JIMMA UNIVERSITY

JIMMA INSTITUTE OF TECHNOLOGY

SCHOOL OF GRADUATE STUDIES

FACULTY OF MATTERIALS SCIENCE AND ENGINEERING

MASTERS OF SCIENCE PROGRAMME IN POLYMER ENGINEERING

Title: Effect of Microwave Irradiation on Structure and Properties of Poly (ethylene terephthalate) (PET)

A thesis Submitted to the School of Graduate Studies of Jimma University in Partial Fulfilment of the Requirements for the Degree of Master of Science in Polymer Engineering

By:

Tigist Merga Gemechu

Advisor: Dr. Rabiul Hussain

Date 02, APRIL 2021

Declaration

This Thesis is my original work and has not been presented for a degree in any other university.

----------	----------	----------
Candidate	Signature	Date

This thesis has been submitted for examination with my approval as a university

I. Supervisor(s).

----------	----------	----------
Advisor	Signature	Date
----------	----------	----------
Co-Advisor	Signature	Date

I. Examiner(s):

i. Internal Examiner:

Name_____Signature _____ Date_____

ii. External Examiner:

Name Tesfamariam Tekle Signature  Date_____

Acknowledgment

First of all I would like to thank God for giving me the courage to work hard and help me throughout my entire life. Then I would like to thank my adviser Dr. Rabiul Hussain for being willing to work with me and Dr. Lodrick Wangatia for his appreciable help, mentoring and sharing knowledge throughout my thesis work. Then thanks to all laboratory assistances of Materials Science and Engineering department in Jimma Institute of Technology, Jimma University for helping and assisting me on the laboratory work. I also appreciate the cooperation of all staff member of Material Engineering Department at Adama Science and Technology University on some laboratory activities. Then I would like to thank all my family members for their support, encouragement, and motivation on my work. Thanks to my husband who has been there for me with all his support, help, encouragement, interest and understanding on all my way to finish this work of mine. At last thanks to all my friends who had helped me throughout this thesis.

Abstract

The application of microwave energy on polymers has got huge interest in the field of organic chemistry. Industrial use of microwave radiation as an alternative to conventional thermal heating has generated interest recently mainly because of the drastic reduction in the processing time. It provides effective, selective and fast synthetic methods by heating the molecules directly through the interaction between the microwave energy and molecular dipole moments of the starting materials. In this research the effect of microwave irradiation on the mechanical and thermal properties Poly (ethylene terephthalate) PET has been investigated. PET has been treated with microwave irradiation under variety of conditions in terms of the power and the time of microwave treatment. The structures of the untreated and treated PET has been investigated with Fourier transform infrared spectroscopy (FTIR), the thermal properties of the untreated and the treated PET has been investigated using Thermo gravimetric analysis (TGA). The effect of microwave irradiation on mechanical properties has been studied using universal testing machine (UTM) and different spectroscopic and analytical equipment.

The analyzed result shows a small change on its tensile strength at an irradiation time of 10 and15 minutes which was due to surface modification of phenyl rings at the surface. The TGA result shows a small reduction of melting temperature as the irradiation time increases. On the FT-IR result also there was a slight change of molecular bonds due to the rearrangement and loss of some particles of PET.

Keyword: *PET, microwave irradiation, structure, thermal and mechanical properties*

Table of Contents

List of Figures

List of Tables

CHAPTER ONE

1. INTRODUCTION

1.1 Background

Poly (ethylene terephthalate) PET was first synthesized in North America in the mid-1940s by DuPont chemists searching for new synthetic fibers. DuPont later branded its PET fiber as **Dacron**. Today, more than half of the world's synthetic fiber is made from PET[1]. In the late 1950s, researchers found a way to stretch a thin extruded sheet of PET in two directions to create PET film, which is now used extensively for video, photo and packaging films. In the early 1970s, the technology was developed for blow-stretch molding PET into bottles. The PET bottle was patented in 1973[2]. PET is one of the most used plastics in our day to day life.

PET is a thermoplastic polymer which belongs to the polyester family. The Polyester polymers are well known for their excellent combination of properties such as mechanical, thermal, chemical resistance and their dimensional stability. PET is the most recyclable polymer. It is highly flexible, colorless and semi-crystalline resin in its natural state. Depending upon how it is processed, it can be semi-rigid to rigid. It shows good dimensional stability, resistance to impact, moisture, alcohols and solvents. Poly(ethylene terephthalate) is one of the most widely used engineering polymer showing excellent thermal and mechanical properties[3, 4]. It is a semi-crystalline thermoplastic polyester with high strength, transparency and safety[5, 6].Polyethylene terephthalate (PET), commonly known as polyester is significant among the verities of polymers due to its high mechanical strength, inertness to chemical reaction and resistance to thermal

environment[7]. It has a wide range of applications in the textile industry, food packaging (especially in water and soft drink bottles), x-ray films etc…[7, 8].

Microwaves are high frequency radio waves which can penetrate many materials that can cause heat to be generated in the process. The application of microwave energy on polymers has got huge interest in the field of organic chemistry. Industrial use of microwave radiation as an alternative to conventional thermal heating has generated interest recently mainly because of the drastic reduction in the processing time[9].The main advantage of microwaves over conventional heating sources is that the irradiation penetrates and simultaneously heats the bulk of the material[3].It provides an effective, selective, and fast synthetic methods by heating the molecules directly through the interaction between the microwave energy and molecular dipole moments of the starting materials. This internal heating is believed to produce an efficient reaction because the reactive sites, which have strong dipole moments, are the primary source of activation in the microwave electromagnetic field.

Microwave application in chemical synthesis reaction began in 1986; Canadian R.Gedye et al. studied the esterification of benzyl alcohol and acid by microwave irradiation, and revealed the sequence of chemical synthesis by microwave. Starting from the date of the study, microwave synthesis has become research focus in the field of chemical synthesis especially in the field of polymer synthesis more shows great potential for development. With traditional high-energy radiation such as ultraviolet ray, r, compared with microwave on the depth of the effect of polymer, no damage, protection of macromolecular chain easy, has the advantages of the operation is simple, clean, safe, and efficient[10]. Microwave irradiation is a powerful technique of non-contact heating by causing vibration and rotation permanent dipoles in the microwave fields[1, 5]. The microwave region of the electromagnetic spectrum corresponds to waves of

wavelength 1 mm to 1 m (frequencies of 300 GHz to 300 MHz respectively).Domestic and industrial microwave ovens generally operate at a wavelength of 2.45 GHz corresponding to a wavelength of 12.2cm and energy of 1.02 x 10^{-s}eV. A material can be heated by applying energy to it in the form of microwaves which are high frequency electromagnetic waves[11, 12]. The rapid heating of food in the kitchen using microwave ovens prompted a number of scientists engaged in different disciplines to explore the potential of microwave technology in a number of useful processes[12, 13]. These include the preparation of samples for analysis, application to waste treatment, polymer technology, drug release or targeting, ceramics, alkane decomposition, hydrolysis of proteins and peptides, etc. Many researches have been done to investigate the advantages of microwave irradiation over the conventional thermal heating processing in heating and in synthesis of polymer materials[4, 14].

