# ผลของไดเอทิลีนไกลคอลและไทรเอทิลีนไกลคอลต่อสมบัติของพอลิเอทิลีนเทเรฟแทเลต

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# EFFECTS OF DIETHYLENE GLYCOL AND TRIETHYLENE GLYCOL ON PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE)

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
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จันท์ฑิมาศ โตชัย: ผลของไดเอทิลีนไกลคอลและไทรเอทิลีนไกลคอลต่อสมบัติของพอลิเอทิลีนเทเรฟแทเลต (EFFECTS OF DIETHYLENE GLYCOL AND TRIETHYLENE GLYCOL ON PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE) ) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร.ศุภวรรณ ตันตยานนท์, 64 หน้า.

โคพอลิเอสเทอร์ 2 ชนิด พอลิ(เอทิลีน-โค-ไดเอทิลีนไกลคอลเทเรฟแทเลต)(พีอีที-โค-ดีอีจีที) และพอลิ(เอทิลีน-โค-ไทรเอทิลีนไกลคอลเทเรฟแทเลต)(พีอีที-โค-ทีอีจีที) ถูกสังเคราะห์ผ่านปฏิกิริยาเอสเทอริฟิเคชันของกรดเทเรฟแทลิก(ทีพีเอ) โมโนเอทิลีนไกลคอล(เอ็มอีจี) และโคมอนอเมอร์ 2 ชนิด ไดเอทิลีนไกลคอล(ดีอีจี)และไทรเอทิลีนไกลคอล(ทีอีจี) และจากนั้นทำปฏิกิริยาพอลิเมอไรเซชันแบบควบแน่น ปริมาณของดีอีจีและทีอีจีถูกแปรจาก 0 ถึง 50 โมลเปอร์เซ็นต์ โครงสร้างทางเคมีของโคพอลิเอสเทอร์ถูกวิเคราะห์โดยเทคนิคฟูเรียทรานฟอร์มอินฟราเรดสเปกโทรสโกปีและนิวเคลียร์แมกเนติกเรโซแนนซ์สเปกโทรสโกปี ผลการทดลองได้แสดงให้เห็นว่าโมลเปอร์เซ็นต์ของดีอีจีและทีอีจีในโคพอลิเอสเทอร์มากกว่าสารป้อนในทุกกรณี นอกจากนี้สมบัติทางความร้อนของโคพอลิเอสเทอร์ถูกวัดด้วยเทคนิคดิฟเฟอเรนเชียลสแกนนิงแคลอริเมทรีและเทอร์มอลกราวิเมทริก อนาไลซิส ผลการทดลองบ่งชี้ว่าการเพิ่มดีอีจีและทีอีจีในโคพอลิเอสเทอร์ทำให้ค่าทีจีและทีเอ็มของโคพอลิเอสเทอร์ลดลง นอกจากนี้โคพอลิเอสเทอร์ทั้งหมดมีการสลายตัวทางความร้อนต่ำลงมากกว่าพีอีที และสมบัติเชิงกลได้ถูกทดสอบ พบว่าเปอร์เซ็นต์การยืดตัว ณ จุดขาดเพิ่มขึ้นเพิ่มขณะที่ค่าความทนต่อแรงดึงลดลงเมื่อปริมาณดีอีจีและทีอีจีเพิ่มขึ้น นอกจากนี้ความสามารถในการย่อยสลายทางชีวภาพถูกศึกษาโดยการทดสอบอินวิโทรเดกกราเดชันในสารละลายฟอสเฟตบัฟเฟอร์เป็นระยะเวลา 2 เดือน ผลการทดลองแสดงให้เห็นว่าโคพอลิเอสเทอร์ทั้งหมดถูกย่อยสลายได้มากกว่าพีอีที

สาขาวิชา…ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์. ลายมือชื่อนิสิต……………………………………...
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# # 5072229723: MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEYWORDS: POLY(ETHYLENE TEREPHTHALATE) / DIETHYLENE GLYCOL / TRIETHYLENE GLYCOL

CHANTIMAS TOCHAI: EFFECTS OF DIETHYLENE GLYCOL AND TRIETHYLENE GLYCOL ON PROPERTIES OF POLY(ETHYLENE TEREPHTHALATE). THESIS ADVISOR: ASSOC. PROF. SUPAWAN TANTAYANON, Ph. D., 64 pp.

Two copolyesters, poly(ethylene-co-diethylene glycol terephthalate)(PET-co-DEGT) and poly(ethylene-co-triethylene glycol terephthalate)(PET-co-TEGT), were synthesized via esterification reaction of terephthalic acid(TPA), monoethylene glycol(MEG) and two comonomers, diethylene glycol(DEG) and triethylene glycol(TEG), and then polycondensation reaction. The content of DEG and TEG were varied from 0 to 50 mol%. The chemical structures of copolyesters were analyzed by Fourier transform infrared spectroscopy and Nuclear magnetic resonance spectroscopy. The results showed that the mol% of DEG and TEG in copolyesters were higher than the feed in every case. In addition, the thermal properties of these copolyesters were measured using Differential scanning calorimeter and Thermogravimetric analysis. The results indicated that the copolyesters with increasing DEG and TEG led to the decrease in $T_g$ and $T_m$ of copolyesters. Moveover, all copolyesters had lower thermal decomposition than PET. The mechanical properties were also measured. It was found that percent elongation at break was higher while the tensile strength was lower when DEG and TGE content increased. In addition, the biodegradability was studied by in vitro degradation test in phosphate buffer solution during the period of 2 months. The results showed that all the copolyesters were more degradable than PET.

Field of Student: Petrochemistry and Polymer Science Student's Signature……………………
Academic Year: 2009 Advisor's Signature………………….

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Finally, I would like to dedicate this thesis to my parents and my family for all support. Many thanks to my friends suggestions supports during the course of my research.

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| | |
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| PET | Poly(ethylene terephthalate) |
| MEG | Monoethylene glycol |
| DEG | Diethylene glycol |
| TEG | Triethylene glycol |
| TPA | Terephthalic acid |
| PET-co-DEGT 10 | Poly(ethylene-co-diethylene glycol terephthalate) with 10 mol% DEG feed ratio |
| PET-co-DEGT 20 | Poly(ethylene-co-diethylene glycol terephthalate) with 20 mol% DEG feed ratio |
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| PET-co-TEGT 50 | Poly(ethylene-co-diethylene glycol terephthalate) with 50 mol% TEG feed ratio |
| BHET | Bis(hydroxylethyl)terephthalate |
| Mw | Molecular weight |
| η | Intrinsic viscosity |

| | |
|---|---|
| $T_g$ | Glass transition temperature |
| $T_m$ | Melting temperature |
| $T_c$ | Crystalline temperature |
| FTIR | Fourier Transform Infrared |
| NMR | Nuclear Magnetic Resonance |
| DSC | Differential Scanning Calorimetry |
| TGA | Thermo Gravimetric Analysis |
| $CDCl_3$ | Deuterated chloroform |
| TFA | Trifluoroacetic acid |
| $CH_2Cl_2$ | Dichloromethane |
| THF | Tetrahydrofuran |

# CHAPTER I

# INTRODUCTION

## 1.1 Background

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester that widely used in various applications such as soft drink bottles, packaging films, synthetic fibers, and engineering plastics due to its good physical and mechanical properties and low cost. However, PET also has unsatisfactory properties like poor flexibility, poor solubility and non-biodegradable, Moreover PET is poor processability, due to high melting temperature [1-5].

Over the past years, there are several approaches to improve poor properties of PET. Copolymerization is one the most attractive techniques to improve undesirable properties of PET. There are many types of comonomers that used for copolyester synthesis. Comonomers, such as diethylene glycol (DEG), 1,3-propanediol (PD), 1,4-butanediol (BD) and isophathalic acid (IPA) can be added to improved poor properties of PET [6]. Among these diethylene glycol (DEG) and triethylene glycol (TEG) are very interesting comonomers to improve undesirable properties of PET. Due to they have both hydroxyl end groups which could be use as monomer for polyester synthesis.

Monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) are straight-chain aliphatic compounds terminated on both ends by a hydroxyl group. Monoethylene glycol (MEG), diethylene glycol (DEG) and triethylene glycol (TEG) have one, two and three ethylene groups, respectively, with the ethylene groups in the last two joined by an ether linkage as following Figure 1.1.

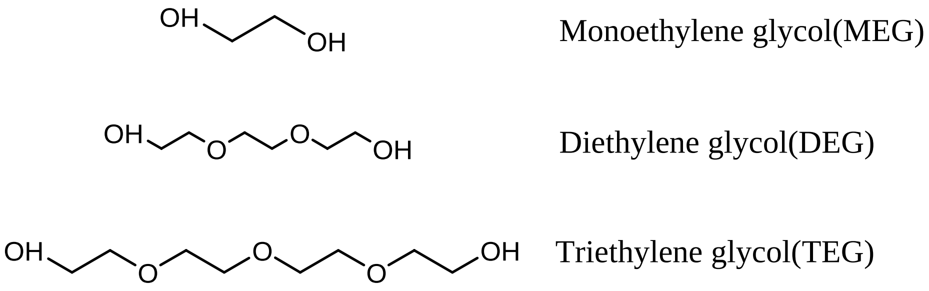
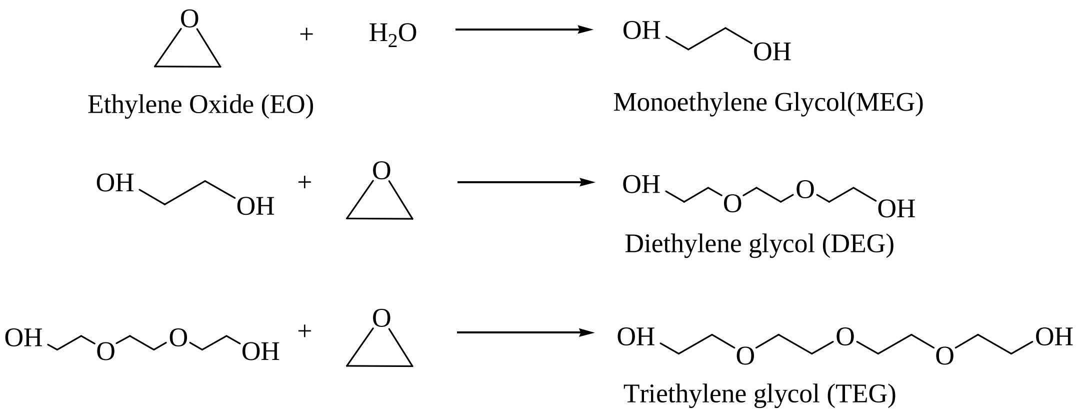


**Figure 1.1** Chemical structures of MEG, DEG and TEG.

Most monoethylene glycol (MEG) is produced by the direct hydration of ethylene oxide. Small amounts of diethylene glycol (DEG) and triethylene glycol (TEG) are by-products in this process. Additional quantities of DEG and TEG can be produced by reacting EG with additional ethylene oxide, as follow in Scheme 1.1.



**Scheme 1.1** Production of DEG and TEG from MEG manufacture.

Large volumes of monoethylene glycol are consumed as polyester fibres, polyethylene terephthalate (PET) plastics, coolants in automobile antifreeze and a solvent in many miscellaneous applications. DEG is an important chemical intermediate in the manufacture of unsaturated polyester resins and plasticisers. The main use for TEG is a liquid desiccant for the dehydration of natural gas and dehumidifiers for air conditioning systems.

DEG and TEG can be added to PET synthesis due to their both hydroxyl end groups which could be used as comonomers to modify the structural properties of PET. Moreover, these glycols have ether functional group which led to increase solubility, flexibility and biodegradability of copolyesters. For the thermal properties of copolyester, the incorporation of these comonomers caused decrease $T_g$ and $T_m$ of polymer chain so it would result in more facilitated and cheaper processing. Besides, the value added by-product (DEG and TEG) from the EG manufacture to synthesize copolyesters, except for desiccant and dehumidifier.

## 1.2 Objectives of the study

1. To synthesize copolyesters, PET-co-DEGT and PET-co-TEGT, using by-product from monoethylene glycol (MEG) manufacture.
2. To study the effect of diethylene glycol (DEG) and triethylene glycol (TEG) on the properties of copolyesters.
3. To investigate the biodegradation of PET-co-DEGT and PET-co-TEGT.

## 1.3 Scope of the research

The scope of this research includes the synthesis and characterization of PET copolyesters containing DEG and TEG as comonomers, employing various amounts of 0-50 mol% of DEG and TEG by using titanium(IV) butoxide as a catalyst. Effects of diol and comonomer molar ratios on thermal, mechanical biodegradable properties of copolyesters are investigated.

# CHAPTER II

# THEORY AND LITERATURE REVIEWS

## 2.1 Poly(ethylene terephthalate)

poly(ethylene terephthalate) (sometimes written Polyethylene terephthalate), commonly abbreviated PET, PETE, or the obsolete PETP or PET-P), is a thermoplastic polymer resin of the polyester family and is used in synthetic fibers; beverage, food and other liquid containers; thermoforming applications; and engineering resins often in combination with glass fiber.

Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline material. The semicrystalline material might appear transparent or opaque and white depending on its crystal structure and particle size. Its monomer (bis-ß-hydroxyterephthalate) can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a byproduct, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a byproduct. Polymerization is through a polycondensation reaction of the monomers (done immediately after esterification/transesterification) with ethylene glycol as the byproduct (the ethylene glycol is directly recycled in production) [7]. The majority of the world's PET production is for synthetic fibers (in excess of 60%) with bottle production accounting for around 30% of global demand. In discussing textile applications, PET is generally referred to as simply "polyester" while "PET" is used most often to refer to packaging applications.

The overall annual world consumption of PET amounts to about 13 million tons, of which 9.5 million tons is processed by the textiles industry, 2 million tons is used in the manufacture of various types of packaging-mainly bottles [8].

## 2.2 History of Poly(ethylene terephthalate)

PET was first synthesized by Carothers and Hill in the late1920s using the melt condensation of dicarboxylic acids and aliphatic diols. However, it had a low melting point and poor hydrolytic stability. Later Whinfield and Dickson [9] discovered poly(ethylene terephthalate)(PET), which possessed a higher melting point (265°C) and showed better chemical resistance due to the presence of more rigid groups in the backbone. In 1949, PET was first commercialized by ICI (Imperial Chemical Industries, Ltd.) under the trade name "Terylene". Later that DuPont bought all legal rights from ICI and manufactured another polyester fiber, which they named Dacron in 1953. Recently, PET is the most important member of polyester group by production volume and sales value.

Nowadays, there are many reports have been studied in synthesis and characterization of PET. In this section, the synthetic methods for the manufacture of PET will be mentioned.

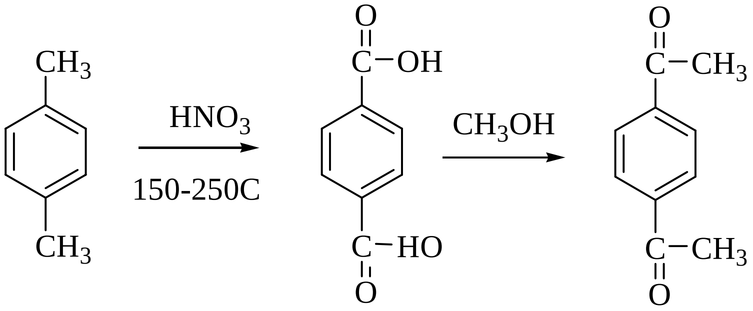
## 2.3 Synthesis of Poly(ethylene terephthalate)

PET is manufactured from monoethylene glycol (MEG) and terephthalic acid (TPA) or dimethyl terephthalate (DMT), the polymerization process involves two steps. The first step is esterification of TPA or transesterification of DMT with EG, followed by the polycondensation by removing excess glycol to promote chain extension.

### 2.3.1 Raw materials

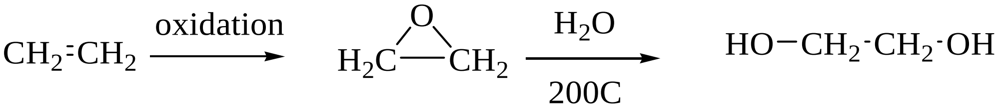
Before 1965, only DMT was used in the large-scale production of polyester because it was easier to obtain the high degree of purity required to produce a high molecular weight polymer without color change. The DMT is obtained by methanol esterification of the crude TPA derived from p-xylene oxidation. Later, development of direct *p*-xylene oxidation followed by purification made pure TPA commercially available. More recently, pure TPA has replaced DMT as the raw material because of advantages in processing, polymer quality and reduced production costs. Thus, in this work we will be synthesized copolyesters via TPA-route.

TPA and DMT could be prepared from *p*-xylene which was reacted by oxidation reaction with nitric acid.



**Scheme 2.1** Process of TPA and DMT.

The monoethylene glycol (MEG) was also used for PET production. The ethylene glycol is derived from ethylene by catalytic oxidation with air to ethylene oxide (EO) followed by acid hydrolysis in Scheme 2.2.



**Scheme 2.2** Process of acid hydrolysis for producing monoethylene glycol.

### 2.3.2 Catalysts and additives

The use of metal compounds as catalysts in the production of PET gave very interest in the study and comparison of their activity, their effectiveness on the polymerization reactions and properties of the final polymers. In the literature various catalysts are described for PET synthesis.

MacDonald studied several catalysts for polycondensation in his paper Germanium oxide is also used. Although it is a more active catalyst than antimony oxide, its high cost precludes common use for commercial PET production [10].

Antimony oxide historically emerged as the catalyst of choice because it demonstrates a good balance between catalytic activity in the presence of the phosphorous-based stabilizer, color, and cost [11]. However, recently antimony containing compounds have become subject to discussion due to their potential hazard to health. Glycol residues from PET have to be burnt in special furnaces or be disposed off as hazardous waste, leading to higher disposal costs. In some PET final products, such as food package or soft-drink bottles, release some antimony compounds, impacting public health [12-15].

