สำนักหอสมุดกลาง พระจอมเกล้าลาดกระบัง

# Unsaturated Polyester Resin from X-ray Film PET

Miss Nidchakarn Krueson
Miss Acharee Seephueng
Miss Natnicha Laorod

เลขหมู่..............................
เลขทะเบียน....46664....
วัน,เดือน,ปี..1 2 ก.ย. 2549

.b..............................
.i..............................

A Special Project Submitted in Partial Fulfillment of the
Requirement for the Degree of Science
Department of Chemistry
Faculty of Science
King Mongkut's Institute of Technology Ladkrabang
Academic Year 2005

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Copyright 2005**
**International Programs, Faculty of science**
**King Mongkut's Institute of Technology Ladkrabang**

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

| | |
|---|---|
| Special Project Title | Unsaturated Polyester Resin from X-ray Film PET |
| Students | Miss Nidchakarn Krueson |
| | Miss Acharee Seephueng |
| | Miss Natnicha Laorod |
| Department | Chemistry, Faculty of Science |
| Program | Polymer Science and Technology |
| Academic Year | 2005 |
| Special Project Advisors | Assoc.Prof.Dr. Ittipol Jangchud |
| | Asst.Prof.Dr. Pathavuth Monvisade |

## Abstract

This project was focused on used PET X-ray film wastes and virgin PET as starting materials for producing unsaturated polyester resins (UPRs) by using depolymerization reaction of PET. First, glycolyzed products were obtained by depolymerizing PET X-ray film flakes or virgin PET with ethylene glycol (EG) and propylene glycol (PG). In this project, diethylene glycol (DEG) was used to improve properties of UPRs. Two molar ratios of EG:PG:DEG (i.e. 1:1:0 and 1:1:0.5) were studied. Then, the glycolyzed products were reacted with maleic anhydride by using hydroxyl:carbonyl ratio of 1.1:1 (mol ratio). In curing reaction, styrene monomer was added by using benzoyl peroxide (BPO) as an initiator and dimethyl aniline (DMA) as an accelerator. Glass fibers (chopped strand mat, CSM) and the synthesized UPRs were fabricated into glass reinforced composites using the hand lay-up technique. Both mechanical and thermal properties of the composites were characterized. It was found that tensile strength, flexural strength, % elongation at break and impact strength of cured UPRs synthesized from both resources of PETs were increased when DEG was added. In contrast, tensile modulus, flexural modulus and hardness of cured UPRs from both resources PETs were decreased when DEG was incorporated. Moreover, adding DEG also had effects on cure characteristic of UPRs, i.e., increasing cure time. The composites of UPRs synthesized from both PETs with glass fibers showed better overall properties than those of pure UPRs. For cost analysis, it was found that the synthesized UPRs were cheaper than commercial UPRs. They seem to be promising materials to be used in composite applications.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# ACKNOWLEDGEMENT

This special project was accomplished due to the attention and aids from our consultants.

First, we wish to thank Assoc.Prof.Dr. Ittipol Jangchud and Asst.Prof.Dr. Pathavuth Monvisade for encouraging guidance, advice, discussion throughout this special project. We are also grateful to Asst.Prof.Dr.Punnama Siriphannon and Asst.Prof.Dr.Chonlada Ritvirulh for serving as the examiners, and their valuable comments.

We gratefully appreciate for all teachers who teach us through four years in the Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang (KMITL).

We would like to thank Heran S. Sevee Co., Ltd for the desilvered PET X-ray films and Charoen Wattana Fiber and Chemicals Co., Ltd for benzoyl peroxide (BPO) and glass fiber used in this project.

We would like to give special thanks to Miss Panruethai Gawborisut, a M.Sc. student at KMITL, Miss Panida Kansomwan, Miss Phensupa Kumperanon and Miss Sirirut Chinarot, graduated students of previous project, for all helps and suggestions throughout this project.

Finally, we would like to thank our parents and our friends for all spirits and encouragements.

Nidchakarn Krueson
Acharee Seephueng
Natnicha Laorod

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# TABLE OF CONTENTS

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

# TABLE OF CONTENTS (CONTINUED)

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# LIST OF TABLES

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# LIST OF FIGURES

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## LIST OF FIGURES (CONTINUED)

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# CHAPTER 1

# INTRODUCTION

## 1.1 Rationale

In recent years, plastics are widely used with rapid consumption rate. Increased consumption of plastics has resulted in an increase in plastic wastes. Currently, three main strategies available for management of plastic wastes are: incineration, landfill and recycling. The limited availability of landfills and the pollution from incineration together with more restrictive customer demands and government legislation about plastics and waste materials drive plastic industries to search for other solutions. One promising solution to solve the problems is to recycle polymers because it is a cheaper way and does not pollute the environment. Thus recycling method is the most worldwide management of plastic wastes.

Poly(ethylene terephthalate) (PET) is a thermoplastic polyester showing excellent thermal and mechanical properties. It is a worldwide used polymer, mostly as a packaging material in several applications such as food packaging, soft-drink bottles and X-ray film. PET is not a hazardous product and relatively expensive compared to other common plastics. Its waste quantity increases drastically so it is a good candidate for recycling. PET waste can be recycled by different methods like physical recycling and chemical recycling.

Because X-ray film is one of many applications that widely used in every day life but most of its wastes are thrown away without any valuable management. If the wastes from X-ray film can be recycled, the amount of plastic wastes and pollution will be reduced. Moreover, silver chloride ($AgCl_2$) that coated on the films can be extracted and converted to high value metal (Ag). So this project involves a glycolysis process of used X-ray PET films that is a chemical recycling technique. The glycolysis is a depolymerization reaction of PET with a glycol leading to bis-hydroxyethyl terephthalate (BHET) and its higher oligomers. However, the bis-

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

hydroxyethyl terephthalate (BHET) and its higher derivatives can be used as a starting material for synthesis of unsaturated polyester resins.

Unsaturated polyester resins (UPRs) are thermoset materials which are most commonly used as a matrix in composite materials. These polymers are made up of at least two separate components; reinforced fibers and embedding matrix. Other additives may be used to improve properties or characteristics. Glass fibers may be used yielding FRP (Fiber Reinforced Plastic) or specifically GRP (Glass Reinforced Plastics). Glass fibers are widely used in construction industry because of their properties: flame retardant, chemically resistant, excellent weather ability, dimensional stability, and rigidity. Unsaturated polyester resins are not only imported from other countries, but also expensive. So this project emphasizes on the synthesis of unsaturated polyester resins to have the properties similar to commercial grades of UPRs in order to reduce cost and PET wastes.

### 1.2 Objectives:

1. To study a method of PET waste recycling techniques by using used PET X-ray films as a starting material in the synthesis of unsaturated polyester resins.
2. To study effects of the ratio of ethylene glycol: propylene glycol: diethylene glycol (EG: PG: DEG) in the synthesis of unsaturated polyester resins on mechanical and thermal properties.
3. To compare the properties of UPRs from different PET resources, i.e., used X-ray films and virgin.

### 1.3 Scopes of Study:

1. Synthesize unsaturated polyester resins(UPRs) from virgin PET and desilvered PET X-ray films with glycolysis process by using ethylene glycol (EG), propylene glycol (PG) and diethylene glycol (DEG) as glycols and zinc acetate as a catalyst.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

2. Study effects of ratios of ethylene glycol, propylene glycol, and diethylene glycol (EG:PG:DEG) at 1:1:0 and 1:1:0.5 on glycolyzed products from both virgin PET and PET X-ray films.
3. Determine molecular weight of glycolyzed products from hydroxyl value.
4. Prepare unsaturated polyester resins (UPRs) from the reaction of glycolyzed products with maleic anhydride. Styrene monomer is added to induce crosslinking in the resin.
5. Fabricate unsaturated polyester resins and glass fiber-reinforced UPRs composite by hand lay-up method.
6. Test for mechanical properties of the composites such as flexural strength, flexural modulus, tensile strength, modulus, % elongation at break, impact strength, hardness and thermal properties.
7. Estimate and compare the cost of unsaturated polyester resins to the commercial ones.

## 1.4 Expected Results:

1. Pollution in environment is reduced by converting wasted PET X-ray films to valuable products, i.e., UPRs for composite applications.
2. Domestic UPRs industries are encouraged and imported resins are reduced.
3. Knowledge gained from this project can be used to improve properties of UPRs that are made from plastic wastes.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# CHAPTER 2

# THEORY AND LITERATURE REVIEWS

## 2.1 Poly(Ethylene Terephthalate)

Poly(ethylene terephthalate) (PET) is one of the most important commercial polyester polymers. Its characteristic properties are the reasons for its many uses. Since it is stronger than cotton and cellulose, yet mixes well with cotton fibers, it is used in fibers. Cloth made from these fibers is resistant to creasing. These fibers are known under the familiar trade names Dacron® and Fortrel® are widely used in consumer goods such as clothing and linens. PET also forms a clear polymer so it is also used in films such as Mylar®, as well as in photographic films and transparencies. Then very large amounts of PET are used in transparent and high strength bottles which are widely used as soft drink bottles and vegetable oil containers. In addition PET has low gas permeation property so it is used as soda bottles also [1].

**Table 2.1** Some typical properties of PET [2]

| **Properties** | **Values** |
|---|---|
| Specific gravity | 1.38 |
| Melting point\($T_m$) | 265°C |
| Glass transition temperature\($T_g$) | 80°C |
| Heat specific at 25°C | 0.315 cal/g-degree |
| Thermal conductivity | $3.63 \times 10^{-9}$ cal/cm.sec.degree |
| Permeability to oxygen | 5.7 g/ $m^2$.hr |
| Permeability to nitrogen | 5.2 g/ $m^2$.hr |

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

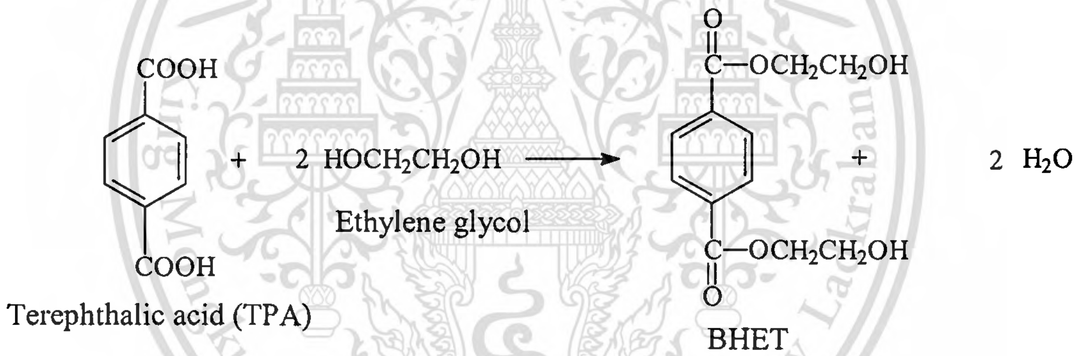
### 2.1.1 Synthesis of Poly(ethylene terephthalate) (PET)

Polyethylene terephthalate (PET) can be synthesized into two ways:

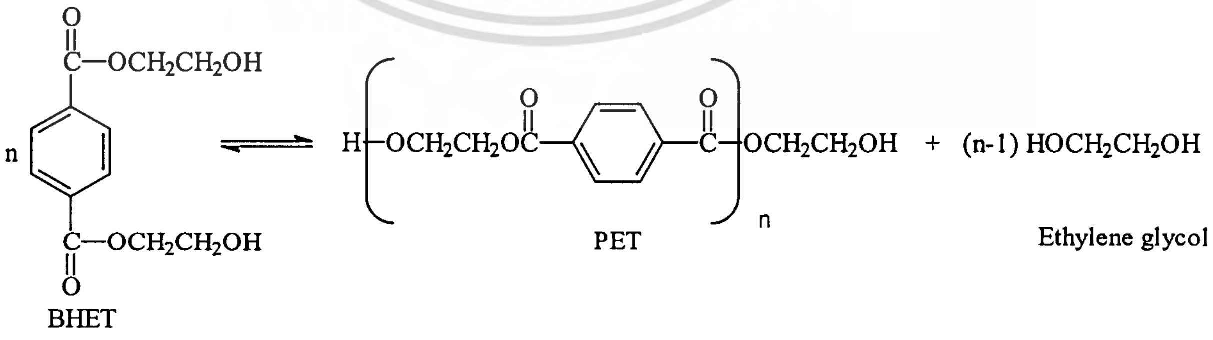
1. Esterification
2. Ester interchange

1. Esterification

Polyethylene terephthalate (PET) may be produced from ethylene glycol and terephthalic acid (TPA). The first step of the reaction is the formation of a prepolymer, bis-hydroxyethyl terephthalate (BHET).



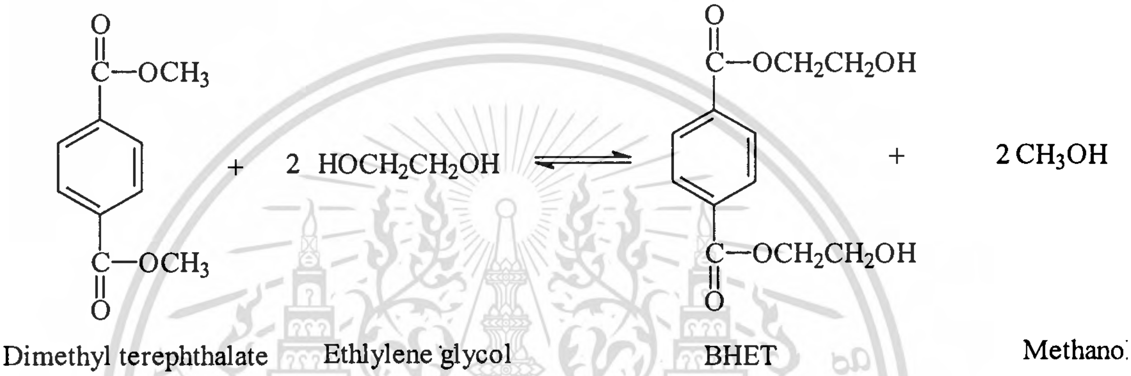
Subsequent polymerization of BHET with the removal of ethylene glycol at 270-285\°C forms the polymeric polyethylene terephthalate.



This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

2. Ester interchange

The other synthesis of PET involves an ester interchange of a diester and a diol. This is a transesterification reaction in which one ester is transformed into another. The synthesis of PET by this method reacts dimethylterephthalate with ethylene glycol as follows.



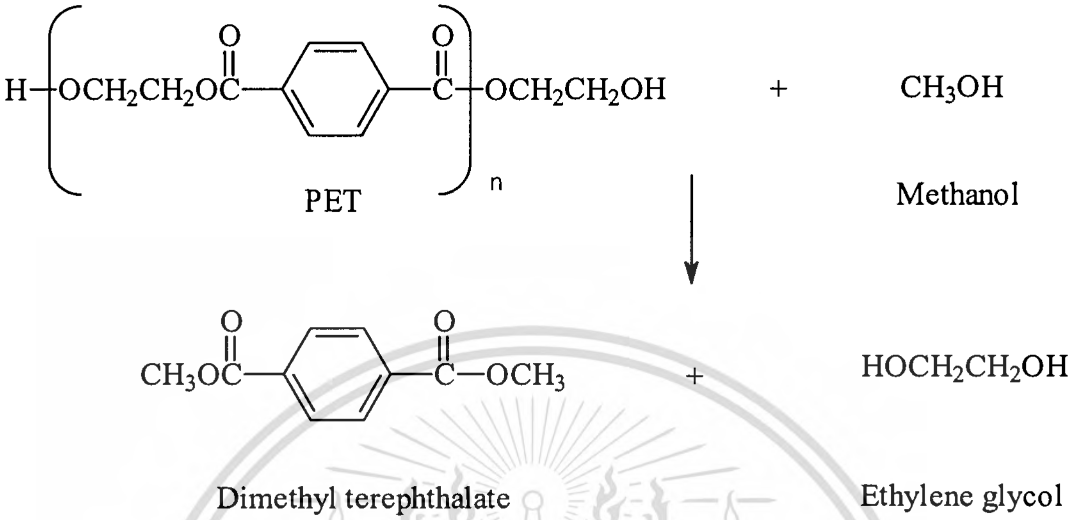
Then polymerization of BHET forms polymeric polyethylene terephthalate with the removal of ethylene glycol also [1].

### 2.1.2 Depolymerization of PET by Using Chemical Recycling Methods

1. Alcoholysis process

Alcoholysis of PET results in the stoichiometric formation of dimethyl terepthalate (DMT) and ethylene glycol (EG). Alcoholysis of PET flakes is performed at temperatures around 200°C and at high pressures.

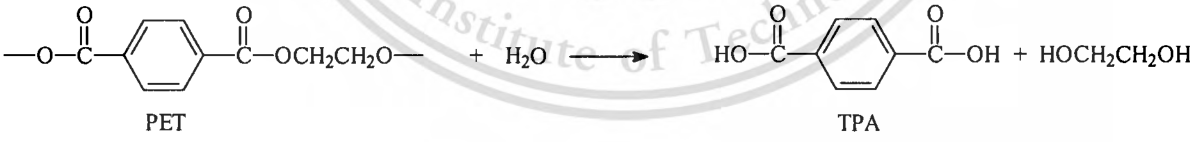
This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.



Alcoholysis is currently being successfully applied to PET scarp. Typical feedstocks for alcoholysis include used films, plant waste, fiber waste and scrap bottles.

2. Hydrolysis process

Hydrolysis relies on the use of high pressures and temperatures to depolymerize PET into terephthalic acid and ethylene glycol.



Hydrolysis of PET flake with water can be classified in to 3 types: [3]

1. Base-catalyzed Hydrolysis Process
2. Acid- catalyzed Hydrolysis Process
3. Neutral Hydrolysis Process

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 3. Aminolysis process

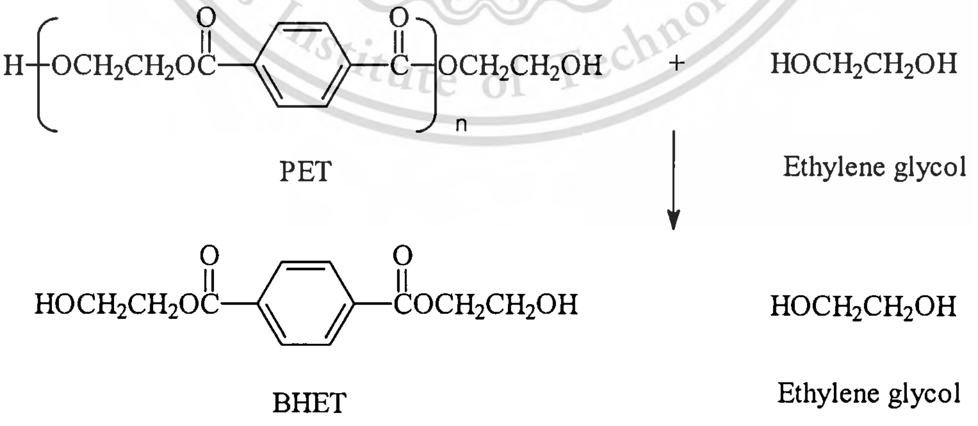
The process that depolymerizes PET by using primary amine such as methyl amine and get ethylene glycol(EG) and diamide of terephthalic acid as products [4].

### 4. Ammonolysis process

The process that uses anhydrous ammonia in ethylene glycol to get amide compound of terephthalic acid as an output [3].

