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PREPARATION OF UNSATURATED POLYESTER RESIN FROM POLYESTER FABRIC SCRAPS

Mr. Kittipoom Klubdee

A Thesis Submitted in Partial Fulfillment of the Requirements
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ผ้าพอลิเอสเทอร์ และผ้าผสมระหว่างพอลิเอสเทอร์กับฝ้าย ถูกนำมารีไซเคิลทางเคมีโดยการไกลโคลิซิสด้วยโพรพิลีนไกลคอล โดยใช้ซิงค์อะซิเตตในปริมาณที่แตกต่างกันคือ 0.5% และ 1% ของน้ำหนักผ้าพอลิเอสเทอร์เป็นตัวเร่งปฏิกิริยา และใช้เวลาในการไกลโคลิซิสที่แตกต่างกันคือ 4 6 และ 8 ชั่วโมง ให้ปฏิกิริยาดำเนินไปที่อุณหภูมิ 180 องศาเซลเซียส ภายใต้การรีฟลักซ์ในบรรยากาศไนโตรเจน โมเลกุลของพอลิเอสเทอร์จะถูกย่อยสลายกลายเป็นผลิตภัณฑ์ไกลโคไลซ์ ซึ่งเมื่อนำสารที่ได้ไปทำปฏิกิริยาเอสเทอริฟิเคชันกับมาเลอิกแอนไฮไดรด์จะได้พอลิเอสเทอร์เรซินชนิดไม่อิ่มตัว ซึ่งสามารถบ่มให้แข็งด้วยการใช้สไตรีนมอนอเมอร์เป็นสารเชื่อมขวาง โดยมีเมทิลเอทิลคีโตนเปอร์ออกไซด์ (MEKPO) เป็นตัววิเริ่ม และโคบอลต์ออกโตเอตเป็นตัวเร่งปฏิกิริยา ผลจากการทดลองเปรียบเทียบสมบัติเชิงกลและเสถียรภาพทางความร้อน ของพอลิเอสเทอร์เรซินที่สังเคราะห์จากการใช้ปฏิกิริยาไกลโคลิซิสที่แตกต่างกัน พบว่าผลิตภัณฑ์จากพอลิเอสเทอร์เรซินที่สังเคราะห์โดยการใช้เวลาในการไกลโคลิซิสที่ 8 ชั่วโมงจะให้สมบัติเชิงกลที่ดีที่สุด ทั้งความแข็ง ความทนแรงดัดโค้ง และความทนแรงกระแทก ส่วนเสถียรภาพทางความร้อนของเรซินที่สังเคราะห์ได้ มีค่าแตกต่างกันขึ้นอยู่กับระยะเวลาที่ใช้ในการไกลโคลิซิส กล่าวคือพอลิเอสเทอร์เรซินที่สังเคราะห์โดยการใช้เวลาในการไกลโคลิซิสที่ 8 ชั่วโมง จะมีเสถียรภาพทางความร้อนดีที่สุด และเมื่อเปรียบเทียบระหว่างพอลิเอสเทอร์เรซินที่สังเคราะห์ได้จากผ้าทั้ง 2 ชนิด กับพอลิเอสเทอร์เรซินทางการค้าพบว่า สมบัติเชิงกลของผลิตภัณฑ์จากพอลิเอสเทอร์เรซินที่สังเคราะห์ได้มีค่าต่ำกว่าสมบัติเชิงกลของเรซินทางการค้า เรซินที่ได้จากผ้าพอลิเอสเทอร์ทั้ง 2 ชนิดนี้สามารถนำไปขึ้นรูปเป็นผลิตภัณฑ์ต่างๆ ได้โดยวิธีการหล่อ เช่นเดียวกับพอลิเอสเทอร์เรซินชนิดไม่อิ่มตัวโดยทั่วไป

ภาควิชา วัสดุศาสตร์ ลายมือชื่อนิสิต…………………………….
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4672208823 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY
KEY WORD: UNSATURATED POLYESTER RESIN / GLYCOLYSIS / DEPOLYMERIZATION

KITTIPOOM KLUBDEE: PREPARATION OF UNSATURATED POLYESTER RESIN FROM POLYESTER FABRIC SCRAPS. THESIS ADVISOR: ASST. PROF. PRANUT POTIYARAJ, Ph.D, 80 pp. ISBN 974-53-1977-5.

Polyester and polyester blended cotton fabrics were chemically recycled by glycolysis. The reactions were carried out in propylene glycol with the presence of zinc acetate catalyst at 0.5% and 1% by weight of the fabric at 180^{o}C under reflux in nitrogen atmosphere. The reaction time was varied at 4, 6 and 8 hours. The glycolyzed products were then esterified using maleic anhydride in order to obtain unsaturated polyester resins. The prepared resins were cured using styrene monomer, methyl ethyl ketone peroxide (MEKPO) and cobalt octoate as a crosslinking agent, an initiator and an accelerator, respectively. The mechanical properties and thermal stability of the products prepared under different conditions were studied. The experimental results indicated that the products from resin prepared under 8-hour glycolysis possessed highest mechanical properties, i.e. hardness, flexural strength and impact strength. The thermal stability was found to be depended on glycolysis time. The products from resin prepared under 8-hour glycolysis exhibited the highest thermal stability. However, the mechanical properties of products from the glycolyzed resins were lower than those of commercial resin. This polyester fabric based resin offers a new class of unsaturated polyester resin that can be fabricated into products by the conventional casting method.

Department Materials Science Student's signature…………….....
Field of study Applied Polymer Science and Textile Technology Advisor's signature……………….
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CHAPTER I
INTRODUCTION

Poly (ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. Tremendous quantities of this material are consumed in the manufacture of video and audiotapes, X-ray films, food packaging and especially of soft-drink bottles, including the production of fibers for ropes, needlework (monofilament) and brushes for domestic cleaning. Another part is destined to molding of automobile parts, plates for vacuum thermoforming, detergent bottles, mantles, carpets, pillows [1].

A very important feature of PET, decisive in the choice of its wide application in the manufacture of packaging for the food industry, is that it does not have any side effects on the human organism. It should be pointed out, that PET does not create a direct hazard to the environment but, due to its substantial fraction by volume in the waste stream and its high resistance to the atmospheric and biological agents, it is seen as a noxious material [2].

PET is one of the most important fibers for industrial production. Due to its high performance, low cost, and recyclability, it is one of the most attractive candidates for high strength fibers [3]. Demand of PET usage as fiber consumption is increased whereas the remaining of PET using that belonged to plastic waste is also increased following as demand of PET usage. Most of plastic wastes are degraded or digested by environmental very hard. The recycling was another way to reduced amount of plastic waste that occurred from PET using.

PET recycling represents one of the most successful and widespread examples of polymer recycling. The main driving forces responsible for the increased recycling of post-consumer PET are its widespread use, particularly in the beverage industry, which had made PET the main target for plastic recycling. The relatively consistent volume supply and easy availability of post-consumer PET bottles from sorting facilities and the fact that generally has the second highest material scrap value after aluminums, makes PET recycling a viable concern. Therefore, the recycling of PET does not only serve as a partial solution to the solid waste problem but also contribute to the conservation of raw petrochemical products and energy.

Among the different recycling techniques, the only one acceptable according to the principles of “Sustainable Development” is the chemical recycling, since it leads to the formation of the raw materials from which the polymer is made of, as well as of other secondary value-added products [4]. A successful recycling program does not only depend on post-consumer waste collection, it also depends on whether the products made out of collected, reclaimed and recycled material respond to consumers’ needs, in other words if recycled products are actually bought. This is the reason why the PET industry constantly researches for reclaimed material new applications. Recently, a growing interest has been observed in the use of PET wastes for the production of specialized products such as unsaturated polyester, polyurethane foams and polymer concrete.

Most of the recent research about PET recycling has been focused on recycling of water drinking bottle PET with glycolysis reaction. In this research, recycling of PET fabric scraps was studied. PET fabric scraps were chemically recycled using glycolysis reaction. PET molecular chains were depolymerized using propylene glycol into smaller molecules (oligomer, tri-mer and di-mer). The glycolyzed products were examinded for its chemical and physical properties using several techniques. These glycolyzed products were bringing into unsaturated polyester resin by esterification reaction.

The cured resin was tested for its physical and mechanical properties i.e. tensile strength, flexural strength, impact strength, hardness and thermal stability. The results were compared with those of commercial resin and resin prepared from PET bottles.

CHAPTER II
LITERATURE SURVEY

2.1 Polyester Resin

Polyester resins are the most widely used resin systems, particularly in the marine industry. By far the majority of dinghies, yachts and workboats built in composites make use of this resin system. These resins are styrene-based, flammable and catalyzed when combined with Methyl Ethyl Ketone Peroxide (MEKPO). When working with these resins in large projects it is advised to use gloves and a chemical respirator to protect yourself from the fumes. These resins can be used with any type of fiberglass, carbon fiber or kevlar, as well as used over urethane foam and other sandwich core materials. These resins tend to be fairly rigid when cured and also slightly more brittle than epoxy resins.

Most of polyester resins are viscous, pale colored liquids consisting of a solution of polyester in a monomer, which is usually styrene. The addition of styrene in amount of up to 30-50% helps to make the resin easier to handle by reducing its viscosity. The styrene also performs the vital function of enabling the resin to cure from a liquid to a solid by 'cross-linking' the molecular chains of the polyester without the evolution of any by-products. These resins can therefore be moulded without the use of pressure and are called 'contact' or 'low pressure' resins. Polyester resins have a limited storage life as they will set or 'gel' on their own over a long period of time. Often small quantities of inhibitor are added during the resin manufacture to slow this gelling action.

For use in molding, a polyester resin requires the addition of several ancillary products. These products are generally: catalyst, accelerator and other additives (such as pigment; filler or chemical/fire resistance etc.

A manufacturer may supply the resin in its basic form or with any of the above additives already included. Resins can be formulated to the molder's requirements ready simply for the addition of the catalyst prior to molding. As has been mentioned, given enough time an unsaturated polyester resin will set by itself. This rate of polymerization is too slow for practical purposes and therefore catalysts and accelerators are used to achieve the polymerization of the resin within a practical time period. Catalysts are added to the resin system shortly before use to initiate the polymerization reaction. The catalyst does not take part in the chemical reaction but simply activates the process. An accelerator is added to the catalyzed resin to enable the reaction to proceed at workshop temperature and/or at a greater rate. Since accelerators have little influence on the resin in the absence of a catalyst they are sometimes added to the resin by the polyester manufacturer to create a 'pre-accelerated' resin.

2.1.1 Classification of Polyester Resin

There are two principle types of polyester resin used as standard laminating systems in the composites industry. Orthophthalic polyester resin is the standard economic resin used by many people. Isophthalic polyester resin is now becoming the preferred material in industries such as marine where its superior water resistance is desirable.

In general industry, polyester resin was classified into two types by chemical structure, saturated and unsaturated polyester resin. Polyester resins are the most Polyester resins such as these are of the 'unsaturated' type. Unsaturated polyester resin, such as alkyd resin, is a thermoset capable of being cured from a liquid or solid state when subject to the right conditions. It is usual to refer to unsaturated polyester resins as 'polyester resins', or simply as 'polyesters'. Whereas saturated polyester resins, such as poly (ethylene terephthalate) (PET), are saturated in their chemical structure by mean of no double bond. Both of them, there are a whole range of polyesters made from different acids, glycols and monomers, all having varying properties.

The Figure below showed the idealized chemical structure of a typical polyester. Note the positions of the ester groups (CO - O - C) and the reactive sites (C* = C*) within the molecular chain.

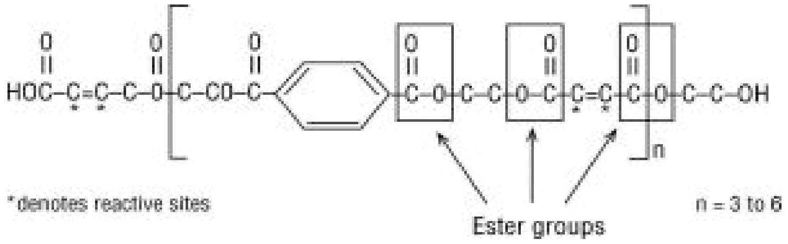
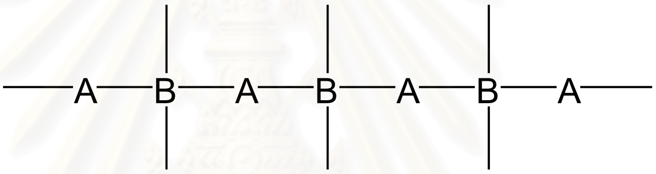


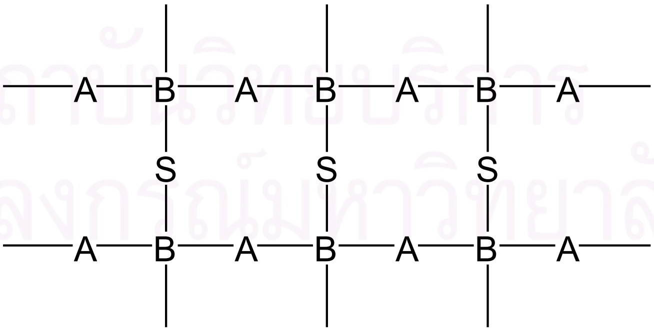
Figure 2.1 Schematic of typical unsaturated polyester

The molecular chains of the unsaturated polyester can be represented as follows, where 'B' indicates the reactive sites in the molecule.



Schematic Representation of Polyester Resin (Uncured)

With the addition of styrene 'S ', and in the presence of a catalyst, the styrene cross-links the polymer chains at each of the reactive sites to form a highly complex three-dimensional network as follows:



Schematic Representation of Polyester Resin (Cured)

The polyester resin is then said to be 'cured'. It is now a chemically resistant (and usually) hard solid. The cross-linking or curing process is called 'polymerization'. It is a non-reversible chemical reaction. The 'side-by-side' nature of this cross-linking of the molecular chains tends to means that polyester laminates suffer from brittleness when shock loadings are applied.

2.1.2 Chemical Reaction for Polyester Resin Synthesis

Polyester resin can be synthesized by many methods. The condensation reaction between polybasic acids and polyhydric alcohols were simply reaction for polyester synthesis with each of reactive groups must have hydroxyl and carboxyl groups at least two groups for each.

- Esterification reaction

Esterification reaction is a direct condensation reaction between dibasic acids and diol with concentration acid or salt of concentration acid are accelerators according to the reaction shown below

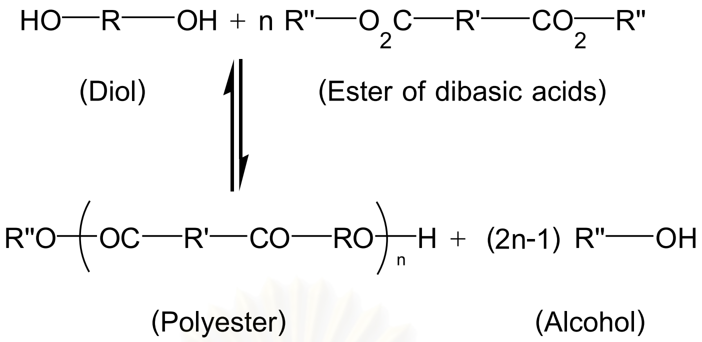
$$HO_2C{-}R{-}CO_2H + HO{-}R'{-}OH \rightleftharpoons HO_2C{-}R{-}CO_2{-}R'{-}OH + H_2O$$

(Dibasic acids) (Diol) (Polyester) (Water)

This reaction can be reacted with fast and easy, suitable for low molecular weight polyester synthesis

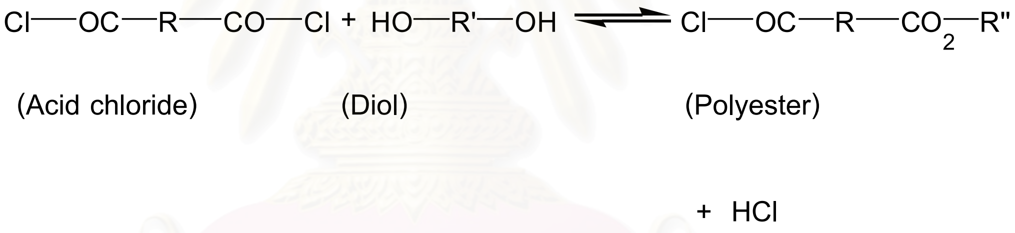
- Ester interchange reaction

Ester of dibasic acids is used instead of dibasic acids, as shown in reaction formula below



This reaction will be used in case of a few dissolved dibasic acids with diol. Methyl ester, R-$COOCH_3$, is an ester of dibasic acids which is potential used for this reaction, suitable for low molecular weight polyester synthesis.

- Reaction between acid chloride and diol



This reaction can be faster than other reaction but spent more times and raw materials because of acid will be changed to acid chloride.

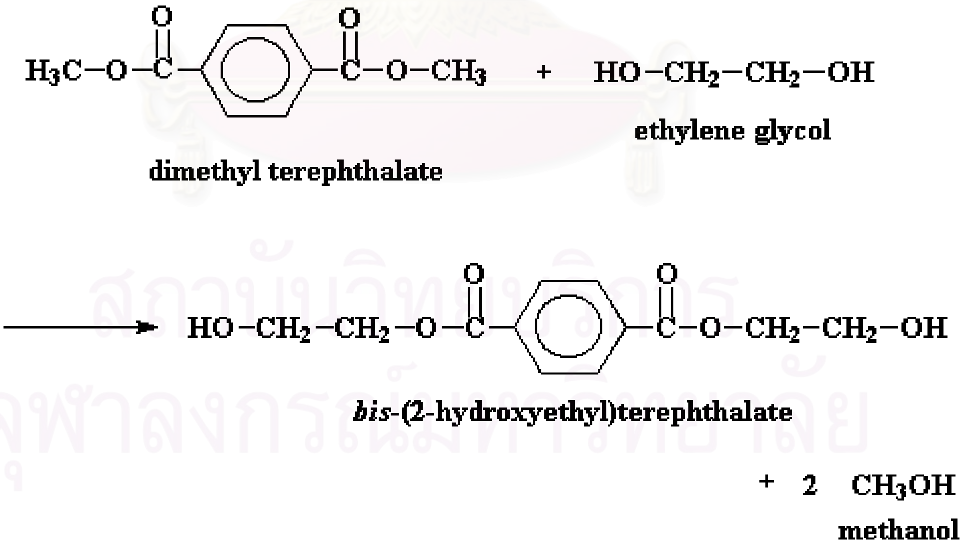
2.2 Poly (ethylene terephthalate), PET

PET was classified into linear saturated polyester and thermoplastic. John Rex Whinfield and James Tennant Dickson [5], patented "polyethylene terephthalate" (also called PET or PETE) in 1941. The saw that Carothers's research had not investigated the polyester formed from ethylene glycol and terephthalic acid. Polyethylene terephthalate is the basis of synthetic fibers such as polyester, dacron, and terylene. Whinfield and Dickson along with inventors W.K. Birtwhistle and C.G. Ritchiethey also created the first polyester fiber called Terylene in 1941 (first manufactured by Imperial Chemical

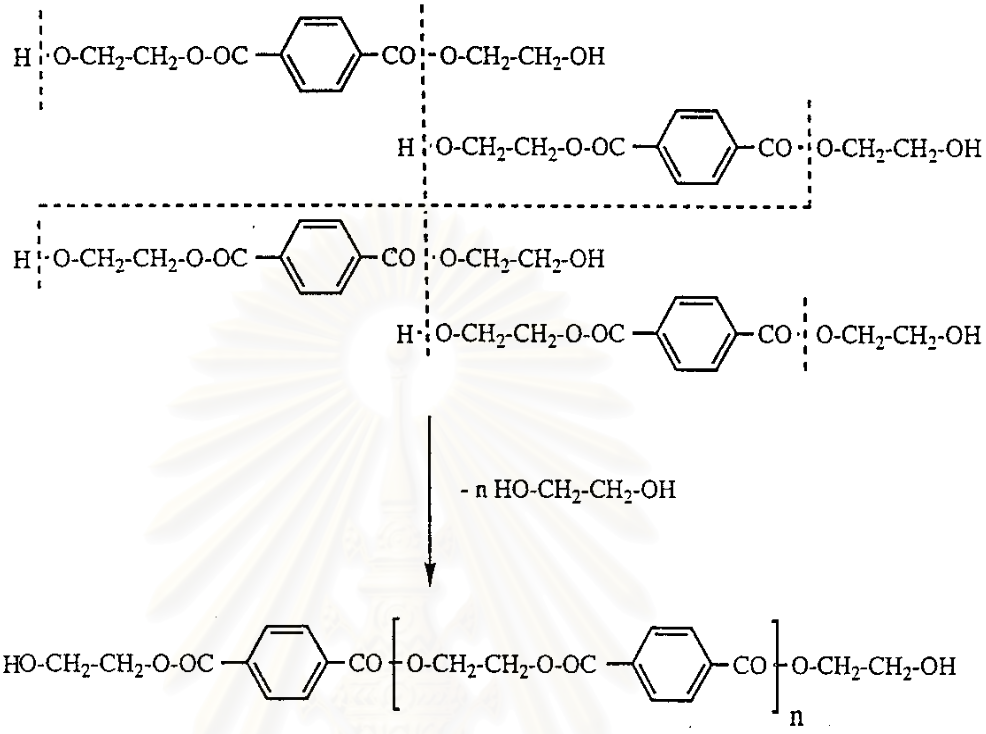
Industries or ICI). The second polyester fiber was Dupont's Dacron. Dupont's polyester research lead to a whole range of trademarked products, one example is Mylar (1952), an extraordinarily strong polyester (PET) film that grew out of the development of Dacron in the early 1950s. Polyesters are made from chemical substances found mainly in petroleum and are manufactured in fibers, films, and plastics.

