

**USE OF HYDROLYSIS PRODUCTS OF
POLYETHYLENE TEREPHTHALATE SCRAPS
TO PRODUCE ALKYD BASED PAINT**

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(08/8053)



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Department of Materials Science and Engineering

University of Moratuwa

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Thesis submitted in partial fulfillment of the requirements for the degree Master of
Philosophy in Materials Science & Engineering

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ABSTRACT

In modern world, plastics play a significant role in our daily life. However Sri Lankans' still have not introduced proper waste management system to daily increasing plastic garbage.

Polyethylene terephthalate (PET) is one of the main plastic used in day today life as packaging material, soft drink and mineral water bottles. Sri Lankan peoples alone consumes 6.5 million PET bottles per month but only 1.5 million bottles collected for recycling. This gives clear indication about the role of PET in environmental pollution.

This report present development of effective chemical recycling process to de-polymerize PET waste into its initial monomers and use of de-polymerized products to synthesized alkyd resin which can be use in coating industry.

Depolymerization of PET was done by hydrolysis method to extract terephthalic acid(TPA) . Here Na_2CO_3 was successfully used as hydrolysis agent instead of highly corrosive NaOH . This overcome the common disadvantages of NaOH .

At 170 °C, 35 minutes and 1:4 PET: EG (ethylene glycol) mole ratio 78.89% PET was reacted with Na_2CO_3 without any catalyst.

Recovered terephthalic acid was used to replace Phthalic anhydride in alkyd resin. Due to the inability of conventional alcoholysis method to making alkyd resin from TPA, a new methodology was developed. New Process was successfully incorporated to produce long oil alkyd resin with soya oil, glycerin, maleic anhydride and recovered TPA. Under this new method alkyd processing time was greatly reduced and minimum time achieved was 120 minutes at 280 °C.

Practical application of this project to the local PET waste will help to reduce the plastic land fill in Sri Lanka and also provide more beneficial effects to the alkyd paint industry by reducing production time and raw material cost.

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LIST OF ABBREVIATION

PET	Polyethylene Terephthalate
TPA	Terephthalic Acid
PA	Phthalic Anhydride
MA	Maleic Anhydride
EG/MEG	Mono Ethylene Glycol
FTIR	Fourier Transform Infrared Spectroscopy
PE	pentaerythritol

Alkyd Calculation

M	Molecular Weight
m	Number of moles
m_0	Total moles present at start of reaction
e_0	Total equivalent present at start of reaction
e_a	Number of acid equivalent
e_b	Number of hydroxyl equivalent
F	Functionality
P	Percentage completion of reaction
AN/AV	Acid Value/Acid Number
HN	Hydroxyl number
W	Weight



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1. INTRODUCTION

Polyethylene terephthalate (PET) is a thermoplastic polymer resin of the polyester family made from Terephthalic acid (TPA) and Ethylene glycol (EG) ^[1] by direct esterification or transesterification processes ^[2]. Large amounts of this material are consumed in manufacture of textile fibers, audio and video tapes, X-ray films, food packaging and soft drinks and mineral water bottles.

The overall world consumption of PET amounts to about 13 million tons per year which 1.5 million tones are used in the manufacture of various types of packaging ^[5]. Sri Lankan consumers use over 6.5 million bottles per month and only 1.5 million collects for recycling. ^[4]

The empty pet packaging is discarded by the consumer after use and it becomes a waste PET (post consumer PET). The huge amount of post consumer PET cause serious environmental pollution, because commonly PET content reaches about 12% in municipal plastic waste showing a slow rate of natural decomposition.

Recycling of post consumer PET more important, firstly to reduce the increasing municipal council waste and secondly to recover or generate value added materials from low cost sources by converting them into valuable materials.

PET can be recycled by mechanically or chemically. However mechanical recycling gives less value to Sri Lanka since the main application of PET in here is beverage and mineral water bottles. Those bottles are categorized under food graded items and mechanically recycled materials are not allowed to use in food graded items.

Glycolysis, methanolysis and hydrolysis are the main chemical recycling processes used for PET ^[3, 6]. Among these, hydrolysis is again divided into three processes called neutral, acidic & basic hydrolysis.

Basic hydrolysis of PET is usually carried out with the use of aqueous alkaline solution of NaOH or KOH ^[8] to de-polymerize PET into its initial chemicals (i.e. terephthalic acid and ethylene glycol). However main disadvantage of these reagents

is, they are more aggressive & highly corrosive .Handling of such aggressive reagents in industrial scale is more difficult and involve with additional costs.

Other disadvantage is TPA and EG can be taken through hydrolysis process is not widely used to produce food graded product because of the cost associated with purification of recycled TPA is high.

Therefore the first goal of this project is to find less aggressive reagent to replace sodium hydroxide in basic hydrolysis process to de-polymerize PET and second Goal is to develop efficient method to use recovered TPA successfully in making of alkyd resin (non food graded product).

Then the second part of the project was aimed to use extracted TPA from PET to synthesized alkyd resin. Use of TPA in alkyd resin synthesis is not very common due to the various problems. One reason is TPA required high temperature than its other isomers. (isophthalic and phthalic acid/anhydride). Another reason is that PA is cheaper than TPA and readily available in market. But compare to the other isomers TPA based resins give good, whether resistance to the alkyd-based paints. Therefore the second goal of the project was to find a suitable method to synthesized TPA based oil modified alkyd resin with commercially acceptable quality.

Finally , the overall aim of this project was to produce alkyd resin by using extracted TPA as main dibasic acid. To achieve this aim following objectives were expected to be fulfill during the project time period .

- To overcome drawbacks involved with basic hydrolysis process to recover TPA from PET scraps.
- To find suitable method to synthesize alkyd resin efficiently from TPA
- To study properties of alkyd resin produced with recovered TPA.
- To reconsider suitable formula for industrial application.

2. LITERATURE SURVEY

2.1 Polyethylene Terephthalate

Polyethylene terephthalate (PET) is a thermoplastic polymer resin of the polyester family. ^[1]

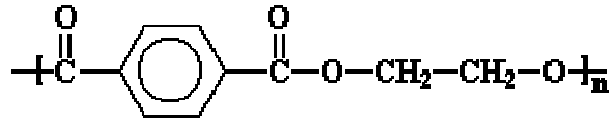


Figure 2-1: Chemical structure of polyethylene terephthalate

2.1.1 History of PET

According to the literature PET was first synthesized in 1941^[2]. In 1953 PET was used to production of textile fibers ^[2]. Initial PET polymers were in crystalline form and hence not used to produce bottles. Amorphous PET was started to produce late 1965^[2] and that provided good toughness and transparency requirement for blow molded bottles. Now, these bottles are extensively used for storing carbonated soft drinks and mineral water.



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2.1.2 Properties of PET

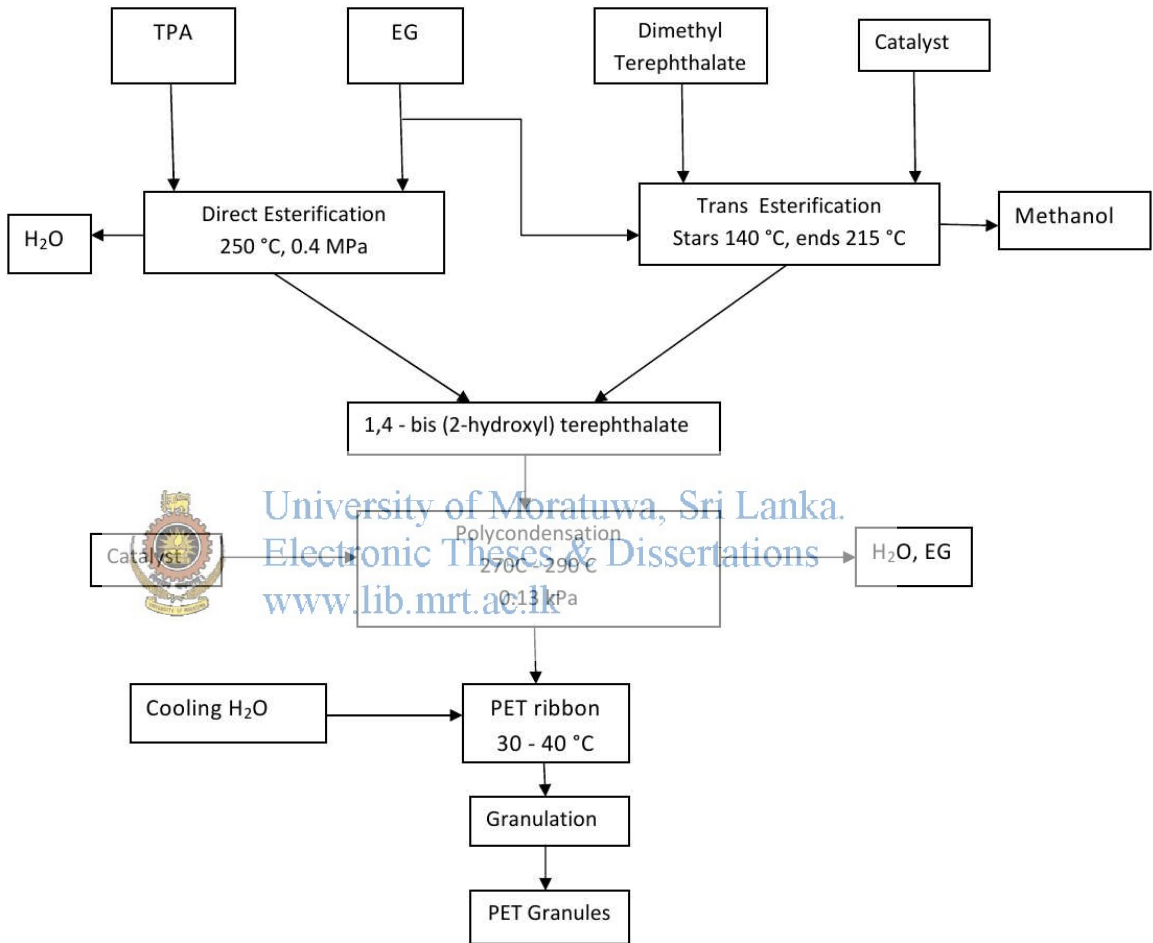
PET has molecular formula of (C₁₀H₈O₄)_n. Amorphous and crystalline densities of the PET are 1370 kg/m³ and 1455 kg/m³ respectively. Table 2-1 shows some other important properties of PET ^[4].

Table 2-1: Properties of PET

Tensile strength	55–75 MPa
Glass transition temperature	75 °C
melting point	260 °C
Thermal conductivity	0.24 W/(m·K)
Specific heat (c)	1.0 kJ/(kg·K)
Refractive Index	1.5750

2.1.3 Production of PET

PET is produced by direct esterification reaction of terephthalic acid with ethylene glycol but at early 1940's due to the insufficient purity of TPA it was synthesized by the trans-esterification of dimethyl terephthalate with ethylene glycol ^[2]. Figure 2-2 illustrates the trans and direct esterification methods used for production of PET.



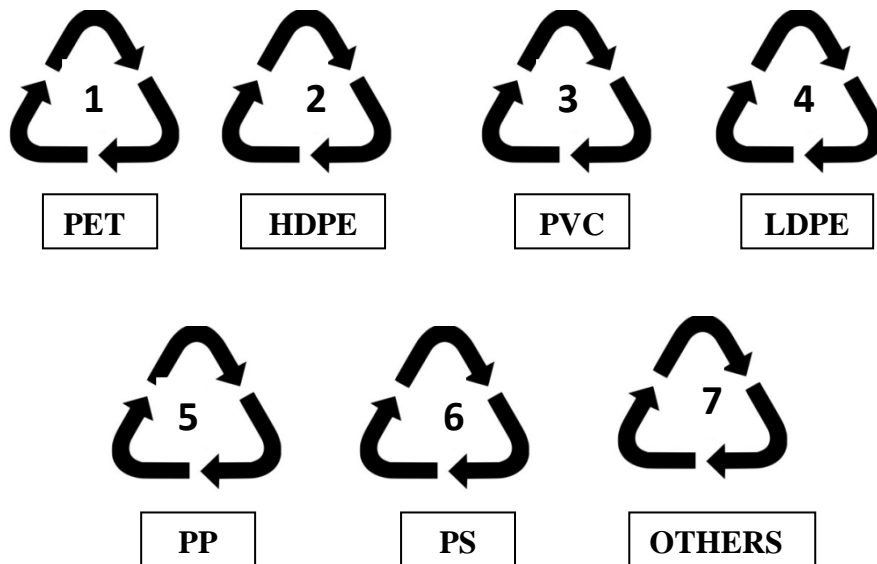
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Figure 2-2 :Preparation of polyethylene terephthalate
Source: Synthetic Polymers, Technology, Properties and Applications', 1st edition

2.1.4 Identification of PET items

To illustrate the recoverable nature of packaging, the American Society of Plastics Industry developed a design that has become the norm ^[3]. This design consist three

arrows chasing one another coupled with the numbering system that identifies the nature of the material, allows the correct identification of PET.



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2.1.5 Polyethylene Terephthalate Recycling

PET can be recycled using various methods. Basically all these methods can be divided in to two categories.

- (1). Mechanical recycling
- (2). Chemical recycling

Mechanical Recycling

Mechanical recycling of PET bottles requires following steps,

- I. Washing
- II. Grinding
- III. Pelletizing
- IV. Blending with virgin polymer

Third and fourth steps are not compulsory. Some PET product making factories use grinded materials directly for the production or mix with virgin materials without doing third step.

Disadvantages of mechanical recycling

- (1). Microscopic level physical contaminations are difficult to remove. ^[3]
- (2). Use of 100 % re-grinded or re-pelletized PET may affect final properties of the product.
- (3). Use of mechanically recycled (grinded) PET is not recommended for food graded items (due to various contaminations).

However the mechanical recycling is economical than chemical recycling and also more environmental friendly.

Chemical Recycling

The most common chemical recycling techniques used for PET are glycolysis, methanolysis, and hydrolysis.

Glycolysis

In glycolysis method, recovered PET is made to react (under pressure at 180 - 240°C) ^[6] with excess amount of ethylene glycol. Bishydroxyethylterephthalate (BHET) is the main product which can be obtained from this process. Melt filtration method is then used to purify the BHET under pressure. That will help to remove most of the physical impurities. Then it is treated with carbon to remove chemical impurities ^[3].