### 5. Glycolysis process

Glycolysis proceeding under the influence of glycol (usually uses ethylene glycol and propylene glycol) is the true reverse reaction to the polycondensation of PET. Glycolysis of PET flake is performed under pressure at temperatures in the range of 180°C-220°C to give BHET and oligomers. The glycolysis reaction is generally performed under a blanket of inert gas (e.g.$N_2$) to prevent oxidation of the polyols which is produced.



This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

BHET can be reacted with anhydride or dicarboxylic acid to produce unsaturated polyester resins. Glycolysis process is widely used because not only it provides the product that can be synthesized further but also it does not need high pressure and high temperature for depolymerization [3,4].

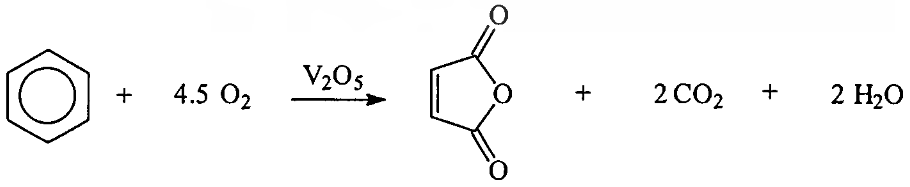
## 2.2 Unsaturated Polyester Resins

Unsaturated polyester resins are mixtures between unsaturated polyester and monomers that can be polymerized. They are viscous, generally pale yellow colored materials of a low degree of polymerization (about 8-10), i.e. molecular weight of about 2000. Many applications can be produced from unsaturated polyester resins because their wide range properties, low cost, mechanical property balance and they can stand for high temperature and chemical reagents. However UPRs have some disadvantages such as low resistance to some solvents and some chemical substances, high shrinkage, low impact strength and high water absorption rate. Thus they should not be used in applications that need high strength especially at high temperature and high humidity [5].

### 2.2.1 Raw Materials for Synthesis of Unsaturated Polyester Resins

1. Unsaturated acids and anhydrides

- Maleic anhydride is the most important unsaturated component used in the manufacture of linear unsaturated polyesters. It is mostly obtained by the oxidation of benzene:

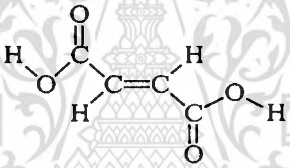


Maleic anhydride

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

The reaction is carried out in the vapor phase by passing a mixture of benzene and excess of air over a vanadium pentoxide catalyst at 350-450°C. The effluent is cooled and most of the maleic anhydride is condensed. The non-condensed material passes to a scrubber where the remaining anhydride is hydrolyzed to maleic acid. The maleic acid solution then passes to evaporators for concentration and dehydration. High-purity anhydride is obtained by distillation under reduced pressure.

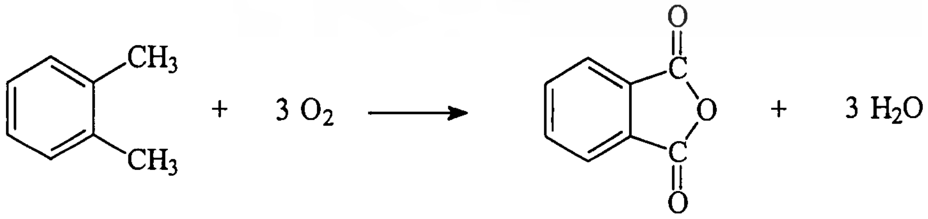
- Fumaric acid is isomerization of maleic acid. It can be prepared by catalytic oxidation of benzene or by bacterial action on glucose. It is found in small amounts in a variety of plants and is essential to the respiration of animal and vegetable tissue. Moreover polymers that are synthesized from fumaric acid have good thermal resistance.



Fumaric acid

2. Phthalic anhydride (Modifying agent)

Phthalic anhydride is one of the most important modifying component used in the manufacture of linear unsaturated polyesters. The anhydride is generally obtained by the oxidation of *o*-xylene:



King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

The reaction is carried out in the vapor phase by passing a mixture of *o*-xylene and air over a catalyst such as vanadium pentoxide supported on silica and promoted with titanium dioxide at about 400°C. The exit gases are cooled and the phthalic anhydride is collected and purified by distillation under reduced pressure.

Phatalic anhydride is a white crystalline solid, m.p.131°C. It gives polyesters which are compatible with styrene and the crosslinked products are hard and rigid [6].

3. Glycols

Glycols provide many properties for polyester resins such as toughness, flexibility, chemical resistance, thermal resistance. Different type of diols give different properties of resins.

Glycols that widely used for the manufacture of unsaturated polyester resins are ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG) and bisphenol A. Instead of glycols, bis-hydroxyethyl terephthalate (BHET) which is the product from depolymerization of PET, can acts as starting material for synthesis of polyester resins also [2].

4. Monomer

Monomer acts as solvent for the molten unsaturated polyester resin, which has high viscosity. It also acts as a crosslinking agent, which links the polyester chains to form strong three-dimensional polymer network also.

Styrene monomer is the most widely used crosslinking monomer because of its compatibility, low viscosity, ease of use and price. Other monomers can be used such as vinyl toluene monomer and methyl methacrylate monomer [6].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

5. Inhibitor

Inhibitor is used to prevent premature polymerization and to modify the reaction times. The common-used inhibitors are hydroquinone,1-4-benzoquinone,tert-butylpyrocatechol, toluhydroquinone and 3,4-di-tert-butyl-p-cresol. All these inhibitors have specific effects and are used for different resin types. In some cases they are added prior to condensation. In other cases they are dissolved in styrene and added after condensation [7].

6. Catalyst

Catalyst is a substance added to the resin to initiate polymerization. Peroxide is very popular for initiation such as Benzoyl Peroxide (BPO) and Methyl Ethyl Ketone Peroxide (MEKPO) [2].

7. Promoter or Accelerator

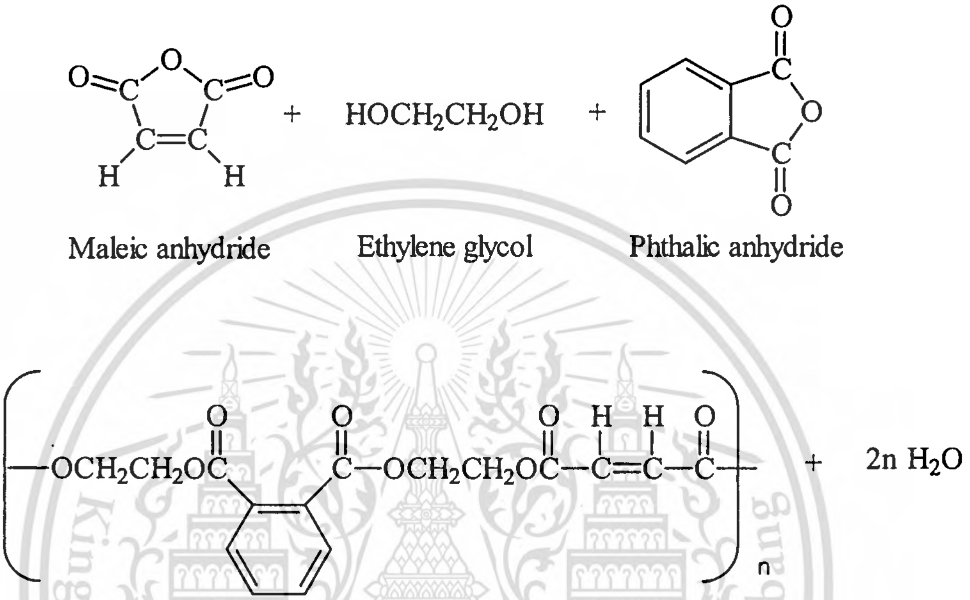
Accelerator is a material which helps decomposition of peroxides and produces free radicals which start propagation reaction resulting in gelation and ultimate cure of polyesters. A choice of accelerator very much depends on the type of organic peroxides selected. Accelerator usually is soaps of Cobalt such as Cobalt octoate, Cobaltnapthenate or certain amines such as Dimethyl aniline, Diethyl aniline [8].

### 2.2.2 Synthesis of Unsaturated Polyester Resin

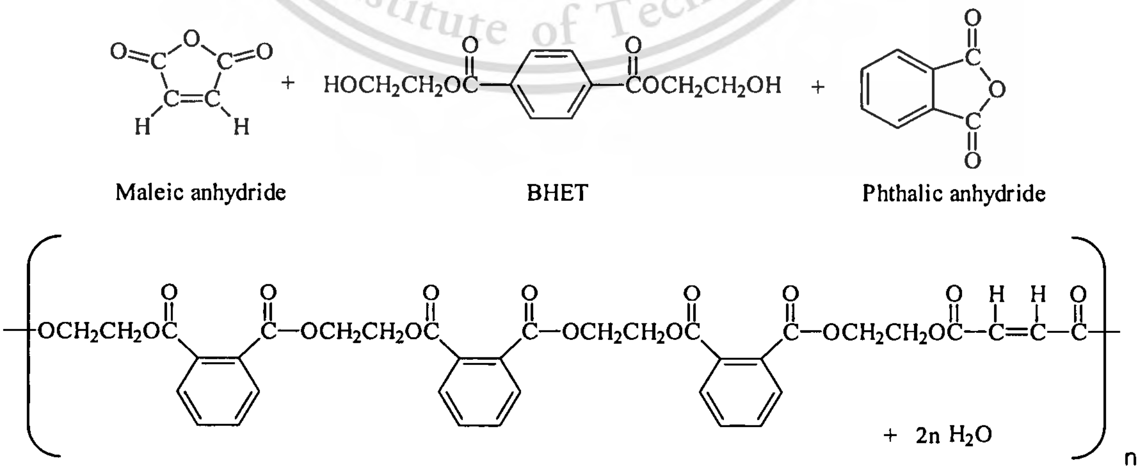
Unsaturated polyester resin is produced by condensing a glycol with both an unsaturated and a saturated dicarboxylic acid (the chemical equation is shown below). The unsaturated acid provides a site for subsequent crosslinking while a saturated acid reduces the number of sites for crosslinking and hence reduces the crosslinking density and brittleness of end products. In practice the polyester resin, which may vary from a very highly viscous liquid to a brittle solid depending on composition, is mixed with a reactive diluent such as styrene. Science crosslinking occurs via an addition mechanism across the double bonds in the unsaturated polyester and styrene which has been added an

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

inhibitor such as hydroquinone in order to obtain a balance of properties in respect of colors, storage stability and gelation rate of catalysed resin.

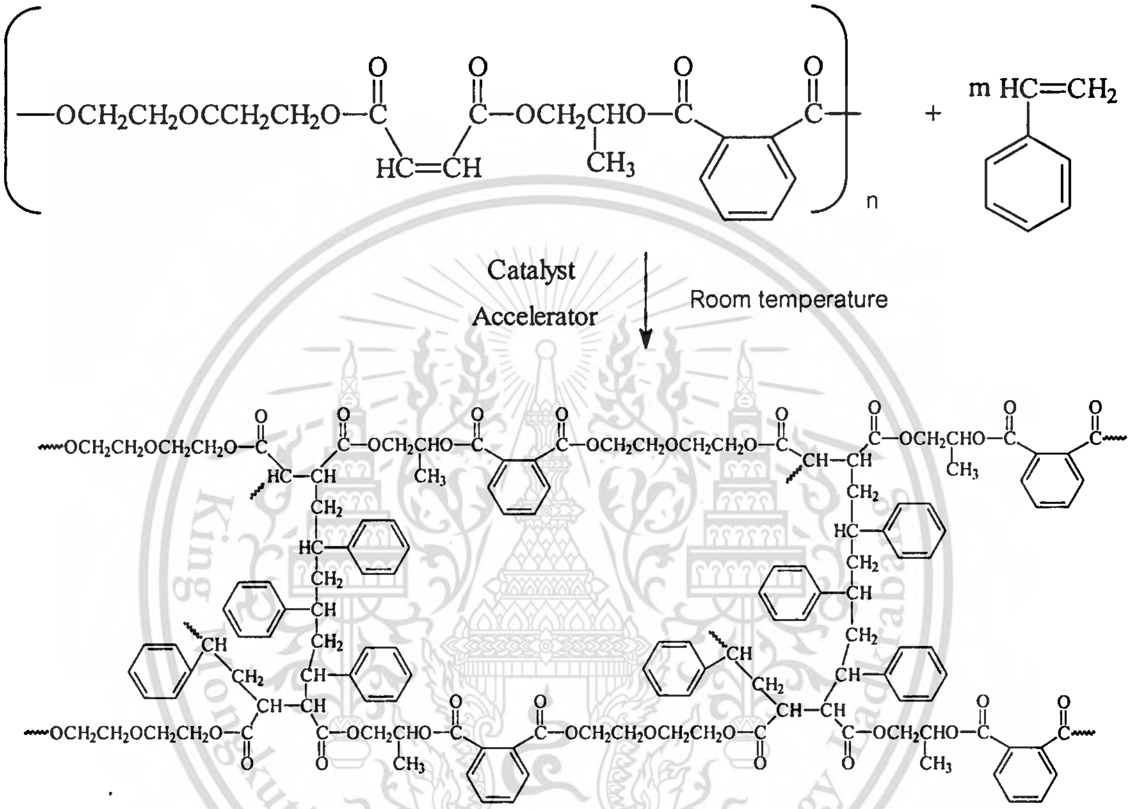


Instead of ethylene glycol, the product of glycolysis process of PET, bis-hydroxyethyl terephthalate (BHET) can be used to produce unsaturated polyester resin also as following equation:



This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

After that initiator and accelerator are added in the mixture of resin and styrene to liberate free radicals then crosslinking occur between the double bonds in the unsaturated polyester and styrene [2, 6, 9].



## 2.2.3 Curing of Unsaturated Polyester Resins

Unsaturated polyester resins can be cured by different ways as follows:

1. By using catalyst and heat.
2. By using catalyst and accelerator, this method is very popular because it is very simple and resins can be cured at room temperature.
3. By using ultraviolet light.
4. By using electron beam.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

Curing reaction takes place from the polymerization between double bonds in styrene monomer and polyester, it can occur at room temperature by activation of catalyst and accelerator. The period of time that start from adding catalyst until the resin form gel like, called "gel time" after that resin will be rigid. This period is called "cure time".

**Factors that affect curing of resins**

1. Temperature : curing rate increases when temperature is increased.
2. Amounts of catalyst and accelerator : amounts of them are proportional to curing rate.
3. Amount of resin : amount of resin is proportional to curing rate also.
4. Moisture : curing rate will decrease if amount of water exceed 0.05% .
5. Amount of oxygen : oxygen acts as inhibitor in curing process of unsaturated polyester resins [2].

## 2.3 Composite Materials

Composite materials are defined as any substance made by combining two or more materials to produce a multiphase system with different physical properties obtained from the constituents. Composite materials may be selected to give unusual combinations of stiffness, strength, weight, high temperature performance, corrosion resistance, hardness, or conductivity generally, a composite material is composed of reinforcement embedded in a matrix [10].

### 2.3.1 Reinforcements

Reinforcement materials are added to the resin system to provide strength to the finished part. The selection of reinforcement material is based on the properties desired in the finished product. These materials do not react with the resin but are an integral part of the composite. There are three basic types of reinforcement materials used and they are aramid fibers, carbon/graphite fibers and glass fibers. Other fibers are also used but these three fibers are most commonly used [15].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

Based on the form of reinforcement, composites can be classified into roughly three types :

1. Particulate : composed of particles in a matrix.

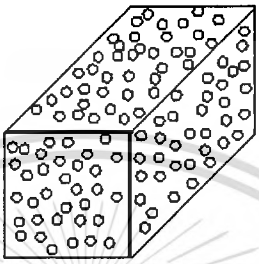


**Figure2.1** Particulate composite

2. Fibrous : composed of fibers in a matrix.

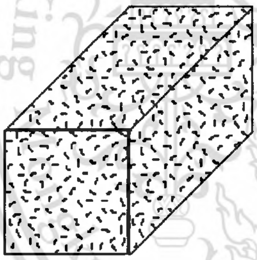


**Figure 2.2** Short fiber reinforced composites

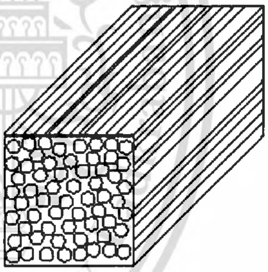


**Figure2.3** Continuous fiber (long fiber) reinforced composites

3. Laminar : composed of layers of materials

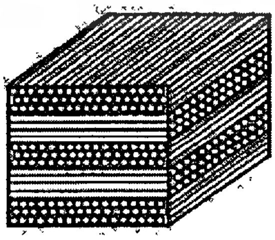


**Figure2.4** Laminar [11]

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

สำนักหอสมุดกลาง พระจอมเกล้าลาดกระบัง

There are several general variables which affect properties of reinforced composite materials and structures, i.e.,

1. Interface bond between matrix and reinforcements: The matrix functions to transfer most of the stress to the reinforcements. In order to accomplish this task, there must be an excellent adhesion between the matrix and the reinforcement.

2. Properties of the reinforcement: It is assumed that the reinforcement is much stronger than the matrix. The actual properties of each reinforcement may vary by composition, shape, size, and number of defects. The production, handling, processing, surface enhancement, or hybridization can also determine for each type of reinforcement.

3. Size and shape of the reinforcement: Some shapes and sizes may help provide superior handling, loading, processing, packing orientation, or adhesion in the matrix.

4. Loading of the reinforcement: Generally, mechanical strength of the composite depends on the amount of reinforcing agent. A part containing 60 percent reinforcement and ten percent resin matrix is almost six times stronger than a part containing the opposite amounts of these two materials.

5. Processing technique: Some processing techniques allow the reinforcements to be more carefully aligned or oriented. These products are more anisotropic. During processing, reinforcements may be broken or damaged, resulting in lower mechanical properties. Depending on processing technique, particulate reinforcements and short fibers are more likely to have random rather than oriented placement in the matrix. This will result in isotropic composite components.

6. Alignment or distribution of or the reinforcement: Alignment or distribution of the reinforcement allows versatility in composites. The processor can align or orient the reinforcements to provide directional properties. In Figures 2.5 and 2.6, the parallel (anisotropic) alignment of continuous strands provided the highest strength;

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

46664

bidirectional (cloth) alignment provides a middle strength range, and random (mat) or isotropic alignment gives the lowest [12].