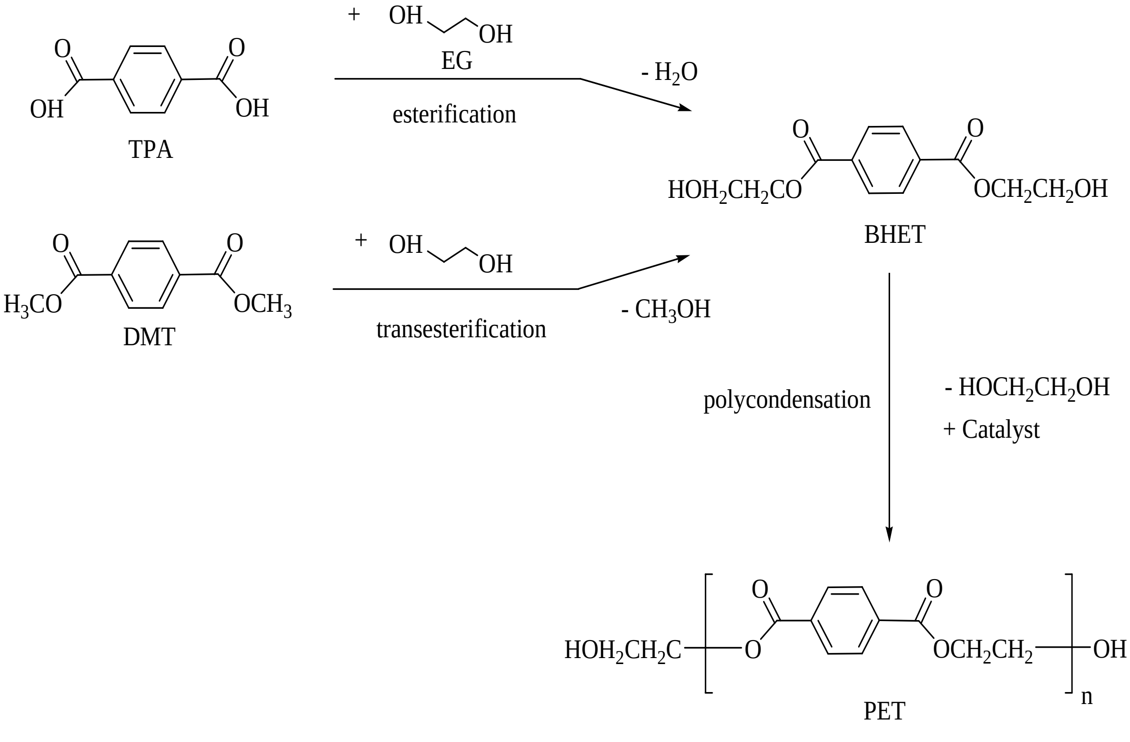
Shan et al. studied the effect of various catalysts on the polymerization reaction of BHET. They polymerized PET with different concentrations of catalysts and reaction temperatures and compared their intrinsic viscosities. The results show that titanium-based catalyst is the most active. The activity of the polycondensation catalysts increases in order Ti>Sn>Sb>Mn>Pb. Moreover, titanium-based catalyst does not give any rise to environmental problems and is available reasonable cost [16]. Thus, in this research we used titanium-based catalyst as a catalyst for the polymerization reaction. Due to this catalyst has effective in both esterification and polycondensation steps.

A phosphorous-based stabilizer is commonly added with the catalyst to prevent color-forming thermal degradation during the polycondensation process. Phosphoric acid ($H_3PO_4$), triethyl phosphate (TEP) and triphenyl phosphate (TPP) are widely used as thermal stabilizers. Gumther et al. reported small amount of triphenyl phosphate did not influence the molecular weight, but amounts larger than 0.04% caused a decrease in molecular weight [17].

### 2.3.3 Polymerization method

The first reaction is esterification reaction, the TPA: EG molar ratio used is 1:1.5-3 and the reaction temperature is usually 240-260˚C. The use of a small monomer feed ratio and high reaction temperature are useful to enhance the solubility of TPA [18]. During the reaction, water is collected into a graduated receiver as a by-product to allow estimation of the extent of conversion.

The second reaction is transesterification reaction, the DMT:EG molar ratio is 1:2.1-2.3 and the reaction temperature should be 170-210˚C. Methanol formed during this reaction as by-product should be collected for the estimation of the reaction conversion. The product from the esterification reaction or transesterification reaction is bis-(2-hydroxyethyl terephthalate) (BHET) which is then further polymerized to PET in successive the polycondensation process. The second reaction is the polycondensation polymerization of BHET to form PET and the elimination of excess EG, this step is conducted under vacuum at 270-285˚C. As summarize in Scheme 2.3.



**Scheme 2.3** Polymerization process of PET.

### 2.3.4 Copolymerization of PET

Although PET has excellent thermal and mechanical properties and high chemical resistance, PET has also unsatisfactory properties like poor solubility, peeling, poor adhesion and non-biodegradable. These can be resolved by incorporation of comonomeric units like containing a second glycol unit or aliphatic unit into the polymer backbone. For example, PET copolymers containing 1,3-propanediol and 2,2-di- alkyl-1,3-propanediol, where the alkyl groups were methyl, ethyl or butyl, were synthesized by Kiyotsukuri et al [19]. Both the glass-transition and melting temperatures decreased with increasing content of the substituted 1,3-propanodiols. Kint studied in detail the crystallization behaviour of PET copolymers containing 2,2-butyl-ethyl-1,3-propanediol and concluded that the crystallinity and the crystallization rate decreased significantly upon the incorporation of this comonomer [20].

As another sample which DEG as a comonomer, Frank and Zachman reported that increasing the content of DEG up to 15 mol% caused decrease the crystallization rate of the PET Farikov et al. reported that the glass transition temperature ($T_g$) and melting temperature ($T_m$) were decreased when DEG units incorporation into PET backbone [21].

Though there are many reports about effect of DEG units on the PET thermal properties, there are few data concerning the mechanical and degradable properties of copolyesters which containing DEG and TEG in the copolymer backbone. Thereby, in this work we have synthesized copolyesters which incorporate DEG and TEG as comonomers. In addition, the effect of the presence of these comonomers on the thermal and mechanical properties and degradability of copolyesters were studied.

### 2.3.5 Applications

The majority of the world's PET production is for synthetic fibers, which compose the largest segment of the synthetic fiber industry. PET is also widely used in food packaging, such as beverage bottles and frozen food trays that can be heated in a microwave or conventional oven. Considerably, PET bottles due to its excellent barrier materials so it widely used for soft drinks. For certain specialty bottles, PET sandwiches an additional polyvinyl alcohol to further reduce its oxygen permeability.

In addition, a thin film (biaxially oriented PET film, often known by one of its trade names, "Mylar"), PET can be aluminized by evaporating a thin film of metal onto it to reduce its permeability, and to make it reflective and opaque (MPET). These properties are useful in many applications, including flexible food packaging and thermal insulation, such as "space blankets". Because of its high mechanical strength, PET film is often used in tape applications, such as the carrier for magnetic tape or backing for pressure sensitive adhesive tapes.

For non-oriented PET sheet, it can be thermoformed to make packaging trays and blisters. If crystallizable PET is used, the trays can be used for frozen dinners, since they withstand both freezing and oven baking temperatures. When filled with glass particles or fibers, it becomes significantly stiffer and more durable. This glass-filled plastic, in a semi-crystalline formulation, is sold under the tradename Rynite, Arnite, Hostadur, and Crastin.

While most thermoplastics can, in principle, can be recycled, PET bottle recycling is more practical than many other plastic applications. The primary reason is that plastic carbonated soft drink bottles and water bottles are almost exclusively PET, which makes them easier to identify in a recycle stream than other plastic. PET has a resin identification code of 1. One of the uses for a recycled PET bottle is for the manufacture of polar fleece material. Among its many uses, companies, such as English Retreads use the PET material to line their products. It can also make fiber for polyester products. Because of the recyclability of PET and the relative abundance of post-consumer waste in the form of bottles, PET is rapidly gaining market share as a carpet fiber. Moreover, PET is being used for toiletries, cosmetics, and household and pharmaceutical products. Other applications of PET include molding resins, X-ray and other photographic films, magnetic tape, electrical insulation, printing sheets, and food packaging film [22].

Recently, the biodegradable plastics are interesting in various applications, due to its reducing environmental problems. Among these, PET is important class of biodegradable and hydrolyzable polymers. It is well known that PET copolymer could be potentially biodegradable [23] because of their ester bonds in the main chain, which are sensitive to hydrolysis. Such potentially biodegradable polyesters could easily be produced, as a variety of monomers such as ethylene glycol, 1,4-butanediol, adipic acid, and terephthalic acid is available as bulk chemicals. Current medical applications of PET include implantable sutures, surgical mesh, vascular grafts, sewing cuffs for heart valves and components for percutaneous access devices. The biostability of PET is a result of its chemical structure which promotes resistance to hydrolysis due to hydrophobic aromatic groups and high crystallinity.

## 2.4 Previous research works

Dye et al. [24] investigated the chemical properties of three glycols, MEG, DEG) and TEG. These glycols contain two hydroxyl groups attached to separate carbon atoms in an aliphatic chain. Although they have similar chemical structure, their applications vary mainly with physical properties such as viscosity and boiling point. The properties of three glycols are dependent on the molecular weight of glycols. The molecular weight of MEG, DEG and TEG are 62.07, 106.12 and 150.17, respectively. The viscosity of these glycols, mono-, di- and triethylene glycols at 20°C are 1.4318, 1.4472 and 1.4559 centipoise. As the boiling point of three glycols, MEG, DEG and TEG are 197.6, 245.0 and 287.4°C, respectively.

Lotti et al. [25] studied effect of diethylene glycol on the poly(butylenes terephthalate-co-diethylene terephthalate) copolyesters. They synthesized poly(butyleneterephthalate-co-diethylene terephthalate) copolyesters and characterized chemical structure and thermal and rheological properties. They found that all copolymers are partially crystalline and thermally stable up to about 300°C. Moreover, the main effect of copolymerization is a decrease in melting and glass transition temperatures with respect to PBT homopolymer. The presence of diethylene terephthalate units was found to influence slightly the rheological behaviour in the melt.

Gaofu et al. [26] synthesized poly(ethylene-co-trimethylene terephthalate)s by means of the PTA direct polycondensation technology. The results showed that the contents of trimethylene terephthalate (TT) units in the resulting copolyesters are higher than PDO compositions in original diol. Oligomer content in the copolyesters vary with the compositions and attain a minimum value when the TT ingredient is 49.52 mol %. $T_g$ of the copolyesters varied from 78.5°C for PET to 43.5°C for PTT and decreases monotonically with the components. The copolyesters were amorphous copolymers when TT content in the range of 32.4-40.8 mol %, as calculated from the melting enthalpy measured via differential scanning calorimetry.

Oleg et al. [27] synthesized and characterized diethylene glycol terephthalate oligomers. The polyester polyols were prepared by the reaction of TPA and DEG. Condensation of TPA with DEG in a 1:2 molar ratio was carried out at 225–230°C under reduced pressure (250-300 Torr) by various reaction conditions. NMR spectra of the mixtures showed the lower content of DEG that might have been lost from the reaction mixture during the initial vigorous distillation process. A short vigreux column was used because the vigreux column helps to retain DEG in the reaction.

Lee et al. [28] reported that PET and PET copolyesters containing DEG units that were isothermally crystallized from the melt at a relatively high undercooling exhibited three endothermic peaks, whereas only two peaks were observed when small undercoolings were used. The lowest temperature peak invariably appeared at about 10°C above the $T_c$ and it was attributed to the melting of the crystals formed during secondary crystallization. The second peak shifted to higher temperatures and increased in intensity as the $T_c$ increased, and it was attributed to the fusion of the crystals grown during primary crystallization. The highest peak was interpreted as due to the melting of the crystals formed by melting–recrystallization processes taking place upon the heating of the sample.

Zhi et al. [29] prepared poly(ethylene terephthalate)/poly(ethylene glycol) (PET/PEG) copolymer and studied water absorption and in vitro degradation behaviour of copolymers. The results showed that water absorption of PET/PEG copolymers decreased with increase in concentration of PET segment, and it increased with molecular weight of PEG segment. The degradation rate increased with decrease in PET concentration. Furthermore, PEG molecular weight had different effects on degradation rate, which could be confirmed by the SEM observation.

Helene et al. [30] studied on the thermal decomposition of poly(diethylene glycol terephthalate) (PDEGT). They found that a new degradation mechanism specific to DEG units, where random ether groups along the backbone could back-bite and form cyclic oligomers. The results obtained that PET undergoes one step of mass-loss stretching between 345-480°C, and losing 95% of its initial mass. On the contrary, PDEGT saw 20% of its initial mass evolved in a first step starting at 250°C, before undergoing a second mass-loss step, starting around 370°C. They concluded that the existence of a degradation mechanism specific to DEG units due to an intramolecular backbiting of random DEG units onto the polymer chain.

Ivonete et al. [31] studied the inflammatory responsed in vivo and in vitro to samples of biopolymers composed of poly(ethylene terephthalate-co-diethylene glycol terephthalate) plus 0, 5, 25% of polyethylene oxide. They reported that these biopolymers did not induce inflammatory responses when implanted in the peritoneal cavity of mice for 28 days. No significant adhesion of inflammatory cells were observed in vitro, when poly(ethylene terephthalate-co-diethylene glycol terephthalate) blends were used as substratum to cellular adhesion. These results suggested that blends composed of poly(ethylene terephthalate-co-diethylene glycol terephthalate) induced low inflammatory cell adhesion, since no rejection of biopolymer was observed when implanted in experimental animal models.

Zhang et al. [32] studied on the biodegradability of polyethylene terephthalate fiber and diethylene glycol terephthalate by microbes and 40% by lipase. The degradation of DTP can be described by the first-order reaction model. Although the biodegradation ratio of PET fiber was still weak, they demonstrated with SEM micrographs and HPLC analysis that microbes and lipase could act on the PET fiber and there were some cracks on the surface of the fiber. Microbes screened showed significant degradation of DTP and the degradation ratio could amount to over 90%.

# CHAPTER III

# EXPERIMENTAL

This work is divided into 3 parts : synthesis, characterizations and measurement of thermal and mechanical properties and degradation property of copolyesters.

## 3.1 Materials

1. Terephthalic acid (Siam mitsui PTA, Co., Ltd.)
2. Ethylene glycol (PTT Chemical Public Co., Ltd.)
3. Diethylene glycol (PTT Chemical Public Co., Ltd.)
4. Triethylene glycol (PTT Chemical Public Co., Ltd.)
5. Titanium(IV) butoxide
6. Chloroform-d
7. Trifluoroacetic acid
8. Dichloromethane
9. Tetrahydrofuran

## 3.2 Equipments

1. FTIR, Perkin-Elmer Spectrum One Spectrometer
2. NMR, Varian Mercury (400MHz)
3. DSC, Mettler Toledo, TGA/SDTA 851
4. TGA, PerkinElmer DSC-7 instrument
5. Instron 1011 universal testing machine
6. Scanning electron microscope (SEM), JEOL model JSM-5800LV

## 3.3 Synthesis of copolyesters

The copolyesters were synthesized by direct esterification and polycondensation. EG, DEG or TEG (vary mol% 0, 10, 20, 30, 40 and 50), TPA and $Ti(OBu)_4$ were placed in a 500 ml round bottom flask under nitrogen. The reaction mixture was stirred for 30 minutes to mix the reaction mixture as homogeneous as possible. The reaction temperature was heated to 220°C for 2 h under atmospheric pressure, and then the reaction temperature was raised to 270°C for 3 h under vacuum to facilitate polymerization. Care was taken to see that the stirring was continuous and atmospheric leak into the system was avoided. Then the reaction was stopped, the resultant melt was poured in another flask. The synthesis procedure is summarized in Scheme 3.1.

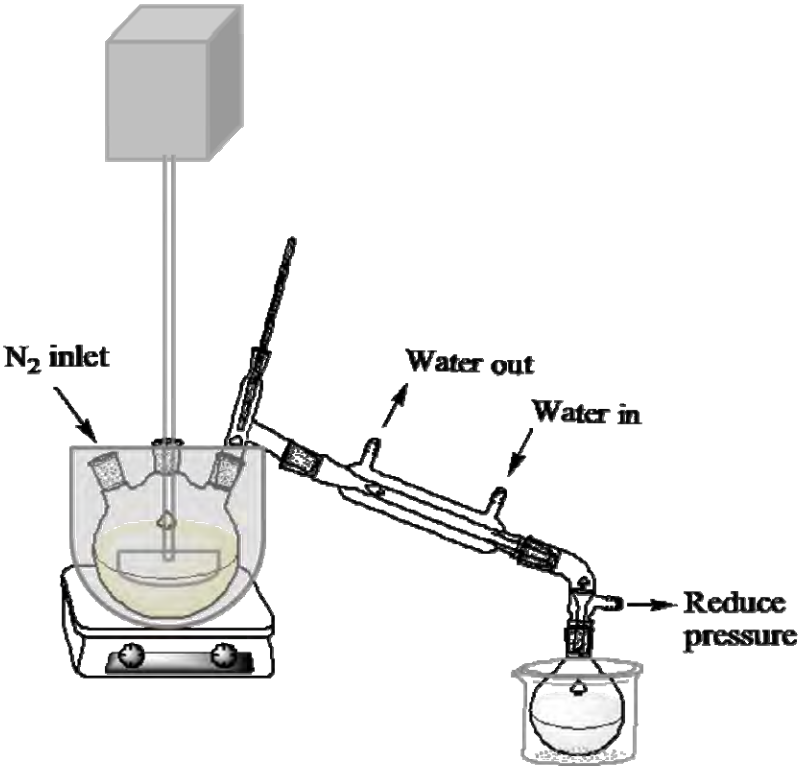
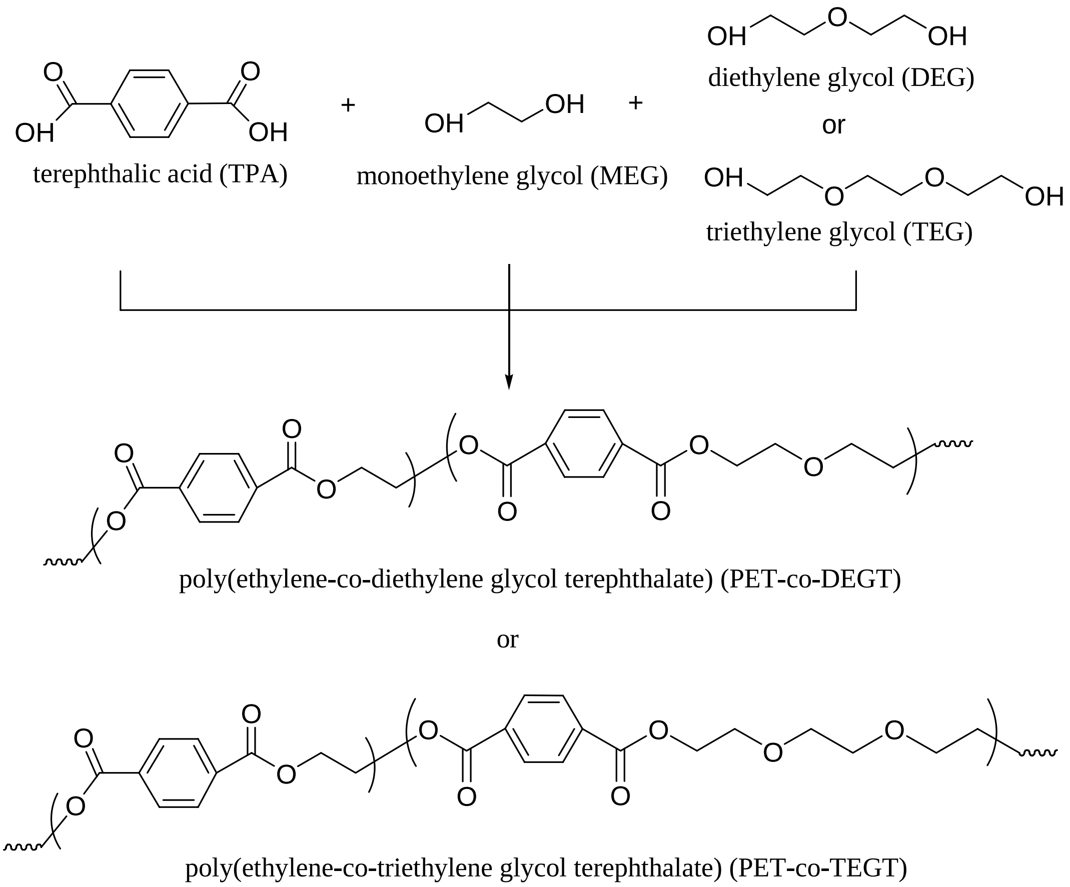


**Figure 3.1** Graphical illustration of the synthesis procedure.



**Scheme 3.1** Summary of the synthesis reaction of copolyesters.

## 3.4 Characterizations of copolyesters

### 3.4.1 Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded on Perkin-Elmer Spectrum One Spectrometer using a transmission mode. The solid sample was prepared into the KBr pellet by mixing with KBr powder.