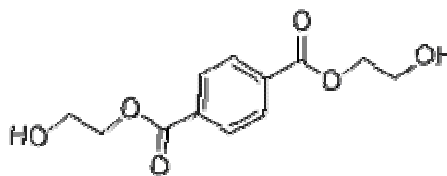


Figure 2-4: Structure of BHET

Methanolysis

As the name implies PET methanolysis is based on the treatment of PET with methanol. This process should be carried out at relatively high temperatures

(180 – 280°C) ^[6] and pressure (20 - 40 atm) ^[6]. Main products obtained through methanolysis process are dimethyl terephthalate (DMT) and ethylene glycol (EG). The reaction proceeds usually in the presence of typical transesterification catalysis, the most widely used being zinc acetate ^[6]. Other than that magnesium acetate, cobalt acetate and lead dioxide are commonly used as catalysts ^[6].

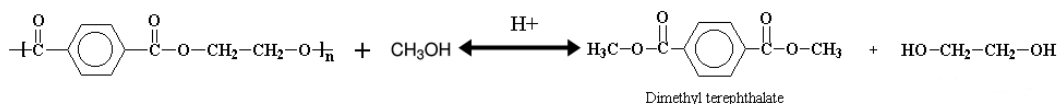


Figure 2-5: Chemical de-polymerization of post-consumer PET by methanol

Purified products of the methanolysis usually obtained by distillation or crystallization.

Disadvantages of methanolysis

- Some of the organic impurities present with reaction products cannot be completely removed. (this may cause some poor colour)
- Continuation of methanolysis process is difficult. (Introducing the solid PET wastes into the methanolysis reactor under high pressure is difficult). ^[6]

Hydrolysis.

Hydrolysis process can be carried out under three different conditions; namely neutral, acidic or basic ^[6].

Neutral hydrolysis of PET generates terephthalic acid and ethylene glycol (Figure 2.6). This process requires high temperature and high pressure with no additives ^[7] and the reaction time ranges from a few to 30 minutes.

In acidic hydrolysis process PET is reacted with an excess amount of strong acid in solution. (E.g. concentrated sulfuric acid). Here the reaction temperature ranges from room temperature to 95°C. Within that temperature strong acid acts in a very short period of time by dissolving the starting PET with formation of terephthalic

acid. Acidic hydrolysis method is not very common because of the high corrosiveness of the reaction system. This method also produces a huge amount of salt solution for neutralizing the employed acid ^[8] .

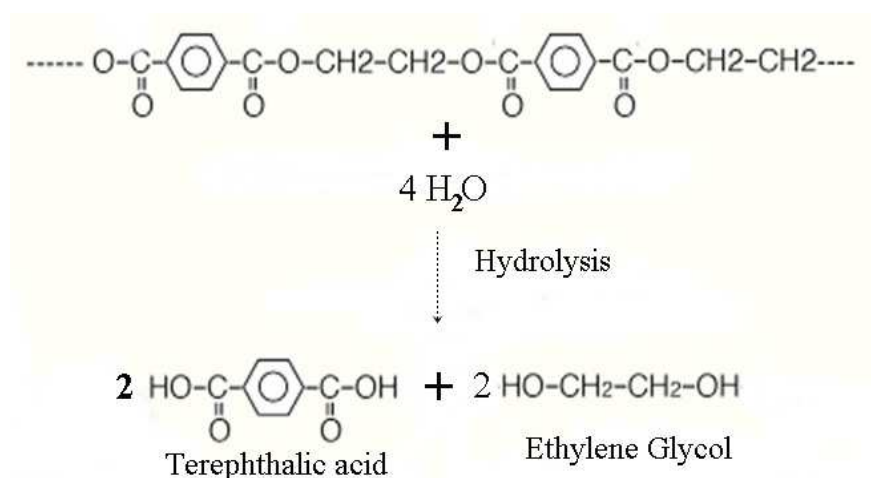


Figure 2-6: Reaction of PET with of high temperature high pressure water.

Source: <http://www.kobelo.co.jp/eneka/p14/sfeos.htm> ^[7]

Alkaline hydrolysis process is almost always carried out by use of alkaline hydroxides most commonly sodium or potassium hydroxides. However use of ammonium hydroxides also possible and if so the process is called as ammonilysis. All these bases lead to formation of aqueous solutions of the corresponding salt of terephthalic acid.

If Sodium hydroxide (NaOH) is used as the base, sodium terephthalate will be the result. (Sodium salt of terephthalate acid) . It is a white paste. To dissolve a 15g of sodium terephthalate 100ml of cold water is required. ^[9]

Mechanical impurities in these solutions can be easily removed by filtering, flocculating or settling process.

2.2 Terephthalic acid (TPA)

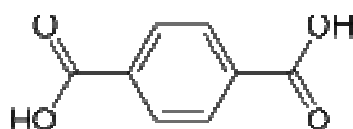


Figure 2-7: Atomic Structure of Terephthalic acid.

Phthalic acid has three isomers and Terephthalic acid is one of them. Above Figure 2-7 shows the atomic structure of terephthalic acid. It finds important use as a starting compound for the manufacture of polyester (specially PET), used in clothing and to make plastic bottles ^[10]. It is also known as 1, 4-benzenedicarboxylic acid, and it has the chemical formula $C_6H_4(COOH)_2$.

2.2.1 History of TPA

In 1836, French chemist Auguste Laurent was first to obtain Phthalic acid. He obtained this by oxidizing naphthalene tetrachloride. However, he believed that this substance was a naphthalene derivative, therefore he gave it the name naphthalenic acid ^[11]. But later Jean Charles Galissard, a chemist from Switzerland, found that the previous supposition was incorrect and he determined its actual chemical formula and gave it the present name ^[11].

2.2.2 Production of TPA

In the laboratory, terephthalic acid can be produced by oxidizing para-derivatives of benzene, or best by oxidizing caraway oil with chromic acid. Caraway oil is a mixture of *cymene* and *cuminal* ^[10].



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Production of TPA in an industry is done by oxidation of *p*-xylene. This is done using acetic acid as solvent, in the presence of a catalyst such as cobalt manganese, using a bromide promoter ^[10].

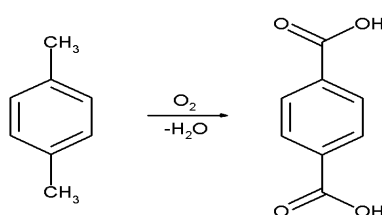


Figure 2-8: Production of TPA

Henkel process is an alternative method which can be used to convert phthalic acid into terephthalic acid.

2.2.3 Properties of terephthalic acid

TPA is white crystal (or powder) with molecular formula of $C_6H_4(COOH)_2$. It has molar mass 166.13 g/mol. Most important property of TPA is water insolubility. At 25 °C solubility of TPA in water is 0.0017 g in 100 g . It's dipole moment is zero.

2.2.4 Identification of TPA

Terephthalic acid can be identified by using following methods.

2.2.5 Fourier transformation infrared spectroscopy (FTIR)

FTIR is most useful method which can be used to identify chemicals that are either organic or inorganic. It can be applied to the analysis of solids, liquids, and gasses^[12]. Also it can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum.

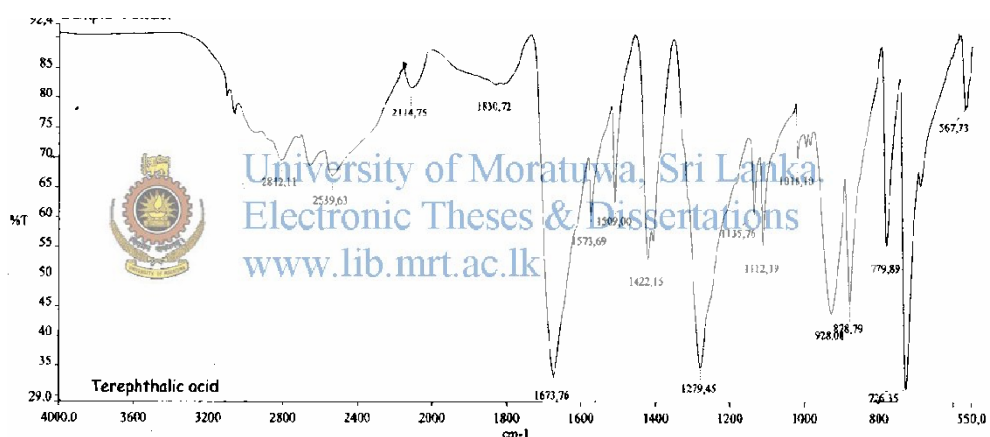


Figure 2-9: FTIR spectrum of Terephthalic acid

Acid Value

Acid value measures the amount of carboxylic acid groups in a chemical compound. (such as a fatty acid, or in a mixture of compounds.) To measure the acid value a known amount of test sample dissolved in organic solvent and then titrated with a potassium hydroxide solution of known concentration and with phenolphthalein as a color indicator.^[13]

2.3 Paints

The main purpose of applying paints on surfaces of objects is to protect them from left in sun light , rain, fog, ice and snow will results corrosion, oxidation, discoloration and etc... Paint also give decorative finish to the surface of the objects.

Main ingredients of the paints are,

1. solvent, medium or matrix
2. resin
3. pigment (If pigment is omitted material is usually called as varnish ^[14])
4. Additives

2.3.1 Resins (binders)

The binder provides the physical structure to support and contain the pigments and additives. It binds itself to these components and to the metal surface, hence its name. It also acts somewhat as a skin: the amounts of oxygen, ions, water, and ultraviolet (UV) radiation that can penetrate into the cured coating layer depend to some extent on which polymer is used.

Type of Binders

1. Epoxies
2. Acrylics
3. Polyurethanes
4. Polyesters
5. Alkyds
6. Chlorinated Rubbers
7. Other Binders
 - I. Epoxy Esters
 - II. Silicon-Based Inorganic Zinc-Rich Coatings

2.3.2 Alkyds in paints

In commercial use since 1927 ^[15] , alkyd resins are among the most widely used anticorrosion coatings. They are one-component air-curing paints ^[16] and, therefore, are fairly easy to use. Alkyds are relatively inexpensive. Alkyds can be formulated into both solvent-borne and waterborne coatings .

Table 2-2: Consumption of synthetic resins in Paints and coatings 1999 ^[17]

Type of Resin	Millions of Pounds
Alkyd	738
Acrylic	955
Epoxies	275
Other Resins	1702
Total Resins	3670

Source: Paints and coatings to 2004 Report - The Freedonia Group, Inc.



Alkyd resins represent a class of polymers that are used in surface coating formulations because of their low cost and versatility. The term “alkyd” is derived from “al” of alcohol and “cid” of acid; “cid” was later changed to “kyd.”^[18]

The main materials used for preparing alkyd resins are polyhydric alcohols (polyols) and dibasic acid (or corresponding anhydrides) together with the modifying oil.^[19]

Theoretically, any polyol or polyacid can be used for the manufacturing of alkyd Resins. However, when considering processability, paint performance and pricing, few of them have commercial acceptance for industrial applications.

2.3.3 Acids used in alkyd resins

Table 2.3 shows most common polybasic acids and polyols which are used as raw materials to produce alkyd resins.

Table 2-3: Common polybasic acids & alcohols used in Alkyd resins

Acids	Alcohols
Phthalic anhydride	Ethylene glycol
Isophthalic anhydride	glycerol
Succinic acid	penterythritol
Adipic acid	Diethylene glycol
Sebacic acid	1,2-propylene glycol
Trimellitic anhydride	Trimethylol propane
Maleic anhydride	Neo-pentyl glycol



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Due to ease of handling, good balance of properties, and economy, orthophthalic acid is the most important polybasic acid for alkyds. It is almost exclusively used in its anhydride form. Isophthalic acid is more suitable than phthalic anhydride if tougher, faster drying, and more chemical- and heat-resistant coating is required^[18]. Isophthalic acid has these properties because of the meta position of its carboxyl groups. It makes the formation of intermolecular cyclic esters more unlikely with isophthalic acid. This improves the molecular weights and viscosities of the alkyds^[18].

Longer aliphatic dibasic acids, in particular adipic and azelaic acid, may be used as minor ingredients to impart flexibility in the alkyd structure^[18]. Tri- and tetra-functional acids or anhydrides, such as trimellitic and pyromellitic anhydride, are incorporated to produce alkyds of high acid value. Chlorinated and brominated compounds (e.g., tetrachloro- and tetrabromophthalic anhydride) are used to impart fire retardant properties to the resin^[18].

2.3.4 TPA in Alkyd Paints

Solubility of TPA in water is about 0.0017g in 100g H₂O at 25°C. So TPA acid is often used in exterior coatings where improved hydrolytic stability is required. [25]

2.3.5 Polyols

Usually, mixtures of polyols having a functionality of 2 to 4 are used in an alkyd formulation. Ethylene glycol, diethylene glycol, propylene glycol, and neopentyl glycol are the most important diols; glycerol and trimethylol propane are commonly used triols; and pentaerythritol is the tetraol of choice. The choice of polyol components is mainly responsible for the degree of branching of the alkyd. The flexibility of the resin is also influenced by the distance between the hydroxyl groups-diethylene glycol, for instance, gives a more flexible product than ethylene glycol. Neopentyl glycol, because of its branched structure, gives heat- and hydrolysis-resistant films.

2.3.6 Oil Length and Type of Oils

Depending on the weight percentage of fatty acid in the resin, alkyds are referred to as short oil (<45%), medium oil (45 to 55%), or long oil (>55%). [18]

For alkyds made directly from oils, the oil length is given by,

$$\text{Oil length} = \frac{(\text{mass of oil used to make alkyd resin}) * 100}{(\text{mass of reactants}) - (\text{mass of water evolved in process})}$$

In the coating industry the oil used are all of vegetable or animal type, and they are divided into three broad categories.

1. Drying or Oxidizing;
2. Semi-drying or Semi-oxidizing;
3. Non-drying or Non –oxidizing oils. [21]

If oil can be oxidized it has good drying properties. Oxygen in the air solidifies suitable oils by reacting with them and converting them from a liquid to a solid form. Thin films of these oils spread on a surface can thus act as varnishes, although the drying would be very slow, the surface tacky and the film soft. Semi-drying oils are

used to impart special properties to other oils while non-drying oils are used to produce special paints which are prepared by mixing with other materials. To make these oils suitable for use in paints and varnishes they need to be suitably modified. This was the basis for the development of oil modified alkyds. The different oils are used or blended to maximize their potential and obtain optimum properties.