1.2 **Problem Statement**

The microwave irradiation has a significant role in the field of polymer science. Nowadays this technology has been applied in synthesis of polymers for enhancement of better and desirable properties of polymers. Most researches which have been done on microwave irradiation are concerned with the depolymerization of PET using reagents and catalysts. This point of view gives a hint that without this reagent the polymer will not under go any depolymerization. So rather than destroying or depolymerizing the polymer why cannot use the microwave irradiation as a modification technique for the polymer properties. From this point of view it is a good opportunity to study effect of microwave irradiation on other properties of polymers. The main reason to do this investigation is to enhance the mechanical and thermal properties of PET. Research on the structural and property changes of PET during the application of microwave irradiation can set the stage for further application of microwave heating in the industry of plastic

technology. The aim of this research is to analyze the effect of microwave irradiation on structure, mechanical and thermal properties of PET using low cost and easy technique. Therefore the changes on the polymer during the microwave irradiation have been investigated. There has not been any research work reported on the effect of microwave irradiation on properties or structure of PET.

1.3 Objective of the study

1.3.1 General objective

The main objective of this research is to investigate the effect of microwave irradiation on the structure and properties mainly mechanical and thermal properties of Poly (ethylene terephthalate) PET.

1.3.2 Specific Objectives

- To apply the microwave irradiation on PET for different time intervals.
- Examine the change in the properties of PET due to the irradiation.
- Analyzing the structural changes.
- To compare the changes before and after the microwave treatment of PET.

1.4 Significance of the study

Most recycling methods and techniques are more of time consuming and costly. The application of microwave irradiation provides effective, selective, and fast synthetic methods by heating the molecules directly through the interaction between the microwave energy and molecular dipole moments of the starting materials. Therefore, it makes microwave irradiation the best technique to improve properties of polymers in short period of time with low cost.

1.5 Research Design

To conduct and investigate this thesis work some investigation techniques were used.

- ✓ Secondary Data collection: Some information related to effect of microwave irradiation on polymers by reading and review of research papers and books to have some hint on the field.
- ✓ Collecting materials used for the research.
- ✓ Designing experimental procedure to analyze and investigate the effect of microwave irradiation on PET.
- ✓ Analyze and explain the experimental characterization result and draw the conclusion.
- ✓ State recommendation for further study depending on the conclusion.

1.6 Research Layout

This thesis contains five main chapters. The first chapter is introduction section which discusses about the background of the study, problem statement, objectives of the study and significance of the study. The second chapter discusses about literature reviews from different research papers, books, and websites. The third chapter is about materials and morphologies used in this research which include material collection, sample preparation, microwave irradiation treatment and characterization techniques. The fourth chapter discusses about the characterization results. The last chapter contains conclusion and recommendation for further investigation and studies.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Recycling Plastic Waste

As the consumption and usage of plastics increases the waste of these plastics is also increasing day by day. Many plastics which are used these days are a single time use items that are only used once and then disposed to the environment[15].In 2015, the annual production of plastic globally reached 381 million tons, a 200times increase from just 2 million tons per year in 1950. In 2010, China produced the most plastic waste at about 60 million tons, followed by the US at 38 million. Germany and Brazil were next in list at 14.5 million and 12 million tons, respectively. About 52% of plastics that were thrown away in 2015 were plastic packaging products. Reports show that only about half of plastic packaging goes to recycling and the rest is added to the growing amount of plastic waste on the environment around us[16, 17]. Around 32% of the 78 million tons of plastic packaging produced in a year end up in the oceans, which is the equivalent of emptying one garbage truck full of plastic into the ocean every minute. This trend is increasing and this could mean by 2050, there will be more plastic waste than fish in the oceans[18].

As a matter of time these wastes are granting huge concern to the environment. That is why better and cost effective recycling technologies are needed. One of the best technologies is the microwave irradiation. Many researches have been done to investigate the advantages of microwave irradiation over the conventional thermal heating processing in heating and in synthesis of polymer materials[4]. In recent years the microwave irradiation technology is already being used in various chemical fields from inorganic to organic reactions, from the

medical chemical industry and the extraction of natural products to food processing, and from simple molecules to complicated biological molecules. It also has great role in the field of polymer science[19, 20]. The technology has been used for synthesis and processing of high polymer materials, for recycling or depolymerization and crystallization of polymers.

There are microwave irradiation assisted chemical depolymerization or degradation of PET. These degradation techniques are divided based on the reagent used in the process[21].Such as;

Hydrolysis: It is the split of bonds in functional groups by reacting with water molecules. This reaction occurs mainly in polymers that take up a lot of moisture and that have water-sensitive groups in the polymer backbone. Synthetic polymers such as polyesters, polyethers, polycarbonates degrade when exposed to moisture. In the case of PET; it is when PET is reacted with an acid, alkaline or neutral environment to produce its monomers terephthalic acid (TPA) and ethylene glycol (EG)[22].

Glycolysis: Glycolysis is the simplest and oldest method of PET depolymerization and mostly is used when the PET that we want to recycle is high valued. It is a slow chemical process in which, at temperatures between 180 and 250 ºC, the reaction of polyethylene terephthalate (PET) with glycols (commonly used ethylene glycol EG) happens, and gives as products PET oligomers. It is when PET is reacted with glycol. Glycols such as ethylene glycol or propylene glycol are used for this degradation process to produce bis (hydroxyalkyl) terephthalate which is an oligomer of PET[23].

Aminolysis: It is a reaction with an amine such as ethanolamine to produce bis (2-hydroxyethyl) terephthalamide (BHETA)[22].

Methanolysis: It is reaction with methanol to produce dimethyl terephthalate and ethylene glycol (EG)[23].

