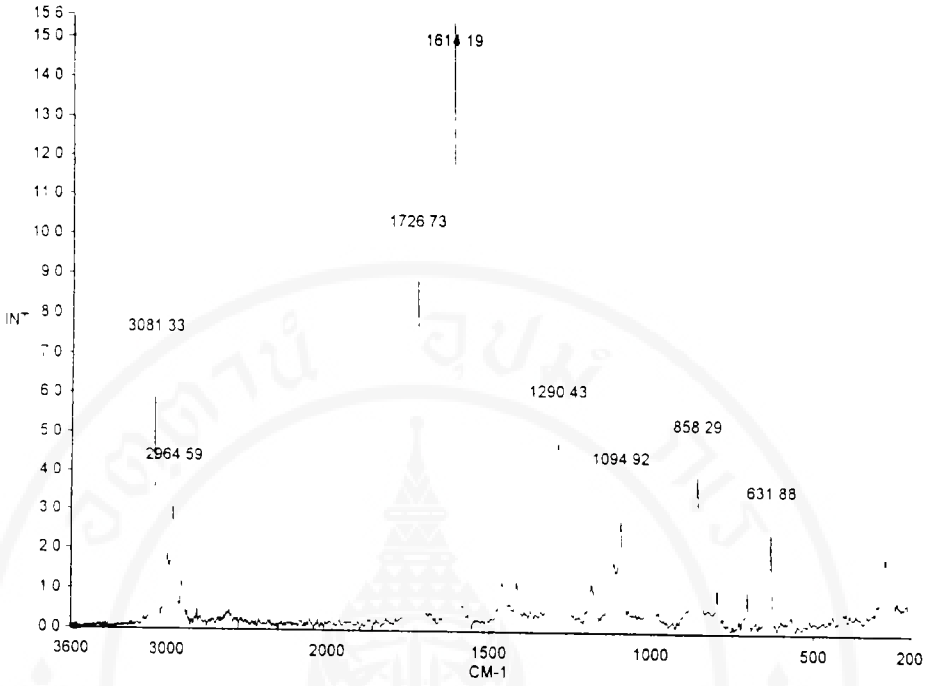



**Figure 3.21** FT-Raman spectrum of ungrafted polyester

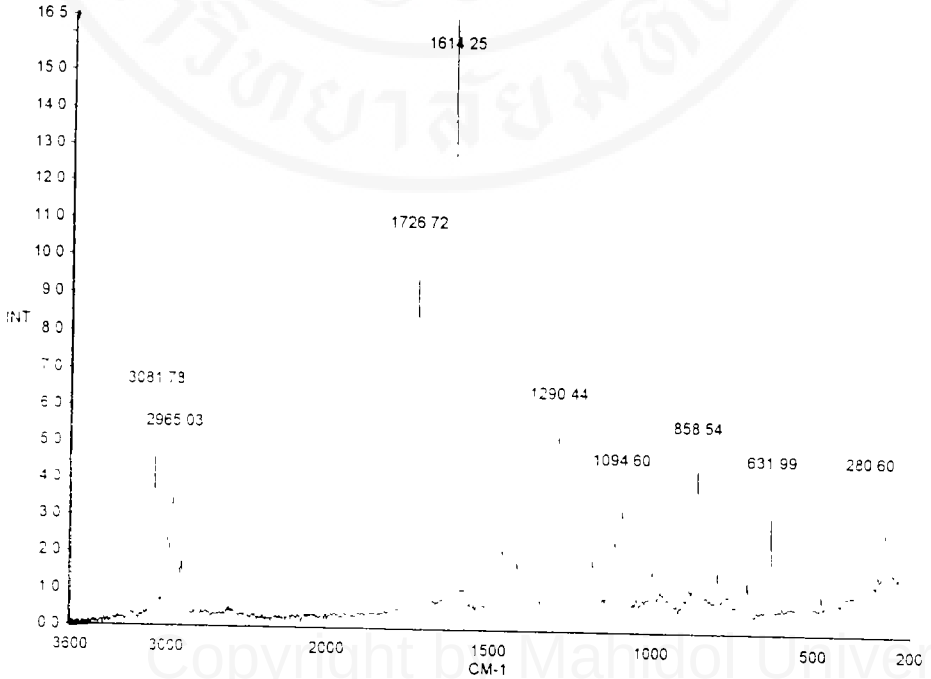



**Figure 3.22** FT-Raman spectrum of polyester fabric grafted with MAA at monomer : fabric ratio 3:1

Copyright by Mahidol University

### 3.3.3 Dynamic Mechanical Analysis (DMA) of Modified Polyesters

The modified polyester fabric was also characterised by DMA. The samples used were in the form of yarns. The results obtained, showing storage modulus (log $E'$) and tanδ curves, are shown in Figures 3.23-3.24.

Copyright by Mahidol University

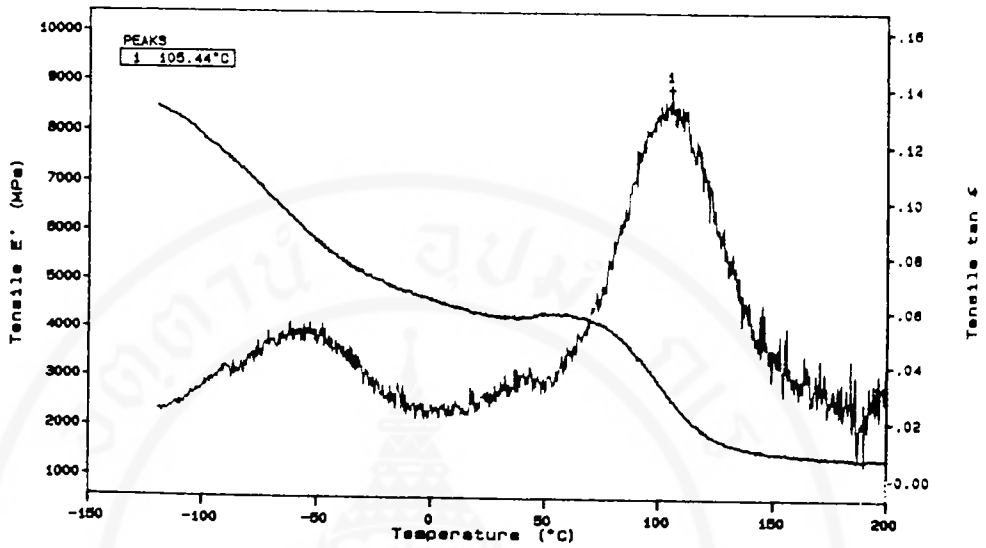
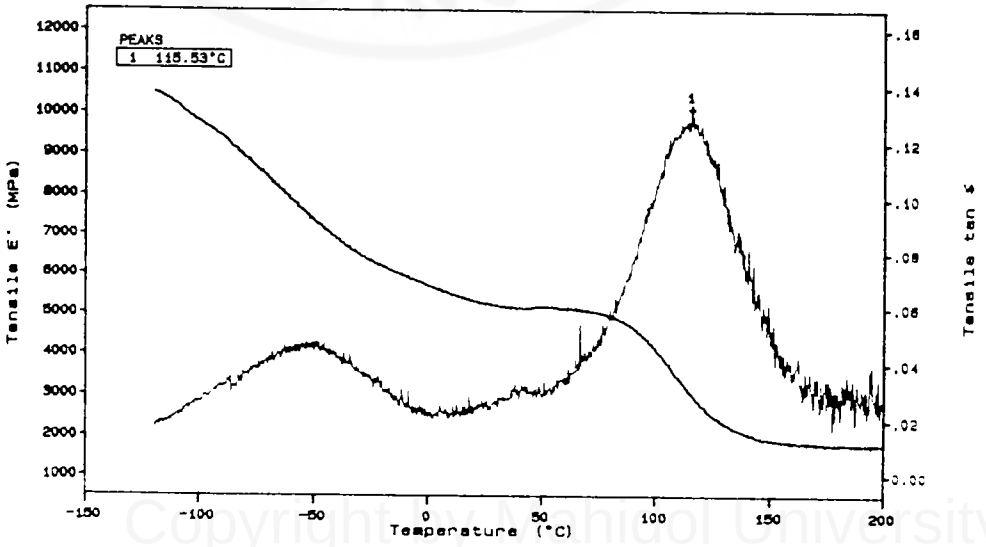



**Figure 3.23** Log E′ and tanδ versus temperature curve for filling yarn of polyester fabric




Copyright by Mahidol University

**Figure 3.24** Log E′ and tanδ versus temperature curve for warp yarn of polyester fabric

The polyester yarn showed transitions both below room temperature and above. The storage modulus showed a series of decreasing steps as the sample softened with increasing temperature. At each of the temperature regions where the storage modulus decreased, there was a peak in the tanδ curve.

