Recycling Of Polyethylene Terephthalate Bottles to Synthesize Alkyd Resins

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1. Introduction

1.1 About PET

The abbreviation PET stands for polyethylene terephthalate, a substance that, from a chemical point of view, is a polyester. Polyesters were first manufactured in the 1930’s, for use as synthetic fibres. Much of the PET produced today is still used to produce fibre. Fleece sweaters, for example, are made of PET. Later, PET came to be used for packaging films. Film and magnetic tape also use PET film as a carrier. Then, in the 1970's, a production process for PET bottles was finally developed. PET bottles were initially used for soft drinks, but gradually their use with bottled water became more popular. PET is manufactured from terephthalic acid (a dicarboxylic acid) and ethylene glycol (a dialcohol). The two substances react together to form long polymer chains, with water as a by-product (Fig 1.1). As in most processes of polymerisation, a catalyst is also required, which in this case is a basic catalyst.

![Fig 1.1: Structure and chemical equation of PET](image)

PET is a virtually unbreakable, colourless, lightweight, transparent polymer. As PET is transparent, it allows the content of the container to remain visible. The robustness of PET is vitally important for beverage packaging since it makes the bottles completely safe for on-the-go...
or sports use. Over recent years, the weight of PET bottles has been constantly reduced and today a bottle can weigh as little as 20 to 30 grams. This process of light weighting represents a true benefit with regard to the environmental impact a bottle will have during its lifetime: production, transport to the consumer and end of life cycle. With such excellent material properties, PET is widely used today as a packaging material for beverages and is one of the most suitable materials for the packaging of natural mineral and spring water (1).

1.1.1 Synthesis Process of PET resins

PET resins are produced commercially from ethylene glycol (EG) and either dimethyl terephthalate (DMT) or terephthalic acid (TPA). DMT and TPA are solids. DMT has a melting point of 140°C, while TPA sublimes (goes directly from the solid phase to the gaseous phase). Both processes first produce the intermediate bis-(2-hydroxyethyl)-terephthalate (BHET) monomer and either methanol (DMT process) or water (TPA process). The BHET monomer is then polymerized under reduced pressure with heat and catalyst to produce PET resins. The primary reaction for the DMT process is: (2)

\[
\text{CH}_2\text{OOC} \underbrace{\text{OCH}_2\text{CH}_2\text{OH}}_{\text{DH}} \rightarrow \text{HO} - (\text{OC} \underbrace{\text{OCH}_2\text{CH}_2\text{O}}_{\text{PET}})_n \text{H} + 2n\text{CH}_2\text{OH}
\]

The primary reaction for the TPA process is:

\[
\text{HOOC} \underbrace{\text{O}}_{\text{TPA}} + \text{HOCH}_2\text{CH}_2\text{OH} \rightarrow \text{HO} - (\text{OC} \underbrace{\text{OCH}_2\text{CH}_2\text{O}}_{\text{PET}})_n \text{H} + 2n\text{H}_2\text{O}
\]

1.1.2 Physical and Chemical Properties of PET

PET exhibits interesting physical properties (morphology). PET, in its purest form, is an amorphous glass-like material. Under the influence of direct modifying additives it develops crystallinity. Also, crystallinity can be developed by heat treatment of the polymer melt. PET is classed as a semi-crystalline polymer and when heated above 72°C changes from a rigid glass-like state into a rubbery elastic form where the polymer molecular chains can be stretched and aligned in either one direction to form fibers, or in two directions to form films and bottles. Because of its rather high transition temperature only a limited amount of crystallization can occur during cooling after injection molding poly (ethylene terephthalate). Such moldings are
transparent and amorphous and are of little value. If the material melt is cooled quickly, while still held in the stretched state, then the chains are frozen, with their orientation remaining intact. Once set in this stretched state the material is extremely tough and confers the properties we see in a typical PET bottle.

Many modifications are introduced to develop specific properties for the various packaging applications and to suit particular manufacturing equipment. Usually the modifications are of a chemical nature to make manipulation of the PET between different crystalline forms easier. For example, small concentrations of an appropriate co-monomer (isophthalic acid—IPA or 1, 4-cyclohexanediol) slow down the rate of crystallization and allow the manufacture of thicker bottle walls, sheets and films\(^{(10)}\).

PET is becoming the package of choice for many food products, particularly beverages and mineral waters. The main reasons for its popularity are the properties of glass-like transparency coupled with adequate gas barrier properties for retention of carbonation. Also it exhibits a high toughness/weight property ratio which allows light weight, large capacity safe unbreakable containers.

Other key properties of PET are given in Table 1.1 \(^{(3)}\)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
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<tr>
<td><strong>Physical Properties</strong></td>
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<tr>
<td>Density</td>
<td>1.3-1.4</td>
<td>g/cm(^3)</td>
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<td>Flammability</td>
<td>Self extinguishing</td>
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<td>Refractive Index</td>
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<td>Water absorption equilibrium</td>
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<td><strong>Thermal Properties</strong></td>
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<td>Coefficient of thermal expansion</td>
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<td>x10(^6) K(^{-1})</td>
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<td>Specific Heat</td>
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<td>Thermal Conductivity (at 23(^0)C)</td>
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<td>Lower working temperature</td>
<td>-40 to -60</td>
<td>(^0)C</td>
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<td>Upper working temperature</td>
<td>115-170</td>
<td>(^0)C</td>
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<td>Heat deflection temperature (0.45MPa)</td>
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<td>(^0)C</td>
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<td>Heat deflection temperature (1.8MPa)</td>
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<td><strong>Mechanical Properties</strong></td>
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<td>Coefficient of friction</td>
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<td>Tensile strength</td>
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<td>Tensile modulus</td>
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<tr>
<td>Young’s modulus of elasticity</td>
<td>2-2.7</td>
<td>Nm(^2)</td>
</tr>
</tbody>
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Table 1.1: Key properties of PET
1.1.3 PET as packaging material

PET is used in the packaging sector in the form of films, trays or bottles, its principle use being in bottles. In 2010, almost 70% of all bottled water and soft drinks sold globally was supplied in PET bottles (Fig 1.2).