### 3.4.2 Nuclear magnetic resonance (NMR) spectroscopy

$^1$H NMR spectra were recorded on a Varian Mercury (400MHz), using chloroform-d / trifluoroacetic acid (TFA) (4/1 mL/mL) as the mixed solvent. The NMR spectra were treated using MestReC 2.1.1 (Magnetic Resonance Companion, NMR Data Processing Program).

### 3.4.3 Thermogravimetric analysis (TGA)

TGA analysis were carried out under nitrogen on a PerkinElmer DSC-7 instrument at heating rate of 20°C/min from 50°C to 650°C using sample of approximately 10 mg.

### 3.4.4 Differential scanning calorimetry (DSC)

DSC analyses were carried out under nitrogen on a Mettler Toledo, TGA/SDTA 851. The samples were heated to 300°C at a heating rate of 20°C/min. Then the samples were quickly cooled to room temperature and heated again to 300°C at rate of 10°C/min, using sample approximately 3-5 mg.

## 3.5 Solubility test

Solubility of copolymers was determined by dissolve 0.5 g of samples in 10 ml of dichloromethane ($CH_2Cl_2$) or tetrahydrofuran (THF) at room temperature. If there are samples undissolved placed them in an ultrasonic water bath for 10 minutes, at 40˚C.

## 3.6 Swelling test

The samples were placed in small bottle containing 10 ml of deionized water and were kept at 37°C for 24 h in an incubator. The samples were taken out and surplus surface to remove excess water with filter paper. Water absorption was calculated according to Eq. (1).

$$\textbf{Water uptake (\%)} = \frac{W_2 - W_1}{W_1} \times 100\% \tag{1}$$

where $W_1$ is the weight of dry samples, and $W_2$ is the weight of humid sample.

## 3.7 In vitro degradation test

The samples were placed in a small bottle containing 10 ml of PBS (pH 7.4) at 37°C. Then remove samples, rinsed thoroughly with distilled water and dried in vacuum at 40°C. Weight loss was calculated according to Eq.(2).

$$\textbf{Weight loss (\%)} = \frac{W_o - W_t}{W_o} \times 100\% \tag{2}$$

where $W_o$ is initial weight, $W_t$ is the weight at degradation time.

## 3.8 Mechanical properties of copolyesters

### 3.8.1 Hardness test

Hardness measurements were performed on a Shore D apparatus according to a standard ASTM D2240.

### 3.8.2 Tensile test

The tensile tests were performed at room temperature on a Instron 1011 tensile testing machine. Tensile test were measured on dumbbell samples at a constant crosshead speed of 100 mm/min. The tensile strength, modulus and elongation at break were calculated from the stress-strain curves on an average of five specimens in accordance with ASTM D638.

### 3.8.3 T-peel strength test

The adhesion properties of copolyester adhesives were studied by T-peel strength tests of PET film/copolyesters/paperboard. The T-peel strength measurements were performed in an Instron 1011 universal test machine using a crosshead speed of 10 mm/min.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Synthesis of copolyesters

### 4.1.1 Synthesis and characterization of PET-co-DEGT

#### 4.1.1.1 Synthesis of PET-co-DEGT

Poly(ethylene-co-diethylene glycol terephthalate) (PET-co-DEGT) was synthesized through two steps : direct esterification and polycondensation reaction from terephthalic acid (TPA), ethylene glycol (MEG) and diethylene glycol (DEG), as shown in Figure 4.1. In this research, titanium(IV) butoxide (TBOT) was used as a catalyst in order to increase the rate of esterification and shortened the distillation time as reported by Oleg et al. [26]. The content of DEG in the feed was varied from 0 to 50 mol%.

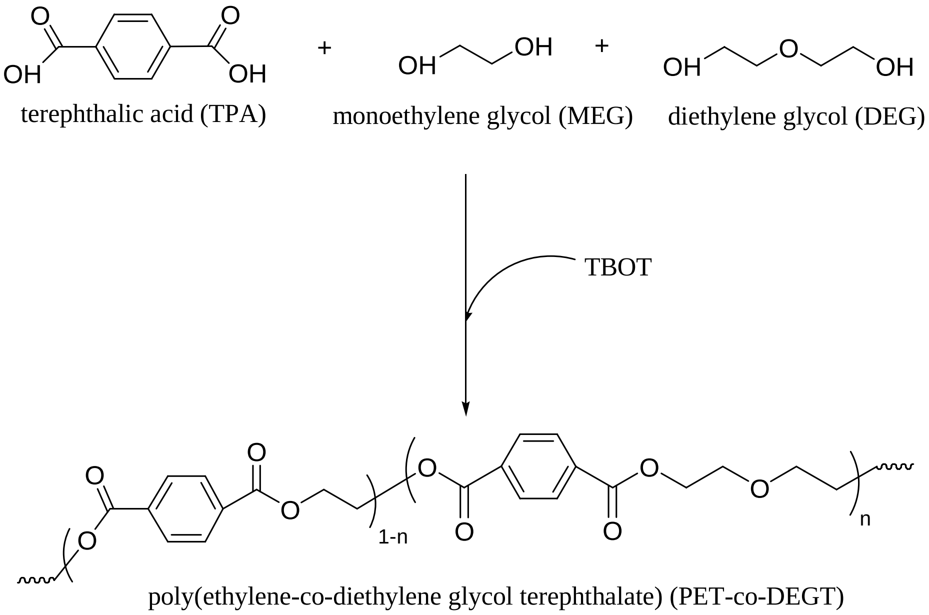


**Figure 4.1** Synthesis of PET-co-DEGT.

Before beginning the esterification, the mixture was purged with nitrogen to ensure that there is no residual oxygen inside the reactor. The polymerization apparatus setup had a short vigreux column to retain DEG in the reaction. The esterification reaction was finished when 18 mL (1 mol) of water as its by-product was discharged.

During the polycondensation reaction, vacuum was applied to remove excess glycol in the reaction. The process of molecular weight build up by the combination of the end groups of terephthalic acid, ethylene glycol and diethylene glycol was allowed to occur until no more distillate was discharged, and the heating was allowed to continue for a total of 3 hours.

The molar ratio and appearance of PET and PET-co-DEGT, at various DEG molar ratio, were showed in Table 4.1.

**Table 4.1** Synthesis data of PET and PET-co-DEGT

| Sample | Molar ratio | | | Product appearance |
|---|---|---|---|---|
| | TPA | MEG | DEG | |
| PET | 0.5 | 1 | 0 | Opaque white solid |
| PET-co-DEGT 10 | 0.5 | 0.9 | 0.1 | Opaque creamy solid |
| PET-co-DEGT 20 | 0.5 | 0.8 | 0.2 | Opaque creamy solid |
| PET-co-DEGT 30 | 0.5 | 0.7 | 0.3 | Opaque yellowish-brown solid |
| PET-co-DEGT 40 | 0.5 | 0.6 | 0.4 | Transparent brown solid |
| PET-co-DEGT 50 | 0.5 | 0.5 | 0.5 | Transparent brown solid |

It was found that copolyesters containing 10 to 30 mol% DEG were opaque, indicated that they had crystallinity. The copolyesters containing 40 to 50 mol% DEG were transparent, and therefore were amorphous.

#### 4.1.1.2 FTIR study of PET-co-DEGT

The Fourier Transform Infrared Spectroscopic technique (FTIR) was used to compare the chemical structures of PET-co-DEGT with PET. The FTIR spectra of PET and PET-co-DEGT are showed in Figure 4.2 and some transmission bands are summarized in Table 4.2. The main characteristic transmission bands of an ester are found at 1680 - 1720 cm$^{-1}$ and 1220 - 1270 cm$^{-1}$, respectively, which are associated to C=O stretching and C(O)-O stretching of ester group, respectively.

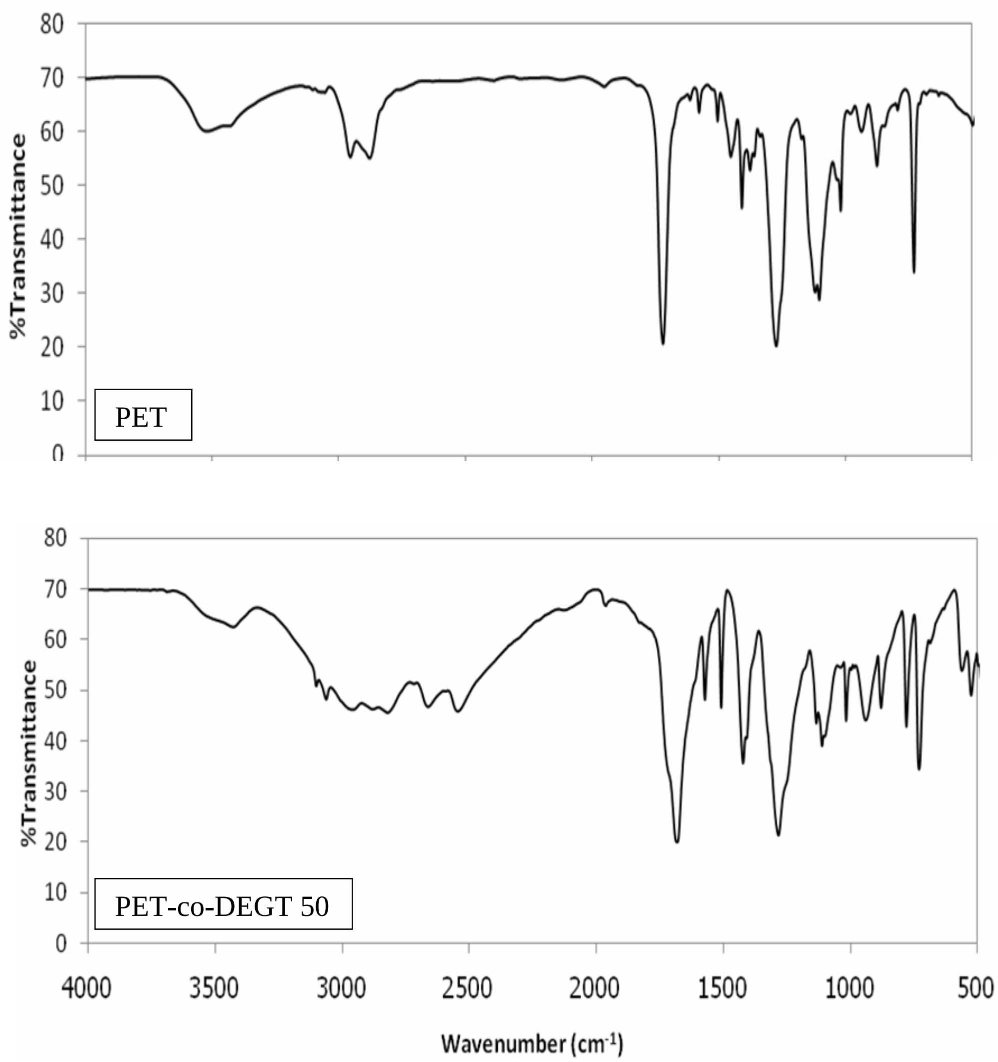


**Figure 4.2** FTIR spectra of PET and PET-co-DEGT 50.

**Table 4.2** Assignment of FTIR absorption bands of PET and PET-co-DEGT

| Wavenumber ($cm^{-1}$) | Assignments |
|---|---|
| 3440 | O-H stretching of glycols end group |
| 3060 | aromatic C-H stretching |
| 3100-2540 | aliphatic C-H stretching |
| 1720-1680 | carbonyl C=O stretching |
| 1450, 1430, 1410 | aromatic skeletal stretching bonds [33] |
| 1270-1220 | C(O)-O stretching of aromatic ester |
| 1175, 1120, 1020 | skeletal ring indicated 1,4-substitution |
| 940 | O-$CH_2$ stretching of glycol [34] |
| 730 | out of plane deformation of carbonyl substituents on the aromatic ring |

The absorption bands of PET-co-DEGT 50 at 1270-1220 $cm^{-1}$ and 1720-1680 $cm^{-1}$ were broader than the ones of PET. These were attributed to the combination of different kinds of ester moieties. In addition, the increase in intensity of O-$CH_2$ stretching at 940 $cm^{-1}$ indicated that more ether bonds in the copolyester than PET.

#### 4.1.1.3 $^1$H NMR study of PET-co-DEGT

The $^1$H-NMR analysis was used to determine the chemical structure of PET and PET-co-DEGT 50. The $^1$H-NMR spectra of PET and PET-co-DEGT 50 are showed in Figure 4.3 and the chemical shifts and assignment of proton signals showed in $^1$H-NMR spectra are listed in Table 4.3.

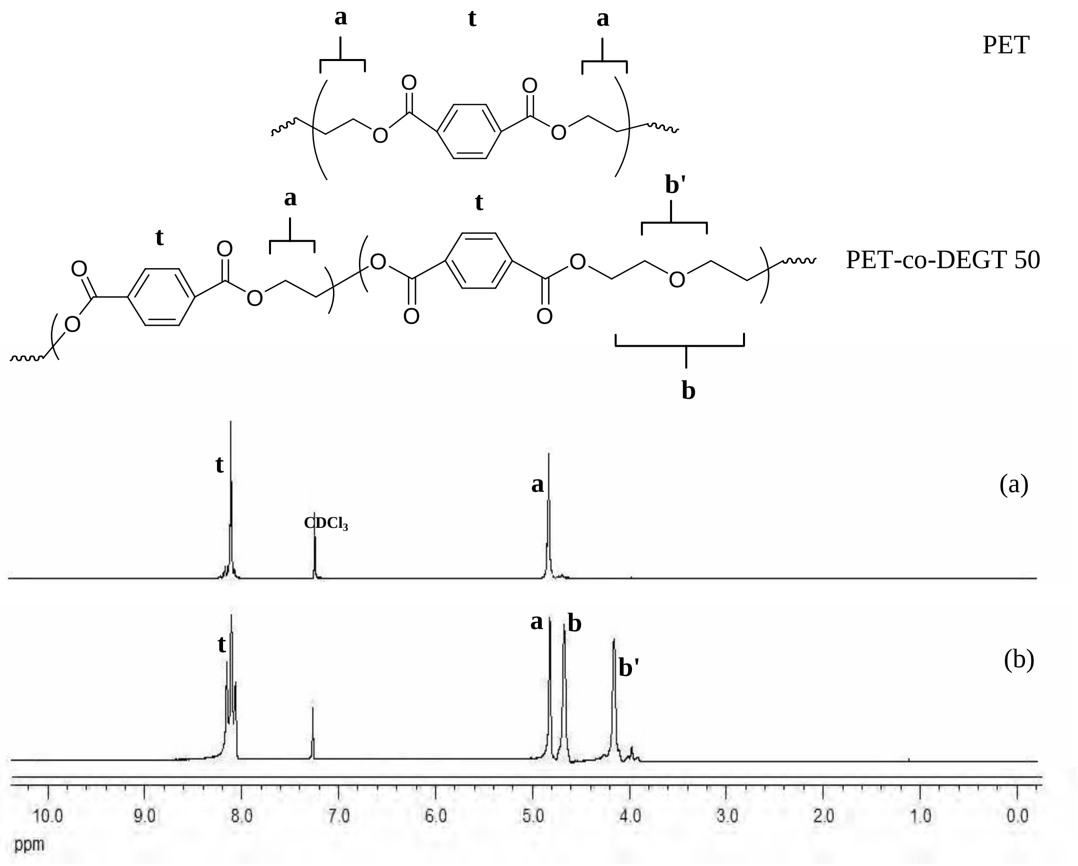
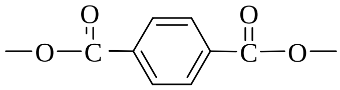


**Figure 4.3** $^1$H NMR spectra (a) PET, (b) PET-co-DEGT 50.

**Table 4.3** Chemical shifts and assignment of proton signal of PET and copolyesters

| Structural unit | Chemical shift (ppm) | |
|---|---|---|
| $-O-CH_2-CH_2-O-$ | a | 4.78 |
| b b' b' b<br>$-CH_2-CH_2-O-CH_2-CH_2-$ | b | 4.63 |
| | b' | 4.12 |
|  | t | 8.16 |

As we can seen in Figure 4.3 and Table 4.3, $^1$H-NMR spectrum (a) showed the typical peaks of PET, the signal at 8.16 ppm indicated the presence of the four phenyl protons and the signal at 4.78 ppm assigned to the methylene group of PET. In the spectrum (b) of PET-co-DEGT 50, we can seen the signal at 4.78 ppm that attributed to –$OCH_2$ in EG units. The two signals between 4.63 and 4.12 ppm are the characteristic of α-methylene group next to ether-oxygen and β-methylene group next to ether-oxygen, respectively.

### 4.1.1.4 $^1$H NMR study of PET-co-DEGT with various DEG mol%

In Figure 4.4, NMR spectra of PET-co-DEGT copolyester with respect to DEG mol ratio. The mole percentage of diethylene glycol terephthalate chain segment unit (DEG mol%) can be calculated from $S_b/(S_a+S_b)$. The results can be observed in Table 4.4 .

