MAJOR PROJECT

Recycling of Polycarbonate from CDs to Epoxy Resin

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

MASTER OF TECHNOLOGY (M. Tech.)

In

POLYMER TECHNOLOGY

Submitted by

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[2K14/PTE/15]

Under the supervision of

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July 2016

DECLARATION

I, **Gaurav Tripathi**, hereby certify that the work which is being submitted in this major project report entitled "**Recycling of Polycarbonate from CDs to Epoxy Resin**" in the partial fulfilment for the award of the degree of Master of Technology (Polymer Technology) at **Delhi Technological University** is an authentic record of my own work carried out by me under the supervision of **Dr. Ram Singh** (Assistant Professor, Department of Applied Chemistry, Delhi Technological University, Delhi.

I, further declare that the project report has not been submitted to any other Institute/University for the award of any degree or diploma or any other purpose whatsoever. Also it has not been directly copied from any source without giving its proper reference.

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CERTIFICATE

This is to certify that the M.Tech. major project entitled entitled "**Recycling of Polycarbonate from CDs to Epoxy Resin**" submitted by **Gaurav Tripathi**, Roll Number 2K14/PTE/15, for the award of the degree of **"Master of Technology in Polymer Technology"** is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements for the submission of the project report.

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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Gaurav Tripathi

Contents

ABBREVIATIONS

S. No.	Symbol	Meaning
1.	PC	Polycarbonate
2.	PVC	Polyvinylchloride
3.	PEG	Polyethylene glycol
4.	CD	Compact Disc
5.	DVD	Digital Versatile Disc or Digital Video Disc
6.	NaOH	Sodium hydroxide
7.	THF	Tetrahydrofuran
8.	HCl	Hydrochloric acid
9.	PE	Polyethylene
10.	H_2O	Water

ABSTRACT

Waste management is the collection, transport, recovery and disposal of waste, including the supervision of such operations and aftercare of disposal sites according to European Union Directive on waste. E-waste is a popular, informal name for electronic products nearing the end of their useful life. E-wastes are considered dangerous, as certain components of some electronic products contain materials that are hazardous, depending on their condition and density. India is fifth largest producer of e-waste, discarding roughly 18.5 lakh tonnes of electronic waste each year. The amount of CDs and DVDs waste are about 4 lakh tonnes.

The recycling of CDs and DVDs has been achieved using sodium hydroxide in THF. The obtained product was further used for the preparation of Epoxy resins. The epoxy resins have been widely used for coatings, electronic materials, adhesives, and matrices for fiber-reinforced composites because of their outstanding mechanical properties, high adhesion strength, good heat resistance, and high electrical resistance. The epoxy resin made above is mixed with white cement to make the mold and for providing high strength to the mold even at high temperatures.

CHAPTER 1

INTRODUCTION

1.1 Waste management

Waste management shall mean the collection, transport, recovery and disposal of waste, including the supervision of such operations and aftercare of disposal sites according to European Union Directive on waste. However the newer concepts of waste management talk about 3Rs: Reduce, Reuse and Recycle. The waste is defined as a product or a substance that is no longer suited for its intended use. According to the Basel Convention, wastes are substances or objects which are disposed or are intended to be disposed or are required to be disposed of by national laws.

Plastics waste is a significant portion of the total municipal solid waste (MSW). It is estimated that approximately 10 thousand tons per day (TPD) of plastics waste is generated i.e. 9% of 1.20 lakhs TPD of MSW in the country. The plastics waste constitutes two major category of plastics; (i) Thermoplastics and (ii) Thermoset plastics. Thermoplastics, constitutes 80% and thermoset constitutes approximately 20% of total post-consumer plastics waste generated in India. The Thermoplastics are recyclable plastics which include; polyethylene terephthalate (PET), low density polyethylene (LDPE), polyvinylcholoride (PVC), High density polyethylene (HDPE), polypropylene (PP), polystyrene (PS) etc. However, thermoset plastics contains alkyd, epoxy, ester, melamine formaldehyde, phenol formaldehyde, silicon, urea formaldehyde, polyurethane, metalized and multilayer plastics etc. The environmental hazards due to mismanagement of plastics waste create a large number of problems.

1.2 STATUS OF E-WASTE

E-waste is a popular, informal name for electronic products nearing the end of their useful life. E-wastes are considered dangerous, as certain components of some electronic products contain materials that are hazardous, depending on their condition and density. The hazardous content of these materials pose a threat to human health and environment. Discarded CDs, DVDs, computers, televisions, VCRs, stereos, copiers, fax machines, electric lamps, cell phones, audio equipment and batteries if improperly disposed can leach lead and other substances into soil and groundwater. Many of these products can be reused, refurbished, or recycled in an environmentally sound manner so that they are less harmful to the ecosystem. Electronic waste from equipment of all sizes includes dangerous chemicals like lead, cadmium, beryllium, mercury, and brominated flame retardants. When we dispose of gadgets and devices improperly, these hazardous materials have a high risk of polluting the air, contaminating soil, and leaching into water sources. When e-waste sits in a typical landfill, for example, water flows through the landfill and picks up trace elements from these dangerous minerals. When it reaches natural groundwater, it introduces lethal toxicity. Health risks range from kidney disease and brain damage to genetic mutations.