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Table 2-4: Effect of Oil Length and Type of Oil on the Properties and Uses of Alkyds

Oil Type	Oil Length	Typical Oil	Properties
Oxidizing	$\geq 60\%$	Linseed, safflower, soybean, tall oil, fatty acids; wood oil in blends with other oils; dehydrated castor oil	Soluble in aliphatic solvents; compatible with oils and medium oil length alkyds; good drying characteristics; films are flexible, with reasonable gloss and durability
Oxidizing	45–55%	Linseed, safflower, soybean, tall oil fatty acids; wood oil in blends with Other oils	Soluble in aliphatic or aliphatic–aromatic solvent mixtures; good drying characteristics, durability and gloss
Oxidizing	$\leq 45\%$	Linseed, safflower, soybean, tall fatty acids; wood oil in blends with other oils; dehydrated castor oil	Soluble in aromatic hydrocarbons; low tolerance for aliphatic solvents; usually cured at elevated temperatures either by heating with manganese driers or with urea or melamine formaldehyde resins
Non-oxidizing	40–60%	Coconut oil, castor oil, hydrogenated castor oil	Soluble in aliphatic–aromatic solvent blends; usually used as a plasticizer for thermoplastic polymers such as nitrocellulose
Non-oxidizing	$\leq 40\%$	Coconut oil, castor oil, hydrogenated castor oil	Soluble in aromatic solvents; used as a reactive plasticizer that chemically combines with other resin entities (e.g. melamine–formaldehyde resin)

Source : Solomon, D.H., “The Chemistry of Organic Film Formers”. [20]

2.3.7 Fatty Acids

Fatty acids are merely carboxylic acids with long hydrocarbon chains. They are divided into two main categories “unsaturated” and “saturated”. What is meant here is that the main chain of the fatty acid has either got double bonds in its backbone (unsaturated) ,or it has not (saturated). Any fatty acid or fatty acid blend can be used to make alkyd resin ^[21]. Normally fatty acids are more expensive than their whole oil counter parts. Fatty acids also have following handling problems.

- More corrosive nature of fatty acids necessitates the use of corrosion resistant equipment.
- the high congealing point of certain fatty acids occasionally introduces the need for heating facilities to maintain the acid in a liquid condition during cold water
- Fatty acids are more susceptible to discoloration during storage.

2.4 Alkyd Preparation Methods.

Most commonly used methods are fatty acid process and Mono-glyceride (alcoholysis) process.



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2.4.1 The fatty acid process

In this method, fatty acids, polyol and phthalic anhydride (Acid/ acid anhydride) are added together to reaction kettle and heated to 205 – 232 °C until the required acid number and viscosity obtained.

2.4.2 Monoglyceride/ Alcoholysis Process

This process is also known as alcoholysis process. This is two step process. In first step, try-glyceride oils and polyols which are immiscible with each other, mixed together and heated to form monoglyceride. The conversion can be satisfactorily accomplished without a catalyst by carrying out reaction at sufficiently high temperature (273 °C). However, it is more expedient to carry out reaction at lower temperatures (175 - 210 °F) ^[21] by resorting suitable catalyst. Some catalysts accelerate the rate of conversion by 10-20 times ^[21].

Lime, $\text{Ca}(\text{OH})_2$, PbO is the most common alcoholysis catalysts. Some of the suitable catalysts are indicated in Table 2-5 ^[21].

Table 2-5: Catalyst use in Alcoholysis Process

	Ba	Ca	Pb	Li	Na	Zn
Oxide	X	X	X			X
Hydroxide	X	X		X	X	
Naphthenate	X	X	X	X	X	

The extent of the alcoholysis is followed by checking solubility of the reaction mixture in methanol. Reaction concludes when one part of reaction mixture shows complete solubility in three part of methanol . ^[23]

Alcoholysis is invariably carried out with no solvent present but alkyd esterification may be carried out either in the absence of solvent (fusion cook) or with solvent present (solvent cook).

2.4.3 Fusion cook method

The fusion method is the older process but is still widely used, especially for alkyds of an oil length of 60% or more ^[20]. The reaction is carried out at a temperature of 220 °C to 250 °C, in an the inert gas spurge, which is used for dewatering, also causes some loss of volatile polyols and of phthalic anhydride.

2.4.4 Solvent cook method

In the solvent method, the esterification is performed in the presence of a small quantity of water immiscible solvent, usually xylene. The process is carried out under continuous azeotropic distillation of the solvent. The xylene–water vapor mixture is condensed, the water is separated, and the organic distillate is returned to the reactor. The reaction temperature is governed by the refluxing temperature that, in turn, depends on the amount of xylene used, 5 % being a normal value. In general, the

solvent method offers better control of the resin composition, as there is virtually no loss of raw materials by volatilization or sublimation.

2.5 Water-Borne Alkyds

Water-reducible alkyds are basically conventional alkyd resins based upon saturated or unsaturated oils or fatty acids, polybasic acids and alcohols modified to confer water miscibility^[28]. Typical components are vegetable oils or fatty acids such as linseed, soyabean, castor, dehydrated castor, safflower, sunflower, tung, coconut and tall oil. Acids include, isophthalic, terephthalic, adipic, benzoic, succinic acids and phthalic, maleic and trimellitic anhydrides. Polyols include glycerol, pentaerythritol, trimethylol propane, trimethylol ethane, ethylene glycol, propylene glycol, diethylene glycol, neopentyl glycol, 1:6 hexane diol, 1:4 butanediol

Typical methods of introducing varying degrees of water miscibility are:-

- Initial maleinisation of the fatty acids followed by reaction with polybasic acids and polyols.
- Make the resin using hydroxyl containing prepolymers eg. polyethylene glycol
- Adding specific acid or hydroxyl containing substance towards the end of the reaction
- Styrenation or acrylation of the alkyd, with the monomer blend containing acidic groups.

In the majority of cases solubility is conferred upon the resin by reaction of the terminal carboxyl or hydroxyl groups with basic or acidic materials, typical examples are dimethyl amino ethanol or acetic acid.

The long term stability of the systems is usually enhanced by the addition of water-soluble or miscible co-solvents such as dimethoxy methyl propanol, methoxy propyl acetate, butyl glycol, butylalcohol, *etc.*

2.6 Summary on Past Researches

Since the post consumer PET acting a main role to increase the plastic waste in many countries past researchers from different areas of the world tried to develop successful and economical PET recycling method.

Lian-chu hu , Akira Oku & Etsu Yamada studied the alkali decomposition of PET in mix media of non-aqueous alcohol and ether^[30] in 1996. They found that ethanol and methanol also can be used as recycling agents.

Gamze gauclu, Tuncer Yalcinyua ,saadet ozumus published a paper in 2003 ^[31]. It titled " Hydrolysis of waste PET & characterization of products by differential scanning calorimetry ".

Recycling of PET waste in alkyd resin basis is a modern trend. Jeane Dullius, Carlo Rucker and Victor Oliveira have successfully make alkyd resin ^[23] by directly replacing part of alcohol and PA with post consumer PET flakes. George P. Karayannidis , Dimitris S. Achilias, Irini D. Sideridou and Dimitris N. Bikiaris derived alkyd resins from glycolized waste PET in 2004 ^[29].

Francis Pardal, Gilles Tersac have studied kinetics of PET glycolysis by diethylene glycol in 2007 ^[32]. They have studied effect of temperature , catalyst and polymer morphology.

D.Spaseska and M.Civkaroska recycled PET by using NaOH with the catalyst trioctyl methyl ammonium bromide ^[33]. This was published in 2010.

There are very few research on acidolysis method and preparation of alkyd by using TPA. Earl F carlston and El Cerrito tried acidolysis triglyceride oil with isophthalic and terephthalic acid to prepare alkyd resin in 1958 ^[34]. They prepared few successful resin using isophthalic acid.

3. MATERIALS AND METHODOLOGY

3.1. Materials

PET

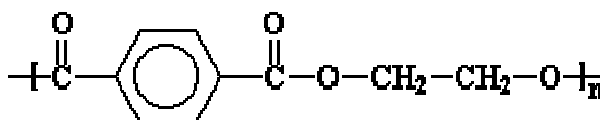
PET used in all experiments was produced from post consumer polyethylene terephthalate bottles which were collected from various locations.

Molecular Formula : $(C_{10}H_8O_4)_n$

Glass Transition temperature : $75\text{ }^\circ\text{C}$

Melting Temperature : $260\text{ }^\circ\text{C}$

Molecular Weight : 192.2 g/mol



3.2 Materials Used for Hydrolysis of PET

1. Sodium Carbonate (Soda Ash)

Sodium carbonate used as reagent to hydrolysis PET . It produces white slurry of sodium terephthalate and MEG.

Appearance : White powder

Formula : Na_2CO_3

Molar mass : 105.9885 g/mol

Density : 2.54 g/cm^3

Melting point : $851\text{ }^\circ\text{C}$

Boiling point : $1,600\text{ }^\circ\text{C}$

Soluble in Water

2. Sodium hydroxide (caustic Soda)

Sodium hydroxide used as reagent to hydrolysis PET . It produces white slurry of sodium terephthalate and MEG.

Formula : $NaOH$

Molar mass : 39.997 g/mol

Density : 2.13 g/cm^3

Melting point : $318\text{ }^\circ\text{C}$

Boiling point : 1,388 °C
Soluble in Water, Methanol, Ethanol

3 Mono Ethylene Glycol

MEG used as reaction media for hydrolysis process.

Appearance : Clear ,colourless liquid

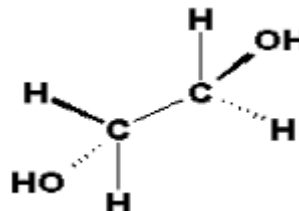
Formula : C₂H₆O₂

Density : 1.11 g/cm³

Melting point : -12.9 °C

Boiling point : 197.3 °C

Molar mass : 62.07 g/mol



4.Sulfuric acid

Sulfuric acid was used at the second stage of hydrolysis process to precipitate TPA.

Appearance : Clear ,colourless liquid

Formula

H₂SO₄
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Molar mass

98.079 g/mol
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Density

1.84 g/cm³
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Melting point : 10 °C

Boiling point : 337 °C

5 .Distilled water

Used to dilute sodium terphthalate solution before titrate with sulfuric acid.

3.3 Materials Used for Synthesis of Alkyd Resin

1. Soya bean Oil

Soya oil bought from local market and it was used to make alkyd resin.

Tested Values

Acid Value :3.47 mg KOH/g

Saponification Number :193mg KOH/g

Colour : Light yellow

2. Glycerin

Glycerine was used as main polyol in the production of alkyd resin by using TPA.

Appearance : Clear ,colourless liquid

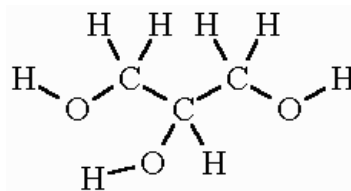
Formula : $C_3H_8O_3$

Density : 1.26 g/cm^3

Melting point : $17.8 \text{ }^\circ\text{C}$

Boiling point : $290 \text{ }^\circ\text{C}$

Molar mass : 92.09382 g/mol



3. Phthalic Anhydride

Phthalic Anhydride is the one of the main polybasic acid (anhydried) used in alkyd industry. here it was used to make reference recipe and first two recipes .

Formula : $C_6H_4(CO)_2O$

Melting point : $131 \text{ }^\circ\text{C}$

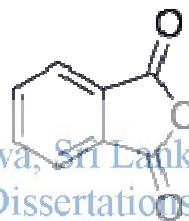
Density : 1.53 g/cm^3

Molar mass : 148.1 g/mol

Boiling point : $295 \text{ }^\circ\text{C}$



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4. Maleic Anhydride

MA added to the alkyd resin to improve drying time and colour.

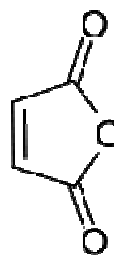
Appearance : White Powder

Formula : $C_4H_2O_3$

Density : 1.48 g/cm^3

Melting point : $52.6 \text{ }^\circ\text{C}$

Boiling point : $202 \text{ }^\circ\text{C}$



5. Pentaerythritol

PE also used as polyol in the alkyd making process similar to the glycerol.

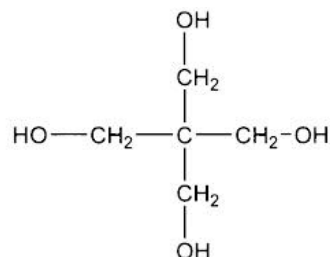
Appearance : White Solid

Formula : $C_5H_{12}O_4$

Melting point : $260.5 \text{ }^\circ\text{C}$

Density : 1.40 g/cm^3

Boiling point : $276 \text{ }^\circ\text{C}$



6. Xylene

Xylene was used as azeotropic media to facilitate easy removal of water from reaction vessel.

Appearance : Clear ,colourless liquid

Formula : C₈H₁₀

Molar mass : 106.16 g/mol

Boiling Point :138.5 °C

Other than the above mentioned chemicals small amounts of following chemicals were also used as catalyst for alcoholysis process.

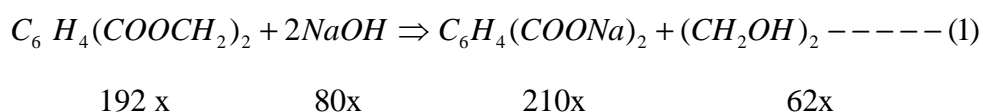
Lead oxide, sodium hydroxide, sodium methoxide, calcium carbonate.

3.4 Methodology

3.4.1 Hydrolysis of PET

Initially PET bottles were washed with water to remove dust and other contaminants . Then the bottles were cut down in to small (approximately 3mm × 3mm size) flakes. After cutting, flakes were further washed first with acetone and then with distilled water to remove the remaining contaminants.

The Basic hydrolysis of PET was carried out in two stages. At the first stage, a reaction between sodium hydroxide and PET was done according to the reaction no. (1).



Firstly PET was reacted with aqueous NaOH (1: 2 mole ratio). Test conditions used are shown in Table 3.1.

Table 3-1: Conditions used for Hydrolysis of PET

Temperature °C	Time (min)	Water (ml)	NaOH (M)
135	10	500	2.08
	15		
	20		
	25		
	30		
145	10		
	15		
	20		
	25		
	30		
155	10		
	15		
	20		
	25		
	30		
135	10	300	3.4
	15		
	20		
	25		
	30		
145	10		
	15		
	20		
	25		
	30		
155	10		
	15		
	20		
	25		
	30		

However, the reaction rate was too slow at atmospheric pressure. Therefore mono ethylene glycol (MEG) was selected as reaction media. Reactions between NaOH with PET (in MEG media) were carried out inside five neck reactor equipped with condensing system , mechanical stirrer and thermometer.