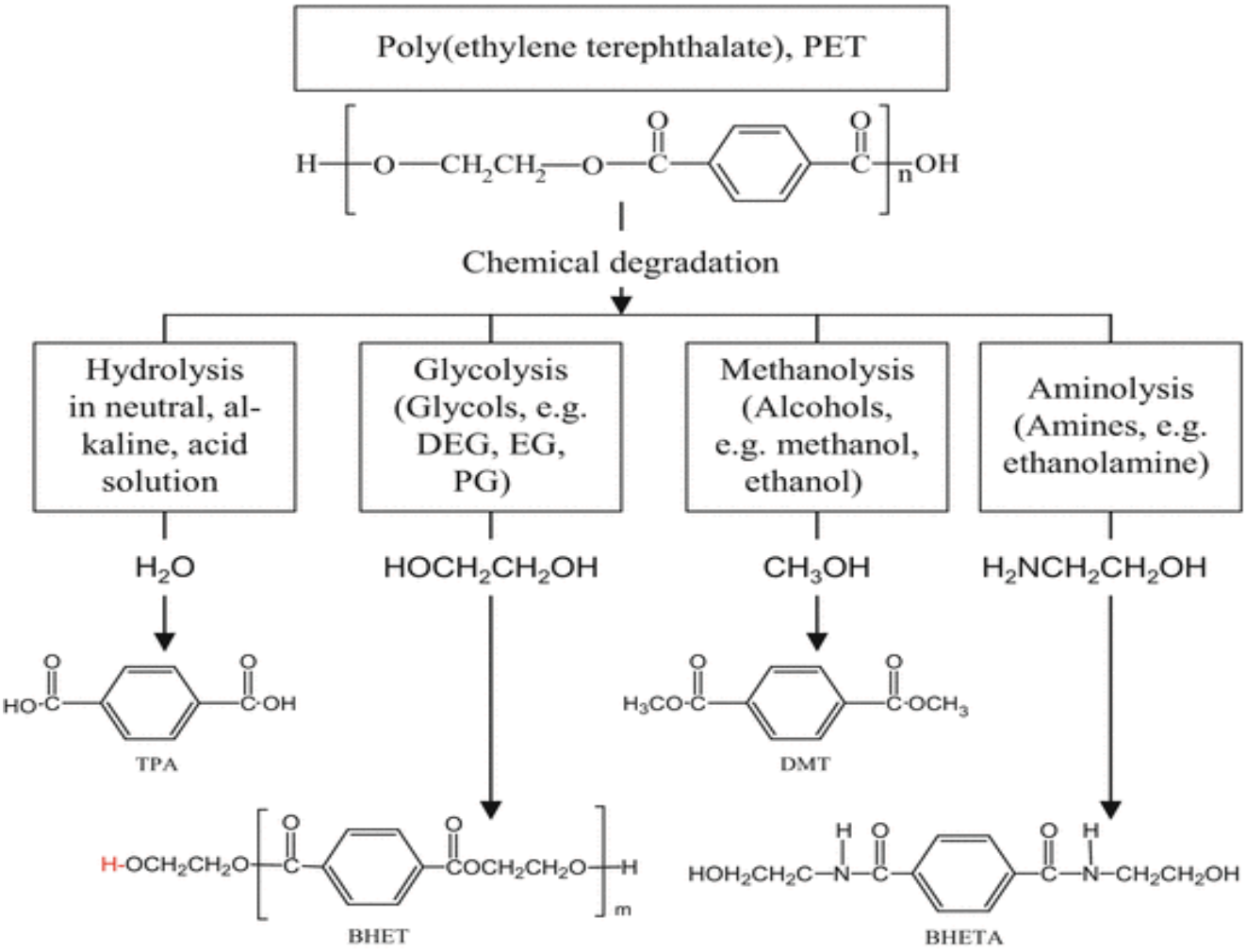

Figure 1: MW assisted chemical degradation of PET

2.2 Structure of PET

PET is produced by the step-growth polymerization of terephthalic acid or dimethyl terephthalate and ethylene glycol. Ethylene glycol is a colorless 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 fibers 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-member carbon (or aromatic) ring and two carboxyl (COOH) groups. Under the influence of heat and catalysts, the hydroxyl and carboxyl groups react to form ester 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 reaction can be represented as follows:

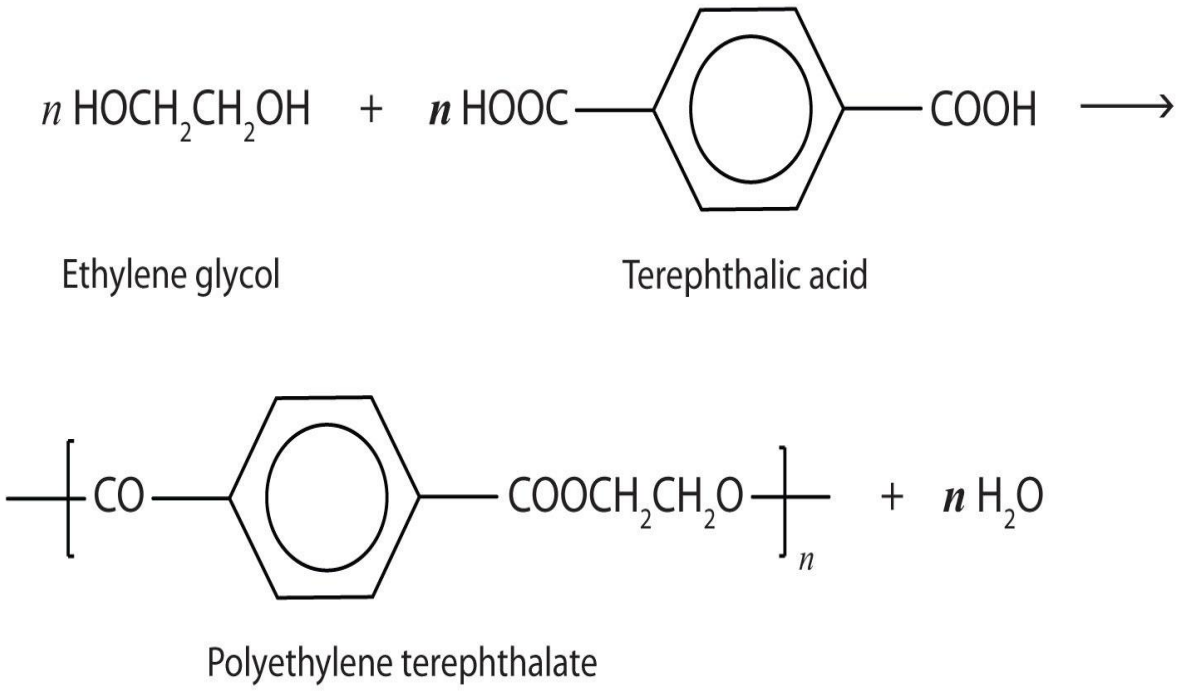

Figure 2: Overall synthesis of PET

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).

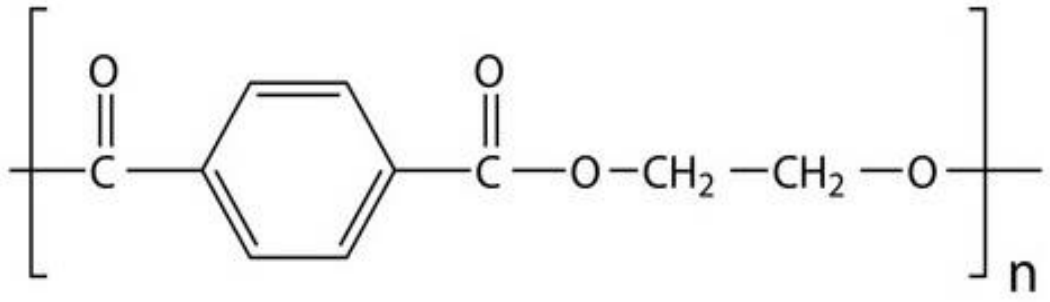

Figure 3: Molecular Structure of Poly (ethylene terephthalate)

2.3 Properties of PET

Polyethylene terephthalate (PET) exists both as an amorphous (transparent) and a semi-crystalline (opaque and white) thermoplastic. Generally, it has good resistance to mineral oils, solvents and acids but not to bases. The semi-crystalline PET has good strength, ductility, stiffness and hardness while the amorphous PET has better ductility. PET also has good process ability and can be recycled for other applications [2].

2.3.1 Mechanical Properties of PET

One of the reasons PET has been the most widely used polymers is its excellent mechanical properties. Even though it has excellent mechanical properties if this investigation is a success it may bring other ways of modification of properties at low cost and easy techniques. The purpose of this research is to investigate if the mechanical properties of PET properties like high tensile modulus and high strength can be obtained by using microwave irradiation.

Table 1: Mechanical properties of PET

Mechanical properties	**Measurement**
Hardness –Rockwell	M94-101
Izod impact strength ($J.m^{-1}$)	13 – 35
Poisson's ratio	0.37-0.44 (oriented)
Tensile modulus (GPa)	2 – 4
Tensile strength (MPa)	80, for biaxial film 190 – 260
Coefficient of friction	0.2 - 0.4

2.3.2 Thermal Properties of PET

The thermal properties of PET are relatively good. Some of the thermal properties of PET are mentioned at the table below[24].

Table 2: Thermal properties of PET

Thermal Properties	**Measurement**
Coefficient of thermal expansion ($x10^{-6}\ K^{-1}$)	20 – 80
Heat-deflection temperature - 0.45 MPa (°C)	115
Heat-deflection temperature - 1.8 MPa (°C)	80
Lower working temperature (°C)	-40 to -60
Specific heat ($J.K^{-1}.kg^{-1}$)	1200 – 1350
Thermal conductivity ($W.m^{-1}.K^{-1}$)	0.15 - 0.4 at 23
Upper working temperature (°C)	115 – 170
Glass transition temperature (^{o}C)	65-81

Melting temperature (^{o}C)	250-260

2.3.3 Chemical Properties of PET

PET has good resistance to weak acids and alkaline solutions, oils, fats, aliphatic and aromatic hydrocarbons, carbon, tetrachloride. On the other hand, it has poor resistance to strong acids and alkaline solutions, phenol, long exposure to hot water. Strong acids such as concentrated sulfuric acid dissolve and depolymerize PET.

