

HYDROLYSIS OF PET AND ITS USE IN CEMENT

A Major Project report submitted in partial fulfilment of the requirement for the award of the degree of

MASTER OF TECHNOLOGY

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POLYMER TECHNOLOGY

Submitted By

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(2K14/PTE/05)



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CERTIFICATE

This is to certify that the M.Tech major project entitled “**HYDROLYSIS OF PET AND ITS USE IN CEMENT**” has been submitted by Hemchand to the Delhi Technological University, for the award of the degree of “Master of Technology” in Polymer Technology is a record of bonafide work carried out by him. Hemchand has worked under our guidance and supervision and fulfilled the requirement for the submission of the thesis. The project work has been carried out during the academic session 2015-16.

To the best of our knowledge and belief the content therein is his own original work and has not been submitted to any other university or institute for the award of any degree or diploma.

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DECLARATION

I, **HEMCHAND (2K14/PTE/05)** a student of Master of Technology (POLYMER TECHNOLOGY), hereby declare that the thesis entitled “**HYDROLYSIS OF PET AND ITS USE IN CEMENT**” is an authentic record of research work done by me. This report work has not been submitted previously for the award of any degree or diploma of this university or any other university/ Institute.

Place: DTU, DELHI

HEMCHAND

Date:

2K14/PTE/05

M.Tech (Polymer Technology)

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CHAPTER 1

INTRODUCTION

Polyethylene terephthalate, commonly abbreviated **PET**, **PETE**, PETP/PET-P, is the most common thermoplastic polymer resin of the polyester family and is used in fibres for clothing, containers for liquids and foods, thermoforming for manufacturing, and in combination with glass fibre for engineering resins. The majority of the world's PET production is for synthetic fibers (> 60%), with bottle production accounting for about 30% of global demand. In the context of textile applications, PET is referred as polyester, whereas the acronym *PET* is generally used in relation to packaging. Polyester makes up about 18% of world polymer production and is the fourth-most-produced polymer after polyethylene (PE), polypropylene (PP) and polyvinyl chloride (PVC), respectively. PET consists of polymerized units of the monomer ethylene terephthalate, with repeating (C₁₀H₈O₄) unit. PET is commonly recycled, and has the number *1* as its recycling symbol. Depending on its processing and thermal history, polyethylene terephthalate may exist both as an amorphous (transparent) and as a semi-crystalline polymer. The semi-crystalline material might appear transparent (particle size < 500 nm) or opaque and white (particle size up to a few micrometres) depending on its crystal structure and particle size. Its monomer bis(2-hydroxyethyl) terephthalate can be synthesized by the esterification reaction between terephthalic acid and ethylene glycol with water as a by-product, or by transesterification reaction between ethylene glycol and dimethyl terephthalate with methanol as a by-product. Polymerization is carried out through a polycondensation reaction of the monomers (immediately after esterification/ transesterification) with water as the by-product, polyethylene terephthalate, a strong, stiff synthetic fibre and resin, and a member of the polyester family of polymers. PET is spun into fibres for permanent-press fabrics, blow-

molded into disposable beverage bottles, and extruded into photographic film and magnetic recording tape. PET is produced by the polymerization of ethylene glycol and terephthalic acid. Ethylene glycol is a colourless liquid obtained from ethylene, and terephthalic acid is a crystalline solid obtained from xylene. When heated together under the influence of chemical catalysts, ethylene glycol and terephthalic acid produce PET in the form of a molten, viscous mass that can be spun directly to fibres or solidified for later processing as a plastic. In chemical terms, ethylene glycol is a diol, an alcohol with a molecular structure that contains two hydroxyl (OH) groups, and terephthalic acid is a dicarboxylic aromatic acid, an acid with a molecular structure that contains a large, six-sided carbon (or aromatic) ring and two carboxyl (CO₂H) groups. Under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester (CO-O) groups, which serve as the chemical links joining multiple PET units together into long-chain polymers. Water is also produced as a by-product. The overall reaction¹ can be represented as below in figure 1.

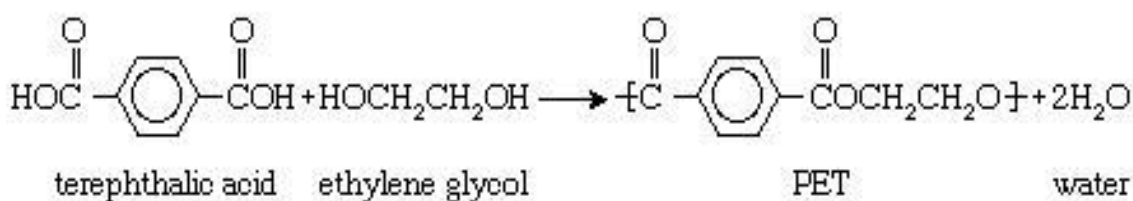


Fig.1 Reaction between EG and TPA

The presence of a large aromatic ring in the PET repeating units gives the polymer notable stiffness and strength, especially when the polymer chains are aligned with one another in an orderly arrangement by drawing (stretching). The stiffness of PET fibres makes them highly resistant to deformation, so they impart excellent resistance to wrinkling in fabrics. They are often used in durable-press blends with other fibres such as rayon, wool, and cotton,

reinforcing the inherent properties of those fibres while contributing to the ability of the fabric to recover from wrinkling. PET is also made into fibre filling for insulated clothing and for furniture and pillows. When made in very fine filaments, it is used in artificial silk, and in large-diameter filaments, it is used in carpets. Among the industrial applications of PET are automobile tire yarns, conveyor belts and drive belts, reinforcement for fire and garden hoses, seat belts (an application in which it has largely replaced nylon), nonwoven fabrics for stabilizing drainage ditches, culverts, and railroad beds, and nonwovens for use as diaper top sheets and disposable medical garments. PET is the most important of the man-made fibres in weight produced and in value.

At a slightly higher molecular weight, PET is made into a high-strength plastic that can be shaped by all the common methods employed with other thermoplastics. Magnetic recording tape and photographic film are produced by extrusion of PET film. Molten PET can be blow-molded into transparent containers of high strength and rigidity that are also virtually impermeable to gas and liquid. In this form, PET has become widely used in carbonated-beverage bottles and in jars for food processed at low temperatures. The low softening temperature of PET approximately 70 °C prevents it from being used as a container for hot-filled foods.

PET is the most widely recycled plastic. PET bottles and containers are commonly melted down and spun into fibres for fibrefill or carpets. When collected in a suitably pure state, PET can be recycled into its original uses, and methods have been devised for breaking the polymer down into its chemical precursors for resynthesizing into PET. The recycling code number for PET is #1 and general structure² of this polymer is given as below.

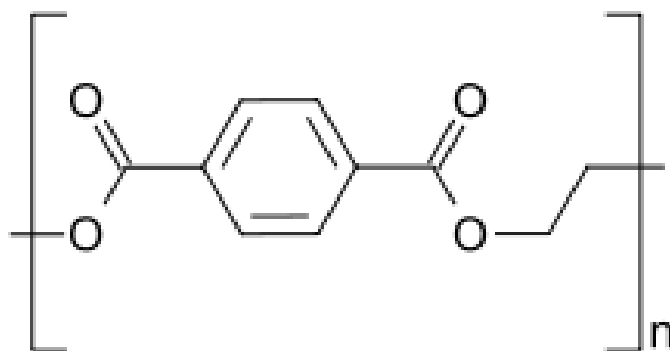


Fig.2 General structure of PET

Characteristic properties of PET

The characteristic properties of PET reported in the literature³ are given in the following table.