2.2.1 Chemical Reaction for PET Synthesis

PET, condensation polyester, is produced by the reaction of a di-acid and a di-alcohol. There are two specific steps involved in PET synthesis. The first is either an esterification of terephthalic acid (TPA) and ethane diol (ED) or the transesterification of dimethyl terephthalate (DMT) and ED. This reaction is performed under pressure. In either case, the result is the bis 2-hydroxyl ethyl terephthalate (BHET), dimers and trimers which both of them are called oligomers. For by product that occurred while react process, but the reaction was heated to around 210 Celsius the methanol or water will boil away.



The second reaction is the polycondensation polymerization of BHET to form PET and the regeneration of ED. This step is conducted under vacuum at 270-285 Celsius



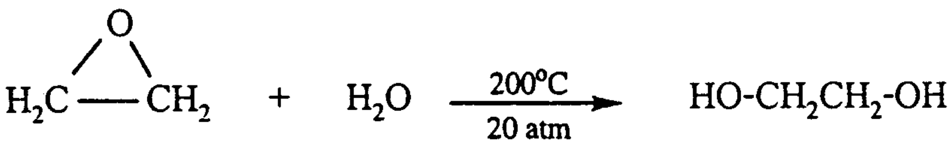
or $$n\ \text{BHET} \rightleftharpoons (\text{PET})_n + (n-1)\ \text{EG}$$

This reaction could be reversible. So, EG would be eliminated while reaction until end of process.

2.2.2 Substance for PET Synthesis

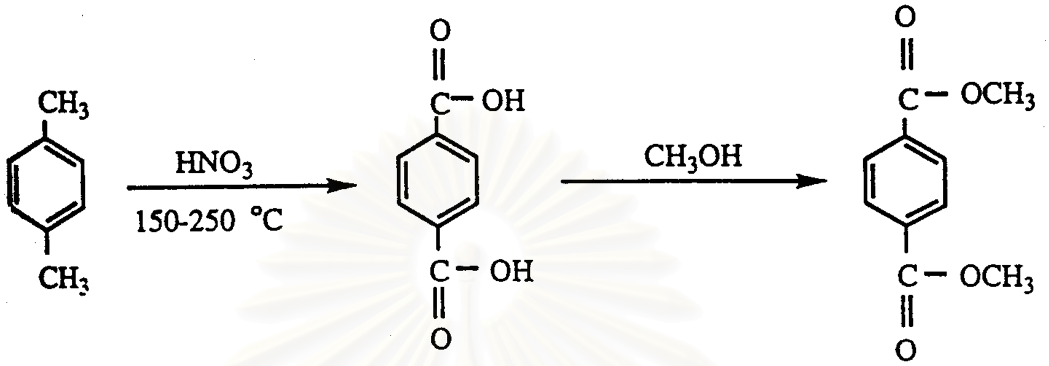
1. Ethylene glycol (EG)

EG could be synthesized by water addition of ethylene oxide reaction at 200 Celsius which shown as below



2. Dimethyl terephthalate (DMT)

DMT could be prepare from p-xylene which was reacted by oxidation reaction with nitric acid



For PET synthesis industrial, PET synthesized by DMT is more favorite than TPA because of high melting temperature, a few dissolved in general solvents and purity of TPA. Although PET were synthesized by condensation between TPA and EG directly. The advantages of DMT was easy to dissolved in EG and by product from reacted with DMT was methanol which had low boiling point can be eliminated easier.

2.3 Unsaturated Polyester Resin (UPR)

UPR is a mixture substance between unsaturated polyester and monomer which can be polymerized to polymer, and had low degree of polymerization about 8-10 (molecular weight about 2000)

Saturated polyester can be synthesized by reaction between glycol and dibasic acid [6], which is a mixture substance between saturated and unsaturated organic acid. When reaction is finished, saturated polyester is dissolved in unsaturated monomer such as styrene monomer. The styrene monomer molecules are introduced between molecules of unsaturated polyester as shown in Figure 2.3

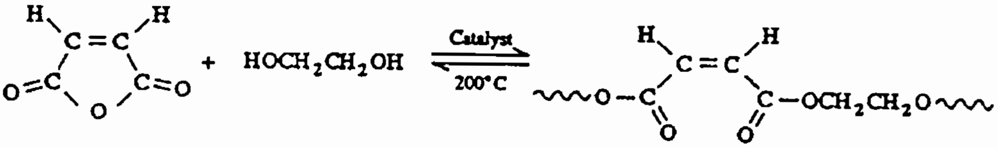


Figure 2.2 Saturated polyester synthesis

Figure 2.3 Styrene monomer were introduced among unsaturated polyester

Both unsaturated bond of polyester and monomer are reacted partially whereas these mixture substance are received heat or accelerator, the reaction are fully reacted. So, styrene monomer is assumed that its duty was cross-linking agent too. The polyester structure are reacted at unsaturated bond as shown in Figure 2.4

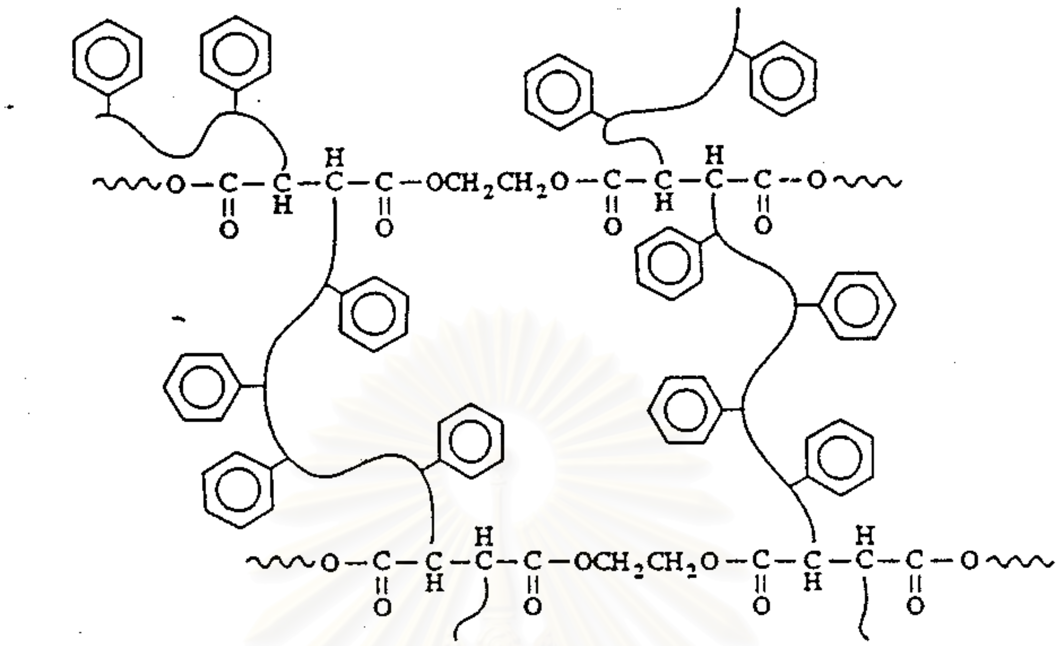


Figure 2.4 Network structure of polyester [6]

2.3.1 Content of Unsaturated Polyester Resin

2.3.1.1 Unsaturated polyester

Unsaturated polyester resins are synthesized by reaction between acid and glycol. There are many types of acid and glycol that used for unsaturated polyester synthesis. The favorite types of glycol are ethylene and propylene glycol. Each types of glycol providing the different properties of polyester.

Table 2.1 Typical types of glycol used for unsaturated polyester synthesis [7]

Name	Formula	Molecular Weight
Ethylene glycol	$HOCH_2CH_2OH$	62
Propylene glycol	HOC_3H_6OH	76
Butylene glycol	HOC_4H_8OH	90
Diethylene glycol	$HOCH_2CH_2O\ CH_2CH_2\ OH$	106
Dipropylene glycol	$HOC_3H_6OC_3H_6OH$	134
Triethylene glycol	$HOCH_2CH_2O\ CH_2CH_2\ O\ CH_2CH_2\ OH$	150

Acids used for unsaturated polyester synthesis are prepared from mixture of saturated and unsaturated organic acid. The ratio of mixing will effect to polyester resin properties. If need polyester resin that had highest of cross linking degree, unsaturated acid were used for synthesis only. In opposite, if ratio of saturated acid were increased, degree of cross linking was decreased too.

Maleic anhydride and fumaric acid are typical unsaturated acids which are preferred to use for unsaturated polyester synthesis

maleic anhydride fumaric acid

Figure 2.5 Chemical structures of maleic anhydride and fumaric acid

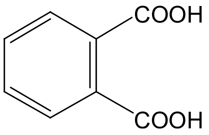
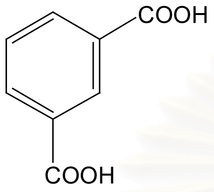
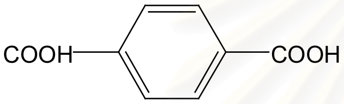
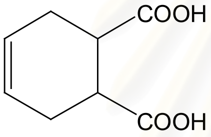
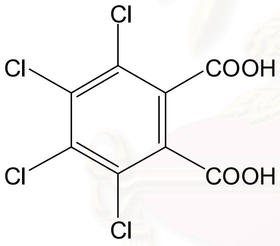
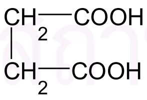
Saturated acid which was used for resin synthesis was phthalic acid. The other types of saturated acid was shown in table 2.2

2.3.1.2 Monomer

Monomer that used for polyester synthesis must be had double bond in its molecule and be dissolved in unsaturated polyester. Monomer would be cross linking among molecule when it was received by heat or curing agent.

Styrene monomer was popular used for this process since cheap, good solvent and can be reacted with polyester while curing. The others type of monomer that were used for polyester resin synthesis was shown in table 2.3

Table 2.2 Saturated acids used for resin synthesis [7]

Formula	Name
	ortho-Phthalic acid
	Isophthalic acid
	Terephthalic acid
	Tetrahydrophthalic acid
	Tetrachlorophthalic acid
 CH_2-COOH CH_2-COOH	Succinic acid
$HOOC-(CH_2)_4-COOH$	Adipic acid

2.3.1.3 Inhibitor

Double bonds in unsaturated polyester had been easy reacted with heat, light and other subject. It could belonging to free radicals easier and takes effect to gelation. So, inhibitor was necessary to addition for prevent over polymerization. Polyester which was added by inhibitor was handling longer than none.

Almost of inhibitor substance were derivative of quinine such as benzoquinone or hydroquinone

2.3.2 Substance for Polyester Curing

2.3.2.1 Catalyst

Almost of catalyst was derivative of peroxide such as methyl ethyl ketone peroxide (MEKPO) or benzoyl peroxide

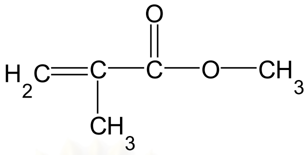
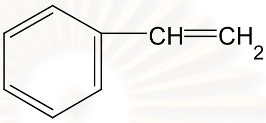
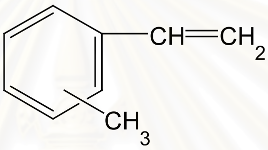
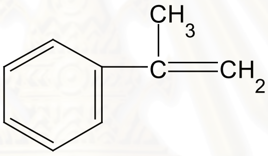
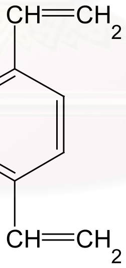
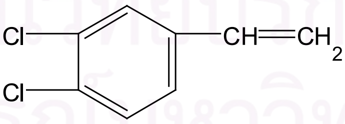
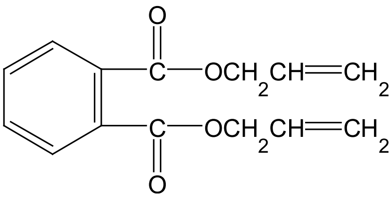
2.3.2.2 Accelerator

Accelerator was a substance that supported polymerization could be reacted at room temperature. Almost of accelerator was salt of metal (such as cobalt octoate, cobalt naphthenate) or derivative of amine such as diethyl aniline or dimethyl aniline.

Each type of accelerator was specifying used with many type of catalyst, for example, cobalt octoate or cobalt naphthenate must be used with MEKPO whereas derivative of amine must be used with benzoyl peroxide.

It is also important to add the accelerator and catalyst in carefully measured amounts to control the polymerization reaction to give the best material properties. Too much catalyst will cause too rapid a gelatin time, whereas too little catalyst will result in under-cure.

Table 2.3 Monomers used for resin synthesis [7]

Name	Formula	Molecular Weight
Methyl Methacrylate	 $H_2C{=}C(CH_3){-}C({=}O){-}O{-}CH_3$	100
Styrene		104
Vinyl toluene		118
α-Methyl styrene		118
Divinyl benzene		130
Dichlorostyrene		170
Diallyl phthalate		246

The process of rigid polyester synthesis was shown in Figureure 2.6

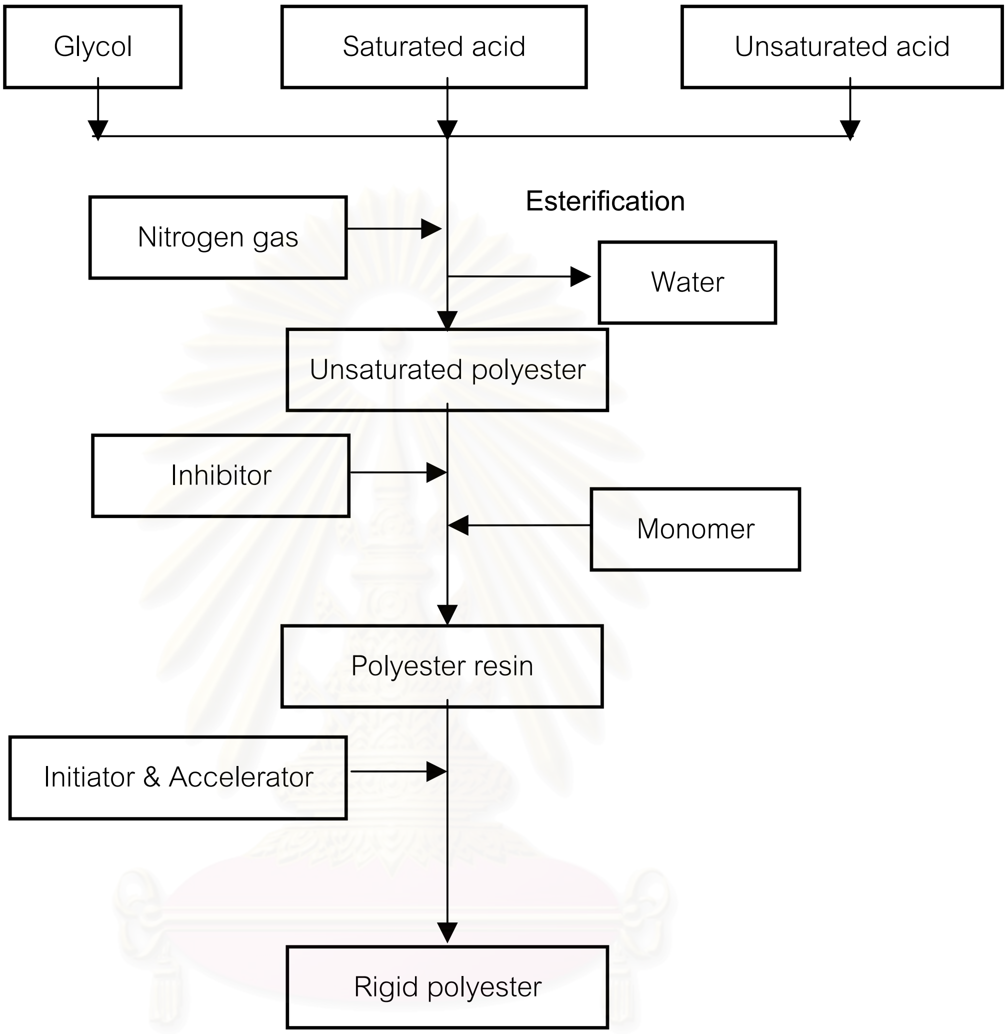


Figure 2.6 The process of rigid polyester synthesis

While polyester was cured by initiator and accelerator, this reaction is polymerization of double bonds between styrene monomer and polyester. In general, resin curing reaction was divided into two times.

First time: Gel time was started until curing agents were added to resins were corrugated to gel

Second time: Cure time

Resin curing was exothermic reaction and had relative between temperature and time as shown as Figure 2.7

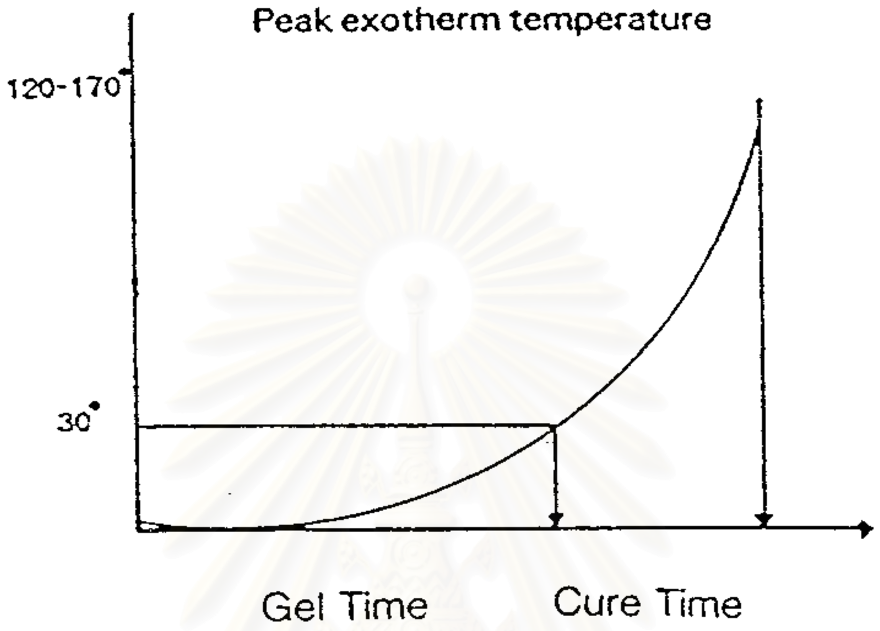


Figure 2.7 Peak exotherm temperature

The hardness of resin was increased while curing reaction was continued until resins were being hard to 95 percent. So, resins were brought to post cure first for prevent resin deformation since not fully hardness. Post cure was be curing at 100-120 Celsius, 3-6 hours.

The factors, which had effected to resin curing, were

1. Temperature; at high temperature resin would be curing faster than low temperature
2. Amount of initiator and accelerator
3. Amount of resin
4. Moisture; water or moisture would be retarded of reaction
5. Amount of oxygen; oxygen would be retarded of reaction same as moisture

2.4 Depolymerization of PET

PET was depolymerized by many chemical reactions;

2.4.1 Hydrolysis

This reaction was divided into 3 types; acid hydrolysis, alkaline hydrolysis and neutral hydrolysis. The hydrolysis of PET was examined in order to take the pure monomer (terephthalic acid) and ethylene glycol from which the polymer is made of. This monomer was used as raw material for the reproduction of PET. Disadvantages of this hydrolysis were spend more times for finished

The hydrolysis of PET was examined in order to take the pure monomer (terephthalic acid) from which the polymer is made of. This monomer was used as raw material for the reproduction of PET.

2.4.2 Methanolysis or Alcoholysis

Methanol was used for solvent at high temperature and pressure. The products were dimethyl terephthalate and ethylene glycol.

Methanolysis of PET affords dimethyl terephthalate (DMT) and ethylene glycol. These products are recycled to the transesterification process of PET production and enjoy some advantages over the products of hydrolysis and glycolysis; for example, easy purification steps. Methanolysis has been attempted by Lotz et al. [8] and Gruschke et al. [9], as described in the references, which are patents. In the process of Gruscheke et al., PET was completely (more than 99%) depolymerized to DMT and EG by reacting molten PET with methanol at 210 °C in the absence of a catalyst. Some patents [10, 11] teach improved processes for increasing the quality of the products and lowering recycling costs

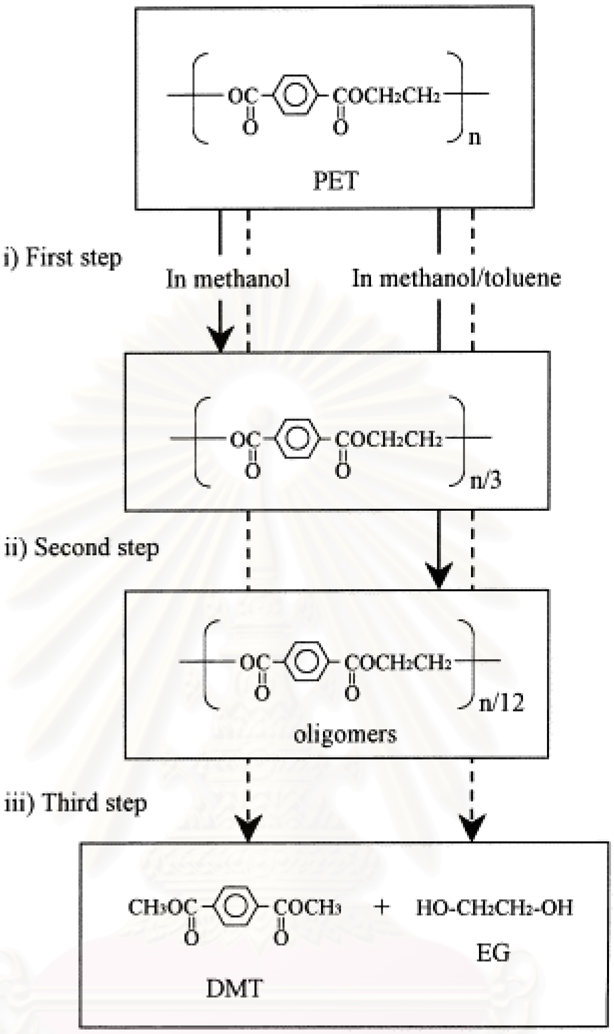


Figure 2.8 Reaction schemes of PET methanolysis.
Solid line: without catalyst; broken line: with catalyst.