The low temperature small peak (β-transition) in the tanδ curve appeared at about -50°C. The higher temperature transition, associated with glass transition temperature (Tg ) of PET, corresponded to the large peak (α-transition) in tanδ at about 105°C and 115°C for filling yarn and warp yarn, respectively. The change in Tg of grafted polyester compared with ungrafted fabrics are shown in Figures 3.25-3.34 and Table 3.15.

Copyright by Mahidol University

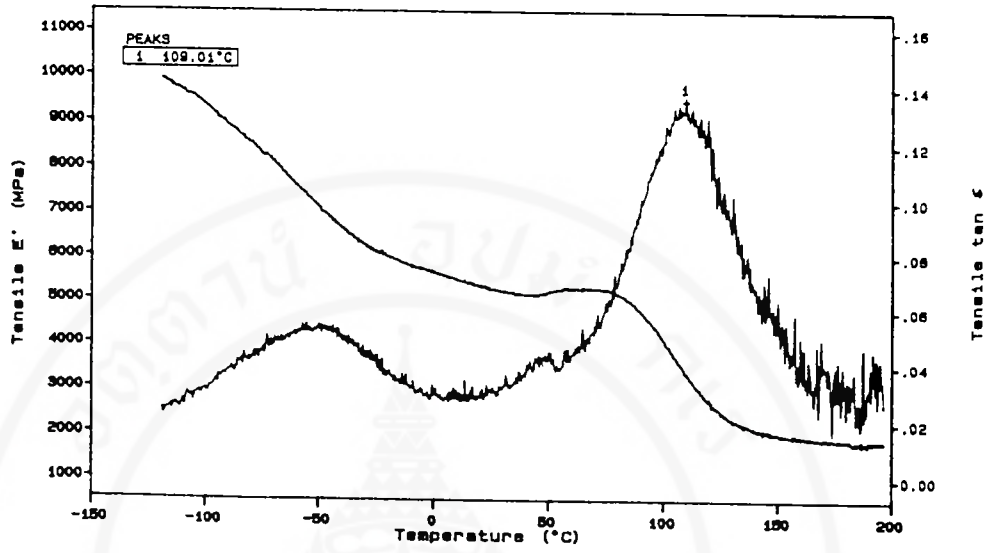



**Figure 3.25** Show the DMTA curves of grafted polyester at monomer : fabric ratio 0.5:1 (filling yarn)

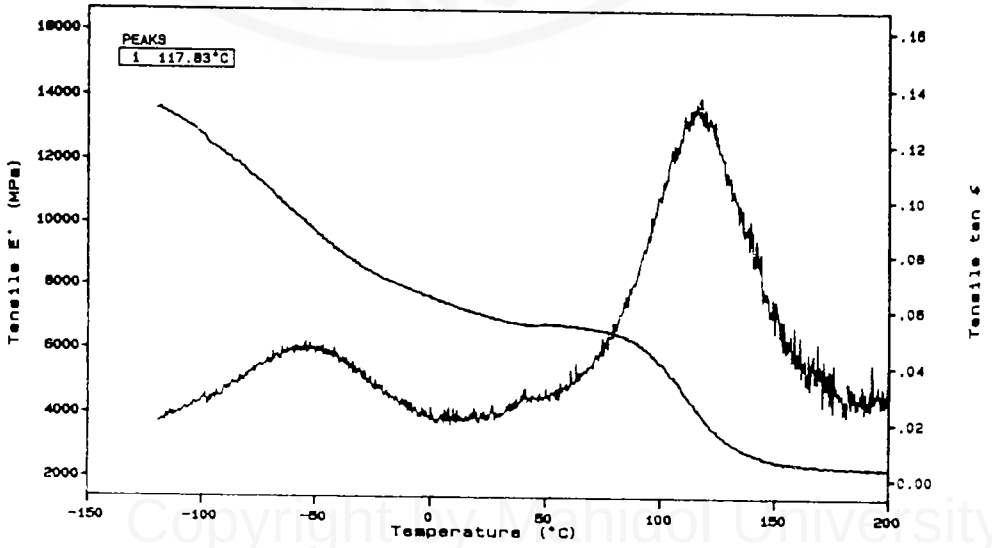



**Figure 3.26** Show the DMTA curves of grafted polyester at monomer : fabric ratio 0.5:1 (warp yarn)

Copyright by Mahidol University

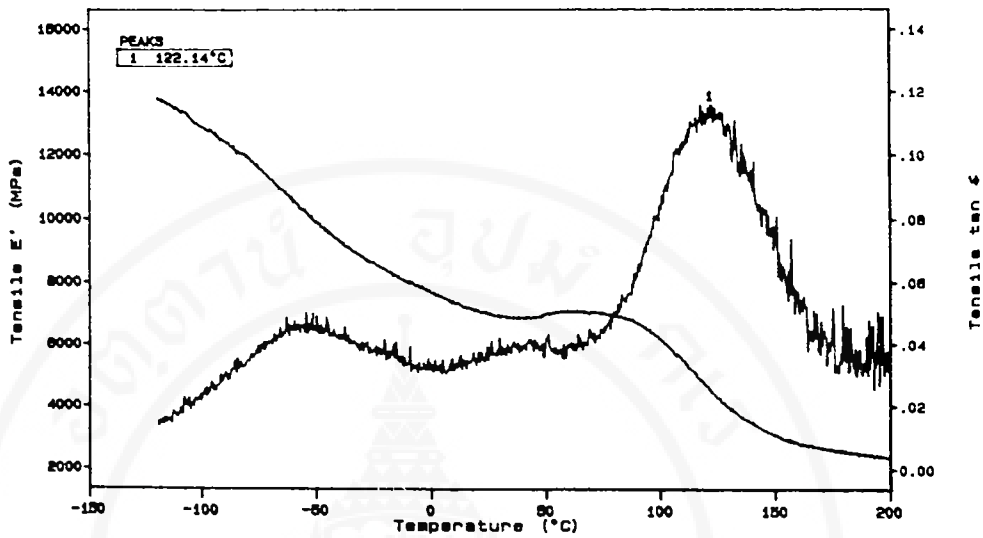
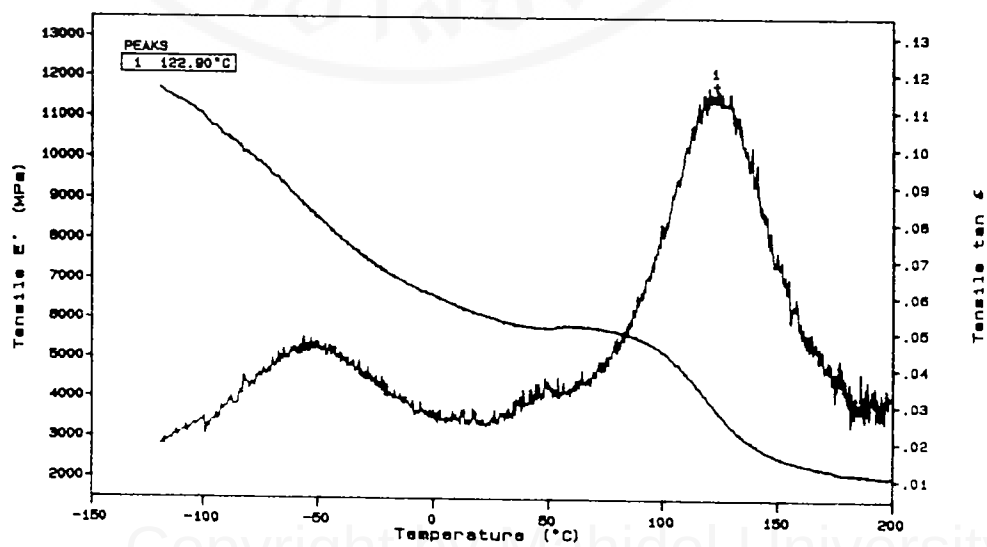