Table 3: Chemical Properties of PET

Chemical	**Resistance ability**
Acids-concentrated	Good
Acids-dilute	Good
Alcohols	Good
Alkalis	Poor
Aromatic hydrocarbons	Fair
Greases and Oils	Good
Halogens	Good
Ketones	Good

2.3.4 Physical Properties of PET

Poly(ethylene terephthalate) (PET) is a polyester that has a high melting point because of the presence of an aromatic ring [25, 26]. PET in its natural state is a colorless, semi-crystalline resin. Based on how it is processed, PET can be semi-rigid to rigid, and it is very lightweight. It has a good gas and fair moisture barrier. PET becomes white when exposed to chloroform and

also certain other chemicals such as toluene[27]. About 60% crystallization is the upper limit for commercial products, with the exception of polyester fibers. Amorphous PET is formed when its molecules are not given enough time to arrange themselves in an orderly, crystalline fashion as the melt is cooled. At room temperature the molecules are frozen in place, but, if enough heat energy is put back into them by heating above the glass transition temperature Tg, they begin to move again, allowing crystals to nucleate and grow. This procedure is known as solid-state crystallization. When allowed to cool slowly, the molten polymer forms a more crystalline material. This material has spherulites containing many small crystallites when crystallized from an amorphous solid, rather than forming one large single crystal[2, 28]. Light tends to scatter as it crosses the boundaries between crystallites and the amorphous regions between them. This scattering means that crystalline PET is opaque and white in most cases[2].

2.3.5 Optical Properties of PET

The high transmission in the visible range makes PET a substrate that is suitable and useful for a number of applications, including optoelectronic and other thin film applications [29-31].Many polymers in everyday use contain fillers and coloring agents that render them opaque. The optical properties of the base polymer are thus obscured. On the other hand the clarity of optical transmission of many polymers and the fact that they are almost colorless, coupled with their low density and excellent mechanical properties. The transparency and colorlessness of a substance arise from the fact that it does not absorb or scatter any significant amount of visible electromagnetic radiation. The reason why many polymers behave in this way is that their molecules consist of atoms linked together either by single bonds, or by isolated double bonds or benzene rings[32]. Semi-crystalline or crystalline polymers such as PE, PP, PET, are translucent

or opaque as there are differences in refractive indices between the crystalline regions and amorphous regions. The light transmission of PET differs greatly according to chemical composition. Although PET is crystalline, films of this material are transparent. This is because these films are bi-axially oriented, stretched in two directions which orientates the polymer molecules in the plane of the film. Hence, when light passes through the film, there is no refraction because of this orientation.

Table 4: Optical Properties of PET

Optical property	Percentage (%)
Gloss	105 - 200 %
Transparency (% Visible Light Transmission)	70 - 90 %

2.4 Related Works

Many researchers investigated the effect of microwave irradiation on modification of polymers properties. The results indicated that the changes in the polymer properties depend on whether cross-linking or degradation dominates during irradiation. However, a wide spectrum of systematic investigation is yet to be carried out to find out the conclusive and definite role of irradiation agents in modification process[33]. Hesek, in 1970s applied microwave technology to analytical chemistry. In 1986, Gedye, et al. published the first paper about the application of microwave technique to organic synthesis. In recent years the microwave irradiation technology is already being used in various chemical fields from inorganic to organic reactions, from the medical chemical industry and the extraction of natural products to food processing, and from simple molecules to complicated biological molecules. It also has great role in the field of polymer science[19, 34]. The technology has been used for synthesis and processing of high

polymer materials, for recycling or depolymerization and crystallization of polymers. Guijuan Li and Yuyuan Shi have studied the effect of microwave irradiation on crystallization behavior of PET/PEN[34]. On the other hand researchers investigated the depolymerization of PET under microwave irradiation.. The main advantage of microwave use are short reaction times, between 4 and 10 min, in which complete PET degradation is achieved[3]. Other researchers like Andrej KrzÏan et al.,Dimitris S Achilias introduced other ways of chemical recycling technique which was assisted under microwave irradiation[20, 35].

Mohammad NahidSiddiqui et al have studied the recycling of poly (ethylene terephthalate) waste through methanolic pyrolysis in a microwave reactor. In their work, they investigated the depolymerization of PET with methanol with or without the use of zinc acetate as a catalyst under microwave irradiation. They found that PET depolymerization, is favored by increasing temperature, time and microwave power. High degrees of depolymerization were measured at temperatures near 180 ◦C and at microwave power higher than 150 W. Most of the degradation was found to occur during the initial 5–10 min. Compared to conventional pyrolysis methods, microwave irradiation during methanolic pyrolysis of PET certainly results in shorter reaction times. As a result of their work, the main product DMT (dimethyl-terephthalate) was produced. Thus they concluded that the microwave irradiation technique is a very beneficial one for the recycling of PET wastes[9].

Dimitris S Achilias et al have studied the Aminolytic depolymerization of poly (ethylene terephthalate) waste in a microwave reactor. In their work, the reaction was carried out with ethanolamine and without the use of any other catalyst in a sealed microwave reactor in which the pressure and temperature were controlled and recorded. Experiments under constant temperature or microwave power were carried out for several time periods. As a result of their

work, PET depolymerization and recovery of the main product, BHETA (bis(2-hydroxyethyl) terephthalamide), are favored by increasing temperature, time and microwave power. In this research they also stated microwave irradiation as a very beneficial technique for their work[35].

KrzÏan et al. did research on the Microwave Irradiation as an Energy Source in Poly (ethylene terephthalate) Solvolysis which is one way of depolymerization technique using microwave irradiation as energy source for the recycling purpose of PET. In their work, they investigated the use of microwave radiation as the energy source in PET solvolysis reactions, and the conditions that govern its effectiveness[3].Solvolysis reagents used were methanol, propylene glycol, and polyethylene glycol 400. As a result they stated that the use of microwave radiation as the energy source in PET solvolysis resulted short reaction times needed for the degradation of PET.

The main difference between the above three works is the reagents they used for the depolymerization of PET. **Mohammad NahidSiddiqui et al.** used methanol with and without the use of zinc acetate as a catalyst to depolymerize PET. **Dimitris S Achilias et al.** used ethanolamine without the use of any other catalyst to depolymerize PET. Reagents **KrzÏanetal.** used was methanol, propylene glycol, and polyethylene glycol 400.

Zhao Xue et al. did research on Effect of Microwave Irradiation on the Physical Properties and Structures of Cotton Fabric. In this work they investigated the effect of microwave irradiation on the physical properties, chemical structure, surface morphological structure and fine structure of cotton fabric. For the investigation cotton fabric was treated with microwave irradiation under variety of conditions in terms of the power and the time of microwave treatment. They concluded that microwave irradiation can impact the breaking strength and elongation at break of wet cotton fabrics. They also stated that microwave irradiation affected the fine structure of cotton.

And they recommended that microwave irradiation treatment has significant potential for wet finishing of cotton fabric and microwave is a clean, environmentally friendly, highly efficient heating technology[5].

Jin Gya Li et al. This researcher studied about the Effect of Microwave treatment on the properties of PET fibers. In this research PET fibers were treated by microwave irradiation at different time and power levels. As a result it is stated that compared to the untreated fiber the microwave treated fibers have enhanced hygroscopicity; this is caused because of the polar groups on the surface of the PET fibers were improved and reduced fiber strength, the fracture strength decreased; reason for this is, that microwave treatment made the fiber surface roughed and the surface molecular structure was broken, the orientation fibers was decreased and the surface crystallinity was destroyed. It is concluded that the optimized values of parameters are the power of 250W, reaction time of 5min, and PH value of 9. And it is concluded that microwave treatment is a technology which can help to support the functional materials for PET fibers[36].