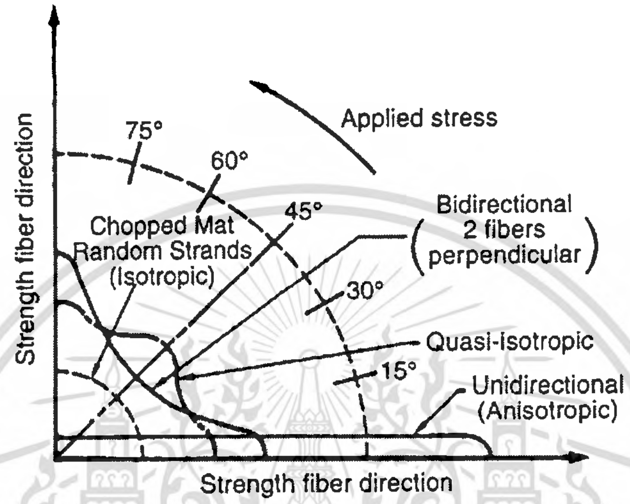


**Figure 2.5** Effect of alignment or distribution of the reinforcement [12]

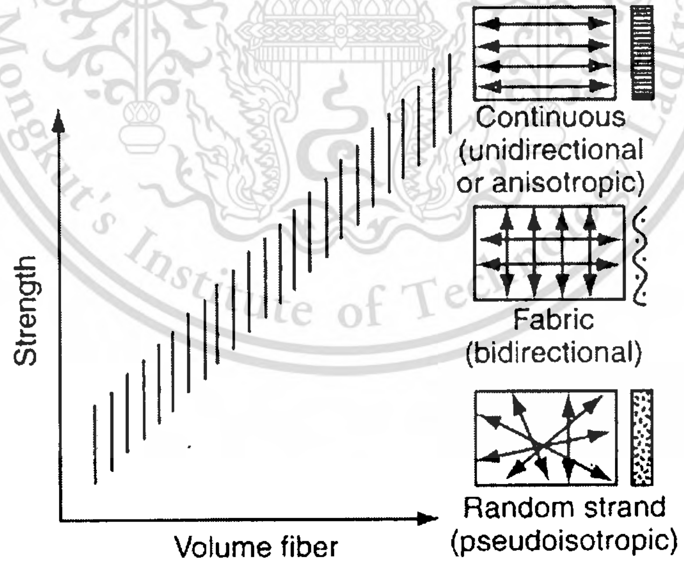


**Figure 2.6** Strength relation to reinforcement alignment and volume of fiber [12]

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 2.3.2 Matrix

The matrix is material that gives body and grips or holds the reinforcements of the composite together, and is usually of lower strength than the reinforcement. The matrix must be capable of being forced around the reinforcement during some stage in the manufacture of the composites. There are a number of matrix materials available, including carbon, ceramic, glass, metal, and polymer [19].

## 2.4 Polymer Composite Materials

Polymer composites were first developed during the 1940's, for military and aerospace applications. Considerable advances have been made since then in the use of this material and applications developed in the construction sector. Load bearing and infill panels have been manufactured using composites. Complete structures have been fabricated where units manufactured from Glass Fiber-Reinforced polyester (GRP) or Fiber Reinforced Plastics (FRP) are connected together to form the complete system in which the shape provides the rigidity. Glass reinforced plastics have been used in many other applications including pressure pipes, tank liners, and roofs. In the present day, many plastic materials that reinforced with glass fiber are widely used including carbon fiber and aramid fiber [16].

### 2.4.1 Glass Fiber

Glass fibers demonstrate excellent thermal and impact resistance, high tensile strength, good chemical resistance and outstanding insulating properties [6]. They can be tailored to create different types of glass fibers. Therefore, they are used in high performance applications in the industry. There are different types of glass fibers like E-Glass, S-Glass, C-Glass, etc. and they are manufactured by varying the composition of the constituents.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Table 2.2** Composition of glass fibers [6]

| **Materials** | **E-Glass Range %** | **S-Glass Range %** | **C-Glass Range %** |
|---|---|---|---|
| Silicon dioxide | 52 to 56 | 65 | 64 to 68 |
| Aluminum oxide | 12 to 16 | 25 | 3 to 5 |
| Boric oxide | 5 to 10 |  | 4 to 6 |
| Sodium oxide and potassium oxide | 0 to 2 |  | 7 to 10 |
| Magnesium oxide | 0 to 5 | 10 | 2 to 4 |
| Calcium oxide | 16 to 25 |  | 11 to 15 |
| Barium oxide |  |  | 0 to 1 |
| Titanium dioxide | Up to 1.5 |  |  |
| Iron oxide | 0 to 0.8 |  | 0 to 0.8 |

The glass fibers used normally have diameter in the range of 6.5 micron to 16 micron and are wet chopped. The chop lengths range from 3mm to 25mm with a moisture content of 10% to 20%. The shelf life is about nine months from the date of manufacture. Glass fibers are strong, inert, high dielectric strength fibers with elastic modulus of 75 GPa. But they are hard to disperse, brittle and hard to bond.

Glass fiber reinforcements have various forms, for example, continuous filament, or discontinuous filament. The continuous filaments are used in the production of woven fabric, roving, knitted and braided reinforcement for special applications. The continuous filaments may be chopped to form discontinuous filament forms such as chopped strands for thermoplastics, mats, spray-up, milled fibers and performs. Depending upon the fabrication process, the form of glass fiber filament is selected accordingly [15].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

The example of different types of glass fiber in several forms:

2.4.1.1 Chopped strand

This is a non-woven planar material in which the glass fiber strands are chopped into short lengths (3 to 50 mm). Chopped strands are usually used in premix molding process [17].

**Figure 2.7** Chopped strand

2.4.1.2 Chopped strand mat

Chopped strand mat is the most widely used form of glass fiber reinforcement, especially in sheet materials. The strands are distributed randomly orientated. The mat is held together by a binder. The glass content of FRP reinforced with chopped strand mat generally varies between 25 and 35 per cent; for FRP reinforced with cloth, the glass fiber content ranges from 50 to 63 per cent [18].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Figure 2.8** Chopped strand mat

2.4.1.3 Continuous strand mat

Continuous strand mat may be used as an alternative to chopped strand mat because their properties and application potential are similar. Continuous strand mat is a non-woven material similar to chopped strand mat except that the fibers are swirled at random and are continuous. The swirled strands are interlocked with a binder. The user should check with the supplier on the compatibility of the binder for a specific resin system.

**Figure 2.9** Continuous strand mat

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 2.4.1.4 Woven rovings

Woven rovings are bidirectional reinforcements constructed from untwisted fibers in parallel tows having a warp array (roll direction) interspersed with a weft array (width of roll). Woven materials allow ease of handling for the construction of large areas of composite. Woven materials produce higher strength and stiffness composites than random fiber reinforcements.

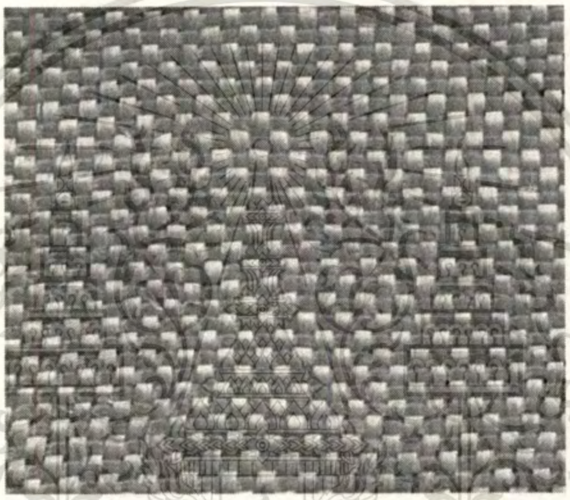


**Figure 2.10** Woven rovings

### 2.4.1.5 Fabrics

Woven fabrics are constructed by interlacing warp and weft yarns, fibers or filaments in a variety of patterns to form fabric styles such as plain, twill, satin, unidirectional and others. Woven fabrics are usually lighter than woven rovings, have less crimp and may achieve volume fractions of over 50% depending on the method of composite compaction [17].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

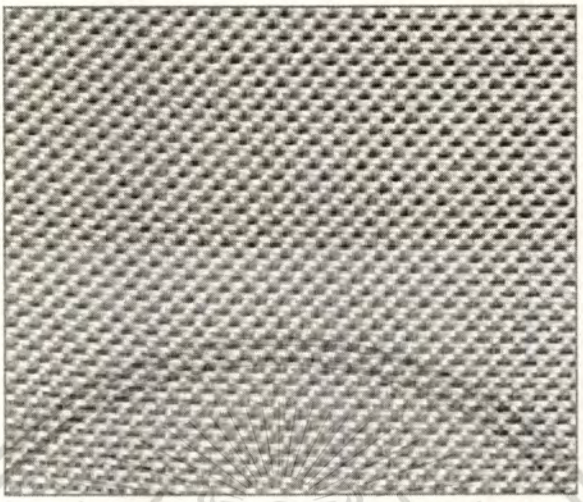


**Figure 2.11** Fabrics

### 2.4.2 Matrices for Glass Fiber Composites

The selection of polymer matrices for use in structural composites will be determined by a number of factors and should not be made without full consultation with materials suppliers and fabricators. Properties required are usually dominated by strength, stiffness, toughness and durability. Account should be taken of the application, service temperature and environment, method of fabrication, cure conditions and level of properties required.

Polymer matrices that usually use for glass fiber composites are thermosetting polymers such as polyester resins, phenolic resins and epoxy resins [17].

## 2.5 Glass Fiber-Reinforced Polyester Composites

Glass fiber-reinforced polyester (GRP) composites are the most popular reinforced plastic materials used in the construction industry. Depending on formulation and use, they may be fabricated into products that are light in weight, transparent, translucent or opaque, colourless or coloured, flat or shaped sheets, with no limit to the size of object that can be made.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 2.5.1 Manufacture of Glass Fiber-Reinforced Polyester Composites

The two components of a GRP composite are the matrix (the continuous phase) and the reinforcing glass. The matrix is based on cured thermosetting polyester resin. The raw material is supplied in the form of a viscous, syrupy liquid comprising the following basic ingredients: a linear unsaturated polyester; a cross-linking monomer (curing agent), usually styrene; and an inhibitor to retard cross-linking. Other ingredients that can be added such as fillers, pigments, fire retardants, ultraviolet (UV) light stabilizers, and thixotropic agents (to prevent excess flow of the resin before cure). When catalyst (initiator) and glass reinforcement are added, the resulting mixture is ready for production of the GRP item. During fabrication the monomer reacts with the polyester, resulting in crosslinking of the polyester chain and final cure. The ultimate result is a rigid solid material in which the matrix has joined chemically and mechanically with the reinforcing glass fibers to provide a composite structure whose properties are very different from and significantly superior to those of either material alone [18].

### 2.5.2 Production Method of Composite by Hand lay-up Process

Hand lay-up process is the most common process in Glass Fiber-Reinforced Polyester (GRP). It is considered as the lowest in capital investment. There are a number of advantages for this method. The size of product has no limit in dimension. Design flexibility is possible. Design components are easily changed; molded inserts and reinforcements are possible. The quantity of parts produced needs not to be numerous. This method requires minimum tooling or equipment. Only brushes, roller, buckets, and other minor items are needed. Figure 2.11 shows the process of hand lay-up technique.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

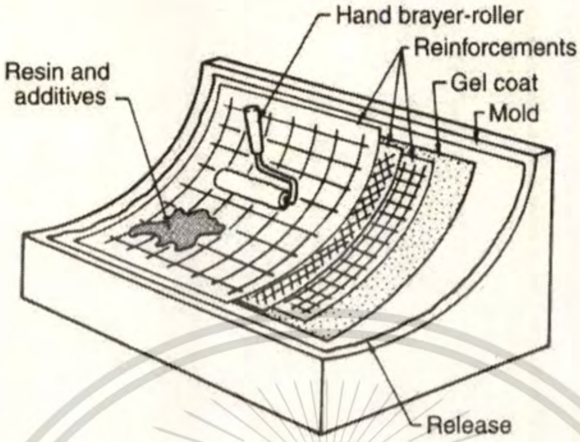


**Figure 2.12** Hand lay-up process [17]

The first layer is a specially formulated gel-coat resin to improve flexibility, blister resistance, surface finish or color, stain resistance, and weatherablity. Gel coats based on neopentyl glycol, trimethylpentanediol glycol, and propylene glycol provide a major advantage as surface treatments for reinforced polyester products. The gel coat forms a protective surface layer through which fibrous reinforcements do not penetrate. A prime cause of deterioration of fibrous reinforced plastics is penetration of water, which takes place when fibers protrude at the surface.

Once the gel coat has partially set, reinforcement is applied. Then, more catalyzed resin is poured, brushed over the reinforcement. This sequence is repeated until the desired thickness is reached. In each layer, the mixture is worked to the mold shape with hand rollers to entrap air, then the reinforced-composite laminate is allowed to harden or cure. External heating is sometimes used to speed polymerization [12].

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 2.6 Advantages and Disadvantages of Composite Materials [20]

Composites offer many advantages over other materials. The many advantages of composites may be summarized as:

- Weight reduction (high strength or stiffness to weight ratio)
- Highly corrosion resistant
- Capable of high continuous operating temperatures
- Tailorable thermal expansion properties, composite materials can be compounded to closely match surrounding structures to minimize thermal stresses.
- High energy absorption or high energy conductivity
- Composites can be formed into many complex shapes during fabrication, even providing finished, styled surfaces in the process.
- Outstanding durability
- Excellent impact habits
- Composites have excellent RAM features (Radar absorbing materials). It is also possible to make special laminates which are radar and sonar transparent.
- Low investment in fabrication equipment

There are some disadvantages of composite materials include:

- Cost of raw materials and fabrication
- Possible weakness of transverse properties
- Weak matrix and low toughness

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

- Environmental degradation of matrix
- Difficulty in attaching
- Difficulty with analysis

## 2.7 Composite Applications

The types of composites and composite design technologies adopted by different sectors of industry can be quite specific to the particular requirements and practice of that particular sector. Since weight reduction in a structural design is critical to the aerospace industry and usually low-volume production is involved, more expensive fibers and resins, long fabrication time, and less automated processing techniques can be tolerated. However, in consumer-oriented industries (automotive and sporting goods, for example), high volume and high production rates are normally required. Automated fabrication, short processing time, and minimization of cost are vital to success of these industries.

Composite materials are used when the total product cost for a given performance is favorable. A need will always exist to develop new cost-effective manufacturing processes closely linked to material design. Although ample evidence can be found of the growing confidence in composite materials and of increasing penetration in many technologies, the application base of composites cannot be broadened without a significant improvement in manufacturing reliability and reproducibility.

Examples for the applications of fiber composites in various industries are given in Table 2.2, illustrating the aggressive penetration of composites into various segments of technology.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Table 2.3** Applications of composite materials [21]

| Industry | Examples |
|---|---|
| Aircraft | Doors, skin on the stabilizer box fin, elevators, rudders, landing gear, fuselage, tail spoiler, flap, body, etc. |
| Aerospace | Space shuttle, space station |
| Automotive | Body frame, chassis components, engine components, drive shaft, exterior body components, leaf springs, etc. |
| Marine | Hulls and masts for recreational boats, submersibles, spars, decks, and bulkheads, etc. |
| Sporting goods | Tennis and racquetball racquets, golf club shafts and heads, bicycle frames, skis, canoes, helmets, fishing poles, tent poles, bobsleds and bobsled track, race cars, pole vaulting poles, etc. |
| Chemical | Pipes, tanks, pressure vessels |
| Construction | Structural and decorative panels, fuel tanks, portable bridges, housings, furniture, etc. |
| Electrical | Printed circuit boards, computer housing, insulators, radomes, battery plates, smart structures |

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 2.8 Literature Reviews

Guoxi Xi , Maixi Lu, and Chen Sun [22] studied depolymerization of post consumer poly(ethylene terephthalate) (PET ) bottles. The glycolysis reaction was carried at 196 °C under nitrogen atmosphere for 5 h. The presence of Zinc acetate as a catalyst. Glycolysis conditions of waste PET were investigated in order to recover its monomer , BHET. It was found that % yield of monomer was increased with increasing ratio of EG to PET , amount of catalyst and reaction time until reaction reached equilibrium. They also found that glycolyzed products were separated into monomer and oligomers. IR, $^1$H NMR, C$^{13}$ NMR and DTA spectra verified the structure of BHET with high purity. Proportion and melting point of oligomers measured by DTA were decreased with increase of degree of depolymerization.

D.J. Sun , O.O. Park , and K.H.Yoon [23] tried to compare properties of unsaturated polyester prepared by glycolysis of PET with propylene glycol (PG) and diethylene glycol (DEG) and their mixtures. Cure behavior and tensile properties of cured resin based on glycolyzed PET were investigated. Glycolysis reaction was obtained by reacting PET with DEG/PG mixtures and zinc acetate as a catalyst. The mixtures were heated for 3 h at 175°C and then held for 5 h at 225°C under nitrogen atmosphere. Then, the glycolyzed products were polycondensed with maleic anhydride in order to synthesize unsaturated polyester at 150°C for 24 h. After that, the unsaturated polyester resins were dissolved in styrene monomer at 60 °C for 30 min. Styrene monomer was added in order to cure the resin and benzoyl peroxide (BPO) was added as an initiator. The results were shown that the extent of depolymerization decreased with increasing amount of DEG in the glycol mixtures and gelation time also delayed. The tensile toughness of cured resin was greatly enhanced by incorporationg DEG units.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

George P. Karayannidis, Dimitris S. Achilias , Irini D. Sideridou,and Dimitris N. Bikiaris [24] studied glycolysis of recycled PET forproduction of alkyd resins used as coatings. PET was taken from common soft-drink bottles and diethylene glycol (DEG) was used for depolymerization at several initial molar ratios. The glycolysis reaction was carried for 4 h at 210 °C in argon atmosphere. Furthermore, the glycolyzed PET was mixed with propylene glycol (PPG) to form unsaturated polyester resins. These were mixed with styrene and cured using the benzoyl peroxide/amine initiator at ambient temperature. They found that the oligoester diols produced from the reaction of DEG with PET consisted mainly of three oilgomers. An increase in the molar ratio of DEG, PET led to better depolymerization and to an increase in the amount of the oilgomers with lower molecular weight. They also found that the replacement of DEG with the glycolyzed PET products gave higher curing rates completed in shorter time periods.

Ph. Radenkov, M. Radenkov, and G. Grancharov, K. Troev [25] investigated the possibility for direct application of PET glycolyzed products in glass-fiber-reinforced plastics (GRP) manufacturing. GRP laminates were made using the cold process moulding technology. They were reinforced with four layers of glass roving textile. The polymer matrix was maleic unsaturated orthophthalic polyester resin which was polymerized in the presence of CHPO as a catalyst and $Co(Oct)_2$ as a promoter. The molding conditions were constant pressure at ambient temperature. BHET was dissolved in the resin at 80°C. The modified GRP samples were produced by addition of different amounts of PET glycolyzed products. After that the proper amount of TDI was added. The last step was the impregnation of the reinforcing glass roving textile placed in the shaping mold cavity with the resin. The cured GRP laminates were post-heated for 24 h at 100 °C. Aiming to achieve maximal degree of resin polymerization process and yielding Barcol hardness of 45-50. They found that moderate amounts of products of PET glycolysis acted as a modifier that improved mechanical properties of the composites. The method also allows effective utilization of even greater amounts of the

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

waste products as resource-saving additives without considerable damage of mechanical properties of the end products.

J.Y. Chen, C.F. Ou, Y.C. Hu, and C.C. Lin [26] studied the process of depolymerization of PET resin by EG glycolysis under pressure and without adding any catalyst. In glycolysis of PET resin they are investigating various temperature, reaction times, ratios of EG/PET and pressure. The kinetics of this pressured depolymerization of PET resin is investigated. It was found that the depolymerization of PET is dependent on pressure, temperature, and EG/PET ratio. The depolymerization rate is very fast and proportional to the square of EG concentration at a constant temperature, pressure, and PET concentration. This implies that EG acts as both reactant and catalyst, Glycolyzed product under pressure consist of the PET monomer, BHET, and oligomers, mostly dimer and trimer. An equilibrium between BHET and oligomer is attained quickly soon after the depolymerization step is completed in the case of high EG/PET ratio. In the case of low EG/PET ratio, the depolymerized products consist of higher molecular weight of oligomers rather than monomer, dimmer and trimer. This indicates that a sufficient amount of EG is needed to depolymerize PET resin to obtain a predominant amount of monomer BHET in the glycolyzed products. This also implies that the equilibrium reaction shifts to the rich BHET content side slowly over a very long period of reaction time.