Industrial revolution followed by the advances in information technology during the last century has radically changed people's lifestyle. Although this development has helped the human race, mismanagement has led to new problems of contamination and pollution.

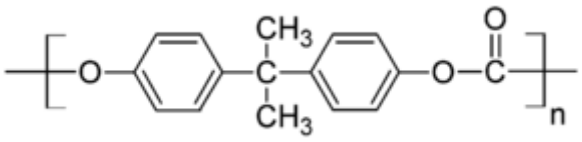
1.3 Polycarbonate

Polycarbonate (PC) is a high performance, sustainable and eco-efficient material used in a large variety of essential everyday applications. It has a unique combination of properties, offering clarity, durability, safety, versatility, and heat and shatter resistance. Products made from polycarbonate include sheets for roofing and glazing, optical media, IT-parts, spectacle lenses, medical devices, leisure articles, and food contact materials. These products contribute substantially to the safety and well-being of consumers. PC is commonly used to manufacture CDs, DVDs, automotive components and also the manufacture of baby bottles and water bottles. However, due to the presence of bisphenol A, many manufacturers have stopped using polycarbonates for applications related to human intake.[1]

PC in landfills is definitely an environmental nightmare. It never biodegrades since it is made of petroleum. The chemicals leach into the environment causing significant damage. Many of these chemicals are consumed by marine organisms and other animals resulting in a lot of damage. It is of concern that the accidental dumping of plastics into oceans have resulted in mammals and birds starving to death and fish ingesting toxins that may make them dangerous to eat. Annually, large amounts of CDs are discarded worldwide. The non-biodegradable polycarbonate results in serious pollution issues. Although there are methods being devised to recycle CDs, these are not very effective and novel methods are being tried out.[2]

Polycarbonate is coded 7 implying that it is difficult to recycle. However, a lot of research has been done in this regard and polycarbonate bottles and CDs are being

extensively recycled and/or degraded.[3]

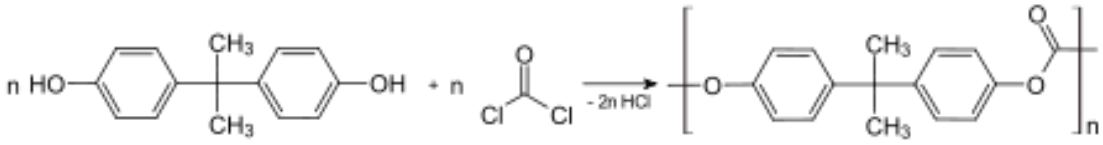


Polycarbonate (PC)

Manufacturing process of PC

A step-growth polymerization is used to synthesize PC from phosgene and Bisphenol A in which elimination of Cl ions are done every time the monomers react (Scheme 1). This is popularly known as condensation.

Firstly, bisphenol A groups are made to react with proton acceptors like sodium hydroxide (NaOH) to result in polymerization functional groups. At a temperature range between 25 and 35°C, phosgene and a catalyst react with the deprotonated Bisphenol A. This forms a PC monomer and the catalyst mostly pyridine is removed with the chloride anion.



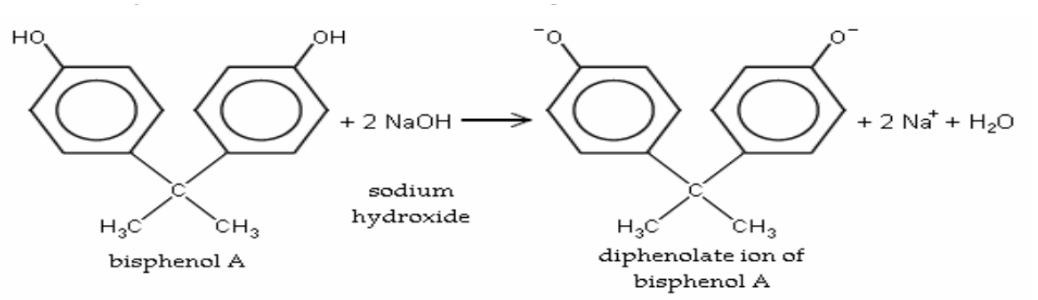
Scheme 1. Synthesis of polycarbonate

In an alternate method, bisphenol A and diphenyl carbonate (R-O-CO-O-R) are made to react in a temperature range between 180 and 220ºC resulting in a phenol molecule and PC. However, this process generates more impurity and incurs more expense especially since high temperatures are not needed. PC is then converted from