**Figure 3.27** Show the DMTA curves of grafted polyester at monomer : fabric ratio 1:1 (filling yarn)




Copyright by Mahidol University

**Figure 3.28** Show the DMTA curves of grafted polyester at monomer : fabric ratio 1:1 (warp yarn)

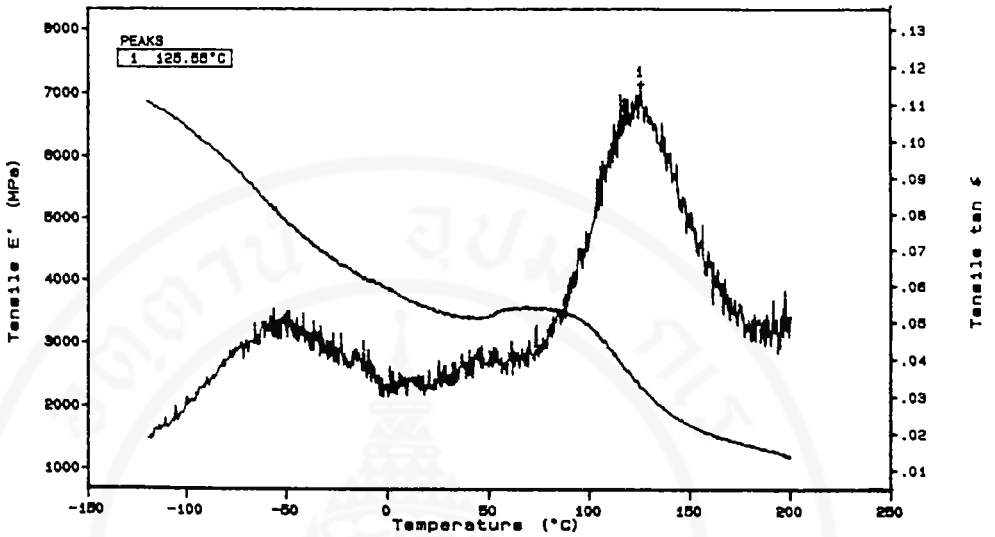



**Figure 3.29** Show the DMTA curves of grafted polyester at monomer : fabric ratio 1.5:1 (filling yarn)

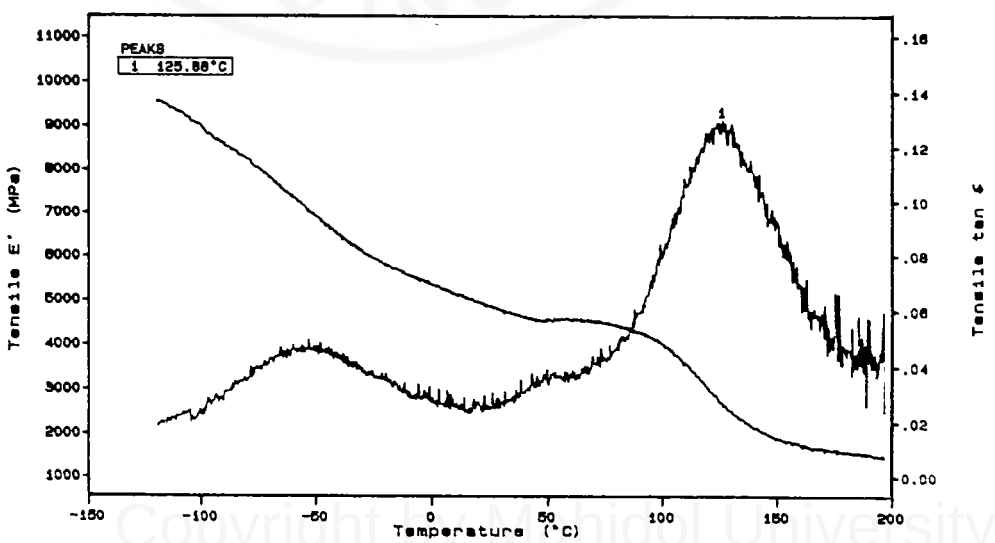



**Figure 3.30** Show the DMTA curves of grafted polyester at monomer : fabric ratio 1.5:1 (warp yarn)

Copyright by Mahidol University

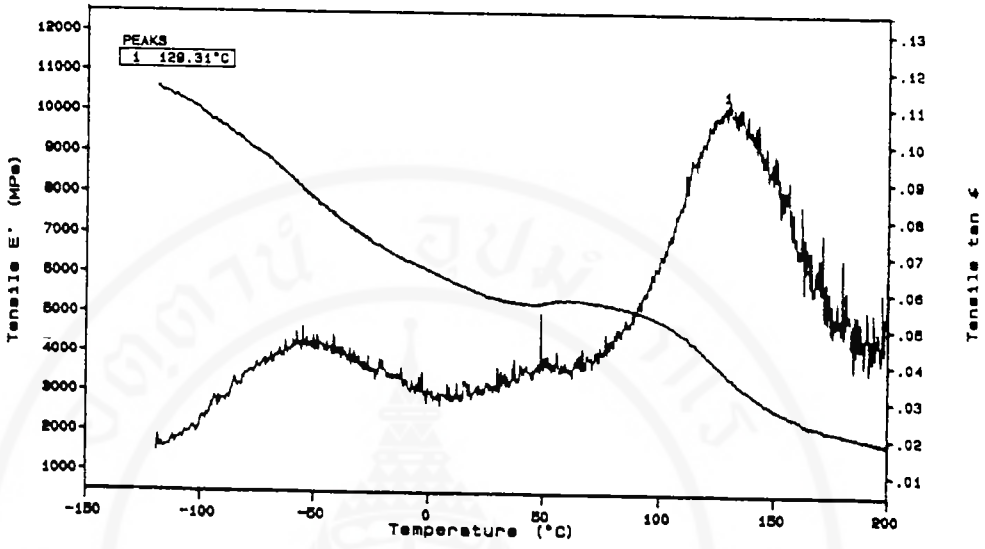



**Figure 3.31** Show the DMTA curves of grafted polyester at monomer : fabric ratio 2:1 (filling yarn)

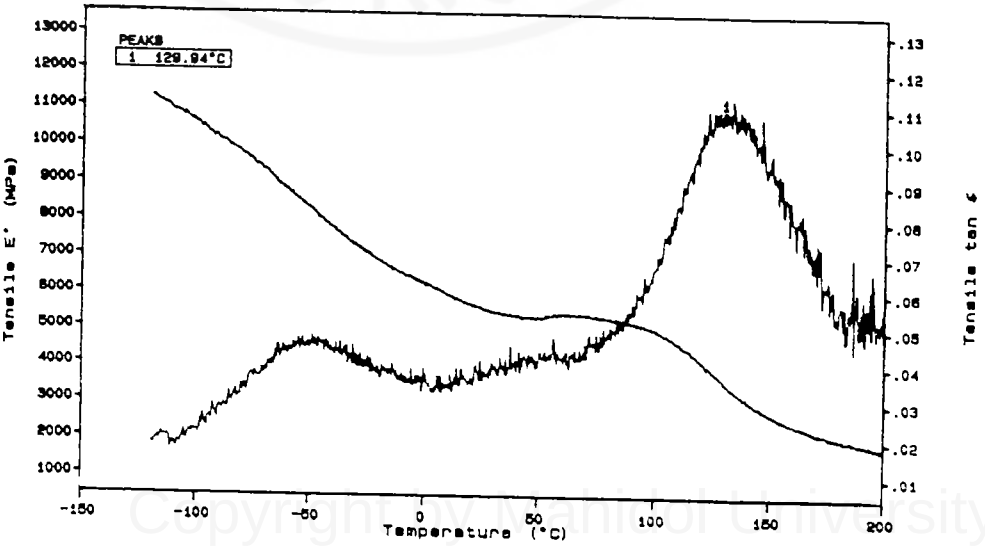



**Figure 3.32** Show the DMTA curves of grafted polyester at monomer : fabric ratio 2:1 (warp yarn)

Copyright by Mahidol University

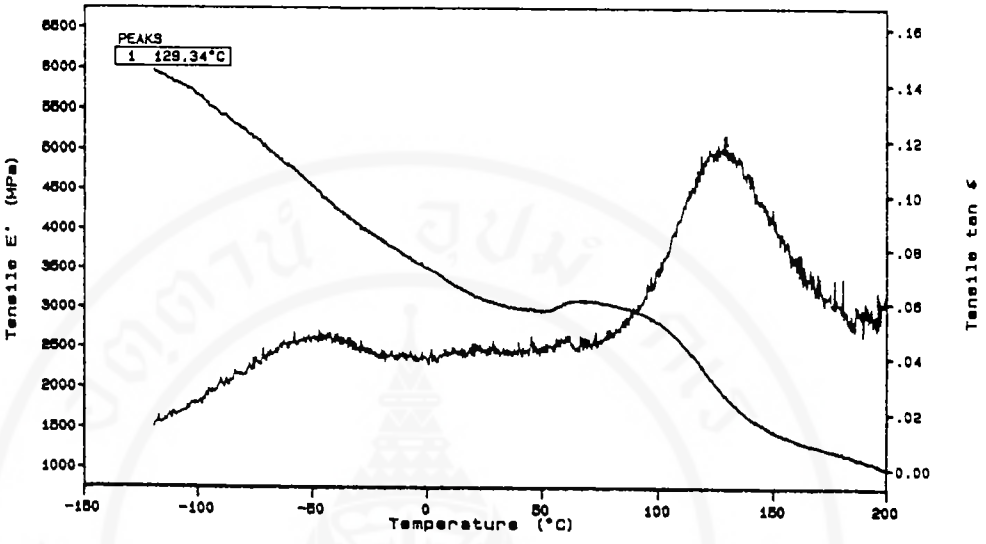
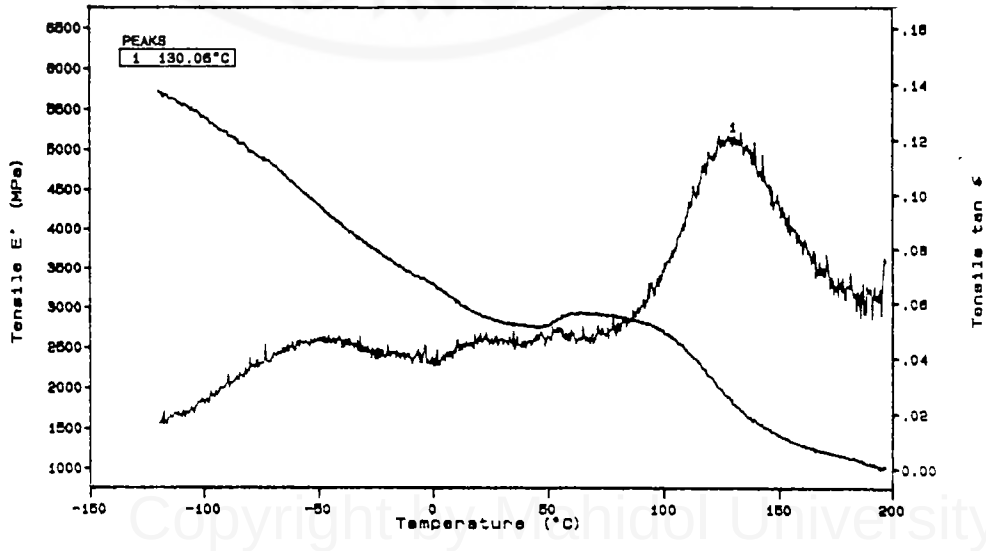



**Figure 3.33** Show the DMTA curves of grafted polyester at monomer : fabric ratio 2.5:1 (filling yarn)




Copyright© by Mahidol University

**Figure 3.34** Show the DMTA curves of grafted polyester at monomer : fabric ratio 2.5:1 (warp yarn)

**Table 3.15** Glass transition temperatures of modified polyester fabrics modified with various monomer to fabric ratios

| Monomer:fabric | Graft yield(%) | Tg (°C) | |
|---|---|---|---|
| | | Filling yarn | Warp yarn |
| ungrafted PET | - | 105 | 116 |
| 0.5 : 1 | 0.7 | 109 | 118 |
| 1 : 1 | 5.3 | 122 | 123 |
| 1.5 : 1 | 11.5 | 126 | 126 |
| 2 : 1 | 21.6 | 129 | 130 |
| 2.5 : 1 | 32.2 | 129 | 131 |

Tg of modified polyesters increased with increasing of the monomer concentration ratios. This effect is believed to result from a change in the structure of the fibre.

Copyright by Mahidol University

**The α-transition**

The mechanical α-transition in polyester is due to the chain motions in the amorphous phase and is, therefore, related to Tg.

The higher temperature transition involves both the motions of the methylene groups and the motion of the benzene rings (31) (see Figure 3.35).

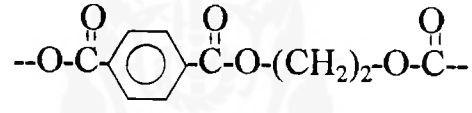