2.4.3 Aminolysis

PET was depolymerized by primary amine solution such as ethyl amine, ethanol amine or methyl amine. The products were di-amide of terephthalic acid and ethylene glycol.

2.4.4 Ammonolysis

Anhydrous ammonia in ethylene glycol was used for PET depolymerization and by products of this reaction was amide of terephthalic acid.

2.4.5 Glycolysis

Glycolysis was PET depolymerized by many types of glycol the most favorable glycol was ethylene glycol and propylene glycol. The products are BHET and polyol which can be reacted with unsaturated dibasic acid and become unsaturated polyester resin. In addition they also can be reacted with isocyanate and become polyurethane.

In this paper, glycolysis of PET is examined as a process for the production of raw materials used in unsaturated polyester resins. Vaidya and Nadkarni were among, the first who systematically studied the formation of unsaturated polyester resins (UPR) from PET glycolysis [14], [15] and [16]. Baliga and Wong [17] carried out the glycolysis of PET with ethylene glycol (EG) using various catalysts. They found that glycolyzed products had 1–3 repeating units depending on the catalyst used. Suh et al. [18] examined the properties of unsaturated polyesters produced from glycolyzed PET with various combinations of the glycols DEG/propylene glycol (PG).

2.5 Unsaturated Polyester Resin Synthesis from PET Scraps

In recent study, Nadkarni et al. [14 and 16] suggested that unsaturated polyester can be synthesized from PET waste. They also investigated the kinetics of glycolysis on several glycols. The glycolyzed product were reacted with maleic anhydride and found that can be homogenious with styrene monomer. After that, accerelator and initiator were added for polyester curing

Water which was occurred while reaction must be eliminated since it could be reversible reaction.

Polyester synthesis was shown as Figure 2.9

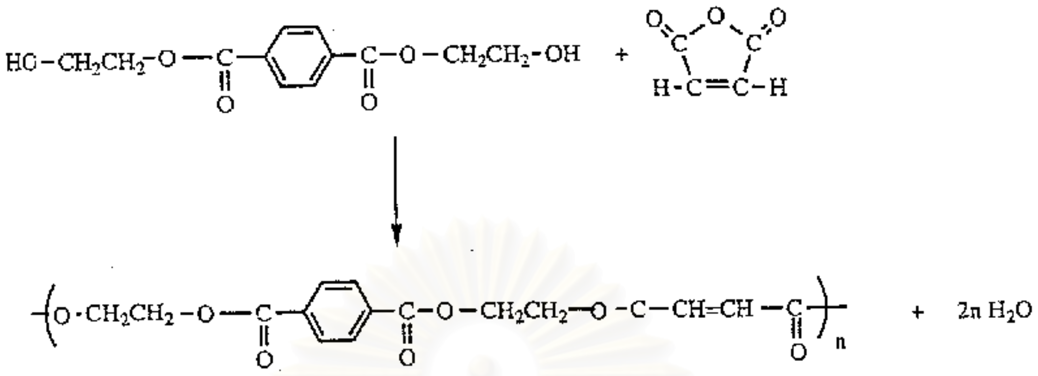


Figure 2.9 Unsaturated polyester synthesis

Farahat et al. also synthesized modified UPR from PET glycolysis using different DEG/PET molar ratios [19] and [20]. In the same process of glass–fiber-reinforced plastics manufacturing, Radenkov et al. [21] investigated the possibility of direct using products from PET glycolysis.

The theory for unsaturated polyester synthesis from PET scraps, was molecular changing from saturated to unsaturated groups by adding unsaturated groups to PET molecule

Polyester was synthesized from recycle PET must be eliminated contaminate substanced. Impurities were affected to physical and mechanical properties. However these problems were solved by good quality control of process and separated impurity substance from PET with high efficiency.

CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

Materials and chemicals are classified into 3 groups according to procedure and chemical reaction.

3.1.1 Glycolysis Reaction

- *PET fabric*: PET fabrics were divided into 2 types, PET fabric and T/C fabric (Cotton fiber was blended with polyester fiber; Polyester/Cotton ratio was 65/35 by weight), from a local fabric procedure.
- *Propylene glycol*: Reagent grade, a product of Fluka, was used as a solvent for PET fabric dissolution in glycolysis reaction.
- *Zinc acetate*: Zinc acetate, a product of Fluka, was used as an accelerator in glycolysis reaction.
- *Hydrochloric acid*: HCl, a product of Merge, were used for cotton part elimination of T/C fabrics.

3.1.2 Esterification Reaction

- *Maleic Anhydride*: Maleic Anhydride, unsaturated acid, a product of Fluka, was used to react with glycolized product.
- *Hydroquinone*: Hydroquinone, a product of Fluka, was used as an inhibitor to prevent setting of unsaturated polyester resin before mold casting.

3.1.3 Cured Polyester Resin Synthesis

- *Styrene Monomer*: Styrene monomer, supplied from Eternal Resin Co., Ltd., was used as a crosslinking agent.
- *Cobalt Octoate*: Cobalt octoate, supplied from Thai Mitsui Co., Ltd., was used as a catalyst for curing polyester resin.

- *Methyl Ethyl Ketone Peroxide*: Methyl Ethyl Ketone Peroxide (MEKPO), a product of Fluka, was used as an initiator.

3.2 Instruments

Details of each instrument are classified according to the experimental procedure as follows.

3.2.1 Chemical Reaction

- Glycolysis reaction

4-Neck round bottom flask attached with nitrogen gas, thermometer, stirrer and condenser was used as a reactor as shown in Figure 3.1

- Esterification reaction

Water reflux were added to the reactor as for prevent reversible of reaction for esterification reaction.

Figure 3.1 Chemical reactor

3.2.2 Physical Property Equipments

- Vernia Caliper

A vernia-carliper (Peacock, Model G, Japan) was used to measure dimension of the samples.

Figure 3.2 Vernia-Carliper

3.2.3 Mechanical Property Equipments

- Tensile Testing Machine

Tensile properties of the samples were tested by universal testing machine LLOYD LR 100K according to the ASTM D638-02a [22].

Figure 3.3 Universal Testing Machines LLOYD LR 100K

- Impact Testing Machine

Impact properties of the samples were tested by ATS Charpy Impact Tester according to the according to the ASTM D6110-02 [23].

Figure 3.4 ATS Charpy Impact Tester

- Flexural Testing Machine

Flexural properties of the samples were examined using Universal Tensile Testing Machine LLOYD500 according to the ASTM D790-02 [24].

Figure 3.5 Flexural Testing Machines

- Hardness Testing Equipment

Hardness properties of the samples were tested by Durometer Shore D according to the ASTM D2240-86 [25].

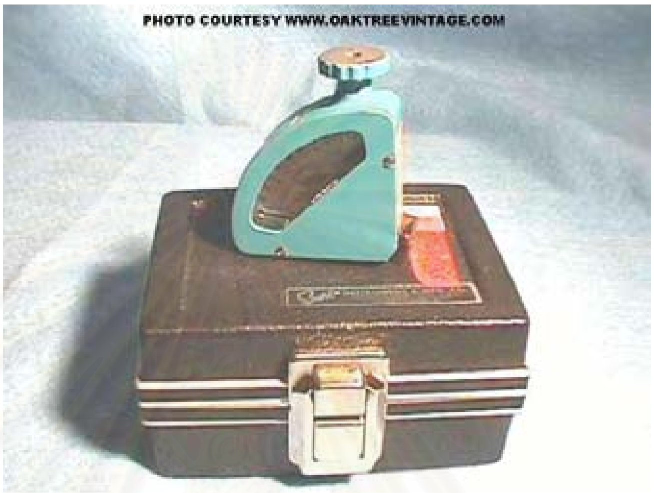


Figure 3.6 Hardness Testing Equipment

3.2.4 Chemical Property Equipments

- Fourier Transform Spectrometer

Functional groups of the samples were characterized by Impact 400D Nicolet

Figure 3.7 FT-IR Testing Machine

- Attenuated Total Reflectance (ATR)

Functional groups of the samples (in the case of fiber) were characterized by Thermo Nicolet Nexus 670.

Figure 3.8 ATR Testing Machine

- Thermogravimetric Analysis (TGA)

Degradation temperature of the samples were characterized by TGA METTLER TOLEDO TGA/SDTA 851^{e}

Figure 3.9 TGA Testing Machine

- Differential Scanning Calorimetry (DSC)

Glass transition and melting temperature of the samples were characterized by NETZSCH DSC 200.

Figure 3.10 DSC Testing Machine

- Gel Permation Chromatography (GPC)

Molecular weight and molecular distribution of each sample were characterized by Waters 150-CV.

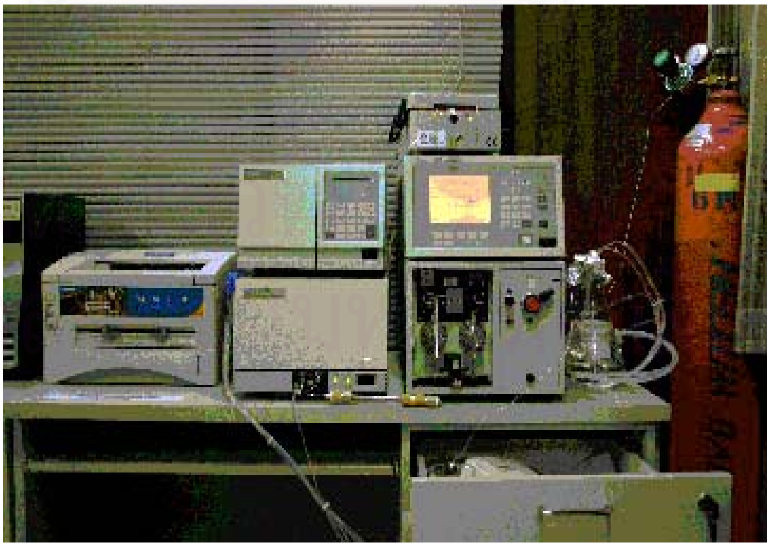


Figure 3.11 GPC Testing Machine

3.3 Experimental Procedure

The experimental flow diagram for synthesis of unsaturated polyester resin was shown in Figure 3.13

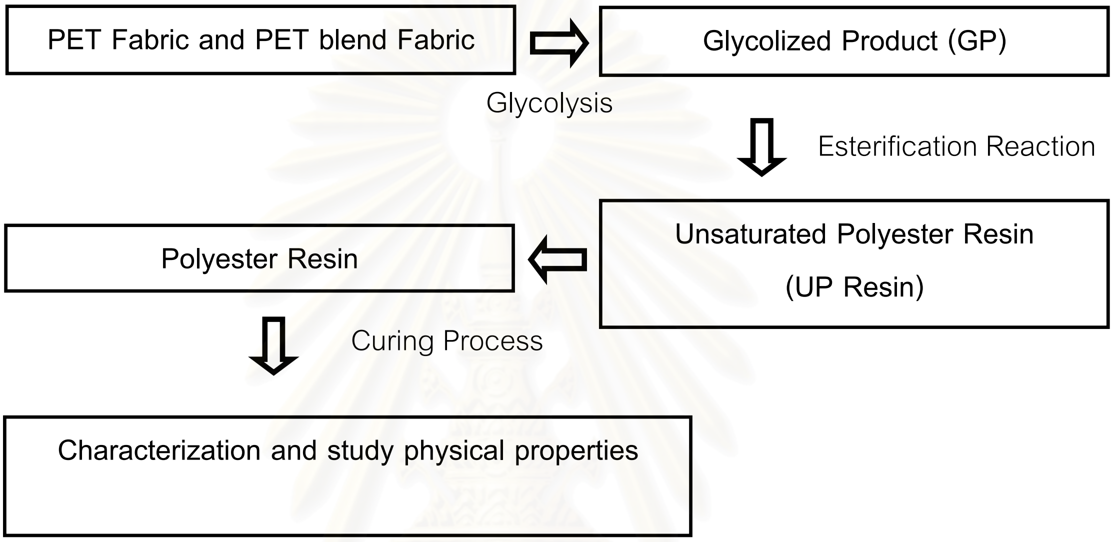


Figure 3.12 The flow diagram of experimental procedure

General preparation of polyester resin was described in three steps as follows:

<u>Step 1</u>: Glycolysis Reaction

PER fabric and PET-blend fabric were glycolized with propylene glycol at molar ratio 0.5 : 1. Zinc acetate was used as a catalyst (add 0.4% depend on PET fabric weight). In this experiment, reaction time was varied to 4, 6 and 8 hours (generally 8 hours for glycolysis reaction), 220^{O}C and nitrogen gas was purged all time. In case of 4 and 6 hours of reaction time, amount of zinc-acetate were increased to 2 times (from 0.4 to 0.8%). Then glycolyzed product was divided into 2 parts, filtered product and non-filtered product. Since almost of PET fabric have titanium dioxide as a filler, the effect of titanium dioxide during polyester resin synthesis on their properties were studied.

Step 2: Esterification Reaction

Glycolized product from glycolysis reaction was added into 4-neck round bottom flask for esterification reaction. Maleic anhydride was added at 1:1 molar ratio with propylene glycol (mole ratio of PET: PG: MA equal to 0.5:1:1). Reaction was carried out at 180^{O}C for at least 6 hours under nitrogen gas. When reaction was finished, hydroquinone (0.45% by weight) was added to prevent gelation before casting.

Step 3: Cured Polyester Resin Synthesis

Styrene monomer (35% by weight of unsaturated polyester resin) was added into resin at 100 ^{O}C and was stirred until homogenous under nitrogen atmosphere. Cobolt octoate and MEKPO were added into resin (0.5% by weight of unsaturated polyester resin) as an accelerator and initiator respectively. Then resins were cast into silicone resin mold and bring it into oven for curing at 100 ^{O}C at least 48 hours.

3.4 Characterization and Testing

3.4.1 Chemical Properties

3.4.1.1 Thermal Analysis

Thermal analysis embraces all methods in which measurements are made of a property that changes as the temperature changes. The equipment used ideally consists of a measurement cell in which the specimen is placed, the measuring apparatus, and the means to change the temperature of the specimen within the measurement cell in a control manner, preferably according to a pre-set programme. A constant rate of change of temperature is normally preferred, and it is desirable to make the property measurements continually.

Differential Scanning Calorimetry (DSC)

DSC thermograms were obtained on a Perkin-Elmer DSC7 calorimeter (Buckinghamshire, UK). Heating scans were carried out at a heating rate of 10 Celsius min^{-1} from 0 to 100 Celsius under a nitrogen gas flow. All of the measurements were conducted at a sufficiently low cooling and heating rate of ± 0.5 K/min to avoid thermal and time delays. At the end of each measurement, the pan was dried under vacuum for 24 h to attain the mass of dry sample.

A differential scanning calorimeter (DSC) is apply suited for precise measurement of the relatively small temperature shifts because of particular sensitivity to exothermic freezing and endothermic melting transitions. The physical basis for the shift is that the equilibrium temperature for a solid–liquid phase transition is determined by the radius of curvature of the interface between the solid and liquid phases.

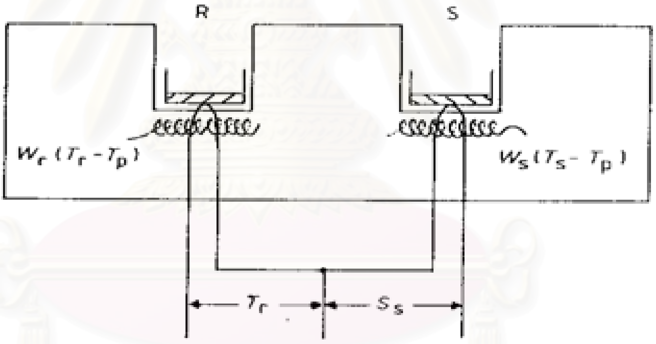


Figure 3.13 Schematic of a DSC apparatus: R. r. reference; S. s. specimen.

Thermogravimetric Analysis (TGA)

TGA thermograms were obtained on a METTLER TOLEDO TGA/SDTA 851^{e}. Heating scans were carried out at a heating rate of 50 Celsius min^{-1} from 30 to 1000 Celsius and run at constant temperature, 1000 Celsius, 10 minutes under a nitrogen gas flow.

With TGA the mass of the sample is recorded continuously while the temperature is increased at a constant rate. Weight losses occur when volatiles absorbed by the polymer are driven off, and at higher temperature when degradation of the polymer occurs with the formation of volatile products. The design of the equipment is most exacting, not only because the weight losses to be measured are very small, demanding a precision weighing mechanism, but also because of the need to avoid convective forces arising within the heating chamber and because of the changes in the density of the gaseous environment. It is important to ensure that volatiles do not condense on the weighing apparatus. It is also necessary to control the atmosphere when this has an influence on the process of degradation.

3.4.1.2 Infra-red Spectroscopy

In attempting to identify and characterize polymeric materials almost invariably recourse will be made to some from of vibrational spectroscopy which is capable of providing detailed information on polymer structure.

Vibration spectroscopy is concerned with the detection of transitions between energy levels in molecules which result from vibrations of the interatomic bonds. The vibrational frequencies are shown to be characteristic of particular functional groups in molecules. They are sensitive to the molecular environment, chain conformations and morphology and so afford a useful method for polymer analysis.

Fourier Transform Spectroscopy (FT-IR)

IR spectra of the samples were characterized by Impact 400D Nicolet. The spectra that shown C=O groups was 1700-1800 cm^{-1}, C-O of ester group and aromatic ester was shown at about 1250-1300 cm^{-1}and 1000-1100 cm^{-1}respectively, C=C (aromatic group in styrene monomer) was 1600-1700 cm^{-1} and the spectra of hydroxyl group (-OH) that be consisted of glycol or water was 2700-4000 cm^{-1}.

Interferometry was first used to investigate the otherwise inaccessible far infra-red (FIR) region of the spectrum. Developments in Fourier transform spectroscopy (FTIR) have extended applications of interferometry to the whole IR region particularly for rapid sampling in such applications as gel permeable chromatography.

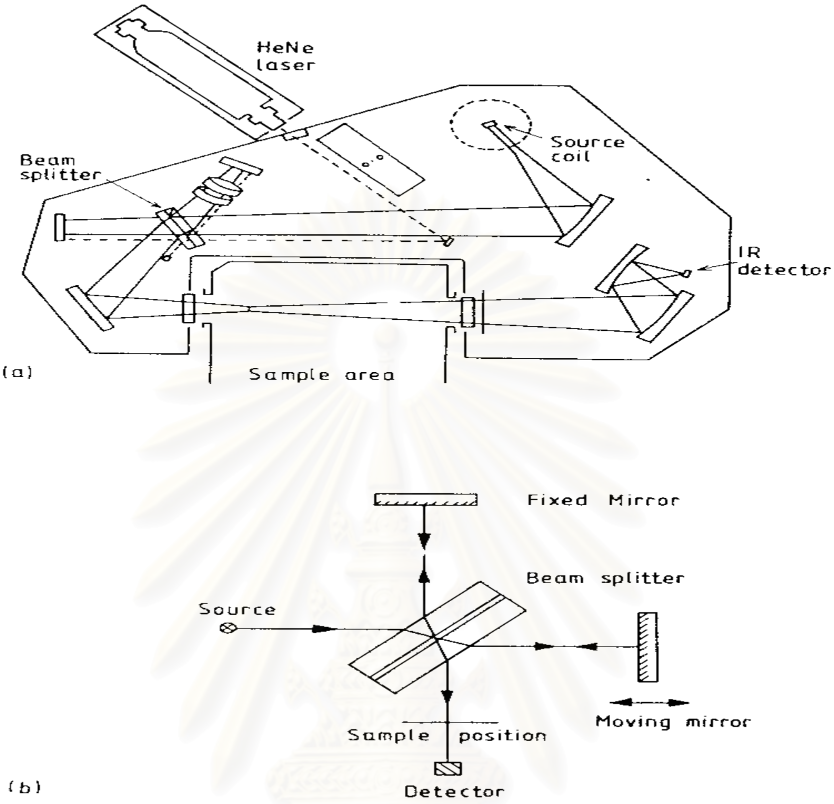


Figure 3.14 Schematic of FT-IR (a) general arrangement of optics (b) Michelson Interferometer (courtesy Perkin Elmer).