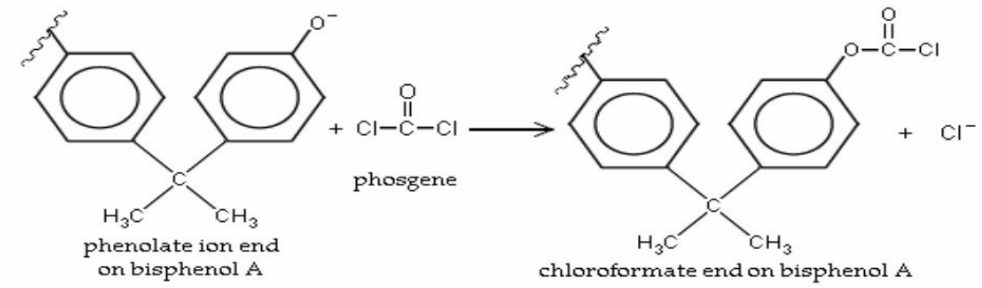
pellets to the desired shape by melting it and forcing it into a die or mold to provide the needed shape based on the application. This process is done repeatedly. In the extrusion process, the molten PC is passed through a die giving the material its final shape. The melt is rapidly cooled after this. Using this process, long pipes and sheets are formed.

The Polymerization steps are:

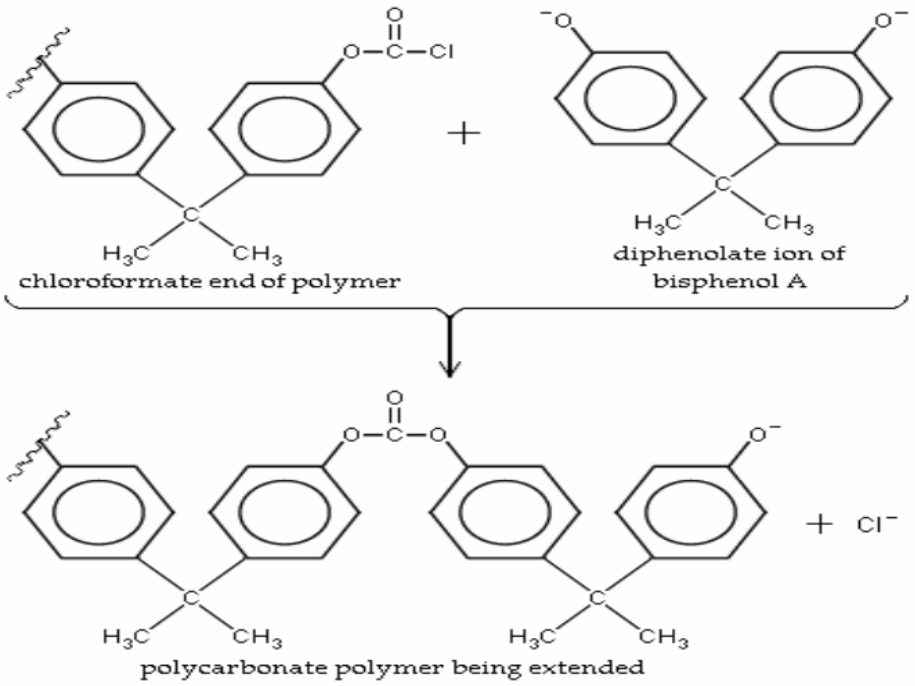
1. The Bisphenol A groups are reacted with proton acceptors such as NaOH to obtain the polymerization functional groups.



2. The deprotonated bispohenol A reacts with phosgene and a catalyst at temperatures between 25 and 35ºC. This way, a polycarbonate monomer is formed, and the catalyst (often times Pyridine), is eliminated along with the chloride anion.[4]



3. In order to react more bisphenol A and phosgene into the chain, chloride anions are always eliminated.



Properties of PC

- It maintains good mechanical properties between -40°F and 280°F.
- High strength that makes it resistant to impact and fracture.
- It can be easily colored, it's non-toxic, and can be absolutely transparent up to 2 In. in width.
- PC also features high electrical and heat resistance.
- It is biologically inert.
- Readily recyclable and cost effective
- Young's modulus (E): 2.0–2.4 GPa
- Tensile strength (σt): 55–75 MPa
- Elongation (ε) at break: 80–150%
- Compressive strength (σc): >80 MPa
- Poisson's ratio (ν): 0.37

- Hardness—Rockwell: M70
- Izod impact strength: 600–850 J/m
- Notch test: 20–35 kJ/m2
- Abrasive resistance: ASTM D1044 10–15 mg/1000 cycles
- Coefficient of friction (μ): 0.31

Thermal Properties

- Glass transition temperature (Tg): 147 °C (297 °F)
- Heat deflection temperature: 0.45 MPa: 140 °C (284 °F)
- 1.8 MPa: 128–138 °C (262–280 °F)
- Vicat softening point at 50 N: 145–150 °C (293–302 °F)[1]
- Upper working temperature: 115–130 °C (239–266 °F)
- Lower working temperature :−40 °C (−40 °F)[2]
- Thermal conductivity (k) at 23 °C: 0.19–0.22 W/(m·K)
- Thermal diffusivity (a) at 25 °C: 0.144 mm²/s[3]
- Linear thermal expansion coefficient (α): 65–70 × 10−6/K
- Specific heat capacity (c): 1.2–1.3 kJ/(kg·K).