Hydrolyzing Procedure

Measured amount of MEG and NaOH were charged into the reactor and heated to pre-determined temperature (eg: 135 °C). After achieving the desired temperature PET flakes were added and continuously stirred for pre determined period of time (eg:

10 min). So that slurry of sodium salt of terephthalic acid was obtained. According to the reaction (1) Other than the sodium terephthalate , slurry consists of sodium chloride, ethylene glycol and remaining PET flakes. Then the slurry was dissolved by adding measured amount of distilled water. Insoluble impurities and remaining PET flakes were separated by filtration.

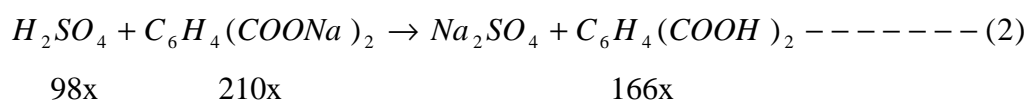
Weight of the remaining PET flakes was measured using analytical balance to calculate the reacted PET percentages.

Above mentioned procedure was repeated for different reaction conditions. Time, temperature, pressure, size of the PET flakes and MEG: PET ratio was identified as the main reaction parameters for this reaction. All reactions were done at atmospheric pressure and therefore pressure was considered as constant.

PET bottles were cut down in to nearly similar size flakes and hence assumed that it was constant. Therefore only the time, temperature and MEG: PET ratio was considered as the main variable reaction parameters. Table 3-1 shows how the above parameters were changed in hydrolysis reaction. Initial PET:MEG ratio was selected as 1:1. Then for that ratio experimental works repeated for temperature range from 135 °C - 155 °C and five minutes time intervals from 10 - 35 minutes. Similar test conditions were selected for PET: MEG ratio 1:2.

Preparation of terephthalic acid

In this stage, diluted salt mixture obtained from previous step was reacted with sulfuric acid to form TPA. Following reaction shows how sulfuric acid reacts with sodium terephthalate to form TPA.



Method

Diluted mixture was added to a 500 ml Erlenmeyer flask. Then 5M sulfuric acid was added drop wise while vigorously shaking flask. Obtained TPA was insoluble in water and settled at the bottom of the flask. Precipitated TPA powder was then filtrated.

Filtered precipitate was washed with distilled water to remove remaining chemicals. Then it was dried in an oven to obtain pure TPA powder.

Extracted TPA powder was analyzed by using Fourier Transformation Infrared spectroscopy (FTIR) machine.

3.4.2 Synthesis of Alkyd Resin

Reference alkyd recipe was found from literature ^[21] is shown in Table 3-2:

Table 3-2: Reference Alkyd Recipe

	W (g)
Soya Oil	66.5
Phthalic Anhydride (PA)	24
Pentaerythritol (PE)	12.9
Total	103.4



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Before synthesis, soya oil was tested for following properties.

1. Acid Value
2. Saponification Number

Then the synthesis of alkyd resin from the reference recipe was done by alcoholysis process. Alcoholysis process is a two step process. First step, convert try glyceride oil to monoglycerides by reacting it with a calculated amount of polyol. In the second stage, alkyd resin is made by adding remaining polyol and acid/ anhydride to the monoglyceride.

Formation of monoglyceride

Reaction was carried out in a 500 ml four necked reaction flask equipped with mechanical stirrer, thermometer, reflux condenser and nitrogen inlet. Reactor was placed inside a heating mantle.

As a first step, 0.06 % (w/w) catalyst and 66.5 g soya oil were put in to the reactor. The temperature was then increased to 240(±5) °C. After achieving that temperature, part of PE was added and temperature was maintained until monoglyceride formed.

The completion of alcoholysis was monitored by taking a sample from the reaction mixture in every 15 minutes. These samples were mixed with laboratory grade methanol at 1:3 ratio and the reaction was stopped when the mixture gave a clear solution. When the alcoholysis step was concluded heaters of the heating mantle were switched off and mixture was allowed to cool down to around 190 °C. Mechanical stirrer was used to mix the reaction mixture throughout the reaction time.

Above procedure was repeated with four different catalysts (Sodium hydroxide, Sodium methoxide, lead oxide and calcium carbonate) to find the most efficient one.

Esterification (alkyd forming) reaction

This reaction was also carried out in a 500 ml five necked reaction flask equipped with mechanical stirrer, thermometer, reflux condenser and nitrogen inlet. Additionally dean and stark was connected to the reflux column to collect water emitted during reaction. Xylene was supplied to the system as azeotropic solvent. Phthalic anhydride and remaining PE were added to previously formed monoglycerides and mixture was then heated to 240 °C. Samples were taken at each 30 minutes intervals to evaluate the acid value until it achieved desired level. Then the recipe was modified by replacing part of phthalic anhydride with varying amount of recovered terephthalic acid (according to Table 3-3) .

Table 3-3: Different Compositions used for Synthesis of Alkyd Resins

	Soya Oil (g)	PA (g)	TPA (g)	Glycerol (g)	PE (g)
Reference	66.5	24.00	-	-	12.90
Recipe 1 (R1)	66.5	11.99	13.46	-	12.90
Recipe 2 (R2)	66.5	17.90	6.81	-	12.90
Recipe 3 (R3)	66.5	22.20	1.99	-	12.90

Above recipes were synthesized at 240 °C, 250 °C and 260 °C temperatures.

Development of new methodology

Alcoholysis process was not successful for TPA. Therefore as the next step order of materials feeding to reactor was changed and new recipe (R4) was formulated without PA.

Recipe 4 (R4)

Soya Oil - 66.5 g

TPA - 26.9 g

PE - 12.9 g

Initially, soya oil and terephthalic acid were fed in to the reactor and heated to 260 °C. Reaction mixture was continuously stirred for a one hour period while maintaining temperature at 260° C. Then the polyol was added to the reactor. That caused to the higher rate of water emission and control of the reaction become uncontrollable. Therefore, for as the next step system (oil & TPA) was first heated to 260° C and just after reaching to the desired temperature polyol was started to add in a uniform rate for a period of one hour. Due to the difficulties of feeding solid polyol continuously to the reactor PE was replaced by glycerol.



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Recipe 5 (R5)

Soya Oil - 66.5 g

TPA - 26.9 g

Glycerol - 11.66 g

Experiments were continued until reach the acid value less than 12 or until gelation occurred. Samples were taken at each 30 minutes time intervals to measure the acid values.

Process was repeated for 250 °C and 270°C temperatures. Final acid value, hydroxyl value, touch drying time, non volatile matter content and bending test were done for each resin samples. Finally recipe was modified by adding 1g Maleic anhydride (MA) to improve the colour, reaction speed and drying properties of the film.

Recipe 6 (R6)

Soya Oil	- 66.5 g
TPA	- 26.9 g
Glycerol	- 11.66 g
Maleic Anhydried	- 1.0 g

R6 was synthesized at 260 °C, 270 °C and 280°C temperatures and all above mentioned tests were done for each recipe.

3.6 Testing Procedures

3.6.1 Determination of acid value

This test was done with reference to ASTM D 1639-90 standards.

Sample of specimen was taken and weight (S) was measured. Then it was transferred into a 250 ml Erlenmeyer flask and 100ml of neutral solvent was added. All the materials were mixed until dissolved. Warming was done if sample didn't dissolve properly at room temperature. After cooling to the room temperature 1 ml of phenolphthalein indicator solution was added and titrated with 0.1 N KOH solution to the end point, which was a pink colour persists for 30 second.

Neutral solvent mixture for above step was prepared by mixing equal parts of isopropyl alcohol and industrial toluene. The mixture was then neutralized by adding 1 ml of phenolphthalein and titrated with 0.1N KOH solution (V) until the pink colour persists 1 min.

$$\text{Acid Value} = \frac{V \times 56.1 \times N}{S}$$

3.6.2 Determination of hydroxyl value

Hydroxyl Value was measured with reference to ASTM D 1957- 86(2011). [36]

The sample of 0.9 to 1.1 g was weighed into flask and 5 ml of pyridine was mixed until dissolved the entire sample. 5.0 ml of pyridine-acetic anhydride solution was added in to the flask containing the specimen. The mixture was thoroughly mixed. Another 5.0 ml of pyridine-acetic anhydride solution was added into an empty flask for the reagent.

Condensers were connected to flasks and flasks were placed in steam bath for 1 hr period of time. 10 ml of distilled water was added to each flasks and the temperature was maintained for another 10 minutes. The flasks were then cooled to room temperature with condensers still attached. 1ml of phenolphthalein was added to each flasks and titrated with 0.5N alcoholic KOH solution.

$$\text{Hydroxyl value} = \frac{(B - V) \times N \times 56.1}{S} + \text{Acid Value}$$

Where:

V- Volume of KOH (ml) required for sample

B – Volume of KOH (ml) required for blank

N – Normality of the KOH

S – Weight of Specimen in gram.

3.6.3 Saponification number

1 mg of specimen was weighed to an Erlenmeyer flask. Then a condenser was connected to a flask and heated on the steam bath for 1 hour. The mixture was cooled to the room temperature and titrated with HCl of known normality until the pink colour disappeared.

Then 25 ml of alcoholic KOH was added to another flask (blank) and similar procedure was followed.

Then the;

$$\text{Saponification number} = \frac{(B-V) \times 56.1 \times N}{S}$$

Where:

V- Volume of HCl (ml) required for titration of specimen

B – Volume of HCl (ml) required for titration of blank

N – Normality of the HCl

S – Weight of Specimen in gram.

This value was measured according to ASTM D5558 - 95(2011)

3.6.4 Adhesion Test

This test was done according to the ASTM D 3359 -97 standard.

Resin layer was applied on smooth steel sheet with a brush until the thickness become 100 μm . Then it was left for 24 hours air drying.

The area free of blemishes was selected and six parallel cuts were made by using cross-hatch cutter device. Length of the cut should be approximately 3/4 inch and cutting edges should be good conditions.

Then the adhesive tape was placed over the grid and the area of grid was smoothed into place by a finger. The colour under the tape is good indicator to understand contact behavior between tape and coating. Within 30 seconds of application, tape should be removed and back upon itself to an angle of 90°.

Then cross cut area was inspected for the removal of coating from the substrate and the adhesion was rated according to the scale which is varied from 0B to 5B. 0B indicated poor adhesion.

3.6.5 Determination of Touch Drying Time

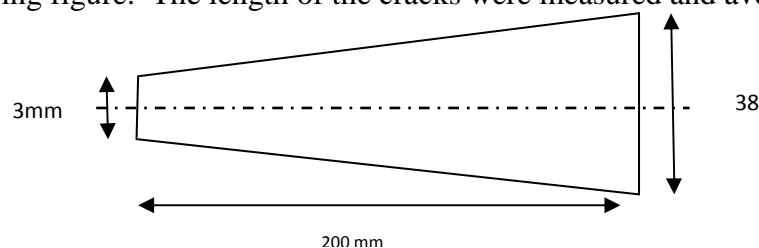
This test was done according to the ASTM D 1640-03(2009) Standard.[37]

Here the 1.4 zirconium Octate, 0.45 % calcium octate and 0.28 % cobalt octate were mixed with 70% of resin. Then the 50 μm thick layer were applied on glass substrate. Then the film was dried in open air.

To determine the touch drying time film was slightly touched with tip of finger and then it was quickly removed. The appearance of the finger print was observed. The time taken to make no finger mark on film was consider as touch drying time.

3.6.6. Bending Test

Bending test was done according to ASTM D 522-13 [37]. The Diluted alkyd resin samples were uniformly applied on the metal sheet and properly dried in an open air. Then coated sheet panels were bent over a conical mandrel having dimensions as shown in following figure. The length of the cracks were measured and average value was calculated.



4. RESULTS AND DISCUSSION

Alkyd resins are products which are mostly used in paints. This project was specially aimed to synthesis alkyd resin using commercially available soya oil, pentaerithritol (or glycerol) together with terephthalic acid extracted from waste PET. First part of the research aimed to completely de-polymerize post consumer PET in to its initial chemicals effectively and efficiently. For this purpose, the most common method used is hydrolysis with NaOH. Firstly, It was decided to find the applicability of that method for our laboratory conditions.

4.1 Hydrolysis of PET

Hydrolysis of crushed post consumer PET was carried out by using NaOH in the aqueous media under different reaction temperatures and time periods. Pressure was kept constant (atmospheric pressure) throughout the reactions. PET:NaOH mole ratio selected according to the following reaction (1).



100g of PET (100/192 = 0.52 mole) was selected for each test. According to the above reaction required weight of NaOH was 41.67 g (1.04 M). The results obtained are given in a Table 4.1 and 4.2

Table 4-1: Hydrolysis conditions of PET with aqueous NaOH (2.08 M)

Temperature °C	Time (min)	Water (ml)	NaOH (M)	Reacted PET %
135	10	500	2.08	0.15
	15			0.24
	20			0.50
	25			0.81
	30			1.30
145	10			0.18
	15			0.29
	20			0.57
	25			0.97
	30			2.47
155	10			0.40
	15			0.65
	20			0.99
	25			1.25
	30			1.39

Table 4-2: Hydrolysis conditions of PET with aqueous NaOH (3.4 M)

Temperature °C	Time (min)	Water (ml)	NaOH (M)	Reacted PET %
135	10	300	3.4	0.19
	15			0.28
	20			0.55
	25			0.91
	30			1.35
145	10			0.26
	15			0.38
	20			0.68
	25			1.03
	30			2.58
155	10			0.49
	15			0.72
	20			1.05
	25			1.31
	30			1.65

Above results clearly show that the reaction rate of PET with aqueous NaOH is very low for the selected temperatures at atmospheric pressure. Therefore it is less practical to use water as media for the above reaction.

According to the available literature ^[21] some of the alcohols like methanol, ethanol, isopropyl alcohol, MEG can be used to improve the reaction behavior between PET and NaOH.

As the next step mono ethylene glycol was selected as the solvent. The main reason is MEG is the one of reaction products produce by de-polymerization of PET. Uses of other alcohols make difficulties in separation of liquid products after the reaction.

Table 4.3 shows how MEG improves reaction behaviour between PET and NaOH at different temperatures and time periods.