Table1 1: Physical and mechanical properties of PET

| Physical Properties | ASTM Test Method | Units | PET |
|---|------------------|----------------|---------------------|
| Density | D792 | lbs/cu in | 0.0499 |
| Water absorption, 24 h | D570 | % | 0.10 |
| Mechanical Properties | ASTM Test Method | Units | PET |
| Specific Gravity | D792 | g/cu cm | 1.38 |
| Tensile Strength at break | D638 | psi | 11,500 |
| Tensile Modulus | D638 | psi | 4 X 10 ⁵ |
| Elongation at break | D638 | % | 70 |
| Flexural Strength, | D790 | psi | 15,000 |
| Flexural Modulus | D790 | psi | 4 X 10 ⁵ |
| Izod Impact Strength, Notched | D256 | ft-lbs/in | 0.7 |
| Rockwell Hardness | D785 | ---- | R117 |
| Coefficient of Friction @ 40psi, 50 fpm | ---- | Static/Dynamic | 0.19/0.25 |

CEMENT:

The **cement** is a binder, used in construction that sets and hardens and can bind other materials together. The most important types of cement are used as a component in the production of mortar in masonry, and of concrete, which is a combination of cement and an aggregate to form a strong building material. The properties of the cement are given as below:

1. It possesses a high compressive strength.
2. It is a corrosion resistance material and atmospheric agent has no appreciable effect on it.
3. It hardens with age the process of hardening continues for a long time after the concrete has attained sufficient strength. It is this property of cement concrete which gives it a distinct place among building materials.
4. It is more economical than steel.
5. It has a tendency to be porous. This is due to the presence of voids which are formed during and after its placing. The two precautions necessary to avoid this tendency are as follows:
 - There should be proper grading and consolidating of the aggregates.
 - The minimum water-cement ratio should be adopted.
6. It forms a hard surface, capable of resisting abrasion.
7. It should be remembered that apart from other materials, the concrete comes to the site in the form of raw materials only. Its final strength and quality depend entirely on local conditions and persons handling it. However, the materials which concrete is composed may be subjected to rigid specifications.

Properties of good Cement

It is always desirable to use the best cement in constructions. Therefore, the properties of a good cement must be investigated. Although desirable cement properties may vary depending on the type of construction, generally a good cement possesses following properties which depend upon its chemical composition, thoroughness of burning and fineness of grinding.

- Provides strength to masonry.
- Stiffens or hardens early.
- Possesses good plasticity.
- An excellent building material.
- Easily workable.
- Good moisture-resistant.

Cement should be tested for its following properties:

1. Fineness

Fineness, or particle size of portland cement affects rate of hydration, which is responsible for the rate of strength gain. The smaller the particle size, the greater is the surface area-to-volume ratio, which means more area available for water-cement reaction per unit volume. Approximately 95% of cement particles are smaller than 45 μ with the average particle size about 15 μ . Fineness is measured in terms of surface area per unit mass. Fineness can be tested by *Wagner turbidimeter* test, *Blaine Air-permeability* test, 45 μ sieve and electronic particle size analyzer.

2. Soundness

Soundness refers to the ability of a hardened cement paste to retain its volume after setting. Lack of soundness is observed in the cement samples containing excessive amounts of hard burnt free lime or magnesia. *Autoclave expansion test* is used to determine soundness of cement.

3. Consistency

Consistency of a cement paste refers to its ability to flow. Normal consistency pastes are required to be prepared for testing cement specimens. A paste is said to have a normal consistency when the plunger of *Vicat apparatus* penetrates it by 10 ± 1 mm.

4. Setting Time

Initial setting time is the time that elapsed from the instance of adding water until the paste ceases to behave as fluid or plastic. Whereas, the final setting time referred to the time required for the cement paste to reach certain state of hardness to sustain the load. Setting time is tested by *Vicat apparatus* or *Gillmore needle*.

5. Compressive Strength

Compressive strength of cement is tested by 50 mm mortar cubes made by using standard sand and cured in a prescribed way. The cubes are tested under a *compression testing machine*. The strength of cement varies with time, therefore in general it is reported as 3, 7 or 28 days strength.

6. Heat of hydration

The heat generated during the reaction of cement and water is known as heat of hydration. The factors affecting heat of hydration are C3A, C2S, water-cement ration, fineness of cement and curing temperature. *Conduction calorimeter* is used to test heat of hydration.

7. Loss on Ignition

A cement sample of known weight is heated between 900 - 1000°C until a constant weight is obtained. The weight loss of the sample due to heating is then determined. A high loss on ignition (> 3%) indicates prehydration and carbonation, which may be due to inappropriate storage or adulteration.

8. Specific gravity (relative density)

Specific gravity is generally required in mix proportioning for concrete. The particle density (measured by excluding the air between particles) of OPC is found to be in the range of 3.1 to 3.25 Mega gram/cu.m. The relative density of OPC is assumed as 3.15. The density of cement is determined by Le Chatelier apparatus.

9. Bulk Density

The bulk density can be determined by dividing the mass of cement particles and air between particles by the volume of cement sample. Bulk density of OPC ranges from 830 to 1650 kg/cu.m. This test can be done with the help of two beaker shaving same amount of cement. The cement in one beaker is slightly vibrated which shows a decrease in the volume.

Disadvantages of Cement

- The tensile strength of cement is relatively low.
- Cement is less ductile.
- The weight of compared is high compared to its strength.
- Cement contains soluble salts. Soluble salts cause efflorescence.

How to overcome these disadvantages of cement?

By using PET, the above drawbacks can be reduced. Because, PET has high tensile strength, compressive strength etc., so it can increase the properties of cement to some extent.

Mechanical Tests

Compressive strength evaluation of all concrete cylindrical specimens was carried out in an universal testing machine.

ASTM D638

The most common testing machine used in tensile testing is the universal testing machine. This type of machine has two *crossheads*; one is adjusted for the length of the specimen and the other is driven to apply tension to the test specimen. There are two types: hydraulic powered and electromagnetically powered machines.

The machine must have the proper capabilities for the test specimen being tested. There are four main parameters like force capacity, speed, precision and accuracy. Force capacity refers to the fact that the machine must be able to generate enough force to fracture the specimen. The machine must be able to apply the force quickly or slowly enough to properly mimic the actual application. Finally, the machine must be able to accurately and precisely measure the gauge length and forces applied; for instance, a large machine that is designed to measure long elongations may not work with a brittle material that experiences short elongations prior to fracturing.

Alignment of the test specimen in the testing machine is critical, because, if the specimen is misaligned, either at an angle or offset to one side, the machine will exert a bending force on the specimen. This is especially bad for brittle materials, because it will dramatically skew the results. This situation can be minimized by using spherical seats or U-joints between the grips and the test machine. If the initial portion of the stress–strain curve is curved and not linear, it indicates the specimen is misaligned in the testing machine.

The strain measurements are most commonly measured with an extensometer, but strain gauges are also frequently used on small test specimen or when Poisson's ratio is being measured. Newer test machines have digital time, force, and elongation measurement systems consisting of electronic sensors connected to a data collection device (often a computer) and software to manipulate and output the data. However, analog machines continue to meet and exceed ASTM, NIST, and ASM metal tensile testing accuracy requirements, continuing to be used today.

Process

The test process involves placing the test specimen in the testing machine and slowly extending it until it fractures. During this process, the elongation of the gauge section is recorded against the applied force. The data is manipulated so that it is not specific to the geometry of the test sample. The elongation measurement is used to calculate the *engineering strain*, ϵ , using the following equation:

$$\epsilon = \Delta l / l_0 = (L - L_0) / L_0$$

where, ΔL is the change in gauge length, L_0 is the initial gauge length, and L is the final length. The force measurement is used to calculate the *engineering stress*, σ , using the following equation:

$$\sigma = F_n / A$$

Where, F is the tensile force and A is the nominal cross-section of the specimen. The machine does these calculations as the force increases, so that the data points can be graphed into a stress-strain curve.