**Figure 3.35** Chemical structure of poly(ethylene terepthalate)

The influence of polarity next to the main chain, or farther removed from the main chain are found to increase Tg (α-transition shifts to higher temperature) (32). Therefore, the increases in Tg of both filling yarns and warp yarns were believed to be due to the presence of grafted PMAA on the PET molecules. Tg of MAA is 228°C (33). Therefore, the Tg of modified polyester was not effected from interference of PMAA. Such increases with increasing monomer to fabric ratio indicated the occurrence of greater number of grafted chains.

Copyright by Mahidol University

The formation of two types of macroradical in PET were suggested to be mostly on the aliphatic segment and to a much lesser extent on the aromatic segments of the PET chains (29). Therefore, the formation of grafted side chain (PMAA) should occur mainly in the aliphatic segment of PET and the minor quantity formed on the aromatic segment.

The shoulder peak at 50°C (see Figures 3.25-3.34), it may be effect of orientation of polyester by grafting of MAA onto polyester fabric. In ungrafted polyester (see Figures 3.23 and 3.24), there is high orientation, the loss peak at 50°C did not appear (The molecular motions are hinder by orientation of the polymer). When grafted polyester fabric with MAA, the orientation of PET decreases. It is this state which gave rise to the loss peak at 50°C. These interpretation were based on the orientation study of PET by Illers and Breuer(34).

**The β-transition**

From Figure 3.23-3.24, it is seen that these appeared a peak at -50°C for unmodified PET. For PMAA modified polyester, similar peak also appeared -50°C (see Figure 3.25-3.34). The presence of this peak (call β peak) was also reported by Schmidt and Gray (35) and was attributed to the motions of -COO group in trans conformation. (-COO can appearing two

Copyright by Mahidol University

conformations, gauche and trans- see Figure 3.36. The gauche conformation peak appears at-105°C.)

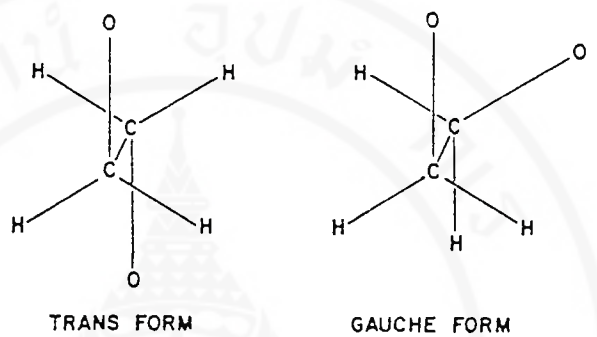



**Figure 3.36** Gauche and Trans-form for the -O-$CH_2$-$CH_2$-O- group in PET

Therefore, the β-transition of modified polyester was not affect by grafting. This may be because the grafted side chain (PMAA) occured mainly in the -$CH_2$ segment of PET.

### 3.3.4 Tensile Properties

The tensile properties of the modified polyester fabrics MAA were measured. The results obtained are shown in Table 3.16 and Figure 3.37.