Utpal R. Vaidya and Vikas M. Nadkarni [27] studied the result of synthesis, resin characterization and prepared a new class of unsaturated polyesters resin to use in the fiber-reinforced plastics (FRP). The processing characteristics like viscosity, gelation time, exotherm temperature of all resin were investigated. Commercially available general purpose resin (GP), prepared from maleic anhydride, phthalic anhydride, and propylene glycol was used as the reference resin. PET waste was polymerized by using different amount of propylene glycol. The reaction carried out at about 200° C for 8 h in a nitrogen atmosphere. These glycolyzed products were reacted with maleic anhydride and mixed with styrene monomer to get unsaturated polyester resin. Moreover, at a given

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

styrene amount, the viscosities of the polyesters containing higher aliphatic PG segment content. In general, the waste-based polyester resin and the reference GP resin had comparable chemical composition in terms of the aliphatic and aromatic blocks these two samples exhibited a similar viscosity behavior. For the gel times and exotherm temperature of the resins depended on the another of the initiator and accelerator. Processing characteristics of PET-based resin were comparable with that of GP resins. Hence, it could successfully replace the conventional GP resin in FRP as a new class of unsaturated polyesters resin.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# CHAPTER 3

# THE EXPERIMENTAL DETAILS

## 3.1 Materials

1. Desilvered PET X-ray films : HERAN S. SEVEE CO., LTD
2. Virgin PET : CHAROEN WATTANA FIBER AND CHEMICALS CO., LTD
3. Ethylene glycol (EG): CARLO ERBA REAGENTI, Analytical grade
4. Propylene glycol (PG): CARLO ERBA REAGENTI, Analytical grade
5. Diethylene glycol (DEG): CARLO ERBA REAGENTI, Analytical grade
6. Zinc acetate: CARLO ERBA REAGENTI, Analytical grade
7. Potassium hydrogen phthalate (KHP): CARLO ERBA REAGENTI, Analytical grade
8. Phenolphthalein
9. Potassium hydroxide (KOH): FLUKA, Analytical grade
10. Maleic anhydride: FLUKA, Analytical grade
11. Phthalic anhydride: FLUKA, Analytical grade
12. Ethanol: CARLO ERBA REAGENTI, Analytical grade
13. Acetone: CARLO ERBA REAGENTI, Commercial grade
14. Pyridine: CARLO ERBA REAGENTI, Analytical grade
15. Hydroquinone: FLUKA, Analytical grade
16. Styrene monomer: LADKRABANG RESIN, Commercial grade
17. Glass fiber: CHAROEN WATTANA FIBER AND CHEMICALS CO., LTD
18. Dimethyl aniline (DMA): CHAROEN WATTANA FIBER AND CHEMICALS CO., LTD
19. Benzoyl peroxide (BPO): CHAROEN WATTANA FIBER AND CHEMICALS CO., LTD
20. Grease

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 3.2 Equipments and Instruments

1. Three-necked flask
2. Round-bottle flask
3. Buret
4. Pipet
5. Micropipet
6. Thermometer
7. Glasswear
8. Oil bath
9. Reflux condenser
10. Mechanical stirrer with appropriate bearing
11. Nitrogen gas tank
12. Hot plate
13. Thermostat
14. Silicone mold
15. Metal mold
16. Metal plate
17. Thick glass
18. Ultrasonic bath
19. Universal testing machine, LLOYD INSTRUMENT, model LR 5K
20. Brookfield viscometer, THE BROOKFIELD ENGINEERING LABS. INC
21. Dynamic Mechanical Analyzer (DMA), GABO, model EPLEXOR QC 25
22. Hardness tester, INTRO ENTERPRISE COMPANY LIMITED

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 3.3 Experimental

### Part 1 Preparation of Glycolyzed Product from Depolymerization Reaction of PET

### 3.3.1 Depolymerization of PET

In this experiment, PET flakes were prepared from waste desilvered PET X-ray films. The desilvered PET X-ray films were washed, dried and cut with a size of 2x10 mm as starting material.

1. PET flakes were washed and dried again.
2. Then they were added into the reactor together with glycols (EG, PG and DEG) in every formula, the molar ratio of PET flakes to glycols (EG, PG and DEG) was the same as 1:5.04. The compositions of PET flakes to glycols were shown in Table 3.1.

**Table 3.1** The compositions of PET flakes to glycols

| Formula | PET flakes: Glycols (mol) | EG:PG:DEG (mol) | PET flakes (g) | EG (g) | PG (g) | DEG (g) |
|---|---|---|---|---|---|---|
| 1 | 1:5.04 | 1:1:0 | 192 | 156.24 | 191.52 | 0 |
| 2 | 1:5.04 | 1:1:0.5 | 192 | 124.99 | 153.22 | 106.85 |

3. Zinc acetate, 0.5wt% based on weight of PET, was added as transesterification catalyst.
4. A three-neck flask 1000 ml glass reactor equipped with thermostat, reflux condenser, and mechanical stirrer, as shown in Figure 3.1, was used for all glycolysis experiments.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

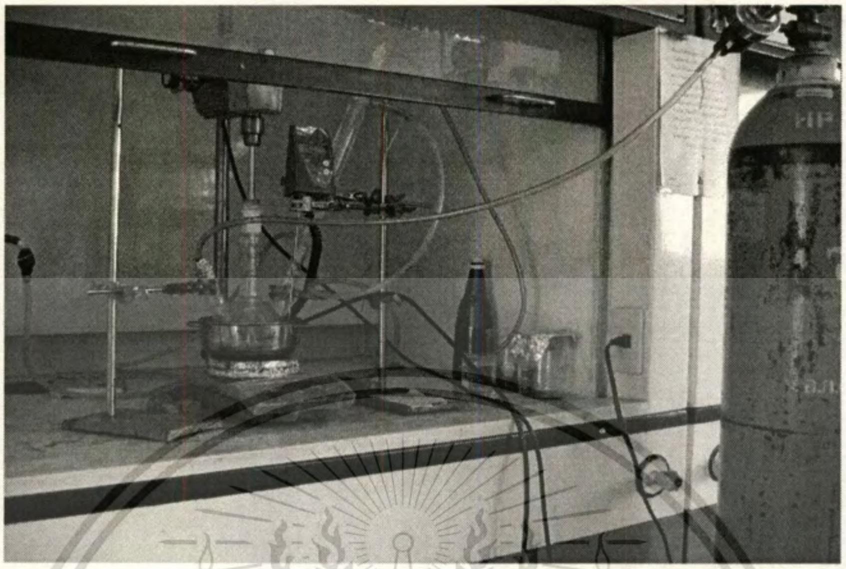


**Figure 3.1** Set-up of reactor for the preparation of glycolyzed product from depolymerization reaction of PET

5. The experiments were allowed to proceed at 190-200°C for 8-11 h under nitrogen atmosphere. The reactor was then allowed to cool at room temperature.
6. The above operations were performed but virgin PET was used instead of desilvered PET X-ray films.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

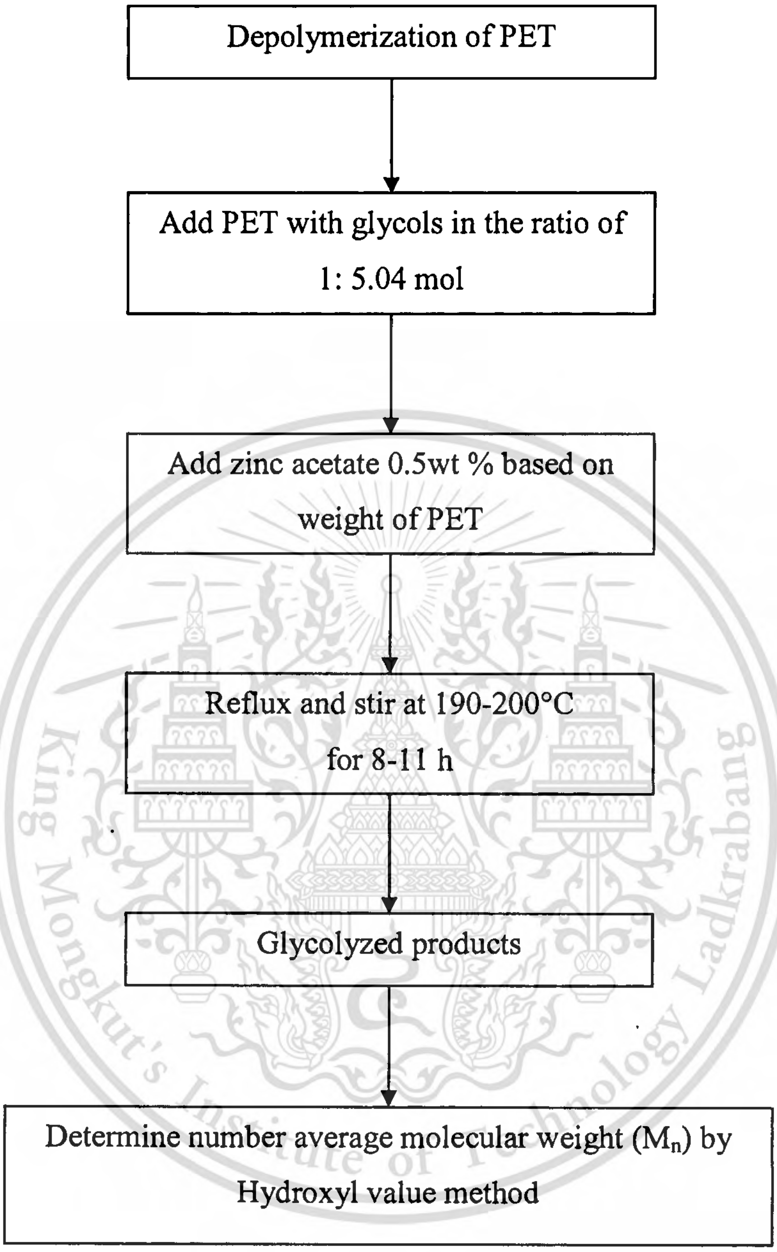


**Figure 3.2** Preparation step of glycolyzed product from depolymerization reaction of PET

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 3.3.2 Determination of Hydroxyl value of glycolyzed product according to ASTM 2849-69 [29]

The content of Hydroxyl end-groups (Hydroxyl number, HN) of the glycolyzed product was determined by titration of glycolyzed product with 0.5N KOH solution. The values obtained provide a means of the number average molecular weight ($M_n$).

1. 1 g of the glycolyzed product was weighed and transferred into a round-bottom flask.
2. The esterification reagent was prepared as follows: Weigh 15.71 g of phthalic anhydride into a beaker. Add 100 ml of pyridine and stir in a beaker with stirring rod until solution is complete.
3. 25 ml of the phthalic anhydride-pyridine reagent was added into a round-bottom flask to mix with the glycolyzed product and shook the flask vigorously until solution was completely homogeneous.
4. A round-bottom flask was equipped with a vertical reflux condenser and heated at 115°C for 1 h. It was then allowed to cool to room temperature.
5. After cooling, the vertical reflux condenser was rinsed with 50 ml of pyridine.
6. The resultant system was subjected to titration with 0.5 N KOH in the presence of several drops of phenolphthalein solution to determine an end point when a pale red state of the system (by the phenolphthalein indicator) was kept for 15 sec.
7. The above operations were performed without adding the glycolyzed product as a blank test.
8. The hydroxyl value of the glycolyzed product was calculated according to the following formula:

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

$$\boxed{\text{Hydroxyl value} = \frac{\left[(\text{B-A})\text{N}\times 56.1\right]}{\text{W}} \quad \text{mgKOH/g}}$$

When A = Volume of KOH consumed in the sample test (ml)
B = Volume of KOH consumed in the blank test (ml)
N = Concentration of KOH (N)
W = Weight of sample (g)

9. The number average molecular weight ($M_n$) of glycolyzed product was calculated according to the following formula:

$$\boxed{M_n = \frac{112200}{\text{OH value}} \quad \text{g/mol}}$$

**Part 2 Preparation of Unsaturated Polyester Resins**

### 3.3.3 Preparation of unsaturated polyesters

1. The unsaturated polyesters were prepared by reaction of the glycolyzed product and maleic anhydride. The compositions of glycolyzed product to maleic anhydride were shown in Table 3.2.

**Table 3.2** The compositions of glycolyzed product to maleic anhydride.

| Formula | PET flakes: Glycols (mol) | EG:PG:DEG (mol) | Glycolyzed product (g) | Maleic anhydride (g) |
|---|---|---|---|---|
| 1 | 1:5.04 | 1:1:0 | 100 | 83.01 |
| 2 | 1:5.04 | 1:1:0.5 | 100 | 77.65 |

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

2. The polyesterification reaction was carried out in a three-necked flask 500 ml glass reactor having an oil bath, thermostat, reflux condenser, and mechanical stirrer as same as Part 1. The reactants were heated at 150°C under nitrogen atmosphere and were then held for 6-7 h to complete the reaction (sampling was done in every 1 h to determine acid value).

### 3.3.4 Determination of acid value of unsaturated polyesters

1. Sampling the same amount of the sample into an Erlenmeyer flask in every hour.
2. The mixed liquid, 20 ml of acetone and 0.5 ml of phenolphthalein was added to dissolve the sample.
3. The sample solution was titrated with 0.1 N KOH solution.
4. The above operations were performed without adding the sample as a blank test.
5. The acid value was calculated according to the following formula:

$$\boxed{\text{Acid value} = \frac{[(A-B)\,N \times 56.1]}{W}\ \text{mgKOH/g}}$$

When A = Volume of KOH consumed in the sample test (ml)
B = Volume of KOH consumed in the blank test (ml)
N = Concentration of KOH (N)
W = Weight of sample (g)

6. The reaction was stopped when acid value was in the assign range shown in Table 3.3 to make unsaturated polyesters had the same properties.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Table 3.3** Acid value of unsaturated polyesters

| Formula | EG:PG:DEG (mol) | Acid value (mgKOH/g) |
|---|---|---|
| 1 | 1:1:0 | 70±5 |
| 2 | 1:1:0.5 | 70±5 |

### 3.3.5 Preparation of unsaturated polyester resins

1. The unsaturated polyesters were dissolved in styrene monomer at 60°C for 25 min. The amount of styrene was 35wt% of unsaturated polyesters. In order to prevent premature curing the unsaturated polyester resins, hydroquinone (0.2wt% based on weight of unsaturated polyesters) was added as inhibitor.
2. After reaching 30 min, the heated resins were allowed to cool to room temperature.
3. Then the resins were measured viscosity by Brookfield viscometer (used spin no.3 and 12 rpm of its velocity).

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

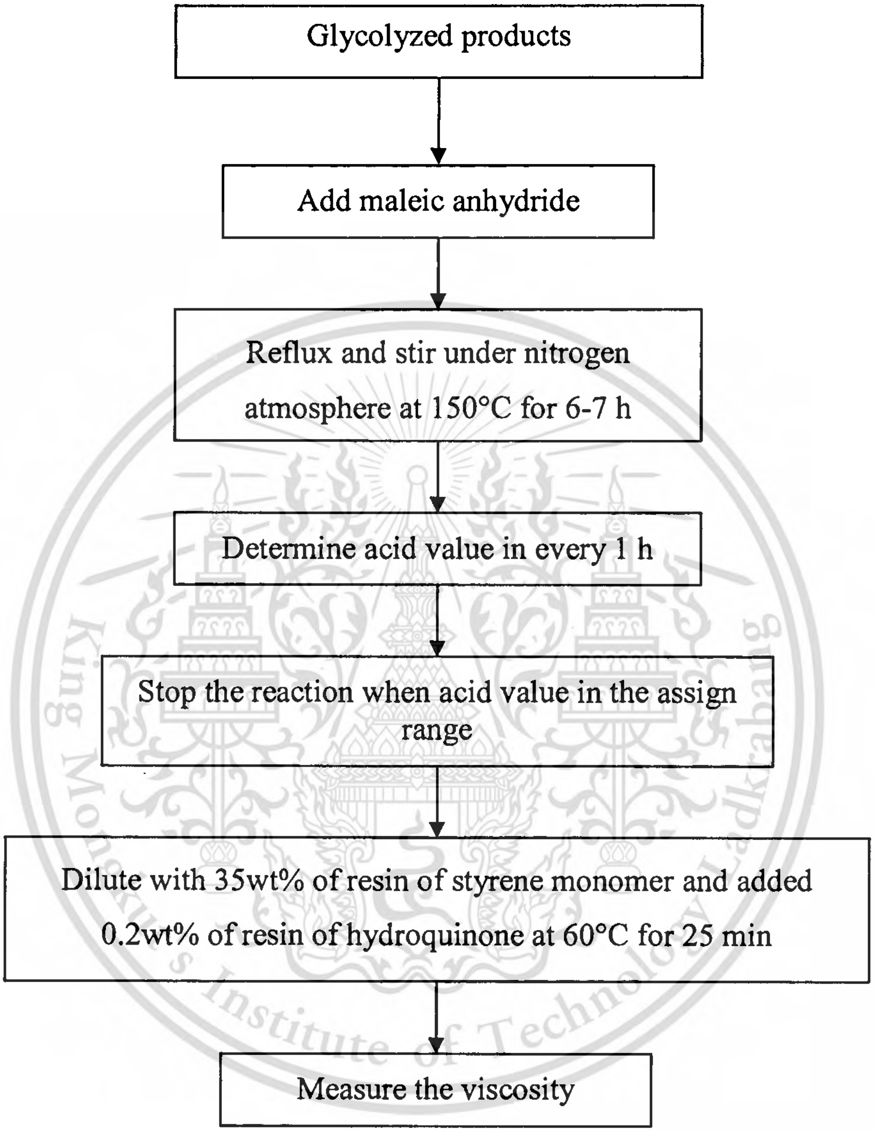


**Figure 3.3** Preparation step of unsaturated polyester resins

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Part 3 Curing reaction of Unsaturated Polyester Resins**

1. In a 100 ml beaker, benzoyl peroxide (56 g/1 kg of resin) was added into the resins which were already dissolved in styrene.
2. Air bubbles were removed by using ultrasonic bath for 25 min.
3. Then dimethyl aniline (DMA) was added (3 ml/1 kg of resin) as accelerator in order to promote the decomposition of peroxides and generate free radicals which start the propagation reaction resulting in the gelation and ultimate cure of resins.
4. When resins were poured into the clean mold (transparency), the mold was closed slowly by another one in order to prevent air bubbles in the product.
5. After that the mold was pressed with metal plate or thick glass at ambient temperature until resins completely cured (measure the curing of resins by ASTM D1650 method).
6. The curing time of resin was recorded in every formula.

