

เมทานิลไฮซิสและการวิเคราะห์ไอโซพาทาลิกแอซิดในฟีดที่เรซินโดยแก๊สโครมาโทกราฟี



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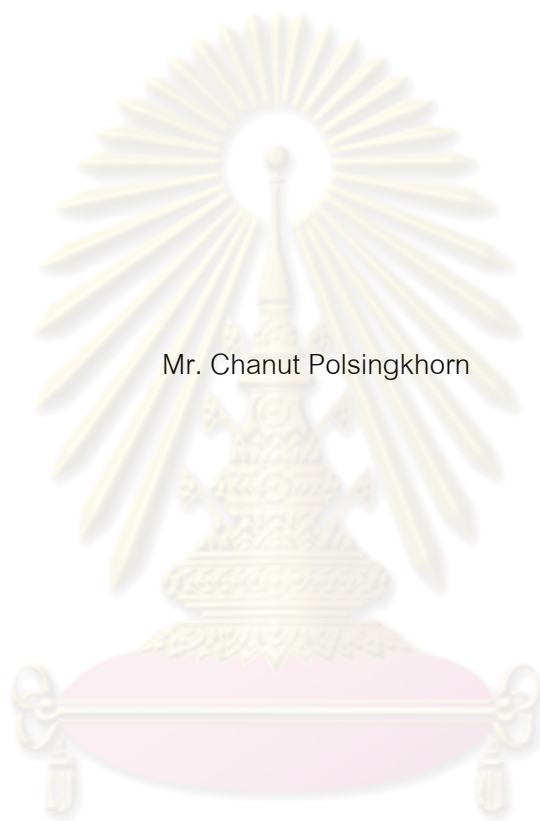
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2552

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

METHANOLYSIS AND ANALYSIS OF ISOPHTHALIC ACID IN PET RESIN BY GAS
CHROMATOGRAPHY

Mr. Chanut Polsingkhorn



ศูนย์วิทยทรัพยากร

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Petrochemistry and Polymer Science
Faculty of Science


Chulalongkorn University

Academic Year 2009


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Thesis Title METHANOLYSIS AND ANALYSIS OF ISOPHTHALIC ACID IN
 PET RESIN BY GAS CHROMATOGRAPHY
By Mr. Chanut Polsinghorn
Field of Study Petrochemistry and Polymer Science
Thesis Advisor Associate Professor Amorn Petsom, Ph.D.


Accepted by the Faculty of Science, Chulalongkorn University in Partial
Fulfillment of the Requirements for the Master's Degree

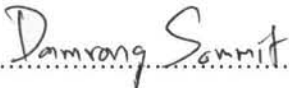

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ชัญญ์ พลสิงขร : เมทาโนไลซิสและการวิเคราะห์ไอโซพทาติกแอซิดในพีอีทีเรซินโดยแก๊สโครมาโทกราฟี (METHANOLYSIS AND ANALYSIS OF ISOPHTHALIC ACID IN PET RESIN BY GAS CHROMATOGRAPHY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. อมร เพชรสม, 48 หน้า.

กรดไอโซแทลิก ถูกใช้เพื่อช่วยเพิ่มคุณสมบัติของพีอีทีในกระบวนการผลิตและจำเป็นต้องทราบปริมาณของไอโซแทลิก อย่างไรก็ตามการวัดในเชิงปริมาณของไอโซแทลิกในพีอีทีเรซินทำได้ด้วยเทคนิคฟูเรียรทรานส์ฟอร์ม อินฟราเรด สเปกโตรสโคปี ซึ่งเป็นวิธีการเฉพาะของผู้ผลิตเท่านั้นและเป็นวิธีที่ใช้เวลานาน ดังนั้นงานวิจัยนี้จึงได้เสนอวิธีการวิเคราะห์เชิงปริมาณของไอโซแทลิกในพีอีทีเรซินด้วยเทคนิคแก๊สโครมาโทกราฟี ในวิธีนี้กรดไอโซแทลิกสามารถวิเคราะห์เชิงปริมาณได้โดยละลาย พีอีทีเรซิน ด้วยเมทานอลในสภาวะที่มีต่างเป็นตัวเร่งปฏิกิริยาในเตาปฏิกรณ์ขนาดเล็กและวิเคราะห์เมทิลเอสเทอร์ที่ได้โดยใช้ไดเอทิลพาเทเลตเป็นสารอ้างอิงมาตรฐาน ซึ่งผลการวิเคราะห์ด้วยเทคนิคแก๊สโครมาโทกราฟีให้ผลถูกต้องกว่าเทคนิคฟูเรียรทรานส์ฟอร์ม อินฟราเรด สเปกโตรสโคปี นอกจากนี้การวิเคราะห์ปริมาณกรดไอโซแทลิกในพีอีทีสามารถทำได้ได้ในเวลาอันสั้นอีกด้วย

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ลายมือชื่อนิติ

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KEYWORDS : PET/ ISOPHTHALIC ACID/ DIMETHYISOPHTHALATE/ METHANOLYSIS

CHANUT POLSINGKHORN: METHANOLYSIS AND ANALYSIS OF ISOPHTHALIC ACID IN PET RESIN BY GAS CHROMATOGRAPHY. THESIS ADVISOR: ASSOC. PROF. AMORN PETSOM, Ph.D., 48 pp.

Isophthalic acid (IPA) has been used to help improve the properties of polyethylene terephthalate (PET) and in the production process precise amount of IPA to be added into PET resin must be known. However, the only known quantitative monitoring of the concentration of IPA in PET resin is the FTIR analysis which is an in-house method and time consuming. In this research a gas chromatographic method for the quantitative analysis of IPA has been proposed. In this method the IPA was quantified by dissolving the PET resin in methanol in the presence of base catalyst in a micro-reactor and the resulting methyl ester was analyzed using diethylphthalate as an internal standard. The results indicated that the gas chromatographic method was more accurate than the FTIR method. Moreover, the analysis of IPA in PET resin was carried out within a short time.

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Field of Study : Petrochemistry and Polymer Science

Academic Year : 2009

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ACKNOWLEDGEMENTS

I have many people to thank for their support and encouragement for this project. First of all, I would like to express my sincere appreciation and gratitude to my beloved advisor, Associate Professor Dr. Amorn Petsom, for all his valuable suggestions, guidance, and encouragement throughout my study.

I am also grateful to the other members of my committee, Associate Professor Dr. Supawan Tantayanon, Assistant Professor Dr. Voravee P. Hoven and Dr. Damrong Sommit for their comments, technical guidelines, and advice given to me especially during the final presentation.

Gratefully thanks are extended to Graduate School, Chulalongkorn University and Excellent Center for Petroleum, Petrochemical and Advanced Materials, NCE-PPAM.

Moreover, I am also extended grateful thanks to Thai PET Resin Co., Ltd. in affiliate of SCG Chemical Co., Ltd. for the good working environment, helpful, opinion, and encouragement. Without all of them as mentioned, this thesis would not be possible.



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LIST OF ABBREVIATIONS

PET	Polyethylene terephthalate
EG	Ethylene glycol
TPA	Terephthalic acid
DMT	Dimethylterephthalate
IPA	Isophthalic acid
DMI	Dimethylisophthalate
DEG	Diethylene glycol
H ₂ SO ₄	Sulfuric acid
NaOH	Sodium hydroxide
GC	Gas chromatography
FT-IR	Fourier transform infrared spectroscopy
°C	Degree Celsius
mg	milligram
g	gram
h	hour
min	minute
dL	deciliter
ml	milliliter
Cpk	process capability
R	range
P/T ratio	precision-to-tolerance

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CHAPTER I

INTRODUCTION

1.1 Polyethylene Terephthalate (PET)

Polyethylene terephthalate (PET) is a well-known plastic used in great quantities around the world to make products such as bottles, fibers, and packaging. Polyethylene terephthalate (PET) is a polymer formed by step-growth polycondensation from ethylene glycol (EG) and terephthalic acid (TPA). The synthesis of PET requires two reaction steps. The first of these is esterification of TPA with EG, forming a so-called prepolymer which contains the monomer bis-hydroxyethyl terephthalate and short-chain oligomers. The esterification by-product, i.e. water, is removed via a column system. The second reaction step is polycondensation, in which a transesterification reaction takes place in the melt phase. The by-product, EG, is removed from the melt by using high vacuum. High-viscosity PET grades for bottles or technical yarns are typically produced by further polycondensation in an additional solid-state process under vacuum or in an inert gas atmosphere, respectively.

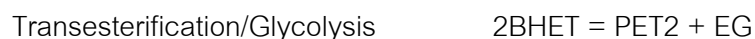
Direct Esterification



Transesterification



Melt -Phase Polycondensation



Solid-State Polycondensation



Figure 1.1 Stoichiometric equations for the synthesis of PET

The formation of prepolymer can also be achieved by transesterification of dimethyl terephthalate (DMT) with EG, releasing the by-product methanol. High-purity DMT is easily obtained by distillation and in the early years of PET production, all processes were based on this feedstock. During the late 1960s, highly purified TPA was produced for the first time on an industrial scale by re-crystallization. Since then, more and more processes have shifted to TPA as the feedstock and today more than 70% of global PET production is based on TPA. The TPA-based PET production saves approximately 8% of total capital investment and 15% of feedstock cost. Two PET grades now dominate the global market, i.e. fiber-grade PET and bottle-grade PET. These standard grades differ mainly in molecular weight or intrinsic viscosity (IV), respectively, optical appearance and the production recipes. The latter differ in the amount and type of co-monomers, stabilizers and metal catalysts, as well as colorants. Textile fiber-grade PET contains 0.03 to 0.4wt% of titanium dioxide (TiO_2) as a delustering agent. This grade has a molecular weight (number-average molecular weight, M_n) of 15 000 to 20 000 g/mol, which refers to an IV of between 0.55 and 0.67 dL/g. The standard textile fiber grade has an IV of 0.64 dl/g. PET fiber grades for technical yarns such as tyre cord are high-modulus low-shrinkage types with very high molecular weights, respectively, with an IV above 0.95 dL/g.

Bottle-grade PET appears 'glass-clear' in the amorphous state. Special requirements for bottle-grade PET are a brilliant white color and a composition fulfilling the regulations for food packaging. The average molecular weight ranges from 24 000 to 36 000 g/mol, which refers to an IV of between 0.75 and 1.00 dl/g. The standard bottle grade has an IV of 0.80 dl/g. Other PET grades are manufactured for packaging films, as well as for the production of video and audio tapes. These PET types are often standard grades with an IV of 0.64 dL/g. To reduce the sticking tendency of the final product, solid additives such as SiO_2 or china clay with specific particle sizes and

particle-size distributions are incorporated by master-batch processes. The final product, the so-called BOPET, is a biaxial oriented PET film with high mechanical strength and a thickness between 1 and 180 μm [1,2].