ASTM D790

THREE POINT FLEXURAL TEST



Fig.3 Test fixture on universal testing machine for three-point flex test

The **three point bending flexural test**⁴ provides values for the modulus of elasticity in bending, flexural stress, flexural strain and the flexural stress-strain response of the material. The main advantage of a three-point flexural test is the ease of the specimen preparation and testing. However, this method has also some disadvantages such as the results of the testing method are sensitive to specimen and loading geometry and strain rate.

ASTM D256

Izod Impact strength Test

Izod impact testing is an ASTM standard method of determining the impact resistance of materials. A pivoting arm is raised to a specific height (constant potential energy) and then released. The arm swings down hitting the sample, breaking the specimen. The energy absorbed by the sample is calculated from the height the arm swings to after hitting the sample. A notched sample is generally used to determine impact energy and notch sensitivity.

The test is similar to the Charpy impact test but uses a different arrangement of the specimen under test. The Izod impact test differs from the Charpy impact test in that the sample is held in a cantilevered beam configuration as opposed to a three-point bending configuration.

Impact Energy

Impact is a very important phenomenon in governing the life of a structure. For example, in the case of an aircraft, impact can take place by a bird hitting a plane while it is cruising, or during takes off and landing the aircraft may be struck by debris that is present on the runway, and as well as other causes. It must also be calculated for roads if speed breakers are present, in bridge construction where vehicles punch an impact load, etc. Impact tests are used in studying the toughness of material. A material's toughness is a factor of its ability to absorb energy during plastic deformation. Brittle materials have low toughness as a result of the small amount of plastic deformation that they can endure. The impact value of a material can also change with temperature. Generally, at lower temperatures, the impact energy of a material is decreased. The size of the specimen may also affect the value of the Izod impact test because it may allow a different number of imperfections in the material, which can act as stress risers and lower the impact energy.

APPLICATION OF PET IN CEMENT

Because PET is an excellent water and moisture barrier material, plastic bottles made from PET are widely used for soft drinks. For certain specialty bottles, such as those designated for beer containment, PET sandwiches an additional polyvinyl alcohol layer to further reduce its oxygen permeability. PET film can be aluminized by evaporating a thin film of metal onto it to reduce its permeability, and to make it reflective and opaque (MPET). These properties are useful in many applications, including flexible food packaging and thermal insulation.

Because of its high mechanical strength, PET film is often used in tape applications, such as the carrier for magnetic tape or backing for pressure-sensitive adhesive tapes. PET is also used as a substrate in thin film solar cells.

PET can be used in cement for increasing its properties such as tensile strength. And this can also help in reducing the wastage of PET. Recently, Japanese scientist estimated that after few years plastic is more than fishes in ocean. So this can also reduce garbage dumping. The various mechanical properties⁵ of the cement are given in the following table.

Table 2: Mechanical properties of cement

| S.No. | PROPERTIES | VALUE |
|-------|-----------------------|----------------------------|
| 1 | DENSITY | 2240-2400Kg/m ³ |
| 2 | COMPRESSIVE STRENGTH | 20-40MPa |
| 3 | FLEXURAL STRENGTH | 3-5MPa |
| 4 | TENSILE STRENGTH | 2-5MPa |
| 5 | MODULUS OF ELASTICITY | 14000-41000MPa |

HYDROLYSIS OF PET

Hydrolysis is usually means the cleavage of chemical bonds by the addition of water. Hydrolysis can be the reverse of a condensation reaction in which two molecules join together into a larger one and eject a water molecule. Thus hydrolysis adds water to break down, whereas condensation builds up by removing water. If hydrolysis occurs in the acidic phase then it is known as **Acidic Hydrolysis**.

ACIDIC HYDROLYSIS

Poly(ethylene terephthalate) powder was hydrolysed⁶ at atmospheric pressure in precalculated wt% of H₂SO₄ for some time. The monomer TPA and EG are obtained after some time which depends upon the concentration and time.

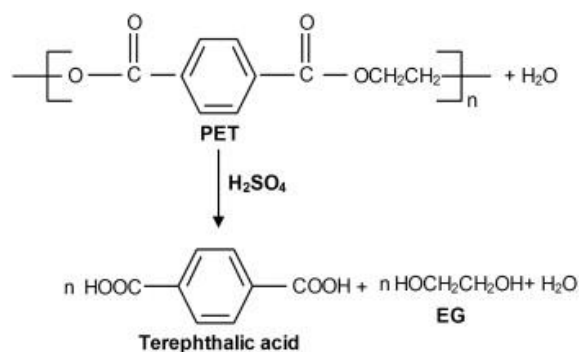


Fig.4 Acidic Hydrolysis of PET

ALKALINE HYDROLYSIS

Poly(ethylene terephthalate) powder was hydrolysed at atmospheric pressure in precalculated wt% of aqueous NaOH for some time using some phase transfer catalyst with an intention to recover the starting monomer from the waste PET. The one monomer TPA was produced in the presence of PTC during alkaline hydrolysis⁷ of PET.

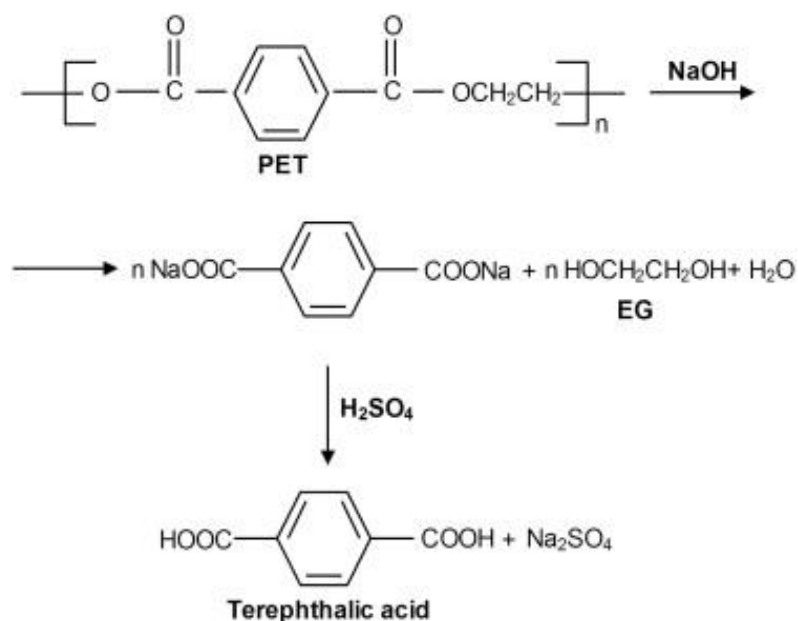


Fig.5 Alkaline Hydrolysis of PET using NaOH or KOH

Objectives:

The objective of my project is to recycle the PET and then use in cement for increasing its properties. Tensile strength of cement would be enhanced and other properties such as compressive strength, flexural strength would be increased by using additives. And properties of cement depend upon the size of PET particles and concentration of medium whether it is acidic or basic.

Need for PET Recycling

PET is saturated polyester of terephthalic acid and ethylene glycol. The growing interest in PET recycling is due its widespread use mainly as jars and bottles. Since the middle of the 1970s, first in the USA and Canada and subsequently in Western Europe, increased quantities of PET are used for the production of soft drink bottles, and a further increase in its application in this area is predicted. The overall world consumption of PET currently amounts to about 13 million tons, of which 9.5 million tons is processed by the textiles

industry, 2 million tons is used in the manufacture of audio and video tapes, and 1.5 million tons is used in the manufacture of various types of packaging mainly bottles and jars. PET is seen as a noxious material due to its high resistance to the atmospheric and biological agents. Ecological as well as economic considerations advocate the introduction of wide-scale PET recycling, similar to the recycling of traditional materials such as glass, paper, or metals.