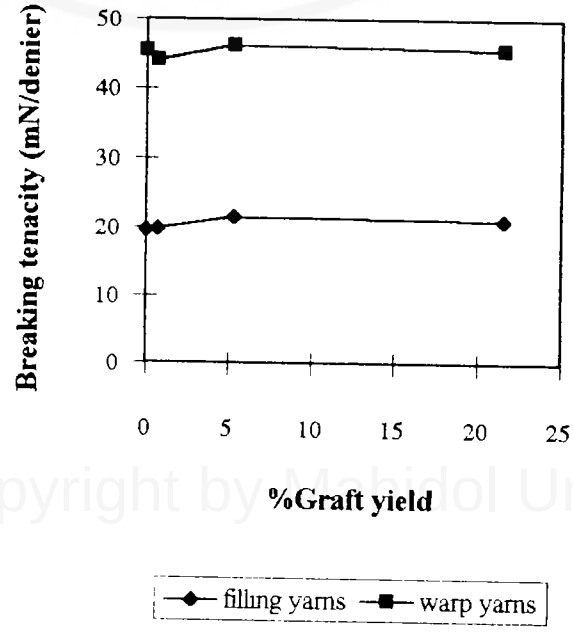
Copyright by Mahidol University

**Table 3.16** Tensile property of modified polyester yarns

| Monomer:fabric | Graft yield(%) | Tensile strength (mN/denier) | |
|---|---|---|---|
| | | Filling yarns | Warp yarns |
| polyester yarn | 0 | 19.7 | 45.4 |
| 0.5 :1 | 0.8 | 19.8 | 44.0 |
| 1 : 1 | 5.6 | 21.5 | 46.2 |
| 2 : 1 | 20.1 | 21.1 | 45.6 |

Conditions : reaction temperature 90°C

reaction time 2 hours




Copyright by Mahidol University

**Figure 3.37** Effect of graft yield on tensile property of polyester yarns

The grafting of MAA onto polyester fabric was found to have almost no effect on the tensile property of the fibres making up the fabrics. This may provide the evidence that grafting occurred only on the surface of the polyester fabric. If modification occurred throughout the fibre structure, change in tensile property would be expected.

### 3.3.5 Measurement of Thickness of Modified Polyester Fabrics

The thicknesses of polyester fabrics grafted with MAA were measured. The results obtained are given in Table 3.17 and Figure 3.38.

**Table 3.17** Thickness values of MAA grafted polyester fabrics

| Condition | Graft yield (%) | Thickness (mm) |
|---|---|---|
| ungafted polyester | 0 | 0.38 |
| 0.5 : 1 | 0.7 | 0.39 |
| 1 : 1 | 5.3 | 0.39 |
| 1.5 : 1 | 11.5 | 0.42 |
| 2 : 1 | 21.6 | 0.47 |
| 2.5 : 1 | 32.2 | 0.50 |

Condition : polymerisation time 90 minutes

Copyright by Mahidol University

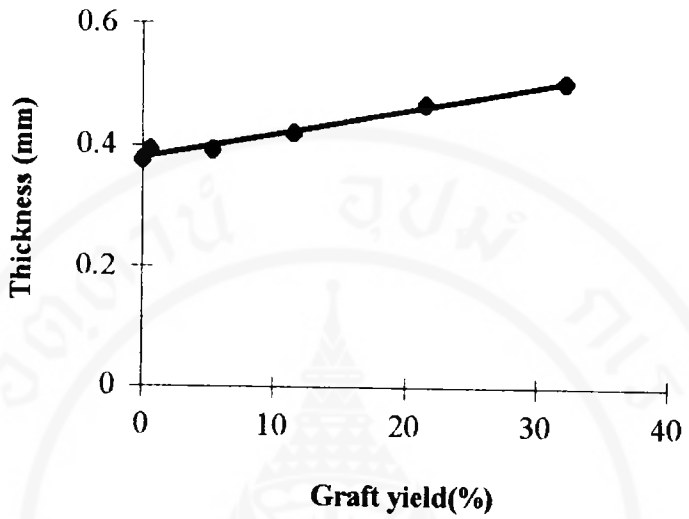


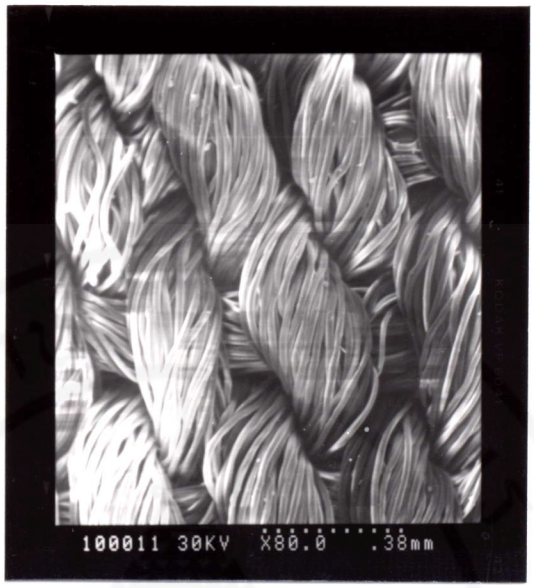

**Figure 3.38** Relation between percent graft yield and thickness of polyester fabrics

It will be seen from Table 3.17and Figure 3.38 that the thicknesses of the fabrics increased with increasing graft yield. Furthermore, the stiffnesses (from feeling) of fabrics also increased with increasing monomer to fabric ratios. Scanning electron micrographs were also taken to see any changes in the structure of the grafted polyester fabrics. Figures 3.39-3.41 show scanning electron micrographs of ungrafted polyester and MAA grafted polyester fabrics. As a result of grafting, the fabric structure became much more densely packed. The fibre surface became increasingly rough with small clusters of the MAA attached to it.

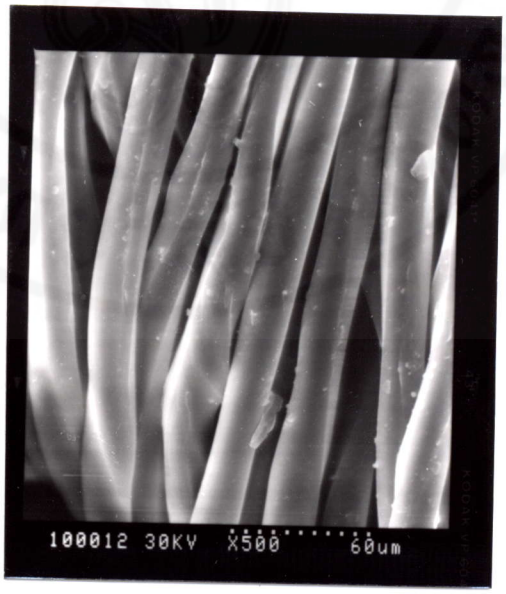
Copyright by Mahidol University

The increases in the size of the fibres after modification reaction were also reported by Celik and coworker (36). The results obtained from both the thickness measurement and the SEM might be the evidence that grafting of PET fabrics took place mostly on their surfaces. A strong evidence to support this conclusion was that the thickness of the fabrics, or more precisely the diameter of the fibres, showed increases with increases in graft yield.