Attenuated Total Reflectance (ATR)

When light is incident at an interface between materials having different refractive indices (*n*) such that the angle of incidence exceeds the critical angle, α_c, where sin $\alpha_c = n_2/n_1$ then the light is reflected from the surface rather than reflected (Fig. 3.16 (a)). At the interface the electric field component of the EM radiation penetrates to some small extent into the surface layers of the less dense materials (n_2). The depth of penetration depends both on the wavelength of the light, increasing with increasing wavelength, and on the relative values of the reflective indices and is typically of the order of several microns. As a consequence, light having wavelengths corresponding to the absorption spectrum will be absorbed in proportion in the depth of penetration. This implies that there will be greater absorption of the longer wavelength light.

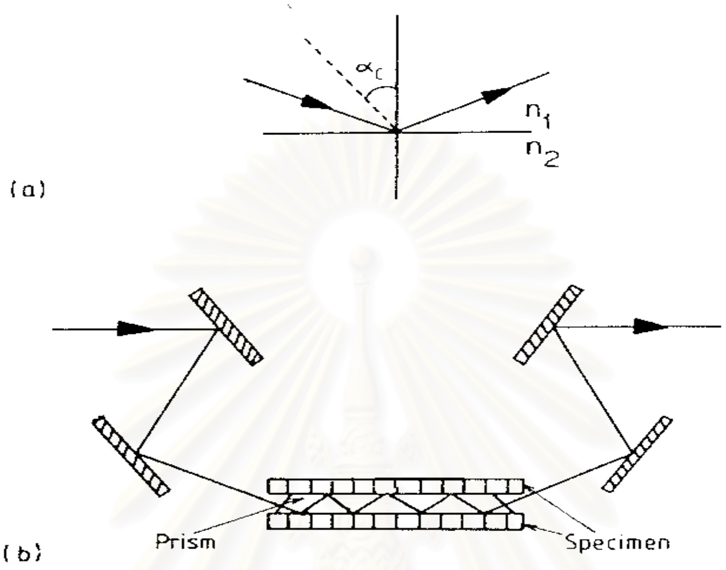


Figure 3.15 (a) Total internal reflection of light when angle of incidence > α_c , (b) optical arrangement for multiple reflection ATR

The spectral distribution of the reflected light is then representative of the surface regions of the material. The effect can be used to examine in particular the surface layers of polymeric material and so provide information on, for example, surface oxidation or to obtain spectra of samples having very high absorptivities not readily examinable by transmission spectroscopy.

In order to obtain measurable absorption spectra, it is normal practice to use multiple reflection prisms (Fig. 3.16 (b)) and these are available as standard spectrometer accessories. A common material for the prisms is thallium bromoiodine. A trapezoidal prism having an angle of incidence of 45° securely in order to provide good optical contact with the prism and, where possible, the sample should be placed on both surfaces of the prism to give optimum sensitivity.

3.4.1.3 Gel Permeation Chromatography (GPC)

GPC has developed into one of the most useful methods for routine determination of average molecular weights and molecular distributions of polymers. It is the latter facility that makes the technique so attractive to polymer scientists and technologists allied to the development of on-line microprocessor based data handling which facilitates the calculation of the molecular weight average from the size distribution chromatograms. In addition, only very small sample sizes are required permitting.

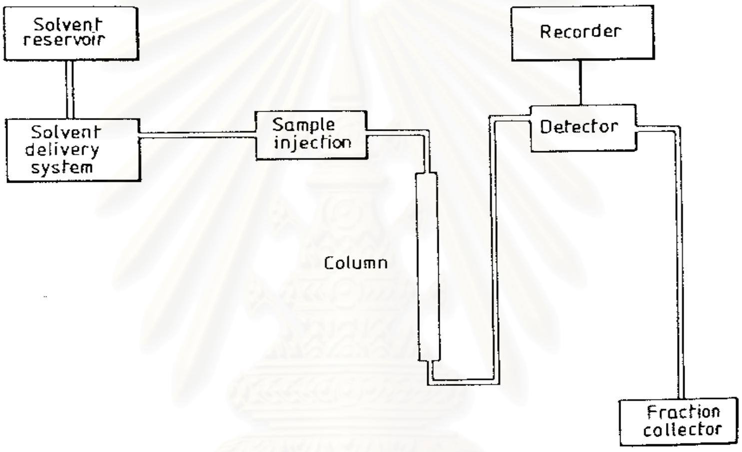
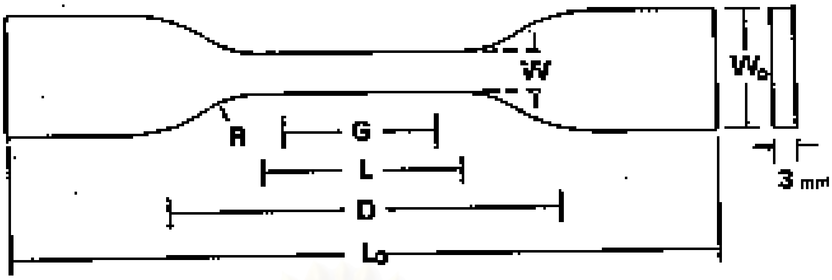


Figure 3.16 Schematic of typical gel permeation chromatograph

3.4.2 Mechanical Properties

Tensile Testing

The tensile stress at maximum load and tensile modulus of the samples were measured by Universal Testing Machine (Model LLOYD LR 100K). The test was carried out according to ASTM D 638-82a standard method, with initial grip separation of 100 mm, crosshead speed of 10 mm min^{-1}, and load cell of 1,000 N.



W: 13 mm L: 57 mm G: 50 mm R: 76 mm

W_o: 19 mm L_o: 165 mm D: 115 mm

Figure 3.17 Schematic of tensile test specimen

The tensile modulus is defined as the slope of the tangent to the stress strain curve at low strain. Tensile stress at maximum load is the value of the stress on the stress-strain curve where the curve occurred at maximum load.

Flexural Testing

The flexural strength at maximum load of the samples was measured by Universal Tensile Testing Machine LLOYD500. The test was carried out according to ASTM D 790-81 standard method, with crosshead speed of 50 mm min^{-1}, load cell of 2,500 N, and span length (L) 50 mm.

The flexural strength is defined as following calculated formula that shown below

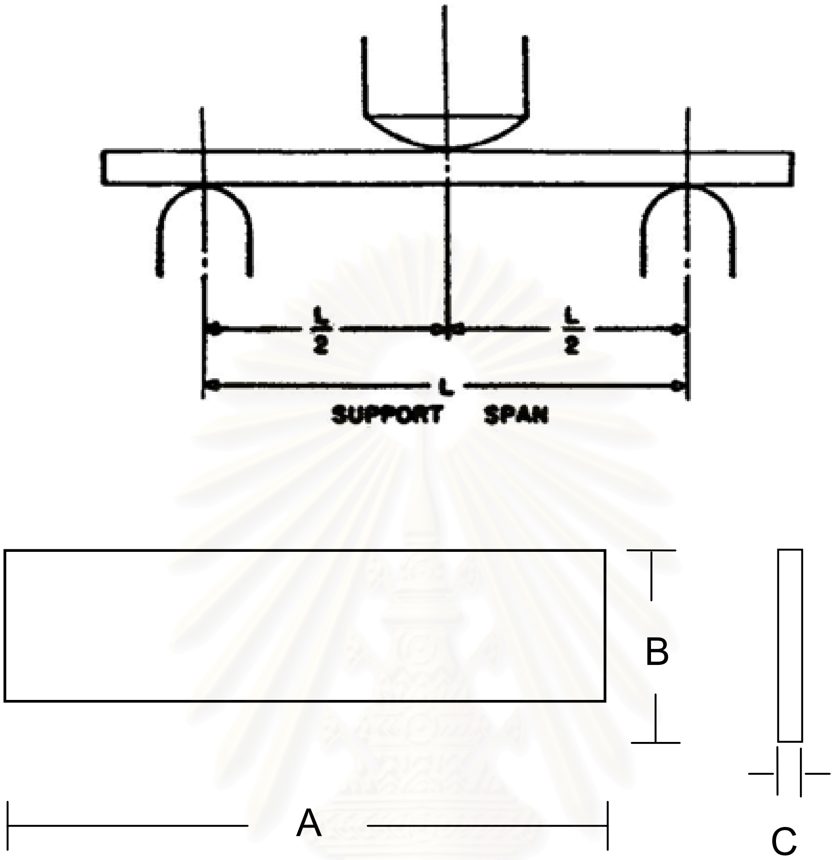
Flexural Strength (N/mm^2); $F = \dfrac{L^3F}{4bh^3}$

Where as; F = force (N)

L = span length (mm)

b = sample width (mm)

h = sample thickness (mm)



A: 80 mm B: 25 mm C: 3.2 mm

Figure 3.18 Schematic of flexural test specimen

Impact Testing

The Impact strength of the samples was measured by Charpy impact testing machine. The test was carried out according to ASTM D 256 standard method, with load of pendulum and the dimension of the sample that shown in figure 3.20

The impact strength is defined as following calculated formula that shown below

Impact strength $= (W / hb) \times 10^3$

Where as; W = Work (J)

h = Sample thickness (mm)

b = Sample width (mm)

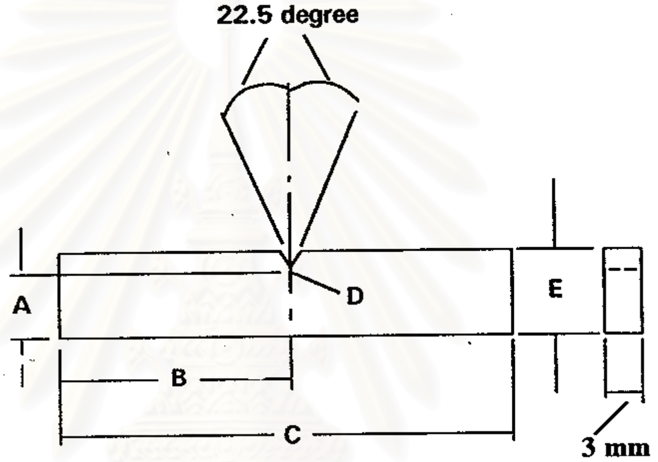


Figure 3.19 Schematic of charpy type test specimen

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of T/C Fabrics

T/C fabrics, composing of polyester and cotton at 65/35 ratio, were immerged in hydrochloric acid (HCl) 2.5 mol for cotton elimination. In order to confirm that cotton was removed after immerging in hydrochloric acid, ATR was used to analyze relevant functional groups. The ATR spectrum of T/C before immerging in HCl as shown in Figure 4.1 exhibits primary hydroxyl fingerprint, the major characteristic of cellulose materials. This fingerprint did not appear in the ATR spectrum of T/C after immerging in HCl as shown in Figure 4.2. Moreover this ATR spectrum shown in Figure 4.2 is similar to the spectrum of PET fabric as shown in Figure 4.3 where the fingerprints of cellulose were disappeared. This due to the fact that most of cotton part in T/C fabric was removed after immerging in HCl.

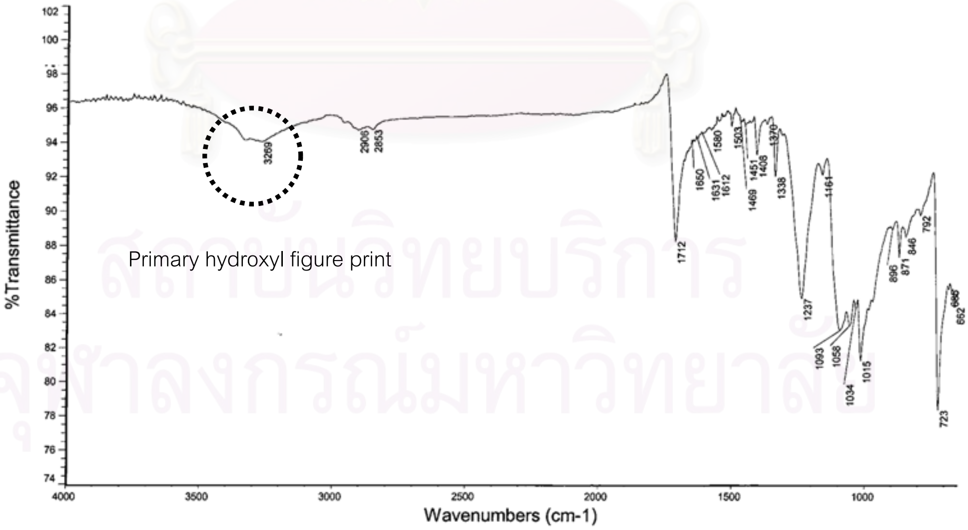


Figure 4.1 ATR spectra of T/C fabrics (before immerge in hydrochloric acid)

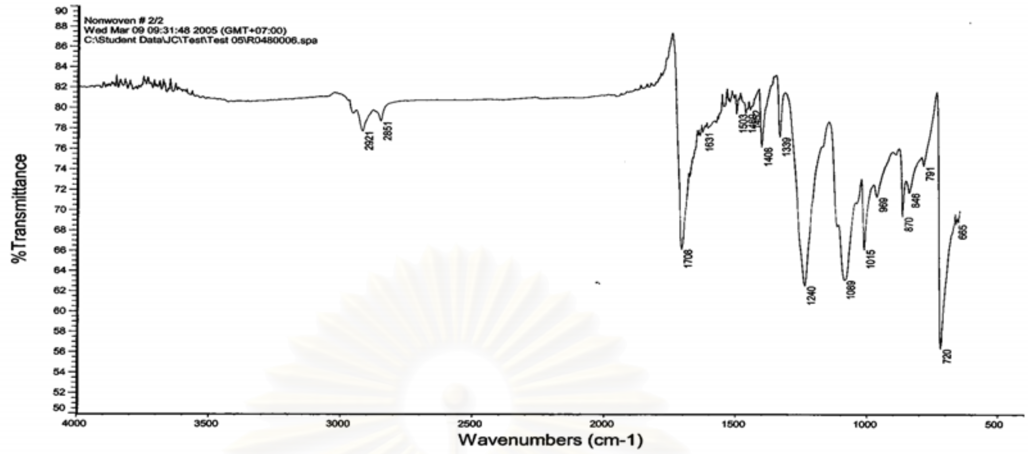


Figure 4.2 ATR spectra of T/C fabrics (after immerge in hydrochloric acid)

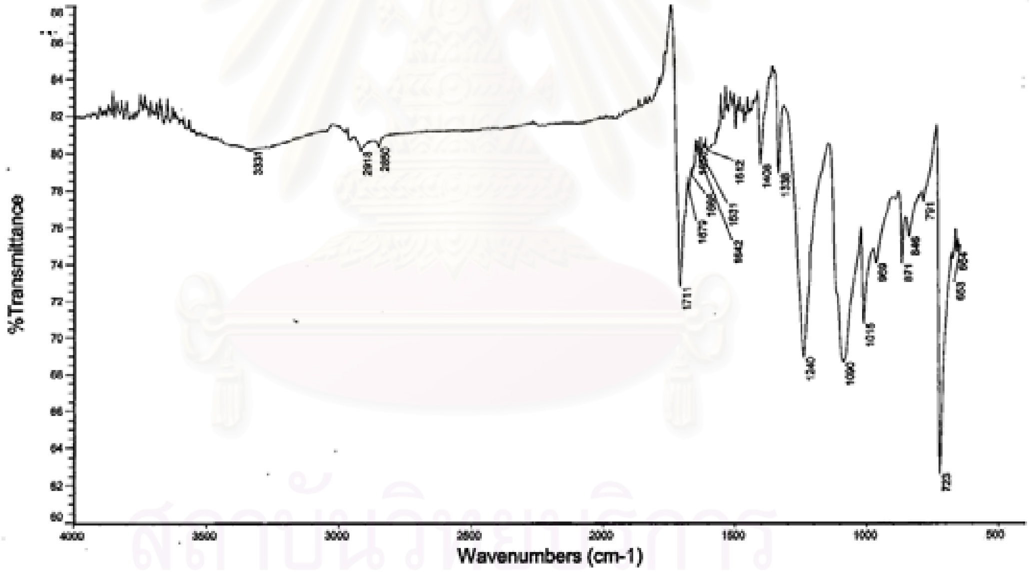


Figure 4.3 ATR spectrums of 100% PET fabrics

4.2 Degradation of PET Fabric Scraps

PET fabric and T/C fabric (after cotton elimination) were glycolyzed with propylene glycol. Molar ratio between fabric and propylene glycol was 0.5:1.0 in the presence of zinc acetate as a catalyst. Glycolysis time was varied at 8, 6 and 4 hours while the amount of catalyst was also varied.

4.2.1 The Results of PET Fabrics Scraps Glycolysis

The results of PET fabrics scraps glycolysis, which were varied in reaction times and amount of catalyst, were shown in Table 4.1. Baliga and Wong [7] found that the almost metal acetate, zinc acetate is the best in terms of the extent of depolymerization. Amount of catalyst, which were used for glycolysis, were 0.5% PET weight.

Table 4.1 The results of PET fabrics scrap glycolysis which was varied in reaction times and amount of catalyst.

Formula	Glycolysis time	Amount of zinc acetate	Glycolyzed product appearance
PET fabric			
1	8 Hrs.	0.5%	yellow liquid solution, fine white dust
2	6 Hrs.	0.5%	creamy viscous solution
3	6 Hrs.	1.0%	creamy viscous solution
4	4 Hrs.	0.5%	creamy highly viscous solution
5	4 Hrs.	1.0%	creamy highly viscous solution
T/C fabric			
6	8 Hrs.	0.5%	yellow liquid solution, fine white dust
7	6 Hrs.	0.5%	creamy viscous solution
PET bottle			
8	8 Hrs.	0.5%	yellow with transparent liquid solution
PET with HCl			
9	8 Hrs.	0.5%	yellow liquid solution with fine white dust

Later on the mechanical properties of Formula 6 and 9 would be compared in order to study the effect of HCl.

4.2.2 FT-IR Spectroscopy

FT-IR was used for inspection of functional groups of the glycolyzed products. The results are shown in Figure 4.4.

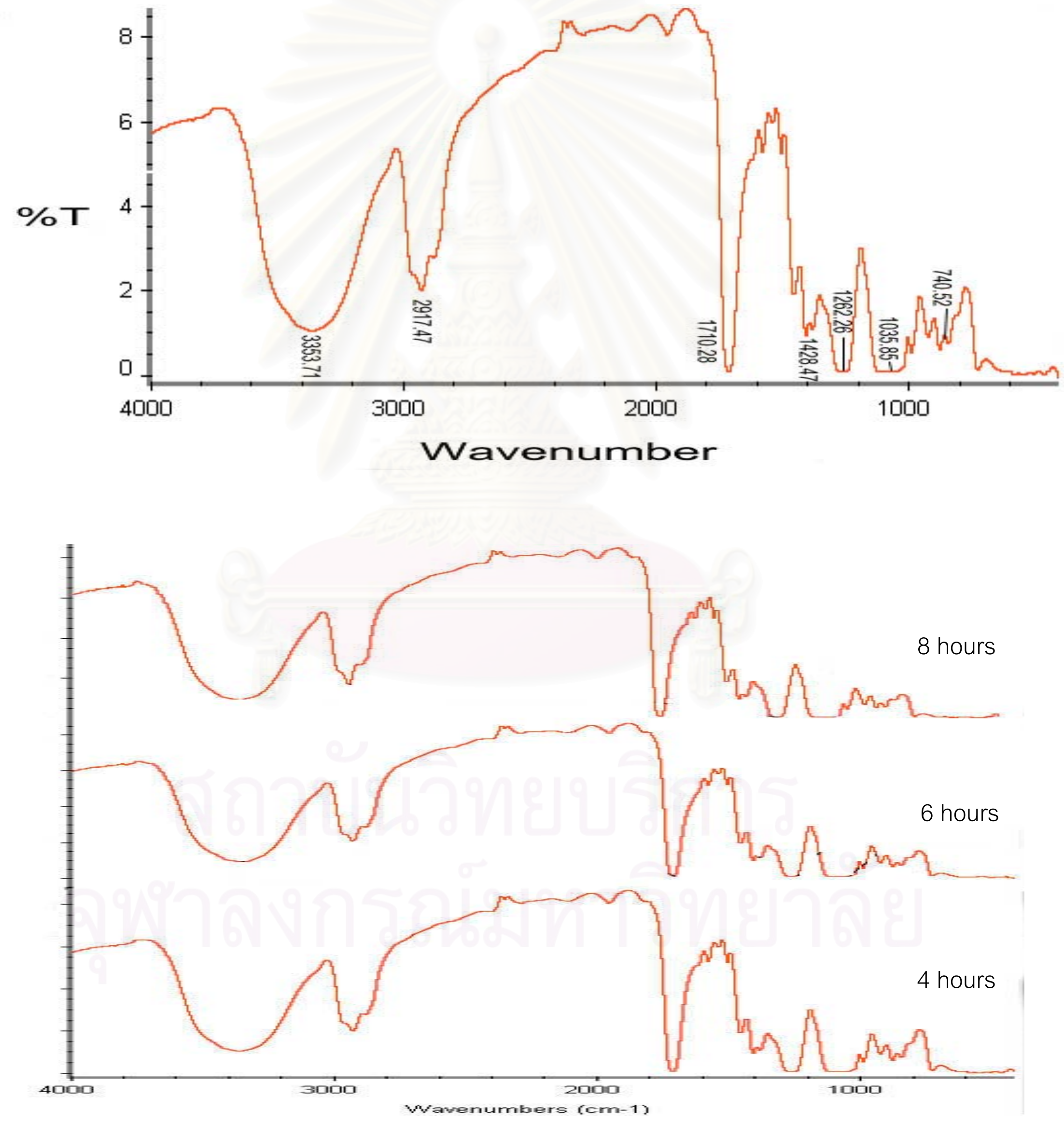


Figure 4.4 FT-IR spectra of GP (a) 8 Hours. Zinc acetate 0.5%, (b) varying 8, 6 and 4 hours of reaction times, respectively

From Figure 4.4 it was found that

1. Figure 4.4 (a) shown spectrum of propylene glycol (characteristics) at 2917.47 cm^{-1}
2. Carbonyl group (C=O) of ester spectrum was shown at about 1600-1800 cm^{-1}.
3. Spectrum of hydroxyl group shown at about 3200-3600 cm^{-1}.
4. Spectrum of –C-O-C- shown at 1200-1400 cm^{-1}.
5. Spectrum of –C-OH shown at 1000-1100 cm^{-1}.
6. Spectrum of ester aromatic ring shown at ~800 cm^{-1}.
7. Figure 4.4 (b) shown the same spectrum of each sample

In the spectrum shown in Figure 4.4 (a), the peak representing hydroxyl groups was broad and low %transmittance because PET molecule was depolymerized into short molecular chains and the end groups of each chain were hydroxyl groups.