![Figure 1.2: Global uses of PET packaging in 2010 (excluding fibre), amounting to a total of 11.5 million metric tonnes](image)

1.1.4 Manufacturing of PET bottles

PET bottles are mainly manufactured in a two-stage process. The PET granulate is first melted at about 280 °C and processed into what are called preforms. These preforms already have the bottle cap threads and are small and easy to transport. Shortly before the filling process, the preforms are again heated to about 120 °C and blown into their final bottle shape. "One stage" process can also be used where the preform goes directly from the injection to the blowing stage. After cooling, bottles are filled with the beverage. This "stretch blow-moulding process" causes the PET to partially crystallise, which whilst reducing its transparency, improves the stability of the bottle and enhances its barriers against oxygen and carbon dioxide. Non-crystalline PET is highly transparent while fully crystalline PET is opaque and is used, for example, to make microwave dishes and trays \(^1\).
1.2 Recycling of PET

Polymer industry causes serious environmental problems because of the large amount of waste discarded in the urban centres. In recent years, recycling of polymers has received a great deal of attention. Chemical recycling, applied to the post-consumer condensation polymers, might be of great interest. The overall world consumption of PET amounts to about 13 million tons. A great percentage of PET is recycled by various methods and for several applications \(^{(4)}\). PET is polyester with functional ester groups that can be cleaved by some reagents, such as water (hydrolysis), alcohols (alcoholysis), acids (acidolysis), glycols (glycolysis), and amines (aminolysis). The recycled PET is mostly used in the form of fibres, films, foams, sheets, bottles etc. Thus, chemical-recycling processes for PET are divided as follows: (i) hydrolysis, (ii) glycolysis, (iii) methanolysis and (iv) other processes \(^{(5)}\).

![Chemical Recycling of PET](image)

**Fig 1.3: Routes for Chemical Recycling of PET**

1.2.1 Glycolysis

Glycolysis can be described as a molecular depolymerisation process by transesterification between PET ester groups and a polyol in excess, glycerol in this case, to obtain the monomer bis(2- hydroxyethyl terephthalate) (BHET), according to the following reaction scheme:
In this process ester linkages are broken and replaced with hydroxyl terminals. The main advantage of this strategy is that it can be easily integrated into a conventional PET production plant and the recovered BHET can be blended with fresh BHET \(^6\). Further, the monomer (and higher oligomers) thus obtained can be used as building blocks to synthesise other polymers with higher economical values such as unsaturated polyesters, polyurethane foams, polyisocyanurate foams, copolyesters, polyurethane coatings, alkyd resins, low temperature curable resins, or UV curable resins \(^7\). These numerous applications, in turn, provide an economical flexibility when using the raw recycled monomer for the most profitable option upon demand.

Moreover, glycolysis avoids the use of, supercritical in some cases, methanol used in methanolysis and limits the environmental impact of the recycling strategy since strong acids or alkalis (necessary in PET hydrolysis) are not employed. The reaction is typically performed under relatively mild conditions, 180-260°C and atmospheric pressure, but metal catalysts are often required to increase the rate. Two major drawbacks of this process are, one hand, the non-biodegradable and toxic nature of heavy metal catalysts such as Zn salts, which are reported as the most active glycolysis catalysts and, on the other hand, the low selectivity of the reaction towards BHET avoiding the formation of higher oligomers (dimers and trimers), which are difficult to purify by conventional separation methods \(^8\).
1.2.2 Methanolysis

This process consists of the degradation of PET by methanol at high temperatures and under high-pressure conditions. The main products of PET methanolysis are dimethyl terephthalate (DMT) and ethylene glycol (EG), which are the raw materials necessary for production of this polymer \(^9\). Catalysts such as zinc acetate, magnesium acetate, cobalt acetate, and lead dioxide enhance the reaction; however, the most commonly used catalyst is zinc acetate. There are examples of using arylsulfonic acid salts as catalysts for methanolytic degradation of PET. Methods for the conduction of methanolysis have similar basic parameters, e.g., pressures of 2–4 MPa and temperatures of 180–280°C. The polymer degradation takes place with the release of ethylene glycol. After the termination of the reaction, it is necessary to deactivate the catalyst \(^5\). Otherwise, in subsequent stages of the process, there could occur is possible DMT losses as a result of transesterification with ethylene glycol. The DMT obtained is precipitated from the post reaction mixture after its previous cooling and then is centrifuged and crystallized.

1.2.3 Hydrolysis

Nowadays there is growing interest in hydrolysis for the chemical recycling of PET, since it is the only method with the reaction products terphthalic acid (TPA) and ethylene glycol (EG), i.e. the monomer from which PET is produced. This is associated with the trend in the new factories for PET synthesis to produce it directly from TPA and EG, thus replacing dimethyl terphthalate (the traditional monomer) from the technological process. The main disadvantage of this method is the use of high temperature (200–250°C) and pressure (1.4–2 MPa) as well as long time needed for complete depolymerisation. Commercially, hydrolysis is not widely used to produce food-grade recycled PET, because of the cost associated with purification of the recycled TPA. Hydrolysis of PET can be carried out as (a) alkaline hydrolysis, (b) acid hydrolysis and (c) neutral hydrolysis \(^5\).

1.2.4 Aminolysis

Aminolysis processes have seldom been used for PET chemical recycling, at least for deep polymer degradation. The superficial partial aminolytic degradation of PET fibers has been the subject of numerous research studies, and is currently applied on an industrial scale. Such
modification processes improve the quality of fiber coloration and other technical and application parameters of the fibers. From the available literature, it can be seen that in most cases the aminolytic modification processes of PET fiber surfaces are conducted using primary amines in aqueous solutions or less commonly in the gas form. The most frequently used amines are methyamine, ethylamine, and butylamine. Other amines used are ethanolamine and triethylenetetramine.