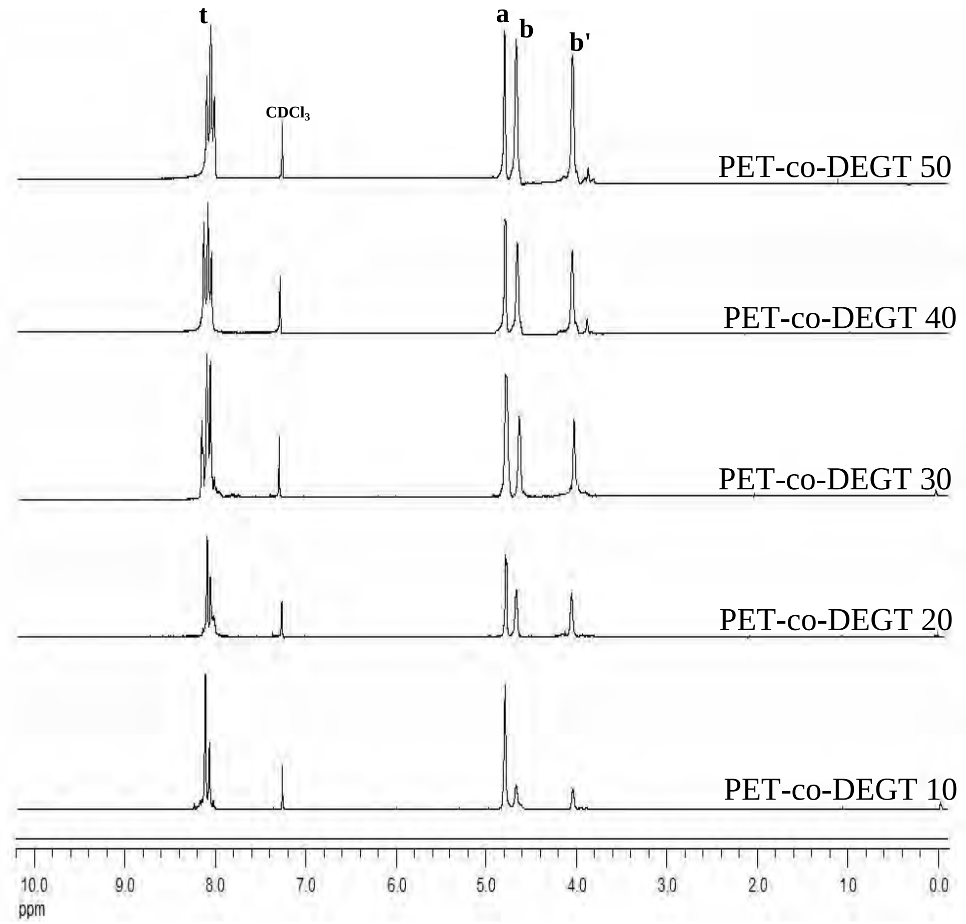


**Figure 4.4** $^1$H NMR spectra of PET-co-DEGT with various DEG mol%.

**Table 4.4** DEG content incorporated in PET-co-DEGT

| Sample | DEG in feed (mol%) | DEG in copolyester (mol%) |
|---|---|---|
| PET-co-DEGT 10 | 10 | 18.2 |
| PET-co-DEGT 20 | 20 | 35.6 |
| PET-co-DEGT 30 | 30 | 39.2 |
| PET-co-DEGT 40 | 40 | 50.7 |
| PET-co-DEGT 50 | 50 | 64.8 |

As showed in Table 4.4, all the PET-co-DEGT had more mol% DEG copolyester than MEG in the feed. The reactivity of diethylene glycol is higher than that of monoethylene glycol. These results can be explained by the presence of oxygen heteroatoms in DEG, which has strong electronegativity, the stronger electronegativity of the oxygen atom in DEG than that of the oxygen atom in EG. Thus, the polar interaction occurs between DEG and terephthalic acid (TPA) easily, these resulted in the DEG unit content (DEG mol%), which heightened in the copolyester.

Moreover, due to the higher boiling point of DEG, the EG composition will be easily volatilized during polycondensation reaction, which leads to an increase in mol%DEG. Besides, during the synthesis of PET, DEG was formed as a by-product due to dimerization of EG [35], it can be incorporated in the polymer chain. These resulted in an increase in DEG content in the copolyesters.

## 4.1.2 Synthesis and characterization of PET-co-TEGT

### 4.1.2.1 Synthesis of PET-co-TEGT

The poly(ethylene-co-triethylene glycol terephthalate), (PET-co-TEGT) was synthesized from terephthalic acid (TPA), monoethylene glycol (MEG) and triethylene glycol (TEG), as shown in Figure 4.5 The content of TEG in the feed was varied from 0 to 50 mol%. The method for synthesis of PET-co-TEGT was the same as PET-co-DEGT preparation.

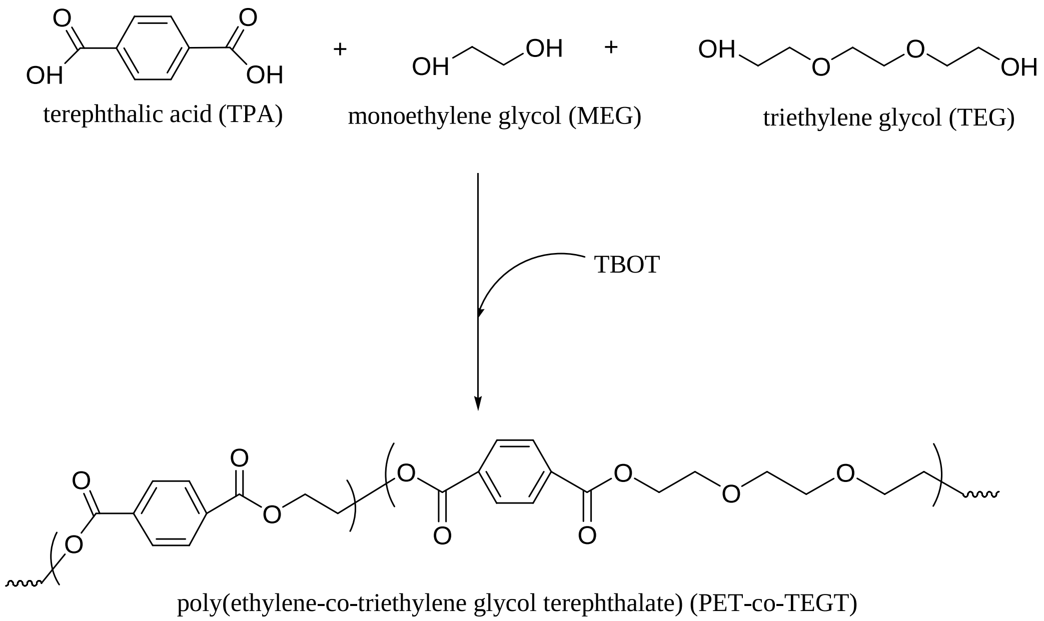


**Figure 4.5** Synthesis of PET-co-TEGT.

The chemical structure of PET-co-TEGT was confirmed by $^1$H NMR and FTIR spectroscopy, as showed in Figure 4.5 and the chemical shift and assignment of proton signal showed in Table 4.5.

**Table 4.5** PET and PET-co-TEGT data

| Formula | Mole ratio | | | Product appearance |
|---|---|---|---|---|
| | TPA | MEG | TEG | |
| PET | 0.5 | 1 | 0 | Opaque white rigidity |
| PET-co-TEGT 10 | 0.5 | 0.9 | 0.1 | Opaque creamy flexibility |
| PET-co-TEGT 20 | 0.5 | 0.8 | 0.2 | Opaque brown flexibility |
| PET-co-TEGT 30 | 0.5 | 0.7 | 0.3 | Opaque brown flexibility |
| PET-co-TEGT 40 | 0.5 | 0.6 | 0.4 | Transparent, brown flexibility |
| PET-co-TEGT 50 | 0.5 | 0.5 | 0.5 | Transparent, brown liquid |

In case of PET-co-TEGT the results showed the same trends as PET-co-DEGT, that copolyesters containing 10 to 30 mol% TEG were opaque, indicated that they had crystallinity. The copolyesters containing 40 to 50 mol% TEG were transparent, and therefore were amorphous. Consideration for flexibility of polymer, PET-co-TEGT showed more flexibility than PET-co-DEGT.

#### 4.1.2.2 FTIR study of PET-co-TEGT

The FTIR spectra of PET-co-TEGT are shown in Figure 4.6 The main characteristic transmission bands are found at 1680 - 1720 cm$^{-1}$ and 1220 - 1270 cm$^{-1}$, respectively, which are associated to carbonyl C=O stretching and C(O)-O stretching of ester group, respectively.

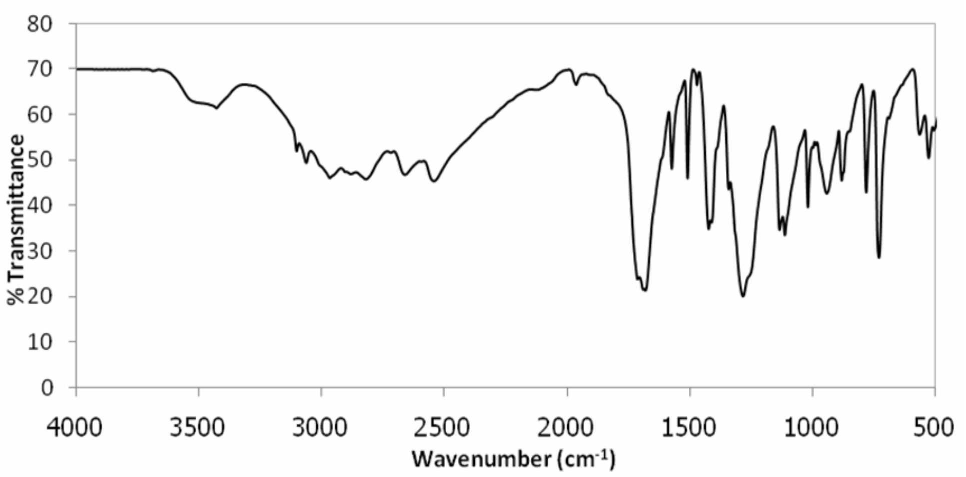


**Figure 4.6** FTIR spectra of PET and PET-co-TEGT 50.

The transmission bands of PET-co-TEGT 50 as the same assignment as PET and PET-co-DEGT 50, however PET-co-TEGT 50 more increased intensity and width peak of C=O stretching and C(O)-O stretching of ester group performed increased ether bonds than both of PET and PET-co-DEGT 50 due to there are present appearance of other new carbonyl species. Furthermore, the assignment of PET-co-TEGT 50 increased intensity of O-$CH_2$ stretching at 940 $cm^{-1}$ performed increased ether bonds in the copolymers.

#### 4.1.2.3 $^1$H NMR study of PET-co-TEGT

$^1$H NMR spectrum of PET-co-TEGT 50 was showed in Figure 4.7. We found that the new characteristic signal appeared in 3.82 ppm, which was not found for the homopolymer and PET-co-DEGT 50. This signal is assigned to TEG group -$OCH_2$-$CH_2O$- in TEG units. The signal at 4.78 ppm is attributed to –$OCH_2$ in EG units. We can also observe two signals one at 4.63, 4.12 ppm which is attributed to the resonances of -$CH_2$-O-$CH_2$- and another at 3.82 ppm is assigned to TEG group -$OCH_2$-$CH_2O$- in TEG units, respectively. Finally, the signal at 8.16 ppm is attributed to the presence of four phenyl protons.

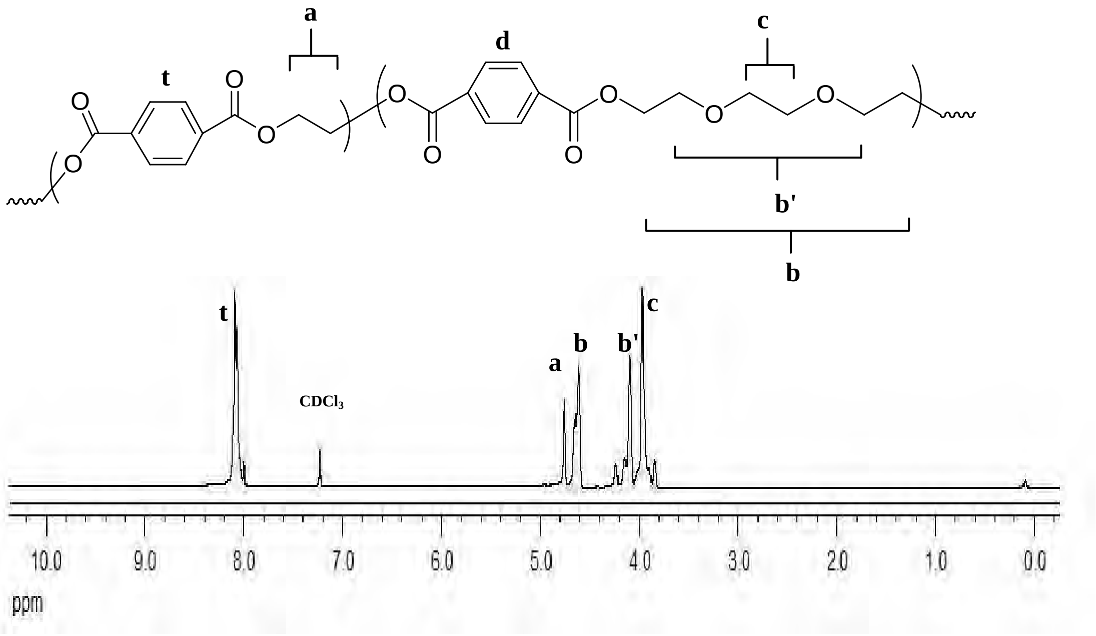


**Figure 4.7** $^1$H NMR spectrum of PET-co-TEGT 50.

#### 4.1.2.4 $^1$H NMR study of PET-co-TEGT with various TEG mol%

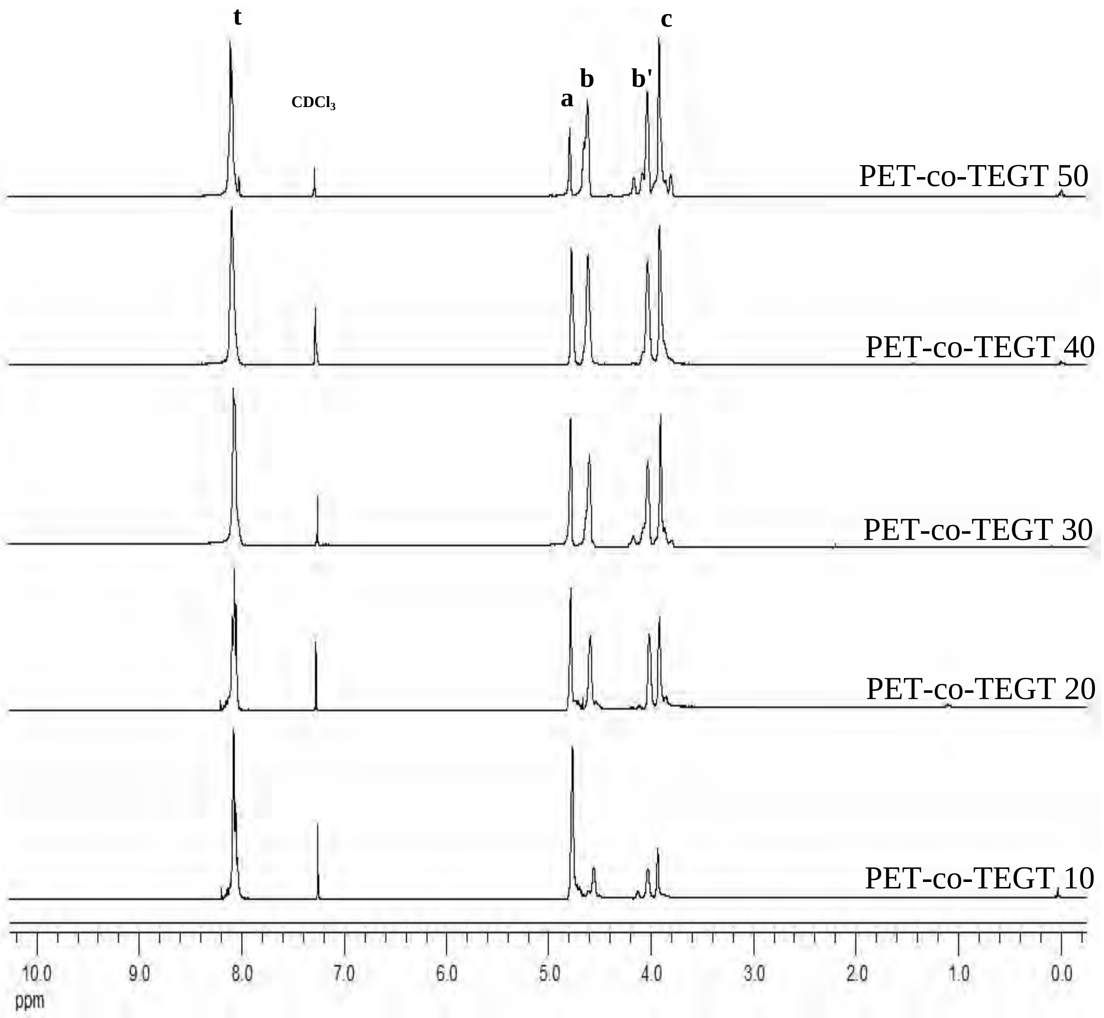


**Figure 4.8** $^1$H NMR spectra of PET-co-TEGT various TEG mol%.

**Table 4.6** Composition of mol% TEG of PET-co-TEGT

| Sample | Feed ratio of TEG (mol%) | TEG (mol%) in copolyester |
|---|---|---|
| PET-co-TEGT 10 | 10 | 21.1 |
| PET-co-TEGT 20 | 20 | 44.9 |
| PET-co-TEGT 30 | 30 | 57.9 |
| PET-co-TEGT 40 | 40 | 62.9 |
| PET-co-TEGT 50 | 50 | 86.4 |

From Table 4.6 and Figure 4.8, the results are similar to that of the DEG mol% in copolyester. The mole percentage of triethylene glycol terephthalate unit (TEG mol%) can be calculated from $S_c/(S_a+S_c)$.