Table 4-3: Hydrolysis conditions of PET with 3.4 M aqueous NaOH

Hydrolysis Conditions									
PET/MEG Mole Ratio	Temperature (°C)	Time (min)	Reacted PET %	PET/MEG Mole Ratio	Temperature (°C)	Time (min)	Reacted PET %		
1:1	135	10	60.25	1: 2	135	10	61.15		
		15	63.27			15	66.77		
		20	69.96			20	70.21		
		25	75.25			25	72.13		
		30	79.4			30	77.24		
		35	81			35	80.50		
	145	10	66.71		145	10	68.36		
		15	73.42			15	77.83		
		20	78.43			20	81.85		
		25	83.21			25	85.80		
		30	90.31			30	91.00		
		35	93.43			35	93.75		
	155	155	10		70.12	155	155	10	75.00
			15		86.11			15	88.44
			20		93.16			20	94.63

Here maximum conversion obtained was 94.63% that occurred at 155 °C in 20 minutes. That conversion is sufficient and therefore further increment of temperature or time has not been done.

During the reaction PET react with NaOH and form white slurry of sodium terephthalate in MEG media. With increasing reaction time amount of slurry gradually increased and hence reaction media becoming more viscous. Therefore reaction rate was reduced with the time. It was observed this effect can be eliminated

by increasing the PET: EG ratio. Figure 4-1 shows percentage conversion of PET at PET: EG =1:1 while Figure 4.2 shows results when PET: EG mole ratio was 1:2 under same conditions (temperatures and time periods).

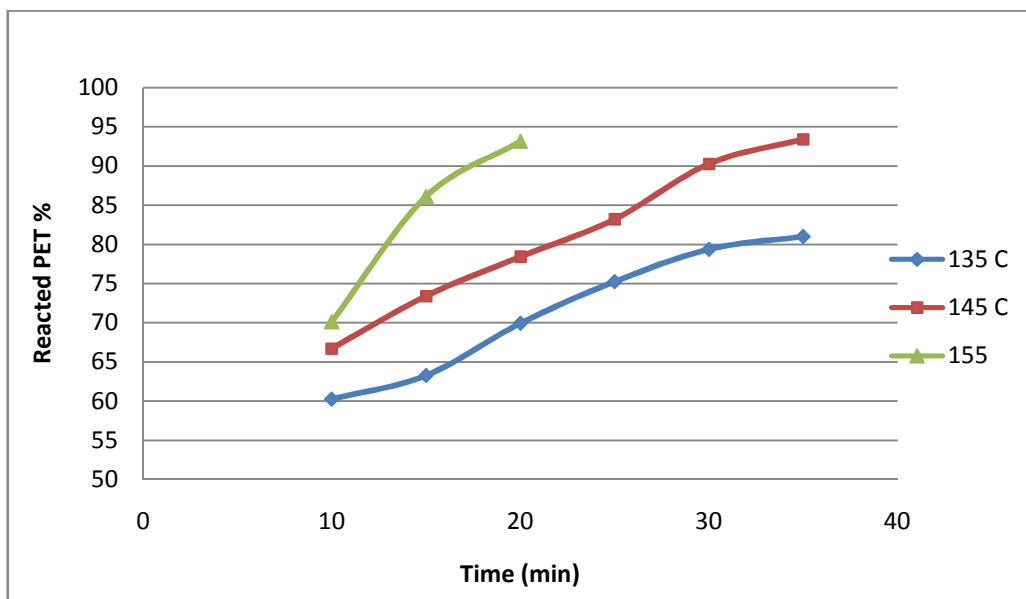


Figure 4-1: Time vs Reacted PET percentage graph for PET: EG 1:1

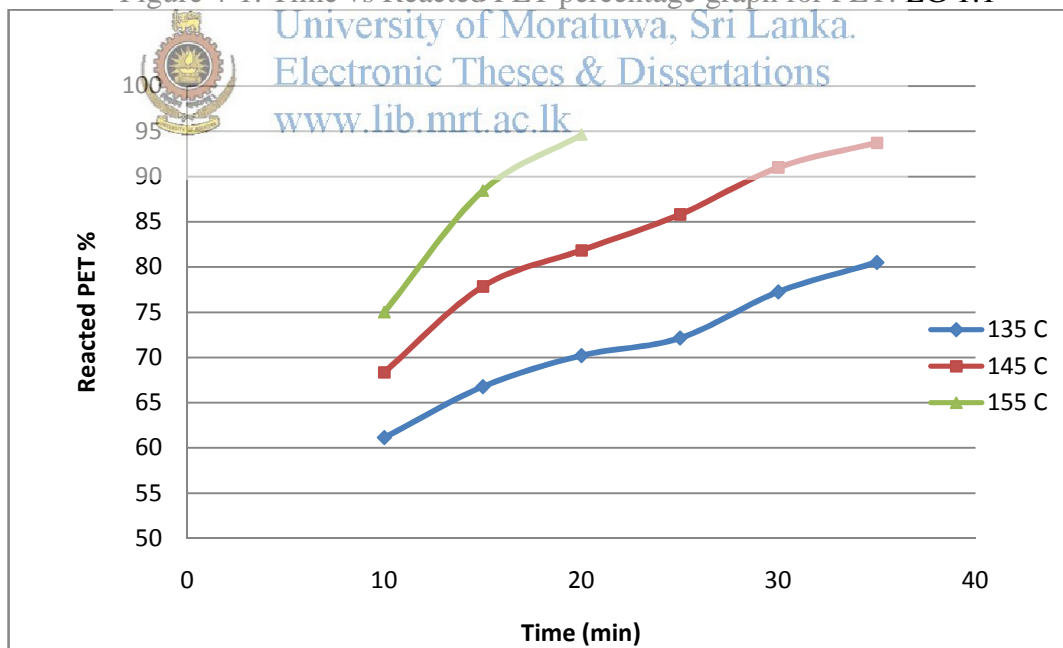


Figure 4-2: Time vs Reacted PET percentage graph for PET: EG 1:2

Above results clearly indicate that when PET: MEG ratio increases reacted PET percentage increases. This was clearly due to the reduction of viscosity with increasing of liquid content.

Quality of TPA extracted by titrating above reaction mixture (after dilution with distilled water) with H_2SO_4 was nearly similar to the commercially available TPA bought from local market. Figure 4-3 gives a clear evidence for that. It shows the comparison of FTIR spectra of commercial TPA and Extracted TPA. Both spectra almost have very similar peak patterns. It doesn't mean the extracted TPA is very pure. However this quality is enough to make alkyd resins because those are not the food graded products.

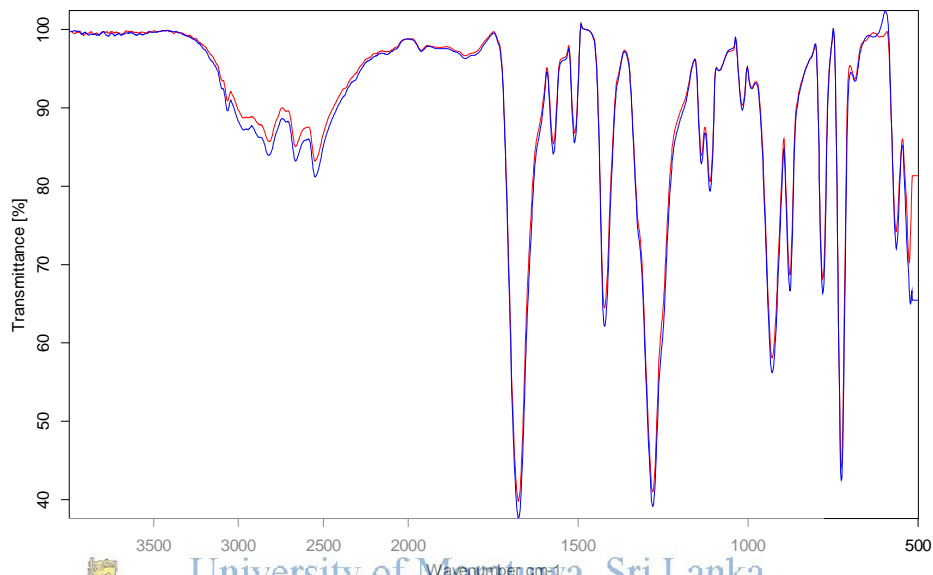


Figure 4-3: Comparison of FTIR spectra of Extracted and Reference TPA



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Above all results, clearly indicated that the NaOH is a good reagent which can be used to depolymerize PET in to its initial monomer. However it has some drawbacks as a hydrolysis agent. The main drawback connected with NaOH is difficulties in manipulating these types of very aggressive reagents by operators. In addition, modifications in the plants are required to adopt together with a series of technical expedients implant construction due to the big problems connected with corrosion. Specially in countries like Sri Lanka most of the laborers don't have enough experience and skills to handle aggressive chemicals. When thinking about commercialization of this project, in future, it is essential to have less aggressive and less corrosive reagent than NaOH.

According to the literature reagent used for hydrolyzing of PET should be a chemical consisting of one or more metal salts of weaker acid than TPA [8]. Here Na_2CO_3 (soda ash) was selected as reagent to replace NaOH. Because it fulfills the above requirements and commercial grade of soda ash is readily available in local market.

Results obtained from the reaction between Na_2CO_3 and PET in MEG media are shown in table 4- 4.

Table 4-4: Reacted PET percentages with Na_2CO_3 at different conditions.

Time (min)	PET:MEG Weight Ratio	Reacted PET percentage						
		135°C	140°C	145°C	150°C	160°C	170°C	180°C
15	1:2	4.1	13.38	15.9	23.73	40.01	45	49.9
20		6.5	14.1	18.2	24.8	41.17	49.5	54.2
25		8.7	16.46	20.1	29.63	44.53	53.5	57.1
30		11.3	19.41	22.7	32.89	48.05	56.3	59.5
35		13.2	20.28	25.4	38.3	49.31	59.9	61.5
40		15.1	22.3	27.9	39	52.2	61.1	63.2
45		16.8	24	29.1	41.4	56.3	62	65

Above results are graphically illustrated in Figure 4-4

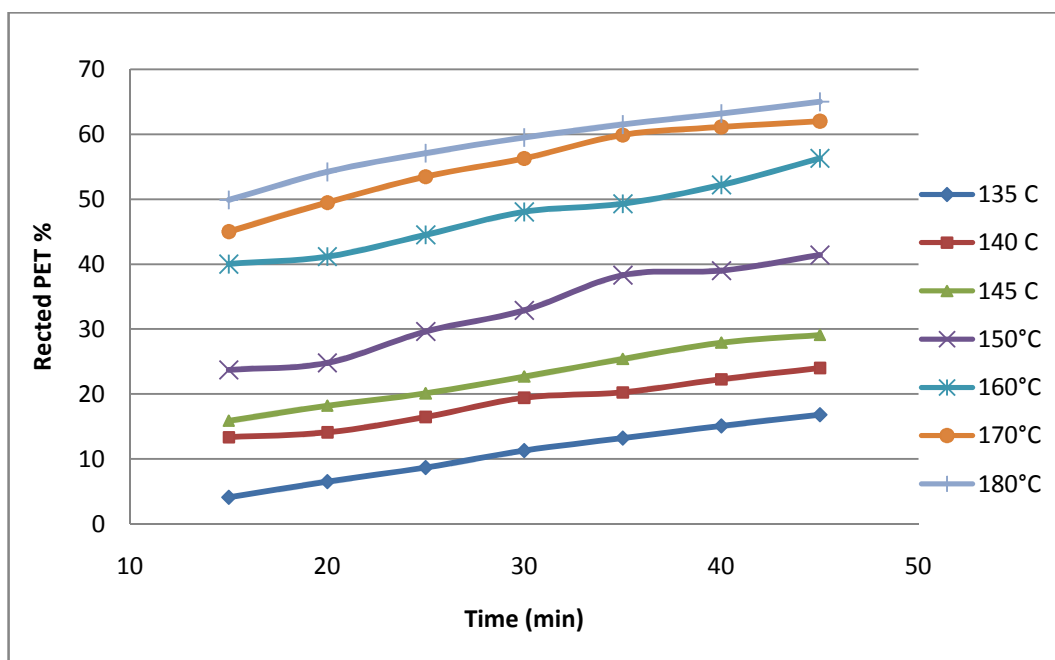


Figure 4-4: Percentage conversion of PET with Na_2CO_3 when PET:EG = 1:2

Similar to the reaction between NaOH, here also reaction rate increases with temperature. However reaction rate of PET with Na₂CO₃ is less compared to the NaOH. Therefore comparatively high reaction temperature and longer reaction time is required. Here maximum conversion of PET obtained was 65% that is at 180 °C. However by increasing PET: EG ratio the percentage conversion can be increased. Table 4-5 shows the percentage conversion of PET at 170 °C, when the PET: EG ratio is 1:4.

Table 4-5: Percentage conversion of PET with Na₂CO₃ when PET: EG = 1:4

Reaction time (min)	Reacted PET %
15	54.6
20	60.19
25	66.61
30	72.45
35	78.89

One can argue that it is not economical. However MEG was just reacted as solvent and does not participate any reaction. Therefore it can be recovered after the precipitation of TPA. Figure 4-5 shows comparison of FTIR spectrums of recovered MEG (1) after the reaction and reference MEG (2). Recovered MEG again can be used as solvent for the next batch of materials.

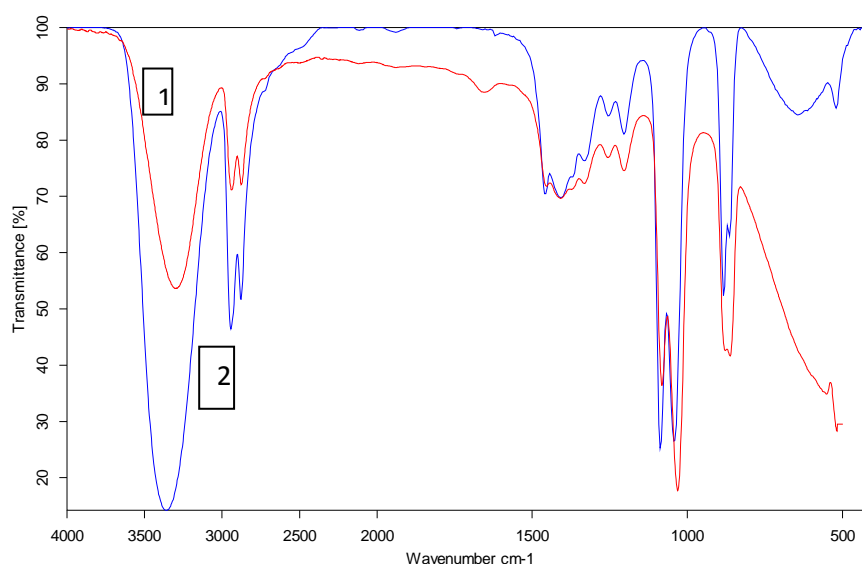


Figure 4-5: Comparison of FTIR spectrums of Extracted (2) and Reference MEG (1).