Classification of Polymer Recycle

Polymer recycling can be classified into four categories, e.g., primary, secondary, tertiary and quaternary recycling. The energy content of the plastics waste can be recovered by incineration. When the collection, sorting and separation of plastics waste are difficult or economically not viable, or the waste is toxic and hazardous to handle, the best waste management option is incineration to recover the chemical energy stored in plastics waste in the form of thermal energy. This is carried out in special type of reactors called incinerators, to burn wastes in the presence of air in a controlled manner to convert hydrocarbons of the plastic into carbon dioxide and water. The heat produced by burning plastics in the waste in the form of superheated steam can be utilized for generating electricity through turbine generators and the residual heat from the waste stream for heating residential and industrial buildings. The melt residue from the incinerator is free from toxicity hazards and may be disposed off by landfill. It should admit that it is not possible to have zero-emission in the incineration of waste plastic. Apart from the aforementioned methods, direct reuse of a plastic material (i.e., PET) could be considered as a “zero-order” recycling technique. Worldwide, the main end-use of post-consumed PET is for the production of fibers (almost 70 %), with only 4 % of PET recycled with chemical methods.

Among the above recycling techniques, the only one acceptable according to the principles of sustainable development is chemical recycling, since it leads to the formation of the raw

materials (monomers) from which the polymer is made. In this way the environment is not surcharged and there is no need for extra resources (monomers) for the production of PET.

PET Chemical-Recycling Techniques

The world's most recyclable polymer is polyester. 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 fibers, 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 etc.

According to the reagent used, different products are obtained. The main depolymerization processes that have reached commercial maturity up to now are glycolysis and methanolysis. Nowadays there is growing interest in hydrolysis for the chemical recycling of PET, since it is the only method with the reaction products TPA and 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 DMT 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 depolymerization. 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. Among previous chemical recycling methods, a recent growing interest has been applied for the production of specialized products such as saturated, unsaturated polyester resins, polyurethane and polymer concrete using glycolysis due to consumer needs and cost.

Glycolysis

Another most important method in chemical processing of PET is glycolysis. This process is used widely on a commercial scale. The glycolysis reaction is the molecular degradation of PET polymer by glycols, in the presence of trans-esterification catalysts, mainly metal acetates, where ester linkages are broken and replaced with hydroxyl terminals. Research concerning this process has been mainly conducted from the point of view of the utilization of the products obtained; very few works have been devoted to the description of the kinetics of glycolysis reactions. The process is conducted in a wide range of temperatures, 180–250 °C, during a time period of 0.5–8 h. Usually 0.5 % by weight of catalyst (most often zinc acetate) in relation to the PET content is added. Much attention has been devoted to glycolysis by EG. In this system, the effect of the reaction parameters, i.e., temperature (190–240 °C), pressure (0.1–0.6 MPa) and PET to EG ratio on the reaction rate has been investigated. It has been observed that the rate of the reaction is proportional to the square of the EG concentration at constant temperature, pressure and PET concentration.

1. Primary Recycling (Pre-Consumer Industrial Scrap)

It is the recycling of clean, uncontaminated single-type waste which remains the most popular, as it ensures simplicity and low cost, especially when done “in-plant” and feeding with scrap of controlled history. The recycled scrap or waste is either mixed with virgin material to assure product quality or used as a second-grade material. Primary recycling of industrial scrap produced during the manufacture of food-contact articles is not expected to pose a hazard to the consumer.

2. Mechanical Recycling (Secondary 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.

3. Chemical Recycling (Tertiary Recycling)

Unlike physical recycling, chemical recycling involves transformation of polymer chain. The polymer backbone under the recycling process is degraded into monomer units (i.e., depolymerization) or randomly ruptured into larger chain fragments (i.e., random chain scission) with associated formation of gaseous products. The chemical recycling is carried out either by solvolysis or by pyrolysis; the former through degradation by solvents including water and the latter through degradation by heat in absence of air or vacuum. Chemical recycling yields monomers, petroleum liquids and gases.

CHAPTER 2

METHODOLOGY & CHARACTERIZATION TECHNIQUES

This chapter describes the various materials and methods used for the hydrolysis of PET followed by the characterization of sample specimen.

2.1 Materials for recycling of PET & specimen design

For recycling of PET, we need flakes of waste PET bottles, sulphuric acid, distilled water, cement, flask, magnetic stirrer, brick mould etc.

2.2 Methods Used

2.2.1 Chemical recycling of PET

PET powder of 0.1-0.3 mm was prepared from PET bottles. Then, **a 5g PET powder was added to 20 ml H₂SO₄ in a sealed container and stirs** it for some time. Thereafter, TPA insoluble in acid solution was precipitated again in the filtrate containing H₂SO₄. The degree of degradation of PET and yield of TPA were determined by weight. The paste like material was poured in petri dish and kept it for few hours for drying purpose.



Fig.6 Recycling symbol of PET⁸

2.2.2 Preparation of specimen for testing

The test specimen was prepared by taking 220gm of cement and different proportion of PET paste. In case of first sample specimen, we have taken 25% (55 gm) PET paste and 220gm of cement and then mixed it. Similarly, for second and sample specimen, we have taken 50% (110gm) and as 75% (165gm) PET paste, respectively along with 220gm of cement. A little amount of water was poured in to these mixtures and then fills the brick mould. After some time, it hardens and specimen was taken out after opening the mould. These steps are shown in the following figure. The testing was performed on the sample specimen.



Fig.7(a) Cement mixed with PET and (b) Brick formed of PET and cement

2.3 Scanning electron microscopy

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nm. Specimens can be observed in high vacuum, in

low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

The most common SEM mode is detection of secondary electrons emitted by atoms excited by the electron beam. The number of secondary electrons that can be detected depends, among other things, on the angle at which beam meets surface of specimen, i.e., on specimen topography. By scanning the sample and collecting the secondary electrons that are emitted using a special detector, an image displaying the topography of the surface is created. In a typical SEM, an electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten is normally used in thermionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be electrically heated for electron emission, and because of its low cost. The electron beam, which typically has an energy ranging from 0.2 to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 to 5 nm in diameter. The beam passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 5 μm into the surface. The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density. The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The

beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a computer monitor (or, for vintage models, on a cathode ray tube). Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. In older microscopes images may be captured by photography from a high-resolution cathode ray tube, but in modern machines they are digitised and saved as digital images. A pictorial view of scanning electron microscope⁹ is shown in the Fig. 8.