Concerning the TEG mol% as compared to the TEG mol% in the copolymer, the results showed that the TEG mol% in PET-co-TEGT were higher than the DEG mol% in PET-co-DEGT. That is caused by the reactivity of TEG is higher than DEG due to electronegativity of the oxygen atom in TEG is greater than that of the oxygen atom in DEG. Hence, the esterification reaction between TEG and TPA is easier than the esterification reaction between DEG and TPA. Furthermore, the boiling point of TEG is higher than that of DEG, resulting in lower volatility of TEG when compared to that of DEG.

## 4.2 Intrinsic viscosity

The intrinsic viscosity of all samples was measured by using the solvent mixture 60/40 phenol/1,1,2,2 trichloroethane at 30°.

**Table 4.7** Composition of mol% comonomers, intrinsic viscosity and molecular weight of PET and copolyesters.

| Polymer | mol% of diol in feed[a] | mol% of diol in copolyester[b] | [η] (dl/g) |
|---|---|---|---|
| PET | 0 | 2.76 | 0.561 |
| PET-co-DEGT 10 | 10 | 18.2 | 0.608 |
| PET-co-DEGT 20 | 20 | 35.6 | 0.621 |
| PET-co-DEGT 30 | 30 | 39.2 | 0.676 |
| PET-co-DEGT 40 | 40 | 50.7 | 0.706 |
| PET-co-DEGT 50 | 50 | 64.8 | 0.733 |

**Table 4.7(cont.)** Composition of mol% comonomers, intrinsic viscosity and molecular weight of PET and copolyesters.

| Polymer | mol% of diol in feed[a] | mol% of diol in copolyester[b] | [η] (dl/g) |
|---|---|---|---|
| PET-co-TEGT 10 | 10 | 21.1 | 0.617 |
| PET-co-TEGT 20 | 20 | 44.9 | 0.660 |
| PET-co-TEGT 30 | 30 | 57.9 | 0.681 |
| PET-co-TEGT 40 | 40 | 62.9 | 0.724 |
| PET-co-TEGT 50 | 50 | 86.4 | 0.740 |

[a] Mol% of DEG and TEG comonomers in feed.

[b] Determined by$^1$H NMR spectroscopy.

The intrinsic viscosities of the synthesized polyesters were between 0.608 to 0.740 dl/g for the copolyesters and 0.561 dl/g for the homopolyester, PET, depending on the %mol of diols (see Table 4.7). These results suggest that molecular weight of the polyesters under study should be reasonably high molecular weight.

## 4.3 Thermal properties

### 4.3.1 DSC thermograms of PET and PET-co-DEGT

The DSC thermograms of PET and copolyester recorded during second heating and cooling are showed in Figure 4.9 and the results are summarized in Table 4.8. The sample was heated to 300°C at a heating rate of 20°C/min. Then the samples were quickly cooled to room temperature and heated again to 300°C at rate of 10°C/min. The glass transition temperature ($T_g$), melting temperature ($T_m$), melting enthalpy ($\Delta H_m$), crystallization temperature ($T_c$) and crystallization enthalpy ($\Delta H_c$) were obtained from DSC curves.

Figure 4.9 showed the DSC crystallization and melting curves of pristine PET and PET-co-DEGT with different %mol DEG and the corresponding transition temperature values are listed in Table 4.8 The results showed that the $T_g$ and $T_m$ of copolyesters decrease with increase of DEG content, due to the different flexibility of the molecular chains. Further decreasing of the %mol DEG led to the decrease of $T_g$ of the copolyesters, due to the incorporation of flexible segments of DEG units. The DSC thermograms illustrate a significant shift of the melting temperatures to lower temperatures with increasing mol% of DEG. It is noticed that PET and all the copolyesters exhibited one glass transition temperature, indicating the formation of homogeneous phase. In addition, the existence of DEG contents restricted the crystallization of copolyesters, resulting in not presence the crystallization curves of the copolyester as DEG mol% reached 20mol% DEG.

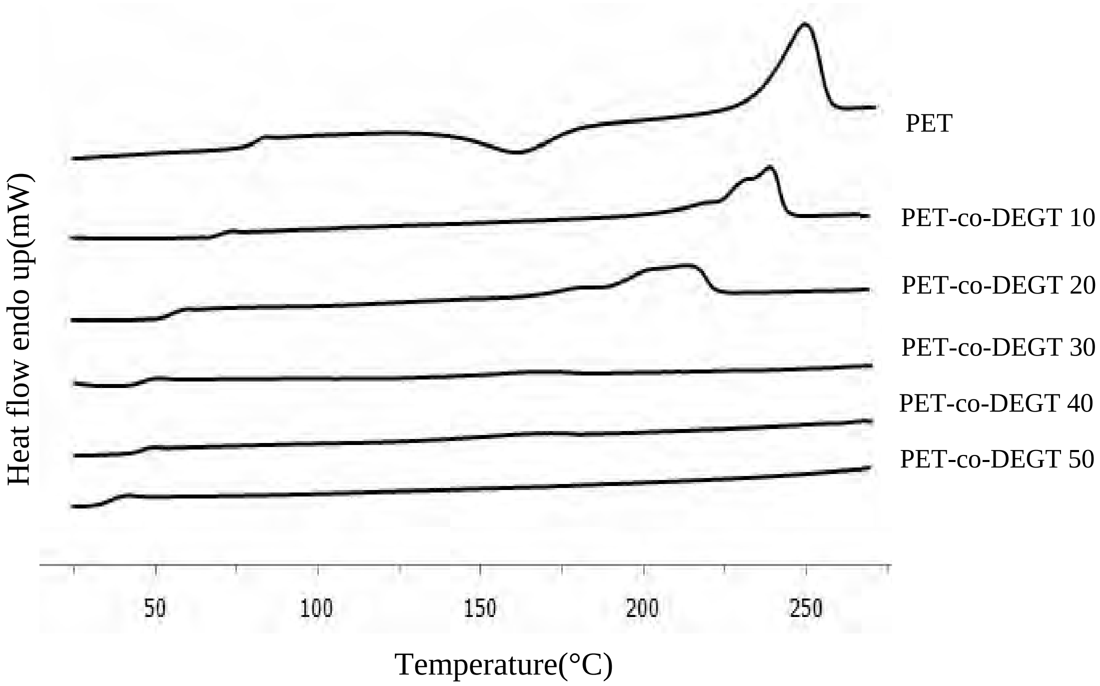


**Figure 4.9** DSC heating curves of PET and PET-co-DEGT with various DEG mol%.

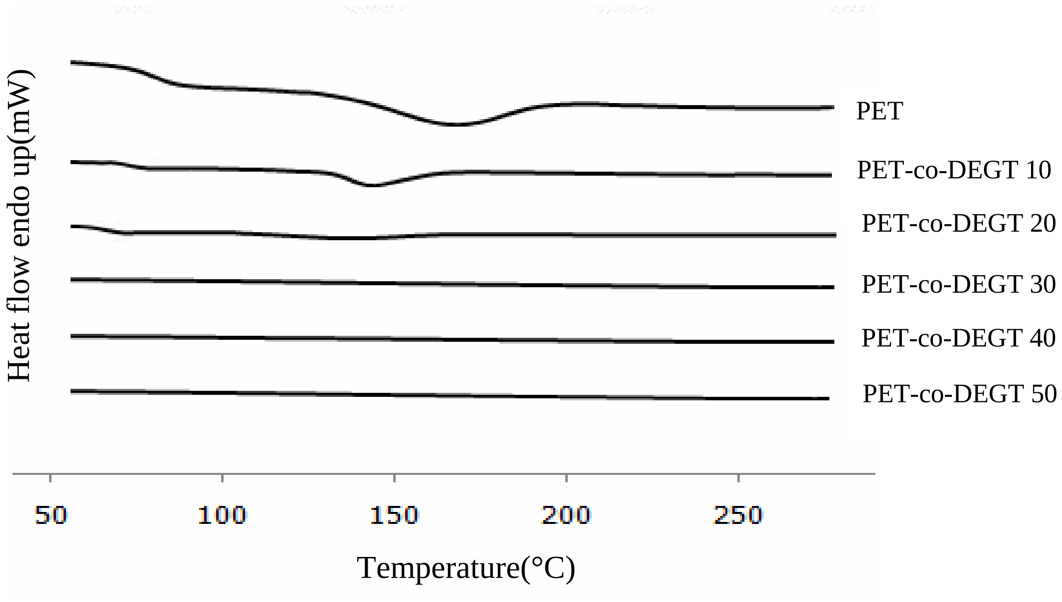


**Figure 4.10** DSC cooling curves of PET and PET-co-DEGT with various DEG mol%.

**Table 4.8** DSC data for PET and PET-co-DEGT copolyester

| Sample | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|
| PET | 78.5 | 254.2 | 27.8 | 187.7 | 28.0 |
| PET-co-DEGT 10 | 72.1 | 247.5 | 21.2 | 148.4 | 22.8 |
| PET-co-DEGT 20 | 54.5 | 221.4 | 18.3 | 146.2 | 4.8 |
| PET-co-DEGT 30 | 50.7 | - | - | - | - |
| PET-co-DEGT 40 | 49.6 | - | - | - | - |
| PET-co-DEGT 50 | 47.4 | - | - | - | - |

### 4.3.2 DSC thermograms of PET and PET-co-TEGT

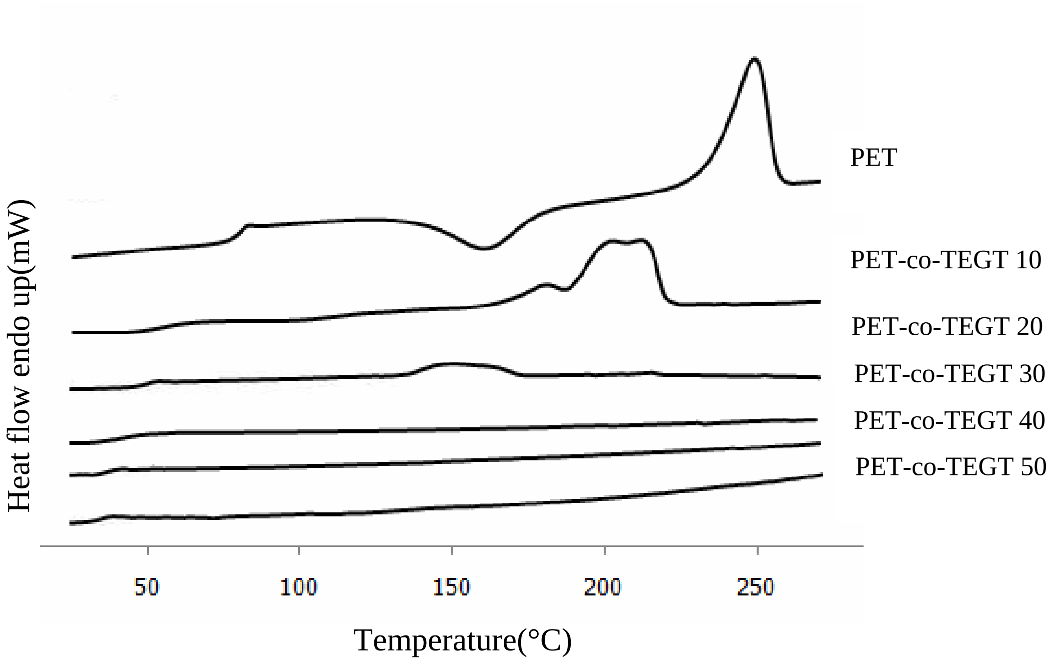


**Figure 4.11** DSC heating curves of PET and PET-co-TEGT with various TEG mol%.

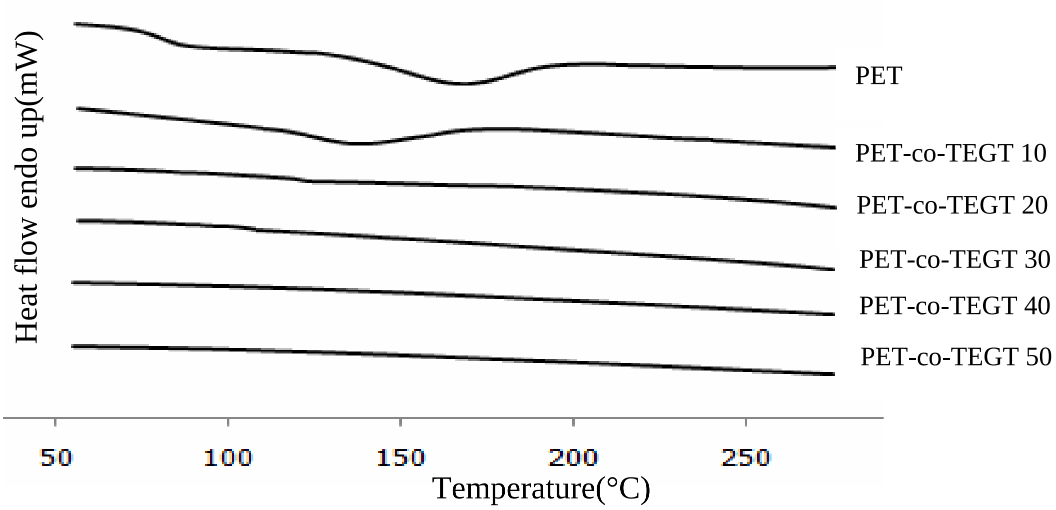


**Figure 4.12** DSC cooling curves of PET and PET-co-TEGT with various TEG mol%.

**Table 4.9** DSC data for PET and PET-co-TEGT

| Sample | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_m$ (J/g) | $T_c$ (°C) | $\Delta H_c$ (J/g) |
|---|---|---|---|---|---|
| PET | 78.5 | 254.2 | 27.8 | 187.7 | 28.0 |
| PET-co-TEGT 10 | 55.8 | 211.7 | 32.6 | 147.5 | 37.2 |
| PET-co-TEGT 20 | 54.5 | 150.5 | 15.9 | - | - |
| PET-co-TEGT 30 | 49.4 | - | - | - | - |
| PET-co-TEGT 40 | 48.5 | - | - | - | - |
| PET-co-TEGT 50 | 47.0 | - | - | - | - |

In Figure 4.11 and Table 4.9, it can be seen that the increasing TEG content caused the $T_g$ and $T_m$ of copolyesters decrease. Considerably, the results obtained from DSC thermograms of PET-co-TEGT, thermal properties of PET-co-TEGT showed the same trends as PET-co-DEGT thermograms. However, at the same mol% of glycols feed, PET-co-TEGT presented lower $T_g$ and Tm than PET-co-DEGT due to the oxygen atom in a chain segment unit of PET-co-DEGT leads to more flexible molecular chain than PET.

### 4.3.3 Thermal gravimetric analysis (TGA)

Thermal stability of the copolyester was investigated by using TGA experiments. The thermograms of the copolyesters are showed in Figure 4.13, where $T_{id}$ is the temperature of initial decomposition and final residue of samples are summarized in Table 4.10.

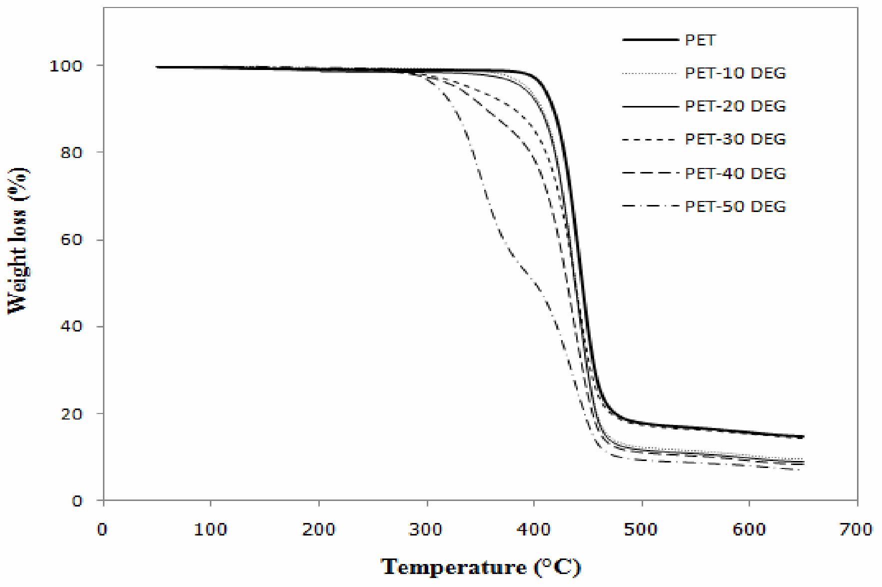


**Figure 4.13** TGA thermograms of PET and PET-co-DEGT.

**Table 4.10** Thermal degradation of PET, PET-co-DEGT and PET-co-TEGT

| Sample | $T_{id}$ (˚C) | Final residue (%) |
|---|---|---|
| PET | 418.9 | 16.6 |
| PET-co-DEGT 10 | 409.0 | 14.4 |
| PET-co-DEGT 20 | 408.3 | 12.0 |
| PET-co-DEGT 30 | 407.2 | 10.8 |
| PET-co-DEGT 40 | 322.3 | 9.0 |
| PET-co-DEGT 50 | 318.7 | 7.9 |
| PET-co-TEGT 10 | 408.6 | 13.1 |
| PET-co-TEGT 20 | 403.6 | 11.1 |
| PET-co-TEGT 30 | 402.5 | 10.5 |
| PET-co-TEGT 40 | 303.6 | 6.7 |

According to Figure 4.13 and Table 4.10, it is clear that the weight loss of the PET takes place in one step. We can be seen that the temperature decomposition of all copolymer was shifted to lower temperatures with increasing the DEG content. In Figure 4.13., weight loss of the copolyester containing 10 mol% DEG take place one step but copolyester containing PET-co-DEGT 50 exhibited two steps of weight loss. Due to the higher ether oxygen atom in the main chain caused the formation of volatiles. The second step of degradation is produces $CO_2$, acetaldehyde and various other degradation products [36].