1.2.5 Ammonolysis

TPA amide is produced by the action of anhydrous ammonia on PET in an ethylene glycol environment. This can be converted into terephthalic acid nitrile and further to p-xylylenediamine or 1,4-bis(aminoethyl) cyclohexane. Very good results were obtained from the ammonolysis of PET waste from postconsumer bottles; the process was carried out under a pressure of about 2 MPa in a temperature range of 120–180°C for 1–7 hrs. After the reaction was completed, the amide produced is filtered, rinsed with water, and dried at a temperature of 80°C. The product has a purity of not less than 99%, and the yield is above 90%. A low-pressure method of PET ammonolysis, in which the degradation agent is ammonia in an ethylene glycol environment, is also known. The process is catalyzed by zinc acetate in a quantity of 0.05 wt%, conducted at a temperature of 70°C and a molar ratio of PET: NH₃ of 1:6. TPA amide was produced with a yield of about 87% (5).

1.2.6 Mechanical Recycling

In this approach, the polymer is separated from its associated contaminants and it can be readily reprocessed into granules by conventional melt extrusion. Mechanical recycling includes the sorting and separation of the wastes, size reduction; melt filtration and reforming of the plastic material. The basic polymer is not altered during the process. The main disadvantage of this type of recycling is the deterioration of product properties in every cycle. This occurs since the molecular weight of the recycled resin is reduced due to chain-scission reactions caused by the presence of water and trace acidic impurities. A secondary recycling process presents some unique problems that may cause it to be inappropriate for the production of food-contact articles, particularly if the recycler had little or no control over the waste stream entering the recycling facility (7).
1.3 Alkyd Resin

Alkyd resins are any of a large group of thermoset resins that are essentially polyesters made by heating polyhydric alcohol with polybasic acids or their anhydride and used chiefly in making protective coatings with good weathering properties.

These resins are useful as film forming agents in paint, varnished and enamels & as thermosetting plastics that can be moulded into solid objects. Hence, alkyd resins are one of the important ingredients in the synthetic paint industry.

The paint factories in India currently produce a variety of paint which can broadly be categorized as synthetic enamel. This type of paint is used for the exclusive use in internal/ exterior walls and ceilings of architecture. This type consists of alkyd based products which are used as metallic & wood paints, varnishes & lacquers, antirust, etc \(^{(11)}\).

Alkyd coatings are a class of polyester coatings derived from the reaction of an alcohol and an acid or acid anhydride hence the term alkyd from “alcohol and acid or anhydride” and are the dominant resin or “binder” in most “oil-based” coatings sold to the consumer market. Alkyd coatings today are typically manufactured from acid anhydrides such as phthalic anhydride or maleic anhydride and polyols such as glycerine or pentaerythritol and are modified with unsaturated fatty acids (from plant and vegetable oils soya oils) to give them air drying properties. The unsaturated oils react with oxygen from the air which cause the oils to polymerize or crosslink with each other \(^{(12)}\).

Alkyd resins are not only the major important binders but also they are the largest volume base of coatings and paints especially for decorative applications \(^{(13)}\). Studies are available on preparation and application of alkyd resins using fatty acids or oils \(^{(14-16)}\). Alkyd resins are used more than other binders because of their low processing cost, inexpensive raw material, easy manufacturing. Besides they can be dissolved in less expensive solvents. In addition, alkyd resins are used in other applications such as air drying, matt and semi matt varnishes of wood furniture.

Poly alcohols which are mainly used for condensational polymerization reactions of alkyd resins comprise ethylene glycol, propylene glycol, diethylene glycol and pentaerythritol. In addition poly carboxylic acids are divided into two different branches: aromatic based poly acids and aliphatic-based poly acids. For the synthesis of alkyd binders, aromatic poly carboxylic acids derived from phthalic anhydride and isophthalic acid, are usually employed. Cycloaliphatic
anhydrides such as hexahydrophthalic anhydride, and malic anhydride have also been used for alkyd resins esterification reactions. Careful selection of the type of poly basic acids and poly alcohols may help in preventing gelation of alkyd resin of choice, and offers easy control of the process of polymerization of alkyd resins. Benzoic acid and other mono basic carboxylic acid are used for alkyd resins formulation including high functionality system to act as chain stopper (17).

1.3.1 Synthesis Process:

Alkyd coatings are produced in two processes fatty acid process and the alcoholysis or glyceride process. Higher quality higher performance alkyds are produced in the fatty acid process where the composition of the resulting resin can be more precisely controlled. In this process an acid anhydride, a polyol and an unsaturated fatty acid are combined and cooked together until the final product has achieved a predetermined level of viscosity as suitable for its intended use. More economical alkyd resins are produced from the alcoholysis or glyceride process where end product quality control is not as paramount. In this process raw vegetable oil, high in unsaturated component, is combined with additional polyol and heated to cause transesterification of the triglycerides into a mixture of mono- and diglyceride oils. To this resulting mixture acid anhydride is added to build molecular weight of the resin into roughly the same product as in the fatty acid process. However the alcoholysis or glyceride process produces a more randomly oriented structure. In both cases the resulting product is a polyester resin to which pendant drying oil groups are attached. At the conclusion of both processes the resin is purified, diluted in solvent and sold to paint and varnish makers (12).

Two processes are used for the production of alkyd resins, namely the solvent and the fusion process. The solvent process uses a small amount of solvent, 5-10%, in the esterification reaction to act as a reflux medium.

The advantages of this process are:

1. Uniformity of product
2. Increased speed of reaction
3. Lower material losses.
4. Light colour
In the solvent process, the production of alkyds can be carried out either in a single stage or a two stage process. Under the single stage process, the drying oil (linseed oil), polyalcohol and phthalic anhydride are converted simultaneously. This method of alkyd preparation is not satisfactory because of the incompatibility of the phthalic anhydride with drying oil (linseed oil) and the difficulty of controlling the reaction to produce the desired end-products.

In the first stage of the two stage solvent process, monoglyceride is produced from drying oil and polyalcohol and in the second stage the monoglyceride is esterified with phthalic anhydride to convert it into alkyd resin. This process is more satisfactory and is the one recommended for the envisaged plant because it eliminates the problems of the first option.

In the two-stage solvent process, the first operation is the alchoholysis reaction which takes place under different duration of time (varying form 40 minutes to 4 hours) and temperature (from about 240 to 260°C). The completion of this stage is shown by the solubility of the product in about twice its weight of methanol (11).