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

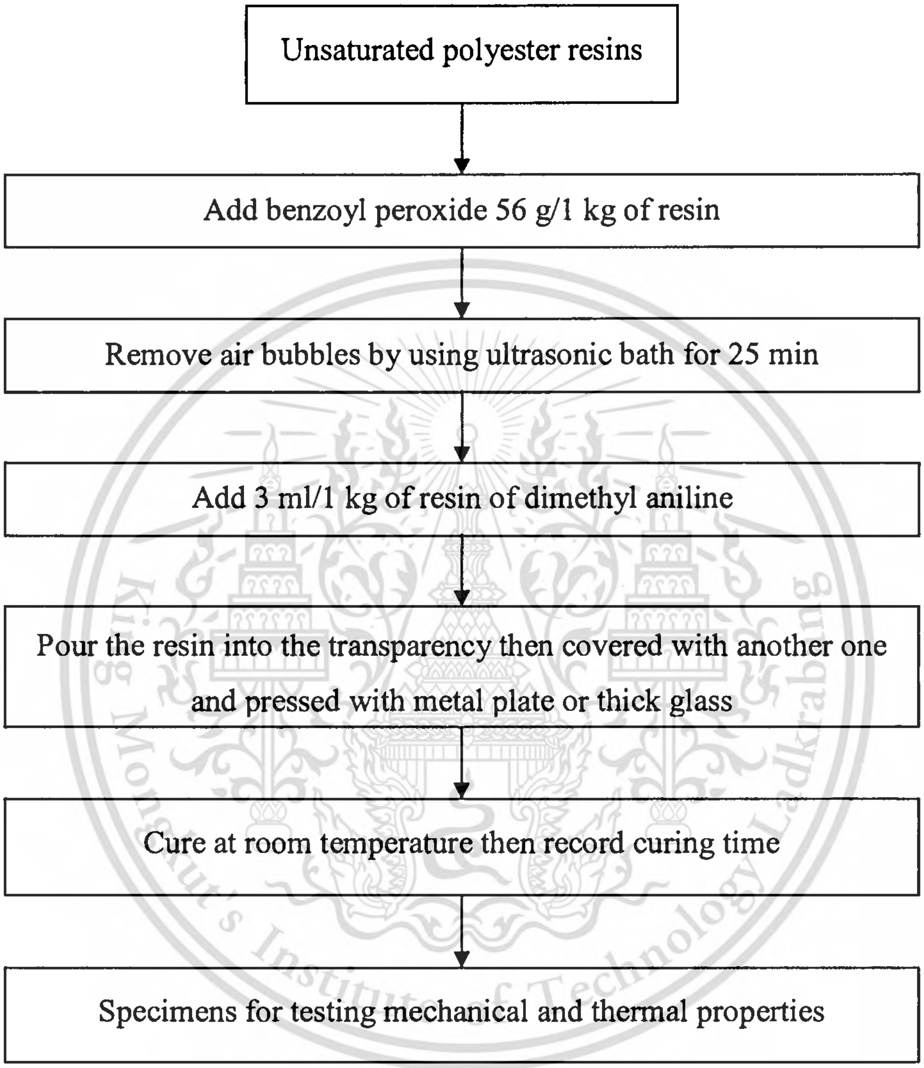


**Figure 3.4** Curing step of unsaturated polyester resins

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Part 4 Drying Time Testing** [30]

According to ASTM D1650, two steps for drying time measurement can be used:

1. Set-to-Touch Time

Lightly touch the test film with the tip of the finger and immediately place the finger tip against a piece of clean clear glass. Observe if any of the varnish is transferred to the glass. However the pressure of the finger shall not be greater than that required to transfer a spot of the varnish from 3.2 to 4.8 mm in cross section. The film shall be considered set-to-touch when it still shows a tacky condition but none of it adheres to the finger.

2. Dry-Hard-Time

With one end of the thumb resting on the test film and the forefinger supporting the test panels exert a maximum downward pressure (without twisting) of the thumb on the film. Lightly polish the contacted area with a soft cloth. The film shall be considered dry-hard when any mark left by the thumb is completely removed by the polishing operation.

In this work, Set-to-Touch Time method was used to test for drying time.

**Part 5 Mechanical Property Testing**

**1. Tensile strength, tensile modulus, %elongation at break and work done** [31]

Tensile strength is a measuring of the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point.

Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. The data is often used to specify a material, to design parts to withstand application force and as a quality control check of materials.

% Elongation at break is the increase in the length produced by stretching a test specimen to the breaking point or the strain at failure or percent change in length at failure.

Work done is the area under the load deformation curve which depends on fracture of materials. The less area under the curve, the lower energy needed to break the material, the more brittle the material.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

Since the physical properties of many materials (especially thermoplastics) can vary depending on ambient temperature, it is sometimes appropriate to test materials at temperatures that simulate the intended end use environment.

ASTM specifications for tensile strength, tensile modulus, % elongation at break and work done testing of reinforced and unreinforced plastics is ASTM D638;

1. Specimens were prepared as a dumb-bell shape according to ASTM D638 (Gauge length = 35 mm, Cross-head speed = 1mm/min, Load cell 30 kN)
2. Specimens were placed in the grips of the Instron Universal Tester and pulled until failure.
3. Tensile strength, Tensile modulus and % Elongation at break of each sample were determined.

**2. Hardness** [32]

Hardness is one property of materials to resist plastic deformation, usually by penetration. However, the term hardness may also refer to resistance to bending, scratching, abrasion or cutting.

Durometer Hardness is used to determine the relative hardness of materials, usually plastic or rubber. The test measures the penetration of a specified indenter into the material under specified conditions of force and time. The hardness value is often used to identify or specify a particular hardness of materials or as a quality control measure on lots of material.

According to ASTM 2240, specimens are tested by Shore D hardness scale at room temperature with the thickness at least 6 mm.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 3. Flexural strength and flexural modulus [33]

The flexural strength of a material is defined as its ability to resist deformation under load.

Flexural modulus was the ratio of stress to strain with in the elastic limit and similar to the tensile modulus. This property was used to indicate the bending stiffness property of a material.

According to ASTM 790,

1. Specimen size is 2.5x25x60 mm
2. Span length is 40 mm
3. Cross-head speed is 10 mm/min
4. Load cell is 5 kN

Flexural strength and Flexural modulus values were determined by using Universal testing machine with Three-Point Loading System.

### 4. Impact strength [34]

Impact strength is a measurement of the energy required to cause a material to fracture when struck by a sudden blow (high rate of deformation). Materials that are sensitive to the stress concentrations at the notch would perform poorly in the notched izod test.

Notched Izod Impact is a single point test that measures a materials resistance to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Izod specimens are notched to prevent deformation of the specimen upon impact. This test can be used as a quick and easy quality control check to determine if a material meets specific impact properties or to compare materials for general toughness.

The standard specimen for ASTM D256 is 3.2 x 12.7 x 60 mm. The depth under the notch of the specimen is 2.54 mm. Then, specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## **<u>Part 6</u> Thermal Property Testing**

### **Dynamic Mechanical Thermal Analysis (DMTA)**

DMTA studies the molecular motions and viscoelastic nature of a material by applying a stress to the sample and monitoring its response. Two parameters can be determined: the modulus (shear, G, or bending, E) and the loss (tan δ). The modulus contains real and imaginary contributions. The real part, G' (E') is a measure of the elastic response of the material, while the imaginary part, G" (E") reflects the viscous response. Glass transitions temperature ($T_g$), manifested as a peak in tan δ, can be determined by this method.

The specimen geometry is 2x10x40 mm

Condition for testing:

Mode : Tension
Temperature : 0-200 °C
Static strain : 0.5%
Dynamic strain : 0.05%
Frequency : 1 Hz
Rate : 2 °C/min

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## Part 7 Fabrication of Glass Fiber-Reinforced Polyester Composites by Hand lay-up Technique

1. Mat of glass fiber reinforcement (Chopped Strand Mat or CSM) was prepared by cutting similar size as mold.
2. Unsaturated polyester resins (80 g/1 piece of CSM) and benzoyl peroxide (56 g/1 kg resin) were mixed together in a beaker. Ultrasonic bath was used to remove air bubbles for 25 min. Dimethyl aniline was then added (3 ml/1 kg resin) into the resins.
3. Mat of glass fiber reinforcement (CSM) was placed in the mold. Then the resins were poured on the glass fiber reinforcement (CSM).
4. Mat of glass fiber reinforcement (CSM) was "wetted out" with resins, and then rolled out to remove air bubbles.
5. After that, resins were allowed to cure and solidify at room temperature the composite was then released out from mold.
6. The product was cut by a cutter with size as 2.5x25x60 mm, 8-10 pieces, for flexural testing

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

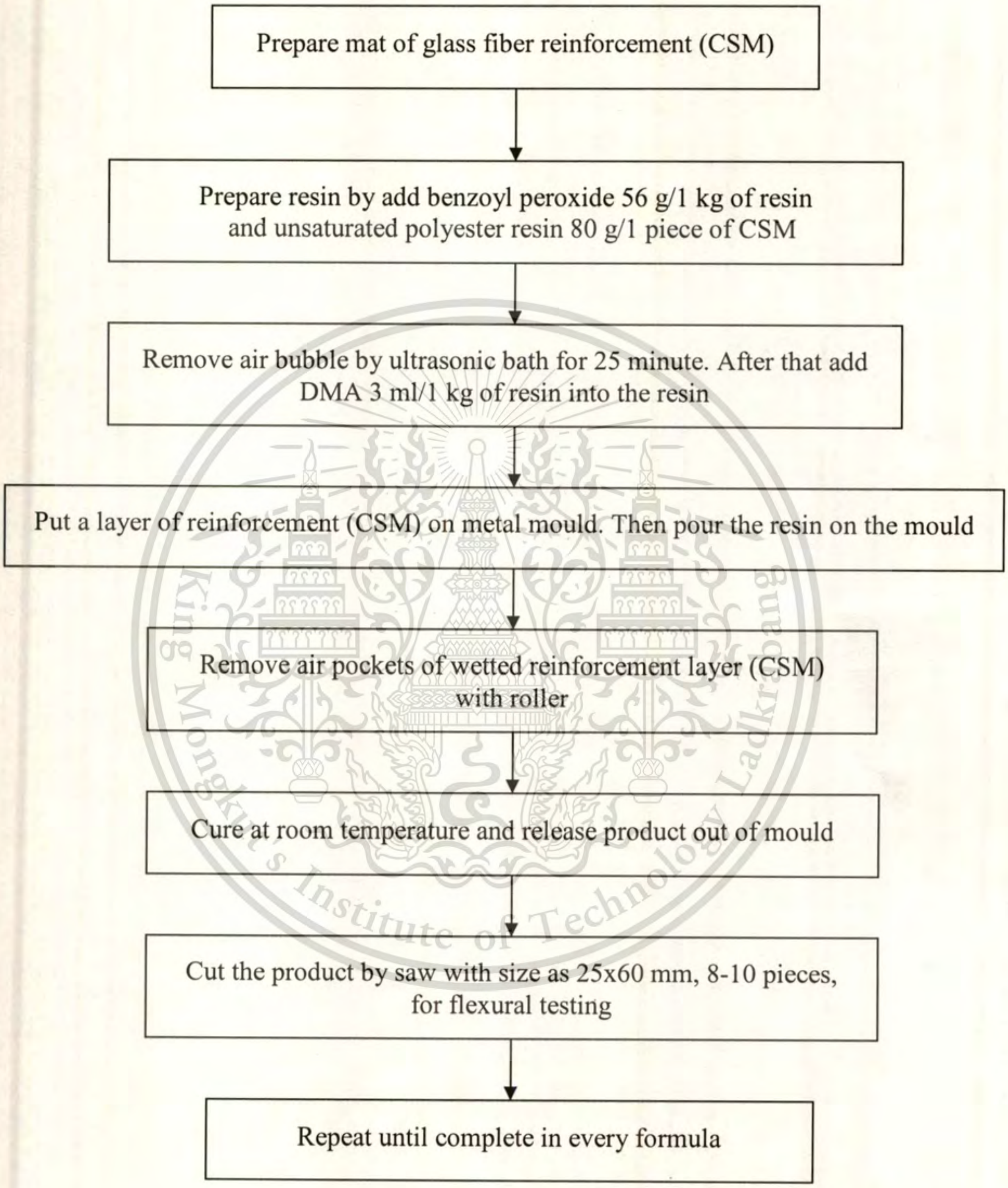


**Figure 3.5** Fabrication step of glass fiber-reinforced polyester composites

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 Preparation of Glycolyzed Product from Depolymerization Reaction of PET

Poly(ethylene terephthalate) (PET) was depolymerized with ethylene glycol (EG), propylene glycol (PG) and diethylene glycol (DEG). The molar ratio of PET to glycols was 1:5.04 while the ratio of EG:PG:DEG in Formula 1 was 1:1:0 and in Formula 2 was 1:1:0.5, as shown in Table 3.1. Zinc acetate was used as a catalyst at 190°C -200°C for 8-11 h under nitrogen atmosphere. After the reaction, glycolyzed products which looked like paste was obtained as shown in Figures 4.1 and 4.2. Glycolyzed product that synthesized from virgin PET was a paste or viscous liquid in white color while glycolyzed product from PET X-ray films was a paste in blue color because the color component in the films might not be removed.

**Figure 4.1** The glycolyzed product synthesized from PET X-ray films

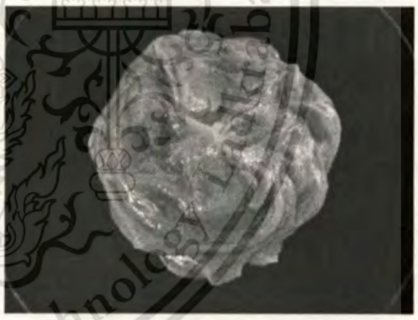


**Figure 4.2** The glycolyzed product synthesized from virgin PET

After that, the number average molecular weight ($M_n$) of the glycolyzed products was determined by using hydroxyl value determination method. In fact, gel permeation chromatography (GPC) could be used to determine $M_n$ value more accurately than hydroxyl value determination method. However, determination of hydroxyl value is an easy and cheaper method that can yield $M_n$ value close to the value from GPC method. The OH values, $M_n$ of resins and glycolysis time were shown in Table 4.1.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Table 4.1** Glycolysis time, hydroxyl value (OH value) and number average molecular weight ($M_n$) of glycolyzed product in each formula from PET X-ray films and virgin PET

| Starting Material | Formula | EG:PG:DEG (mol) | Glycolysis time (hr) | OH value (mgKOH/g) | $M_n$ (g/mol) |
|---|---|---|---|---|---|
| PET X-ray films | F1 | 1:1:0 | 11 | 355.45 | 316 |
| | F2 | 1:1:0.5 | 8 | 359.84 | 312 |
| Virgin PET | V1 | 1:1:0 | 11 | 364.37 | 308 |
| | V2 | 1:1:0.5 | 8 | 390.74 | 287 |

**Note**: The calculation of $M_n$ of glycolyzed product from OH value was shown in appendix A.

In this experiment, the hydroxyl values were controlled in the range of 350-400 mgKOH/g to eliminate molecular weight variation in the products. The effects of DEG and different sources of PET on properties of resins were mainly focused in this research.

## 4.2 Preparation of Unsaturated Polyesters

Unsaturated polyesters were prepared from reaction of glycolyzed products which have hydroxyl as a functional group and maleic anhydride which has carboxyl as a functional group. The molar ratio of glycolyzed product to maleic anhydride or Hydroxyl to Carboxyl was 1.1:1. The composition of each formula was shown in Table 3.2.

Because maleic anhydride provides double bonds to unsaturated polyesters, the acid value shows the quantity of maleic anhydride which does not react with the resins. Thus, resins from each formula need to control acid value being in the same range of 65-75 in order to eliminate amount of double bond variation in the unsaturated polyesters.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 4.3 Effects of Diethylene Glycol (DEG) and Different Sources of PET on Viscosity and Curing Time of Unsaturated Polyester Resins

### 4.3.1 Viscosity of unsaturated polyester resins by Brookfield viscometer

Viscosity is an important parameter for studying fluid flow, which depends on molecular weight and molecular structure of polymers. When polymer chains are subjected to force, they will align and disentangle. The long chains tend to resist alignment and disentanglement. So, the viscosity will be increased.

In this experiment, average viscosity of resins synthesized from both PET X-ray films and virgin PET were shown in Tables 4.2.

**Table 4.2** Viscosity of resins from PET X-ray films and virgin PET

| Starting Material | Formula | EG:PG:DEG | Average viscosity (cP) |
|---|---|---|---|
| PET X-ray films | F1 | 1:1:0 | 767 |
| | F2 | 1:1:0.5 | 867 |
| Virgin PET | V1 | 1:1:0 | 900 |
| | V2 | 1:1:0.5 | 1075 |

If the effect of DEG was studied, it was found that the average viscosity of both types of resins synthesized from PET X-ray films and virgin PET in Formula 2 were higher than those of Formula 1. It should be pointed out that DEG has higher molecular weight and longer linear chain than EG and PG, as shown in Figure 4.3, so it resists to align and disentanglement. This was the reason why the average viscosity values in Formula 2 were higher than those of Formula 1.

For the effect of starting material, it was observed that the average viscosity of resins from virgin PET (V1 and V2) were higher than those of resins from PET X-ray films (F1 and F2).

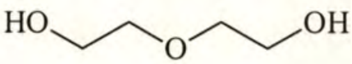


**Figure 4.3** Molecular structure of diethylene glycol (DEG)

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

### 4.3.2 Curing time

From the experiment, curing time of both types of resins in each formula were shown in Tables 4.3.

**Table 4.3** Curing time of resins synthesized from PET X-ray films and virgin PET

| Starting Material | Formula | EG:PG:DEG | Curing time (min) |
|---|---|---|---|
| PET X-ray films | F1 | 1:1:0 | ~ 45 |
| | F2 | 1:1:0.5 | ~ 60 |
| Virgin PET | V1 | 1:1:0 | ~ 45 |
| | V2 | 1:1:0.5 | ~ 60 |

The curing time in Formula 2 of both resins synthesized from PET X-ray films and virgin PET were higher than those of Formula 1. Due to the long linear ether linkage structure of DEG, it would increase distance between double bonds or crosslink points in polymer chains. Then the chance for styrene monomers to react with double bonds in resins would be decreased. Moreover DEG would make the resins more flexible so the resins in Formula 2 used time for curing longer than those in Formula 1.

However, in this experiment "Set-to-Touch Time" method was used to test the curing of resins according to ASTM D1650. The curing time of resins was controlled in 30-60 min because it was the period that generally used in many industries.

However, the curing time of resins from PET X-ray films and virgin PET were not different.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 4.4 Effects of Diethylene Glycol (DEG) and Different Sources of PET on Mechanical Properties of Unsaturated Polyester Resins

### 4.4.1 Tensile strength, tensile modulus and % elongation at break

Tensile strength, tensile modulus, and % elongation at break are important properties of materials. Tensile strength is a measurement of the maximum force per unit area of the specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile modulus is the ratio of stress to elastic strain in tension. A high tensile modulus means that the material is rigid. % Elongation at break is the increase in the length produced by stretching a test specimen to the breaking point or the strain at failure or percent change in length at failure.

From this experiment, % elongation at break of resins from both PET X-ray films and virgin PET would increase when quantity of DEG was increased as shown in Figure 4.4. Due to the structure of DEG which has ether linkages, resins with high amount of DEG possessed high flexibility. Moreover, it would increase distance between crosslink at double bond points so crosslink density was decreased. If structure has high crosslink density which called "Tight Network", the motion of molecular chains would be limited and the chains could not dissipate energies when it was subjected with force causing stiff but brittle materials as shown in Figure 4.6. In contrast, if the structure has low crosslink density, three dimensional networks would move easily. Therefore, elongation at break of the resins was increased.