PC can be blended to enhance its properties. PC/ABS blends exhibit high ductility and impact strength at temperatures below those of pure PC. PC tends to scratch easily, Silicone-polycarbonate copolymers can yield a hard thermoplastic that doesn't get scratched. Many more properties can be achieved depending on the composition.

The amount of PC production has been rising recently, leading to a continuous increase in the generation of the plastic waste. Disposal of the waste plastic has posed serious environmental as well as economic problems. Chemical recycling of PC waste is becoming an increasingly important method for the conversion of waste PC into valuable chemicals.

Manufacturing of Compact Discs

Ever since the invention of the phonograph in 1876, music has been a popular source of home entertainment. In recent years, the compact disc has become the playback medium of choice for recorded music. A compact disc, or CD, is an optical storage medium with digital data recorded on it. The digital data can be in the form of audio, video, or computer information. When the CD is played, the information is read or detected by a tightly focused light source called a laser (thus the name optical medium).[5]

By the late 1970s, a common set of standards for the optical storage discs had been developed by the joint efforts of Sony and Philips. A consortium of 35 hardware manufacturers agreed to adopt this standard in 1981 and the first compact discs and compact disc players were introduced in the market in 1982.

A compact disc is a deceptively simple looking device considering the technology required to make it. CDs consist of three layers of materials:

- A base layer made of a polycarbonate plastic.
- A thin layer of aluminum coating over the polycarbonate plastic.

- A clear protective acrylic coating over the aluminum layer.

Some manufacturers use a silver or even gold layer instead of the aluminum layer in the manufacture of their compact discs.

The compact disc is designed strictly according to the standards established by Sony and Philips in order to maintain universal compatibility. A CD is 4.72 inches (120 millimeters) in diameter and .047 inches (1.2 millimeters) thick. The positioning hole in the middle is 0.59 of an inch (15 millimeters) in diameter. A CD usually weighs around 0.53 of an ounce (15 grams). A standard CD can store up to 74 minutes of data. However, most CDs contain only about 50 minutes of music, all of which is recorded on only one side of the CD (the underside). The recorded data on the CD takes the form of a continuous spiral starting from the inside and moving outward. This spiral or track consists of a series of indentations called pits, separated by sections called lands. A tiny laser beam moving along the track reflects light back to a photo sensor. The sensor sees more light when it is on a land than when it is on a pit, and these variations in light intensity are converted into electrical signals that represent the music originally recorded.

Compact discs must be manufactured under very clean and dust free conditions in a "clean room," which is kept free from virtually all dust particles. The air in the room is specially filtered to keep out dirt, and occupants of the room must wear special clothing. Because an average dust particle is 100 times larger than the average pit and land on a CD, even the smallest dust particle can render a disc useless.[6]

Indian Scenario of E-waste:

India is fifth largest producer of e-waste, discarding roughly 18.5 lakh tonnes of electronic waste each year.[7] The amount of CDs and DVDs waste are about 4 lakh tonnes. The increasing levels of e-waste generation in India have been a matter of concern in recent years. The best example is the use of mobile phones. The annual e-waste is about 25% of about 100 crore mobile phones in circulation.[7]

The Ministry of Environment, Forest and Climate Change has notified e-waste management rules, 2016, in which producers are for the first time covered under extended producers' responsibility (EPR).

CHAPTER 2

MATERIALS AND METHODS

2.1 Procedure

Firstly the waste CDs and DVDs is being collected from e-waste site near local shop in Rohini area, Delhi, India. Further, the collected CDs and DVDs were burnished. The burnishing was done to remove the aluminum coating present. Burnishing of CDs/DVDs is majorly carried out by rubbing them with sand papers. Now the burnished CDs/DVDs was washed with ethanol. Ethanol acted as solvent for dissolving dyes. Now the disc obtained was completely of polycarbonate. The disc was further washed with water and dried in air. The treated discs were shreded into smaller pieces.