1.3.2 Market Potential

Alkyd resin, which is used in the production of a wide variety of paints, is supplied to the Indian market both from domestic production and import. As Indian industries are producing paint of amount approximately Rs.15000 crores which needs Alkyd Resin of amount near about Rs. 3000 crores. Due to construction of apartments, buildings, roads there is huge demand of paint in this sector. Increased demand of paint will need the basic raw material of paint i.e. alkyd resin simultaneously (11).

1.3.3 Applications of Alkyd Resin

a) Very long oil alkyds (>75%)

The use of very long oil alkyd is restricted to printing ink industry. At these oil lengths, orthophthalic based alkyds give very low viscosities and consequently isophthalic alkyds are preferred. Alkyds of the type are frequently used as modifiers for heat-set and quick-set inks where they improve pigment wetting and scuff resistance. They are also used as binders for metal decorating inks.
In recent years, isophthalic alkyds have been used as modifiers for latex based paints. Modified latexes of this type show improved adhesion when applied over chalky substrates.

Very long non drying oil based alkyds find limited use as plasticizers. Plasticizers of this type are mainly used with ethyl cellulose and nitrocellulose where they show excellent compatibility and retain flexibility at low temperatures.

b) Long oil alkyds (60-75%)

All the resins in this range are soluble in low odour aliphatic solvents, permitting excellent brushing properties with good flow characteristics and easy brush cleaning. Their main use is in architecture and maintenance as brushing enamels, undercoats, primers, and also marine paints (fortified with chlorinated rubber).

Most architectural high gloss enamels for consumer market are formulated on long oil soya based alkyds. Safflower oil based alkyds give slightly better drying and non yellowing properties. Tall oil based alkyds give good non yellowing properties with reasonable drying time.

Rosin additions are not normally made to long oil alkyds since gloss and colour retention are downgraded. These alkyds do give better flow and speed of set, and are used in architectural undercoats.

Long oil alkyds modified with polyamide resins are used to produce thixotropic architectural paints. These resins are also used in fairly high proportions in some undercoats, where they show excellent non penetrating properties and ease of brushing.

c) Medium oil alkyds (45-60%)

Products in this range are probably the most versatile of all the alkyds. Alkyds of this type are extensively used in anti corrosive primers and in general maintenance painting applications. Medium oil linseed and soya alkyds are used in automotive refinishing and implement enamels. A specific application for medium oil length alkyds is in flat wall paints.
Rosin and phenolic modifications are frequently made to medium oil length alkyds, to give them excellent hard drying properties, with improved resistance to abrasion, water and alkali. They are extensively used in maintenance paints, industrial primers and some marine paints (18).

d) Short oil alkyds (<40%)

Short oil alkyds generally give films of high quality with regard to color and gloss retention but low flexibility and with poor adhesion. Short oil alkyds are soluble in aromatic but not aliphatic solvents. The air-drying type is used in baking primers and enamels, either as the sole binder or together with other resins, such as urea or melamine resins. The nondrying type is mainly used as plasticizing resin in nitrocellulose lacquers and in combination with urea or melamine resins in stoving and acid curing finishes (19).
2. Experimental work

2.1 Materials Used

Waste PET bottles of the same size and company were collected from a local vendor near the institute. Acetone, glycerol, phthalic anhydride, were ordered from SD Fine Chem Ltd, along with the analytical grade reagents, 99.5% isopropyl alcohol, xylene, butanol, sodium hydroxide & potassium hydroxide pellets, and phenolphthalein. Catalyst zinc acetate was bought from Thomas Baker. Dehydrated Castor oil was obtained as a gift sample from Jayant Agro Organics, Mumbai. The cobalt and zirconium driers were purchased from Aryavart Chemicals Ltd. Rutile TiO$_2$ pigment was purchased from Ankush Enterprise, whereas the paint emulsifier soya lecithin was received as gift sample from KTech India Ltd.

2.2 Glycolysis of PET

Glycolysis reaction was carried as per the reaction scheme in Fig 1.4, in a 500 ml four neck flask with water reflux condenser, in presence of nitrogen blanket and at a temperature of 210$^\circ$C. The PET bottles were first cut into small pieces (0.2cm$^2$) and washed with acetone and water to remove the dust and other impurities. Washed PET flakes were dried thoroughly in oven before charging them in the reaction flask.

Quantity of glycerol added was varied on the basis of weight ratio. The ratio of PET flakes to glycerol was varied from 1:1 to 1:3 (w/w). The mixture was stirred for 3 hours at the desired temperature. (Refer Fig 2.1 to check the process route for glycolysis of PET)

To check the effect of catalyst on the depolymerisation reaction via glycolysis, 1% (w/w) of zinc acetate powder was added to the reaction flask along with the PET flakes and glycerol.

After completion of 3 hours, the mixture was continued to stir as it cooled down to 100$^\circ$C, and was then collected in pre-weighed sample bottles.
2.3 Synthesis of Alkyd Resins

Monoglyceride Process was followed for synthesizing long oil alkyd. The glycolyzed product was first reacted with castor oil in presence of sodium hydroxide catalyst, at 200°C. The reaction was continued till monoglyceride was formed, which was confirmed by testing solubility of the product in methanol.

After monoglyceride was formed, phthalic anhydride was added to the reaction flask at 130°C and the temperature was raised to 200°C. A Dean Stark assembly was setup and xylene was added to the mixture, which facilitates removal of water by formation of azeotrope. Acid value of the reaction mixture was checked after regular intervals, and the reaction was stopped once the acid value fell below 10mgKOH/g. Reaction can also be monitored on the basis of stoichiometric amount of water collected in the Dean Stark.

A standard alkyd was prepared for the purpose of comparative study of experimental samples. For the standard alkyd, glycerol was used as the hydroxy functional compound instead of glycolyzed product (BHET). Reaction scheme followed for standard alkyd synthesis is shown in Fig 2.2.

\[
\text{Oil} + 2\text{Gly} \rightarrow 3\text{MG} \quad \text{(1)} \\
3\text{PA} + 3\text{MG} + 2\text{Gly} \rightarrow \text{alkyd} + 3\text{H}_2\text{O} \quad \text{(2)}
\]

Fig 2.2: Reaction Scheme for Alkyd synthesis
The amount of raw material to be charged was estimated based on the concept of equivalent base and equivalent acid concept, with an underlying assumption- functionality of the glycolyzed product is 2 (since functionality of BHET is 2).