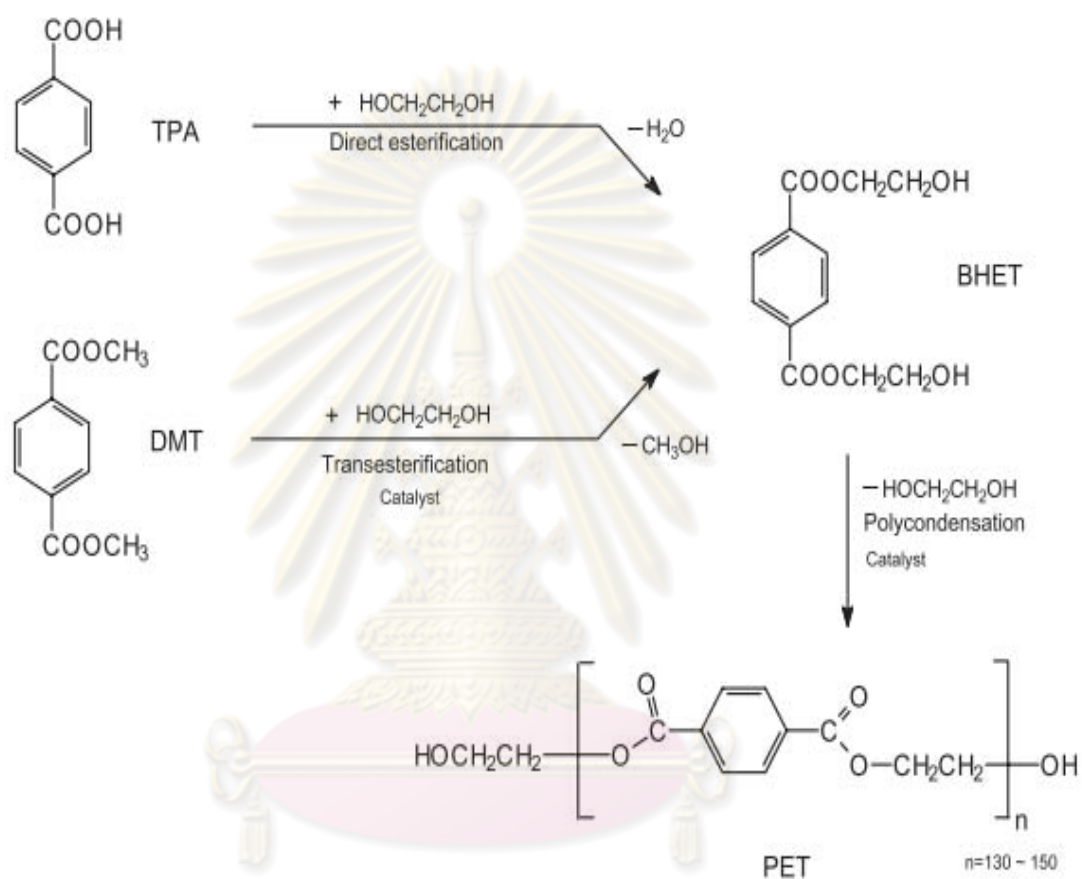


Figure 1.2 Process of PET production in manufacturer

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1.2 Isophthalic acid (IPA)

Often PET is modified with a carboxylic acid other than TPA and/or a diol other than ethylene glycol to enhance particular physical properties. For example, isophthalic acid is added as a partial replacement to terephthalic acid in commercial polyester production processes to change the morphology of the resultant polyester product. Typical modification levels are 0-5 mole % replacement of primary terephthalic acid, resulting in more desirable properties of the polyester produced. These improved properties include, for example, reduced crystallization rate and improved barrier properties for packaging resins.

isophthalic acid (IPA) typically is produced using the same basic process steps as terephthalic acid, but starting with a meta-xylene feed. Commercial isophthalic acid contains low levels of impurities. Like commercial terephthalic acid, this is important for most applications where isophthalic acid is used in significant quantities. It can be appreciated that the importance of absolute purity of the isophthalic acid diminishes as the amount of isophthalic acid used is a lower overall fraction of the monomer mix for making the polyester.

The isophthalic acid production process can be divided into the oxidation zone and the hydrogenation zone. Crude isophthalic acid is produced in the oxidation zone. The crude (or non-hydrogenated) IPA is purified (or hydrogenated) in the hydrogenation zone. The hydrogenation zone typically includes the following steps: (1) replacing the mother liquor of the crude IPA-containing slurry with water, (2) heating the crude IPA/water slurry to dissolve the crude IPA in water, (3) catalytically hydrogenating the crude IPA/water solution to convert impurities to more desirable and/or easily-separable compounds, (4) precipitating the resulting purified IPA from the hydrogenated solution via multiple crystallization steps, and (5) separating the crystallized purified IPA from the

remaining liquids. Although effective, this type of conventional purification process can be very expensive. Individual factors contributing to the high cost of conventional crude IPA purification methods include, for example, the heat energy required to promote dissolution of the crude IPA in water, the catalyst required for hydrogenation, the hydrogen stream required for hydrogenation, the yield loss caused by hydrogenation of some isophthalic acid, and the multiple vessels required for multi-step crystallization[3].

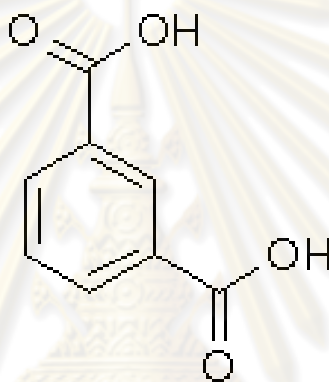


Figure 1.3 Structure of Isophthalic acid

1.3 Research goal

At the present, FT-IR is an in-house method use for the analysis of IPA in PET. The sample is molded to a film with 100 – 200 μm thickness by a 280°C hot-plate. Afterwards the film is measured with an infrared spectrophotometer at 700 – 600 cm^{-1} and the spectrogram is recorded. Seek the absorbency D632 at the key band 632 cm^{-1} , and determine IPA content using the calibration curve. However, FT-IR method requires a proprietary standard and it is not commercially available. Thus, the analysis of IPA in PET cannot be done in other laboratories. Moreover, PET sample film with 100 – 200 μm thickness is non- homogeneous as reveals by FT-IR (as shown in figure 1.4) which causes fluctuation of IPA quantity in PET resin.

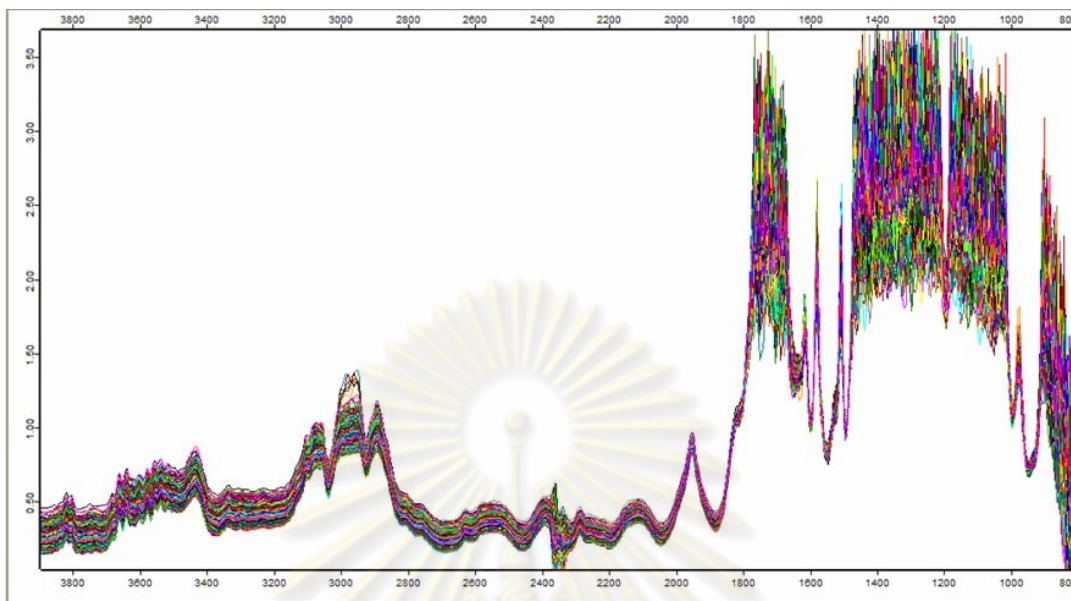


Figure 1.4 FT-IR spectrogram of non-homogeneous PET film.

The process capability (Cpk) of analysis of IPA in PET by FT-IR is 0.43 that means result of analysis of IPA in PET by FT-IR is fluctuated. Cpk from theoretical for suitable analysis is more than 1.00 at 90% confidential. Therefore, in this work, a more general method for analysis of IPA content in PET based on gas chromatographic analysis was developed. The process was carried out by methanolysis of PET to convert IPA to dimethyl isophthalate (DMI) and then analyzed by gas chromatography (GC).

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CHAPTER II

THEORETICAL

2.1 Transesterification/Methanolysis

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis (Figure 2.1). In this review, the term transesterification will be used as synonymous for alcoholysis of carboxylic esters, in agreement with most publications in this field. The transesterification is an equilibrium reaction and the transformation occurs essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high yield of the ester, the alcohol has to be used in excess.