The shredded discs were treated with sodium hydroxide (NaOH) (in gram, table 1) and tetrahydrofuran (THF) and the solution was heated for different time interval such as 10, 15, 20 mins at 110^{o}C. The reaction mixture was filtered and treated with 1M hydrochloric acid (HCl). The solid obtained was thought to be bis-phenol A (BPA).
The obtained solid product was mixed with epichlorohydrin under basic condition to give bisphenol A diglycidyl ethers. Increasing the ratio of bisphenol A to epichlorohydrin during the process produces higher molecular weight linear polyethers with glycidyl end groups. The obtained product was semi-solid to hard crystalline materials at room temperature.

Table 1: Percentage of possible BPA yield

Sample	PC (g)	Water (mL)	NaOH (g)	Time (min)	% BPA
1	2.5	5	0.75	10	58
2	2.5	5	0.75	15	72
3	2.5	5	0.75	20	78

Table 2: Percentage yield of Resin

BPA (g)	Epichlorohydrin (ml)	NaOH (g)	% Resin
1.5	5	0.25	62
1.5	5	0.25	58
1.5	5	0.25	60

Bisphenol A diglycodyl ether is then mixed with the hardner and then further added in white cement to make the desired mold. Compressive strength of concrete depends on many factors such as water-cement ratio, cement strength, quality of concrete material, quality control during production of concrete etc.

Test for compressive strength is carried out either on cube or cylinder. Various standard codes recommend concrete cylinder or concrete as the standard specimen for the test. American Society for Testing Materials ASTM C39/C39M provides Standard Test Method (Table 3)

Table 3: Percentage increase in strength of the mold

Compressive strength of mold without resin(MPA)	Compressive strength of mold with resin(MPA)	Percentage increase in strength
36	48	33.34

CHAPTER 3

RESULTS AND DISCUSSION

Curing epoxy resins

Epoxy resins are produced from combining epichlorohydrin and bisphenol A to give bisphenol A diglycidyl ethers. Epoxy resins are low molecular weight polymers or higher molecular weight polymers which normally contain at least two epoxide groups. The epoxide group is also sometimes referred to as a glycidyl or oxirane group.Generally epoxy resins are produced industrially. The raw materials for epoxy resin production largely petroleum derived.

In general, uncured epoxy resins have only poor mechanical, chemical and heat resistance properties. However, good properties are obtained by reacting the linear epoxy resin with suitable curatives to form three-dimensional cross-linked thermoset structures. This process is commonly referred to as curing or gelation process.Curing of epoxy resins is an exothermic reaction and in some cases produces sufficient heat to cause thermal degradation if not controlled. Curing may be achieved by reacting an epoxy with itself (homopolymerisation) or by forming a copolymer with polyfunctional curatives or hardeners. In principle, any molecule containing reactive hydrogen may react with the epoxide groups of the epoxy resin. Common classes of hardeners for epoxy resins include amines, acids, acid anhydrides, phenols, alcohols and thiols. Relative reactivity (lowest first) is approximately in the order: phenol < anhydride < aromatic amine .Epoxy resin/ hardener combinations will cure at ambient temperature, or, with temperatures up to 150^{o}C being common, and up to 200^{o}C . Insufficient heat during cure will result in a network with incomplete polymerisation, and thus reduced mechanical, chemical and heat resistance. Cure temperature should

attain the glass transition temperature (T_g) in order to achieve maximum properties. Hence Epoxy resin is obtained. The epoxy form above can be used in coatings, adhesives and composite materials such as those using carbon fiber and fiberglass reinforcements. Epoxies have excellent adhesion, chemical and heat resistance, good-to-excellent mechanical properties and very good electrical insulating properties.Epoxy form above can be use in paints and coatings because they provide a tough, protective coating with excellent hardness. Epoxy systems are used in industrial tooling applications to produce molds, master models, laminates, castings, fixtures, and other industrial production aids.

Bisphenol A diglycodyl ether is obtained by reacting bisphenol A with epichlorohydrin in presence of NaoH. Bisphenol A diglycodyl ether is mixed with hardner to get the best mechanical properties.

SEM Analysis

Scanning electron microscopy (SEM) Fig. 1(a) show the SEM of Polycarbonate. And Fig. 1(b) show SEM of Bisphenol A. The morphology of the Polycarbonate changes. In the as-synthesized sample very large crystals are seen together with aggregates of intergrown crystals.