2.4 Formulation of Paint

The alkyd resins synthesized were used for formulating paint and thus check its performance in an application. A basic formulation was prepared with minimum raw materials, including resin (alkyd), pigment (TiO₂), emulsifier (soya lecithin), and solvent (70:30 xylene: butanol (w/w)). Pigment volume concentration (PVC) of 30% was maintained for all the batches. All the materials were taken in a vessel and stirred in high speed disperser (max rpm= 19000) for 1 hr. The formulated paint was then diluted with solvent mixture and applied on metal panels for film testing.

2.5 Characterization- Fourier Transform Infrared Spectroscopy

FT-IR Shimadzu IR Tracer 100 was used for analysis of the glycolyzed samples and alkyd resins. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some passes through (is transmitted). The resulting signal at the detector is a spectrum representing a molecular ‘fingerprint’ of the sample. The usefulness of infrared spectroscopy arises because different chemical structures (molecules) produce different spectral fingerprints. Therefore FTIR proves to be an effective analytical instrument for detecting functional groups and characterizing covalent bonding information.

2.6 Tests Performed

2.6.1 Hydroxyl value

The hydroxyl value is given in mg KOH per g sample and gives information about the degree of depolymerization of the PET in this case. 1-2 g sample is taken in a conical flask and 10ml acetic acid-pyridine mixture is added to it. The flask is then kept on reflux for 2 hrs. In this course of time, acetic acid reacts with the hydroxy (OH) functionalities to form acetate. The remaining acetic acid is back titrated with alcoholic KOH soln and phenolphthalein indicator. A blank run
is conducted simultaneously. The difference between the reading of blank and sample is equivalent to OH content.

\[ \text{Hydroxyl value} = \frac{(\text{Blank} - \text{Sample}) \times N_{\text{KOH}} \times 56.1}{\text{sample weight}} \]

### 2.6.2 Acid value

The acid value obtained corresponds to the amount of carboxylic acid groups in alkyd resins, and is given in mg KOH per gram sample. Low acid value is an indication of completion of reaction of alkyd synthesis.

1-2 g sample is drawn out from the mixture and 25ml neutral alcohol is added to dissolve the sample (heat if necessary). Titration is carried out using KOH solution and phenolphthalein indicator, end point being colourless to pink.

\[ \text{Acid value} = \frac{(\text{Burette reading} \times N_{\text{KOH}} \times 56.1)}{\text{sample weight}} \]

### 2.6.3 Instrumental Analysis- Gel Permeation Chromatography

Gel Permeation Chromatography (GPC) is a type of size exclusion chromatography (SEC), which separates analytes on the basis of size. This differs from other separation techniques which depend upon chemical or physical interactions to separate analytes. Separation occurs via the use of porous beads packed in a column.

GPC is often used to determine the relative molecular weight of polymer samples as well as the distribution of molecular weights. What GPC truly measures is the molecular volume and shape function as defined by the intrinsic viscosity. GPC allows for the determination of PDI as well as \( M_v \) and based on other data, the \( M_n \), \( M_w \), and \( M_z \) can be determined.

The molecular weight of glycolyzed products were estimated using the 1260 Infinity II multi detector GPC/SEC system.

*Sample Preparation:* 0.05g of sample is dissolved in 5ml tetrahydrofuran (THF) and passes through plane and hollow fibre membrane into vials which store 1ml of the sample. 1µl aliquot enters the GPC column for analysis.
2.6.4 Film Testing of Paint

The paint was diluted in xylene solution before applying a coat (using brush) on the metal panels. Cobalt and zirconium driers were added to the paint mixture to facilitate drying. The surface preparation of metal panels was done by rubbing sand paper on it, and the application of resin was using a brush. The following tests were carried out to check the film properties of the paint:

a) Impact Testing

Falling dart impact testing employs a ball-end dart, or tup, to be raised to a specified height then dropped onto the test sample. The measure of toughness is done by noting the drop height and weight of the tup (60 cm & 2.5 Kg in this case) that cause sample rupture.

For coated metal panels, it is done both inwards and outwards. After the testing the impacted area is observed for cracks. If there are no cracks the sample is considered to be passed for that particular load and height (2.5 Kg & 60 cm). There should also be no cracking at the circumference of the impact. Along with the toughness it also gives us a measure of the flexibility of the sample (20).

ASTM-D1709 is the standard which is generally followed.

b) Pencil Hardness

This method is used to determine the hardness of clear and pigmented organic coating films. A coated panel is placed on a firm horizontal surface. The pencil is held firmly against the film at a 45° angle and pushed away from the operator. The process is started with the hardest pencil and continued down the scale of hardness to either of two end points: one, the pencil that will not cut into film (pencil hardness), or two, the pencil that will not scratch the film (21).


| Softer | Harder |

Fig 2.3: Scale of hardness

ASTM-D3363 is the standard which is generally followed.
c) Gloss Testing

Gloss is a measurement of how a surface reflects light in the specular direction. Some factors that affect gloss are the refractive index of the material, the angle at which light is directed from the surface, and the roughness of the coated surface.

Common angles of incidence for gloss measurement are: 20°, 60°, and 85°.

- 20° - Gloss surface
- 60° - Semi-gloss surface
- 85° - Flat (matte) surface

ASTM-D523 is the method used.

Gloss measurements are always referenced against a standard, and the angle of reflection (20°, 60°, or 85°) must be specified. The Glossmeter is set to the proper angle, calibrated, then checked with the standard supplied with the meter. The meter is then placed on the test sample and a reading is taken. The scale of measurement varies from 0 to 100, 0 indicating poor gloss and 100 indicating high gloss.

d) Flexibility

The coated panels are bent over a conical mandrel and the resistance to cracking of the coating is determined.