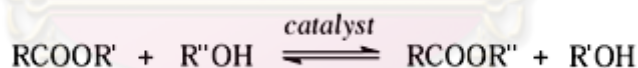


Figure 2.1 General equation of transesterification reaction

The applicability of transesterification is not restricted to laboratory scale. Several relevant industrial processes use this reaction to produce different types of compounds 1. An example is the production of PET (polyethylene terephthalate), which involves a step where dimethylterephthalate is transesterified with ethylene glycol in the presence of zinc acetate as catalyst (Figure 2.2) 2. Furthermore, a large number of acrylic acid derivatives is produced by transesterification of methyl acrylate with different alcohols

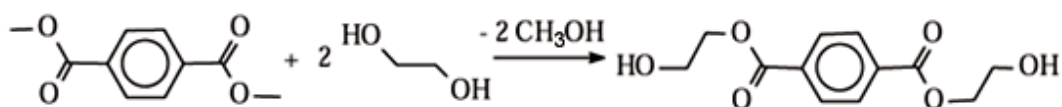


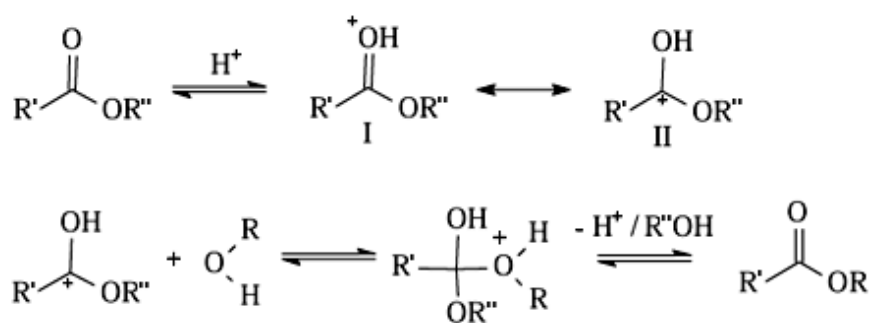
Figure 2.2 Transesterification of dimethylterephthalate with ethylene glycol

2.1.1 Acid – catalyzed of transesterification reaction

The transesterification process is catalyzed by Brnsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 oC and more than 3 h to reach complete conversion. The methanolysis of soybean oil, in the presence of 1 mol% of H₂SO₄, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and methanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 h, respectively.

The alcohol/vegetable oil molar ratio is one of the main factors that influences the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the ideal alcohol/oil ratio has to be established empirically, considering each individual process.

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in figure 2.3, for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H⁺.



R = alkyl group of alcohol

R' = carbon chain of polymer

Figure 2.3 Mechanism of the acid – catalyzed transesterification of polymer

According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.1.2 Base – catalyzed of transesterification reaction

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reaction. Due to this reason, together with the fact that the alkaline catalysts are less corrosives than acidic compounds, industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in figure 2.4. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2)11,40, from which the alkyl ester and the corresponding anion of the diglyceride

are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol.

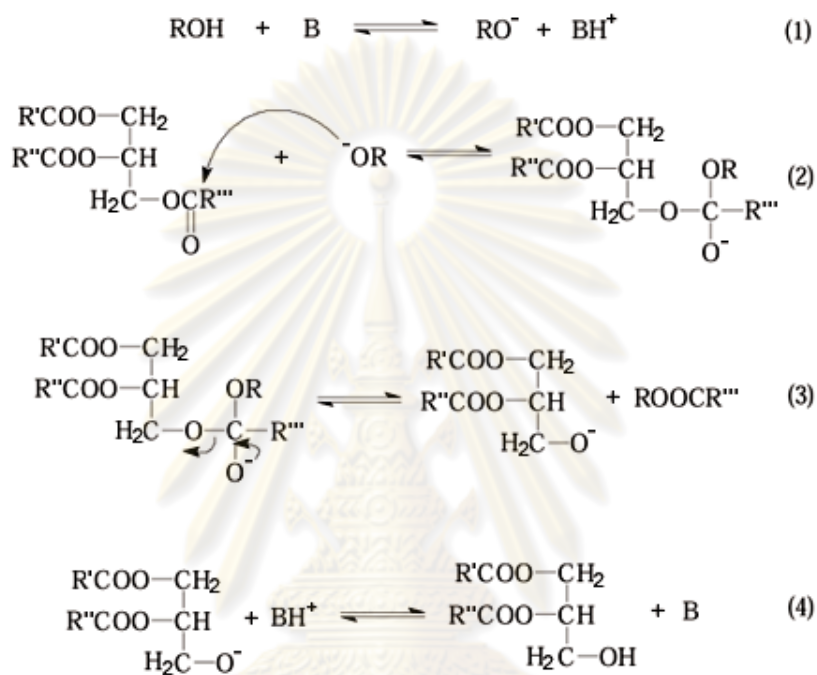


Figure 2.4 Mechanism of the base – catalyzed tranesterification of polymer

R = alkyl group of alcohol

R' = carbon chain of polymer

Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields (> 98%) in short reaction times (30 min) even if they are applied at low molar concentrations (0.5 mol%). However, they require the absence of water which makes them inappropriate for typical industrial processes³⁰. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just by increasing the catalyst concentration to 1 or 2

mol%. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation (Figure 2.5). This undesirable saponification reaction reduces the ester yields and considerably difficults the recovery of the glycerol due to the formation of emulsions³⁰. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters [4].

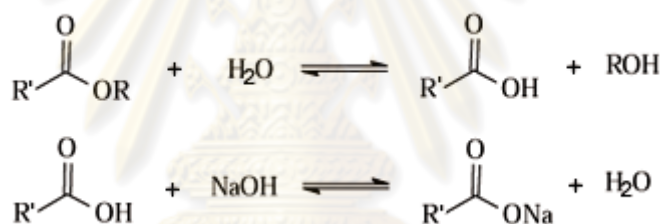


Figure 2.5 Saponification reaction of the produced alkyl ester

R = alkyl group of alcohol

R' = carbon chain of polymer

2.3 Literature reviews

In 2007, Liptik V., T. and coworker developed procedure for the simultaneous determination of phthalic acid isomers; the procedure includes the preparation of diisoamyl esters by reaction with isoamyl alcohol in a benzene solution in the presence of sulfuric acid with the distillation of an azeotrope mixture of benzene with water, the neutralization of acid with triethylamine, and the separation of esters by gas-liquid chromatography on a steel column (1 m × 3 mm) filled with Chromaton N-AW-HMDS

with 5% Apiezon L in the temperature programming mode with flame-ionization detection. The time of separation is 13 min. The time of the sample preparation step is 2 – 2.5 h. The lower determination limit is 20 ng. The procedure allows the determination of phthalic acids in the concentration range from 0.02 to 2 mg/L in liquid samples and from 0.03 to 3 mg/m³ in air [5].

In 2003, Kurokawa H. and coworker used Aluminium triisopropoxide (AIP) promoted the methanolysis of polyethylene terephthalate (PET) to form monomers, dimethylterephthalate (DMT) and ethylene glycol (EG), in an equimolar ratio. The methanolysis at 200°C in methanol with an AIP catalyst gave DMT and EG in 64% and 63% yields, respectively. The yields were increased by using a toluene/methanol mixed solvent containing 20–50 vol.% toluene; maximum yields, 88% for DMT and 87% for EG, were obtained at 20 vol.% toluene. These results indicate that the rate of methanolysis strongly depends on the solubility of PET. The results of GPC analysis suggest that the methanolysis of PET in the absence of the catalyst includes three steps. In the first step, the depolymerisation occurred at a tiemolecule connecting PET crystals and the chain length was shortened to about 1/3. The shortened chain was depolymerized to oligomers in the second step. The GPC curve of the oligomers tailed to low molecular weight, clearly indicating that the depolymerization took place at random positions on the polymer chain. The third step, the depolymerisation from the oligomers to the monomers, was promoted only in the presence of the AIP catalyst [6].

In 2003, Guclu G. and coworker study neutral hydrolysis of waste polyethylene terephthalate (PET) has been carried out with different amounts of water and different catalysts, in the presence of xylene. The organic solvent made it possible to employ very little amounts of water, lower temperatures and pressures and providing concentrated ethylene glycol (EG) solutions in contrast with previous methods, yielding intermediates

suitable for PET preparation. These intermediates were characterized by FTIR spectroscopy, acid value (AV), hydroxyl value (HV), viscosity average molecular weight (Mv) determinations as well as by DSC. Multiple heating/cooling runs in DSC apparatus were carried out and a deconvolution procedure was applied using Haarhoff–Van der Linde (HVL) function to verify the presence of the same components and also to compare polymerization tendency of these various hydrolysis products [7].

In 2005, Xi G. and coworker study on depolymerization of waste polyethylene terephthalate (PET) into monomer bis(2-hydroxyethyl terephthalate) (BHET) in order to obtain with high purity and significant yield. The glycolysis reaction was carried out at 196 °C with a weight ratio of ethylene glycol (EG) to PET from 0.5 to 6; weight ratio of catalyst to PET from 0 to 1.5% and time of 1e5 h in the presence of zinc acetate as a transesterification catalyst. The optimal conditions are reaction time of 3 h, weight ratio (EG to PET) of 5, weight ratio (catalyst to PET) of 1% and the yield of BHET is 85.6% under these conditions. The glycolysed products were separated into monomer and oligomers and identified by IR, DTA (differential thermal analysis), ¹H NMR and ¹³C NMR [8].

In 2002, Holland B. G. and coworker analysis concentrations of diethylene glycol (DEG) and isophthalate unit present in two commercial polyesters by using Fourier transform infrared (FT-IR) spectroscopy and by a lowering of the melting point as measured by differential scanning calorimetric (DSC) method. To carry out the FT-IR spectroscopic analysis, it was necessary to synthesize poly(diethylene glycol terephthalate) and poly(ethylene isophthalate). With FT-IR spectroscopy, it was possible to measure with reasonable accuracy the DEG content of the two commercial polyesters, whereas by DSC, the presence of IPA in one material affected the result. Cyclic oligomers of the two commercial polyesters were extracted using chloroform and

analyzed by preparative high performance liquid chromatography and electrospray mass spectrometry. It was found that polymer containing more DEG units promoted the formation of oligomers less than trimer in size, whilst the polymer containing more IPA units promoted the formation of oligomers greater than trimer in size [9].

In 2002, Yang Y. and coworker study on Methanolytic depolymerization of polyethylene terephthalate (PET) was carried out in a stainless stirred autoclave at temperatures of 523–543 K, pressures of 8.5–14.0MPa, and with a weight ratio of methanol to PET from 3 to 8. The solid products mainly composed of dimethyl terephthalate and small amounts of methyl-(2-hydroxyethyl) terephthalate, bis (hydroxyethyl) terephthalate, dimers and oligomers were analyzed by high performance liquid chromatography (HPLC). The liquid products composed of ethylene glycol and methanol were analyzed by gas chromatography (GC). It was found that both the yield of dimethyl terephthalate and the degree of PET depolymerization were seriously influenced by the temperature, weight ratio of methanol to PET, and reaction time, whilst the pressure has insignificant influence when it is above the critical point of methanol. The optimal depolymerization conditions are temperature of 533–543 K, pressure of 9.0–11.0 MPa, and the weight ratio (methanol to PET) from 6 to 8. The depolymerization of several PET wastes collected from the Chinese market was investigated under the optimal conditions [10].