Bo Qu et al. this researcher studied Enhancement of mechanical properties of bucky papers/polyethylene composites by microwave irradiation. This work the mechanical properties such as tensile strength and stiffness of the composite were developed using microwave irradiation. It is denoted in this work that, the desirably improved properties of BPs/PE composites can be characteristics to the physical improvement of impregnation of PE into BPs, the chemical improvement of interfacial bonding strength between PE and carbon nanotubes as well as crystallization behavior of PE. These results suggest a new process employing microwave irradiation to prepare stronger and stiffer buckypaper/ thermoplastic resin composites[37].

CHAPTER THREE

3. MATERIALS AND METHDOLOGY

This experimental section is primarily concerned with the investigation of effect of microwave irradiation on PET on the structure and properties of the polymer also. Most commodity polymers are disposed inappropriately to the environment. PET bottles are the most disposed plastic nowadays. Recycling these wastes is getting a huge interest. Getting cost effective and easy ways will be the biggest concern. Considering this issue this research was carried out to investigate effect of microwave irradiation on the structural changes and properties such as mechanical properties and thermal properties of PET polymer and as a result finding the effect of the microwave irradiation on increasing mechanical properties of PET following the testing procedure of specifications of ASTM.

3.1 Materials and Methodology

In this section the materials used in the experiment and the methodology to investigate the microwave irradiation effect on PET has been discussed. The characterization techniques to investigate the changes on mechanical properties, thermal properties and molecular structure are also studied in this chapter.

3.1.1. Sample Selection

Most commodity materials especially which are used for food and beverage storage are made of PET. Due to the abundance and inappropriate disposal, used clear PET bottles are selected for this research. The other reason for selecting PET is that, from the literature review survey it can be concluded that microwave irradiation can improve some properties of the polymer.

3.1.2. Experimental Sites

Used clear PET plastic bottles were collected from Jimma town where waste materials are disposed. The chemicals used for the washing the bottles is acetone which is collected from Jimma university materials science and engineering lab. The sample preparation and most of the characterization has been done at Jimma University, Jimma Institute of Technology Material Science and Engineering lab.

3.1.3. Apparatus and Equipment

In this experiment the following laboratory apparatuses have been used to accomplish the objectives of the thesis; beakers, cutter, microwave oven, digital caliper, mechanical cutter, digital beam balance. For the characterization; Fourier Transform Infrared Spectroscopy (FT-IR), Thermo gravimetric Analysis (TGA), UTM, Rockwell and Brinell Hardness Tester were used.

3.2. Methodologies

3.2.1. PET Bottles

Used clear PET bottles were collected and the labels glued on the bottles were removed. Then washed using water and different detergents to remove the dirt then dried. After that the bottles were washed again with distilled water to remove remaining dirt.

3.2.2 Sample Preparation

After washed and dried; the PET bottles were cut in to smaller shapes having size of 200cm^2 which was measured using digital calipers. Then the samples were dispersed in acetone in a 500ml beaker for about 5 to 10 minutes to remove some impurities on the surface. Then the flasks were removed from the beaker and put aside to dry at room temperature in an open air.

3.2.3. Microwave Irradiation

After the samples were prepared they were exposed to the microwave irradiation for different time intervals. The microwave used in this research was Nikai microwave oven model NMO2020B having a fixed output power of 1100W, input power of 700W, microwave frequency of 2450MHz.The temperature used for all samples was room temperature the irradiation exposure time intervals used for this research are 10min, 15min, 20min and 30min.

3.3. Characterization Techniques

The molecular structure of the microwave irradiation treated and the untreated PET were characterized by FT-IR. The thermal properties were characterized by TGA (Thermo gravimetric analysis).

Mechanical Test

Mechanical properties of the microwave irradiation treated and untreated PET samples were measured. Tests such as tensile strength and elongation at break were conducted using tensile testing following the ASTEM standard D638-02a at room temperature using UTM model with 50N as cell load. The test speed is 5mm/min. The films were cut in to bone shaped specimens. All specimens have same width of 6.5mm, length of 50mm and thickness of 2.5mm which were measured using digital caliper.

Rockwell hardness test: The hardness tests were performed with a hardness tester (Jinan Lian gong Testing Technology Co., Ltd) model HR-150A. For this test all the samples were measured under same conditions of test. Applied force of 10kgF, scale used is scale B; scale B is used because of the sample thickness was thin and for soft sample scale B is used.

Brinell hardness Test: The hardness tests were performed with a hardness tester (Jinan Hensgrand Instruments Co., Ltd) model 3000B. For this test all the samples were measured under same conditions of characterization and environment. Applied force is 62.5kgF, time is 12 sec, and ball diameter is 2.5mm.

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1 Introduction

In this chapter the results of microwave irradiation treated and untreated PET samples has been analyzed and discussed briefly. The characterization results on structure, thermal and mechanical properties of microwave irradiation treated and the untreated samples are discussed.