With the operating lever of the apparatus in a horizontal position, slip the test specimen between the mandrel and the drawbar with the finish side towards the drawbar. Rigidly clamp the specimen in a vertical position adjacent to the mandrel by placing the long edge behind the clamping bar in such a manner that the panel is always set up to the narrow end of the mandrel. Move the lever through about 180° at uniform velocity to bend the specimen approximately 135°. Examine the bent surface of the specimen immediately with the unaided eye for cracking. The mandrel diameter at which cracking ceased is taken as the resistance to cracking value (23).

ASTM-D522 is followed.
e) **Adhesion**

A lattice pattern with either six or eleven cuts in each direction is made in the film to the substrate, pressure-sensitive tape is applied over the lattice and then removed, and adhesion is evaluated by comparison with descriptions and illustrations.

Select an area free of blemishes and minor surface imperfections, and make parallel cuts. After making the required cuts brush the film lightly with a soft brush or tissue to remove any detached flakes or ribbons of coatings. Make the additional number of cuts at 90° to and centered on the original cuts. Brush the area as before and inspect the incisions for reflection of light from the substrate. If the metal has not been reached make another grid in a different location.

Place the center of the tape over the grid and in the area of the grid smooth into place by a finger. The color under the tape is a useful indication of when good contact has been made. Within 60-120 sec of application, remove the tape by seizing the free end and rapidly. Inspect the grid area for removal of coating from the substrate.\(^{(24)}\)

Rate the adhesion in accordance with the following scale:

- **5B** - The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
- **4B** - Small flakes of the coating are detached at intersections; less than 5 % of the area is affected.
- **3B** - Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15 % of the lattice.
- **2B** - The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35 % of the lattice.
- **1B** - The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65 % of the lattice.
- **0B** - Flaking and detachment worse than Grade 1.
f) Drying time

The coated panel were allowed to air dry, and the time when the film was completely adhered to the surface, leaving no tack and wetness was recorded.

g) Dry film thickness

Digital coating thickness gauges (Elcometer) are ideal to measure coating thickness on metallic substrates. Electromagnetic induction is used for non-magnetic coatings on ferrous substrates such as steel, whilst the eddy current principle is used for non-conductive coatings on non-ferrous metal substrates.

h) Acid and Alkali resistance

5% HCl and 5% NaOH solution (w/w) were used for testing acid and alkali resistance. A small area of the panel was covered with both the solutions and allowed to stay for 24 hrs. Changes in the areas covered respectively were then observed and recorded.
3. Results & Discussion

3.1 Glycolysis of PET

The glycolysis of PET in this study was carried out using five batches where the parameter studied included effect of nitrogen blanketing, polyol quantity, and effect of catalyst. 1:2 mass ratio of PET: GLY was used for studying effect of nitrogen blanketing and catalyst. The sample code for glycolyzed product corresponding to the batch in absence of nitrogen is GP 1, and that conducted in presence of nitrogen is GP 2. Glycolyzed product for PET: GLY mass ratio 1:3 is GP3. To study the effect of catalyst, zinc acetate powder was added (1% w/w) and the product obtained is coded GP4. A batch with 1:1 PET: GLY mass ratio was also studied, but no valid results were obtained as the product formed was solid and not suitable for further analysis and process. Fig 3.1 shows the different glycolyzed products obtained.

Fig 3.1 (clockwise from left): GP1; GP2; GP3; GP4; GP5

Effect of Nitrogen blanketing- The colour difference in GP 1 and GP 2 clearly indicates the effect of nitrogen blanketing in the reaction. The dark colour of GP 1 can be attributed to the fact that the material has degraded under the presence of oxygen and high temperature. Also the results from GPC (Fig 3.2 (a)) show that two peaks are obtained for the sample GP 1 indicating the presence of two oligoesters, whereas in case of GP 2 only one oligoester is formed (in this case, monomer BHET). Thus nitrogen blanketing has contributed in obtaining higher yield of the product.
Fig 3.2: Gel permeation chromatography plots of Glycolyzed products

Results on the average molecular weights (number avg molecular weight $M_n$, and weighted avg molecular weight $M_w$) of the four glycolyzates are presented in Table 3.1. In this table the hydroxyl value of the GPs, and the polydispersity of the molecular weight distribution of these samples obtained from GPC are also included.

*Effect of Polyol quantity*- As the amount of GLY was increased the area under the peak corresponding to the lowest molecular weight was increased (Refer Fig 3.2). Also the hydroxyl
value of the product decreases as the GLY quantity increases, which is expected as the functionality of GP (BHET) is less (2) than glycerol (3). Low hydroxyl value is also an indication of less amount of free glycerol present in the sample. Hence, with increased amount of GLY a better depolymerisation of PET was obtained (25).

Effect of catalyst- When zinc acetate catalyst was added in 1% (w/w) during glycolysis reaction, the product obtained showed comparable properties to the GP 3 (Refer Table 3.1 and Fig 3.2 (b)). Thereby indicating that the depolymerization of PET can be increased by addition of a catalyst, instead of increasing the polyol quantity. This proves to have a significant impact on the economics of the process.

<table>
<thead>
<tr>
<th>Glycolyzed Product</th>
<th>Mass Ratio (PET: GLY)</th>
<th>Hydroxyl number</th>
<th>Data from GPC</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP 1</td>
<td>1:2</td>
<td>164.25</td>
<td>334 667 1.99</td>
</tr>
<tr>
<td>GP 2</td>
<td>1:2</td>
<td>101.12</td>
<td>340 651 1.91</td>
</tr>
<tr>
<td>GP 3</td>
<td>1:3</td>
<td>151.27</td>
<td>259 406 1.58</td>
</tr>
<tr>
<td>GP 4</td>
<td>1:2</td>
<td>91.33</td>
<td>263 414 1.57</td>
</tr>
</tbody>
</table>

Table 3.1: Hydroxyl value and Average molecular weights of the Glycolyzed products