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CHAPTER III

EXPERIMENTAL

3.1 Materials and Chemicals

Polyethylene Terephthalate (PET) (bottle grade and fibre grade) was supplied from Thai PET Resin Co., Ltd. (Rayong, Thailand). Dimethyl terephthalate (DMT), ethylene glycol (EG), diethylene glycol (DEG) and sodium hydroxide were reagent or analytical grades purchased from Merck (Germany). Dimethyl isophthalate (DMI) was analytical grades purchased from Fluka, diethyl phthalate was purchased from Sigma-Aldrich and analytical grade methanol was purchased from RCILabscan (Bangkok, Thailand).

3.2 Instrument and Equipments

The gas chromatographic (GC) analyses was carried on HEWLETT PACKARD model HP 6890, performed on DB-WAX column model J&W 125-7062, column length 60.0 m diameter 530 μm and film thickness 1.00 μm with flame-ionization detector (FID). Fourier transform infrared spectroscopy (FT-IR) was carried on BRUKER model TENSOR27, measured with a infrared spectrophotometer at 700 – 600 cm^{-1} . Mini Reactor was carried on HACH mini reactor with temperature control.

3.3 Methanolysis of isophthalic acid in PET

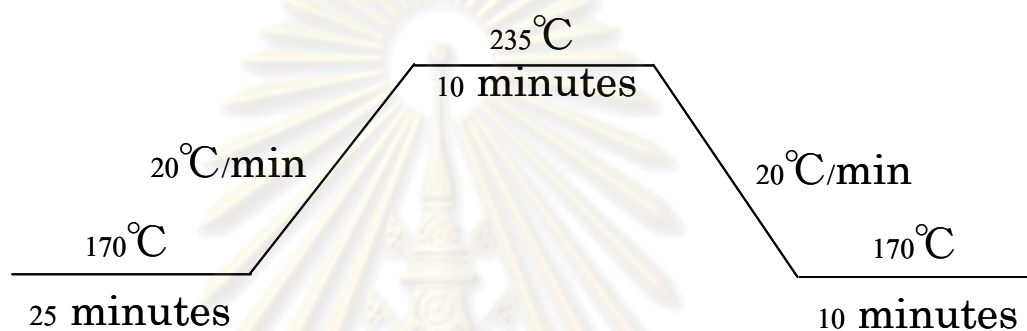
3.3.1 Gas chromatographic condition

The separation of a mixture containing dimethylterephthalate (DMT), dimethylisophthalate (DMI), ethylene glycol (MEG) and diethylene glycol (DEG) was carried out by gas chromatography (GC) under the following condition

Column: Capillary column DB-WAX model J&W 125-7062, 60 m length, 530 μm diameter, 1.00 μm film thickness.

Inlet: 250°C temperature, 20.00 psi pressure, 50:1 split ratio, 583.4 ml/min split flow, Helium as a carrier gas.

Temperature program: Initial temperature 170°C, 20°C/min until 235°C holding time 10 minute then decrease 20°C/min until 170°C



Detector: Flame Ionization Detector (FID)

Temperature: 250°C

Hydrogen flow: 30.0 ml/min

Air flow: 300.0 ml/min

Makeup Gas Type: Nitrogen

Makeup flow: 23.0 ml/min

3.3.2 Determination of methanolysis of isophthalic acid in PET resin

3.3.2.1 Calibration curve of dimethylisophthalate in PET

Standard dimethylisophthalate concentration at 0.9 mol%, 2.3 mol%, 4.7 mol% and 9.4% were prepared and analyzed by GC.

3.3.3 Sample preparation for methanolysis of isophthalic acid in PET resin

3.3.3.1 Efficiency of catalyst in methanolysis of isophthalic acid in PET resin

Weighting 0.3 g of PET sample and dissolve in 5 ml methanol in the presence of catalyst into a glass tube of mini-reactor and heated up to 150°C. Similar processes of methanolysis were also carried out with various types of sample and catalyst (Table 2.1).

Table 3.1 Type of sample, catalyst and reaction time in the methanolysis of isophthalic acid in PET resin.

Sample	Catalyst	Solvent
Fiber PET resin	Acid catalyst	Methanol
Bottle PET resin		
Fiber PET		
Bottle PET		
Fiber PET resin	Antimony (III) acetate in acid solution	Methanol
Bottle PET resin		
Fiber PET		
Bottle PET		
Fiber PET resin	Cobalt (II) acetate in acid solution	Methanol
Bottle PET resin		
Fiber PET		

Bottle PET		
Fiber PET resin	Base catalyst	Methanol
Bottle PET resin		
Fiber PET		
Bottle PET		

3.3.3.2 Effect of reaction type for methanolysis of isophthalic acid in PET resin

PET samples were dissolved in methanol in methanolysis reaction in the presence of catalyst using open reflux and mini-reactor experiments. Different reaction processes of methanolysis were also carried out at various temperatures. Open reflux was carried out at 200°C but mini-reactor was carried out at 150°C.

3.3.3.3 Optimization of reaction time for methanolysis of isophthalic acid in PET resin

Weighting 0.3 g of PET sample and dissolved in methanol in the presence of catalyst in a glass tube of mini-reactor and heated to 150°C. Similar process of methanolysis was also carried out with various types of reaction time by increasing reaction time at 10 min interval until reaction was completed.

3.3.3.4 Optimization of PET particle size for methanolysis of isophthalic acid in PET resin

Weighting various size of 0.3 g of PET sample and dissolved in in the presence of catalyst in a glass tube of mini-reactor and heated to 150°C. Similar processes of methanolysis were also carried out with various size of PET samples (PET chip resin size 2 mm, grinding PET size 355 µm – 425 µm by coffee mill and grinding PET size 425 – 710 µm by freezer mill).

3.3.3.5 Optimization of amount of PET sample for methanolysis of isophthalic acid in PET resin

Various amount of PET samples were dissolved in methanol in the presence of catalyst in a glass tube of mini-reactor and heated to 150°C. Similar processes of methanolysis were also carried out with various amount of PET samples (PET fiber and PET bottle grade at 0.1 – 1 g).



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CHAPTER IV

RESULT AND DISCUSSION

4.1 Methanolysis of isophthalic acid in PET

Two reaction types of methanolysis of isophthalic acid in PET including open reflux on hotplate at temperature 200°C and closed reaction in mini-reactor at temperature 150°C were carried out. It was found that methanolysis of PET resin was complete in a closed reaction in mini-reactor at temperature 150°C. Under various types of catalysts and with many trials on various concentrations of catalysts, it was found that based catalysts were suitable for methanolysis of isophthalic acid in PET resin. Therefore, this study had focused on the effect of catalyst type, concentration of base catalyst, sample types, sample weight and reaction time.

4.1.1 Effect of catalysts for methanolysis of isophthalic acid in PET

The catalysts for the methanolysis of PET, such as Antimony (III) acetate, Cobalt (II) acetate, acid catalyst and hydroxides of alkali metals were investigated. Result of effect of various types of catalysts for methanolysis of isophthalic acid in PET at 150°C in closed reaction in mini-reactor with sample amount of 0.3g, particle size of PET sample between 355 µm – 425 µm, and reaction time 20 min are shown in Table 4.1.1.

Table 4.1.1 Effect of type of catalysts for methanolysis of both fiber grade PET and bottle grade PET in a closed reaction in mini-reactor with 0.3 g of PET sample, sample size between 355 μm – 425 μm , and 20 min. reaction time.

Sample types	Sample weight	Type of Catalysts	Reaction Time	Physical appearance
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	Antimony (III) acetate	20 min	Cloudy
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	Cobalt (II) acetate	20 min	Cloudy
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	H_2SO_4	20 min	Cloudy
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	NaOH	20 min	Clear
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	Antimony (III) acetate	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	Cobalt (II) acetate	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	H_2SO_4	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	NaOH / methanol	20 min	Clear

The methanolysis of isophthalic acid in PET was complete using NaOH in methanol but incomplete with other catalysts such as Antimony (III) acetate, Cobalt (II) acetate and sulfuric acid (H_2SO_4) (Figure 4.1). Therefore, the best catalyst for methanolysis of isophthalic acid in PET was NaOH in methanol.

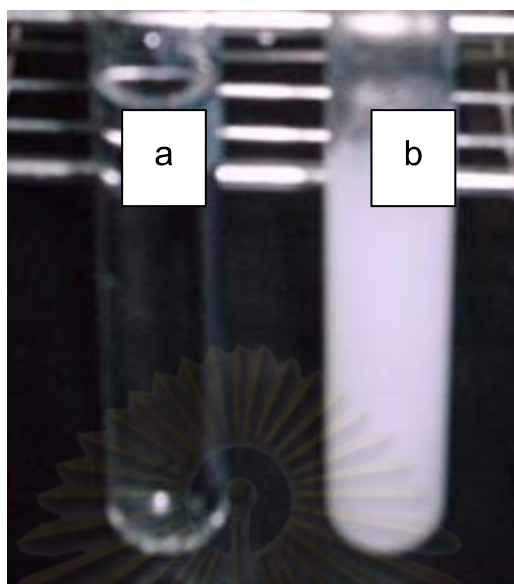


Figure 4.1 Pictures showed the reaction mixture of methanolysis of isophthalic acid in PET with various types of catalysts (a) prepared by base catalyst with 1% NaOH in methanol, (b) prepared by Antimony (III) acetate, Cobalt (II) acetate and sulfuric acid.

4.1.2 Optimization of concentration of NaOH in methanolysis of isophthalic acid in PET

The concentration of NaOH in methanolysis of isophthalic acid in PET was investigated. The reaction was performed in a mini reactor, 150°C, 3 g sample, particle size 355 μm – 425 μm , and 20 min. reaction time. The result showed that at 1% concentration of NaOH, the reaction was completed in 20 min. as shown in Table 4.1.2. At higher concentration, however, the reaction gave cloudy appearance as shown in Fig. 4.2. Thus the appropriate amount of NaOH for methanolysis of isophthalic acid in PET resin was 1%.

Table 4.1.2 Effect of concentration of NaOH for methanolysis of both fiber grade PET and bottle grade PET in a closed reaction in mini-reactor using 0.3g of PET sample, sample size between 355 μm – 425 μm , and 20 min. reaction time.