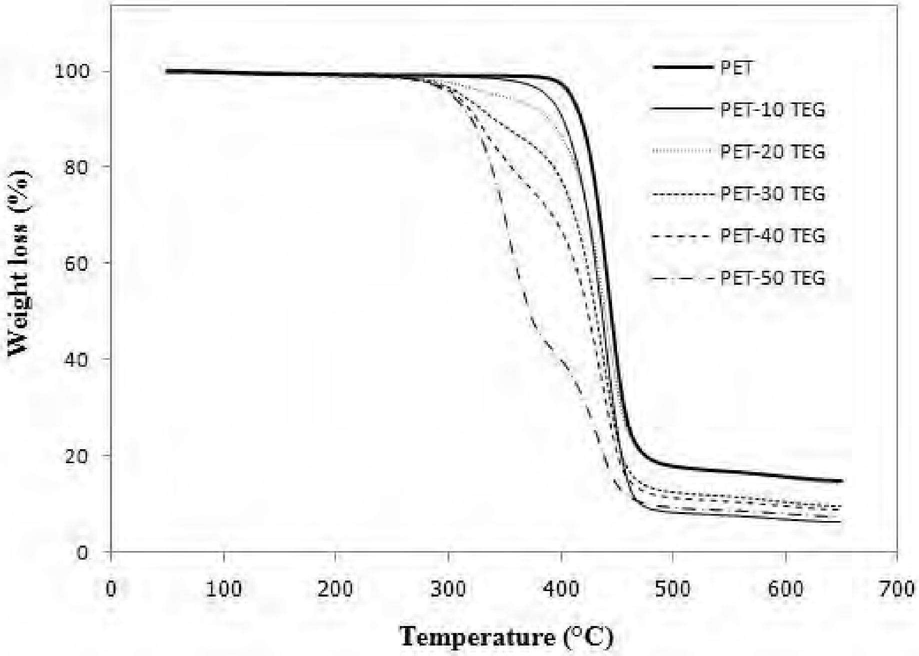


**Figure 4.14** TGA thermograms of PET and PET-co-TEGT.

According to Figure 4.14 the thermal stability of PET-co-TEGT compared to PET-co-DEGT, the results indicated that PET-co-TEGT has lower temperature decomposition than PET-co-DEGT because PET-co-TEGT has longer methylene sequence and has more ether bond than PET-co-DEGT copolymer. This also leads to lower thermal stability for the copolymers.

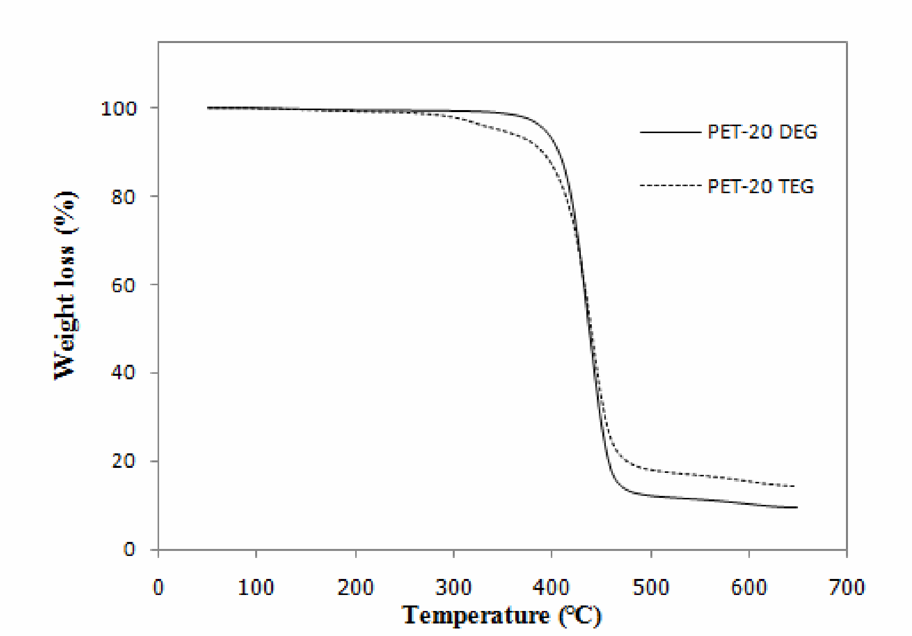


**Figure 4.15** Comparision of TGA thermograms of PET-co-DEGT and PET-co-TEGT.

Comparing the decomposition temperatures of PET-co-TEGT and PET-co-DEGT, we can conclude that PET-co-TEGT has the same stability as PET-co-DEGT. However, the copolyester containing 40 to 50 mol% TEG take place two steps decomposition. This is probably due to thermal degradation of low molecular weight fraction of copolyesters such as acetaldehyde, $CO_2$ and various other degradation products.

## 4.4 Solubility test

Solubility tests were conducted to examined the ability of the copolymers to dissolve in common solvents; i.e. dichloromethane ($CH_2Cl_2$) tetrahydrofuran (THF) at ambient conditions. $CH_2Cl_2$ and THF are both interest solvent because they can dissolve a wide range of nonpolar and polar chemical compounds. The solubility test of PET and copolyester as shown in Table 4.11

**Table 4.11** Solubility of PET, PET-co-DEGT and PET-co-TEGT in $CH_2Cl_2$ and THF

| Sample | Solubility | |
|---|---|---|
| | $CH_2Cl_2$ | THF |
| PET | - | - |
| PET-10DEG | - | - |
| PET-20DEG | - | - |
| PET-30DEG | + | + |
| PET-40DEG | ++ | ++ |
| PET-50DEG | ++ | ++ |
| PET-10TEG | - | - |
| PET-20TEG | - | - |
| PET-30TEG | + | ++ |
| PET-40TEG | ++ | ++ |
| PET-50TEG | ++ | ++ |

The solubility is indicated by number of '+'. If a complete dissolution within one second at ambient temperature, solubility is rated as '++', while the rating of '+' indicates that the samples are poorly soluble in solvents at 40˚C within 10 minutes in ultrasonic bath, respectively. If samples are insoluble in solvents solubility is rated as '-'.

Regarding to the resulting of homopolymer, it was obvious that it could not dissolve in both, $CH_2Cl_2$ and THF, with agreement to the literature. It was interesting when the ratio of DEG or TEG: PET of sample was increased, the polymer would be incorporated more polar units of DEG and TEG, resulting the higher solubility of the sample. In addition, the highest solubility of sample in both $CH_2Cl_2$ and THF solvents were observed when PET-co-DEGT and PET-co-TEGT contain 40-50 mol% glycols.

## 4.5 Swelling test

The absorption of water by the PET and the copolyester films after 24 h was measured. The PET sample absorbed about 0.01mass% of water, confirming the low hydrophilicity of the homopolyester film, while the PET-co-DEGT copolyesters absorbed in the range from 0.13 to 2.27 mass%, increasing with increasing content of hydrophilic soft segments. Also, the water uptake of PET-co-TEGT absorbed in the range from 0.16 to 2.07 mass% with increasing content of TEG units due to the increased hydrophilicity of the copolyesters (Figure 4.16).

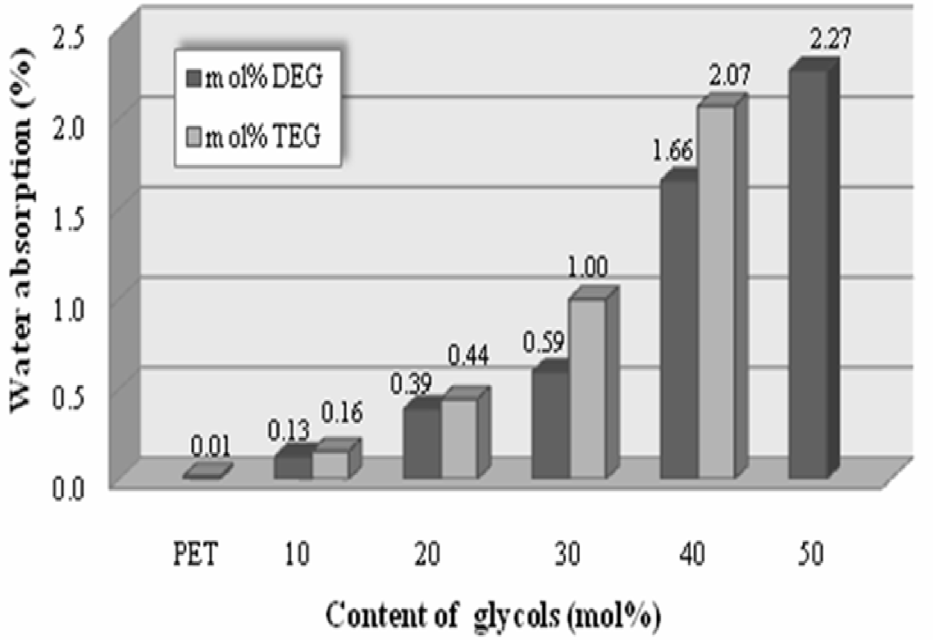


**Figure 4.16** Effect of glycols content on water absorption behaviour of PET and copolyesters.

## 4.6 Degradation properties

### 4.6.1 In vitro degradation

The weight losses of PET and the copolyester films in buffer solution (pH=7.4) after 2 months (Figure 4.17). The increase of the content of the incorporated DEG and TEG units soft segments provides more amorphous domains and imparts good chain hydrophilicity, which would facilitate the diffusion of water molecules and attack at the ester bond and hence accelerates the hydrolytic degradation. Furthermore, a high degree of water absorption generally results in a swollen polymer matrix with a greater free volume for mass transfer, leading to an increase of soluble degradation products.

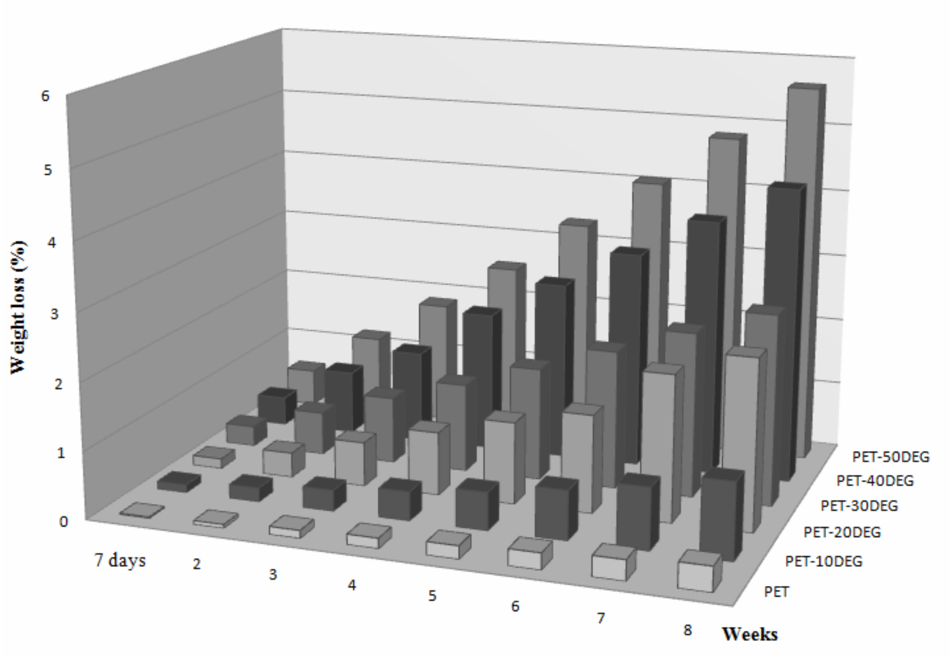


**Figure 4.17** Percent weight loss of PET and PET-co-DEGT.

As shown in Figure 4.17, the weight losses of the PET films in the buffer solution around 0.15 mass% after 4 weeks and increased slightly with time. The weight losses of the PET-co-DEGT based on mol% of DEG increased from 0.12 to 2.54 mass% with increasing content of DEG after 4 weeks to 2.54 to 5.63 mass% after 2 months.

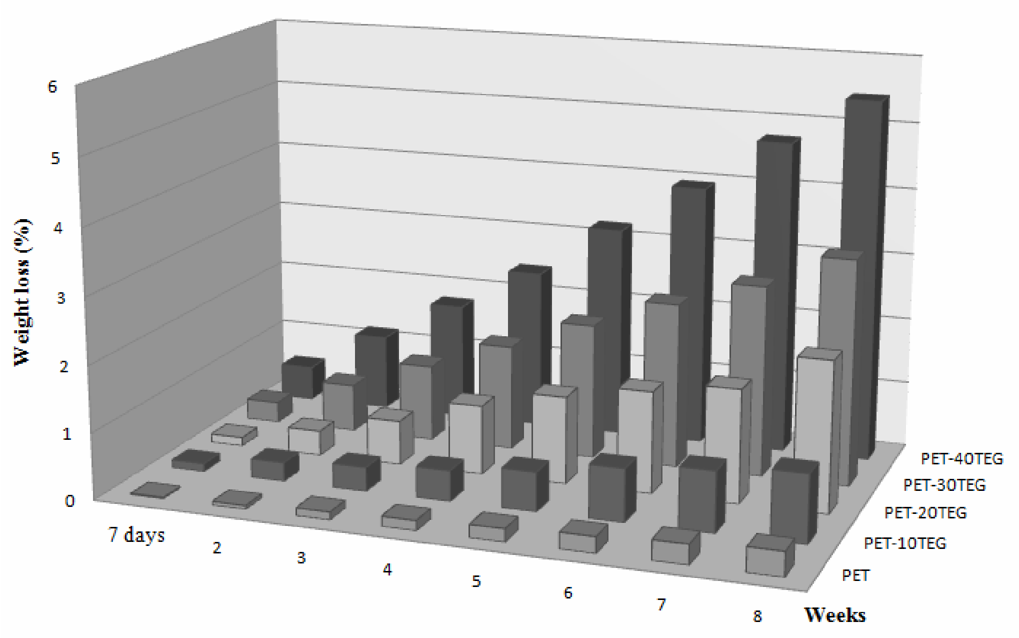


**Figure 4.18** Percent weight loss of PET and PET-co-TEGT.

For the weight loss of PET-co-TEGT (Figure 4.18) as the same trend as PET-co-DEGT. PET-co-TEGT which containing 10 and 20 mol% TEG, no significant weight loss is observed during the first week. Then weight loss was gradually increased and reached almost about 5.44 mass% after 2 months. The earlier results indicate that the incorporation of DEG and TEG comonomers into the PET main chain led to the change of the degradation behavior of PET. More content of comonomers units resulted in the easier degradation of the copolyesters due to the existence of large amount of aliphatic ester bonds.

### 4.6.2 Surface morphology

The surface morphology of the PET and copolyester films after degradation test was investigated by scanning electron microscope (SEM). Figure 4.13 shows the SEM images of PET and the copolyesters films before and after degradation for 1 and 2 months. It is observed that the surface of the films was smooth without holes before the degradation. After degradation for 1 month, the holes on the surfaces of the samples representing biodegraded parts were observed. The film became cracked or porous after 2 months due to the degradation of the DEG or TEG units in copolyesters.

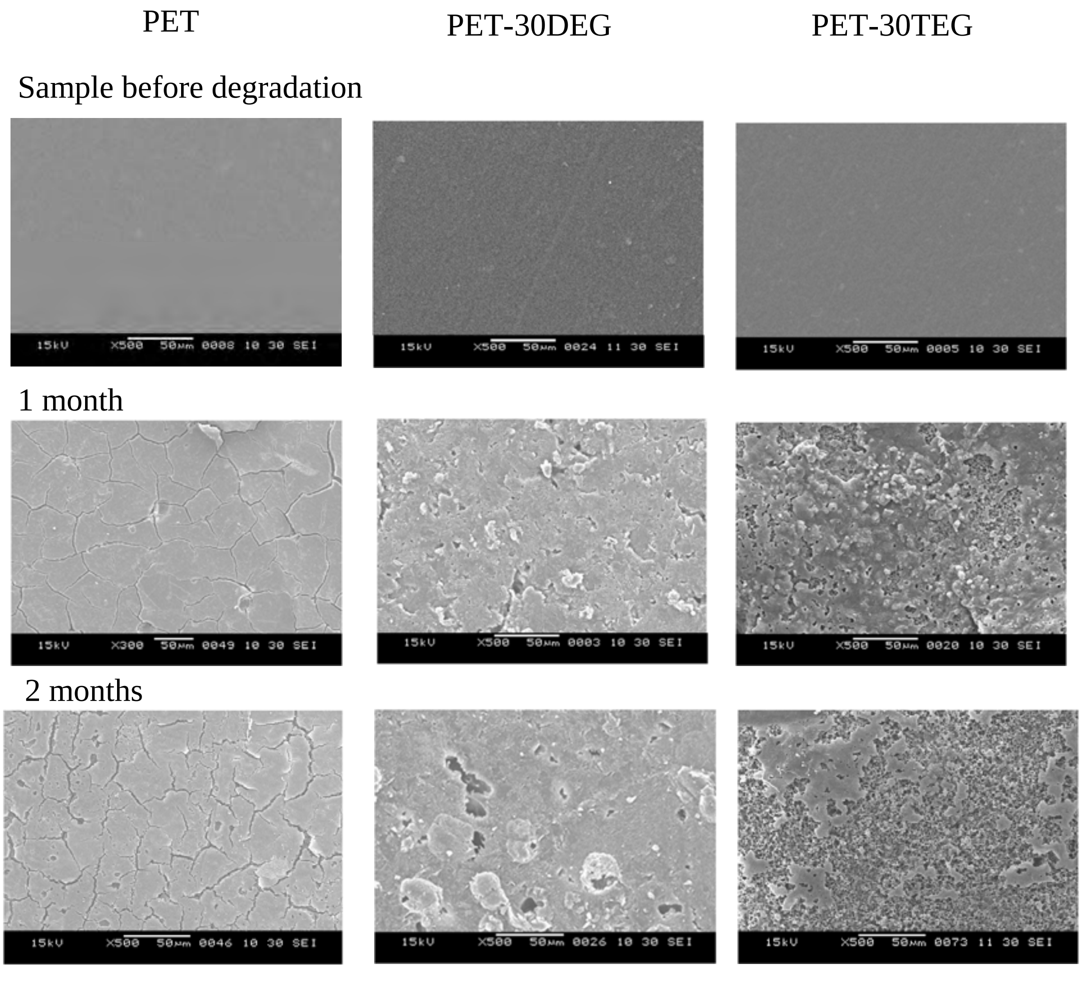


**Figure 4.19** Scanning electron micrographs of the surface of PET, PET-co-DEGT 30 and PET-co-TEGT 30.

## 4.7 Mechanical properties

### 4.7.1 Hardness test

The results are shown in Table 4.12 and Figure 4.20, it was found that comonomers ratio affected the hardness of polymer. Hardness was decreased following the increasing of mol% of DEG and TEG. Moreover, the hardness of PET-co-DEGT was higher than PET-co-TEGT at the same ratio because the PET-co-TEGT has longer methylene sequence and higher ether bond than PET-co-DEGT leads to PET-co-TEGT more flexibility than PET-co-DEGT.