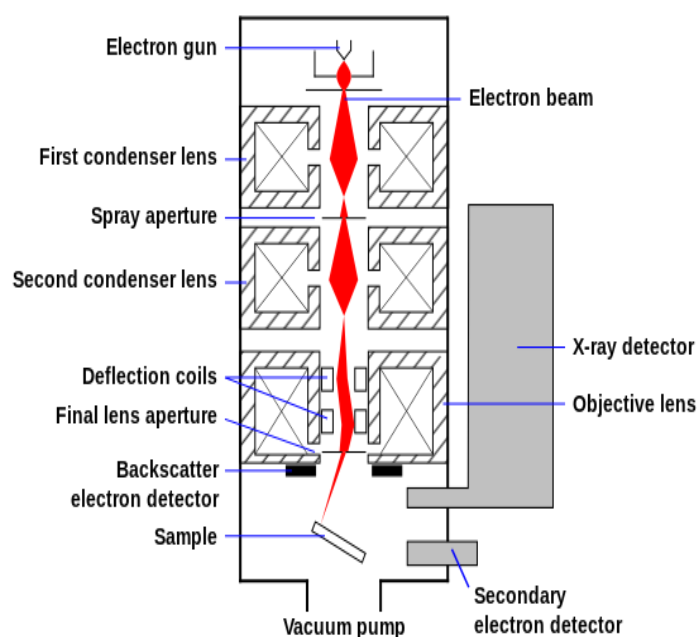


Fig. 8 Schematic representation of scanning electron microscope

2.4 Fourier transform infrared (FT-IR) spectroscopy

Fourier Transform Infra-red Spectroscopy¹⁰ (FTIR) is a sensitive technique particularly for identifying organic chemicals in a whole range of applications although it can also characterise some inorganics. Examples include paints, adhesives, resins, polymers,

coatings and drugs. It is a particularly useful tool in isolating and characterising organic contamination. FTIR relies on the fact that the most molecules absorb light in the infra-red region of the electromagnetic spectrum. This absorption corresponds specifically to the bonds present in the molecule. The frequency range is measured as wave numbers typically over the range $4000 - 400 \text{ cm}^{-1}$. The background emission spectrum of the IR source is first recorded, followed by the emission spectrum of the IR source with the sample in place. The ratio of the sample spectrum to the background spectrum is directly related to the sample's absorption spectrum. The resultant absorption spectrum from the bond natural vibration frequencies indicates the presence of various chemical bonds and functional groups present in the sample. FTIR is particularly useful for identification of organic molecular groups and compounds due to the range of functional groups, side chains and cross-links involved, all of which will have characteristic vibrational frequencies in the infra-red range. A pictorial view of FTIR is given in the Fig. 9.



Fig.9 Pictorial view of FTIR

CHAPTER 3

RESULTS & DISCUSSION

Cement is a useful material for the purpose of civil engineering building construction. It has many beneficial properties such as good compressive strength, fine durability, specific gravity and fire/ moisture resistance. Cement has some better properties, like low tensile strength, brittleness, lower impact strength, heavy weight, etc. Still concrete is a better option than any other available materials for civil engineering constructions. Some of the properties can be enhanced by adding fibers with other ingredients in the concrete. The fibers inclusion in concrete acts as unwanted micro crack arrester. In presence of fibers, the crack prorogation is delayed which helps in improvement in static and dynamic properties of concrete.

The consumption of plastic has grown substantially all over the world as it leads to create large quantities of plastic-based waste. Plastic waste is the one of the challenge to dispose and manage as it is non-biodegradable material which is harmful to our beautiful environment. The polyethylene terephthalate (PET) bottles are recycled and used for different purposes. Further research to evaluate the use of plastic waste in concrete production is therefore attracting the attention of researchers. Therefore, it is the background of the present study. The waste PET bottles were converted into fibers and added in to the concrete as an additional ingredient of concrete. The cube and cylinder compressive strength of conventional and plastic fiber reinforced concrete samples were determined.

Materials: Portland Pozzolana cement (Flyash) was used in this experimentation conforming to IS: 1489-1991. The chemical compositions of cements are shown in table 3.

Table 3: Chemical composition of cements

| <i>Chemical Composition</i> | <i>CPJ-CEM III/A (%)</i> |
|--------------------------------|--------------------------|
| Loss on Ignition | 2.09 |
| SiO ₂ | 21.82 |
| Al ₂ O ₃ | 6.57 |
| Fe ₂ O ₃ | 4.01 |
| CaO | 63.43 |
| MgO | 0.21 |
| SO ₃ | 1.86 |
| CaO free | 0.24 |

Compressive strength values of concretes made with PET analysis in terms of (a) PET particle size, (b) PET particle concentration, and (c) curing time was realized. Values of concrete strength range from 10 to 21.3 MPa, with a maximum improvement of 40% when a 1.5 mm PET particle is added. Concretes without PET particles show moderate values, but when adding different sizes and volume percentages of PET particles, compressive strength increases. Moreover, the compressive strength values increase progressively for curing times ranging from 7 to 28 days given the condition that PET particle sizes do not exceed 1.5 mm as found in this investigation. Such behaviour can be related to the presence of non-degradable material (PET), which in principle can reduce the cement hydration. This is based on the results, due to the fact that compressive strength at 7 days is less than the one obtained at 28 days.

According to PET particle size, the values are higher for concrete with 1.5 mm PET particles and lower for those with 3.0 mm PET particles. Moreover, the highest values are obtained for 2.5% by volume of PET particles. As it is known that the strength of materials can be improved by blending, insertion of fibres, using fillers, and/or combinations of these

techniques. Smaller particles usually provide more reinforcement. Compressive strength of cement with different proportion of hydrolysed PET is given in the following Table 4.

Table 4: Compressive strength data

| Compressive Strength of cement (100%) with 0% hydrolyzed PET | Compressive Strength of cement (75%) with 25% hydrolyzed PET | Compressive Strength of cement (50%) with 50% hydrolyzed PET | Compressive Strength of cement (25%) with 75% hydrolyzed PET |
|--|--|--|--|
| 35MPa | 28MPa | 15Mpa | 9MPa |

Hydrolysis of PET occurs with conc. H_2SO_4 greater than 60%. Below 60% conc. H_2SO_4 , PET cannot hydrolyse. As the result shows that the maximum compressive strength observed in the cement and as we are adding hydrolyzed PET, the compressive strength gets reduced.

Further, we also get to know that the compression strength of the prepared bricks decreases when the acidity of the mixture increases. And various other properties improve well such as tensile strength, brittleness etc. and other properties can also increase by adding additives.

It is also noticed that the more surface area of plastic fibers was available at higher aspect ratio, at same volume fraction which causes an adhesion and holding of other ingredients of concrete together. The dry density was also found decreases on increasing the plastic fiber content in the concrete.

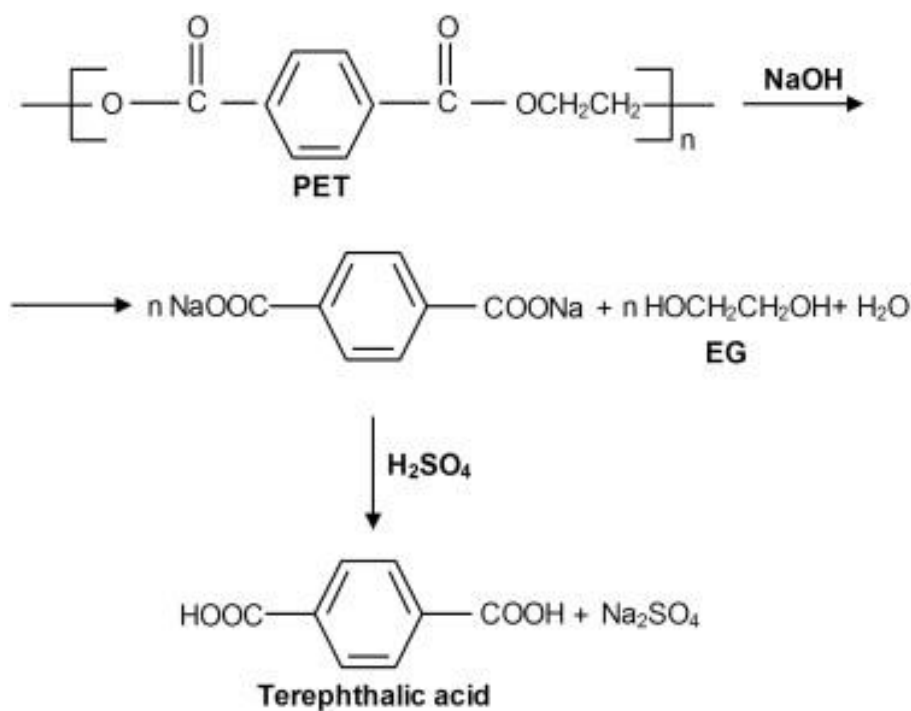


Fig 10: Hydrolysis of PET

5.2 SEM Analysis

Scanning electron microscopy (SEM) is an important tool to study the morphological behaviour of the samples under investigation. Fig. 11(a) shows the SEM micrographs of PET waste while Fig. 11(b) shows SEM micrographs of PET grated sample. The morphology of the PET changes greatly upon activation after grating. In the as-synthesized sample, the very large crystals are seen together with aggregates of intergrown crystals. Fig. 11(c) shows the SEM image of hydrolysed PET. After mixing PET with H_2SO_4 , the SEM image clearly shows that the size of granules becomes very small and equally distributed.