Sample types	Sample weight	Concentration of NaOH	Reaction Time	Physical appearance
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	2% NaOH / Methanol	20 min	Cloudy
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	3% NaOH / Methanol	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	2% NaOH / Methanol	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	3% NaOH / Methanol	20 min	Cloudy

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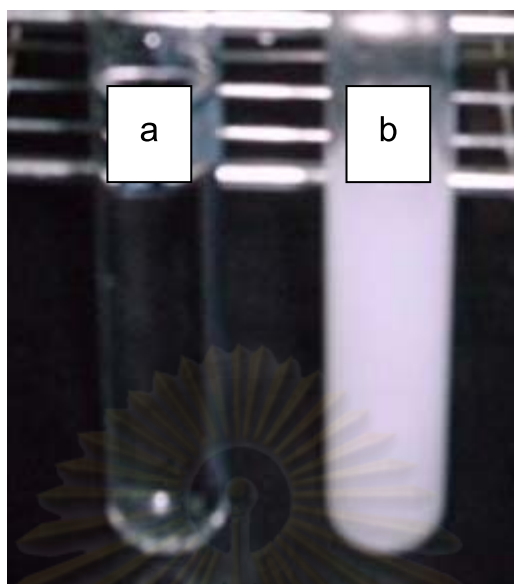


Figure 4.2 Pictures showed the reaction mixture of methanolysis of isophthalic acid in PET with various concentrations of NaOH in methanol (a) prepared by methanolysis with 1% NaOH in methanol, (b) prepared by methanolysis with 2% NaOH and 3% NaOH in methanol.

4.1.3 Optimization of particle size of PET for methanolysis of isophthalic acid in PET

The effect of various PET particle sizes in methanolysis of isophthalic acid in PET at 150°C in a mini-reactor in the presence of 1% NaOH in methanol (5 m), 0.3g sample and 20 min. reaction time were investigated and the results are shown in Table 4.1.3. It was found that the particle size between 355 μm – 425 μm were the most suitable. It was also observed that at higher particle size the reaction was incomplete as shown by a cloudy reaction mixture in Fig. 4.3.

Table 4.1.3 Effect of particle size of both fiber grade PET and bottle grade PET in methanolysis using 0.3g of PET, 1% NaOH in methanol and 20 min. reaction time in closed reaction in a mini-reactor.

Sample types	Sample weight	Concentration of NaOH	Reaction Time	Physical appearance
PET fiber resin (Particle size between 1500 μm – 2500 μm)	0.3 g	1% NaOH / Methanol	20 min	Not dissolve
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
PET bottle resin (Particle size between 2000 μm – 3000 μm)	0.3 g	1% NaOH / Methanol	20 min	Not dissolve
Grinding PET bottle resin (Particle size between 425 μm – 710 μm)	0.3 g	1% NaOH / Methanol	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear

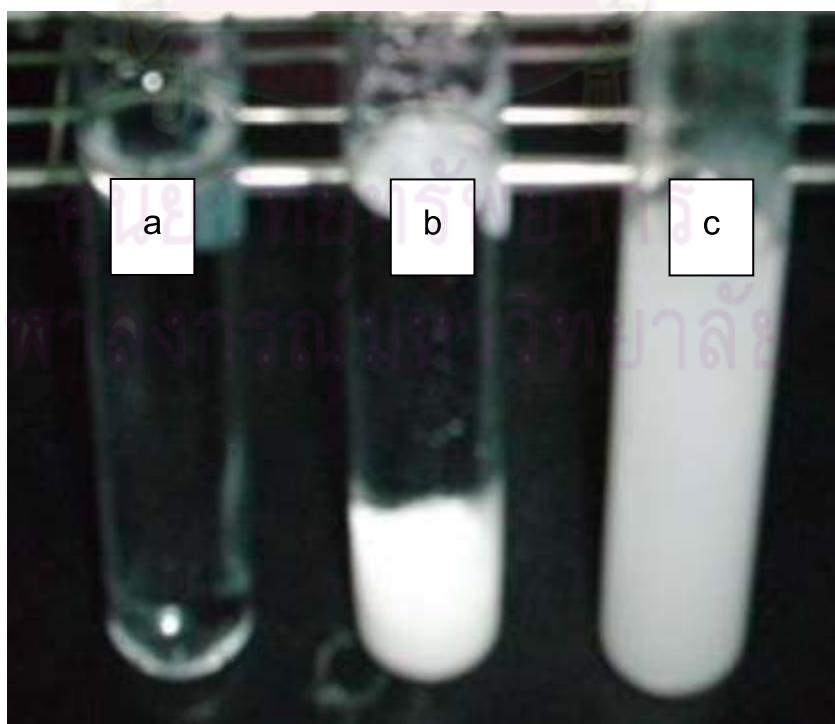


Figure 4.3 Pictures showed the reaction mixture of methanolysis of isophthalic acid in PET at various size of both fiber grade PET and bottle grade PET (a) PET fiber resin & PET bottle resin (Particle size between 355 μm – 425 μm), (b) PET fiber resin & PET bottle resin (Particle size between 1500 μm – 2500 μm), (c) PET bottle resin (Particle size between 425 μm – 710 μm).

4.1.4 Optimization of the amount of PET sample in methanolysis of isophthalic acid in PET

The reaction was carried out using various amounts of PET samples in closed reaction in mini-reactor at 150°C in the presence of 1% NaOH in methanol (5 mL), particle size of PET sample between 355 μm – 425 μm , 20 min reaction time and the results are shown in Table 4.1.4 and Fig. 4.4. Sample amount of both fiber grade PET and bottle grade PET from 0.1 g – 1 g were used and it was observed that at higher amount of sample the methanolysis of isophthalic acid in PET was incomplete. At sample size less than 0.3 g the reaction gave a clear reaction mixture.

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Table 4.1.4 Effect of sample amount of both fiber grade PET and bottle grade PET in methanolysis in closed reaction in mini-reactor with PET particle size between 355 μm – 425 μm , 1% NaOH and 20 min. reaction time.

Sample types	Sample weight	Concentration of NaOH	Reaction Time	Physical appearance
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	1 g	1% NaOH / Methanol	20 min	Not dissolve
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.5 g	1% NaOH / Methanol	20 min	Cloudy
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.2 g	1% NaOH / Methanol	20 min	Clear
Grinding PET fiber resin (Particle size between 355 μm – 425 μm)	0.1 g	1% NaOH / Methanol	20 min	Clear
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	1 g	1% NaOH / Methanol	20 min	Not dissolve
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.5 g	1% NaOH / Methanol	20 min	Cloudy
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.2 g	1% NaOH / Methanol	20 min	Clear
Grinding PET bottle resin (Particle size between 355 μm – 425 μm)	0.1 g	1% NaOH / Methanol	20 min	Clear

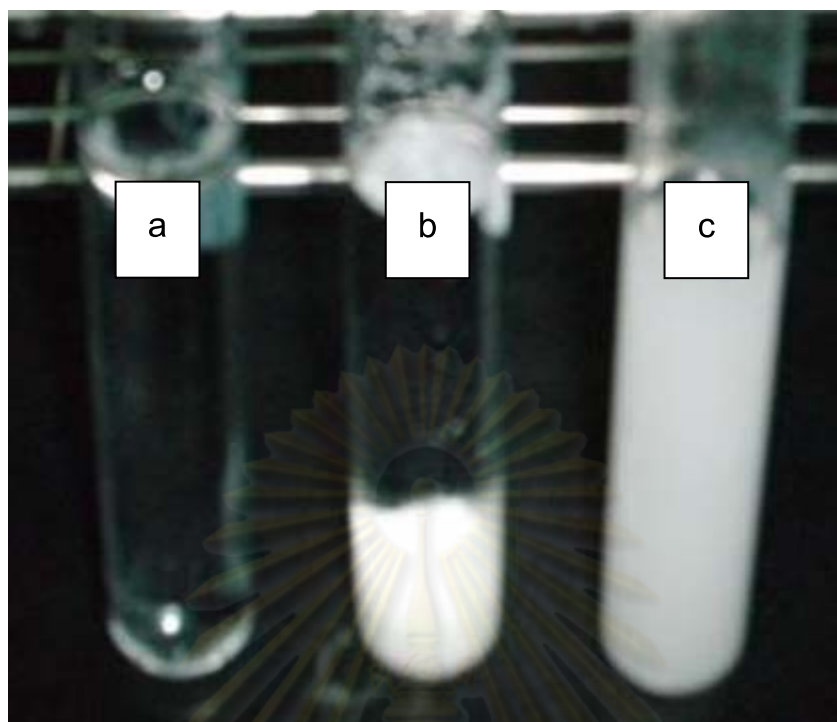


Figure 4.4 Pictures showed the reaction mixture after methanolysis of isophthalic acid in PET using various amount of both fiber grade PET and bottle grade PET (a) grinding PET fiber grade resin & PET bottle grade resin (Particle size between $355\ \mu\text{m}$ – $425\ \mu\text{m}$) sample amount lower than 0.3g, (b) grinding PET fiber grade resin & PET bottle grade resin (Particle size between $355\ \mu\text{m}$ – $425\ \mu\text{m}$) sample amount more than 1.0g, (c) grinding PET fiber grade resin & PET bottle grade resin (Particle size between $355\ \mu\text{m}$ – $425\ \mu\text{m}$) sample amount 0.5g.

4.1.5 Optimization of reaction time in mini-reactor for methanolysis of isophthalic acid in PET

Various reaction times in methanolysis of isophthalic acid in PET resin were investigated in a mini-reactor at 150°C in the presence of 1% NaOH in methanol (5 ml), PET particle size between $355\ \mu\text{m}$ – $425\ \mu\text{m}$ and 0.3 g sample and the results are shown in Table 4.1.5. Reaction times from 10 min – 60 min were investigated. It was found that

the reaction time of 20 min. was appropriate to complete the reaction as shown in Table 4.1.5 and Fig. 4.5.

Table 4.1.5 Effect of reaction time in methanolysis of both fiber grade PET and bottle grade PET in closed reaction in mini-reactor using PET particle size between 355 μm – 425 μm , 0.3g sample, 1% NaOH in methanol.

Sample types	Sample weight	Concentration of NaOH	Reaction Time	Physical appearance
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	10 min	Cloudy
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	20 min	Clear
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	30 min	Clear
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	40 min	Clear
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	50 min	Clear
Grinding PET fiber & bottle resin (Particle size between 355 μm – 425 μm)	0.3 g	1% NaOH / Methanol	60 min	Clear

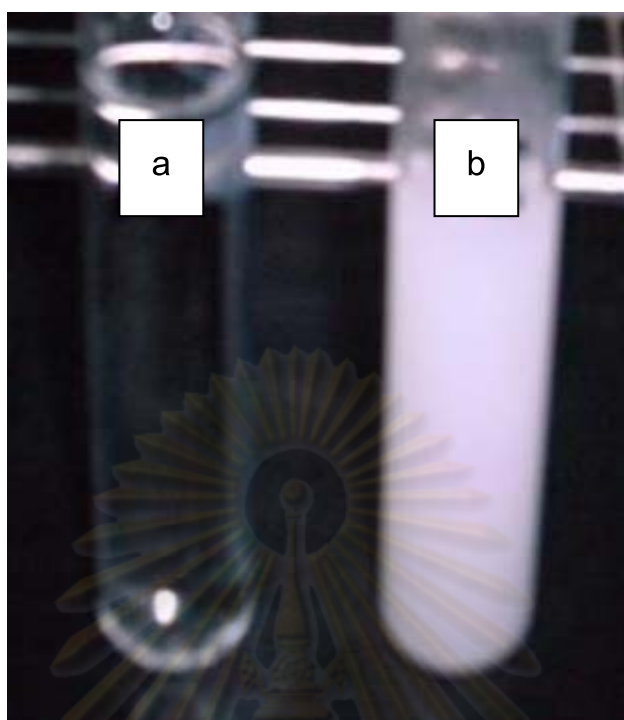


Figure 4.5 Pictures showed the result from methanolysis of isophthalic acid in PET at various reaction time of both fiber grade PET and bottle grade PET (a) grinding PET fiber grade resin & PET bottle grade resin (Particle size between 355 μm – 425 μm) reaction time higher than 20 min, (b) grinding PET fiber grade resin & PET bottle resin grade (Particle size between 355 μm – 425 μm) reaction time 10min.