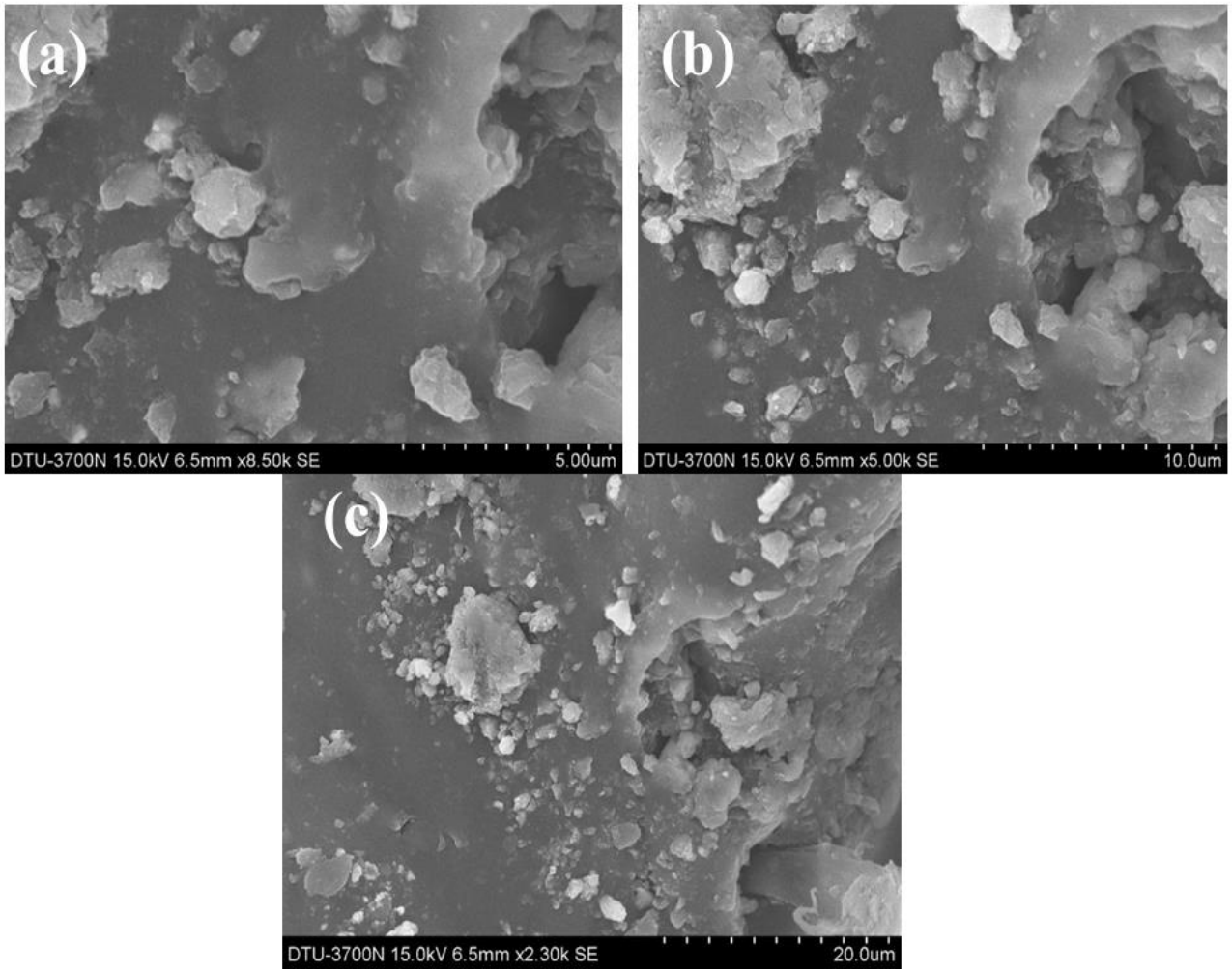


Fig. 1: (a) SEM image of Polycarbonate, b) SEM image of Bisphenol A and (c) SEM image of Epoxy resin

Fig. 1(c) shows the SEM image of Epoxy Resin. After mixing bisphenol A with Epichlorohydrine in presence of NaOH. And observe SEM image we see the size of granules becomes very small and equally distributed.

We observe the SEM image of cement as shown in fig. 2(d). And fig. 2(e) show the SEM image of Epoxy with Cement. After mixing with Epoxy in cement we observe that the aggregates of Epoxy and sheets of cements are uniformly distribute all over the surface. The surface become more rough and seen large aggregates (image e).