FTIR Characterization

Figure 3.3 shows the FTIR peaks obtained for the glycolyzed products. Bands from –C=O stretching and stretching vibration of C-O which appear at ~1715 cm\(^{-1}\) and ~1270 cm\(^{-1}\) respectively, are a key bands that confirmed ester bond formation during the glycolysis of PET. Band around ~3300 cm\(^{-1}\) is due to the free hydroxyl group presents in glycolyzed PET oligoesters. The peaks around ~2940 and ~2880 cm\(^{-1}\), were assigned to the stretching vibrations of C-H bands in the structure of methyl and methylene groups. FT-IR spectra show the bands around ~1420 cm\(^{-1}\) of bending vibration of methylene groups in the polyol chains. Furthermore, the peaks at ~1100 and ~1030 cm\(^{-1}\) corresponding to a C-O group of ether primary and secondary hydroxyl end-groups in the structure of GLY (25).
Fig 3.3: FTIR peaks of glycolyzed products
3.2 Synthesis of Alkyd Resins

The alkyd resin was synthesized using the equivalent base and equivalent acid based calculation. The equivalent base was the glycol component whereas the equivalent acid was phthalic anhydride. 200g batch was prepared for every GP, and 60% oil length was maintained to prepare long oil alkyd using dehydrated castor oil.

Since the base component has to be in excess to prevent gellation, equivalent base was taken to be 2.4 and equivalent acid to be 2. Since the functionality of GP was considered to be 2, 1.2 moles of GP were required, whereas 1 mole of PA (functionality = 2) was required to complete the reaction.

Table 3.2 (a) gives details regarding the input materials for synthesis of alkyd using GP 2. This alkyd was coded as ARGP 2. Similar pattern was followed for preparing the other alkyds and similar coding was also done to the respective products.

Table 3.2 (b) gives details regarding the input materials for the synthesis of standard alkyd resin (SAR) using pure glycerol as the polyol component. The quantities to be charged were determined on the basis scheme shown in Fig 2.2.

<table>
<thead>
<tr>
<th>Input</th>
<th>Mol wt (g)</th>
<th>Moles</th>
<th>Wt charged</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP 2</td>
<td>651</td>
<td>0.10</td>
<td>67.18</td>
</tr>
<tr>
<td>DCO</td>
<td>880</td>
<td>0.14</td>
<td>120</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>148</td>
<td>0.086</td>
<td>12.72</td>
</tr>
</tbody>
</table>

(a) - Formulation of Alkyd resin - GP 2

<table>
<thead>
<tr>
<th>Input</th>
<th>Mol wt (g)</th>
<th>Moles</th>
<th>Wt charged</th>
</tr>
</thead>
<tbody>
<tr>
<td>GLY</td>
<td>92</td>
<td>0.3</td>
<td>27.6</td>
</tr>
<tr>
<td>DCO</td>
<td>880</td>
<td>0.14</td>
<td>120</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>148</td>
<td>0.41</td>
<td>60.56</td>
</tr>
</tbody>
</table>

(b) - Formulation of Standard Alkyd resin

Table 3.2: Formulation of Alkyd resin

The reaction was monitored by measuring the acid value of the material in reaction flask at regular intervals, after the addition of PA to synthesized monoglyceride. An acid value below 10 mgKOH/g is desired for an ideal alkyd. Fig 3.4 shows the graphical representation of drop in
acid value for different batches of alkyd. It can be noticed that an acid value up to 2 mgKOH/g was obtained for the samples within a time period of 60-70 min.

![Graph showing drop in acid value during alkyd synthesis](image)

**Fig 3.4: Drop in acid value during alkyd synthesis**

Different alkyds prepared as per the formulations shown above can be observed in Figure 3.5

![Images of alkyd samples](image)

**Fig 3.5 (clockwise from top left): SAR, ARGP 1; ARGP 2; ARGP 3; ARGP 4**
FTIR Characterization

Figure 3.6 shows the FTIR peaks obtained for the alkyd resins. Peak observed at ~3520 cm$^{-1}$ was attributed to the OH group stretching vibration. Overlapping stretching vibrations of the CH$_3$ and CH$_2$ groups, asymmetric and symmetric, were located at ~2925 and ~2852 cm$^{-1}$, respectively, and the corresponding bending vibrations appeared at ~1450 and ~1385 cm$^{-1}$, respectively. The stretching vibration of the ester carbonyl group appeared at ~1726 cm$^{-1}$. In the FTIR spectrum of the alkyd resins, the band at ~980 cm$^{-1}$ corresponded to the C=C stretching (skeletal) vibration of the benzene ring. The two sharp and moderate bands observed at ~735 and ~705 cm$^{-1}$ were assigned to the skeletal deformation, $\gamma$(CH), vibration of the benzene ring$^{(26)}$.

(a)- SAR
(b)- ARGP 1

(c)- ARGP 2.
Fig 3.6: FTIR of synthesized alkyd resins
3.3 Paint formulation and Testing

PVC of 30% was kept constant for all the paint batches. Density of alkyd resins was estimated by measuring the mass of a given volume of sample. The formulation for paints were decided based on the densities of alkyd resin and TiO$_2$, and the resulting quantities of inputs are mentioned in Table 3.3

<table>
<thead>
<tr>
<th>Paint Resin</th>
<th>Sample code</th>
<th>Resin density (g/cc)</th>
<th>Resin input (g)</th>
<th>TiO$_2$ input (g)</th>
<th>Emulsifier input (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SAR</td>
<td>P0</td>
<td>0.89</td>
<td>32.25</td>
<td>67.74</td>
<td>1</td>
</tr>
<tr>
<td>ARGP 1</td>
<td>P1</td>
<td>0.93</td>
<td>34.06</td>
<td>65.93</td>
<td>1</td>
</tr>
<tr>
<td>ARGP 2</td>
<td>P2</td>
<td>0.80</td>
<td>32.33</td>
<td>68</td>
<td>1</td>
</tr>
<tr>
<td>ARGP 3</td>
<td>P3</td>
<td>1.03</td>
<td>36.18</td>
<td>63.8</td>
<td>1</td>
</tr>
<tr>
<td>ARGP 4</td>
<td>P4</td>
<td>1.01</td>
<td>35.96</td>
<td>64.04</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3.3: Paint formulation for alkyd resins

Panel testing was carried out as per discussed in section 2.6. The results are shown in Table 3.4