Copyright by Mahidol University




a

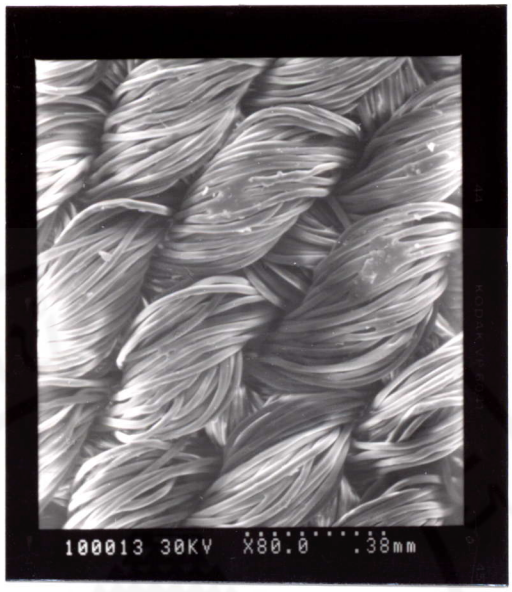



b

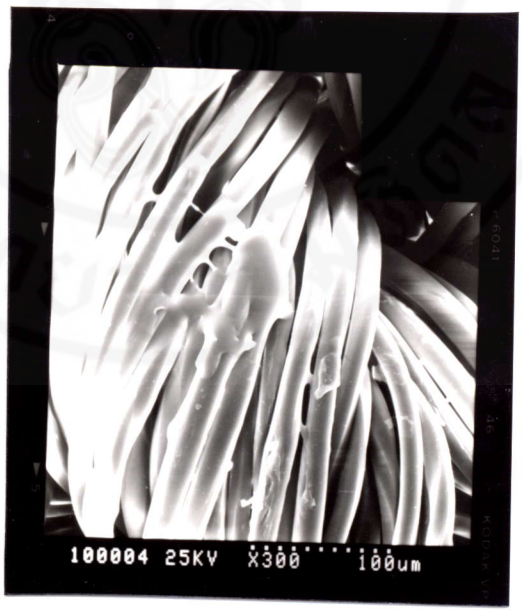
Copyright by Mahidol University

**Figure 3.39** SEM micrographs of an ungrafted polyester

a. magnification 80 x b. magnification 500 x




a




b

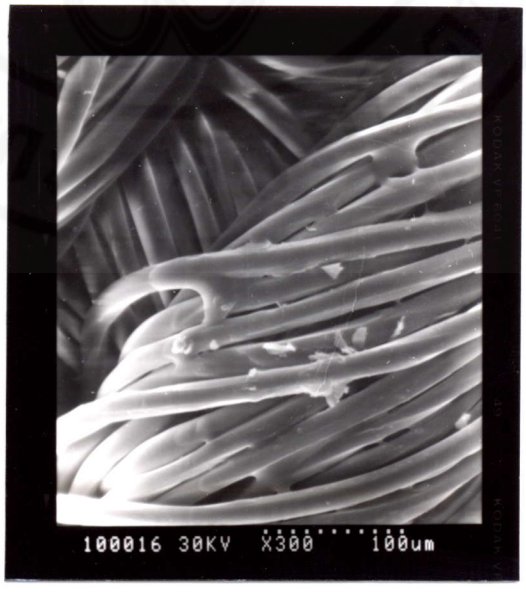
**Figure 3.40** SEM micrographs of polyester fabric grafted with MAA at monomer tofabric ratio 1: 1 a. magnification 80 x

b. magnification 300 x c. magnification 300 x

d. magnification 300 x e. magnification 500 x

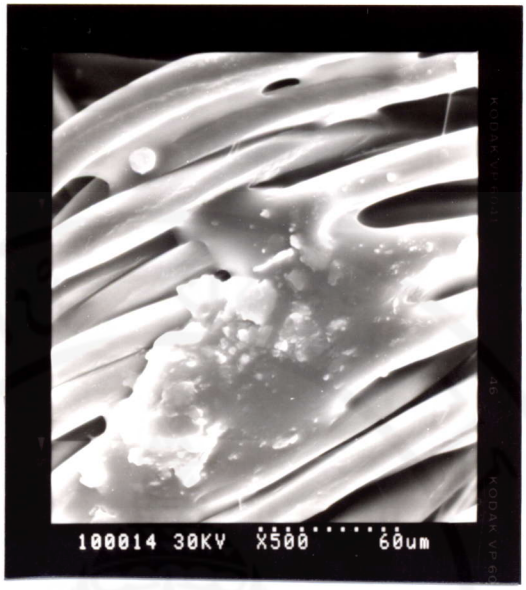
Copyright by Mahidol University

c



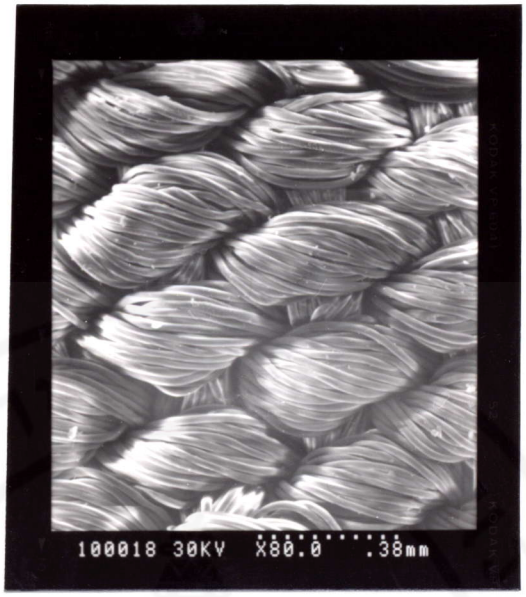

d

Copyright by Mahidol University

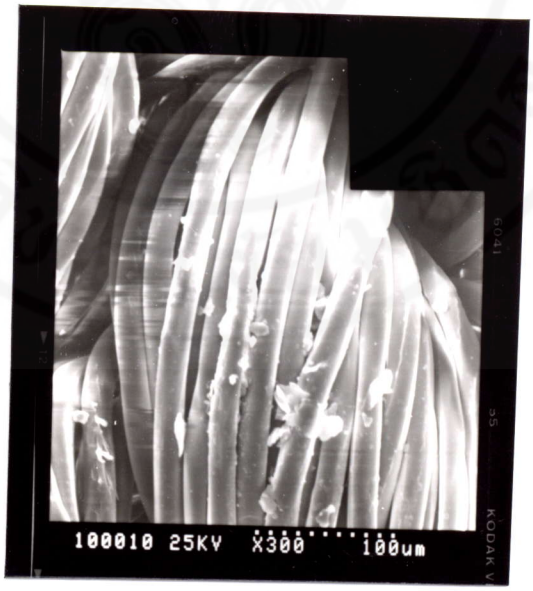



e

Copyright by Mahidol University




a




b

Copyright by Mahidol University

**Figure 3.41** SEM micrographs of polyester fabric grafted with MAA at monomer to fabric ratio 2.5 : 1

a. magnification 80 x b. magnification 300 x

### 3.3.6 Treatment of Modified Polyester with NaOH

Since the modified polyester fabrics obtained were noticetably stiff, it was thought interesting to try treating the modified fabrics with NaOH, in order to see whether the modified fabrics could be made softer with this treatment. The effects of treating ungrafted polyester fabric and polyester fabrics grafted with MAA are shown in Table 3.18.

**Table 3.18** Percentage weight loss of polyester fabrics after treatment with NaOH solution

| Monomer:fabric | NaOH (%w/v) | Treatment time (min) | Weight loss (%) |
|---|---|---|---|
| ungrafted polyester | 2 | 60 | 8.0 |
| | 4 | 60 | 21.5 |
| 1 : 1 | 4 | 10 | 49.7 |
| 2.5 : 1 | 4 | 5 | sample - disintegrated |
| | 0.1 | 60 | 3.3 |

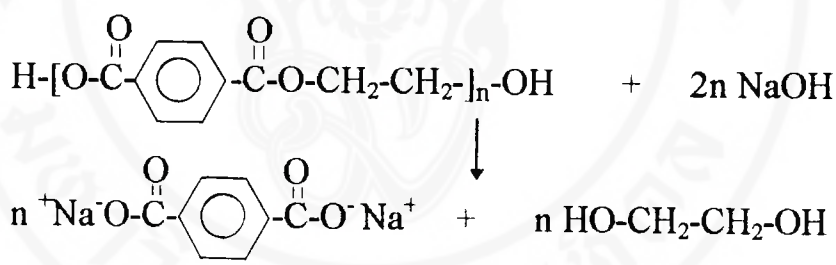
Conditions : material to liquor ratio 1: 30

temperature 95°C

Copyright by Mahidol University

It will be seen that weight loss of polyester fabrics, both ungrafted and grafted, occurred following the alkali treatment. The % weight loss of the ungrafted polyester showed increase with the increase in the concentration of NaOH.

Treatment of PET with NaOH cause hydrolysis of the former. The reactions that occur are believed to be as shown below (37).




Disodium terephthalate Ethylene glycol

For grafted PET fabrics, hydrolysis by treatment with NaOH occurred more quickly and more extensively than ungrafted polyester fabric. The data of Table 3.18 showed that the % weight loss of the modified fabric after treatment with 4% NaOH was 49.7% and occurred in only 10 minutes compared with the loss of 21.5% in 60 minutes exhibited by the ungrafted PET.

Copyright by Mahidol University

For highly-modified polyester fabric (monomer : fabric ratio of 2.5:1), treatment with 4% NaOH solution caused disintegration of the fabric in 5 minutes. This was surpeising and could not be understood at present. Further work will be required in order to elucidate this behaviour of modified PET.