According to the above results both NaOH and Na₂CO₃ can be used as hydrolyzing reagents to depolymerize post consumer PET.

Figure 5-6 shows FTIR spectra of TPA acid which was extracted using Na₂CO₃ and H₂SO₄. This spectrum also matches with spectra in Figure 4-3. There is no difference in quality of extracted TPA in both reactions.

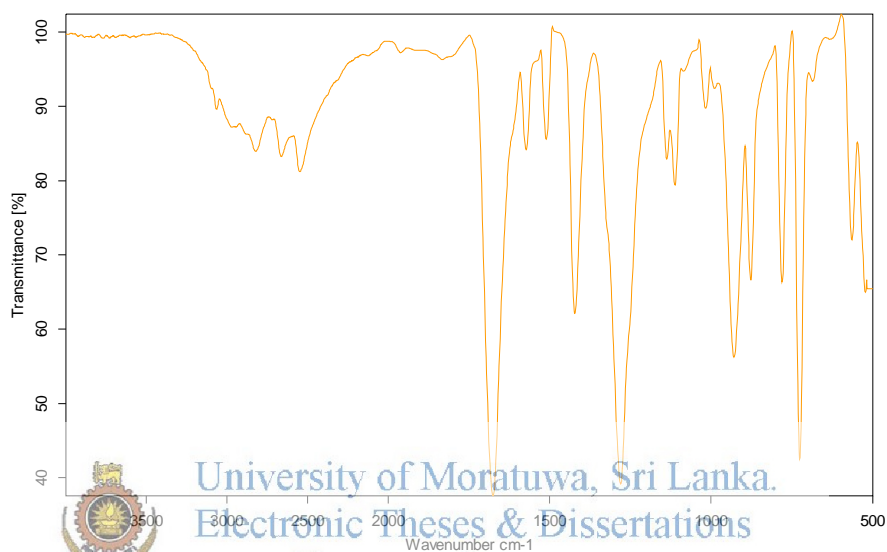


Figure 5-6 : FTIR spectrum of the Extracted TPA by using Na₂CO₃

4.2 Synthesize of alkyd resin using extracted TPA

Properties of the soya oil were tested according to the ASTM standards. Test results are shown in table 4.6

Table 4-6: Tested properties of Oil

Property	Value
Acid Value	3.47 mg KOH/g
Saponification number	193 mg KOH/g

Above test results indicated that alcolysis processes could be started without any pre-treatment.

Following Table 4.7 shows the selected reference alkyd resin and its breakdown.

Table 4-7: Reference alkyd formula

	Charge			Break Down			
	W (g)	E	e ₀	e _a	e _b	F	m ₀
Soya Oil	66.5	293	0.227	0.227		1	0.227
PA	24	74	0.324	0.324		2	0.162
PE	12.9	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	103.4			0.551	0.607		0.560

Before the synthesis theoretical $P_{gel\ point}$ was calculated to check whether this reaction can be completed without gelation.

$$P_{gel\ point} = \frac{m_0}{e_a} = \frac{0.560}{0.551} = 1.015 = 101.4\%$$

Above calculation indicated that reference recipe can be cooked without gelation.

The most common way of preparing oil modified alkyd resin is alcoholysis^[21]. It is a two step process. As a first step triglyceride oil partly converted to monoglyceride by reacting with pentaerythritol. Initially Sodium methoxide was used as a catalyst for alcoholysis step. But reaction mixture turned in to dark colour. Hence another three catalysts which were mentioned in literature were also tested. Table 4-8 shows the test results.

Table 4-8: Time taken to form monoglyceride with different catalysts

Catalyst	Weight (g)	Time taken to form monoglycerides (min)			Average time (min)	Other Observations
		Experiment 1	Experiment 2	Experiment 3		
PbO	0.06	45 min	60 min	45 min	50.0	
NaOH	0.06	50 min	55 min	50 min	51.6	Reaction mixture became dark brown
	0.03	55 min	65min	65 min	61.6	
Sodium methoxide	0.06	50 min	55 min	51 min	52.0	Reaction mixture became dark brown
	0.03	57 min	58min	59 min	58.0	
CaCO ₃	0.06	55min	50 min	52 min	52.3	
	0.03	62 min	60min	58 min	60.0	



According to the experimental results, there is not much difference among the time periods. However sodium compounds tends to darken the reaction mixture. Therefore calcium carbonate and lead oxide were selected as most suitable catalyst for monoglyceride formation.

Formation of monoglyceride from soya oil was carried out inside a five neck reaction vessel equipped with mechanical stirrer, dean & stark, spiral condenser Nitrogen inlet and thermo meter. Nitrogen is required to facilitate neutral environment inside the reaction vessel. Presence of oxygen may helps to form cross links and promote the gelation process. Monoglyceride formation considered as successful after checking the miscibility of 1 volume of monoglyceride with 3 volume of methanol. Addition of PA at high temperature causes excess phthalic loss (evaporation) and higher amount of water emissions. Therefore monoglyceride mixture was cooled down to about 190°C. Second step was also carried out in side same reactor as describe in section 3.4.2. Initial acid values were calculated depending on theoretical values and then samples were taken at each thirty minutes to check the acid value of the reaction mixture. Water was removed continuously as a byproduct until finish the reaction.

This meant that the reaction was not as controllable as would be desired. Therefore 15 % Xylene was gradually added to the reaction mixture via dean stark to produce an azeotrope with the water. Figure 4-7 sows the variation of acid value with time for the reference recipe.

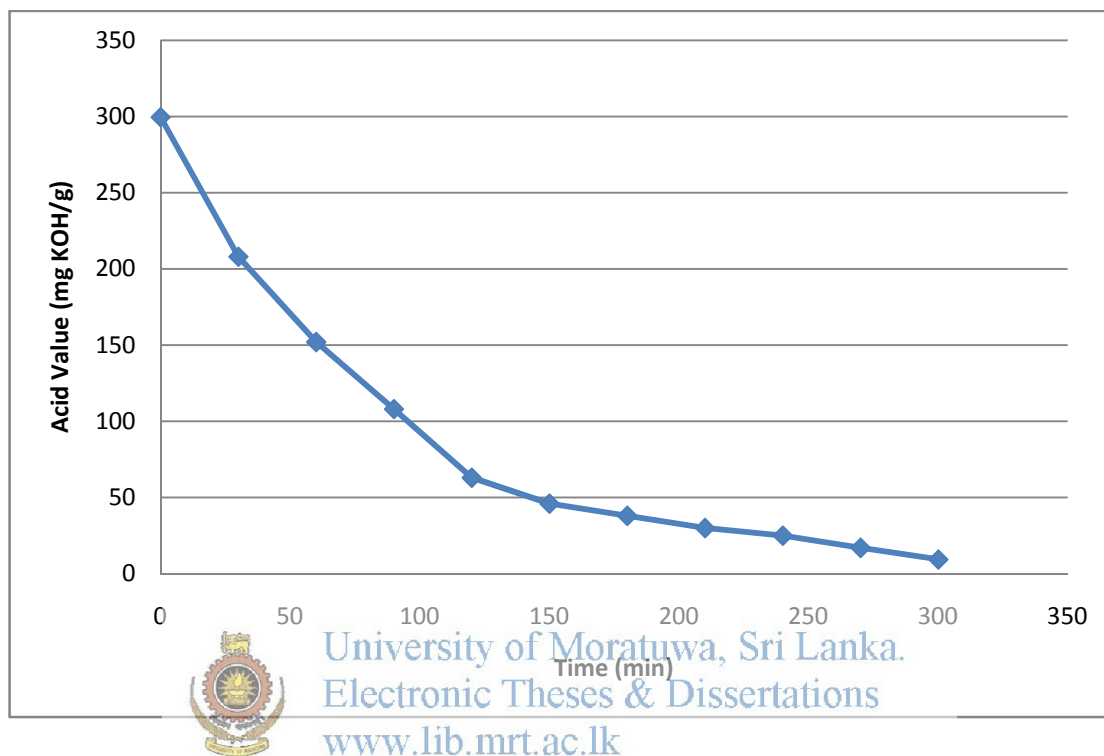


Figure 4-7: Time vs acid value variation graph for Reference Recipe

Alkyd formation reaction was continued until reach the acid value to the commercially acceptable range (<10). Table 4-9 shows some of the tested results for reference alkyd resin.

Table 4-9: Tested Properties for Reference Resin

Property	Value
Acid Value	9.3 mg KOH/g
Hydroxyl number	38.7 mg KOH/g
Non Volatile Matters	94.7%
Water emitted during reaction	2.88 g

According to the results in Ttable 4-9, it was concluded that synthesis of alkyd using above recipe (Table 4-7) was successful. The next step was to modify above recipe using extracted TPA from waste PET. Since the $P_{gel\ point}$ is depend on M_0 and e_a values were kept constant. It ensured completion of reaction without geletion. Therefore in the next step recipe 1 (R1) was formulated by adding 13.46 g TPA to the reference recipe. To kept e_a constant, Weight of PA was reduced to 11.99 g. New recipe and its breakdown were shown in Table 4-10.

Table 4-10: Alkyd recipe 1 (R1)

	Charge			Break Down			
	W	E	e_0	e_a	e_b	F	m_0
Soya Oil	66.50	293	0.227	0.227		1	0.227
PA	11.99	74	0.162	0.162		2	0.081
TPA	13.46	83.1	0.162	0.162		2	0.081
PE	12.90	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	104.85			0.551	0.608		0.560

R 1 was synthesized using same procedures and equipment setup. Variation of acid value with for R1 is shown in Figure 4-8.

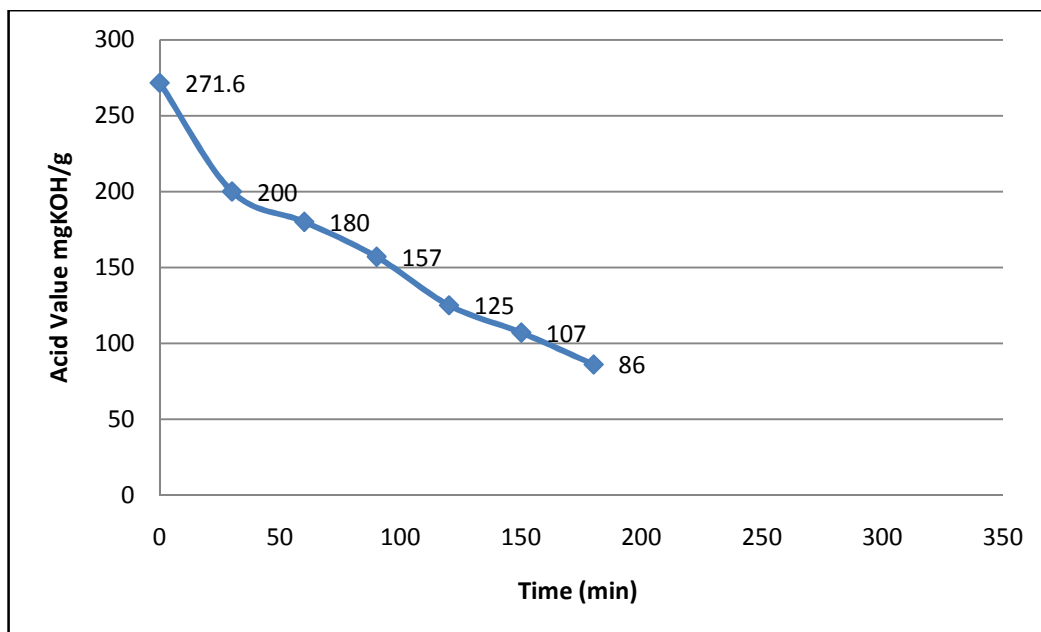


Figure 4-8 : Time vs Acid value variation graph for R1

Since the m_0 and e_a was not changed, the theoretical percentage completion of reaction at the gel point is similar to the reference recipe. However practically gelation occurred before the completion of reaction.



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Table 4-11: Tested Properties of R1

Property	Value
Approximate Acid Value (tested) before gelation	86 mg KOH/g
Approximate Time taken to reach above acid value	210 min
Water emitted until gelation occur	1.4 g

Only the modification done for reference recipe to make recipe 1 was the replacement of part of PA with TPA. All other ingredients and reaction conditions were kept constant. Therefore, addition of terephthalic acid would be the only reason to occur gelation before completion of the reaction.

To further study this matter another two recipes (R2 & R3) were designed by reducing amount of TPA. Recipes and breakdowns of the R2 and R3 are show in Table 4-12

and 4-13 respectively. Figure 4-8 and 5-9 shows the variation of acid value with time respectively.