4.2.3 Molecular Weight Determination

Molecular weights and molecular weight distributions of GP were determined by GPC method, using tetrahydrofuran (THF) as a diluent. The weight average molecular weight, number average molecular weight, and polydispersity index of GP were analyzed by comparing with the standard calibration curves of polystyrene standard having a molecular weight range of 5,460-1,290,000.

During the experiment, trace of fine particle was appeared, even after ultrafiltration. As a result, the molecular size and molecular distribution as shown in Table 4.2 were not precise. The viscosity of GP was brought to investigate instead.

From Table 4.3, it was found that reaction times affected the viscosity of GP significantly. The viscosity of GP was reduced as reaction time increased. The viscosity of 8-hour reaction time GP was less than that of 4-hour reaction time GP. This is because the molecular chains were getting smaller when the reaction time was prolonged.

Table 4.2 M_w, M_n and PDI of GP

Formula		M_n	M_w	PDI
Glycolyzed time	% Catalyst			
8 hours	0.5 %	1053	1134	1.076612
6 hours	1.0 %	1032	1088	1.054726
6 hours	0.5 %	1030	1091	1.059122
4 hours	1.0 %	1003	1050	1.046611
4 hours	0.5 %	1040	1107	1.064161

Table 4.3 Viscosity of GP

Formula		Viscosity (Centipoise)
Glycolyzed time	% Catalyst	
8 hours	0.5 %	1232
6 hours	1.0 %	1664
6 hours	0.5 %	1456
4 hours	1.0 %	1936
4 hours	0.5 %	1616

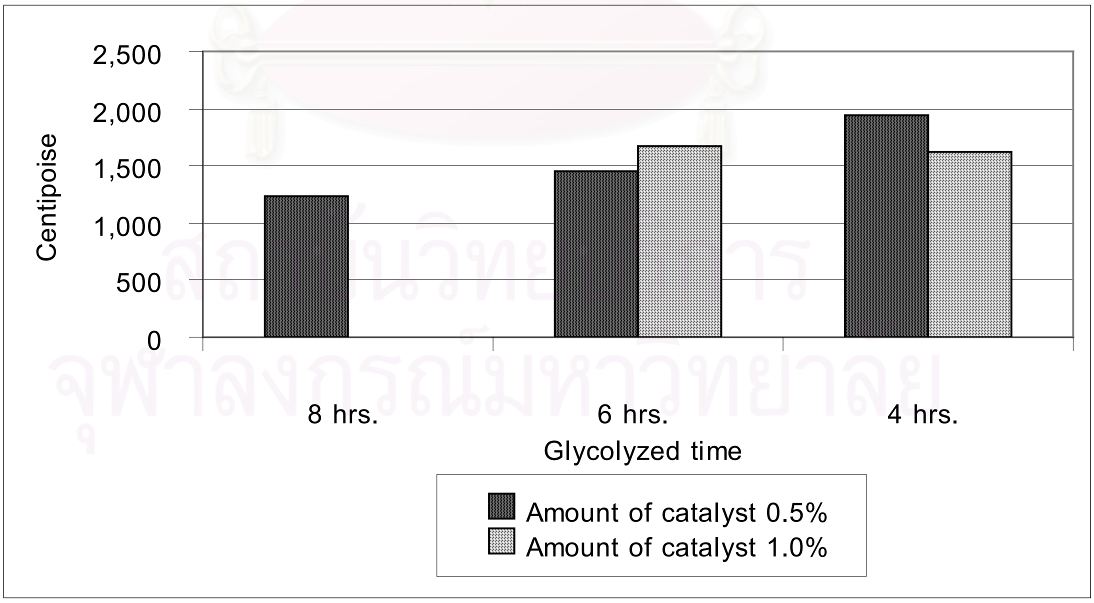


Figure 4.5 Viscosity of GP

Figure 4.5 shows that the amount of zinc acetate did not affect the viscosity of GP. Thus, it can be assumed that the amount of catalyst has not effect on glycolysis reaction.

4.3 The Results of Polyester Synthesis

There was fine white residue appeared in glycolyzed products from fabric scraps. This was assumed to be titanium dioxide (TiO_2) since most of PET fiber process added titanium dioxide as a filler. UPR were synthesized from GP by esterification with maleic anhydride at the molar ratio of 0.5:1.0. The results of unsaturated polyester synthesis were shown in Table 4.4.

It was not possible to obtain rigid cured UPR synthesized from GP without TiO_2 elimination as TiO_2 may interfere with curing reaction.

Table 4.4 The results of unsaturated polyester synthesis

Fabric type	Glycolyzed time	% Catalyst	Resin appearance	Remark
PET fabrics				
1 (a)	8	0.5	yellow, rigid	TiO_2 filtration
1 (b)	8	0.5	not setting to rigid, gelation	Non-filtration
2	6	1.0	yellow rigid resin	
3	6	0.5	yellow rigid resin	
4	4	1.0	creamy rigid resin	
5	4	0.5	creamy rigid resin	
T/C fabrics				
6	8	0.5	yellow rigid resin	
7	6	0.5	yellow rigid resin	
PET bottle				
8	8	0.5	transparent brown rigid resin	

Table 4.4 The results of unsaturated polyester synthesis (cont.)

Fabric type	Glycolyzed times	% Catalyst	Resin appearance	Remark
Commercial resin 9	None	None	transparent magenta rigid resin	
PET with HCl 10	8	0.5	yellow rigid resin	

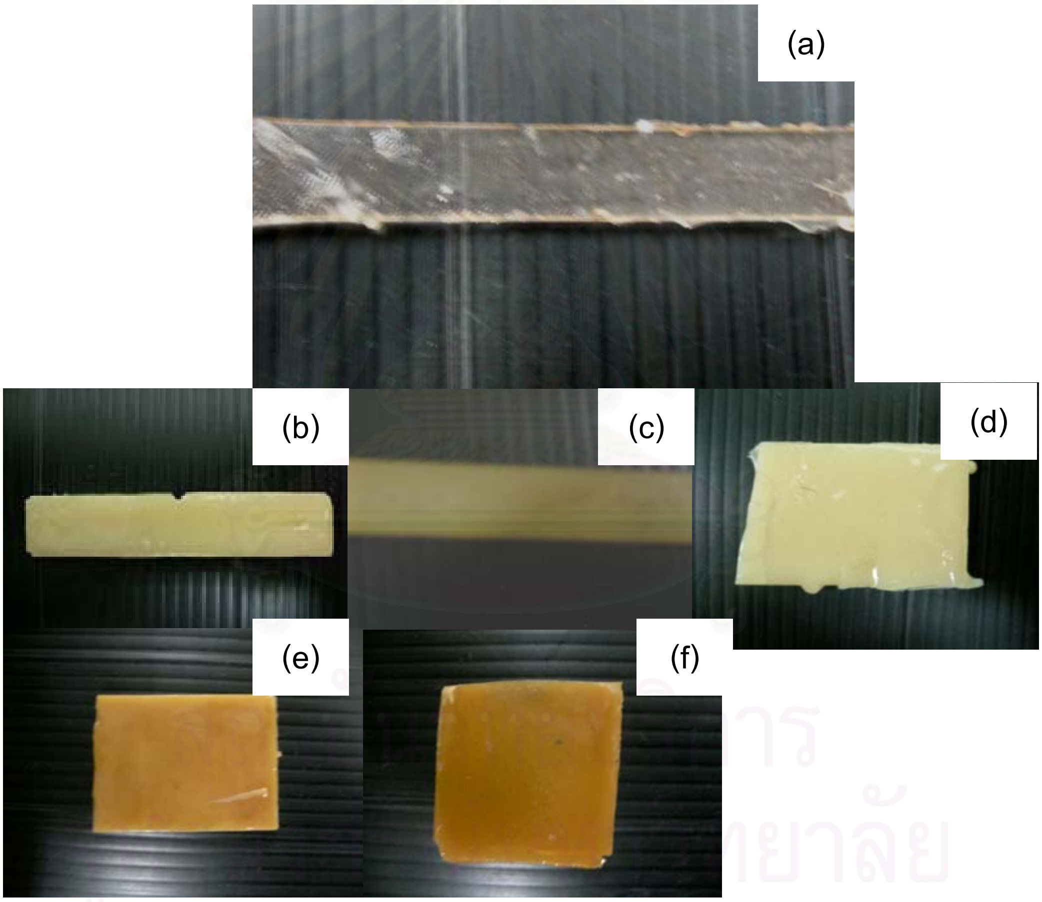


Figure 4.6 The appearance of cured polyester resin

(a) Commercial polyester resin, (b) resin from PET fabric glycolyzed for 8 hours, (c) resin from PET fabric glycolyzed for 6 hours, (d) resin from PET fabric glycolyzed for 4 hours, (e) resin from T/C fabric glycolyzed for 8 hours, (f) resin from T/C fabric glycolyzed for 6 hours.

4.4 Mechanical Properties

4.4.1 Hardness

Hardness of cured resins was tested by Shore D Durometer. The results are shown in Table 4.5 and Figure 4.7. From Figure 4.7, it was found that reaction time affected the hardness of resin. Hardness was increased following the increasing of reaction time. Hardness of resin from 8-hour glycolysis GP was highest when compare with resin from 6- and 4- hour glycolysis GP. However, these values are closed to that of commercial resin and that of UPR prepared from PET bottles.

4.4.2 Impact Strength

Impact strength of cured resin was tested with charpy impact tester. The results are shown in Table 4.6 and Figure 4.8.

In Figure 4.8, most of UPR which was synthesized from PET fabric showed the highest impact strength at 8 hours glycolysis time. It was assumed that there were lots of smaller size molecules rather than mixed size molecules as found in GP with less glycolysis time. Therefore, crosslink density was presumably higher. As a result impact strength of cured resin from 8-hour glycolysis GP was found to be the highest.

4.4.3 Flexural Strength

The results of flexural strength testing are shown in Table 4.7. It can be pointed out that flexural strength of cured resin prepared from PET fabric, which was glycolyzed for 8 hours, is similar to that of cured commercial UPR.

Table 4.5 The results of hardness testing

Formula	Hardness (Shore D)						
	1	2	3	4	5	Average	SD
PET fabrics							
1	71	70	70	71	70	70.6	1.09
2	63	63	63	63	65	63.4	0.89
3	60	65	60	65	65	64.2	2.74
4	60	60	60	63	60	61.2	1.64
5	63	60	60	60	60	60.6	1.34
T/C fabrics							
6	69	68	70	70	72	69.2	0.89
7	63	62	63	64	63	63.0	1.09
PET bottle							
8	70	71	71	70	70	70.4	0.55
Commercial resin							
9	72	70	71	71	72	71.2	0.84
PET with HCl							
10	68	70	70	68	68	68.8	1.09

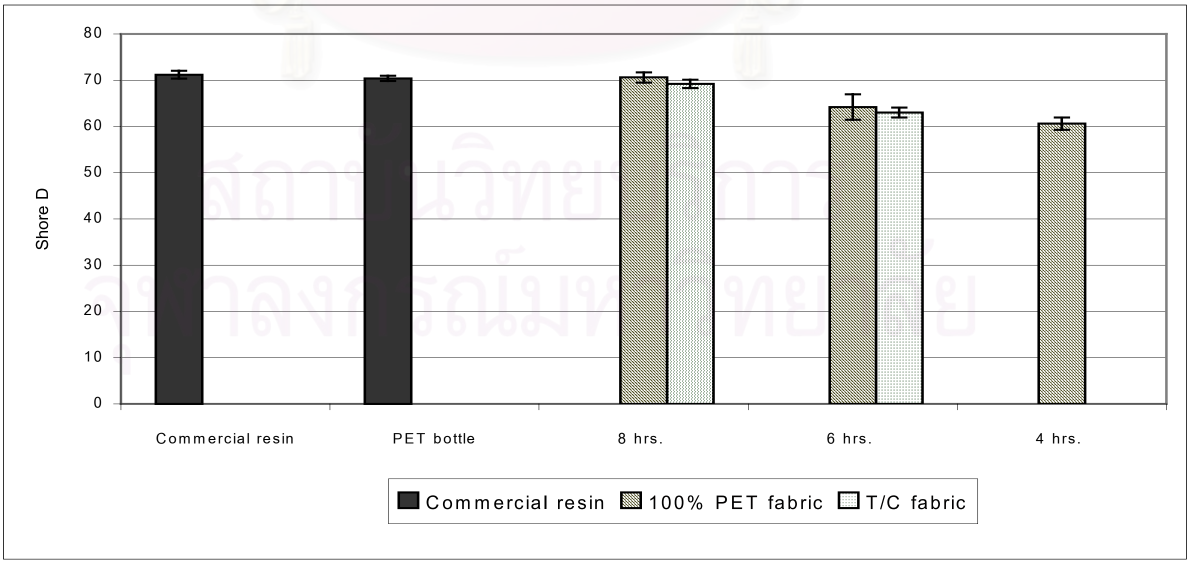


Figure 4.7 Hardness of polyester resin. Amount of catalyst was 0.5%

Table 4.6 Impact properties of polyester resins

Formula	Width (mm)	Thickness (mm)	Work (J)	Impact strength (J/mm^2)	SD
PET fabrics					
1	10.55	3.25	0.050	1.46	0.0055
2	10.45	3.25	0.045	1.32	0.0120
3	10.35	3.25	0.040	1.19	0.0027
4	10.35	3.25	0.040	1.19	0.0044
5	10.30	3.25	0.035	1.05	0.0059
T/C fabrics					
6	10.35	3.25	0.045	1.32	0.0089
7	10.35	3.25	0.040	1.19	0.0052
PET bottle					
8	10.25	3.25	0.050	1.50	0.0440
Commercial resin					
9	10.25	3.25	0.055	1.65	0.0089
PET with HCl					
10	10.25	3.25	0.045	1.35	0.0047

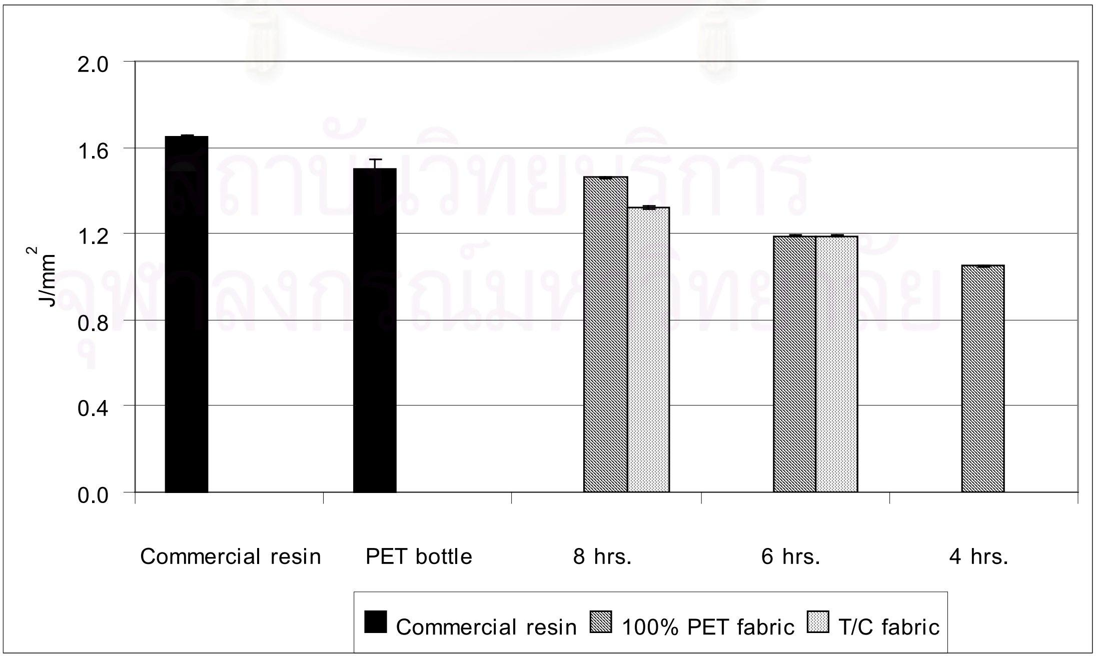


Figure 4.8 Impact strength of polyester resin, amount of catalyst was 0.5%

Table 4.7 Flexural strength of polyester resin

Formula	Flexural Strength (N/mm^2)	SD
PET fabric		
1	644.43	142.95
2	348.84	66.87
3	354.83	84.55
4	386.12	174.16
5	346.25	104.23
T/C fabric		
6	589.46	174.15
7	349.81	127.44
PET bottle		
8	745.26	121.69
Commercial resin		
9	832.15	22.13
PET with HCl		
10	601.25	135.23

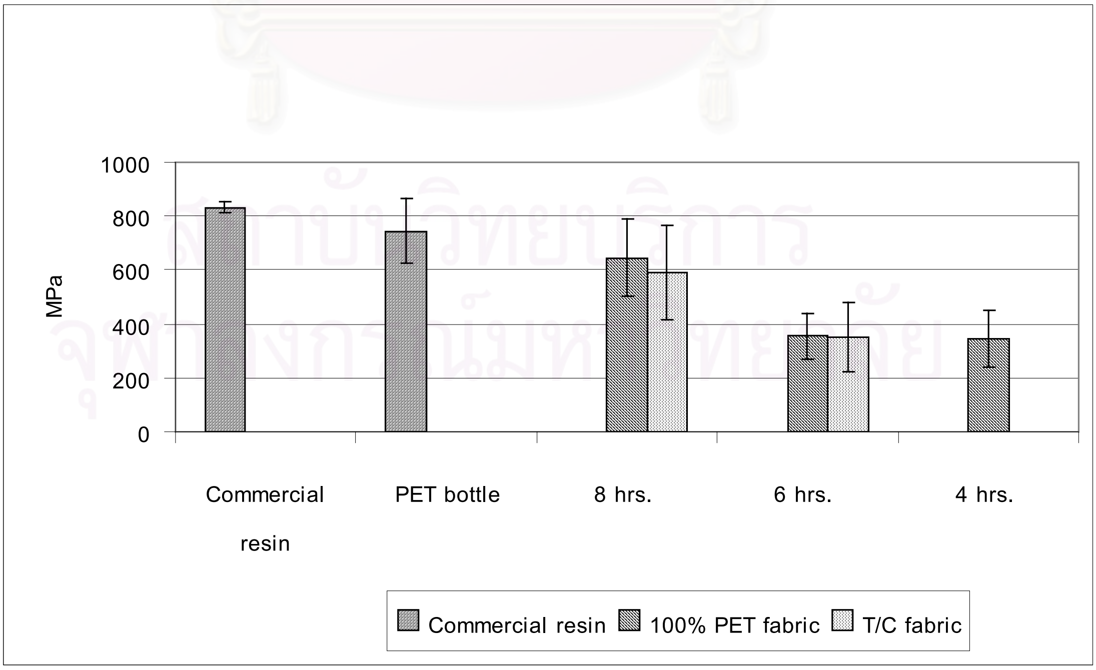


Figure 4.9 Flexural strength of polyester resin, amount of catalyst was 0.5%

4.4.4 Tensile Properties

The results of tensile strength and Young's modulus are shown in Table 4.8. These results suggested that the longer glycolysis time, the higher Young's modulus and tensile strength.