4.2 FT-IR Analysis

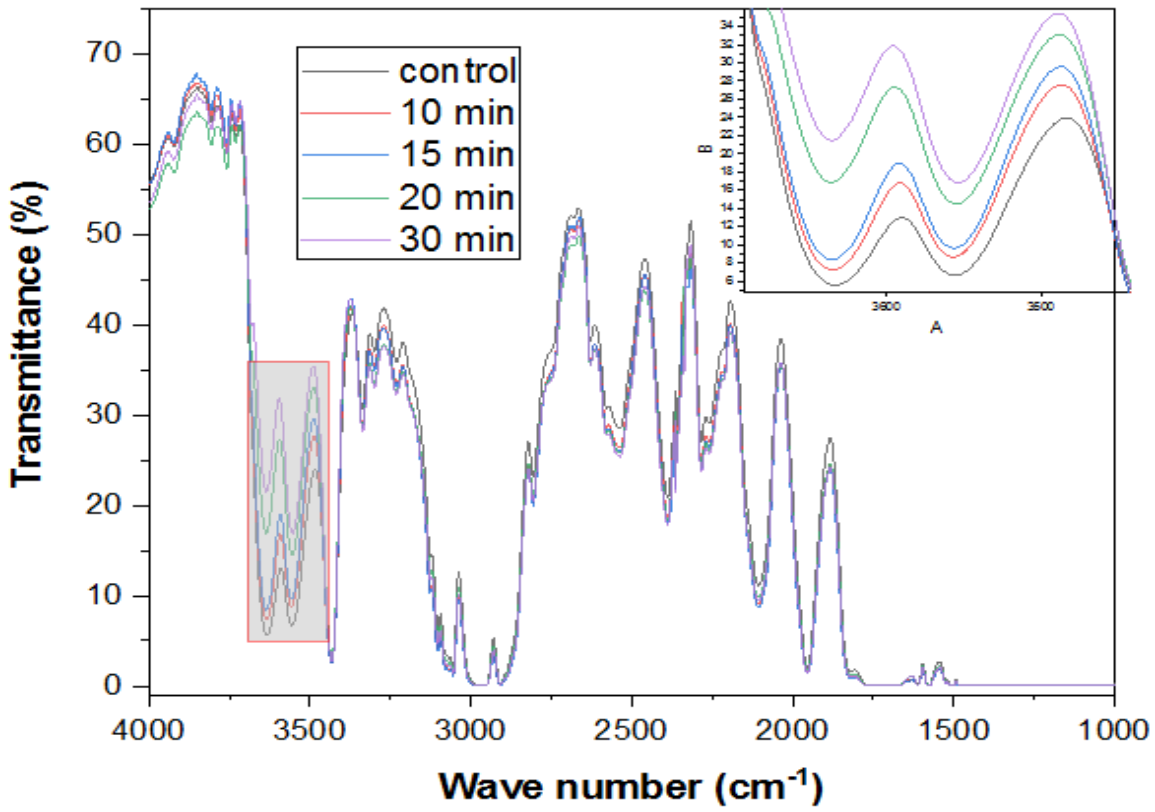

Figure 4: FT-IR Results of MW Irradiation Treated and Untreated PET Samples

Figure 4 displays the FT-IR spectra of microwave irradiated and the non-irradiated PET samples. As a result most of the peaks remain unchanged even after the microwave irradiation. This might be due to that the irradiation gets the chains which are align on the surface. But at around the wavenumber 3000 $cm^{-1}$to 3700cm^{-1}which is attributed for the C-O-H stretching shows slight change as the irradiation time increases. As the time of microwave irradiation increases, the absorbance of C-O-H decreases. This shows that the PET molecule undergoes decomposition at some extent. At 10min of microwave irradiation the absorption is higher which shows more bonds exist in the PET molecule. The absorbance is reducing as time increases, which mean more and more bonds are breaking. It can be said that as the microwave irradiation time increases the degradation of PET will also be increases which shows that not only the bonds at the surface but also the molecular bonds will also be affected by the MW irradiation.

4.3 TGA Results

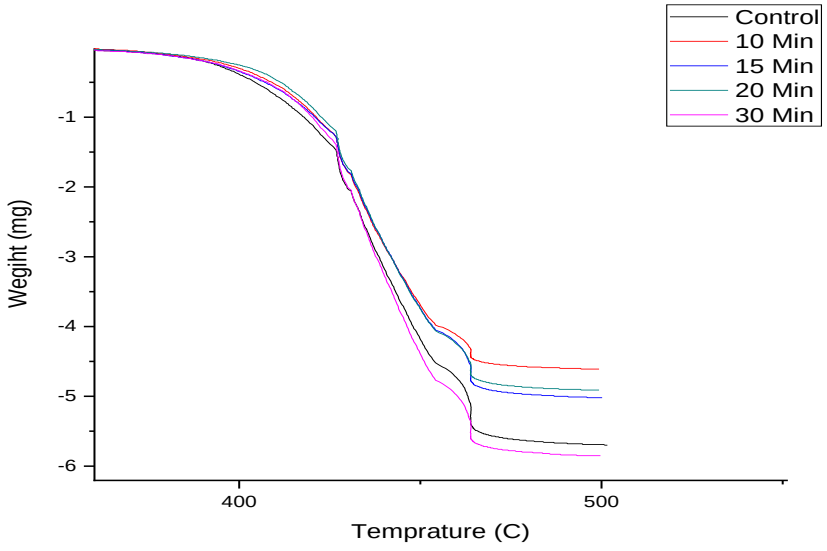

Figure 5: TGA result of MW Irradiation Treated and Untreated PET

Figure 5 shows the TGA results of MW irradiation treated and the untreated samples of PET which was carried out under the nitrogen environment with heating rate of 10^0c/min. The samples remain stable until it reaches around 375^0C. As seen from the figure the decomposition starts at around 380^OC to 400^OC which is almost the same decomposition starting temperature for all the samples. The weight loss in the temperature span referred to the boiling point of PET, where the actual boiling point of PET is 350^0C. The increase in the boiling temperature might be because of the rearrangement of the chains at the surface. The other potential reason can be cross-linkage of chains due to the longer irradiation time. The weight loss continues till it reaches at around 500^OC with weight loss of 85.5 %. The result a small change rather than that it can be said that there is no significant change on the thermal stability of PET due to the irradiation.

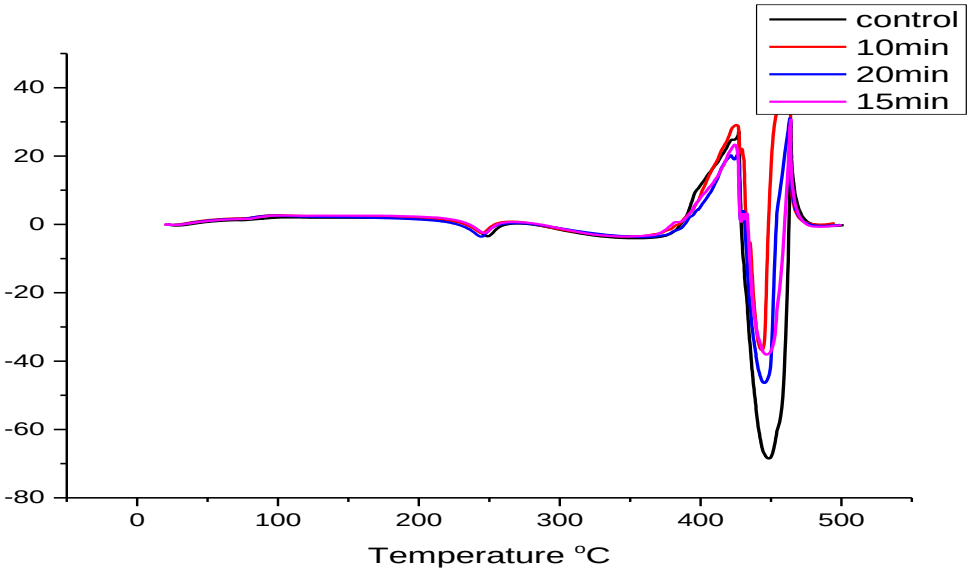

Figure 6: DTA results of MV Irradiation Treated and Untreated PET

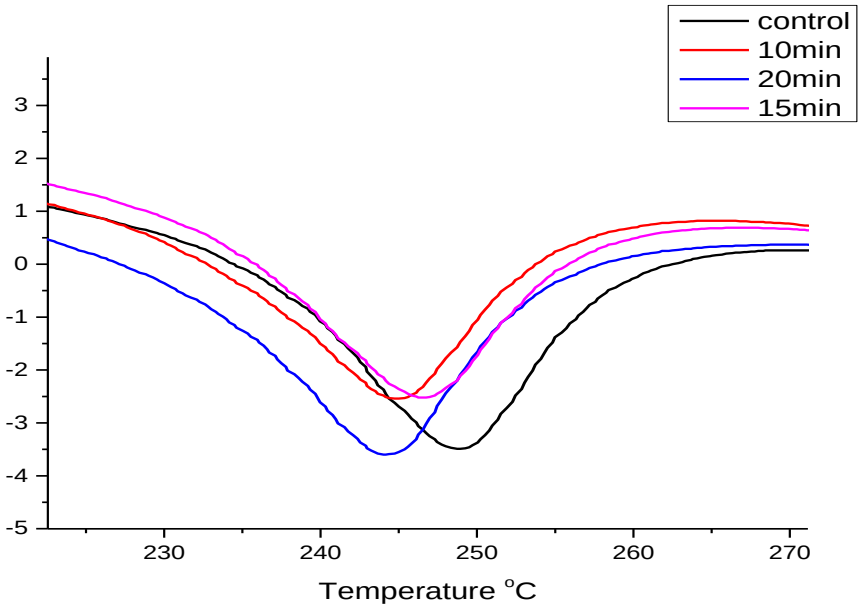

Figure 7: DTA results

Figure 6 shows the DTA curves of the MW irradiation treated and untreated PET samples. The thermal analysis of the samples shows peaks which are corresponding to the melting temperature of the samples. In this result there is a reduction on the melting temperature as the irradiation time increases but it cannot be said there is big difference on that. The comparative analysis of the thermal properties represents the melting temperature of PET lowering 242^0C which was actually 252.2^0C. At the irradiation time 20min the temperature is reduced to around 242^0C from the control which is around 252.2^0C, at irradiation time 15 min 246.97^0C, for 10 min 250^0C. These reductions could be because of the surface modification which was discussed at the FT-IR result above. The decomposition stage of the samples clearly defined between 400^0C and 480^0C.