4.2 GC condition for analysis of dimethylisophthalate

4.2.1 GC separation of mixture of dimethylisophthalate and dimethylterephthalate

A mixture obtained from mixing of methanol, ethylene glycol, diethylene glycol, dimethylterephthalate (DMT), dimethylisophthalate (DMI) and diethylphthalate as an internal standard was separated by gas chromatography using temperature programming mode as shown in the experimental section. The analysis time was 51 minute. The GC chromatogram is shown in Fig. 4.6. It was clear that the separation of

DMT and DMI was very good and they did not overlap with the peak of internal standard. Thus quantitative analysis was further carried out.

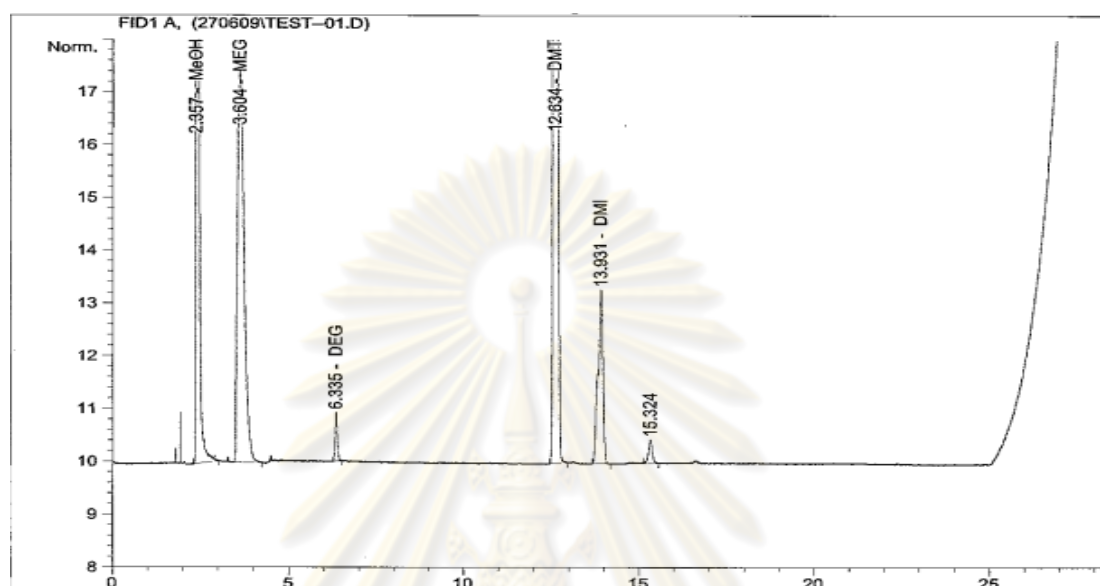


Figure 4.6 GC chromatogram of a mixture of methanol, ethylene glycol, diethylene glycol, dimethylterephthalate, dimethylisophthalate and diethylphthalate.

4.2.2 Analysis of reaction mixture obtained from methanolysis of isophthalic acid in PET

When methanolysis of isophthalic acid in PET was completed, the reaction mixture was subjected to GC analysis using the same condition as in 4.2.1. and the gas chromatograms are shown in Figure 4.7 and 4.8.

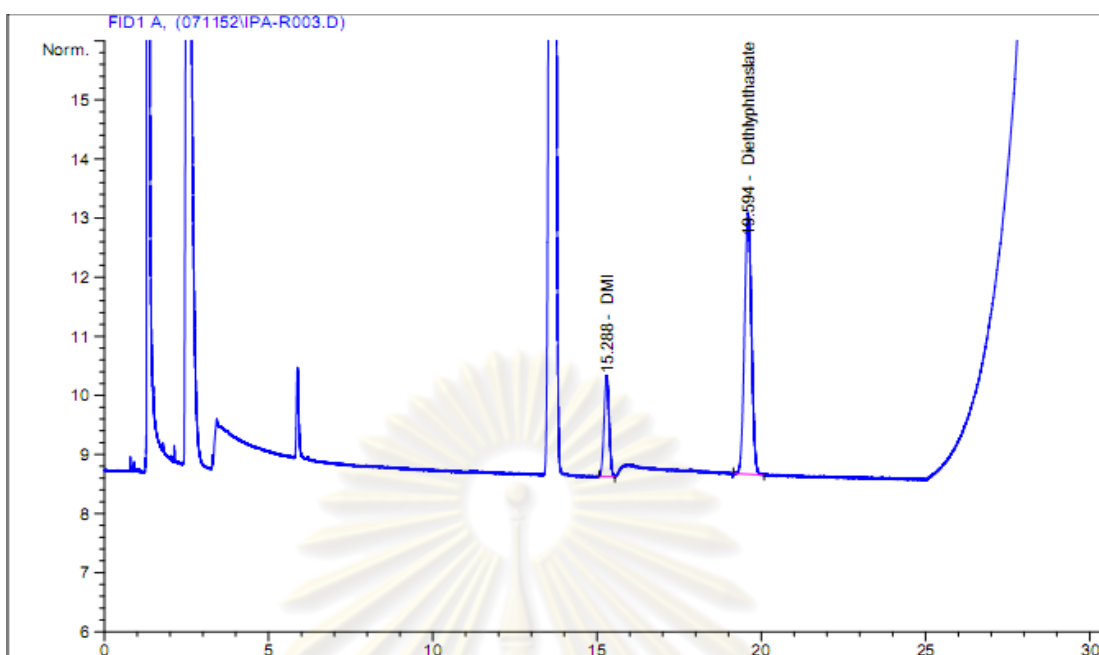


Figure 4.7 GC chromatogram of mixture obtained from methanolysis of isophthalic acid in PET fiber grade resin.

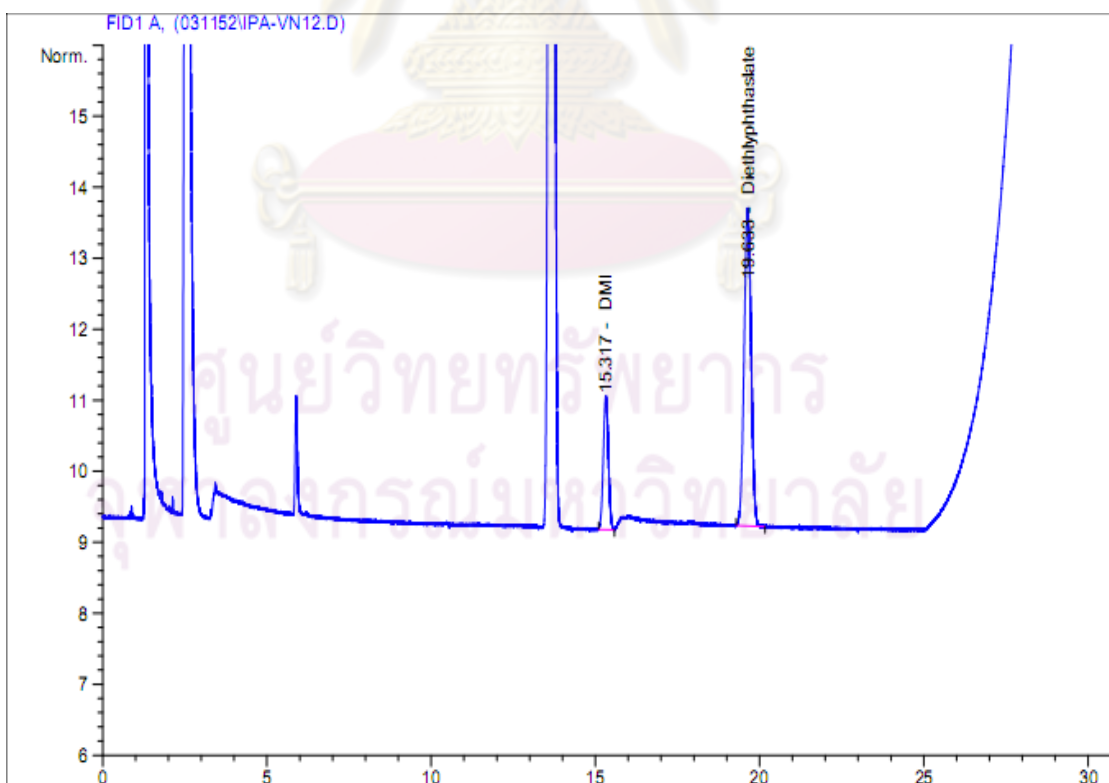


Figure 4.8 GC chromatogram of mixture obtained from methanolysis of isophthalic acid in PET bottle grade resin.

4.3 Determination of IPA in PET resin

4.3.1 In-house method of determination of IPA in PET resin using FT-IR

Determination of IPA in PET by FT-IR is an in-house method. The calibration curve at wave number 632 cm^{-1} in IR spectrum was used and the result is shown in Figure 4.9. The standard IPA concentrations at 0.9 mol%, 2.3 mol%, 4.7 mol% and 9.3 mol% in PET were used to construct a calibration curve as shown in Figure 4.10 and the result of analysis of IPA in both fiber grade and bottle grade PET sample in the same batch no. is shown in Table 4.3.1.