Table 4.8 Tensile strength and Young's modulus of polyester resin

Formula	Tensile Strength (MPa)	Young's modulus (MPa)
PET fabric		
1	16.20	448.62
2	3.07	275.62
3	5.24	270.46
4	1.52	206.23
5	1.23	157.96
T/C fabric		
6	16.20	440.33
7	5.24	250.36
PET bottle		
8	20.88	472.56
Commercial resin		
9	29.52	560.57
PET with HCl		
10	15.68	416.69

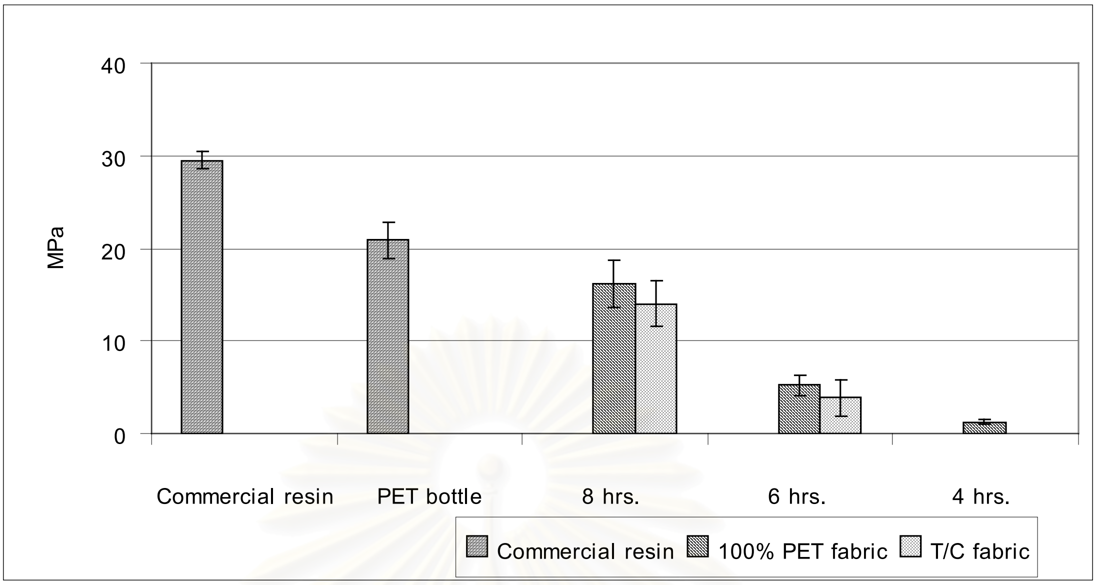


Figure 4.10 Tensile strength of UPR

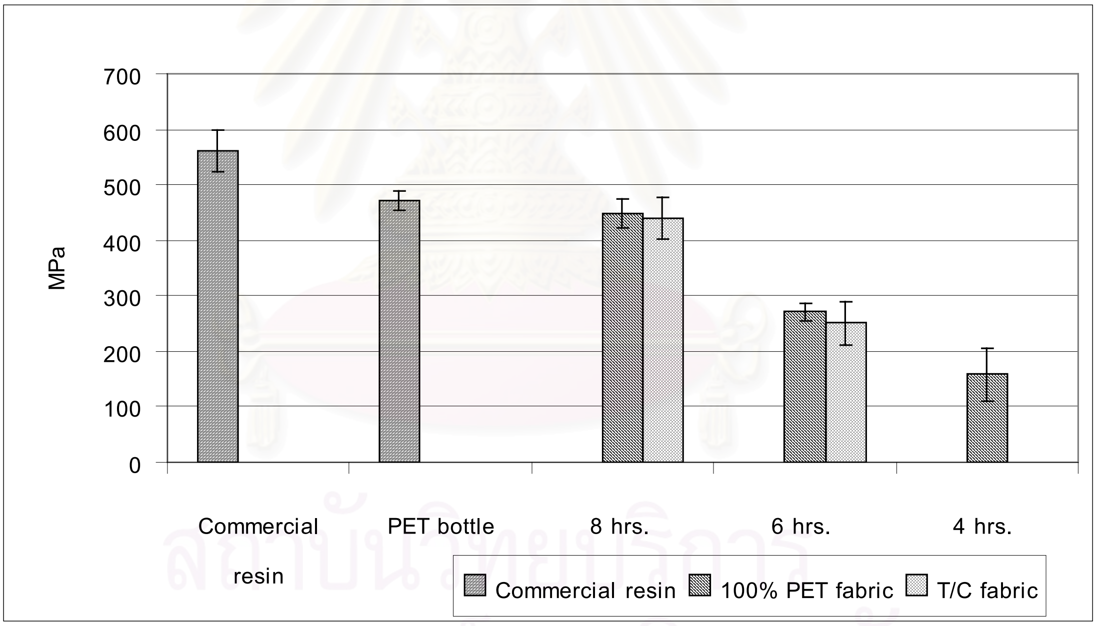


Figure 4.11 Young's modulus of UPR

From mechanical properties results of synthesized polyester resin expressed that the more glycolysis time had the better. These because of most of molecules were depolymerized into more consistent and shorter segments providing higher degree of crosslink. Shorter glycolysis time would give mixture between short and long molecular chains, resulting in the inferior mechanical properties.

4.4.5 Effects of Excess Catalyst Addition

PET is depolymerized by glycolysis reaction with the presence of a metal acetate catalyst. Amount of catalyst, which was used for glycolysis, was 0.5% by PET weight in the almost earlier research. This research was trying to reduced reaction time so increasing of the amount of catalyst was studied.

The results, as shown in Figure 4.12, indicate that the excess amount of catalyst did not affect the mechanical properties of UPR.

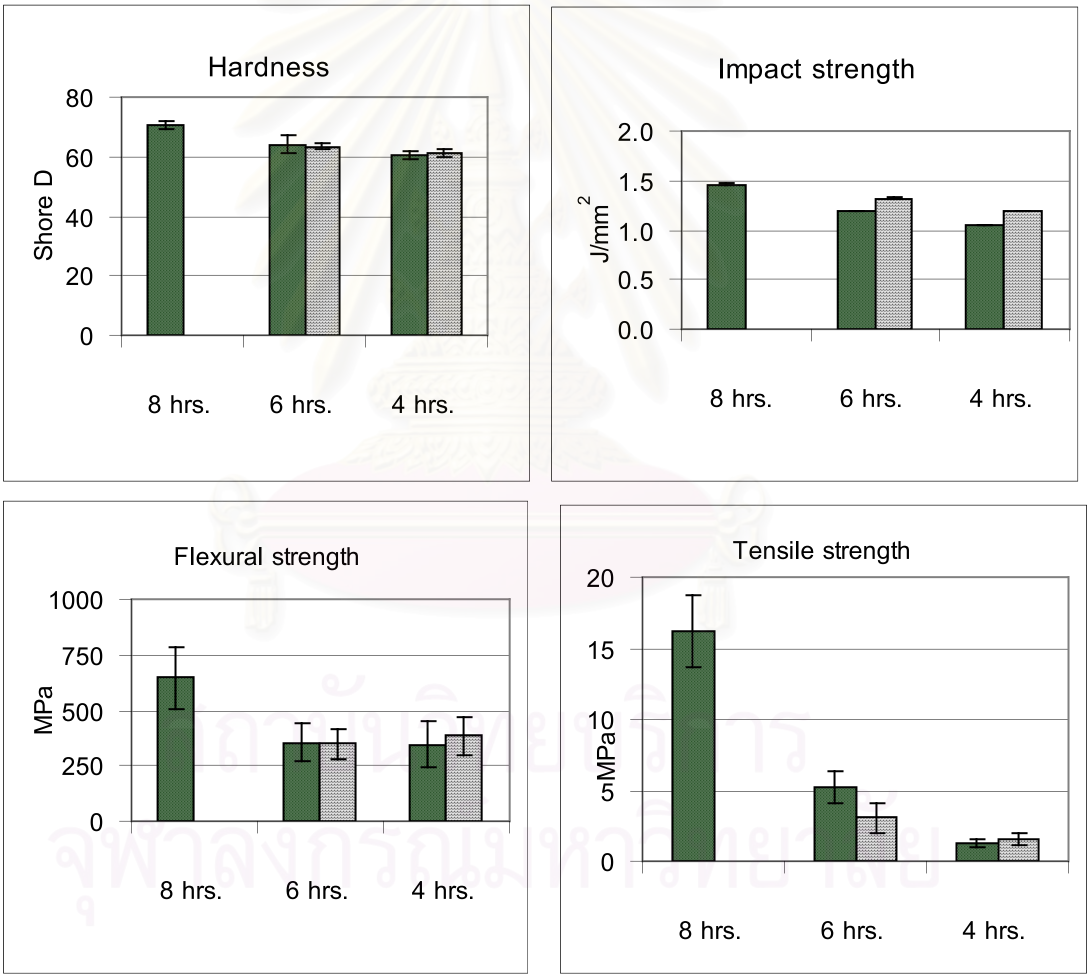


Figure 4.12 Comparison of mechanical properties at different weight of catalyst

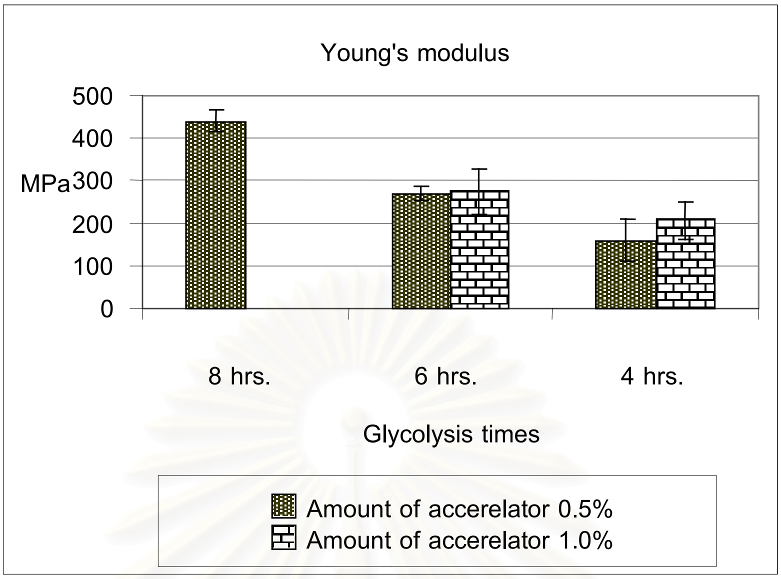


Figure 4.12 Comparison of mechanical properties at different weight of catalyst (cont.)

4.4.6 Effects of HCl

2.5 mole HCl acids were used for removing cotton from T/C fabrics. So, effects of HCl on mechanical properties of cured resin were investigated as shown in Figure 4.13. From the results, HCl usage did not affect to the mechanical properties of UPR.

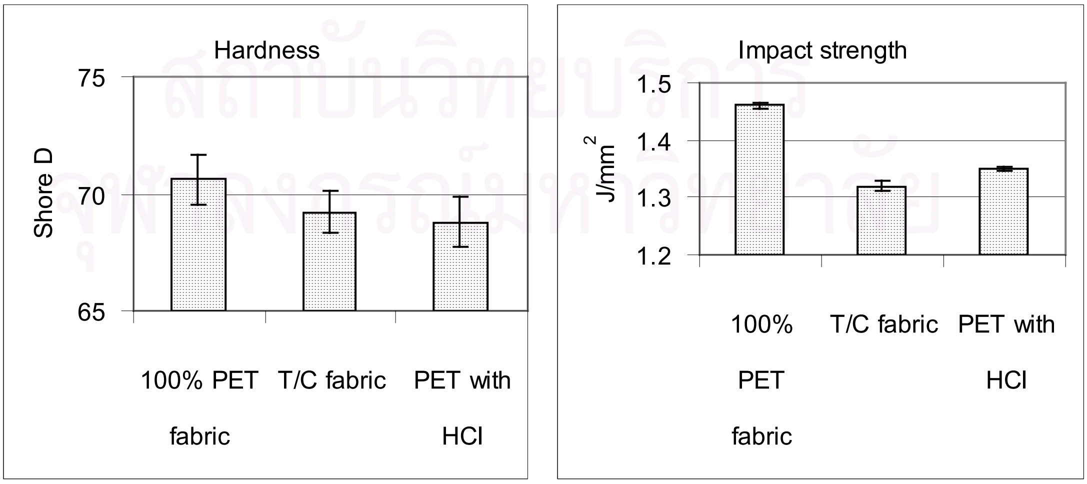
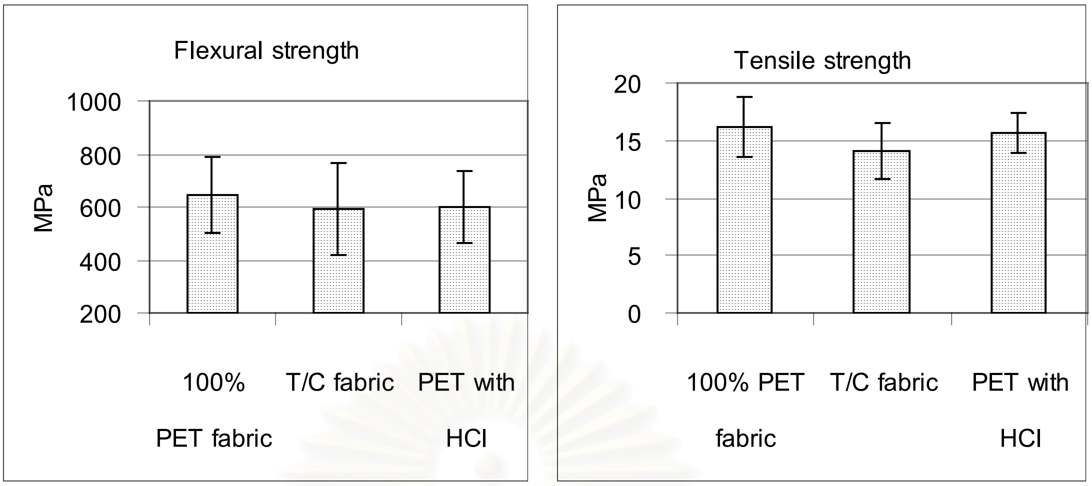


Figure 4.13 Effects of HCl with mechanical properties



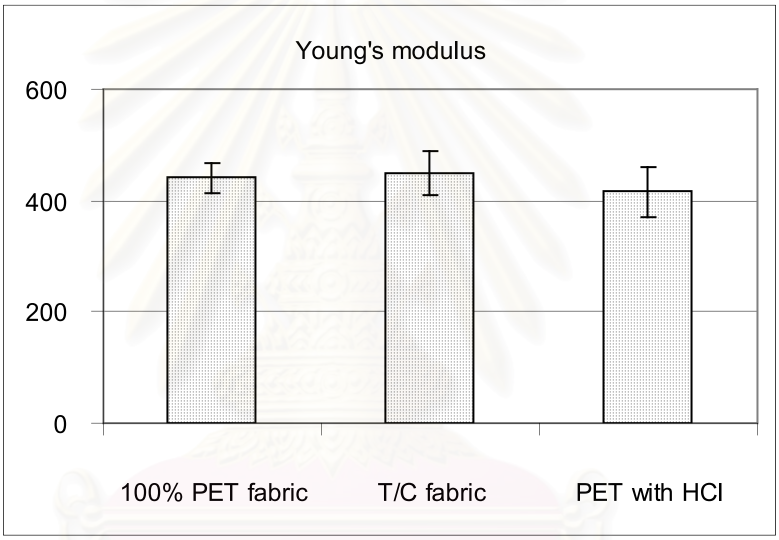


Figure 4.13 Effects of HCl with mechanical properties (cont.)

4.5 Thermal Stability

4.5.1 Glass-Transition Temperature (T_g)

The result of glass-transition temperature (T_g), was tested by DSC machine as shown in Table 4.9 and T_g of UPR graph was shown in Figure 4.14

Table 4.9 Glass transition temperature of UPR

Formula	Glass transition temperature (Celsius)	
	PET fabrics	T/C fabrics
4 hrs Zn 0.5%	15	-
6 hrs Zn 0.5%	19	20
8 hrs Zn 0.5%	23	22
PET bottle	45	
Commercial resin	N/A	

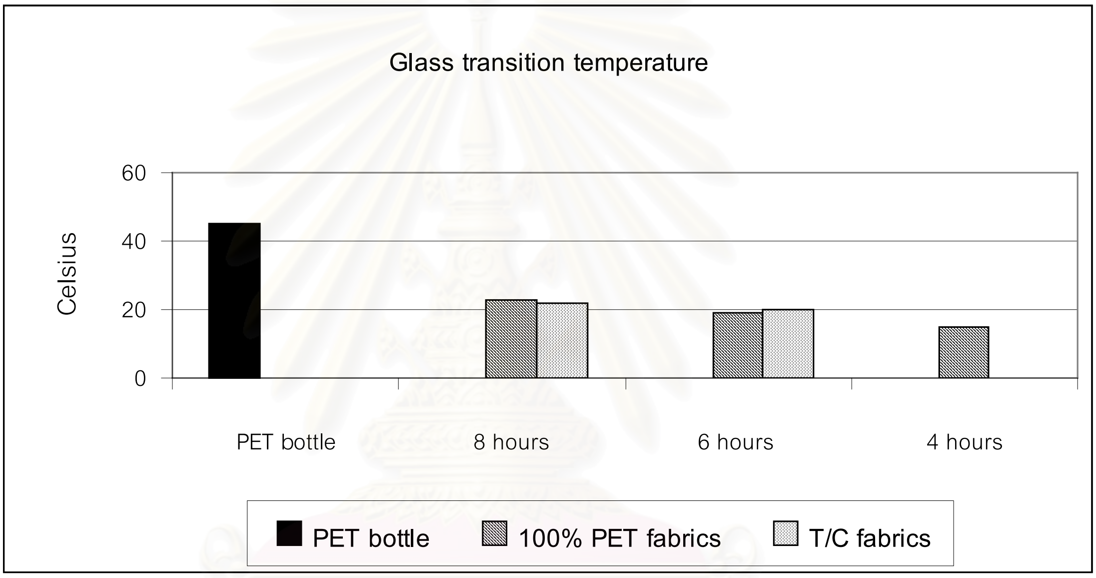


Figure 4.14 T_g graph of UPR

From Figure 4.14, the more glycolysis time the higher T_g of UPR. These because of most of molecules were depolymerized into short segments providing high degree of crosslink. Whereas short glycolysis time would be providing short and long molecular chain that give high flexibility and low T_g.

4.5.2 Thermal Degradation (degradation temperature, T_d)

The result of degradation temperature (T_d), was tested by TGA machine as shown in Table 4.10 and TGA thermogram comparison was shown in Figure 4.15.

Table 4.10 Thermal degradation of UPR

Formula	Thermal degradation (Celsius)	
	PET fabrics	T/C fabrics
4 hrs Zn 0.5%	319	-
6 hrs Zn 0.5%	335	327
8 hrs Zn 0.5%	345	371

From Figure 4.15 the different in glycolysis times (8, 6 and 4 hours) was effected to thermal stability of UPR. T_d of 8 hours glycolysis times was the highest whereas 4 hours glycolysis times shown the lowest T_d. In case of T/C fabrics, the result was same as PET fabrics as shown in Figure 4.16. Thermal stability of resin was increased when reaction time was increased. However, reaction time should not over 8 hours because equilibrium of glycolysis was at 8 hours [15].

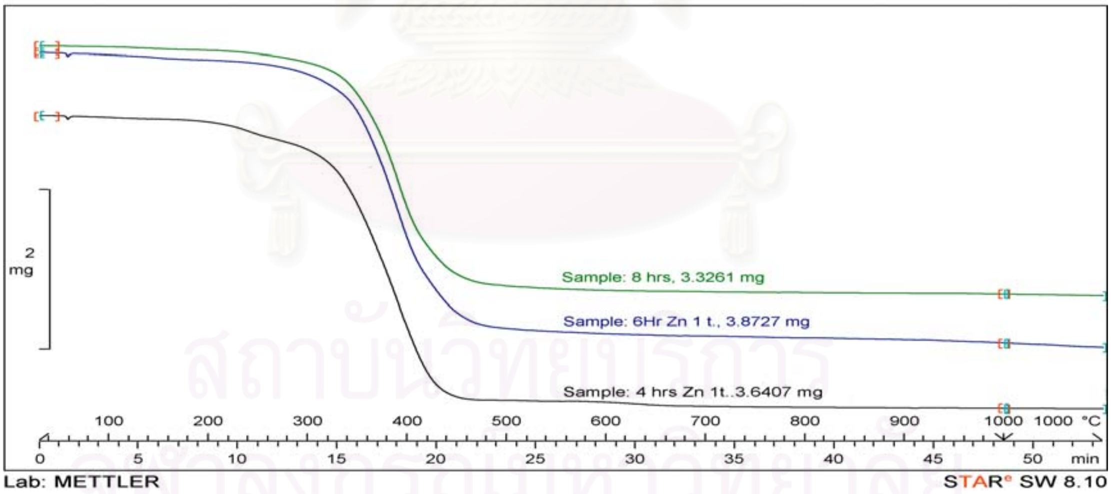


Figure 4.15 TGA thermogram of polyester resin (PET fabrics)

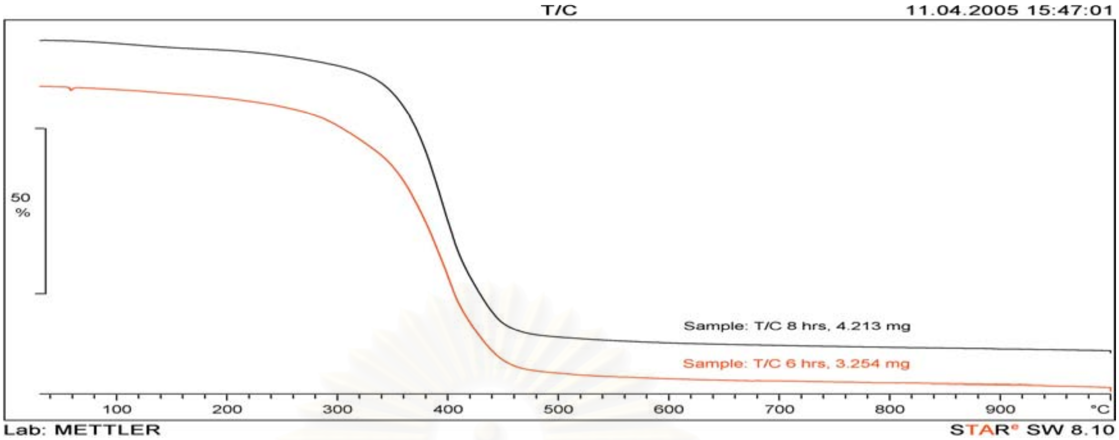


Figure 4.16 TGA thermogram of polyester resin (T/C fabrics)

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From the experimental results, several conclusions can be drawn as follows.