For tensile strength, resins from PET X-ray films and virgin PET in Formula 2 gave higher tensile strength than resins from Formula 1, as shown in Figure 4.5. It was pointed out that resins in Formula 2 had higher % crosslinking than the other. Due to long linear ether linkage structure of DEG which made the resins more flexible and had lower crosslink density so DEG could flow further to form crosslinking although the resins became stiff after adding initiator (BPO) and accelerator (DMA). It is noted that in this project, the samples were not taken to test for mechanical properties immediately after the resins became rigid.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

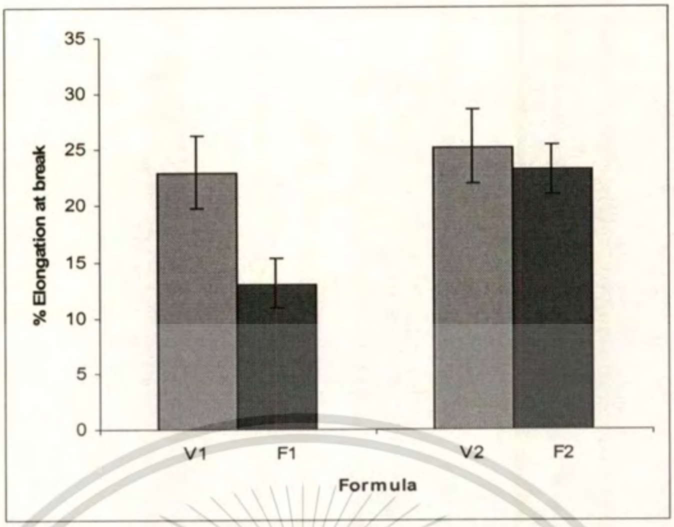


**Figure 4.4** % Elongation at break of resins synthesized from PET X-ray films and virgin PET

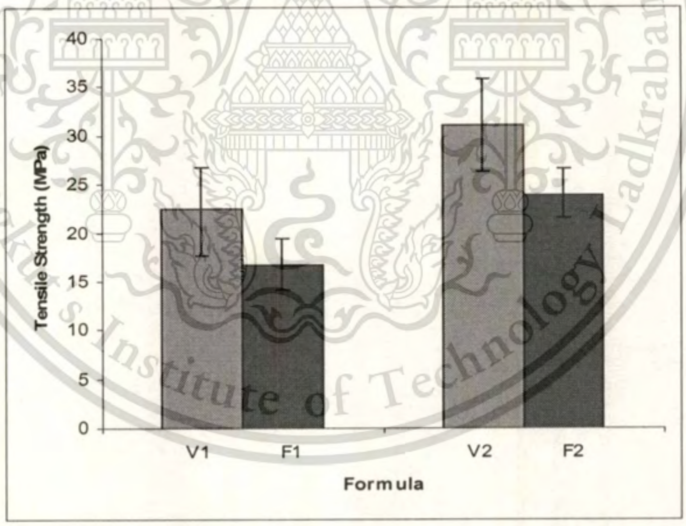


**Figure 4.5** Tensile strength of resins synthesized from PET X-ray films and virgin PET

For the effects of starting materials, it was found that resins derived from PET X-ray films gave % elongation and tensile strength lower than those of virgin PET. From these results, it meant that resins from PET X-ray films were stiffer and more brittle.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

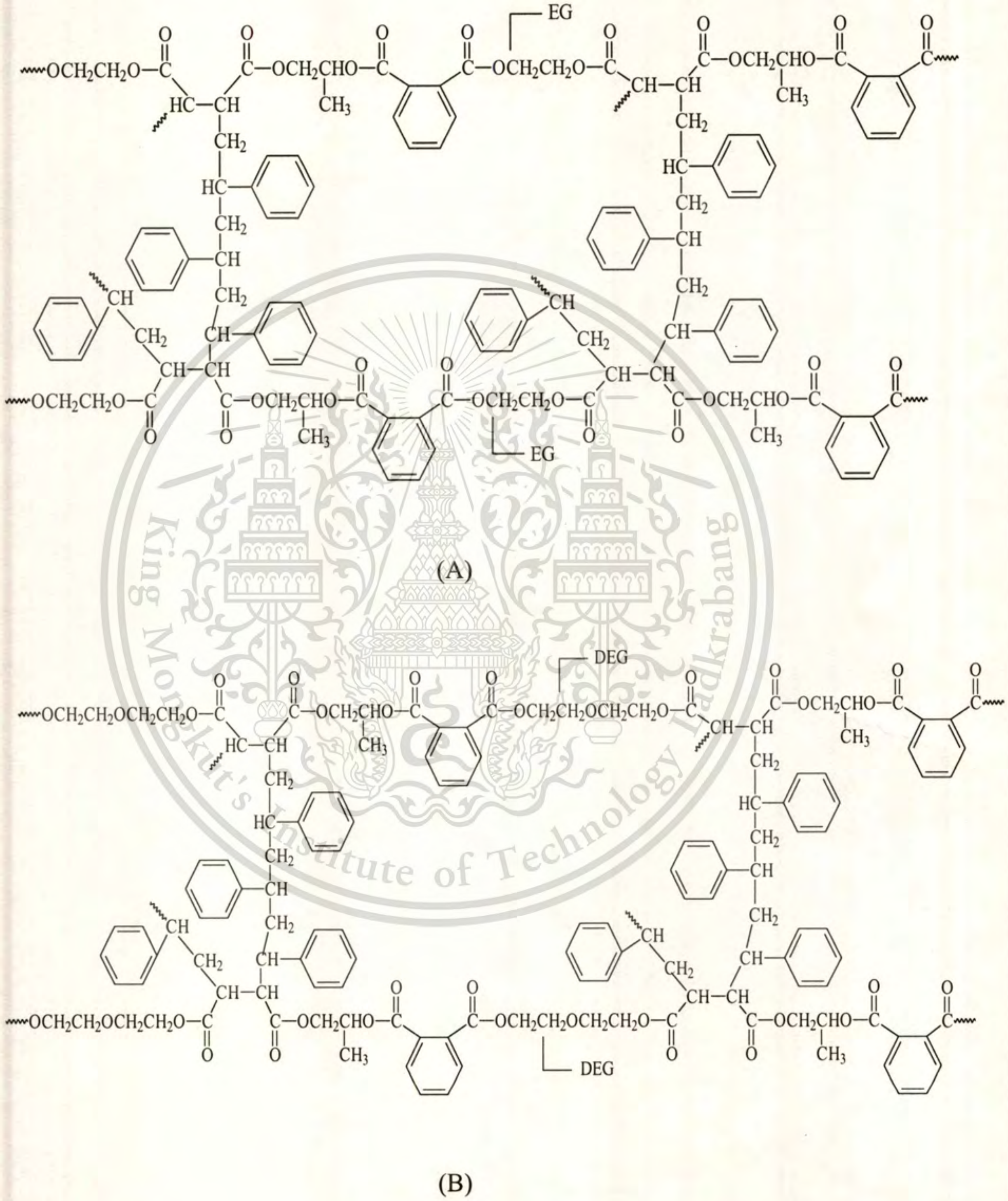


Figure 4.6 Crosslink structures of (A) resin which has no DEG (B) resin which has DEG

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

For tensile modulus, due to the effect of DEG, it was observed that tensile modulus of resins derived from PET X-ray films and virgin PET in Formula 2 were lower than those of the resins in Formula 1, as shown in Figure 4.7. The reason was similar to % elongation and tensile strength, because DEG would decrease crosslink density, so resins in Formula 2 would have high flexibility but low rigidity. In contrast, resins in Formula 1 that had no DEG showed high tensile modulus because they had "tight network" structure then they were stiffer than resins in Formula 2.

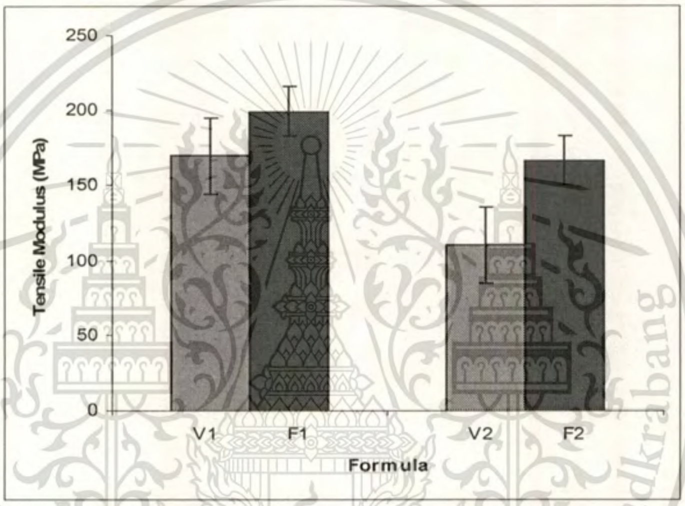


**Figure 4.7** Tensile modulus of resins synthesized from PET X-ray films and virgin PET

On the other hand, when resins from PET X ray films and resins from virgin PET were compared, it was seen that tensile modulus of resins from PET X-ray films were higher than those of virgin PET. It was cleared that resins from PET X-ray films were more rigid than resins from virgin PET.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 4.4.2 Work done

Work done is the area under the load deformation curve which depends on energy needed to fracture materials. The less area under the curve, the lower energy needed to break the material, the more brittle the material.

In experimental data, work done of both resins from PET X-ray films and virgin PET in Formula 1 were lower than Formula 2. For the resins in Formula 1, no DEG was added therefore it was more brittle compared to the resins in Formula 2. The results were shown in Figures 4.8.

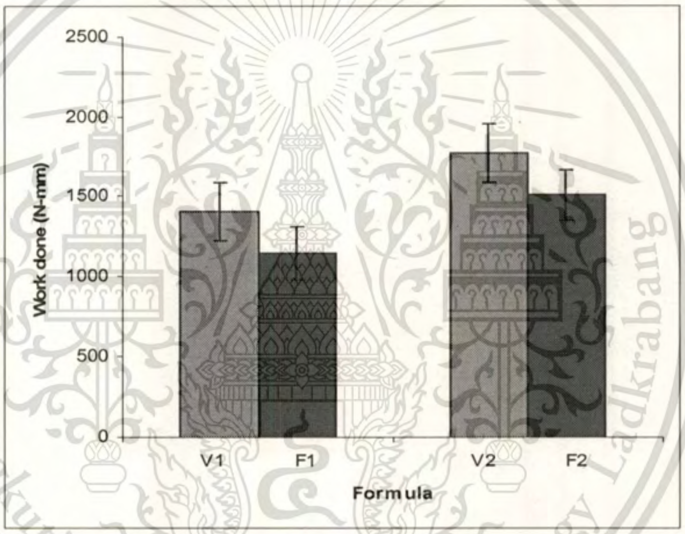


**Figure 4.8** Work done of resins synthesized from PET X-ray films and virgin PET

In addition, work done of resins derived from PET X-ray films was lower than resins derived from virgin PET. This means that PET X-ray films resins were more brittle so they needed lower energy required to break them.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 4.4.3 Hardness

Hardness is one property of materials to resist plastic deformation, usually by penetration. However, the term hardness might also refer to resistance to bending, scratching, abrasion or cutting. The hardness value is derived from a scale while Shore D hardness scale is very common for hard materials.

In this experiment, it could be observed that the hardness of both types of resins in both formulas showed the similar values as shown in Figure 4.9. This could be discussed that DEG was not effect hardness of the resins.

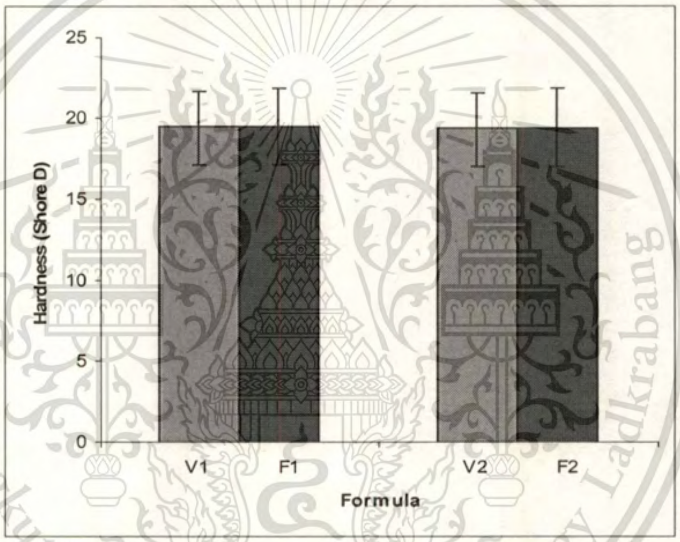


**Figure 4.9** Hardness of resins synthesized from PET X-ray films and virgin PET

If the effect of starting material was considered, it seems that the hardness values of resins from PET X-ray films and virgin PET were not different.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### 4.4.4 Impact strength

Impact strength is a measurement of the energy required to cause a material to fracture when struck by a sudden blow (high rate of deformation). Polymeric materials that are sensitive to the stress concentrations at the notch would perform poorly in the notched izod test.

From experiment, impact strengths of resins which synthesized from PET X-ray film in Formula 2 were higher than these of Formula 1 as shown in Figure 4.10. This could be explained by the structure of DEG. Its structure is flexible long chain with ether linkage structure so the chain would move freely. Furthermore, the chains of DEG was longer than EG and PG, as shown in Figure 4.11. So, crosslink density of the resins in Formula 2 would decrease then toughness of resins would increase. Thus, they could dissipate energy along network better than resins in Formula 1 then impact strength property of resins in Formula 2 would be high.

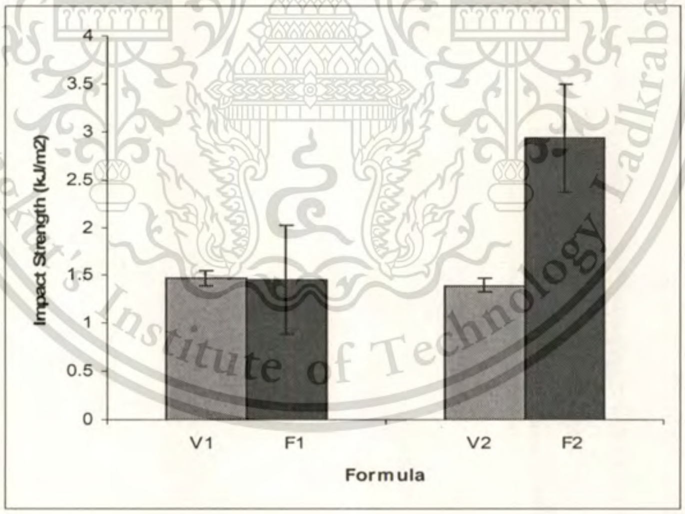
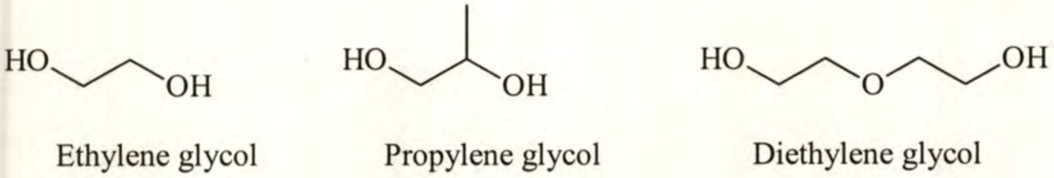


**Figure 4.10** Impact strength of resins synthesized from PET X-ray films and virgin PET

If impact strength of resins derived from PET X-ray films and virgin PET was compared, it was found that impact strength of resins in Formula 1 from PET X-ray films and virgin PET were not different.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.



Ethylene glycol Propylene glycol Diethylene glycol

Figure 4.11 Molecular structures of EG, PG and DEG

### 4.4.5 Flexural strength and flexural modulus

Flexural strength means maximum flexural stress generated when test specimen is supported at its both ends and concentrated load is applied downward at the span. Flexural modulus is the ratio of stress to strain with in the elastic limit and similar to the tensile modulus. This property is used to indicate the bending stiffness property of a material.

From the experimental data, it was shown that flexural modulus in Formula 2 from both resins synthesized from PET X-ray films and virgin PET were lower than those of Formula 1 as shown in Figure 4.12. This means that flexural modulus decreased when DEG was added. It was mentioned in the previous part that DEG would decrease crosslink density of resins because of its long linear chain so the resins in Formula 2 were more flexible. While the resins in Formula 1 that had no DEG would be more rigid because of their high crosslink density. So the resins in Formula 1 would give higher bending stiffness than another one.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

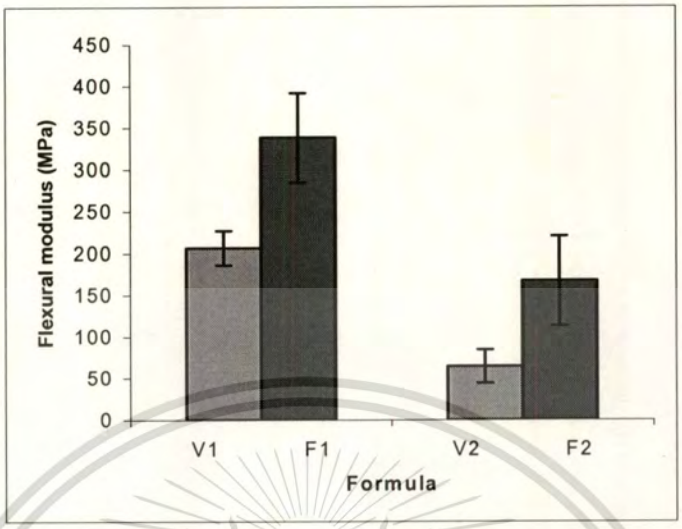


**Figure 4.12** Flexural modulus of resins synthesized from PET X-ray films and virgin PET

If the effect of starting material was considered, it was seen that flexural modulus of PET X-ray films resins was higher than resins derived from virgin PET. This meant that resins from PET X-ray films gave higher bending stiffness property.

For flexural strength, from the Figure 4.13, it was shown that resins derived from virgin PET in Formula 2 gave higher flexural strength than those of Formula 1. This effect was due to DEG. Its structure would make the resins were more flexible so the resins could bend more before they started to break.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

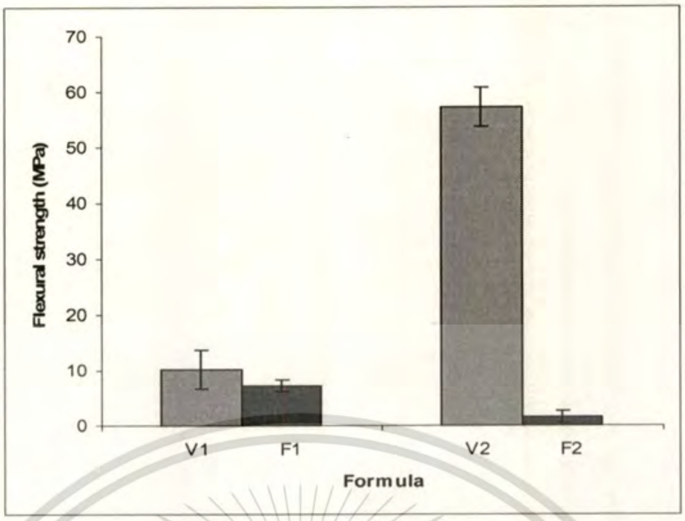


**Figure 4.13** Flexural strength of resins synthesized from PET X-ray films and virgin PET

If flexural strength of both PET X-ray films resins and virgin PET were compared, it could observed that flexural strength of PET X-ray films resins in Formula 1 was lower than virgin PET in Formula 1. Thus PET X –ray films resins generated lower maximum flexural stress than the other.