**Table 4.12** The results of hardness testing

| Sample | Hardness (Shore D) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | Average | SD |
| PET | 88 | 87 | 88 | 87 | 87 | 87.4 | 0.55 |
| PET-10 DEG | 75 | 72 | 72 | 73 | 72 | 72.8 | 1.30 |
| PET-20 DEG | 63 | 64 | 66 | 65 | 65 | 64.6 | 1.14 |
| PET-30 DEG | 55 | 52 | 54 | 54 | 52 | 53.4 | 1.34 |
| PET-40 DEG | 38 | 38 | 38 | 40 | 41 | 39 | 1.41 |
| PET-50 DEG | 31 | 30 | 30 | 31 | 32 | 30.8 | 0.84 |
| PET-10 TEG | 58 | 58 | 60 | 60 | 62 | 60.2 | 1.67 |
| PET-20 TEG | 52 | 52 | 52 | 48 | 48 | 50.4 | 2.19 |
| PET-30 TEG | 42 | 42 | 40 | 38 | 40 | 41.2 | 1.67 |
| PET-40 TEG | 28 | 28 | 28 | 30 | 30 | 28.8 | 1.10 |

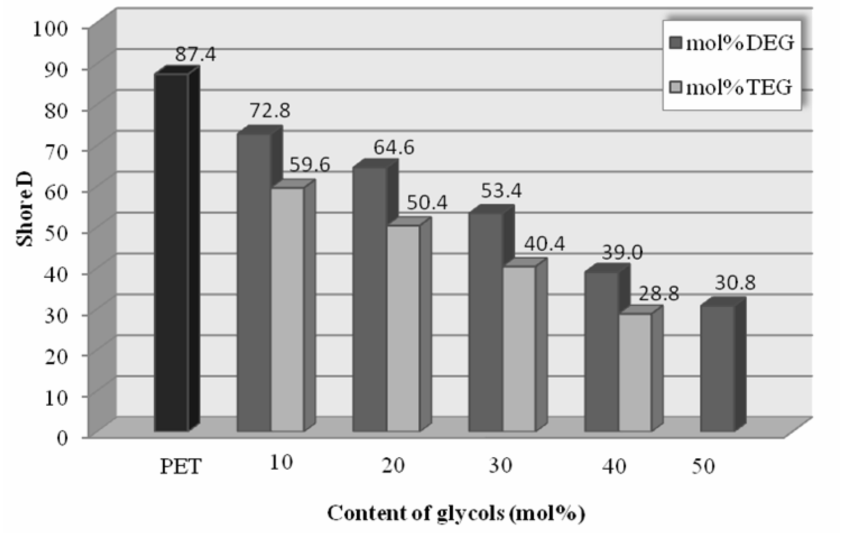


**Figure 4.20** Effect of glycols on the hardness property of PET and copolyesters.

### 4.7.2 Tensile test

The stress-strain curves of PET and copolyesters are presented in Figure 4.21 The tensile strength of all copolymers was lower than PET but all copolymers had higher %elongation than PET. The % elongation at break increased with the increase of DEG and TEG molar ratios due to the incorporation of flexible segment in the polymerchain. The tensile modulus was lower than 8 MPa as the feed molar ratio of copolymers reached to 20, 30 and 40 mol% of DEG and TEG. However, the values of tensile modulus sharply increased as 10 mol% of DEG and TEG. The increase of the DEG and TEG content in the copolyesters made the molecular chain of the copolyesters flexible, leading to the decrease of the tensile modulus. The incorporation of more content of DEG and TEG eventually led to the increase of elongation at break.

It is concluded that the tensile properties of the copolyesters are mainly influenced by the compositions and structures of the molecular chains. The incorporation of DEG and TEG segments into the PET main chain led to the formation of molecular chains with short sequence length of DEG unit. Therefore, the increase of the content of DEG and TEG in the copolyester main chain significantly improved the tensile elongation at break. In addition, due to the flexibility of the DEG and TEG units, the tensile modulus of the copolyesters decreased as the content of both glycols increasing.

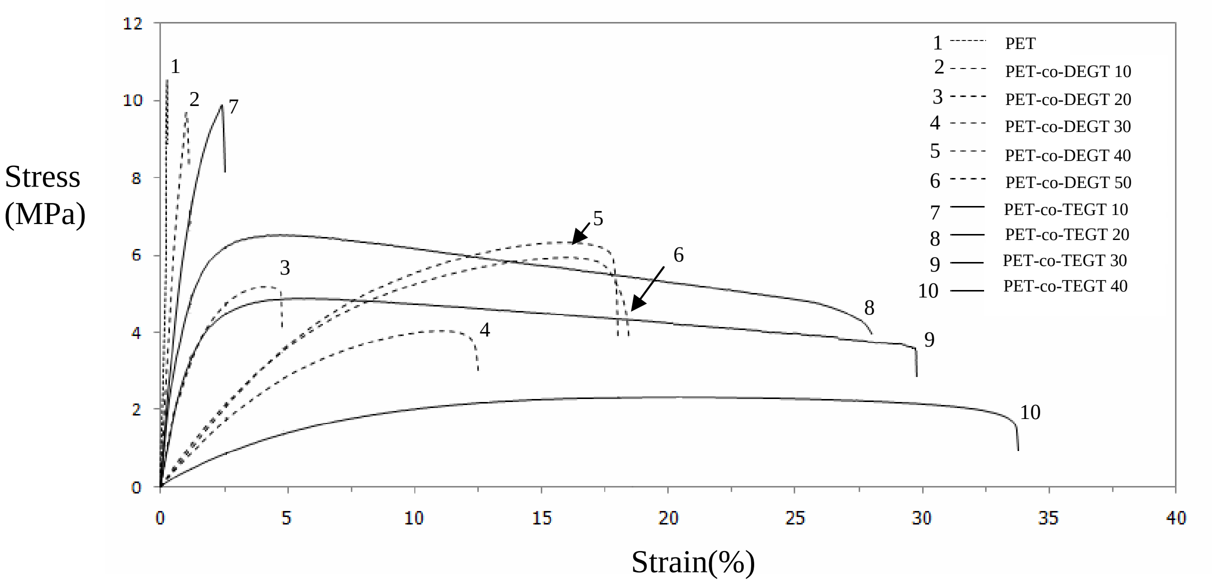


**Figure 4.21** The stress-strain properties of PET and copolyesters.

### 4.7.3 T-peel strength test

The adhesion properties were obtained from T-peel strength test of PET film /copolyesters/ paperboard, depending on the presence of functionalities, such as hydroxyl groups from the cellulose of wood and oxygen atom in copolyester chain. The higher oxygen atoms in the copolyester, the stronger peel strength adhesion between PET film and paperboard. There were reports in the literature had studied peel strength of copolyester containing DEG mol%. Petke and coworker studied peel strength of copolyester containing 30-50 DEG mol%[37]. However, there were no reports about peel strength of PET-co-TEGT.

In this research, we reported results on the comparison of peel strength of PET-co-DEGT and PET-co-TEGT. The results were plotted in Figure 4.22. It was found that the peel strength of both PET-co-DEGT and PET-co-TEGT increase with increasing content of glycols mol% due to PET-co-TEGT containing more oxygen atom than PET-co-DEGT resulted in enhance adhesion between PET film and paperboard. Interestingly, PET film and paperboard couldn’t adhere when PET and PET-co-DEGT containing 10 mol% DEG as adhesive because of crystallization of polymer chain.

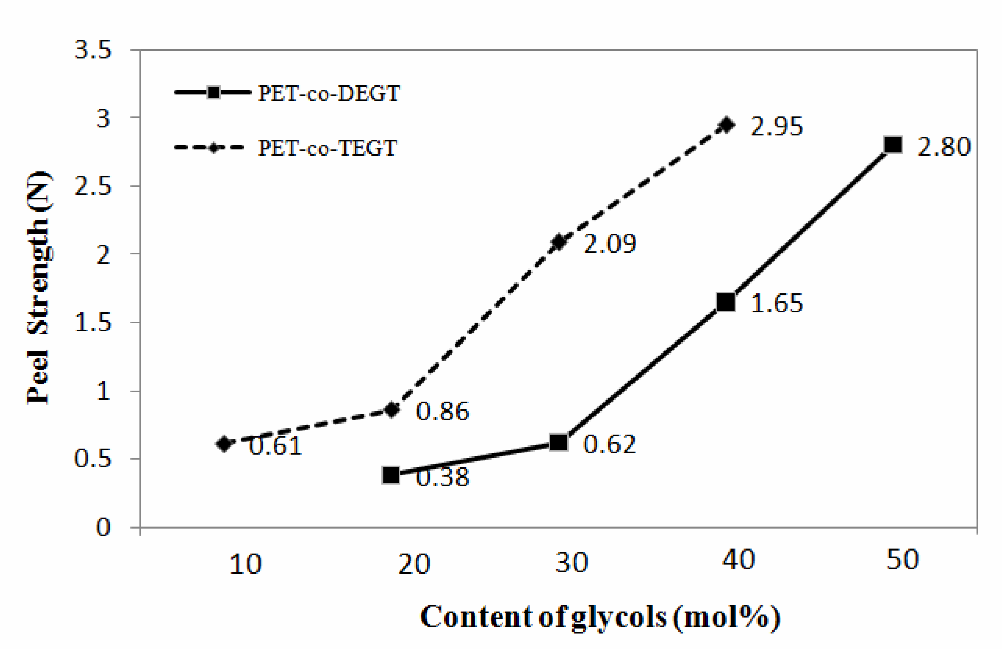


**Figure 4.22** Effect of glycols on the peel strength of polyester to paperboard.

The hot melt adhesives can be used in e.g. packaging and manufacture of disposable articles which are made from degradable materials. The composition is especially useful in bonding parts of ovenable food containers [38].

# CHAPTER V

# CONCLUSION AND RECOMMENDATIONS

## 5.1 Conclusion

Poly(ethylene-co-diethylene glycol terephthalate) (PET-co-DEGT) and poly(ethylene-co-triethylene glycol terephthalate) (PET-co-TEGT) were successfully synthesized by means of direct esterification reaction and then polycondensation reaction. The results showed that when DEG was used, all products were solid, but copolyesters only 10-30 mol% of glycols in the feed were opaque. In case of PET-co-TEGT when the content of TEG 10-20 mol%, the copolyester were solid and opaque, while the rest were all semi-solid and transparent. These indicated that both copolyesters had a regularity of polymer chain. In contrast, at the high mol% of DEG and TEG in the feed, the higher mol% of DEG and TEG content which resulted in the copolyesters were higher irregularity. Regarding for the reactivity of glycols, we found that at the same mol% of glycols in feed, both of glycols, DEG and TEG show higher mol% of glycol in copolyester. These indicated that DEG and TEG have higher reactivity than MEG. Furthermore, when compared between DEG and TEG in copolyester chain. The results showed that higher mol% of TEG than DEG was found in the corresponding copolyesters. These implied that TEG was more reactive than DEG which is consistent with their structures. The thermal properties of copolyester were also studied. The results showed that the copolyesters increasing of DEG and TEG units led to decreased $T_g$ and $T_m$ of copolyesters. In addition, from the DSC thermograms it can be concluded that PET could not be generated in these reactions as indicated by DSC. Moreover, all copolyesters have good thermal stability with the decomposition temperature of 300°C and higher, but lower than PET. For the solubility test, the higher mol% of comonomers, the easier solubility of the copolymers. The increase of content of both glycols units led to the increase of elongation at break and the decrease of tensile strength and tensile modulus. All the copolyesters were found to be able to degrade in phosphate buffer solution.

## 5.2 Recommendations for future work

1. To reduce the reaction time, the microwave irradiation was applied to synthesize of copolyester.
2. To improve the appearance of copolyester, the thermal stabilizer and colorant should be added to the copolymer synthesis.

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# APPENDICES

# APPENDIX A

## Molecular weight determination

**Table A-1** Intrinsic viscosity of PET

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.54 | 327.45 | 328.17 | 327.72 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5016 | 381.03 | 380.21 | 380.83 | 380.69 | 1.1616 | 0.1616 | 0.3222 |
| $C_2$ | 0.4180 | 379.19 | 376.17 | 378.20 | 377.85 | 1.1530 | 0.1530 | 0.3660 |
| $C_3$ | 0.3583 | 375.21 | 375.38 | 376.45 | 375.68 | 1.1463 | 0.1463 | 0.4084 |
| $C_4$ | 0.3135 | 370.76 | 372.60 | 373.36 | 372.24 | 1.1358 | 0.1358 | 0.4333 |
| $C_5$ | 0.2951 | 367.58 | 369.64 | 367.92 | 368.38 | 1.1241 | 0.1241 | 0.4204 |
| $C_6$ | 0.2787 | 365.23 | 364.59 | 366.37 | 365.40 | 1.1150 | 0.1150 | 0.4125 |

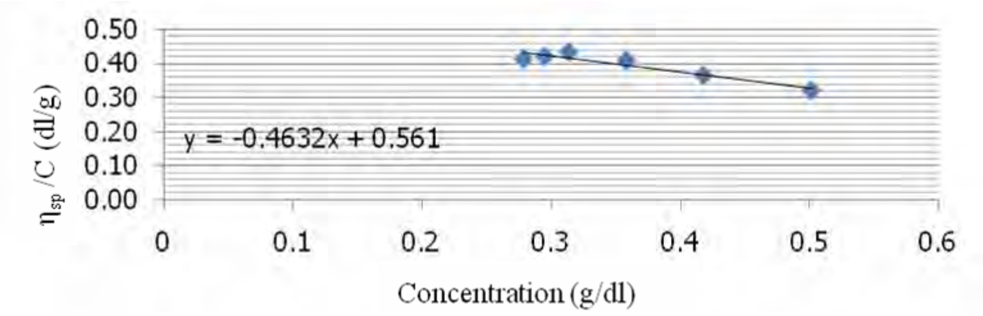

**Figure A-1** Plot of viscosity versus concentration at 30°C for PET.

**Table A-2** Intrinsic viscosity of PET-co-DEGT 10

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.4860 | 390.35 | 392.96 | 388.24 | 390.52 | 1.1920 | 0.1920 | 0.3950 |
| $C_2$ | 0.4050 | 381.70 | 385.15 | 381.92 | 382.92 | 1.1688 | 0.1688 | 0.4168 |
| $C_3$ | 0.3471 | 377.11 | 379.63 | 377.40 | 378.05 | 1.1539 | 0.1539 | 0.4434 |
| $C_4$ | 0.2859 | 370.62 | 374.85 | 371.60 | 372.36 | 1.1366 | 0.1366 | 0.4776 |
| $C_5$ | 0.2430 | 367.20 | 366.46 | 368.07 | 367.24 | 1.1209 | 0.1209 | 0.4977 |
| $C_6$ | 0.2025 | 360.16 | 362.55 | 363.72 | 362.14 | 1.1054 | 0.1054 | 0.5204 |

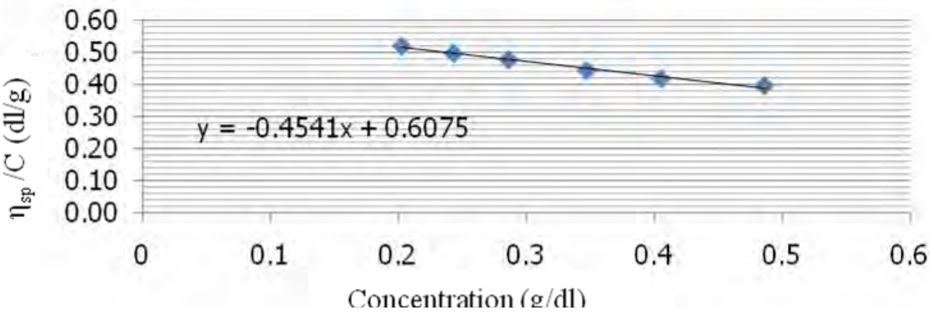

**Figure A-2** Plot of viscosity versus concentration at 30°C for PET-co-DEGT 10.

**Table A-3** Intrinsic viscosity of PET-co-DEGT 20

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}/C$ (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5050 | 426.39 | 425.98 | 423.89 | 425.42 | 1.2985 | 0.2985 | 0.5911 |
| $C_2$ | 0.4208 | 417.92 | 419.46 | 415.78 | 417.72 | 1.2750 | 0.2750 | 0.6535 |
| $C_3$ | 0.3607 | 395.74 | 398.39 | 400.76 | 398.30 | 1.2157 | 0.2157 | 0.5981 |
| $C_4$ | 0.3156 | 390.46 | 391.41 | 393.69 | 391.85 | 1.1961 | 0.1961 | 0.6212 |
| $C_5$ | 0.2658 | 386.58 | 384.29 | 389.52 | 386.80 | 1.1806 | 0.1806 | 0.6796 |
| $C_6$ | 0.2295 | 368.47 | 370.75 | 370.46 | 369.89 | 1.1290 | 0.1290 | 0.5622 |

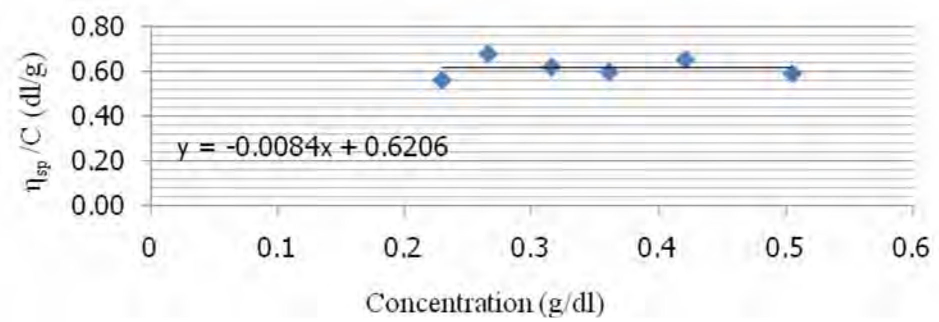

**Figure A-3** Plot of viscosity versus concentration at 30°C for PET-co-DEGT 20.

**Table A-4** Intrinsic viscosity of PET-co-DEGT 30

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}/C$ (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5016 | 394.87 | 395.39 | 395.13 | 395.13 | 1.2061 | 0.2061 | 0.4108 |
| $C_2$ | 0.4180 | 389.19 | 390.17 | 389.44 | 389.60 | 1.1892 | 0.1892 | 0.4526 |
| $C_3$ | 0.3583 | 385.21 | 385.08 | 386.45 | 385.58 | 1.1769 | 0.1769 | 0.4938 |
| $C_4$ | 0.3135 | 379.76 | 380.60 | 380.36 | 380.24 | 1.1606 | 0.1606 | 0.5123 |
| $C_5$ | 0.2951 | 377.58 | 379.64 | 377.92 | 378.38 | 1.1549 | 0.1549 | 0.5250 |
| $C_6$ | 0.2787 | 375.23 | 374.79 | 375.37 | 375.13 | 1.1450 | 0.1450 | 0.5203 |