1. PET fabric scraps can be depolymerization by glycolysis reaction resulting in smaller molecular chains, ideally BHET. However, the extent of depolymerization depends on the reaction time. There was trace of residue presented in glycolyzed products. This inhibited the products from being analyzed by GPC. However, the viscosity which was lower when the reaction increased indicated that the molecular chain is getting smaller. Furthermore, the glycolysis reaction was not affected by the amount of catalyst.

2. In the case of PET/Cotton (T/C) fabric scraps, the cotton must be eliminated using HCl prior to glycolysis. Otherwise, glycolysis would not be possible. The results indicated that HCl did not affect the properties of the prepared resin.

3. Fine white particle residue has been found in the glycolyzed products. This is presumably titanium dioxide (TiO_2) which is typically used as a filler during fiber production processes. This residue must be separated from the glycolyzed product by filtration before esterification step as it can interfere significantly with the reaction.

4. After esterification with maleic anhydride, the products can be cured by using styrene monomer, MEKPO and cobalt octoate as a crosslinking agent, initiator and catalyst, respectively.

5. Test specimens prepared from the cured products were used in order to investigate mechanical properties. It was found that the mechanical properties, i.e.

impact strength, tensile strength and flexural strength were slightly lower than those of commercial resin. Resin prepared from PET and T/C fabric scraps which were glycolyzed for 8 hours possessed highest mechanical properties.

6. Thermal stability of the prepared resins was improved as the glycolysis time increased.

5.2 Recommendations

This research shows that it is possible to prepared unsaturated polyester resin from PET and T/C fabric scraps. There is still further research to be carried out. Few will be pointed out here, as listed below.

1. Investigation of recycling of PET mixed scraps (bottles, fiber, fabrics, etc.) may be carried out to minimize identification and separation steps in recycling process.

2. In order to improve mechanical properties, unsaturated polyester resin may be prepared from mixing the resin from glycolyzed products with commercial resin or reinforcing fillers in the appropriate ratio.

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22. ASTM D638-02a Standard Test Method for Tensile Properties of Plastics.

23. ASTM D6110-02 Determining the Charpy Impact Resistance of Notched Specimens of Plastics.

24. ASTM D6110-02 Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials.

Appendices

APPENDIX A

Mechanical Property Characterization

Table A1 Hardness of polyester resin

Formula	Hardness (Shore D)						
	1	2	3	4	5	Average	SD
100% PET fabrics							
1	71	70	70	71	70	70.6	1.09
2	63	63	63	63	65	63.4	0.89
3	60	65	60	65	65	64.2	2.74
4	60	60	60	63	60	61.2	1.64
5	63	60	60	60	60	60.6	1.34
T/C fabrics							
6	69	68	70	70	72	69.2	0.89
7	63	62	63	64	63	63.0	1.09
PET bottle							
8	70	71	71	70	70	70.4	0.55
Commercial resin							
9	72	70	71	71	72	71.2	0.84
PET with HCl							
10	68	70	70	68	68	68.8	1.09

Table A2 Impact strength of polyester resin synthesis

Formula	Width (mm)	Thickness (mm)	Work (J)	Impact strength (J/mm^2)	SD
100% PET fabrics					
1	10.55	3.25	0.050	1.46	0.0055
2	10.45	3.25	0.045	1.32	0.0120
3	10.35	3.25	0.040	1.19	0.0027
4	10.35	3.25	0.040	1.19	0.0044
5	10.30	3.25	0.035	1.05	0.0059
T/C fabrics					
6	10.35	3.25	0.045	1.32	0.0089
7	10.35	3.25	0.040	1.19	0.0052
PET bottle					
8	10.25	3.25	0.050	1.50	0.0440
Commercial resin					
9	10.25	3.25	0.055	1.65	0.0089
PET with HCl					
10	10.25	3.25	0.045	1.35	0.0047

Table A3 Flexural strength of polyester resin synthesis

Formula	Flexural Strength (N/mm^2)	SD
100% PET fabric		
1	644.43	142.95
2	348.84	66.87
3	354.83	84.55
4	386.12	174.16
5	346.25	104.23
T/C fabric		
6	589.46	174.15
7	349.81	127.44
PET bottle		
8	745.26	121.69
Commercial resin		
9	832.15	22.13
PET with HCl		
10	601.25	135.23

Table A4 Tensile modulus (MPa) and Young's modulus of polyester resin synthesis

Formula	Tensile Strength (MPa)	Young's modulus (MPa)
100% PET fabric		
1	16.20	448.62
2	3.07	275.62
3	5.24	270.46
4	1.52	206.23
5	1.23	157.96
T/C fabric		
6	16.20	440.33
7	5.24	250.36
PET bottle		
8	20.88	472.56
Commercial resin		
9	29.52	560.57
PET with HCl		
10	15.68	416.69

Appendix B

Thermal Stability Characterization

Table B1 Glass transition temperature of polyester resin synthesis

Formula	Glass transition temperature (Celsius)	
	100% PET fabrics	T/C fabrics
4 hrs Zn 0.5%	15	-
6 hrs Zn 0.5%	19	20
8 hrs Zn 0.5%	23	22
PET bottle	45	
Commercial resin	N/A	

Table B2 Thermal degradation of polyester resin synthesis

Formula	Thermal degradation (Celsius)	
	100% PET fabrics	T/C fabrics
4 hrs Zn 0.5%	319	-
6 hrs Zn 0.5%	335	327
8 hrs Zn 0.5%	345	371

Appendix C

DSC Thermogram of Synthesized Polyester Resin

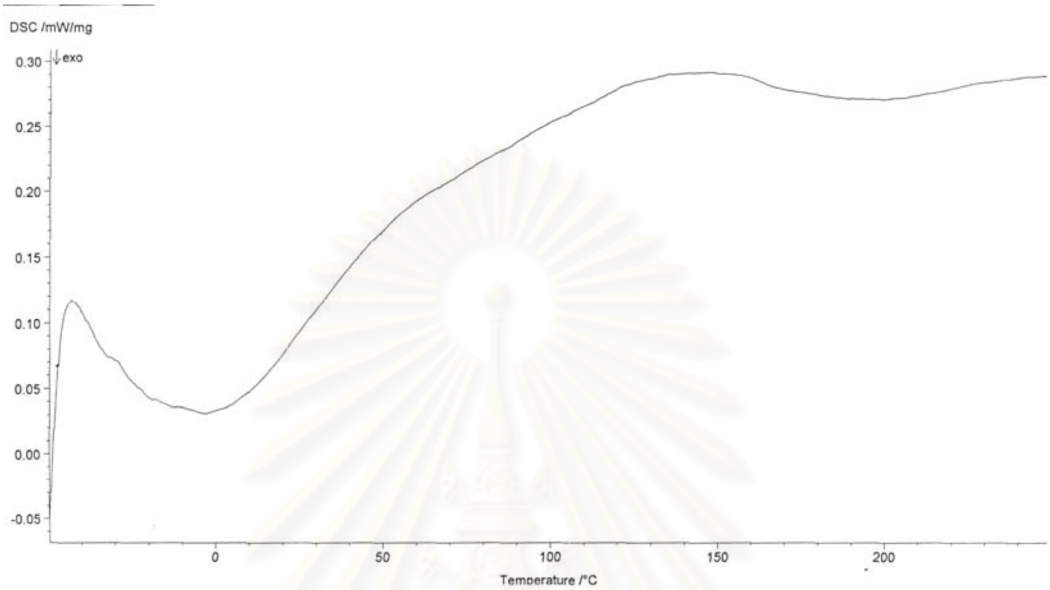

Figure C1. Commercial Resin

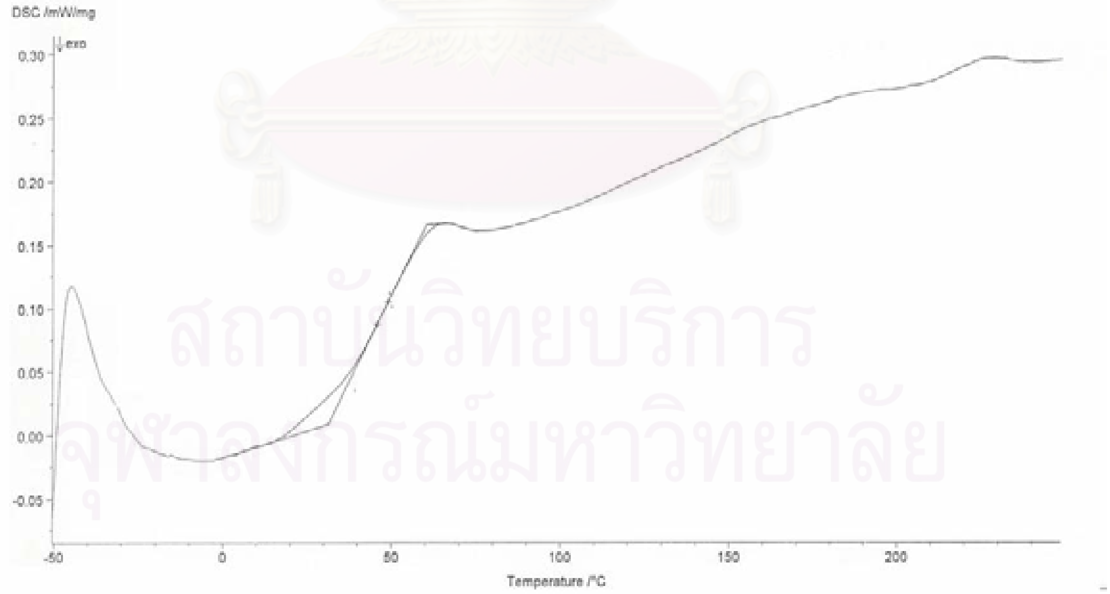

Figure C2. Synthesis from PET bottle

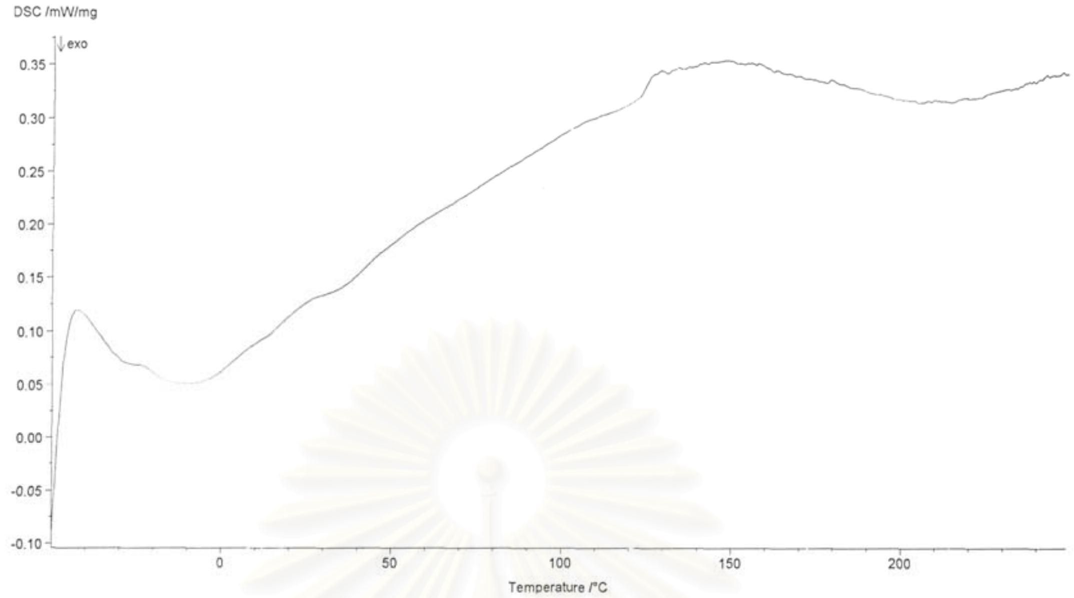

Figure C3. Synthesis from PET fabrics (8 hours of glycolysis times)

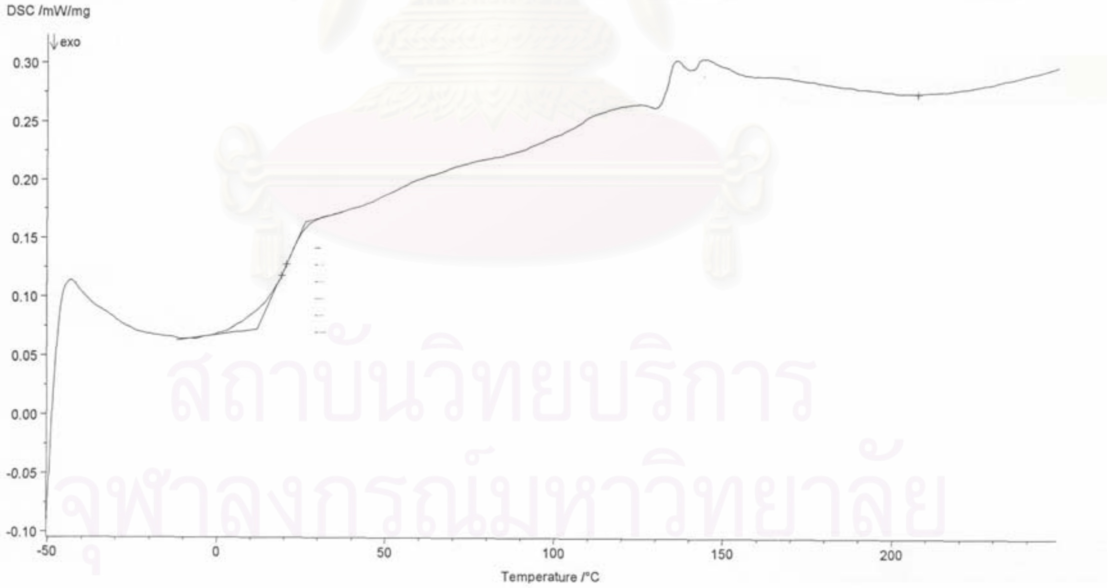

Figure C4. Synthesis from T/C fabrics (8 hours of glycolysis times)

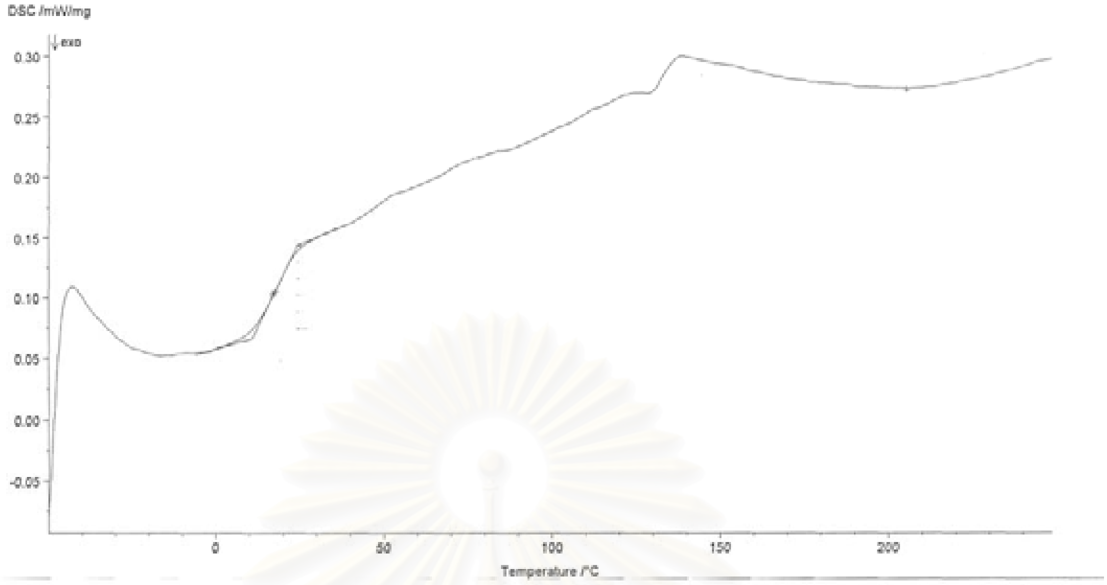

Figure C5. Synthesis from PET fabrics (6 hours of glycolysis times)

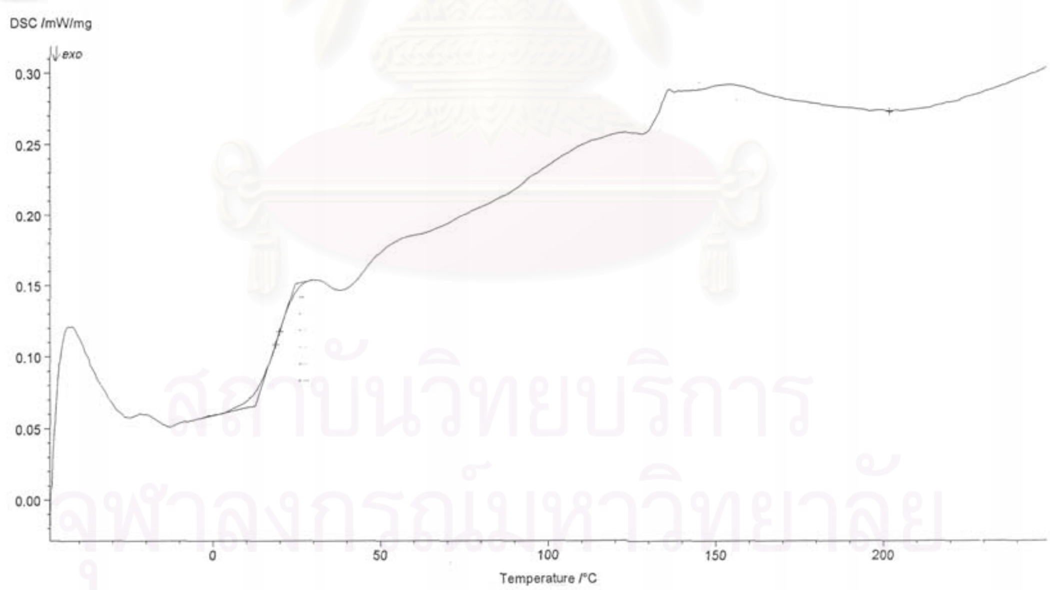

Figure C6. Synthesis from T/C fabrics (6 hours of glycolysis times)

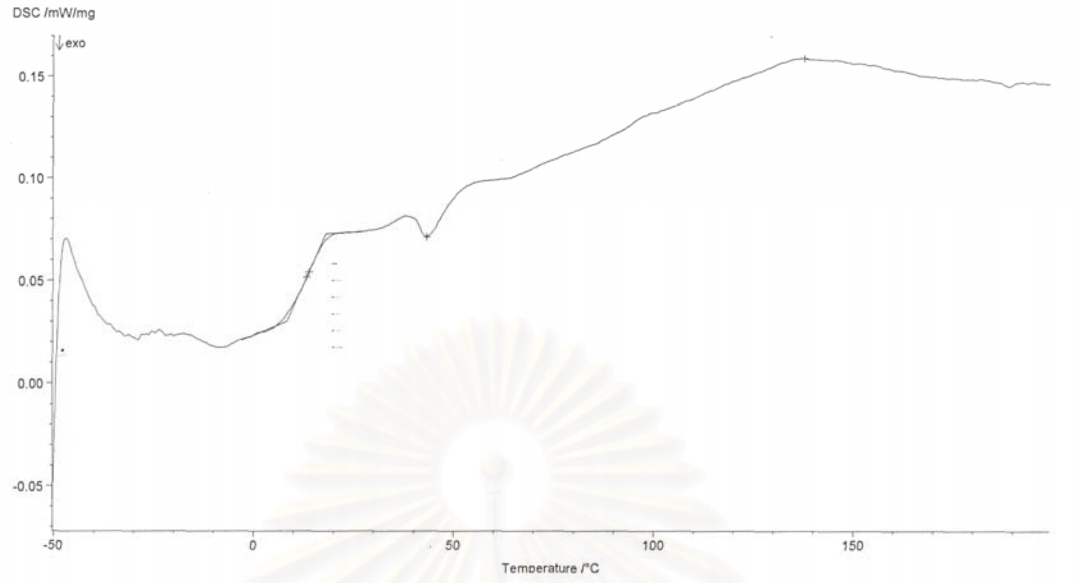

Figure C7. Synthesis from PET fabrics (4 hours of glycolysis times)