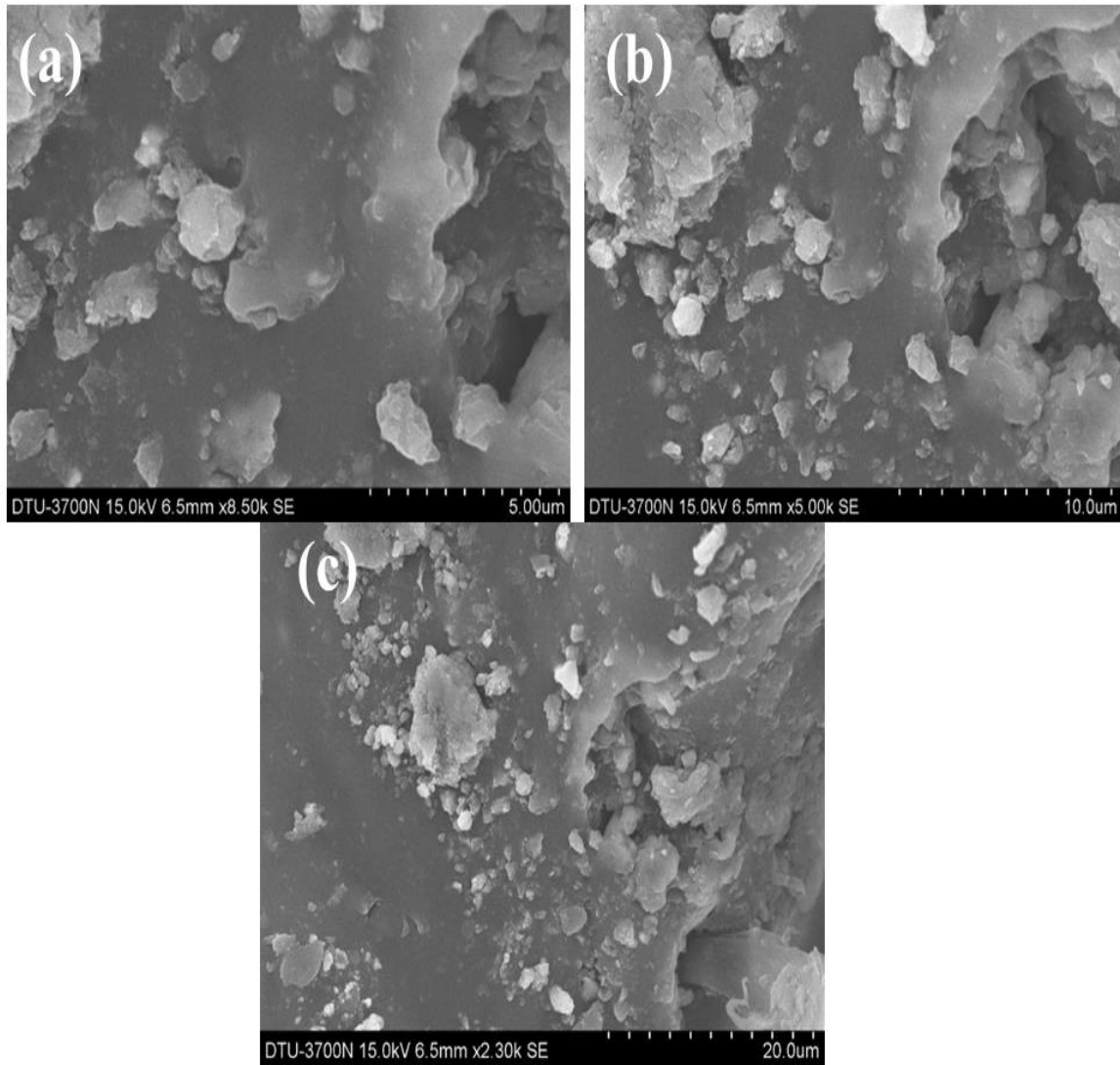


Fig. 11:(a) SEM image of PET waste, b) SEM image of PET grated and (c) SEM image of hydrolysed PET

The SEM micrograph of cement is shown in fig. 12(a). And fig. 12(b) shows the SEM image of PET paste with Cement. After mixing PET in cement, we observed that the aggregates of PET and sheets of cements are uniformly distributed all over the surface. The surface becomes more rough and seen large aggregates as shown in fig. 12 (b).

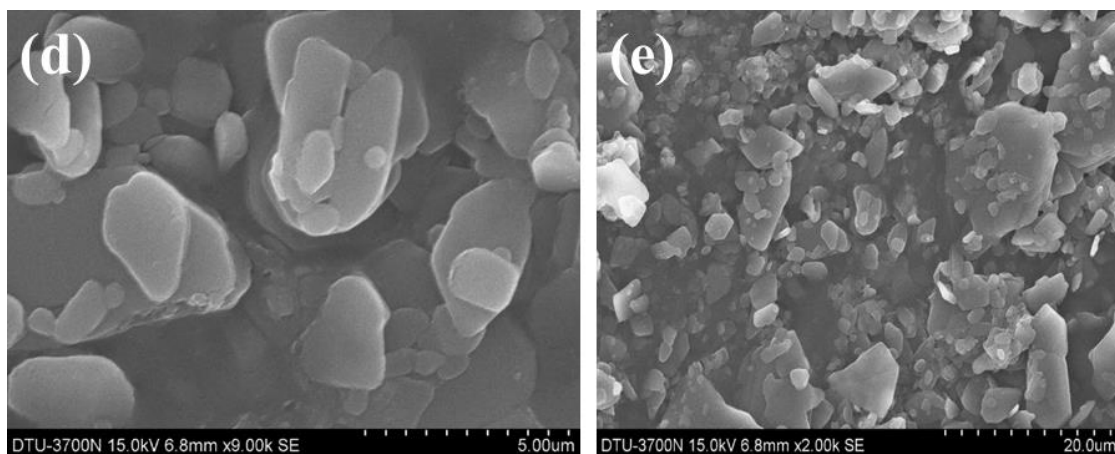


Fig.12 (a) SEM image of cement (b) SEM image of PET paste with cement

5.3 FTIR analysis

Infrared spectroscopy is a powerful tool for studying the qualitative and quantitative analysis of natural and synthetic molecules. IR spectroscopy can provide the information about the nature, concentration and structure of samples at the molecular level in material science. Fig 13 (a) shows the end-group determination in PET by infrared spectroscopy. The investigations shows, the correlations of the hydroxyl and carboxyl units were derived independently for accurate calibration results. This determination stating that the carboxyl and hydroxyl groups are the only end-group units available in PET.