Table 4-12: Alkyd Recipe 2

	Charge			Break Down			
	W	E	e ₀	e _a	e _b	F	m ₀
Soya Oil	66.50	293	0.227	0.227		1	0.228
PA	17.90	74	0.242	0.242		2	0.121
TPA	6.81	83.1	0.082	0.082		2	0.041
PE	12.90	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	104.11			0.552	0.607		0.560



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Variation of acid value with time for the recipe 2 is shown in figure 4-9

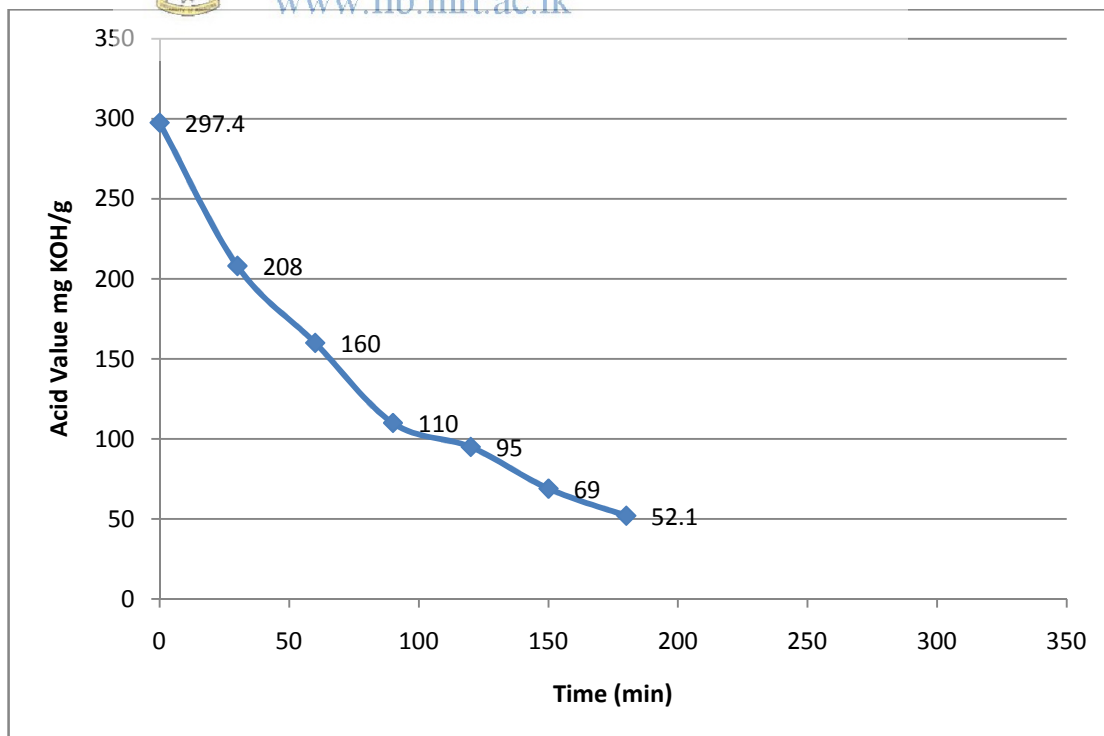


Figure 4-9: Time vs Acid value variation graph for R2

Water emitted during reaction was = 2.1 g

Final acid value observed was = 52.1

Recipe 3 was formulated by further reducing TPA amount to 1.99g

Table 4-13: Alkyd Recipe 3

	Charge			Break Down			
	W	E	e ₀	e _a	e _b	F	m ₀
Soya Oil	66.50	293	0.227	0.227		1	0.227
PA	22.20	74	0.300	0.300		2	0.150
TPA	1.99	83.1	0.024	0.024		2	0.012
PE	12.90	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	103.5			0.552	0.607		0.560



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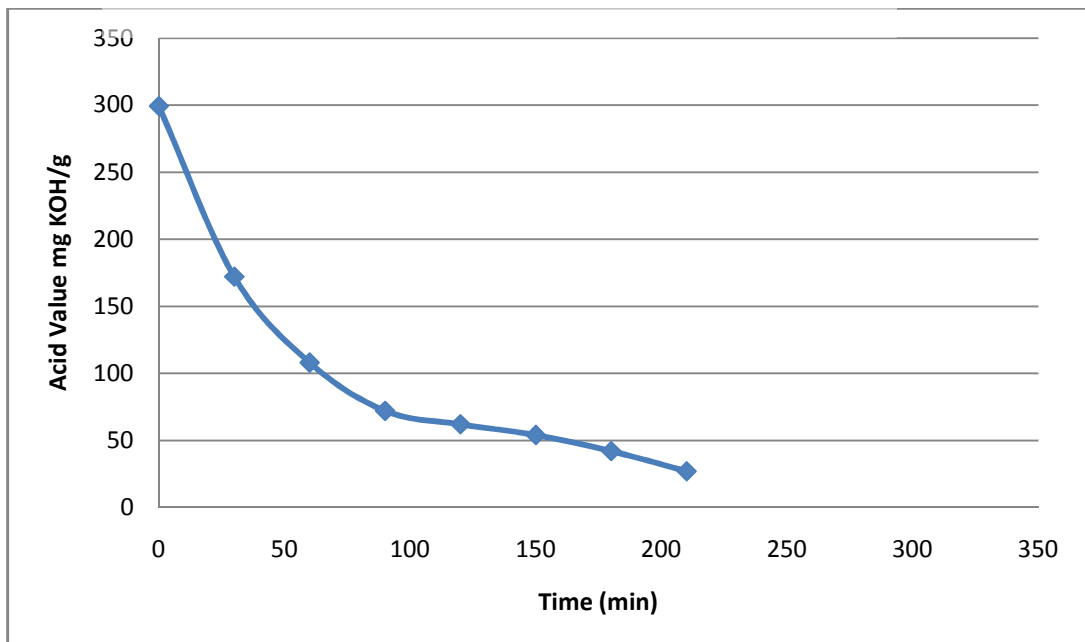


Figure 4-10: Time vs Acid value variation graph for R3

Water emitted 2.59 g

This time an acid value reached to nearly 27 mgKOH/g prior to the gelation occurred.

Table 4-14: Summary Results for alkyd synthesis at 240 (± 5)°C

	PA (g)	TPA (g)	Acid value at Gel point	Water Emitted (g)
Reference	24.00	0.00	-	2.78
R 1	11.99	13.46	86.0	1.4
R 2	17.90	6.81	52.1	2.10
R 3	22.2	1.99	29.0	2.59

Amount of water emitted during the reaction is one of the key factors to understand the successfulness of the reaction. This can be done by comparing emitted amount of water (during synthesis) with theoretical (calculated) value. Amounts of water emitted by all three recipes were tabulated in the Table 4-15 with calculated values. It clearly shows that the actual values are much lesser than calculated values.



Table 4-15: Amount of water emitted by all recipes at 240 °C

Recipe	Calculated water content (g)	Calculated water without TPA (g)	Actual water Emitted (g)
Reference	2.91	-	2.78
R 1	2.91	1.46	1.40
R 2	2.91	2.17	2.10
R 3	2.91	2.70	2.59

Nevertheless the interesting fact is that calculated amounts of water only by considering PA were nearly equal with actually emitted water contents. Accordingly the conclusion made was, at the tested reaction conditions TPA not reacted with other ingredients as PA did.

As a remedy, reaction temperature was increased to firstly 250 °C and then to 260 °C. R1, R2 and R3 recipes were synthesized at those two temperatures and results obtained are shows in Table 4-16 and Table 4-17.

Table 4-16 : Summary results for alkyd synthesis at 250 (± 5)°C

	PA (g)	TPA (g)	Acid value at Gel point	Water Emitted (g)	Expected Water out come (g)
R 1	11.99	13.46	98.0	1.10	2.91
R 2	17.90	6.81	69.1	1.82	2.91
R 3	22.2	1.99	35.0	2.21	2.91

Table 4-17: Summary Results for alkyd synthesis at 260 (± 5)°C

	PA (g)	TPA (g)	Acid value at Gel point	Water Emitted (g)	Expected Water out come (g)
R1	11.99	13.46	102.0	1.20	2.91
R2	17.90	6.81	74.0	1.84	2.91
R3	22.2	1.99	40.2	2.19	2.91

Expected results were not obtained even in 260 °C. Therefore following conclusions were made based on the results.

1. Alocolysis method is not the suitable method to synthesized alkyd resin from TPA.
2. Mixing of PA with TPA is not possible due to the excessive volatilation of PA at high temperatures and less reactivity of TPA at low temperatures.

Both conclusions are valid only for used reaction conditions. Use of catalysts sometimes may help to proceeds reaction under same conditions. Although it may increases the production cost of alkyd resins.

Therefore it was decided to develop new methodology for producing TPA based alkyd resin instead of using catalyst for existing method. This was initialized by changing the order of feeding materials to the rector. New recipe (R4) formulated for new methodology is shown in table 4-18. Based on previously made conclusions, R4 was formulated by purely adding TPA without any PA.

Table 4-18 : Alkyd Recipe 4

	Charge			Break Down			
	W	E	e_0	e_a	e_b	F	m_0
Soya Oil	66.50	293	0.227	0.227		1	0.227
TPA	26.9	83.1	0.324	0.324		2	0.162
PE	12.90	34	0.380		0.380	4	0.095
Glycerol					0.227	3	0.076
	103.5			0.552	0.607		0.560

Here soya oil and TPA was charged in to the reactor followed by addition of polyol.

As learnt from previous results reaction temperature of TPA is higher than that of PA. So 260 °C was selected as initial temperature.

Firstly TPA and soya oil mixture were heated to 260 °C and maintained at that temperature for a one hour period then PE was added. This caused to emission of water at faster rate and controlling of reaction become too hard. After few minutes gel particles started to appear in reaction mixture and sizes of them increased with time. One solution for this was reducing temperature to below 190 °C (similar to alkalosis method) and adding polyol to the reactor and then gradually increases the temperature. Second solution was add alcohol slowly but continuously to the mixture for a period of time while maintaining the temperate at 260 °C. First method is time consuming. Hence the second solution was selected as most suitable method. However since PE is in solid form, continuous feeding is difficult. Therefore, it was decided to select liquid polyol for the reaction and glycerol (which was second mostly use polyol in the alkyd industry) was selected to make alkyd resin. Table 4-19 shows modified recipe for proposed new method.

Table 4-19: Alkyd Recipe 5

	Charge			Break Down			
	W	E	e ₀	e _a	e _b	F	m ₀
Soya Oil	66.50	293	0.227	0.227		1	0.227
TPA	26.9	83.1	0.324	0.324		2	0.162
Glycerol	11.66	30.7	0.380		0.380	3	0.126
Glycerol					0.227	3	0.076
	102.14			0.552	0.607		0.591

Firstly soya oil and TPA heated to 260 °C and just after reaching the maximum temperature addition of glycerol started. This was done by uniformly and continuously for one hour period. After that temperature was maintained at 260 °C while stirring until acid value become less than 12 mg KOH/g or gel formations occur.



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Figure 4-10 shows variation of acid number with time.

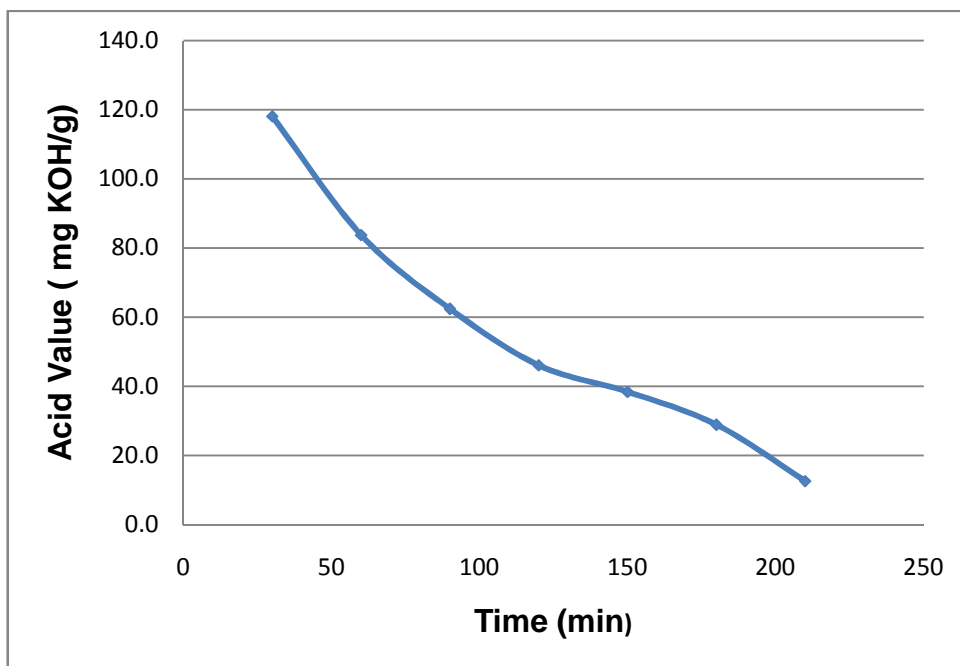
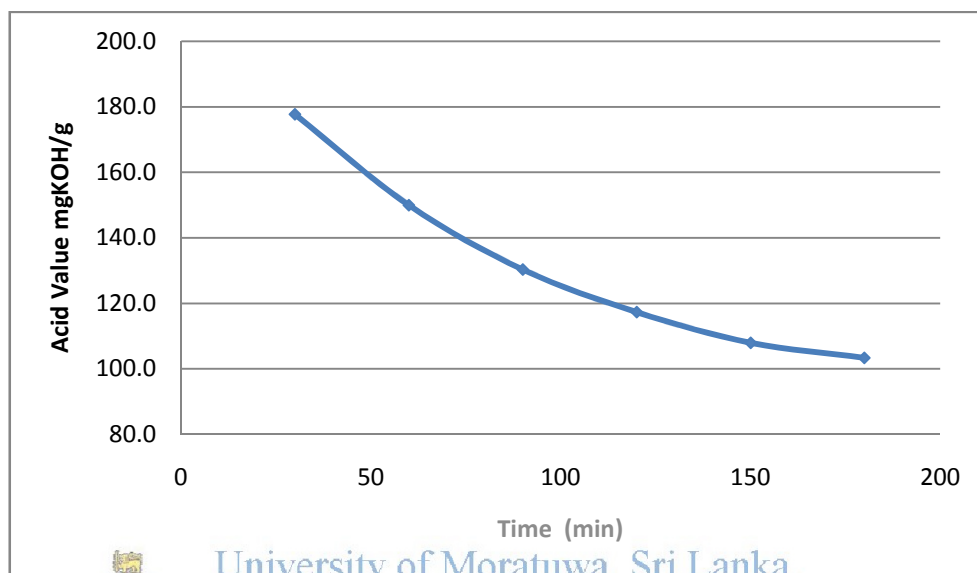


Figure 4-11: Time vs Variation of AV for R5 at 260 °C

R5 produced resin with final acid number 12.5 and time taken to form this resin was nearly 210 minutes. This time was considerably lesser than that of the alcoholysis method. Resin color is light yellow and no evidence about gel formation.

Then the temperature was reduced to 250 °C and same procedure was repeated for R5. Graph in figure 4-12 shows acid value variation for R5 at 250 °C.



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Figure 4-12: Time vs Variation of AV for R5 at 250 °C

Here gel particles start to appear after about 270 minutes and acid value recorded at that point was 103 mg KOH/g. Then the Procedure was repeated for 270 °C and variation of acid value noted down (Figure 5-11).