Appendix D

Molecular Weight and Molecular Distribution Characterization

GPC Data

Instrument : Gel Permeation Chromatograph, Water 150-CV
Test conditions : Eluent : Tetrahydrofuran
Flow rate : 1.0 ml/min
Injection volume : 100 μl
Temperature : 30°C
Column set : PLgel 10 μm mixed B 2 columns
(MW resolving range = 500-10,000,000)
Polymer standard : Polystyrene
Calibration method : Polystyrene standard
calibration
(MW 5,460-1,290,000)
Detector : Reflective Index Detector

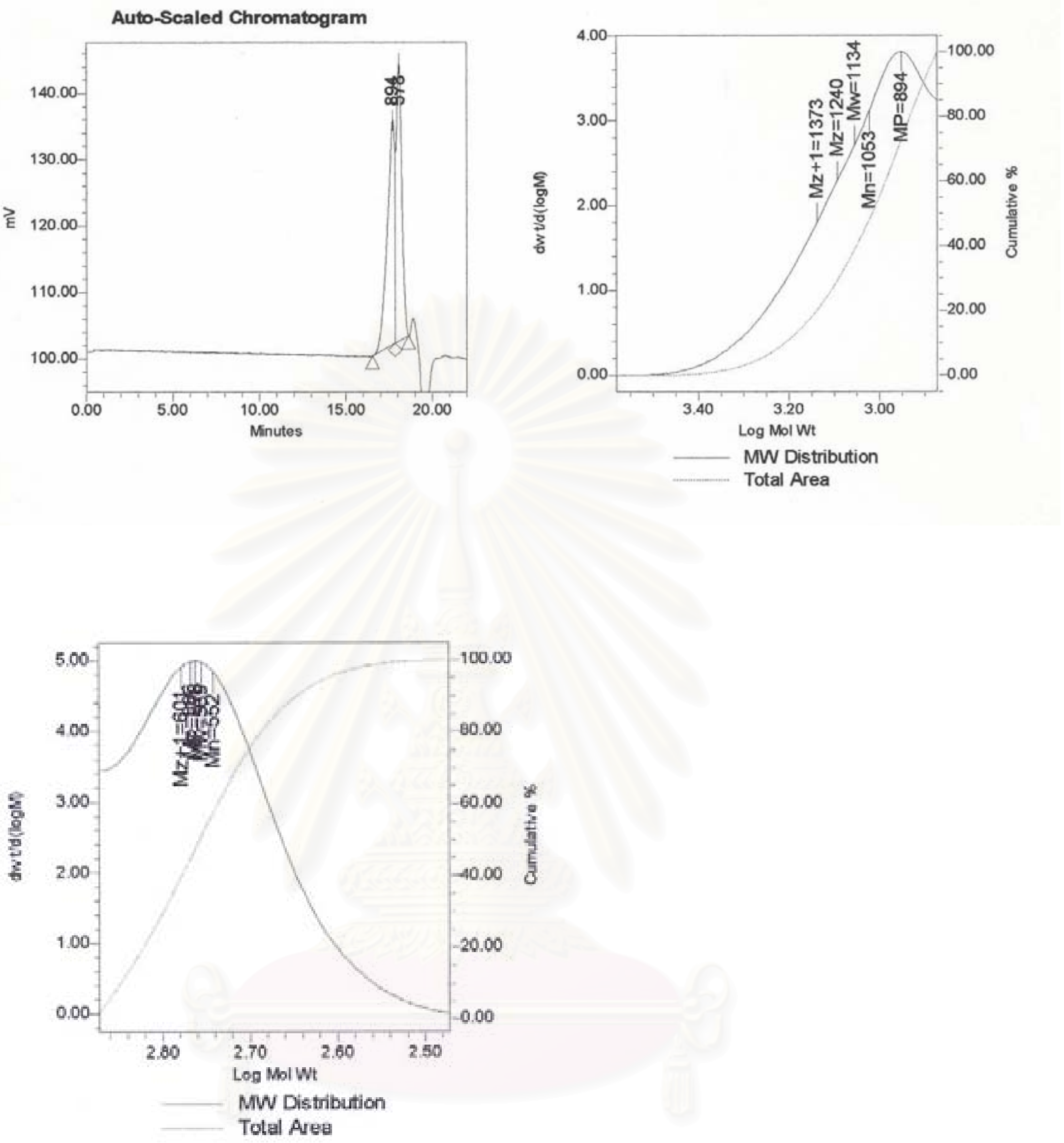

Figure D1. GPC data of glycolyzed product
(8 hours of glycolysis times, amount of catalyst 0.5%)

Table D1. GPC data of glycolyzed product
(8 hours of glycolysis times, amount of catalyst 0.5%)

	Mn	*Mw*	*MP*	*Mz*	*Mz+1*	*Polydispersity*
1	1053	1134	894	1240	1373	1.076612
2	552	569	578	586	601	1.031351

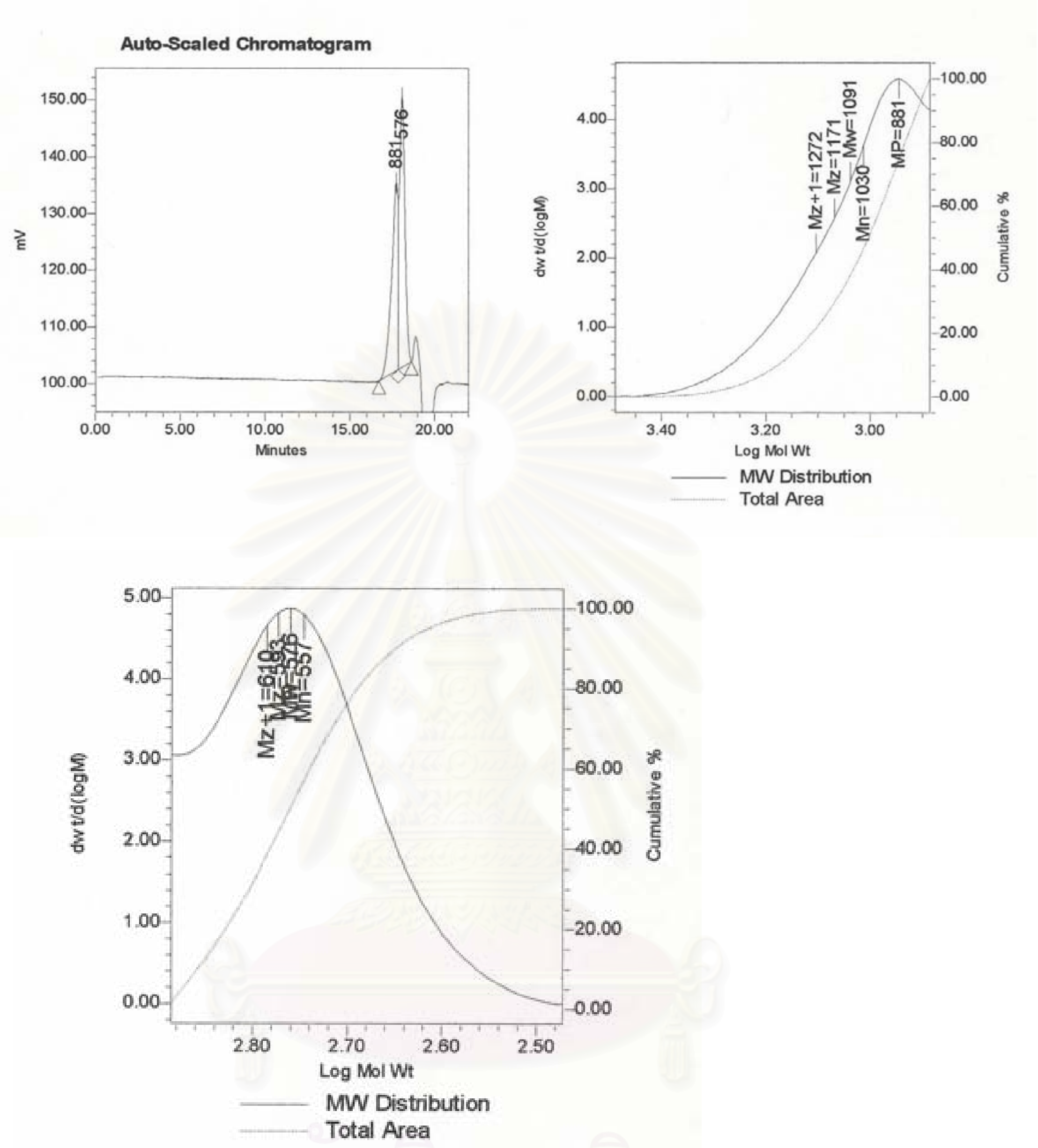

Figure D2. GPC data of glycolyzed product

(6 hours of glycolysis times, amount of catalyst 0.5%)

Table D2. GPC data of glycolyzed product

(6 hours of glycolysis times, amount of catalyst 0.5%)

	Mn	*Mw*	*MP*	*Mz*	*Mz+1*	*Polydispersity*
1	1030	1091	881	1171	1272	1.059122
2	557	576	576	593	610	1.033019

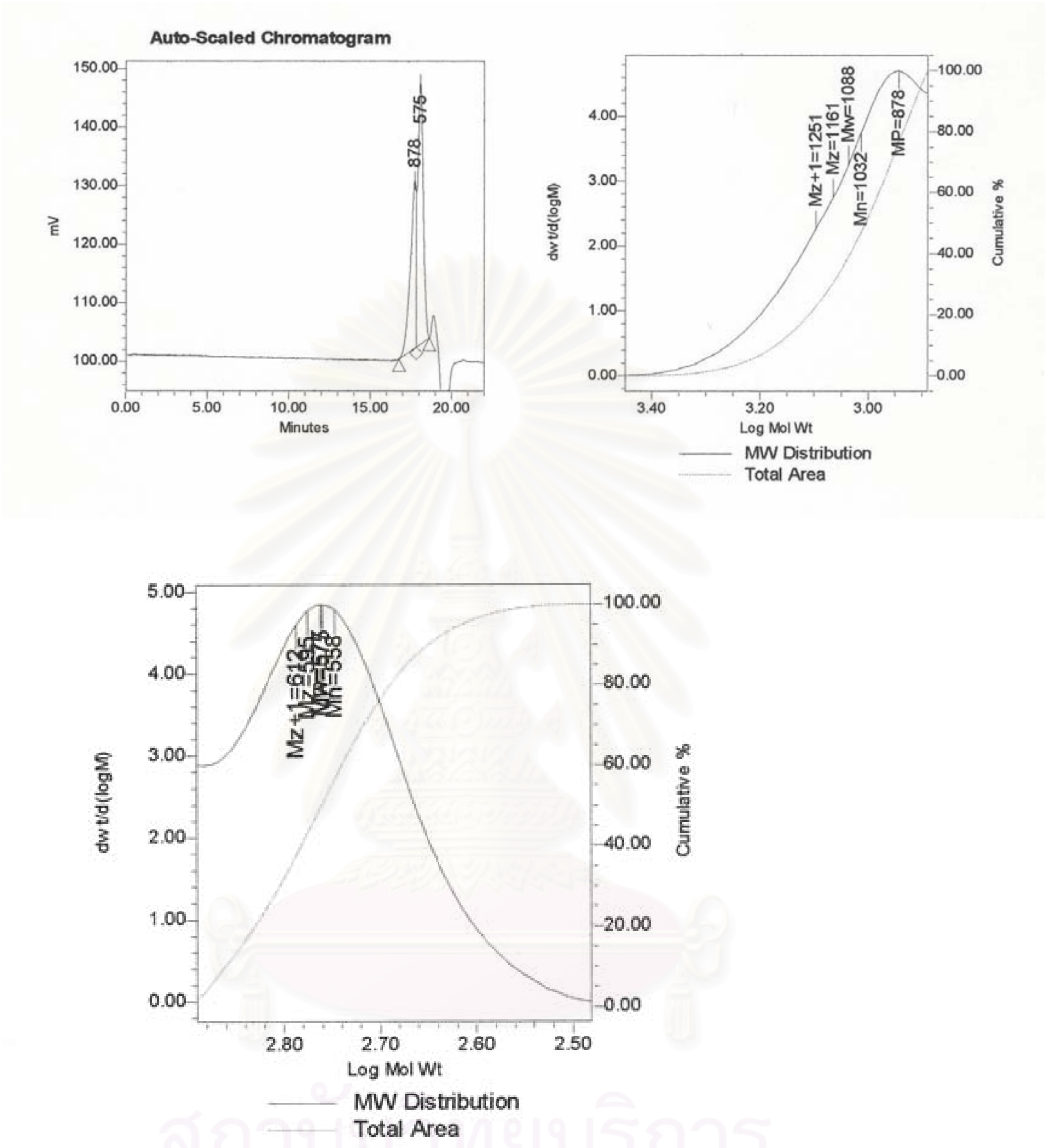

Figure D3. GPC data of glycolyzed product

(6 hours of glycolysis times, amount of catalyst 1.0%)

Table D3. GPC data of glycolyzed product

(6 hours of glycolysis times, amount of catalyst 1.0%)

	Mn	*Mw*	*MP*	*Mz*	*Mz+1*	*Polydispersity*
1	1032	1088	878	1161	1251	1.054726
2	558	577	575	595	612	1.033611

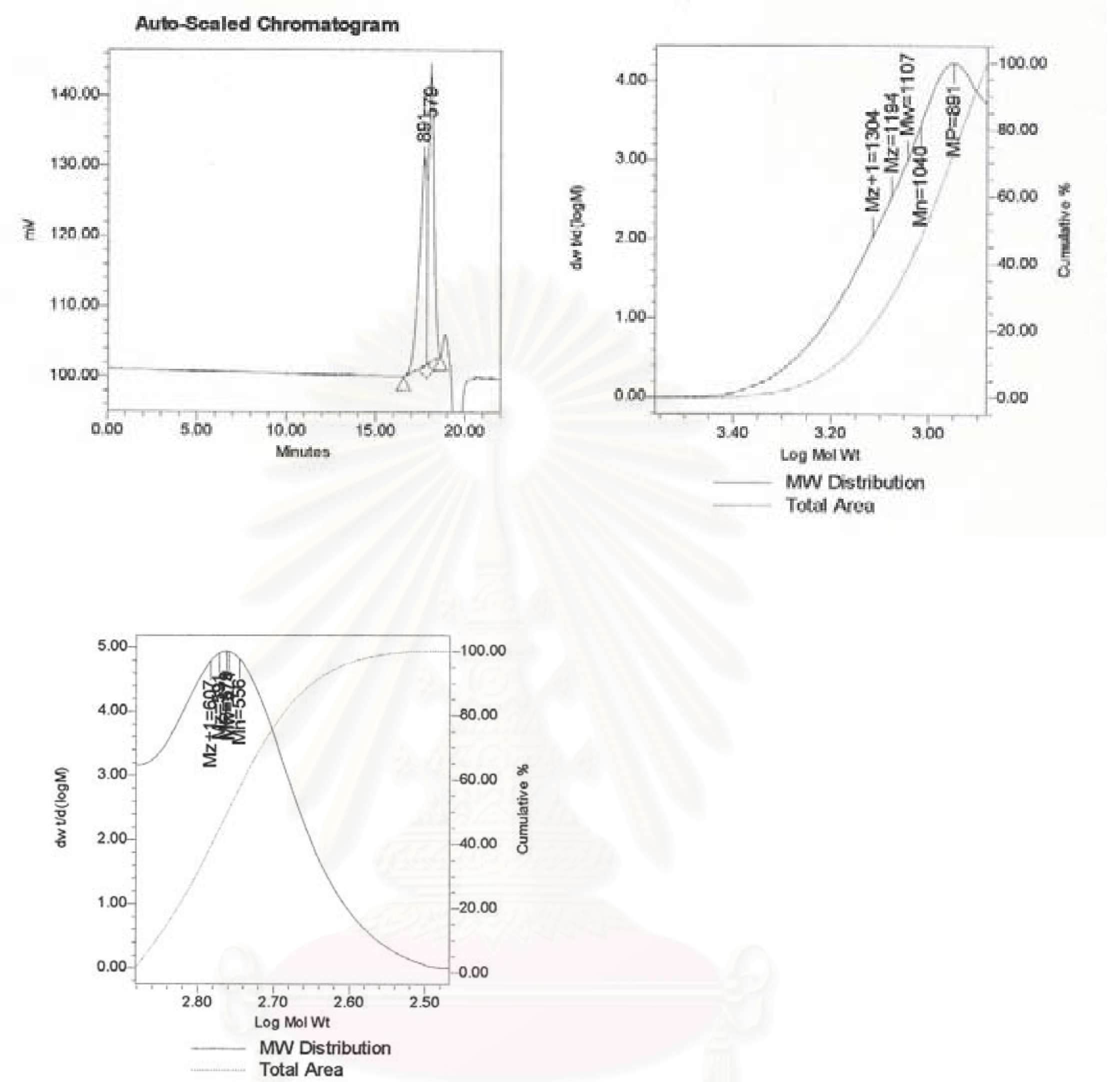

Figure D4. GPC data of glycolyzed product

(4 hours of glycolysis times, amount of catalyst 0.5%)

Table D4. GPC data of glycolyzed product

(4 hours of glycolysis times, amount of catalyst 0.5%)

	Mn	*Mw*	*MP*	*Mz*	*Mz+1*	*Polydispersity*
1	1003	1050	877	1109	1180	1.046611
2	558	575	579	592	608	1.031885

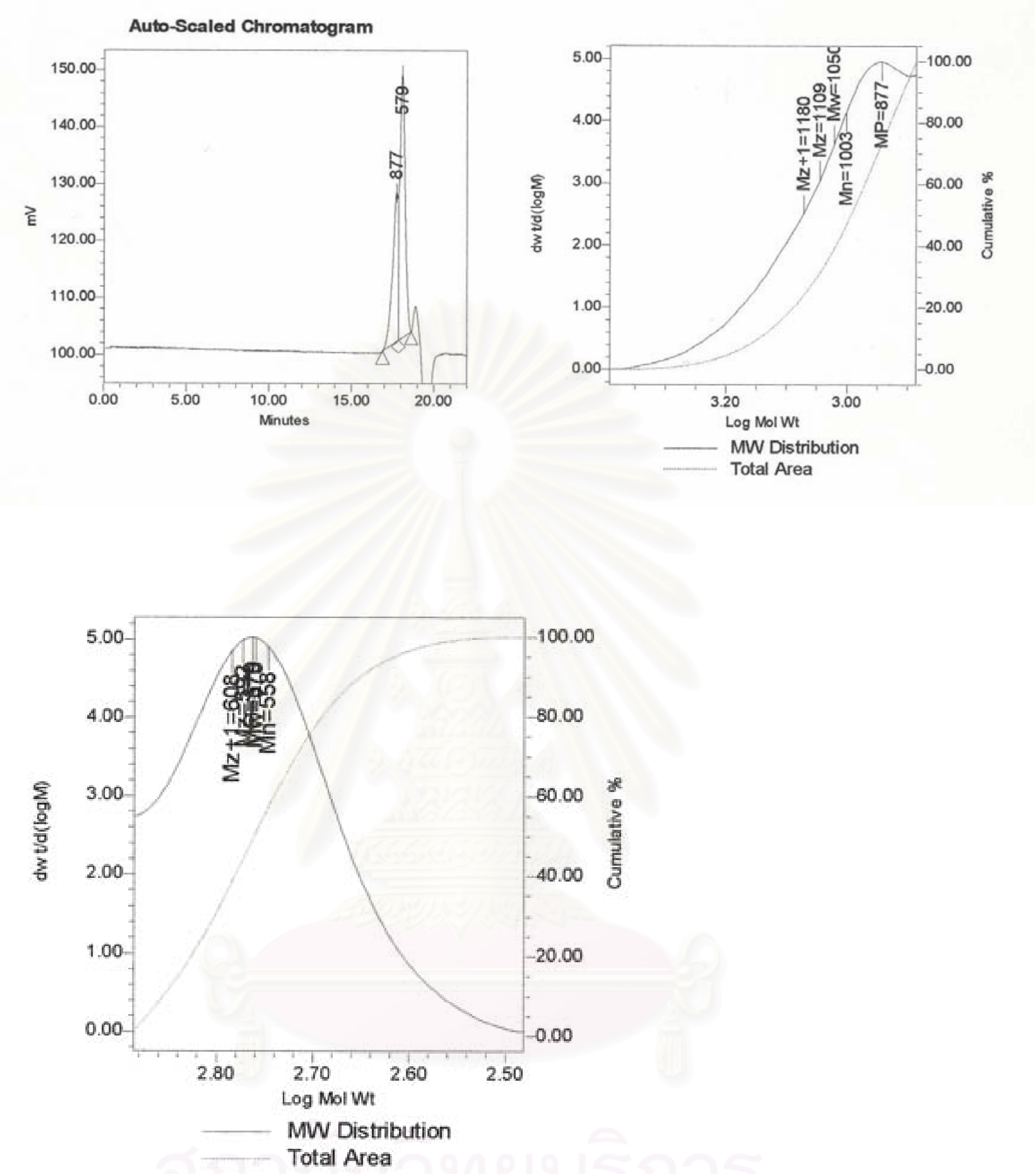

Figure D5. GPC data of glycolyzed product
(4 hours of glycolysis times, amount of catalyst 1.0%)

Table D5. GPC data of glycolyzed product
(4 hours of glycolysis times, amount of catalyst 1.0%)

	Mn	*Mw*	*MP*	*Mz*	*Mz+1*	*Polydispersity*
1	1040	1107	891	1194	1304	1.064161
2	556	574	579	591	607	1.032293

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