The NaOH-treated fabrics were also examined by SEM. The results obtained are shown in Figures 3.42-3.44. It will be seen, by comparison between Figure 3.39a and Figure 3.42, that treatment of PET fabric with NaOH caused loosening of the fabric. The size of the fibre also appeared to become smaller after treatment with NaOH (Figure 3.42b V.S. Figure 3.39b). The reduction in size of the treated fibre was in agreement with the observed weight loss noted.

The loosening, even broken fibre, and thining of PET fibres after treatment with NaOH were more obvious in NaOH-treated modified polyester fabrics. These can be seen in the SEM micrographs of Figures 3.43a and 3.43b.

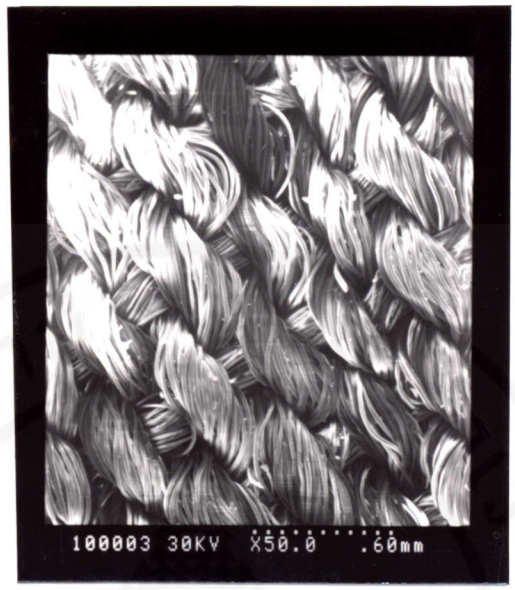
When the monomer : fabric ratio was 2.5:1, the resulting fabrics treated with NaOH showed residues on the surface of the fibres as shown in Figure 3.44a and 3.44b . It was thought that the residues collected on the surfaces of the fibres were hydrolysed PMAA grafted to the surface of the

Copyright by Mahidol University

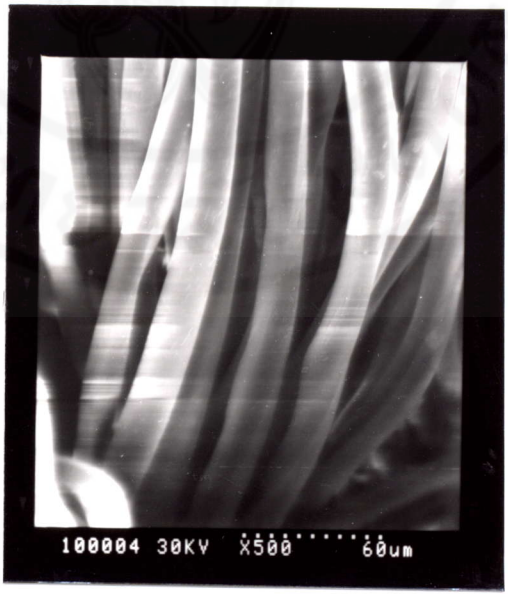
fibre fabrics. If this interpretation was correct, the evidence obtained confirmed that grafting of PMAA onto PET fabrics occured on the surface of the fabrics or, more precisely, the surfaces of the fibres.

It should also be noted that NaOH-treated modified PET fabrics become softer compared with the untreated samples.

Copyright by Mahidol University




a

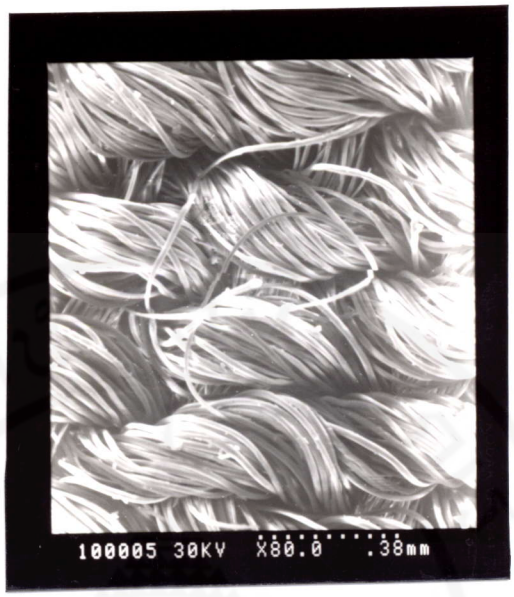



b

Copyright by Mahidol University

**Figure 3.42** SEM micrographs of hydrolysis polyester fabric in 4% NaOH

a. magnification 50 x b. magnification 500 x



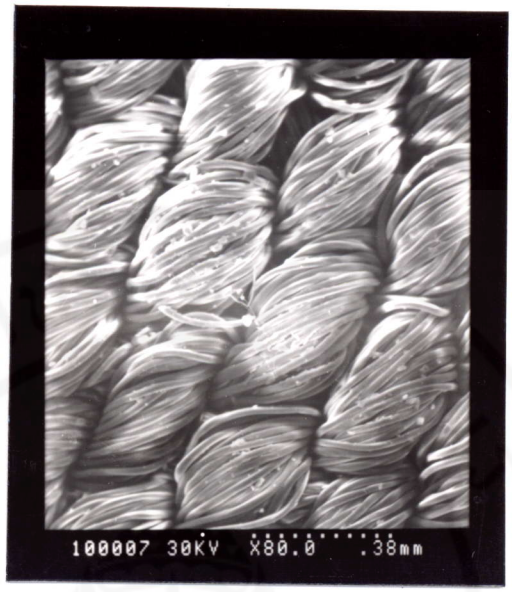

a

b

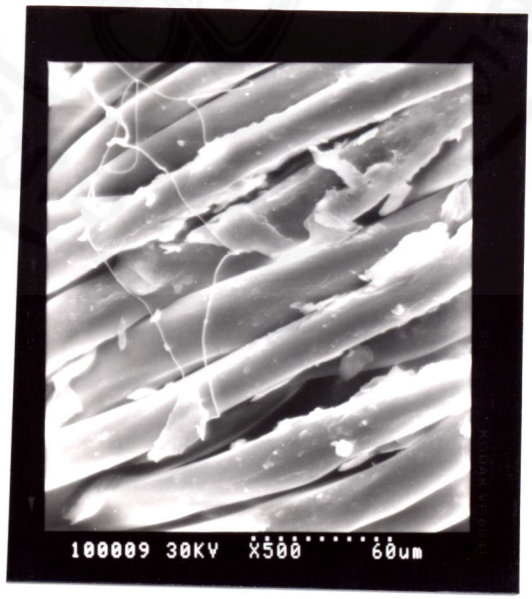
Copyright by Mahidol University

**Figure 3.43** SEM micrographs of hydrolysis polyester fabric grafted with MAA at monomer to fabric ratio 1 : 1 and in 4% NaOH

a. magnitfication 80 x b. magnification 500 x




a




b

Copyright by Mahidol University

**Figure 3.44** SEM micrographs of hydrolysis polyester fabric grafted with MAA at monomer to fabric ratio 2.5:1 and in 0.1% NaOH

a. magnification 80 x b. magnification 500 x

# CHAPTER IV

# CONCLUSIONS

The following conclusions could be made from the present studies of modification of polyester fabrics with MAA,

1. The polyester fabrics could be modified by grafting with PMAA. Swelling of the fabrics in benzyl alcohol was, however, required prior to carrying out the reactions, in water medium. Unswollen fabrics led to no grafting occurring.

2. The extent of grafting (%grafting) was found to depend on the initiator (BPO) concentration, the reaction temperature and the monomer to fabric ratio. Therefore, the % grafting could be controlled by adjusting these three parameters.

3. The amount of water uptake of the modified PET fabrics was found to increase with the increase in the % grafting. For the % grafting between 5 and 32, the moisture regains varied between 1 and 4.6 %

4. The modified polyester fabrics were found to become stiffer than the unmodified fabrics. However, the tensile strengths of the modified fibres were unaffected by grafting.

Copyright by Mahidol University

5. The modified polyester fabrics could be made softer by treatment with aqueous sodium hydroxide solution. The stability of the modified fabrics against sodium hydroxide treatment, however, was found to decrease with increasing % graft yield and increasing concentration of sodium hydroxid. Under unfavourable condition, the modified fabrics could disintegrate within minutes. The reason for the decrease in stability of the modified polyester fabrics toward sodium hydroxide solution was still not known.