## 4.5 Effect of Diethylene glycol (DEG) and Different Sources of PET on Thermal Properties of Unsaturated Polyester Resins

Dynamic Mechanical Thermal Analysis (DMTA) is a technique used to study thermal properties of materials. An oscillating force is applied to a sample of material and the resulting displacement of the sample is measured. From this analysis, the stiffness of the sample could be determined then modulus of sample could be calculated. By measured the time lag in the displacement compared to the applied force, it is possible to determine the damping properties of materials. Materials typically exist in two distinct states. They exhibited the properties of glass (high modulus) at low temperatures and those rubbers (low modulus) at higher temperatures. By scanning the temperature during a DMTA experiment, the glass transition or alpha relaxation could be observed.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

In the experiment, glass transition temperatures ($T_g$) of resins from both PET X-ray films and virgins PET were shown in Table 4.6.

**Table 4.4** Glass transition temperature ($T_g$)

| Starting Material | Formula | EG: PG: DEG mol | Glass transition temperature ($T_g$)(°C) |
|---|---|---|---|
| PET X-ray films | F1 | 1:1:0 | 73.3 |
| | F2 | 1:1:0.5 | 73.2 |
| Virgin PET | V1 | 1:1:0 | 62.3 |
| | V2 | 1:1:0.5 | 62.1 |

It could be observed that the glass transition temperature ($T_g$) of resin from PET X-ray films in Formula 1 was not different to that of Formula 2. Likewise, the glass transition temperature ($T_g$) of resin from virgin PET in Formula 1 was not different to that of Formula 2 as well. Normally, from the theoretical prediction when DEG is added, then the glass transition temperature ($T_g$) should be lower because DEG will increase distance between crosslink points in the structure. However, in this experiment it did not give different $T_g$,. This might be cause from longer curing time of resins in Formula 2 so they would have higher % crosslinking. Then $T_g$ of resins in Formula 2 was higher than they should be.

If $T_g$ of resins from PET X-ray films and virgin PET were compared, it was shown that $T_g$ of resins from PET X-ray films was higher than the other. Thus resins from PET X-ray films had higher thermal resistance than resins from virgin PET.

**Note**: the results of DMTA were shown in Appendix D.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 4.6 Flexural Strength and Flexural Modulus of Composite

Glass fibers (Chopped Strands Mat, CSM) and the unsaturated polyester resins prepared from PET X-ray films and virgin PET were used to fabricate were prepare composites by the hand lay-up technique at room temperature. Glass fiber fraction in the composite was 36% by weight of the resins.

From experiment, flexural modulus of the composites was higher than those of cured resins due to the reinforcing effect. While the influence of DEG would still affect flexibility of the resins as discussed in previous parts, so flexural modulus of resins in Formula 2 were lower than those of Formula 1 as shown in Figure 4.14

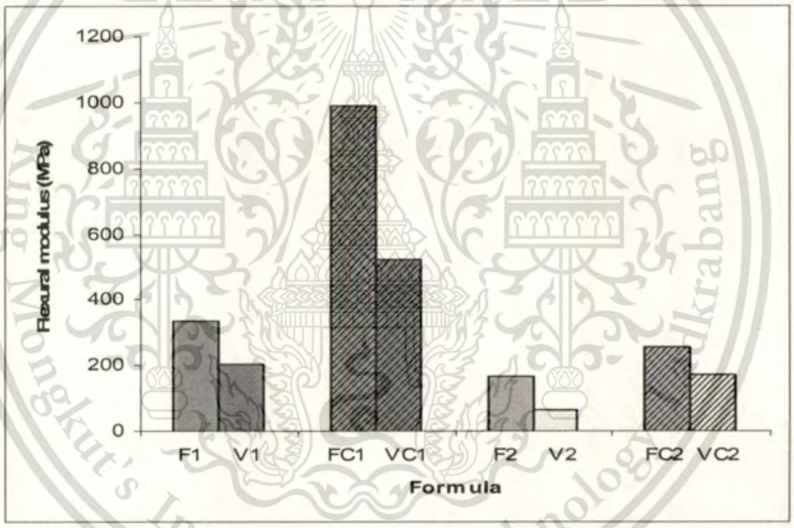


**Figure 4.14** Flexural modulus of composites and cured resins synthesized from PET X-ray films and virgin PET in each formula

**Note:** FC1 means the composite derived from PET X-ray films in Formula 1

FC2 means the composite derived from PET X-ray films in Formula 2

VC1 means the composite derived from virgin PET in Formula 1

VC2 means the composite derived from virgin PET in Formula 2

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

In comparison of flexural strengths of the composites with those of the cured resins, it was found that the composites gave higher values than the resins. In other word, it was shown that the flexural strengths of Formula 1 were less than those of Formula 2 because DEG increased flexibility of the samples. The results of flexural strength are shown in Figure 4.15.

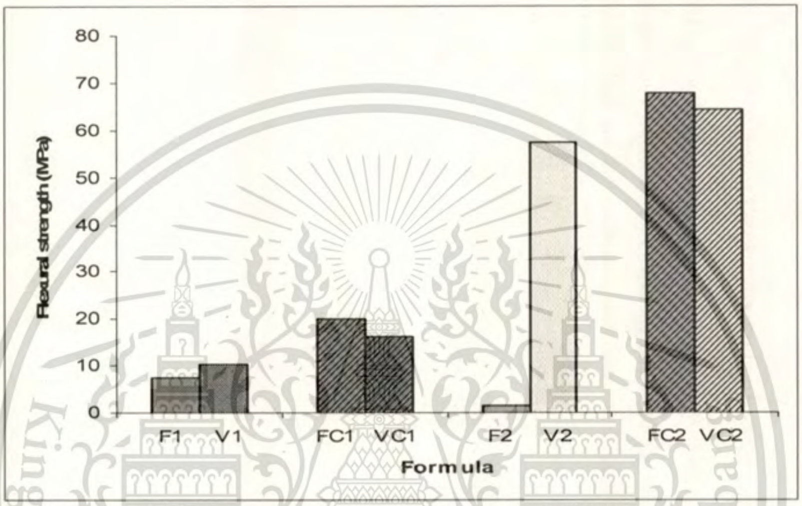


**Figure 4.15** Flexural strength of composites and cured resins synthesized from PET X-ray films and virgin PET in each formula

**Note:** FC1 means the composite derived from PET X-ray films in Formula 1

FC2 means the composite derived from PET X-ray films in Formula 2

VC1 means the composite derived from virgin PET in Formula 1

VC2 means the composite derived from virgin PET in Formula 2

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 4.7 Cost Analysis

From cost analysis (Table 4.5) between synthesized unsaturated polyester resins and commercial products, the costs of both formula resins (55 and 59 bath/kg) were less than those of commercial ones (70 and 90 bath/kg).

**Table 4.5** Comparison of raw material costs for synthesis of unsaturated polyester resins derived from PET X-ray films

| Starting materials | Cost of starting materials per kg (Baht) | Cost of resins in Formula 1 (Baht) | Cost of resins in Formula 2 (Baht) |
|---|---|---|---|
| PET X-ray films waste | 26 | 0.93 | 0.93 |
| Ethylene glycol | 43 | 0.89 | 0.71 |
| Propylene glycol | 67 | 3.32 | 2.66 |
| Diethylene glycol | 42 | 0 | 2.08 |
| Zinc acetate | 235 | 0.04 | 0.04 |
| Maleic anhydride | 65 | 5.43 | 5.04 |
| Styrene | 50 | 3.21 | 3.32 |
| Total cost (Baht) |  | 55.28 | 59.12 |

**Note:** 1. Price of commercial grade of Epoxy Vinyl Ester Resin is 90 bath/kg

2. Price of commercial grade of Polyester Resin General Propose is 70 bath/kg

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 4.8 Comparison of Mechanical Properties between Synthesized UPRs from PET X-ray Films and Commercial Resins

From comparison of mechanical properties between synthesized UPRs from PET X-ray films and commercial resins as shown in Table 4.6. We found that mechanical properties of commercial resins were better than synthesized UPRs from PET X-ray films, except tensile elongation. Therefore, the future research work should be continued to improve those mechanical properties.

**Table 4.6** Comparison of mechanical properties between synthesized UPRs from PET X-ray films and commercial resins

| Properties | Commercial resins (grade A) | Synthesized Formula 1 resins | Synthesized Formula 2 resins |
|---|---|---|---|
| Tensile Strength , MPa | 86 | 16.7 | 23.9 |
| Tensile Modulus, MPa | 3200 | 199.1 | 166.1 |
| Tensile Elongation , % | 5.0-6.0 | 13.1 | 23.2 |
| Impact Strength, kJ/ $m^2$ | n/a | 1.5 | 2.9 |
| Flexural Strength , MPa | 150 | 7.4 | 1.7 |
| Flexural Modulus, MPa | 3400 | 338.3 | 166.6 |
| Hardness, Barcol | 35 | n/a | n/a |
| Hardness, Shore D | n/a | 19.5 | 19.5 |

**Note:** Mechanical properties of unsaturated polyester resins (UPRs) commercial grade (commercial grade A) of The DOW chemical company, as shown in appendix B, Table B.2

n/a = not available

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# CHAPTER 5

# CONCLUSIONS AND SUGGESTION

## 5.1 Conclusions

This project was focused on used PET X-ray films and virgin PET as starting materials for producing unsaturated polyester resins (UPRs) by using depolymerization reaction of PET. Glycolysis process under the influence of glycol (i.e., ethylene glycol (EG) and propylene glycol (PG)) is the reverse reaction to the polycondensation of PET. In this project diethylene glycol (DEG) was used to improve properties of UPRs. Two ratios of EG:PG:DEG (i.e. 1:1:0 and 1:1:0.5) by mole were studied. Then UPRs composites were prepared by the hand lay-up technique at room temperature. In this work, some conclusions could be summarized as follows:

1. PET X-ray films waste could be used as a starting material for synthesis of UPRs and used in composite applications.
2. In comparison of mechanical properties and thermal properties of UPRs from PET X-ray films with those of virgin PET, it was found that UPRs from PET X-ray films gave higher tensile modulus, hardness, flexural modulus and glass transition temperature ($T_g$) than those of UPRs.
3. When DEG was added, tensile strength, flexural strength, % elongation at break and impact strength were increased while tensile modulus, flexural modulus and hardness were decreased. Due to the structure of DEG, that is long linear chain with ether linkage, flexibility of UPRs was increased.
4. UPRs from PET X-ray films had higher glass transition temperature ($T_g$) than UPRs from virgin PET.
5. The composites of UPRs reinforced with glass fibers possessed all properties better than those of pure UPRs.
6. From the cost analysis, it was found that the synthesized UPRs cost seemed to be cheaper than both virgin PET and commercial resins for composite applications.

This material is used for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## 5.2 Suggestion for Future Works

1. Free glycol of glycolyzed products and blue color of UPRs should be eliminated for application of UPRs.
2. Impact property should be improved by adding elastomers such as natural rubber or SBR.
2. Glycolysis reaction of Formula 2, DEG added to react with PET, needed higher temperature than Formula 1 to allow the reaction between DEG and PET.
3. The color of synthesized UPRs from PET X-ray films was transparent blue color. After BPO addition for curing, the color was changed to be cloudy blue color. As a result, selecting grade of BPO should be considered to suit the application of cured resins.
4. Crosslink density of resins should be studied.
5. Instead of ultrasonic bath, vacuum oven is more suitable for removing all air bubbles in the resins.
6. Glycolyzed products and resins from PET X-ray films should be analyzed for metals or impurities by using other techniques, such as, XRF, NMR and IR spectroscopy.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# REFERENCES

[1] www.academic.scranton.edu/faculty/CANNM1/industrialchemistry /industrialchemistrymodule.html

[2] Naroemon Khreuuaongattnukul, "Preparation resin from post-consumer poly (ethylene terephthalate) bottles", Thesis of Faculty of Applied Science, KMITNB,**2002**.

[3] Scheirs,J.,"Polymer Recycling:Science,Technology and Applications", John Wiley&Sons, England, **1998**.

[4] Danniel Paszun and Tadeusz Spychaj, "Chemical Recycling of poly(ethylene terephthalate)", Chapman&Hall,London, **1998**.

[5] Lawrence,J.R., "Polyester Resin",New York,Van Nostrand Reinhold, **1960**.

[6] Saunders,K.J.,"Organic Polymer Chemistry",2nd ed., Chapman&Hall,London, **1988**.

[7] Clarke, J.L., "Structural Design of Polymer Composites", E&FN Spon, London, **1996**.

[8] www.durachemicals.com/polyurethane_catalysts.htm

[9] Brydson,J.A.,"Plastic Materials",7th ed.,Butterworth-heinemann,London, **1999**.

[10] Salomone,J.c.,"In Polymeric materials Encyclopedia";CRC Press,Inc.:USA,vol 2, **1996**.

[11] www.mech.utah.edu/

[12] Richardson, T.L., "Industrial Plastic: Theory and Application", 2nd ed., Delmar Publishers Inc., USA, **1989**.

[15] Neha Vaidya, "The Manufacturing of Wet-laid Hydroentangled Glass Fiber Composites For Industrial Applications", Thesis of North Carolina State University, **2002**.

[16] www.projects.bre.co.uk/

[17] Clarke, J.L., "Structural Design of Polymer Composites", E&FN Spon, London, **1996**.

[18] www.irc.nrc-cnrc.gc.ca/

[19] Richardson, T.L., "Composites: A Design Guide", Industrial Press Inc., New York, **1987**.

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

[20] Schwartz, M.M., "Composite Materials : Properties, Nondestructive Testing, and Repair", Prentice Hall PTR, New Jersey, Vol.1, **1997**.

[21] Jang, B.Z., "Advanced Polymer Composite: Principles and Applications", ASM International, USA, **1994**.

[22] Guoxi Xi, Maixi Lu, Chen Sun., "Study on depolymerization of waste polyethylene terephthalate into monomer of bis(2-hydroxyethyl terephthalate)" *Polymer Degradation and stability*, Vol.87, **2005**, 117-120.

[23] D.J. Suh, O.O. Park, K.H. Yoon., "The properties of unsaturated polyester based on the glycolyzed poly(ethylene terephthalate) with various glycol compositions" *Polymer*, Vol.41, **2000**, 461-466.

[24] George P. Karayannidis , Dimitris S. Achilias, Irini D., Sideridou, Dimitris N. Bikiaris. "Alkyd resins derived from glycolized waste poly(ethylene terephthalate " *European Polymer Journal*, Vol.41, **2005**, 201–210.

[25] Ph. Radenkov , M. Radenkov , G. Grancharov , K. Troev., "Direct usage of products of poly(ethylene terephthalate)glycolysis for manufacturing of glass-fibre-reinforced plastics " *European Polymer Journal*, Vol.39, **2003**, 1223–1228.

[26] J.Y. Chen, C.F. Ou, Y.C. Hu, and C.C. Lin., "Depolymerization of Poly (Ethylene Terephthalate) Resin under pressure" *Applied Polymer Science*, Vol 42, **1991**, 1501-1507.

[27] Utpal R. Vaidya and Vikas M. Nadkarni., "Unsaturated Polyester Resins from Poly (ethylene terephthalate) Waste. 1. Synthesis and Characterization" *Ind.Eng.Chen.Res.* Vol.26, 194-198.

[28] www.derakane.com

[29] The American Society for Testing and Materials., "Standard Methods of Testing Urethane Foam polyol raw materials", ASTM D 2849-69, **1975**, 630-650.

[30] The American Society for Testing and Materials., "Standard Methods of Sampling and Testing Shellac Varnish", ASTM D 1650-91, 277-280.

[31] The American Society for Testing and Materials., "Standard Methods for Tensile Property of Plastic", ASTM D 638-87b, **1992**, 155-166.

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

[32] The American Society for Testing and Materials., "Standard Methods of Rubber Property – Durometer Hardness", ASTM D 2240-91, **1992**, 226-229.

[33] The American Society for Testing and Materials., "Standard Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials ", ASTM D 790-91, **1992**, 269-278.

[34] The American Society for Testing and Materials., "Standard Methods for Impact Resistance of Plastic and Electrical Insulating Materials", ASTM D 256-90b, **1992**, 58-74.

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

# Appendices

## Appendix A Expression of calculation

### A.1 Calculation of the number average molecular weight ($M_n$) of glycolyzed product from hydroxyl value

Molecular weight of glycolyzed product $= W$ g

Volume of KOH consumed in titration $= V$ ml

Therefore, the number of mole of –COOH $= \frac{NV}{1000}$ mol

If 1 molecule of linear chain of glycolyzed product has –COOH two groups

Therefore, the number of mole of glycolyzed product $= \frac{NV}{2(1000)}$ mol

Weight of glycolyzed product $\frac{NV}{1000}$ mol is W g

If weight of 1 mole of glycolyzed product is $\frac{2W(1000)}{NV}$ mol (A.1)

Because of hydroxyl value (OH value) $= \frac{VxNx56.1}{W}$ mgKOH/g

$$\text{Or} \quad \frac{NV}{W} = \frac{\text{OH value}}{56.1} \qquad \text{(A.2)}$$

Substitute (A.2) in (A.1)

Weight of 1 mole of glycolyzed product is $\frac{2x56.1(1000)}{\text{OH value}}$ g

Therefore,

The number average molecular weight (Mn)
of glycolyzed product $= \frac{112200}{\text{OH value}}$ g/mol (A.3)

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Example of calculation of the number average molecular weight (Mn)**

From experiment, glycolyzed product which synthesized from PET X-ray films had hydroxyl value 355.45 mgKOH/g

Substitute OH value in (A.3)

Therefore, the average molecular weight (Mn) $= \frac{112200}{355.45} = 315.66$ g/mol

## A.2 Example of calculation of quantity of diethylene glycol and maleic anhydride that used for synthesis unsaturated polyester resins (UPRs) in both Formula 1 and Formula 2 of glycolyzed product derived from PET X-ray films or virgin PET

**Part1** Preparation of glycolyzed product in Formula F1 or V1

| Starting Materials | Quantity (g) |
|---|---|
| PET X-ray films or Virgin PET | 192 |
| Ethylene Glycol (EG) | 156.24 |
| Propylene Glycol (PG) | 191.52 |
| Zinc Acetate | 0.96 |
| Total | 540.72 |

Preparation of glycolyzed product in Formula F2 or V2

| Starting Materials | Quantity (g) |
|---|---|
| PET X-ray films or Virgin PET | 192 |
| Ethylene Glycol (EG) | 124.992 |
| Propylene Glycol (PG) | 153.216 |
| Diethylene glycol (DEG) | 106.848 |
| Zinc Acetate | 0.96 |
| Total | 578.016 |

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Part 2** Preparation of unsaturated polyesters

| Formula | PET : Glycol (mol) | EG:PG:DEG (mol) | Glycolyzed Product (g) | DEG (g) | Maleic anhydride (g) |
|---|---|---|---|---|---|
| F1,V1 | 1:5.04 | 1:1:0 | 100 | - | 83.00 |
| F2,V2 | 1:5.04 | 1:1:0.5 | 100 | 106.85 | 77.65 |

<u>Formula F1 or V1</u>

EG : PG : DEG = 1 : 1 : 0

PET : (EG+PG) = 1 : 5.04 mol

Hydroxyl : Carbonyl (1.1:1) = 5.04 : 4.58 mol

Therefore, weight of maleic anhydride is 4.58x98 = 448.84 g

But, glycolyzed product is divided into 100 g

Hence, the quantity of maleic anhydride is (100x448.84)/540.72 = 83 g

<u>Formula F2 or V2</u>

EG : PG : DEG = 1 : 1 : 0.5

PET : (EG+PG+DEG) = 1 : 5.04 mol

EG : PG : DEG = 2.016 : 2.016 : 1.008mol

Therefore, weight of diethylene glycol is 1.008x106 = 106.848 g

Hydroxyl : Carbonyl (1.1:1) = 5.04 : 4.58 mol

Therefore, weight of maleic anhydride is 4.58x98 = 448.84 g

But, glycolyzed product is divided into 100 g

Hence, the quantity of maleic anhydride is (100x448.84)/ 578.016 = 77.65 g

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

## Appendix B Some properties of unsaturated polyester resins (UPRs) and glycol

**Table B.1 General properties of unsaturated polyester resins (UPRs) (commercial grade A) of DOW Chemical Company** [26]

| Typical Properties | Values |
|---|---|
| Dynamic Viscosity @ 25°C (77 °F) , mPa.s | 370 |
| Styrene Content , % | 45 |
| Density @ 25°C (77 °F) , g/ml | 1.046 |
| Shelf Life , dark , @ 25°C (77 °F) , months | 7 |

**Table B.2 Mechanical properties of unsaturated polyester resins (UPRs) (commercial grade A) of DOW Chemical Company**[26 ]

| Properties | Values |
|---|---|
| Tensile Strength , MPa/psi | 86/12,000 |
| Tensile Modulus, Gpa/unit $10^5$ psi | 3.2/4.6 |
| Tensile Elongation , % | 5.0-6.0 |
| Flexural Strength , MPa/psi | 150/22,000 |
| Flexural Modulus, Gpa/unit $10^5$ psi | 3.4/4.9 |
| Specific Gravity | 1.14 |
| Heat Distortion Temperature , °C (F°) at 1.82 MPa (264 psi) applied stress | 105/220 |
| Barcol Hardness | 35 |

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

**Table B.3 Properties of EG, PG and DEG**

| Materials | Specific density (g/cm$^3$) | Molecular weight (g/mol) | Melting Point (°C) | Boiling Point (°C) |
|---|---|---|---|---|
| Ethylene glycol | 1.11 | 62.07 | -13 | 117 |
| Propylene glycol | 1.04 | 76.10 | -50 | 188 |
| Diethylene glycol | 1.12 | 106.12 | -10 | 244-252 |

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.