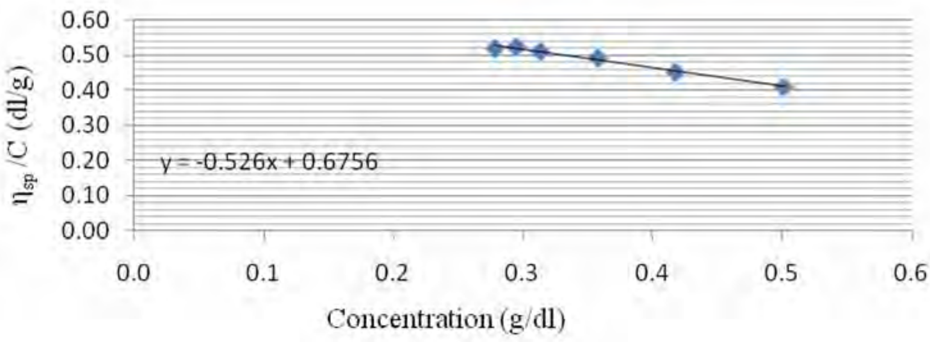

**Figure A-4** Plot of viscosity versus concentration at 30°C for PET-co-DEGT 30.

**Table A-5** Intrinsic viscosity of PET-co-DEGT 40

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}/C$ (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.4708 | 420.48 | 419.85 | 421.94 | 420.76 | 1.2843 | 0.2843 | 0.6038 |
| $C_2$ | 0.3923 | 409.61 | 411.79 | 408.42 | 409.94 | 1.2513 | 0.2513 | 0.6405 |
| $C_3$ | 0.3363 | 398.97 | 396.18 | 399.69 | 398.28 | 1.2157 | 0.2157 | 0.6413 |
| $C_4$ | 0.2769 | 385.86 | 386.41 | 386.72 | 386.33 | 1.1792 | 0.1792 | 0.6472 |
| $C_5$ | 0.1906 | 370.13 | 368.76 | 369.11 | 369.33 | 1.1273 | 0.1273 | 0.6680 |
| $C_6$ | 0.1657 | 364.54 | 365.02 | 362.79 | 364.12 | 1.1114 | 0.1114 | 0.6723 |

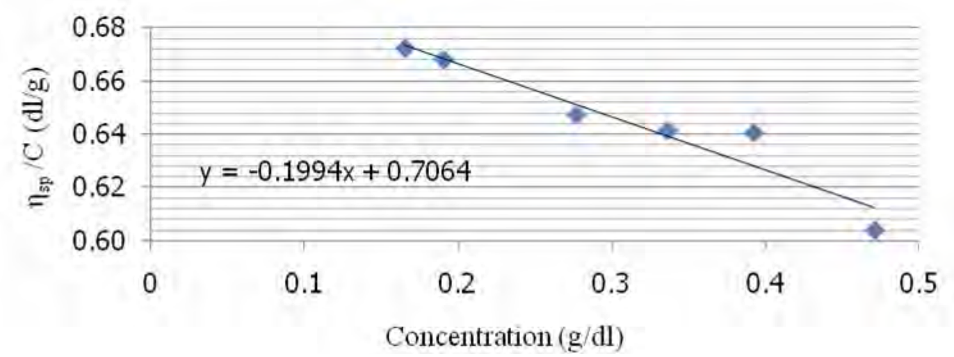

**Figure A-5** Plot of viscosity versus concentration at 30°C for PET-co-DEGT 20.

**Table A-6** Intrinsic viscosity of PET-co-DEGT 50

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}/C$ (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.4620 | 416.46 | 414.63 | 415.75 | 415.61 | 1.2686 | 0.2686 | 0.5813 |
| $C_2$ | 0.3850 | 409.10 | 410.84 | 407.98 | 409.31 | 1.2493 | 0.2493 | 0.6476 |
| $C_3$ | 0.3300 | 397.18 | 395.72 | 392.51 | 395.14 | 1.2061 | 0.2061 | 0.6245 |
| $C_4$ | 0.2718 | 381.74 | 382.38 | 384.43 | 382.85 | 1.1686 | 0.1686 | 0.6202 |
| $C_5$ | 0.2310 | 376.91 | 375.53 | 377.49 | 376.64 | 1.1496 | 0.1496 | 0.6478 |
| $C_6$ | 0.2009 | 373.16 | 373.92 | 373.98 | 373.69 | 1.1406 | 0.1406 | 0.6999 |

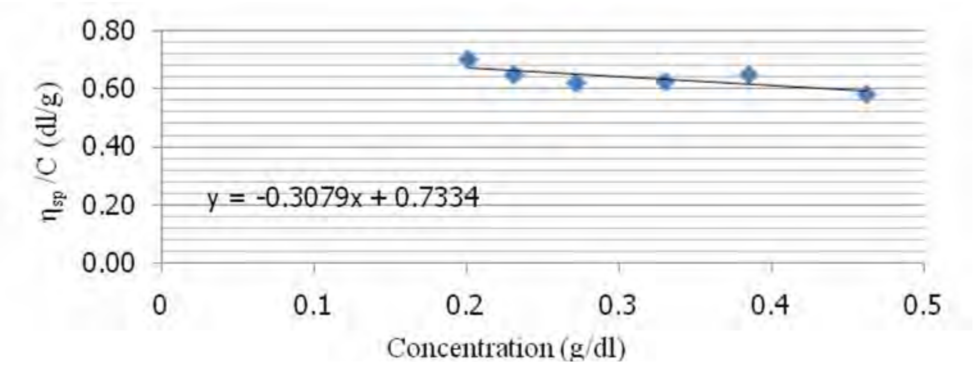

**Figure A-6** Plot of viscosity versus concentration at 30°C for PET-co-DEGT 20.

**Table** A-7 Intrinsic viscosity of PET-co-TEGT 10

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5020 | 415.93 | 418.12 | 419.72 | 417.92 | 1.2756 | 0.2756 | 0.5491 |
| $C_2$ | 0.4183 | 394.73 | 394.28 | 395.24 | 394.75 | 1.2049 | 0.2049 | 0.4898 |
| $C_3$ | 0.3586 | 389.41 | 390.19 | 390.49 | 390.03 | 1.1905 | 0.1905 | 0.5312 |
| $C_4$ | 0.2953 | 387.36 | 387.59 | 386.53 | 387.16 | 1.1817 | 0.1817 | 0.6154 |
| $C_5$ | 0.2510 | 375.62 | 373.84 | 374.65 | 374.70 | 1.1437 | 0.1437 | 0.5726 |
| $C_6$ | 0.2183 | 368.50 | 366.43 | 367.27 | 367.40 | 1.1214 | 0.1214 | 0.5562 |

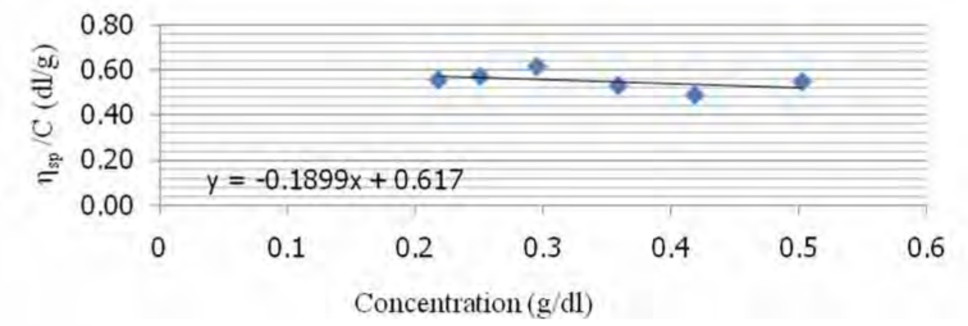

**Figure A-7** Plot of viscosity versus concentration at 30°C for PET-co-TEGT 10.

**Table A-8** Intrinsic viscosity of PET-co-TEGT 20

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.4608 | 424.51 | 425.06 | 423.82 | 424.46 | 1.2956 | 0.2956 | 0.6415 |
| $C_2$ | 0.3840 | 408.72 | 409.43 | 406.06 | 408.07 | 1.2456 | 0.2456 | 0.6395 |
| $C_3$ | 0.3291 | 395.04 | 397.28 | 397.57 | 396.63 | 1.2106 | 0.2106 | 0.6400 |
| $C_4$ | 0.2711 | 386.29 | 384.10 | 384.81 | 385.07 | 1.1753 | 0.1753 | 0.6468 |
| $C_5$ | 0.2425 | 378.13 | 380.09 | 379.09 | 379.10 | 1.1571 | 0.1571 | 0.6480 |
| $C_6$ | 0.2194 | 376.05 | 372.81 | 374.72 | 374.53 | 1.1432 | 0.1432 | 0.6526 |

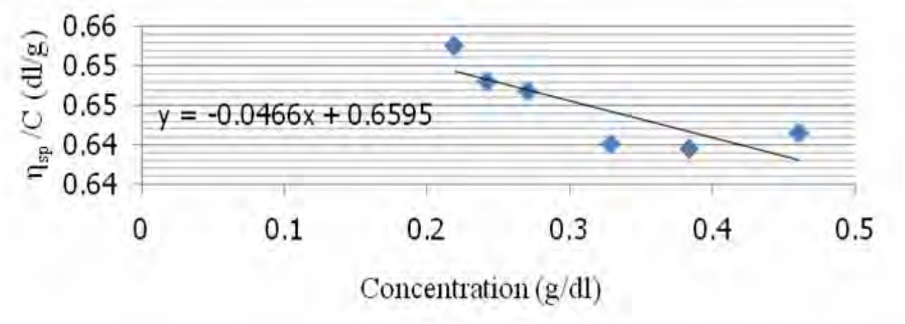

**Figure A-8** Plot of viscosity versus concentration at 30°C for PET-co-TEGT 20.

**Table A-9** Intrinsic viscosity of PET-co-TEGT 30

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5046 | 429.75 | 429.19 | 429.47 | 429.47 | 1.3109 | 0.3109 | 0.6161 |
| $C_2$ | 0.4205 | 426.84 | 422.70 | 423.73 | 424.42 | 1.2955 | 0.2955 | 0.7027 |
| $C_3$ | 0.3604 | 417.03 | 419.24 | 418.11 | 418.13 | 1.2763 | 0.2763 | 0.7665 |
| $C_4$ | 0.3154 | 397.41 | 397.68 | 395.46 | 396.85 | 1.2113 | 0.2113 | 0.6700 |
| $C_5$ | 0.2656 | 383.19 | 382.15 | 380.30 | 381.88 | 1.1656 | 0.1656 | 0.6236 |
| $C_6$ | 0.2294 | 378.64 | 378.82 | 376.22 | 377.89 | 1.1535 | 0.1535 | 0.6689 |

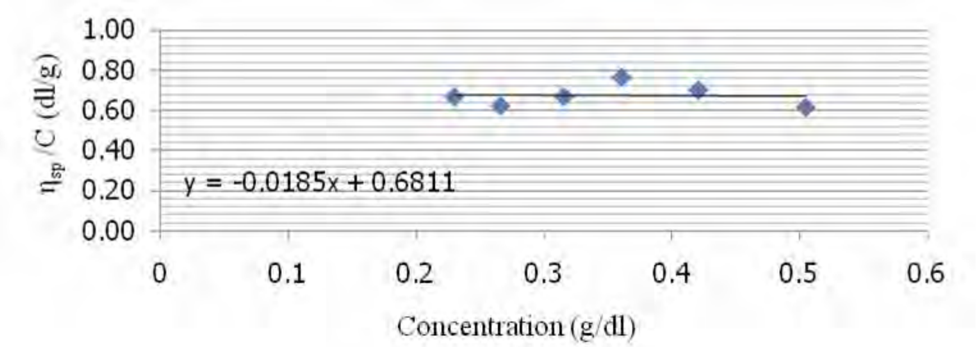

**Figure A-9** Plot of viscosity versus concentration at 30°C for PET-co-TEGT 30.

**Table A-10** Intrinsic viscosity of PET-co-TEGT 40

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}$/C (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.5032 | 389.91 | 390.68 | 390.97 | 390.52 | 1.1920 | 0.1920 | 0.3815 |
| $C_2$ | 0.4193 | 385.82 | 384.79 | 385.80 | 385.47 | 1.1766 | 0.1766 | 0.4211 |
| $C_3$ | 0.3594 | 379.69 | 379.89 | 381.17 | 380.25 | 1.1606 | 0.1606 | 0.4470 |
| $C_4$ | 0.2013 | 364.67 | 364.32 | 365.26 | 364.75 | 1.1133 | 0.1133 | 0.5630 |
| $C_5$ | 0.1677 | 361.03 | 360.51 | 360.86 | 360.80 | 1.1013 | 0.1013 | 0.6039 |
| $C_6$ | 0.1438 | 357.45 | 358.21 | 358.07 | 357.91 | 1.0925 | 0.0925 | 0.6429 |

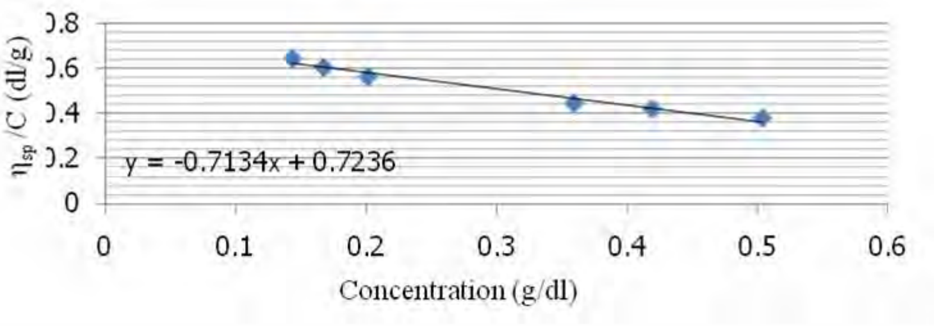

**Figure A-10** Plot of viscosity versus concentration at 30°C for PET-co-TEGT 40.

**Table A-11** Intrinsic viscosity of PET-co-TEGT 50

| Solvent | Concentration (C) (g/dl) | Flow time of solution (sec) | | | | $\eta_r$ | $\eta_{sp}$ | $\eta_{sp}/C$ (dl/g) |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | Average | | | |
| $C_0$ | 0.0000 | 327.24 | 327.45 | 328.17 | 327.62 | 1.0000 | 0.0000 | 0.0000 |
| $C_1$ | 0.4448 | 397.09 | 396.72 | 397.73 | 397.18 | 1.2123 | 0.2123 | 0.4773 |
| $C_2$ | 0.3707 | 385.81 | 386.16 | 386.03 | 386.00 | 1.1782 | 0.1782 | 0.4807 |
| $C_3$ | 0.3177 | 379.04 | 380.19 | 379.54 | 379.59 | 1.1586 | 0.1586 | 0.4993 |
| $C_4$ | 0.2616 | 374.52 | 375.26 | 375.70 | 375.16 | 1.1451 | 0.1451 | 0.5547 |
| $C_5$ | 0.2224 | 372.33 | 372.21 | 372.87 | 372.47 | 1.1369 | 0.1369 | 0.6155 |
| $C_6$ | 0.1853 | 365.59 | 366.12 | 365.96 | 365.89 | 1.1168 | 0.1168 | 0.6304 |

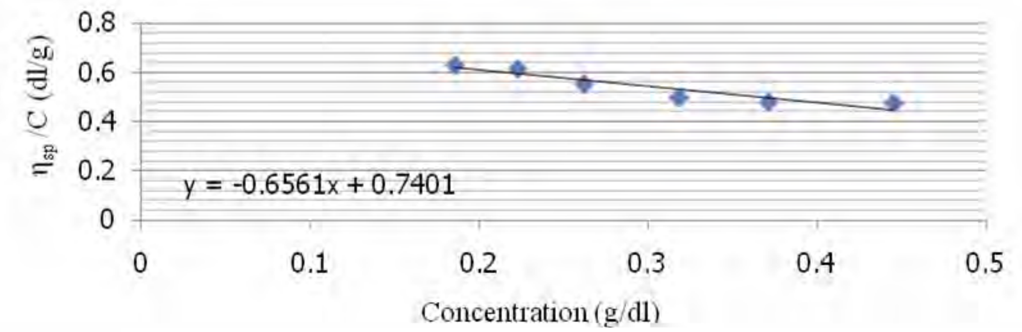

**Figure A-11** Plot of viscosity versus concentration at 30°C for PET-co-TEGT 50.

# APPENDIX B

## Mechanical Property Characterization

**Table B-1** Hardness of PET and copolyesters

| Sample | Hardness (Shore D) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | Average | SD |
| PET | 88 | 87 | 88 | 87 | 87 | 87.4 | 0.55 |
| PET-10 DEG | 75 | 72 | 72 | 73 | 72 | 72.8 | 1.30 |
| PET-20 DEG | 63 | 64 | 66 | 65 | 65 | 64.6 | 1.14 |
| PET-30 DEG | 55 | 52 | 54 | 54 | 52 | 53.4 | 1.34 |
| PET-40 DEG | 38 | 38 | 38 | 40 | 41 | 39 | 1.41 |
| PET-50 DEG | 31 | 30 | 30 | 31 | 32 | 30.8 | 0.84 |
| PET-10 TEG | 58 | 58 | 60 | 60 | 62 | 60.2 | 1.67 |
| PET-20 TEG | 52 | 52 | 52 | 48 | 48 | 50.4 | 2.19 |
| PET-30 TEG | 42 | 42 | 40 | 38 | 40 | 41.2 | 1.67 |
| PET-40 TEG | 28 | 28 | 28 | 30 | 30 | 28.8 | 1.10 |

**Table B-2** Tensile of PET and copolyesters

| No. of sample | Polymer | Tensile strength (MPa) | Elongation at break (%) |
|---|---|---|---|
| 1 | PET | 10.53 | 0.26 |
| 2 | PET-10 DEG | 9.65 | 0.51 |
| 3 | PET-20 DEG | 5.19 | 4.94 |
| 4 | PET-30 DEG | 4.05 | 12.66 |
| 5 | PET-40 DEG | 6.11 | 17.35 |
| 6 | PET-50 DEG | 5.96 | 17.95 |
| 7 | PET-10 TEG | 9.87 | 2.56 |
| 8 | PET-20 TEG | 2.30 | 28.08 |
| 9 | PET-30 TEG | 5.06 | 29.90 |
| 10 | PET-40 TEG | 6.52 | 33.76 |

# CURRICULUM VITAE

Miss Chantimas Tochai was born in Angthong, Thailand. She got a Bachelor’s Degree in major of Materials Science from Chulalongkorn University in 2007. After that, she started her graduate study a Master’s Degree in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and finished her study May in 2010.

## Presentations at the national conference

**2009** Synthesis and Thermal properties of poly(diethylene glycol terephthalate) and poly(triethylene glycol terephthalate) copolyester, October 15-17, 2009, Burapha University, Thailand