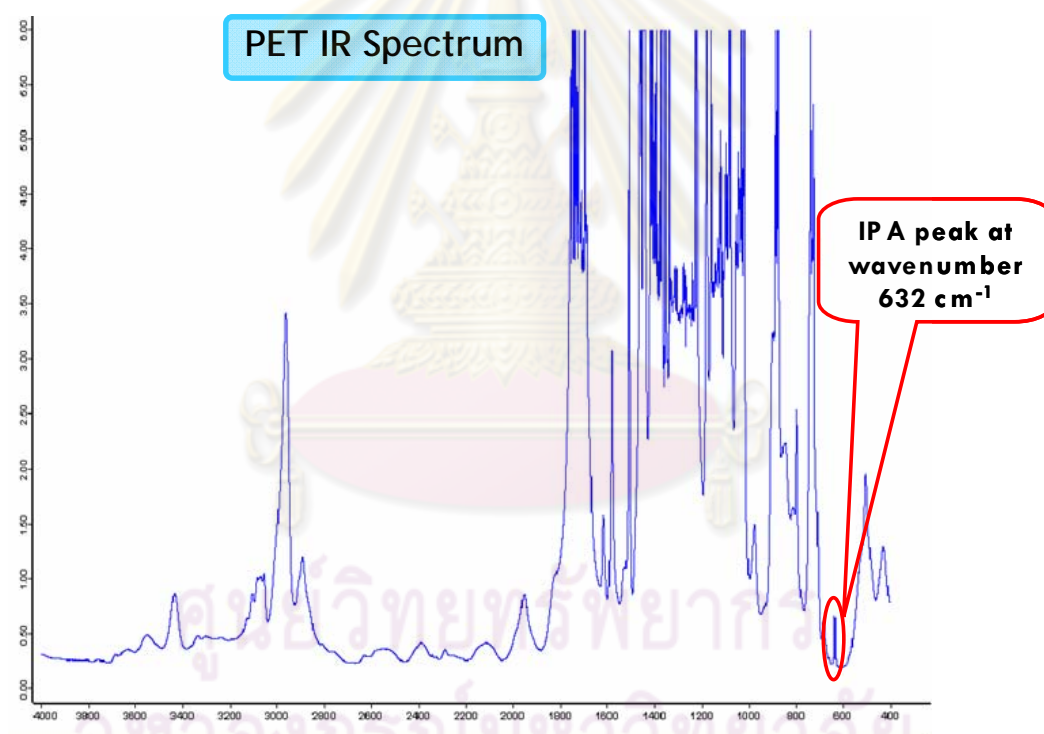


Figure 4.9 FT-IR spectrogram of both bottle and fiber grade PET resin.

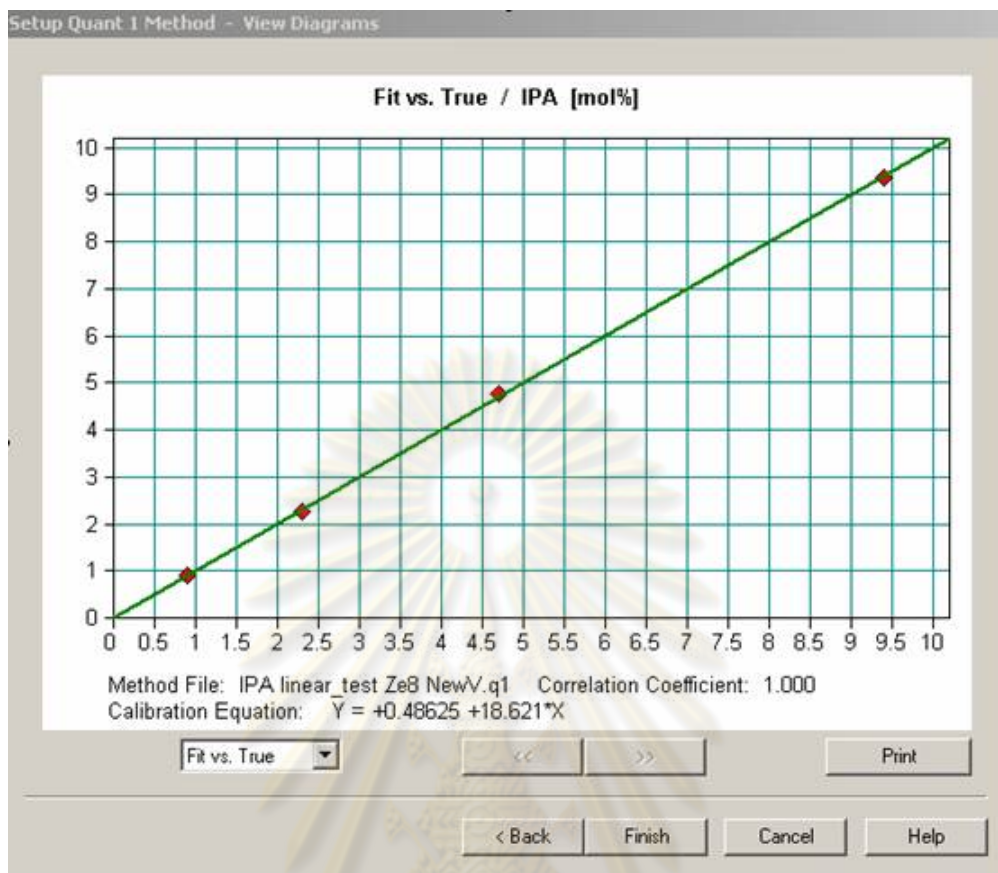


Figure 4.10 Calibration curve of standard IPA in PET by FT-IR.

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Table 4.3.1 The result from FT-IR determination of IPA in both bottle grade and fiber grade PET and checked for repeatability using 5 samples in one batch and repeat 3 times in each sample.

PET sample	Sample name	IPA in PET by FT-IR		PET sample	Sample name	IPA in PET by FT-IR	
		Repeat no.	IPA content			Repeat no.	IPA content
PET bottle resin	A	1	1.870	PET fiber resin	A	1	1.779
		2	1.836			2	1.756
		3	1.825			3	1.735
	B	1	1.902		B	1	1.671
		2	1.874			2	1.635
		3	1.873			3	1.639
	C	1	2.197		C	1	1.602
		2	2.195			2	1.596
		3	2.185			3	1.574
	D	1	1.854		D	1	1.693
		2	1.846			2	1.688
		3	1.821			3	1.677
	E	1	1.783		E	1	1.812
		2	1.767			2	1.787
		3	1.780			3	1.764

4.3.2 Determination of IPA in PET resin using Gas chromatography

The standard curve of DMI with internal standard diethylphthalate was constructed using concentration of IPA at 0.9 mol%, 2.3 mol% and 4.7 mol% in PET and it is shown in Fig. 4.11. The result of determination of IPA in PET by GC is shown in Table 4.3.2.

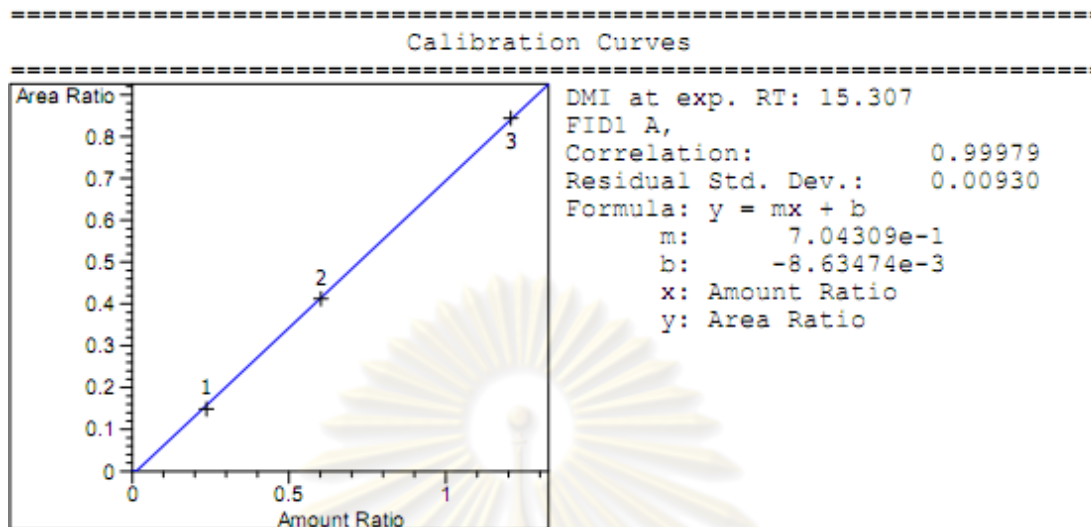


Figure 4.11 Calibration curve of DMI by GC using diethylphthalate as internal standard.

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Table 4.3.2 The results of determination IPA in both bottle grade and fiber grade PET by GC using the same batch of sample as in FT-IR method and checked repeatability for 7 samples and repeat 3 times in each sample.

PET sample	Sample name	IPA in PET by GC		PET sample	Sample name	IPA in PET by GC	
		Repeat no.	IPA content			Repeat no.	IPA content
PET bottle resin	A	1	1.733	PET fiber resin	A	1	1.768
		2	1.743			2	1.793
		3	1.720			3	1.788
	B	1	1.749		B	1	1.776
		2	1.742			2	1.790
		3	1.753			3	1.785
	C	1	1.805		C	1	1.815
		2	1.795			2	1.794
		3	1.803			3	1.796
	D	1	1.766		D	1	1.809
		2	1.759			2	1.800
		3	1.770			3	1.802
	E	1	1.752		E	1	1.749
		2	1.749			2	1.772
		3	1.751			3	1.756
	F	1	1.819		F	1	1.756
		2	1.818			2	1.750
		3	1.812			3	1.753
	G	1	1.704		G	1	1.821
		2	1.694			2	1.813
		3	1.689			3	1.802

4.3.3 Comparison of determination of IPA in PET resin between FT-IR method and Gas chromatographic method

Isophthalic acid (IPA) was a comonomer in PET process to improve some properties in PET resin such as transparency in PET bottle and decrease melting point in injection process in making PET bottle or fiber. Thus the amount of IPA needs to be strictly controlled otherwise the bottle manufacturing process would be altered. Moreover, price of IPA was more expensive than other raw materials of PET producing. Therefore, accuracy and precision of analysis IPA in PET was so important. Process capability (Cpk) was one of statistical tools for investigation of fluctuation of determination of IPA content in PET by comparing with manufacturing specification. The formula on calculation of Cpk is shown in Figure 4.12 and theoretical Cpk should be higher than 1.00 which indicates that the process was producing product that conforms to specifications and is on target. If Cpk is lower than 1.00, it indicates the high variation of analysis or PET process control is shifted to upper or lower specification. Therefore, PET manufacturing process control IPA content in both fiber grade and bottle grade PET in a range of 1.6 – 1.9 mol%.

$$C_{pk} = \min \left(\frac{USL - \mu}{3 \times \hat{\sigma}}, \frac{\mu - LSL}{3 \times \hat{\sigma}} \right)$$

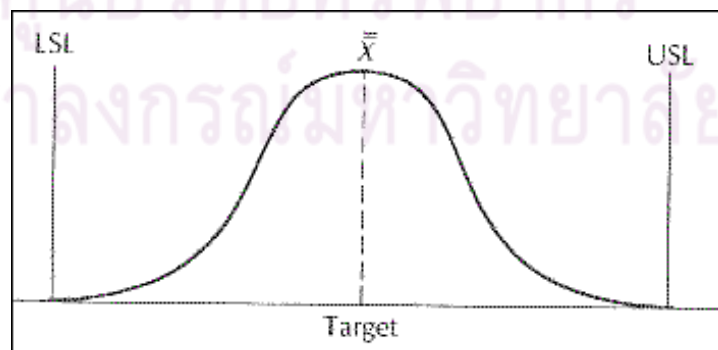


Figure 4.12 Formula for calculation of process capability (Cpk) and normal distribution curve for Cpk > 1.00

Comparison of process capability (Cpk) of determination of analysis IPA in PET between in-house method by FT-IR and GC method are shown in Table 4.3.1 and Table 4.3.2, respectively. It was shown that the process capability (Cpk) of FT-IR method was 0.20 that indicated high variation in analysis method and some result out of specification as shown in Figure 4.13.