6.The modified polyester fabrics could be characterised by solvent extraction with methanol (% graft yield), IR spectroscopy, dynamic mechanical analysis and scanning electron microscopy. Raman spectroscopy did not give useful information.

Copyright by Mahidol University

# BIBLIOGRAPHY

1. Joseph M. Introductory Textile Science. third edition. United States of America : Holt Rinechart, 1977 : 134-398.

2. Jacqueline I. K. Polymer : Fibers and Textiles, A compendium New york: John Wiley &Sons, 1990 : 677-678.

3. Hoechst. Pretreatment of Cotton. Federeal Republic of Germany, 1983:

4. Bilimeyer F.W., JR. Textbook of Polymer Science. second edition. New York : John Wiley &Son, 1971 : 514.

5. Ternon (UK) Ltd. of London Synthetic Markets. *Textile Asia.* 1993; **August** : 96.

6. Nunn D.M. The Dyeing of Synthetic Polymer and Acetate Fibre. West Yorkshire : Dyers Company Publications Trust, 1979 : 132.

7. Cerbman B.P. Textile Fibre to Fabric. six edition. New York : Mc Graw-Hill, 1983 : 374-389.

8. Hermann L. Polyester Fibre Chemistry and Technology. German : Wiley-Interscience, 1971 : 392-393.

9. Hebeish A.,Shalaby S.E., and Bayazeed A. M. $H_2O_2$- Induced Graft Polymerisation of Acrylic Acid on Poly(ethylene terepthalate) Fibers. *J. Appl. Poly. Sci.* 1981; **26** : 3245-3251.

Copyright by Mahidol University

10. Datye K. V. Chemical Processing of Synthetic Fibers and Blends. New York : John Wiley and Sons, 1984 : 493.

11. Allcock H.R. and Lampe F.W. Contemporary Polymer Chemistry. London : Prentic-Hall International, 1989 : 156.

12. Kildal K., Olafsen K. and Stori A. Peroxide-Initiated Grafting of Acrylamide onto Polyethylene Surface. *J.Appl.Poly.Sci.* 1992 ; **44** : 1893-1898.

13. Hsieh Y.-L., Pergh C. and Ellison M.S. The Effect of Selected Organic Solvents on the Polymerisation of Acrylic Acid to Poly (ethylene terephthalate) by Glow Discharge. *J.Appl.Poly.Sci.* 1984 ; **29** : 3547-3560.

14. Sanli O. and Pulat E. Solvent-Assisted Graft Copolymerization of Acrylamide on Poly(ethylene terephthalate) Films Using Benzoyl Peroxide Initiator. *J.Appl.Poly.Sci.* 1993 ; **47** : 1-6.

15. Sacak M., Bastug N.,and Talu M. Azobisisobutyronitril Initiated Graft Copolymerization of Methyl Methacrylate onto Poly(ethylene terephthalate) Fibre. *J.Appl.Poly.Sci.* 1993 ; **50** : 1123-1129.

16. Adwait K., Pati N. C. and Nayak P. L. Grafting Vinyl Monomer onto Polyester Fibers III Graft Copolymerization of Methyl Methacrylate

Copyright by Mahidol University

onto Poly(ethyllene terephthalate) Using Potassium Permanganate-Oxalic Acid Redox System. *J.Appl.Poly.Sci.* 1982 ; **27** : 2131-2138.

17. Osipenko I. F. and Martinovicz V.I. Grafting of the Acrylic Acid on Poly(ethylene terephthalate). *J.Appl.Poly.Sci.* 1990 ; **39** : 935-942.

18. Sacak M., Sertkaya F., and Talu M. Grafting of Poly (ethylene terephthalate) Fibers with Methacrylic Acid Using Benzoyl Peroxide. *J. Appl.Poly.Sci.* 1992 ; **44** : 1737-1742.

19. Lokhande H.T. and Teli M.D. Grafting onto Polyester Fibers IV Synergism During Graft Copolymerization of Binary Mixture of Vinyl Monomers onto Polyester Fibers. *J.Appl.Poly.Sci.* 1984 ; **29** : 1843-1856.

20.Hebeish A., Shalaby S.E. and Bayazeed A.M. Graft Polymerisation of Methyl Methacrylate on Poly (ethylene terephthalate) Fibers Using $H_2O_2$ as initiator. *J.Appl.Poly.Sci.* 1981 ; **26** : 3253-3269.

21.Gawish S.M. and Alfy E. El. Grafting 2-Dimethylaminoethyl Methacrylate On Polyester/Polyester Blend Fabrics. *Am. Dyestuff Reporter.* 1993 ; **September** : 66-68.

Copyright by Mahidol University

22. Hebeish A., Shalaby S. and Bayazeed A.M. $H_2O_2$-Induced Graft Polymerisation of Acrylic Acid/Styrene Mixtures on Poly(ethylene terephthalate) Fibers. *J.Appl.Poly.Sci.* 1982 ; **27** : 197-209.

23.Sacak M. and Oflaz F. Benzoyl - Peroxide - Initiated Graf Copolymerization of Poly(ethylene terephthalate) Fibers with Acrylic Acid. *J.Appl.Poly.Sci.* 1993 ; **50** : 1909-1916.

24. Abdel-Bary E.M., Sarhan A.A., and Abdel-Razik H.H. Effect of Graft Copolymerization of 2-Hydroxyethyl Methacrylate on the Properties of Polyester Fibers and Fabric. *J.Appl.Poly.Sci.* 1988 ; **35** : 439- 448.

25. Hunt B.J. and James M.I. Polymer Characterisation. Glasgow : Blackie Academic & Professional , 1993 : 339-340.

26. Tsukada M., Yamamoto T., Nakabayashi N., Ishikava H., and Freddi G. Grafting of Methyl Methacrylate onto Silk Fibers Initiated by Tri-n-Butylborane. *J.Appl.Poly.Sci.* 1991 ; **43** : 2115-2121.

27. Faterpeker S.A. and Potnis S.P. Thermal Characteristics of Poly (ethylene terephthalate) Fibre Grafted with Poly(vinyl acetate) and Poly (vinyl alcohol). J. Appl. Poly. Sci. 1982 ; **27** : 3349-3356.

28. Rao M.H. and Rao K. N. Radiation Induced Grafting of Mixed Monomers onto Polyester and Polypropylene Fibers. *J.Appl.Poly.Sci.* 1987 ; **33** : 2707-2714.

Copyright by Mahidol University

29. Hsieh Y.L., Shinawatra M. and Castilolo M.D. Postirradiation Polymerisation of Vinyl Monomers on Poly(ethylene terephthalate). *J. Appl.Poly.Sci.* 1986 ; **31** : 509-519.

30. Faterpekar S.A. and Potnis S.P. Dyeing of Grafted Polyester Fibre Part I Effect of Polyvinyl acetate Graft on Dyeing Characteristics. *Textile Res. J.* 1981 ; **July** : 448-453.

31. Farrow G., Mc Intosh J., and Ward I.M. *Symp. Macromolecules.* Verlag Chemie Weinheim Section I. Wiesbaden : 1959.

32. Philip E.S. and Lloyd T.J, Thermal Characterisation Techniques. New york ,Marcel Dekker Inc: 1970; 175-176.

33. Rozinskaya I.N., Kharitonova N.E. and Shtarkman B.P. *Vysokomolekul,Soedin.B.* 1969; 11: 892.

34. Illers and Breure *J. Colloid.Sci.* 1963 ; **18** : 1.

35. Schmidt P.G. and Gay F.P. *Angew. Chem.* 1962 ; **74** : 638.

36. Celik M. and Sacak M., Grafting of Acrylamide-Methacrylic acid Mixture onto Poly(ethylene terephthalate) Fibers by Azobisisobutylonitril *J. Appl. Poly. Sci.* 1966 ; **59**: 609-617.

Copyright by Mahidol University

LIBRARY AND INFORMATION CENTER
MAHIDOL UNIVERSITY



37. Haig Zeronian S., Hui-Zhen Wang and Kenneth W. A. Further Studied on the Moisture-Related Properties of Hydrolyzes Poly (ethylene terephthalate) *J. Appl. Poly. Sci.* 1990 ; **41**: 527-534.

Copyright by Mahidol University

36556