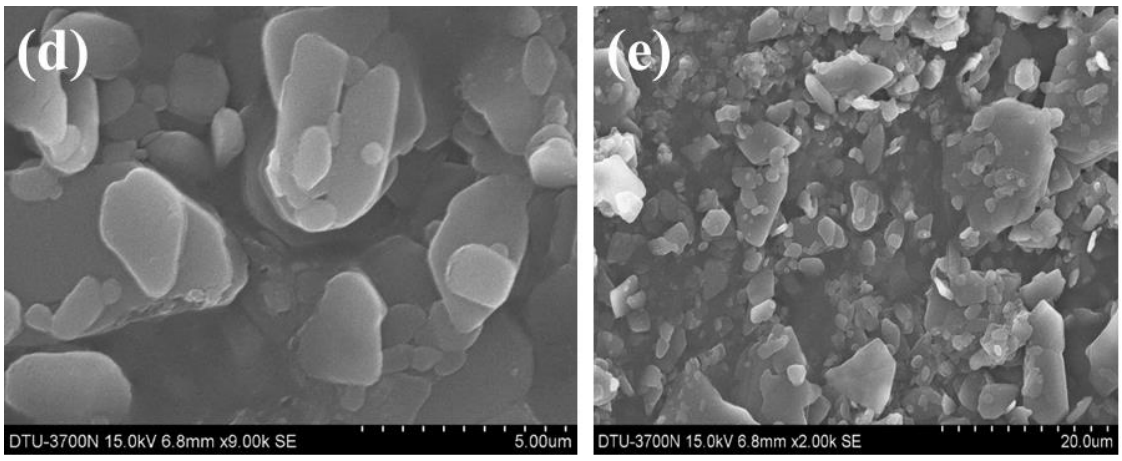


Fig.2 (d) SEM image of mold (e) SEM image of Epoxy paste with mold

3.2 FTIR analysis

Infrared spectroscopy is a powerful tool technique 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 3(a) shows the end-group determination in by infrared spectroscopy. Determination, stating that carbonate are the only end-group units available in polycarbonate.

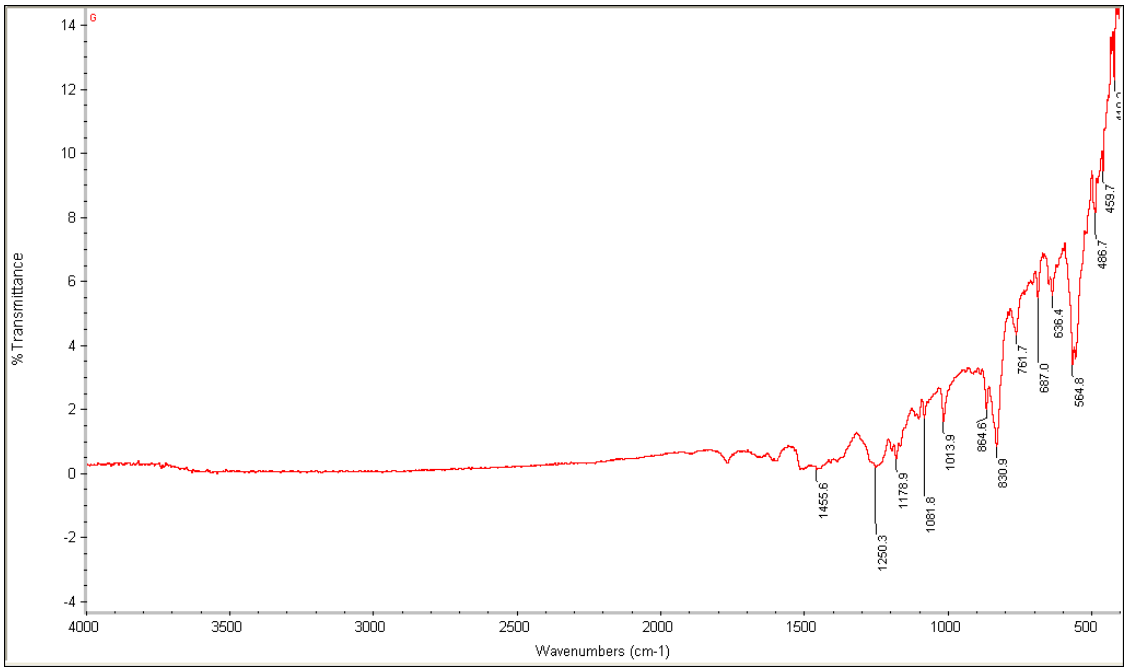


Fig.3(a) FTIR of polycarbonate

Fig 3 (b) shows the end-group determination in by infrared spectroscopy. Determination, stating that two hydroxyphenyl groups are the only end-group units available in bisphenol a.