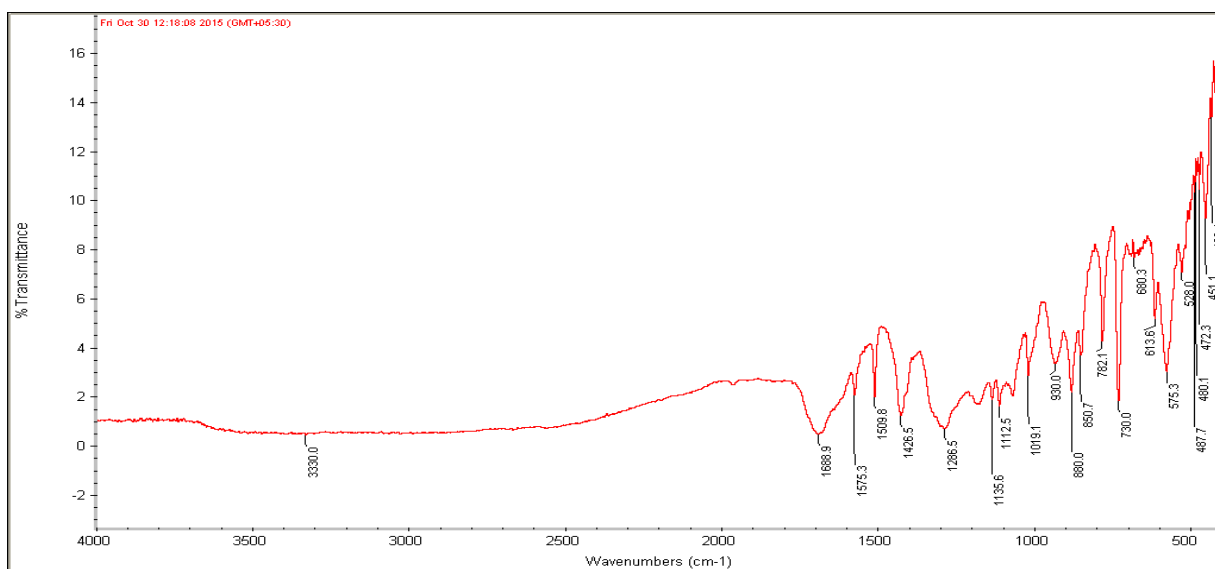


Fig.13 (a) FTIR spectra of PET waste

Table 5: Fourier-transform infrared data of PET in KBr pellet

| Band stretching (cm ⁻¹) | Bands identification |
|-------------------------------------|---|
| 881 | Alternating deformation of benzene, out of the plane (para-disubstituted) |
| 1091 | -C-O |
| 1575-1689 | C=C, aromatic character |
| 1743 | COO- |
| 2963 - 2905 | -CH ₂ - |
| 3330 | OH |

The FT-IR spectra of grated PET as shown in Fig. 13 (b) confirm the presence of a carbonyl group in conjugation with aromatic ring appears at 1716 cm⁻¹. The second strongest peak at 1236 cm⁻¹ is due to the asymmetric C-C-O stretching involving the carbon in aromatic ring. The aromatic C-H wagging appears at 726 cm⁻¹. The characteristic peak at 877 cm⁻¹ corresponds to aromatic C-H out of plane bending. The O-C-C asymmetric stretching splits at 1101 and 1018 cm⁻¹. There are also other characteristic peaks at 2960 cm⁻¹ for C-H asymmetric stretching, 1509 cm⁻¹ for aromatic C-C stretching, and 1453 cm⁻¹ for C-H bending. The characteristic peaks at 1408 and 1339 cm⁻¹ are due to the deformation C-H alkane.

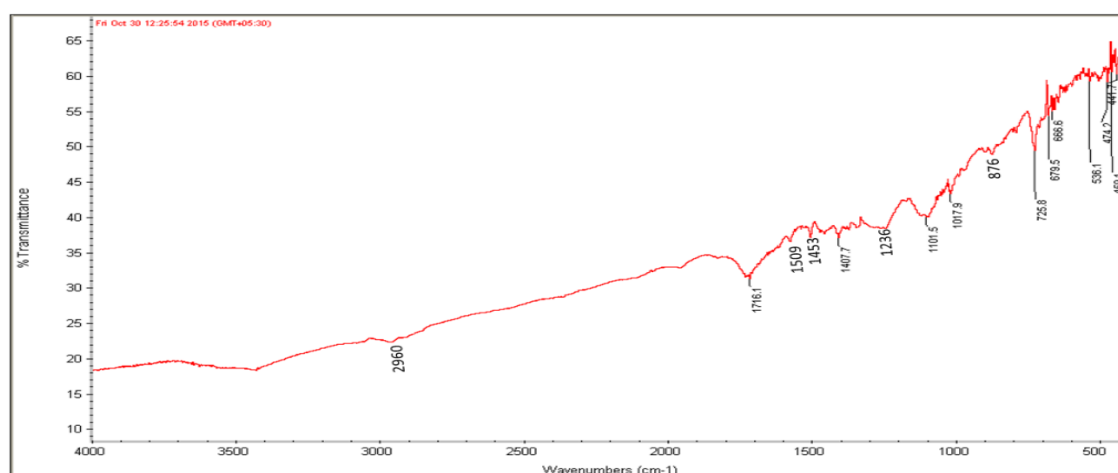


Fig. 13 (b) FTIR of grated bottle

In the carbonyl region of an IR spectrum of PET, there are various carbonyl species overlapped together, including mainly esters and acids (coming from the terminal carboxyl group). During the hydrothermal aging of PET, the hydrolysis leads to the formation of carboxylic and hydroxyl end groups. Therefore, the concentration of carboxylic groups increased with the aging time and that of ester groups decreased, with the profile changed as shown in Fig. 13 (c). Since, the peak positions of the various carboxylic acids and esters do not differ significantly, the superposition of these absorbance leads to a strong and broad band. The characteristic peaks at 1734-1634 cm^{-1} were attributed to the ester groups in main chain and end carboxyl groups, as well as their hydrogen bonded associations. The changes of hydroxyl groups in the region of 3000–3446 cm^{-1} represent the formation of hydroxyl groups at the chain end. However, the hydroxyl groups are not used to study the hydrolysis because they are strongly influenced by water absorbance, and drying samples takes long time and may cause further changes.