<table>
<thead>
<tr>
<th>Sample code</th>
<th>Drying time (hrs)</th>
<th>Dry film thickness (µm)</th>
<th>Gloss</th>
<th>Impact</th>
<th>Flexibility</th>
<th>Resistance</th>
<th>Adhesion</th>
<th>Pencil hardness</th>
</tr>
</thead>
<tbody>
<tr>
<td>P0</td>
<td>24</td>
<td>53</td>
<td>68.9</td>
<td>Pass</td>
<td>Pass</td>
<td>Maximum</td>
<td>Pass</td>
<td>5B 3H</td>
</tr>
<tr>
<td>P1</td>
<td>24</td>
<td>59</td>
<td>69.1</td>
<td>Pass</td>
<td>Fail</td>
<td>Maximum</td>
<td>Fail</td>
<td>4B 1H</td>
</tr>
<tr>
<td>P2</td>
<td>24</td>
<td>50</td>
<td>72.5</td>
<td>Pass</td>
<td>Pass</td>
<td>Maximum</td>
<td>Fail</td>
<td>5B 2H</td>
</tr>
<tr>
<td>P3</td>
<td>24</td>
<td>54</td>
<td>73.1</td>
<td>Pass</td>
<td>Pass</td>
<td>Maximum</td>
<td>Fail</td>
<td>5B 2H</td>
</tr>
<tr>
<td>P4</td>
<td>24</td>
<td>60</td>
<td>72.6</td>
<td>Pass</td>
<td>Pass</td>
<td>Maximum</td>
<td>Fail</td>
<td>5B 2H</td>
</tr>
</tbody>
</table>

Table 3.4: Results of film testing of paint samples

It can be observed that the properties shown by the respective paints are comparable in nature and satisfy most of the parameters. P1 shows inferior properties compared to other paint samples which can be attributed to the fact that GP 1 had shown poor yields and consisted of mixture of oligoesters, which might have hindered the paint processing of ARGP 1.

Failure in Impact resistance was justified when cracks were observed in the film after the test (Refer Fig 3.7). Since the failure was found in case of reverse impact for P1, one can link it to poor film adhesion, which is again supported by the results obtained for its tape adhesion.
Adhesion for P1 is less than all other paint samples. Hence on receiving an impact from the opposite side of the film, the adhesion was weakened and cracks were observed. 5B adhesion is the highest value in the adhesion scale. It is characterized by no defects in the pattern made on the film surface (Refer Fig 3.8).

![Fig 3.7: Direct and Reverse Impact](image)

![Fig 3.8: 5B adhesion](image)

A paint film is said to have maximum flexibility when the cone and mandrel test is operated at minimum steradian and no cracks are observed on the film (Refer Fig 3.9). Since all the samples showed maximum flexibility, it can be inferred that BHET imparts flexibility to the film which is supplemented by the plasticity of the glycol component.
Two different types of failures were observed in case of acid alkali testing. The area covered with acid lost its adhesion, and the film was separated from the panel. Whereas the area covered with alkali was degraded (Refer Fig 3.10). Alkyd resins in general are not alkali resistant as they are oil based and undergo saponification reaction in presence of alkali.

Hydroxy functionality in paint provides strong adhesion to metal surface. Higher adhesion in case of standard alkyd resin formulation can be attributed to use of higher functional polyol (i.e. glycerol) compared to BHET. Complete neutralization of hydroxy groups by acid was difficult in case of glycerol and thus standard alkyd showed positive results for acid resistance test.
Low pencil hardness was observed (Refer Fig 3.11) since the resin is prepared using a plastic component, and also no fillers were added in the formulation.

The gloss of the film was measured using Glossmeter at 60°. Results show that the gloss is high, as the values are close to 70-75. It can be seen in Fig 3.12 that the gloss of the film is maintained even after carrying out all the tests on it.

Fig 3.11: Pencil hardness of film

Fig 3.12: Panel after testing
4. Conclusion

An ecologically friendly technology for production of alkyd resins was suggested which utilizes the waste product- postconsumer polyethylene terephthalate bottles. The technology consists of three stages: glycolysis, alcoholysis and polyesterification. All the stages are performed on the same experimental assembly without interruption of the process.

Glycolysis results in formation of monomer diol, BHET, which is later used as the alcohol component in alkyd synthesis. Different PET: GLY ratios (w/w) were tested for the reaction and it was observed that, an increase in the GLY quantity led to better depolymerization and to an increase in the amount of monomer with lower molecular weight. Using a catalyst, zinc acetate, in 1:2 PET:GLY ratio batch yielded product which was equivalent to the product obtained in 1:3 PET:GLY ratio.

The monomer diol was mixed with castor oil and phthalic anhydride to form unsaturated polyester resin. The properties of the alkyd resins were found to be highly dependent on the functionality and the structure of the employed glycolyzates. These resins were used for formulating paint and check its application performance. The properties were compared with a formulation prepared using standard alkyd resin.

The paint films prepared showed comparable properties to the standard resin, and gave good characteristics. Further formulation developments need to be carried out to improvise on the limitations observed.

After carefully studying all the results, it can be concluded that the most economical way of up-cycling postconsumer bottles to be used as alkyd resin based paint would be following glycolysis in 1:2 PET: GLY ratio (w/w) in presence of 1% zinc acetate catalyst.
5. Future Scope

The need for recycling of PET bottles has become very essential looking at the factors such as rise in population, demand for resources, increased generation of waste, and environment harmful waste disposal techniques.

The study carried out in this investigation is recent and innovative, and thus calls for multiple areas of development to help economize and commercialize the process. The future scope includes the following:

1. In order to economize the process, crude glycerol obtained from Oleochemical industries can be used for glycolysis.
2. Fusion method and MG process routes for synthesizing alkyds can be compared to optimize the process route yielding high quality alkyd.
3. Following the current trend of water based coatings, synthesizing water reducible alkyds can be tried using appropriate monomers.
4. Study of catalyst systems for glycolysis of PET system.
5. Investigate the effect of flake size of PET on glycolysis and optimize the reaction.
6. Performance of alkyd as a resin for paint applications can be improved by structural modification of resins, physical blending of resins, and developing an effective formulation for paint.

6. References

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