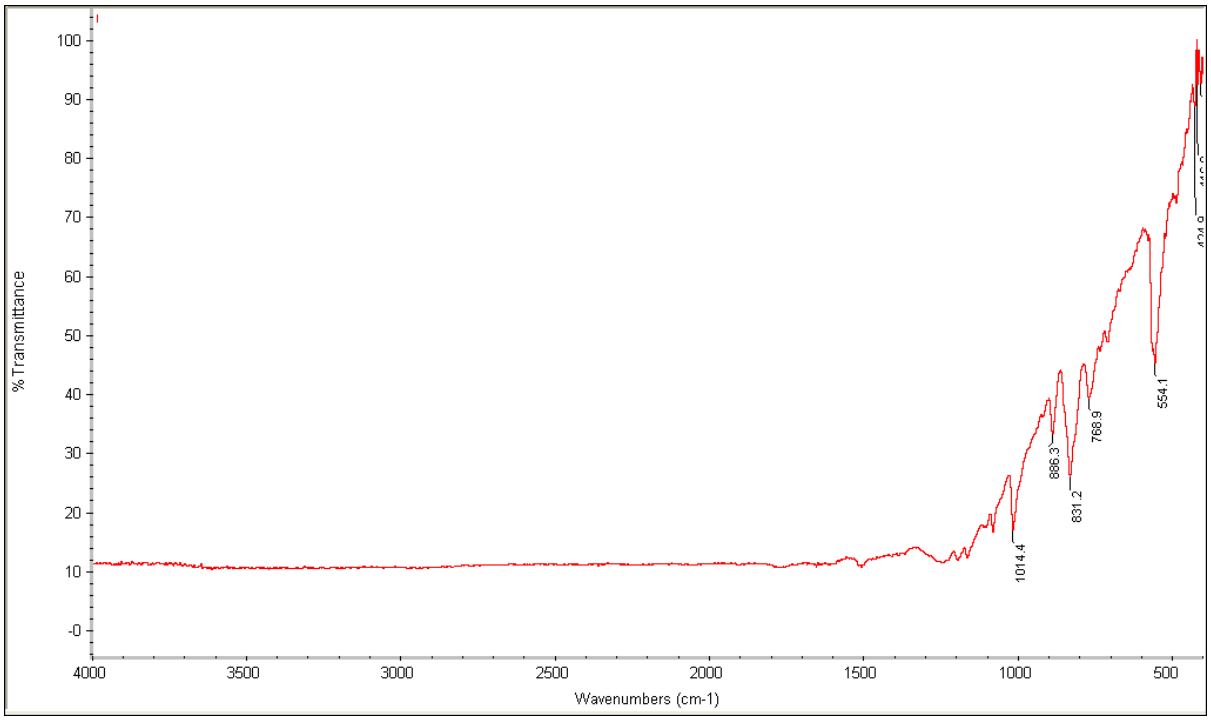


Fig. 3(b)FTIR of bisphenol a

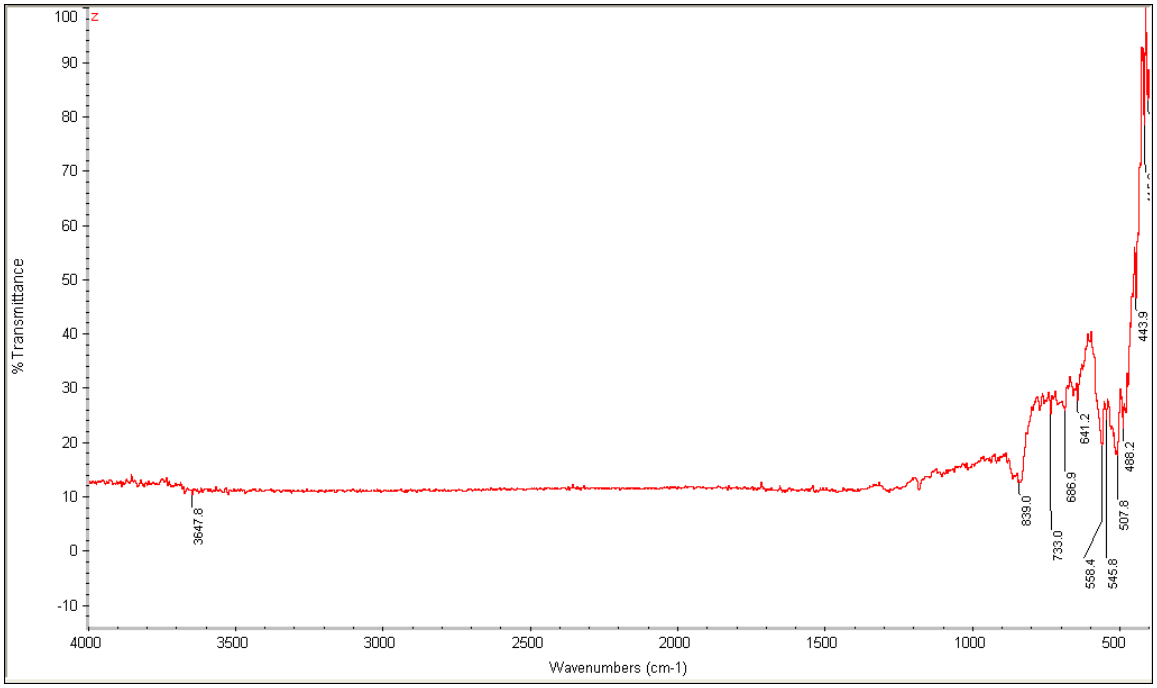


Fig.10(d) FTIR of mold with epoxy

CHAPTER 4

CONCLUSIONS

Waste management is the collection, transport, recovery and disposal of waste, including the supervision of such operations and aftercare of disposal sites according to European Union Directive on waste.

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CHAPTER 5

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