Forbidden to modify the content, and cite the document when use.

## Appendix C The quantity of starting materials that used in this experiment

### C.1 Starting materials that used for preparation of glycolyzed product

| Formula | PET X-ray films (g) | EG (g) | PG (g) | DEG (g) | Zinc acetate (g) |
|---|---|---|---|---|---|
| F1 | 192.00 | 156.24 | 191.52 | 0 | 0.96 |
| F2 | 192.00 | 124.99 | 153.22 | 106.85 | 0.96 |

| Formula | Virgin PET (g) | EG (g) | PG (g) | DEG (g) | Zinc acetate (g) |
|---|---|---|---|---|---|
| V1 | 192.00 | 156.24 | 191.52 | 0 | 0.96 |
| V2 | 192.00 | 124.99 | 153.22 | 106.85 | 0.96 |

### C.2 Acid value and viscosity of unsaturated polyester resins (UPRs)

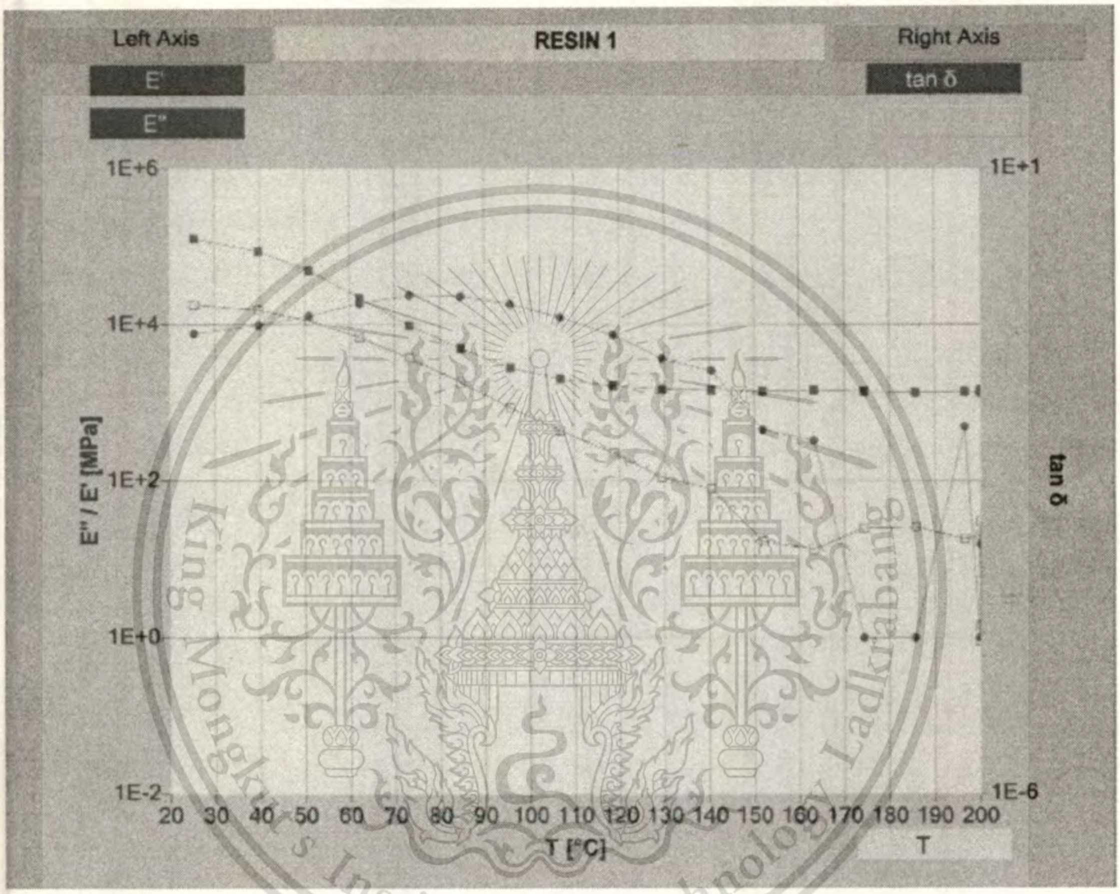
<table>
<tr><th colspan="11">PET X-ray films</th></tr>
<tr><th>Formula</th><th>GP (g)</th><th>MA (g)</th><th>$V_{KOH}$ (ml)</th><th>[KOH] (N)</th><th>W (g)</th><th>Acid value</th><th>Time (hr)</th><th>UPRs (g)</th><th>Styrene (g)</th><th>$\eta$ (cP)</th></tr>
<tr><td>F1</td><td>100.04</td><td>83.03</td><td>6.7</td><td>0.088</td><td>0.44</td><td>74.05</td><td>7</td><td>181.19</td><td>63.42</td><td>750</td></tr>
<tr><td>F2</td><td>100.08</td><td>77.7</td><td>5.9</td><td>0.087</td><td>0.43</td><td>66.14</td><td>6</td><td>175.91</td><td>62.57</td><td>850</td></tr>
<tr><td colspan="11">Composite</td></tr>
<tr><td>FC1</td><td>100.44</td><td>83.55</td><td>6.2</td><td>0.089</td><td>0.43</td><td>70.83</td><td>6</td><td>182.43</td><td>61.80</td><td>720</td></tr>
<tr><td>FC2</td><td>100.66</td><td>78.15</td><td>6.3</td><td>0.090</td><td>0.43</td><td>72.80</td><td>6</td><td>177.45</td><td>62.19</td><td>900</td></tr>
</table>

<table>
<tr><th colspan="11">Virgin PET</th></tr>
<tr><th>Formula</th><th>GP (g)</th><th>MA (g)</th><th>$V_{KOH}$ (ml)</th><th>[KOH] (N)</th><th>W (g)</th><th>Acid value</th><th>Time (hr)</th><th>UPRs (g)</th><th>Styrene (g)</th><th>$\eta$ (cP)</th></tr>
<tr><td>V1</td><td>100.14</td><td>83.10</td><td>6.0</td><td>0.088</td><td>0.40</td><td>66.20</td><td>7</td><td>181.26</td><td>63.48</td><td>855</td></tr>
<tr><td>V2</td><td>100.07</td><td>77.71</td><td>6.5</td><td>0.091</td><td>0.44</td><td>74.26</td><td>6</td><td>175.91</td><td>61.57</td><td>1075</td></tr>
<tr><td colspan="11">Composite</td></tr>
<tr><td>VC1</td><td>100.33</td><td>83.26</td><td>4.8</td><td>0.113</td><td>0.44</td><td>67.99</td><td>6</td><td>182.76</td><td>63.96</td><td>960</td></tr>
<tr><td>VC2</td><td>10016</td><td>77.78</td><td>6.6</td><td>0.089</td><td>0.43</td><td>75.47</td><td>6</td><td>176.70</td><td>62.00</td><td>995</td></tr>
</table>

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

## Appendix D Thermograms of DMTA

### D.1 Graph showing storage modulus (E’), loss modulus (E”) and tan δ of Formula 1 of UPRs from PET X-ray films

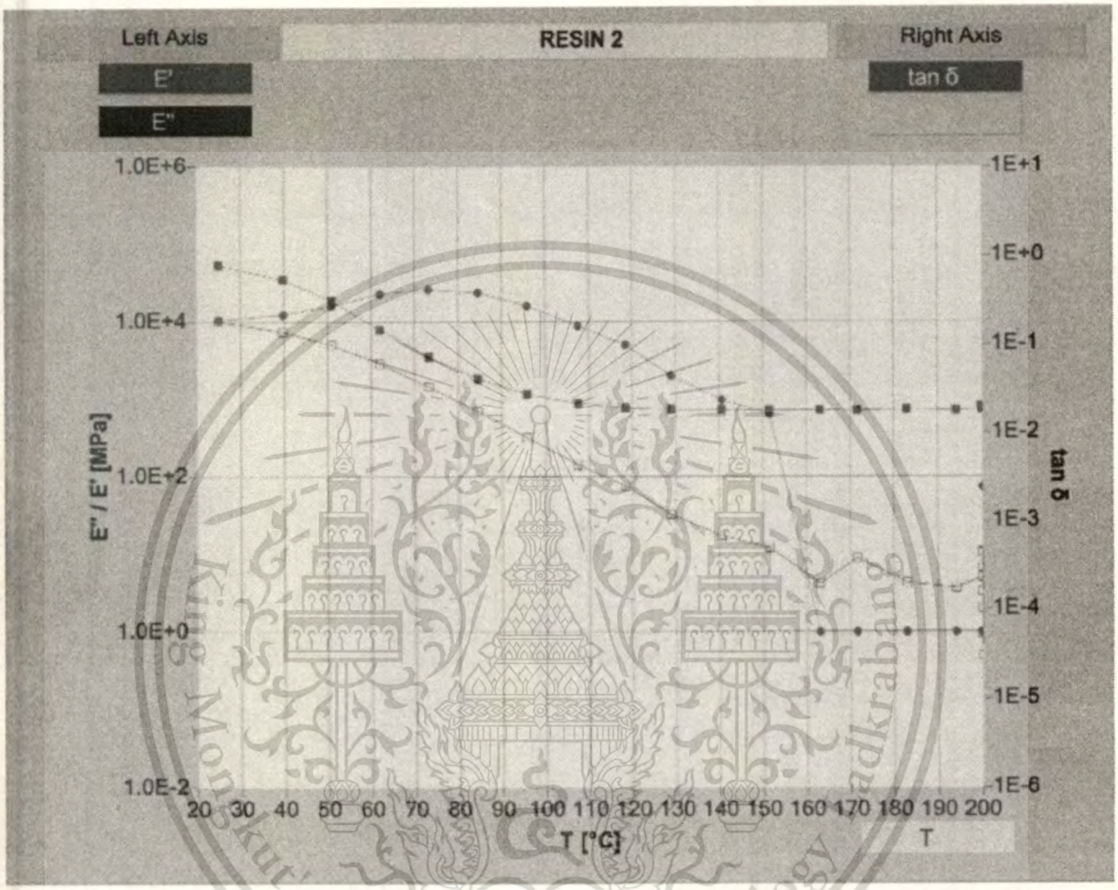


Glass transition temperature ($T_g$) of Formula 1 of UPRs from PET X-ray films is 73.3

King Mongkut's Institute of Technology Ladkrabang

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

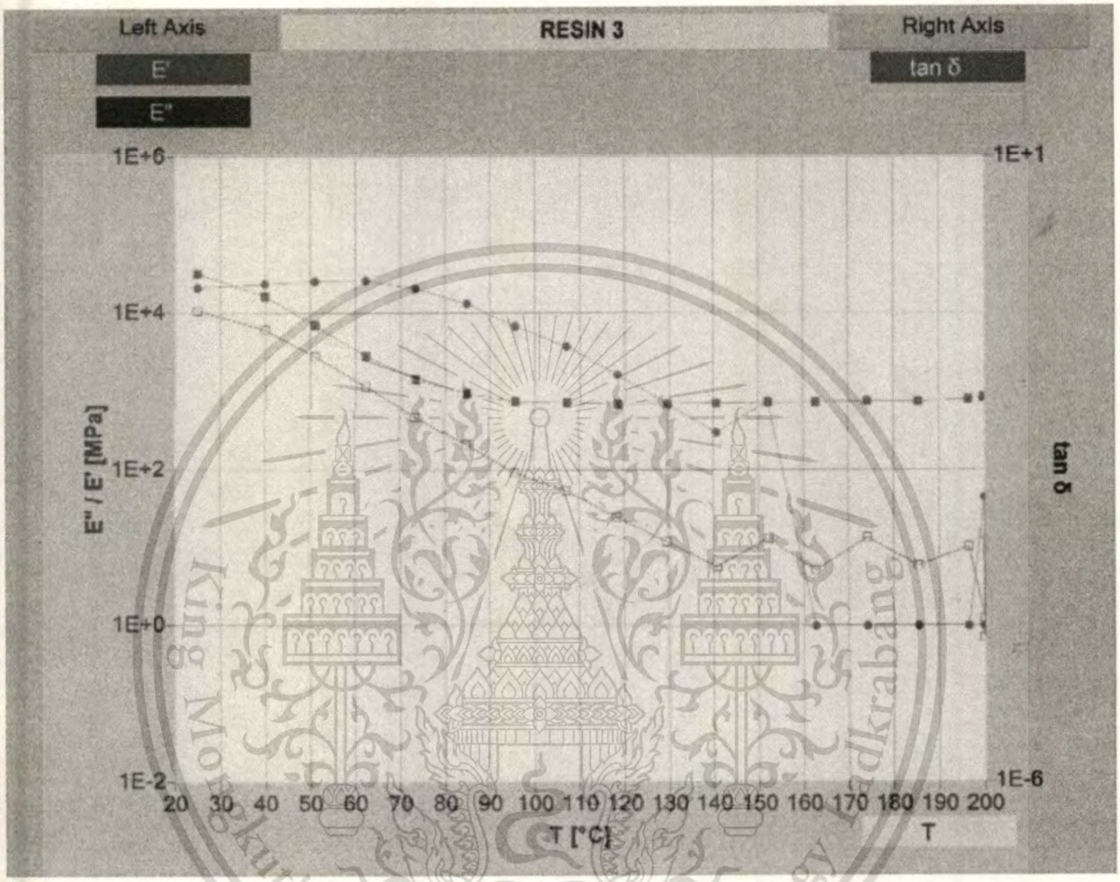
### D.2 Graph showing storage modulus (E'), loss modulus (E") and tan δ of Formula 2 of UPRs from PET X-ray films



Glass transition temperature ($T_g$) of Formula 2 of UPRs from PET X-ray films is 73.2

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

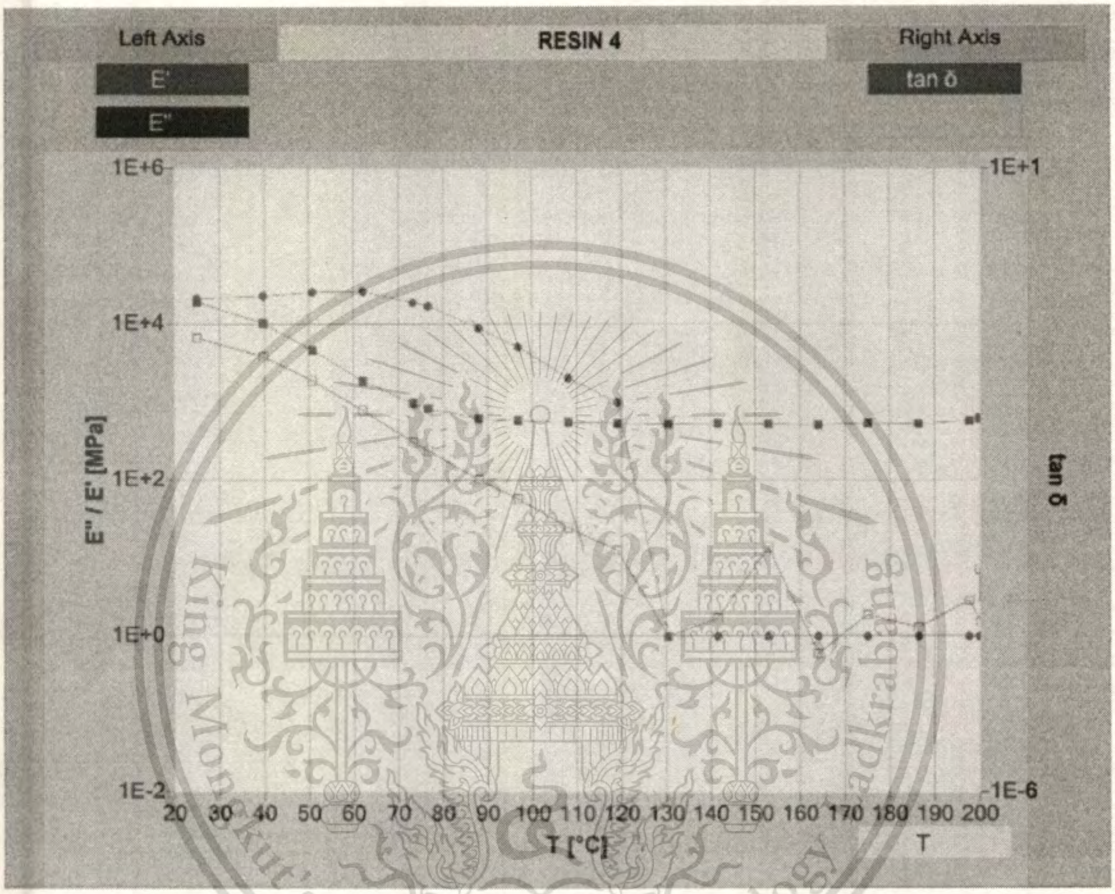
### D.3 Graph showing storage modulus (E'), loss modulus (E") and tan δ of Formula 1 of UPRs from virgin PET



Glass transition temperature ($T_g$) of Formula 1 of UPRs from virgin PET is 62.3

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.

### D.4 Graph showing storage modulus (E'), loss modulus (E") and tan δ of Formula 2 of UPRs from virgin PET



Glass transition temperature ($T_g$) of Formula 2 of UPRs from virgin PET is 62.1

This material is reserved for educational use only, not allowed for commercial use.
Forbidden to modify the content, and cite the document when use.