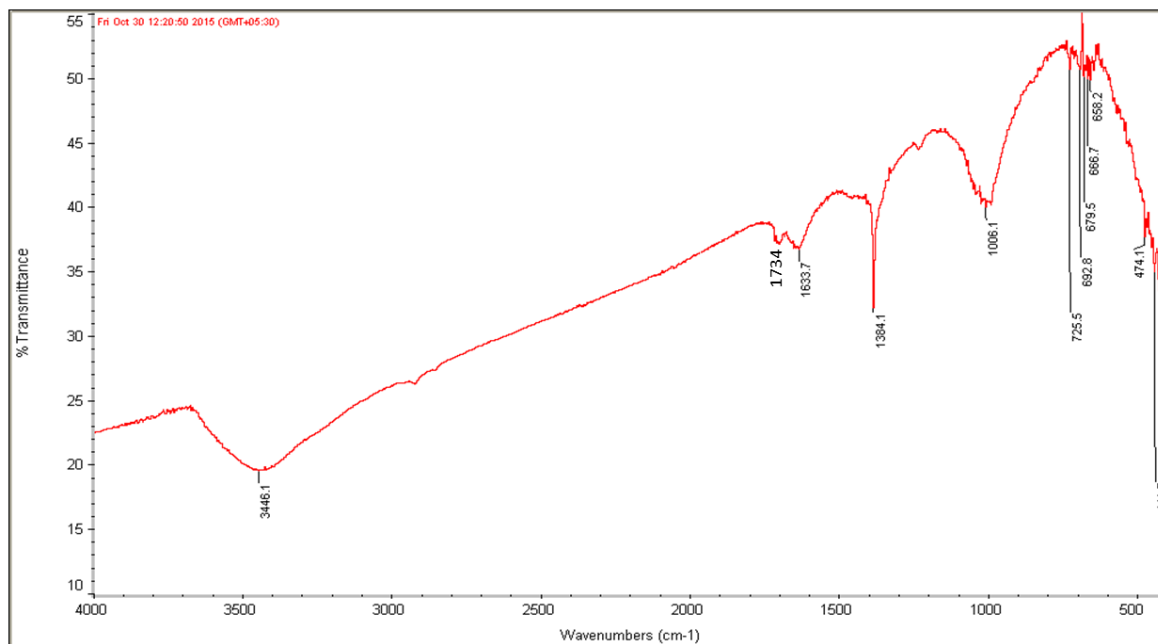


Fig.13 (c) FTIR of hydrolysed PET

Figure 13 (d) presents the infrared spectra of the ordinary Portland cement. In these spectra, it is possible to identify different vibrational bands from the calcium silicates, calcium aluminates, and gypsum, the last one added as setting regulator. The gypsum can lose part of the structure water and the sulphates can be present as bassanite and/or anhydrite. In the IR spectra, the strongest peak is presented at 1105, 1115, and 1076 cm^{-1} , for the gypsum, bassanite, and anhydrite, respectively. The bassanite, and anhydrite present two absorption bands at 669, and 609 cm^{-1} , respectively in gypsum. The characteristic peaks at 537 cm^{-1} is also found in gypsum. For gypsum and bassanite presence, it will also be possible to analyze 4000-3000 cm^{-1} region where ν_1 O-H absorptions can be observed at 3553 and 3399 cm^{-1} for gypsum and 3611 and 3557 cm^{-1} for bassanite.

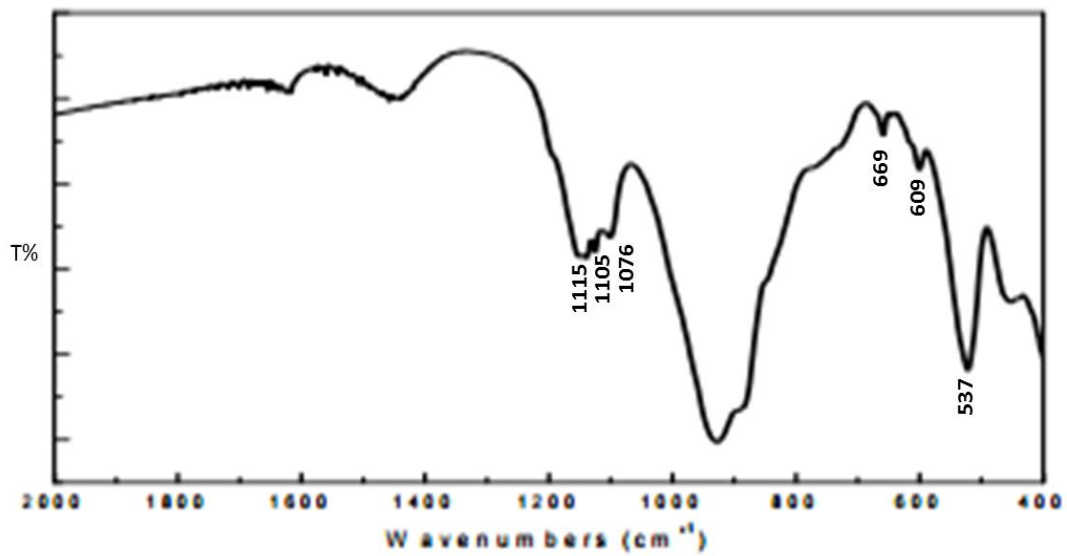


Fig.13 (d) FTIR of cement

In fig. 13 (e), the FTIR spectra show the various peaks which clearly indicate the phase formation. The characteristic peak of PET shows at 1688 cm^{-1} may be attributed due to $\text{C}=\text{O}$. And, also the characteristic peaks at 3440 , 1708 , 1369 , and 1227 cm^{-1} may be due to the presence of $-\text{OH}$, $-\text{C}=\text{O}$, $-\text{CH}$, $-\text{C}-\text{O}$, respectively.

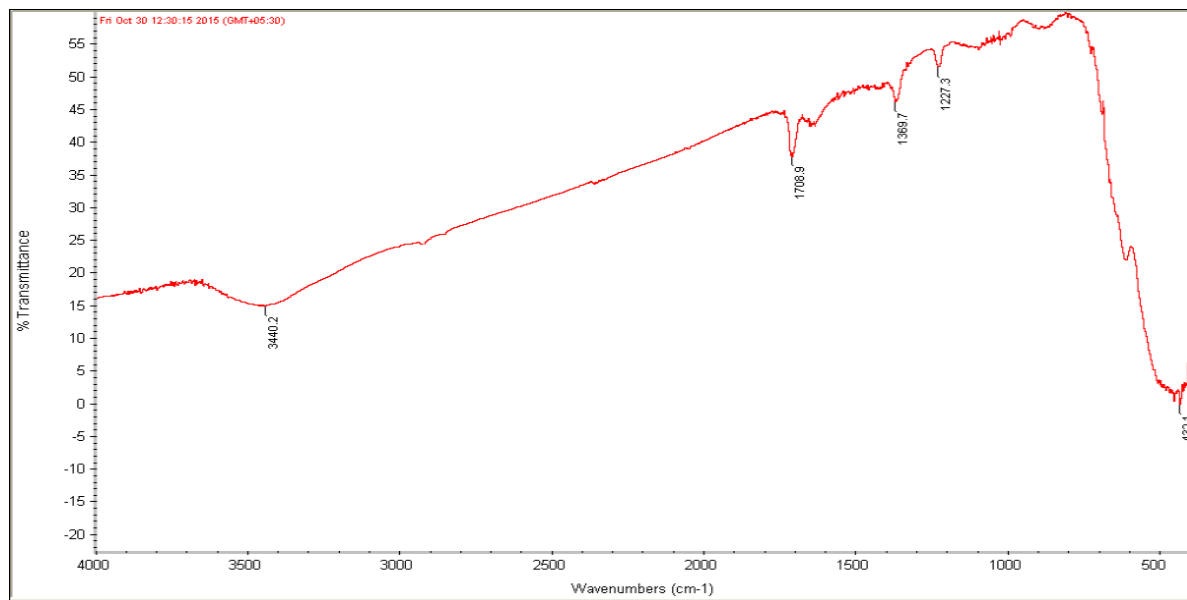


Fig. 13 (e) FTIR of PET paste with cement

CHAPTER 4

CONCLUSION

The project helps us to get to know the concentration of sulphuric acid required to perform the hydrolysis of polyethylene glycol and the time required for different concentrated sulphuric acid to perform hydrolysis. Further, we also get to know that the compression strength of the prepared bricks decreases when the acidity of the mixture increases. So, in order to increase the compression strength of the bricks, we can use a base and hence the hydrolysis of PET could be performed using a base like NaOH, KOH, etc. Thus, the recycling of PET could be done by using the hydrolyzed PET via basic medium, in the mixture for making bricks and ultimately the strength of the bricks could be increased. The recycling of PET will help to reduce a lot of harmful dumping of it in the oceans which is very harmful for sea creatures and this will result in an increase in the compressive strength of the bricks which could be further used in houses, buildings bridges, etc.

FUTURE ASPECTS

The optimum amount of the concentration required for a base could be found out. Also the percentage of base required for obtaining maximum strength could be studied in future. To analyze the variation of size aggregates of PET quantitatively and the water absorption or oil absorption further studies are needed.

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