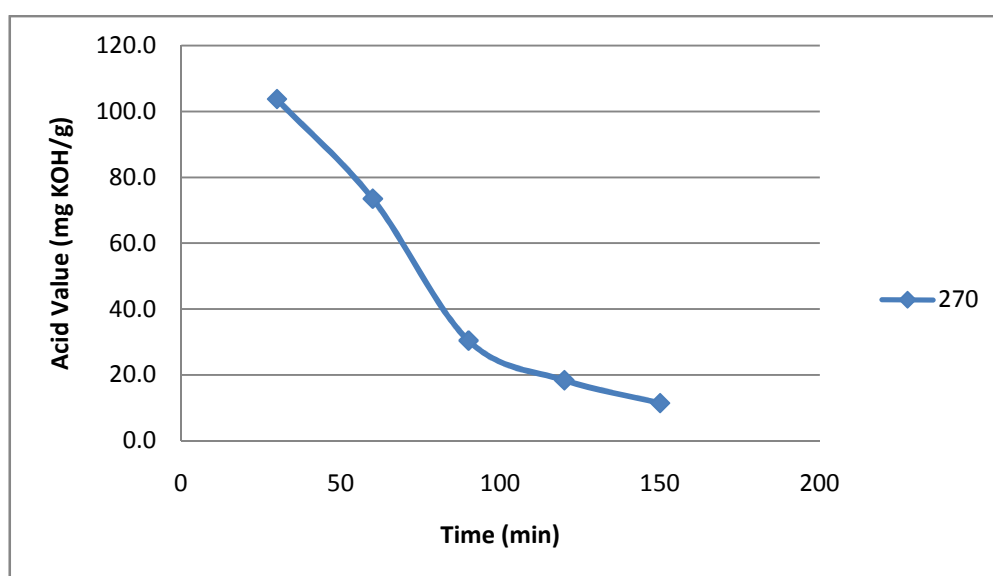


Figure 4-13: Time vs Variation of AV for R5 at 270 °C

Here acid value reached less than 12 within 150 minutes. Resin was clear and no evidence of gelation was observed.

Final acid value, hydroxyl value, non volatile content, viscosity and bending test were done for all resin samples. Mass of emitted water and total processing times were also noted down. Colour of the resins and evidence of gel formation was visually observed. Table 4.20 shows the summary results of all above mentioned tests and observations.



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Table 4-20: Tested Properties of R5 at different temperatures.

Resin	Temp (°C)	AV (mg KOH/g)	Pressing time (min)	Water emitted during reaction (g)	HV (mg KOH/g)	Touch Drying time (min)	Bending	Non volatile content (%)	Viscosity (second B4 cup at 1:1 Diluted)	Resin Color	Evidence of Gel formation	Remarks
R5 Ex 01	250	103	240	2.20	-	-	-	-	-	Light brown	yes	Reject
R5 Ex 02	260	12.5	270	2.75	45	180	<5mm	91.1	82	Light yellow	no	Ok
R5 Ex 03	270	11.4	210	2.70	43.1	185	<5mm	87.2	79	Light yellow	no	Ok



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Oil length of the above resins can be calculated as follows.

$$\text{Oil length} = \frac{(\text{mass of oil used to make alkyd resin}) * 100}{(\text{Mass of reactants}) - (\text{Mass of water evolved in process})}$$

Table 4-21: Oil length of the Resins Produced by R5

Alkyd Resin	Oil Length
R5 Ex 02	66.90%
R5 Ex 03	66.87%

Since the length of oils is greater than 55 % , these resins can be categorized as long oil alkyds.

Most of the alkyd manufacturers adds small amount of maleic anhydride (MA) to improve the colour, reaction speed and specially to improve drying properties of the film. Therefore R5 was modified by adding 1 g of MA. Accordingly amount of TPA reduces to maintain constant m_0 and e_a values. Table 4-22 shows modified recipe 6 (R6) with MA.

Table 4-22: Alkyd Recipe 6

	Charge			Break Down			
	W	E	e_0	e_a	e_b	F	m_0
Soya Oil	66.50	293	0.227	0.227		1	0.227
TPA	25.26	83.1	0.304	0.304		2	0.152
Glycerol	11.66	30.7	0.380		0.380	3	0.126
Glycerol					0.227	3	0.076
MA	1.0	49	0.020	0.020		2	0.010
	102.14			0.551	0.607		0.591

This recipe was cooked at three different temperatures 260°C, 270°C, and 280 °C. Figure 4-14 shows the variation of acid value with time for three different temperatures.

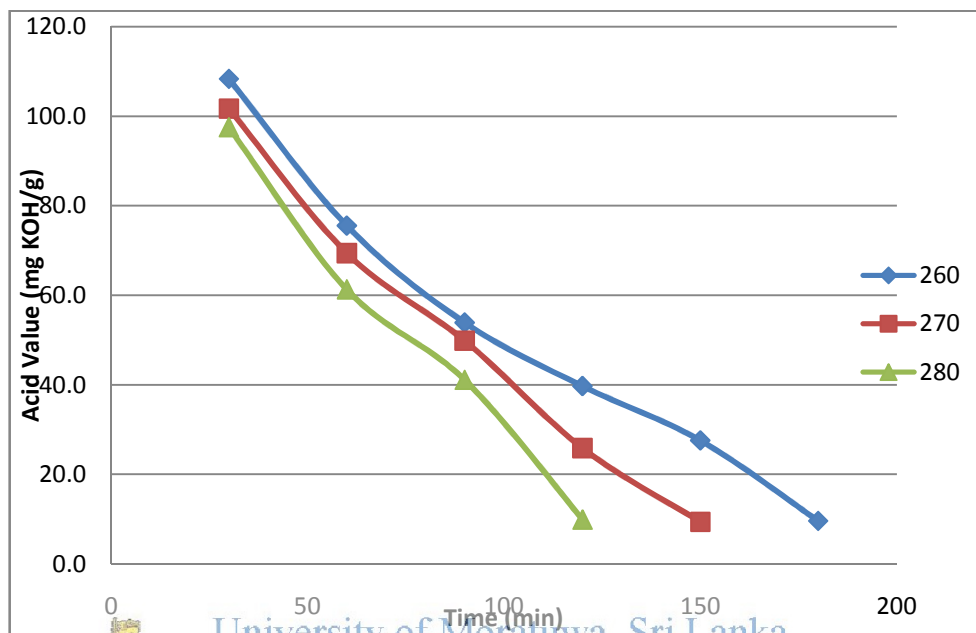


Figure 4-14 Variation of Acid Value of R6 with Time at Different Temperatures

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Test results for above three resins are shown in a following Table 4-24.

Table 4-23: Tested Properties of R6 at different temperatures.

Temp (°C)	AV (mg KOH/g)	Time taken to reach AV (min)	Water emitted during reaction (g)	HV (mg KOH/g)	Touch Drying time (min)	Bending	Non volatile content (%)	Viscosity (second B4 cup at 1:1 Diluted)	Resin Color	Evidence of Gel formation	Remarks
R6 Ex 01	9.6	180	2.80	41.1	189	<5 mm	88.1	71	Light yellow	no	Ok
R6 Ex 02	9.4	150	2.85	41.0	190	<5mm	82.1	75	Light yellow	no	Ok
R6 Ex 03	9.9	120	2.81	43.2	185	<5mm	91.1	79	Light yellow	no	Ok

Table 4-24: Tested Properties of R7 at different temperatures.

Temp (°C)	AV (mg KOH/g)	Time taken to reach AV (min)	Water emitted during reaction (g)	HV (mg KOH/g)	Touch Drying time (min)	Bending	Non volatile content (%)	Viscosity (second B4 cup at 1:1 Diluted)	Resin Color	Evidence of Gel formation	Remarks
R7 Ex 01	9.1	180	2.88	39.3	197	<5 mm	80.2	77	Light yellow	no	Ok
R7 Ex 02	9.0	150	2.88	39.0	200	<5mm	80.0	78	Light yellow	no	Ok
R7 Ex 03	9.3	120	2.85	40.2	192	<5mm	82.2	74	Light yellow	no	Ok

According to the results (Table 4-24) properties of all three resins produced at different temperatures are within the commercially acceptable limit. Time taken to synthesize the resin was decreased with increasing reaction temperature. At 260 °C R6 took 180 minutes to produce a resin with less than 10 mg KOH/g acid value but it took only 120 minutes at 280 °C. This can be further reduced by increasing temperature. However maximum temperature was limited to 280 °C due to inability of operate alkyd cooking equipment at high temperatures than 280 °C. Calculation of the percentage of oil in the alkyd resin shows all three resins are long oil alkyds. (Table 4-26).

Table 4-26: Oil length of the Alkyd Resin Produced by R6 Recipe

Alkyd Resin	Oil Length
R6 Ex 01	66.94 %
R6 Ex 02	66.98%
R6 Ex 03	66.95%



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To compare the quality of extracted TPA with commercial TPA, three reference resin samples were synthesized by using same compositions but with commercially available TPA. So only the difference between R6 and new recipe R7 was R7 had commercial TPA instead of extracted TPA in R6. Tested properties of R7 at 260 °C, 270 °C and 280 °C temperatures are shown in Table 4-25 and calculated oil lengths shown in Table 4-27.

Table 4-27: Oil length of the Alkyd Resin Produced by R7 Recipe

Alkyd Resin	Oil Length
R7 Ex 01	67 %
R7 Ex 02	67%
R7 Ex 03	66.98%

Comparison of results clearly indicated that properties of extracted TPA are as good as commercially available TPA.

Basic difference between the alcoholysis method and proposed new method is an order of feeding raw materials in to the reactor. In the alcoholysis method initial step is formation of monoglyceride by reacting triglyceride oil with polyol and second step (esterification reaction) start after completion of the first reaction. However in the proposed method, oil and terephthalic acid first fed in to the reactor and polyol added to the system just after the initiation of first reaction . Therefore acid - oil reaction (separation of fatty acid from oil) and esterification reaction can occur simultaneously. This reduces the total processing time drastically. New method also reduces gel formation ability by balancing acid-oil reactions and alkyd forming reactions.

The second difference is alcoholysis has a cooling period between monoglyceride forming and esterification reactions. However in proposed method, polyol was added to reactor just after the heating period so no cooling period. This also helps to reduce total processing time. FTIR spectrum can be used as evidence to prove formation of alkyd resins from TPA.

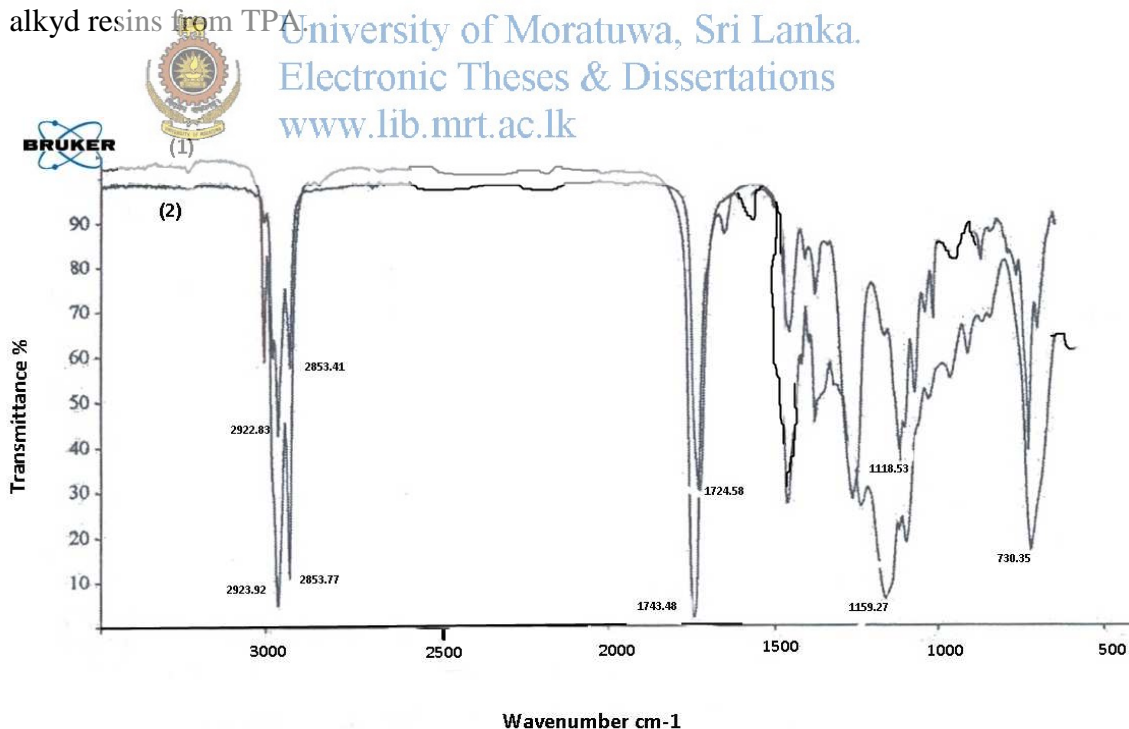


Figure 4-15: FTIR spectra of Soya bean oil (1) and Alkyd Resin (2)

Insertion of terephthalic acid to the soya oil during the esterification reaction can be proved by comparing FTIR spectra of soya oil and alkyd resin. Figure 4-15 (1) shows

the FTIR spectrum of the alkyd resin produced by using R7 recipe at 180 °C. Figure 4-15 (2) shows the FTIR spectrum of the soya oil bought from local market. The band displacement of 1743.48 cm^{-1} to 1724.58 cm^{-1} which belongs to C=O group is evidence for poly esterification reaction ^[23] .

Appearance of peak in 1118.53 cm^{-1} in the spectrum 2 is evidence for TPA acid incorporation ^[23] . This peak refers COO group in the alkyd resin.



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5. CONCLUSIONS

1. Sodium Carbonate can be use to overcome the disadvantages of the Sodium hydroxide as hydrolyzing agent in PET recycling process.

78.89 % PET was recycled under conditions of 170 °C, 35 minutes and PET: EG ratio 1:4.

2. Calcium carbonate and lead oxide are more suitable as catalysts for monoglyceride process than sodium salts which induced dark colour to reaction mixture.
3. Alcoholysis process is not suitable process to synthesize TPA based alkyd resins..
4. Soya oil, TPA and glycerol based alkyd resins can be easily synthesized by proposed new methodology under following conditions.
 - Reaction temperatures 260 °C or above.
 - Continuous and uniform addition of polyol to the system just after the system reaching to its maximum temperature.

5. Alkyd processing time reduces with increasing temperature. Minimum time achieved was 120 minutes at 280 °C.

6. Extracted TPA from waste PET bottles can be successfully used to make long oil alkyd resin with the commercially acceptable properties.




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