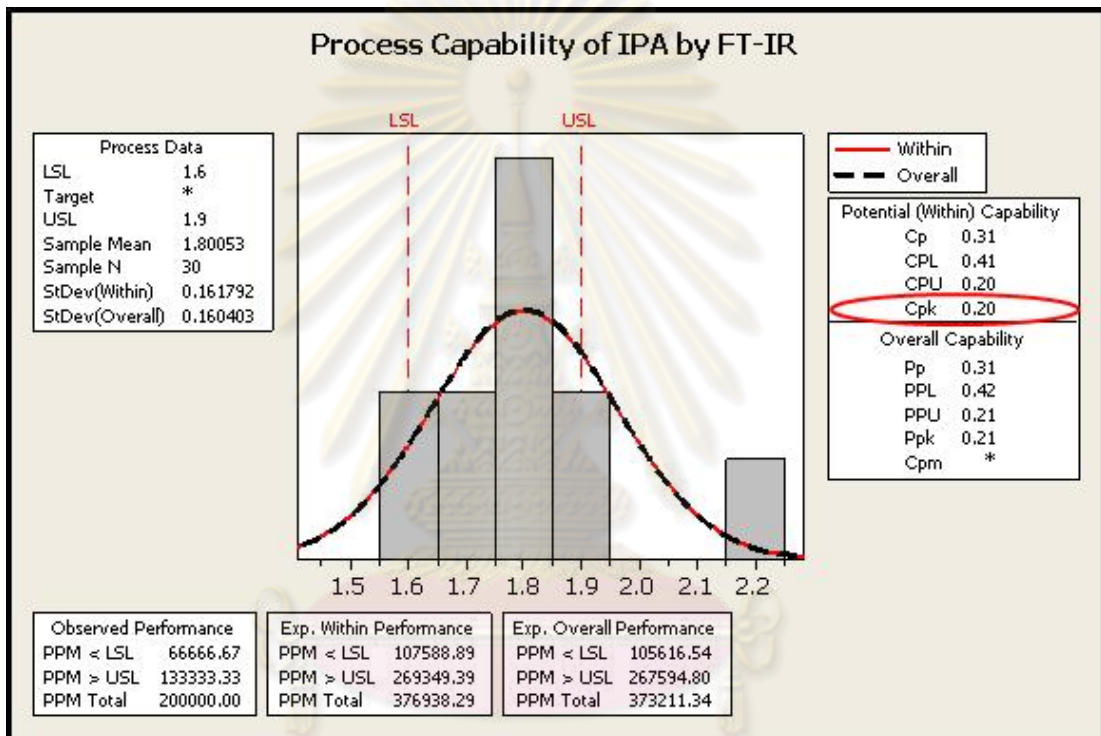


Figure 4.13 Process capability (Cpk) of determination of IPA in PET by FT-IR.

Meanwhile, the process capability (Cpk) for GC was 1.23 which indicated that the analysis of IPA in PET by GC had low deviation and on target in manufacturing specification as shown in figure 4.14.

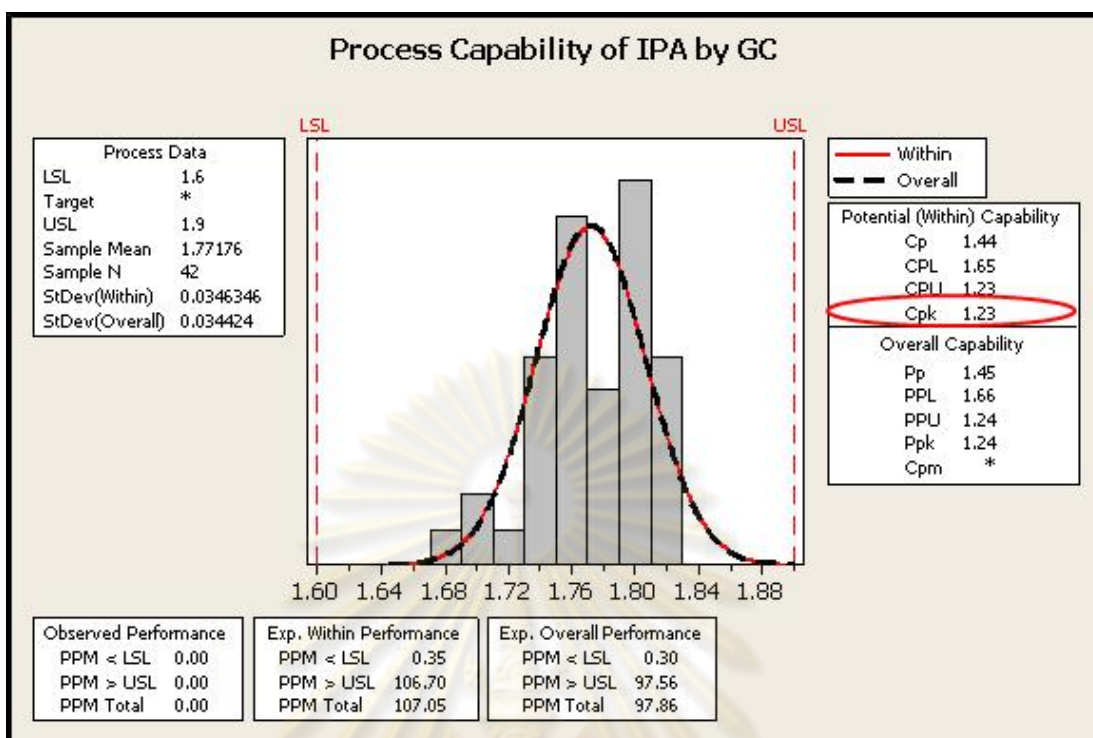


Figure 4.14 Process capability (Cpk) of determination of IPA in PET by GC.

4.3.4 Statistical method for quantitative analysis of determination of IPA in PET resin by Gas chromatography

One of statistical tools for analysis of the precision of determination of IPA in both fiber grade and bottle grade PET resin was gage capability by using Range (R) values which represent the difference between measurements made on the same unit using the same GC instrument and the results are shown in Table 4.3.3.

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Table 4.3.3 The range (R) values of determination of IPA in both bottle and fiber grade PET with repeatability of 7 samples in one batch and repeat 3 times for each sample.

PET sample	Sample name	Measurement no.			R
		1	2	3	
PET bottle resin	A	1.733	1.743	1.720	0.023
	B	1.749	1.742	1.753	0.011
	C	1.805	1.795	1.803	0.010
	D	1.766	1.759	1.770	0.011
	E	1.752	1.749	1.751	0.003
	F	1.819	1.818	1.812	0.007
	G	1.704	1.694	1.689	0.015
	Average				0.011
PET fiber resin	A	1.768	1.793	1.788	0.025
	B	1.776	1.790	1.785	0.014
	C	1.815	1.794	1.796	0.021
	D	1.809	1.800	1.802	0.009
	E	1.749	1.772	1.756	0.023
	F	1.756	1.750	1.753	0.006
	G	1.821	1.813	1.802	0.019
	Average				0.017

The standard deviation of measurement error, $\hat{\sigma}_{\text{gage}}$, can be estimated as follows:

$$\hat{\sigma}_{\text{gage}} = \frac{\bar{R}}{d_2}$$

d_2 from theoretical was 1.693 for repeat 3 time (n=3)

It was a common practice to compare the estimate of gage capability to the width of the specification or the tolerance band (Upper specification limit (USL) – Lower specification limit (LSL)) for the part that was being measured. The ratio of 6 gage capability to the tolerance band was often called the precision-to-tolerance or P/T ratio.

$$\frac{P}{T} = \frac{6\hat{\sigma}_{\text{gage}}}{\text{USL} - \text{LSL}}$$

Upper specification limit for IPA content in quality control for PET manufacturing process was 1.6 mol% and lower specification limit was 1.9 mol%. Therefore, value of P/T in theoretical calculation at 0.1 or less often implies adequate gage capability. The result of GC analysis of IPA in PET from Table 4.3.3 indicated that P/T ratio for PET fiber grade was 0.010 and bottle grade was 0.015 and both P/T ratios were lower than 0.1 which indicated that the analysis of IPA in PET by GC had high precision and low deviation.

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CHAPTER V

CONCLUSION

In this research, methanolysis of isophthalic acid (IPA) in both fiber grade and bottle grade PET resin in a closed mini-reactor in the presence of 1% sodium hydroxide (NaOH) in methanol was carried out in order to convert IPA to dimethylisophthalate (DMI) which was then analyzed using gas chromatography. Optimal particle size, sample amount and reaction time were found between 355 μm – 425 μm , 0.3g and at least 20 min., respectively, for completely conversion of IPA to DMI and quantitative analysis by gas chromatography (GC). The method validation between in-house method using FT-IR and a new method using GC was carried out by using statistical tools. Process capability (Cpk) of GC method was 1.23 compare with Cpk of in-house FT-IR method at 0.20 which meanted that GC method had a low deviation and on target in quality control of PET manufacturing process using lower specification limit (USL) at 1.6 mol% to upper specification limit (USL) at 1.9 mol%. Precision-to-tolerance (P/T ratio) which was one of the statistical tools to imply that precision of GC method to the total tolerance was 0.010 for PET fiber grade and 0.015 for bottle grade. The result of P/T ratio above were lower than 0.1 of the theoretical figure which implied that analysis of IPA in PET by GC had high precision and low deviation.

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