4.4 Mechanical Test

4.4.1 Tensile strength

The tensile strength of all the microwave irradiation treated and untreated PET was conducted which shows the maximum load that PET film can support without fracture when being stretched. The other test is percentage of elongation at break, shows how much PET film can be stretched as a percentage of its original dimensions before it breaks.

Table 5: Tensile strength and elongation at break of MW irradiation treated and untreated PET

Sample	Time of Irradiation (min)	Tensile strength (Mpa)	Elongation at break (%)
1	Not irradiated	18.25	22.12
2	10	25.33	29.812
3	15	22.1	28.31
4	20	15.76	16.22
5	30	14.7	13.51

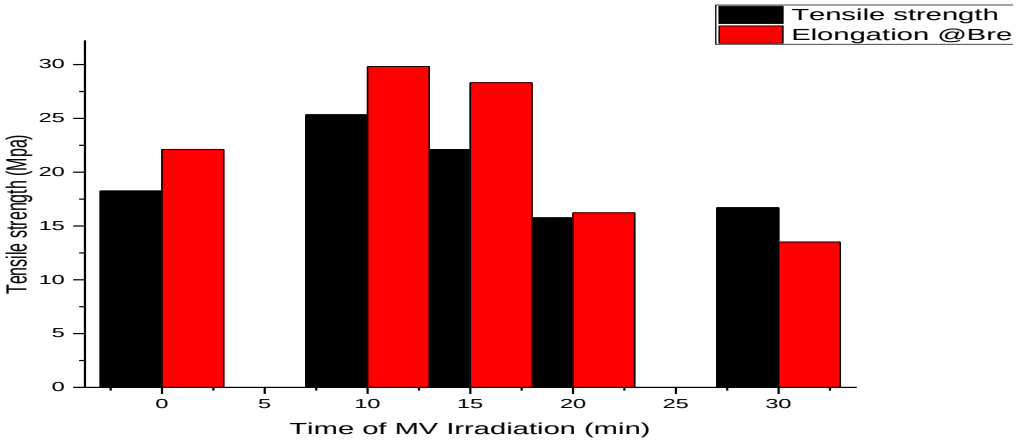

Figure 8: Result of Tensile Strength and Elongation @ Break

The mechanical properties of microwave irradiation treated and untreated PET samples were conducted as shown in figure 6. This result shows that at irradiation time of 10min and 15min the tensile strength increased this is may be due to the temperate microwave irradiation time which have been able to rearrange the PET structure and release of residual stress effectively in PET. In the case of polymers linearly chained structures have higher mechanical properties. This might be the reason at the time MW irradiation of 10 minutes the tensile strength got higher than the other samples this is due to and the molecules arranged themselves. However as the irradiation time increases the mechanical properties decreased this is due to the loss of some components such as ethylene glycol which gives flexibility for PET, which leads to degradation of PET molecules undergo at high irradiation time.

4.4.2 Hardness test

Rockwell hardness test:

Table 6: Rockwell Hardness Test Result of MW Irradiation Treated and Untreated PET

Sample	Time of Irradiation (minute)	Rockwell Hardness Test (HRB)
1	Not irradiated	25
2	10	28
3	15	34
4	20	46
5	30	57

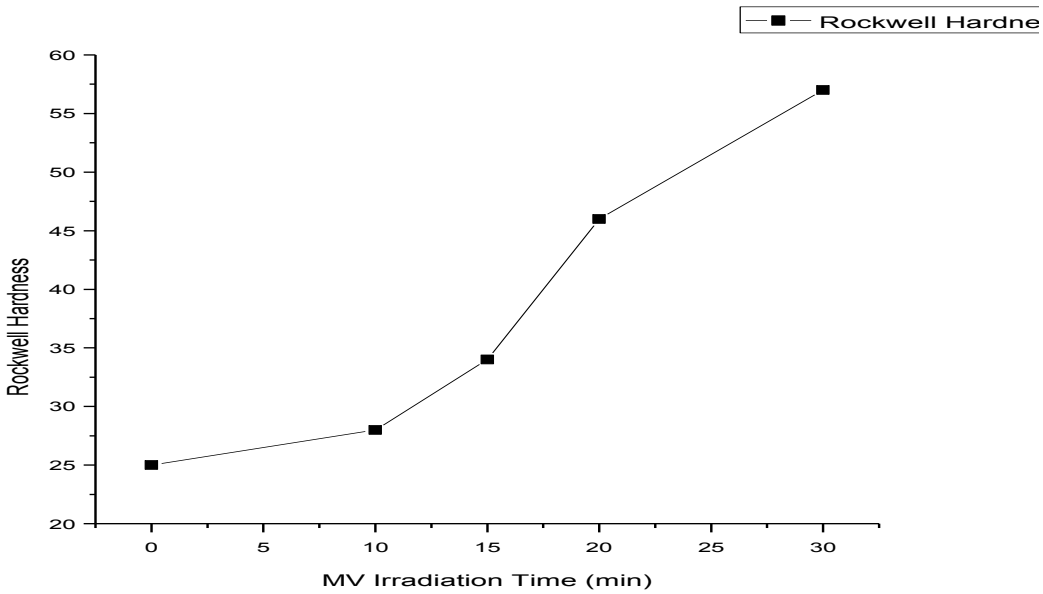

Figure 9: Rockwell Hardness Test Result MW Irradiation Treated and Untreated PET

Brinell Hardness Test:

Table 7: Brinell Hardness test result MW irradiation treated and untreated PET

Sample	Irradiation time (minute)	Brinell hardness test
1	Not irradiated	10.46
2	10	12.06
3	15	13.92
4	20	15.92
5	30	18.09

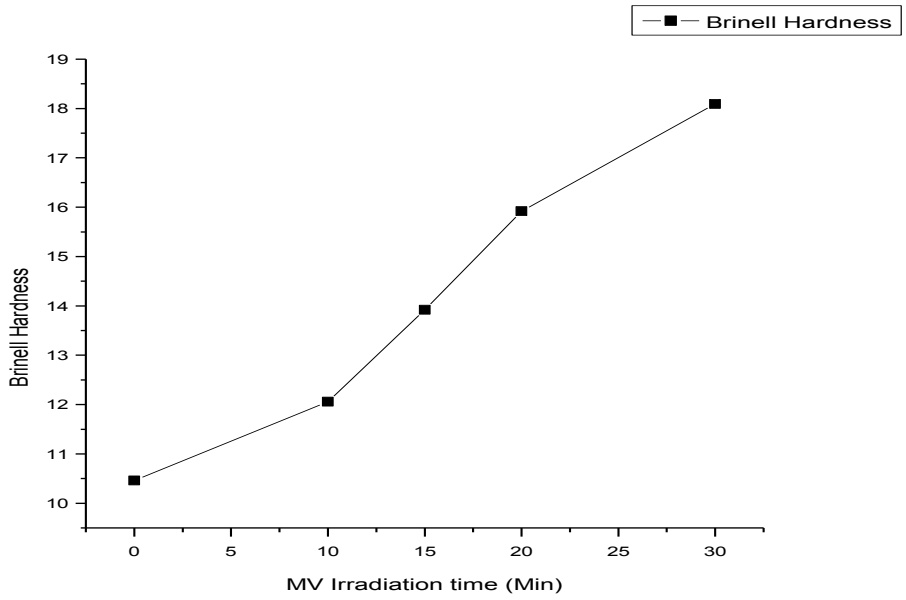

Figure 10: Brinell Hardness Test Result MW Irradiation Treated and Untreated PET

The hardness test result from both Rockwell and Brinell hardness testes show the results of microwave irradiated and non-irradiated samples of PET. The results show an increase on the measured hardness of PET samples as the microwave irradiation exposure time increases as showed in figures8 and 9.The reason for the increase in hardness as the irradiation time increases is due to the decomposition of different PET components and release of some volatile components from the PET molecule. This may cause some void in the chains of PET which leads to the increase in brittleness of the polymer. Since increasing in brittleness is one way of determining a polymer degradation it can be said that as the microwave irradiation time increases PET decomposition and degradation also increases.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Generally, in this study on the application of microwave irradiation on PET then investigation and characterization of the effect of MW irradiation on the polymer's structure and properties leads to conclusions like:

1. The effect of microwave irradiation on the structure, mechanical properties, and thermal properties has been investigated. The result obtained shows that microwave irradiation treatment for exposure time 10 min and 15 min have some changes on some mechanical properties and the surface.
2. Microwave irradiation can be used on surface modification of polyesters, especially for PET which is an effective low cost technique.
3. It can be used where properties like tensile are issues to be increased. At irradiation time 10 minutes has higher tensile strength which is due to the surface modification of the phenyl rings at the surface occurred by the microwave irradiation.
4. The hardness of PET will also be increase due to the microwave irradiation. The result shows a continuous increase on PET samples as the irradiation treatment time increases. This happened due to the loss of some volatile substances and decomposition.
5. Applications where better hardness of PET is needed it can be improved using microwave irradiation.

6. As a matter of facts MW irradiation can be used where more hardness of PET is needed. But it should be noted that the more irradiation treatment the more the polymer losses its properties and starts to degrade.
7. The thermal stability of the microwave irradiation treated PET has no obvious change. But the thermal property melting temperature gets reduced as the irradiation time increased; which is also happened due to the rearrangement of the rings at the surface.
8. As a general point the longer duration of irradiation time the higher the degradation and decomposition of the phenyl rings which provides strength and good mechanical properties.
9. Finally, it can be concluded that microwave irradiation treatment time of 10 minutes is the best to modify the surface of PET bottles. It also gives an inspection that microwave energy safer and easier way of surface modification of PET.

5.2. Recommendation

- ✓ To get better results further investigations are needed which can support and modify this thesis.
- ✓ Future researches can be done by blending PET with other polymers whose properties can be modified by microwave irradiation.
- ✓ Other properties such as physical, chemical which can be affected by the microwave irradiation can be further studied and analyzed.

Reference

1. *Choudhary, R., A. Kumar, and K. Murkute, Properties of waste polyethylene terephthalate (PET) modified asphalt mixes: dependence on PET size, PET content, and mixing process. Periodica Polytechnica Civil Engineering. **62**(3): p. 685-693.*
2. *Ji, L.N. Study on preparation process and properties of polyethylene terephthalate (PET). in Applied Mechanics and Materials: Trans Tech Publ.*
3. *KrÅ¾an, A., Microwave irradiation as an energy source in poly (ethylene terephthalate) solvolysis. Journal of applied polymer science, 1998. **69**(6): p. 1115-1118.*
4. *Fang, X., et al., Ringâ€opening polymerization of Ïµâ€caprolactam and Ïµâ€caprolactone via microwave irradiation. Journal of Polymer Science Part A: Polymer Chemistry, 2002. **40**(14): p. 2264-2275.*
5. *Xue, Z., Effect of Microwave irradiation on the physical properties and structures of cotton fabric. Journal of Engineered Fibers and Fabrics. **13**(2): p. 155892501801300201.*
6. *Siddiqui, M.N., et al., Hydrolytic depolymerization of PET in a microwave reactor. Macromolecular Materials and Engineering. **295**(6): p. 575-584.*
7. *Al-Sabagh, A.M., et al., Greener routes for recycling of polyethylene terephthalate. Egyptian Journal of Petroleum. **25**(1): p. 53-64.*
8. *Awasthi, K., et al., Optical, chemical and structural modification of oxygen irradiated PET. Radiation Measurements. **45**(7): p. 850-855.*
9. *Siddiqui, M.N., H.H. Redhwi, and D.S. Achilias, Recycling of poly (ethylene terephthalate) waste through methanolic pyrolysis in a microwave reactor. Journal of Analytical and Applied Pyrolysis. **98**: p. 214-220.*
10. *Bai, X. and Z. Mu. Research and Development of Microware Irradiation Technology in Polymer Synthesis. in IOP Conference Series: Materials Science and Engineering: IOP Publishing.*
11. *Kumar, V., et al., Study of chemical, optical and structural properties of 120 MeV Ni 11 ions beam irradiated poly (ethylene terephthalate) film. Int. J Appl Eng Res. **2**(2): p. 419-430.*
12. *Nguyen, D.T., et al., Effect of Microwave Irradiation on Polyvinyl Alcohol as a Carrier of Silver Nanoparticles in Short Exposure Time. International Journal of Polymer Science. **2019**.*
13. *Natalâ€™ia, V.A., et al., Effect of microwave irradiation on the structuring of polyvinyl alcohol. Mendeleev Communications, 2005. **4**(15): p. 170-172.*
14. *Cai, R., K.K.M. Nthoiwa, and C. Ge, Effect of microwave heating on the migration of additives from PS, PP and PET container into food simulants. Journal of Applied Packaging Research. **6**(1): p. 3.*
15. *Chowreddy, R.R., K. Nord-Varhaug, and F. Rapp, Recycled poly (ethylene terephthalate)/clay nanocomposites: Rheology, thermal and mechanical properties. Journal of Polymers and the Environment. **27**(1): p. 37-49.*
16. *Geyer, B.r., G.n. Lorenz, and A. Kandelbauer, Recycling of poly (ethylene terephthalate)-A review focusing on chemical methods. Express Polymer Letters. **10**(7).*
17. *Brems, A., et al., Thermogravimetric pyrolysis of waste polyethylene-terephthalate and polystyrene: A critical assessment of kinetics modelling. Resources, Conservation and Recycling. **55**(8): p. 772-781.*
18. *Ritchie, H. and M. Roser, Plastic pollution. Our World in Data.*
19. *Parab, Y.S., N.D. Pingale, and S.R. Shukla, Aminolytic depolymerization of poly (ethylene terephthalate) bottle waste by conventional and microwave irradiation heating. Journal of applied polymer science. **125**(2): p. 1103-1107.*

20. *KrÅ¾an, A., Poly (ethylene terephthalate) glycolysis under microwave irradiation. Polymers for Advanced Technologies, 1999.* ***10****(10): p. 603-606.*
21. *Achilias, D.S., Polymer degradation under microwave irradiation. Microwave-assisted Polymer Synthesis: p. 309-346.*
22. *Thomas, S., et al., Recycling of Polyethylene Terephthalate Bottles: William Andrew.*
23. *Ragaert, K., L. Delva, and K. Van Geem, Mechanical and chemical recycling of solid plastic waste. Waste Management.* ***69****: p. 24-58.*
24. *Mishra, D.D., Thermal Analysis of Polyethylene Terephthalate (PET)â€“Coke Composites Prepared by Mechanical Alloying Technique.*
25. *Tseng, K.-S. and Y.-L. Lo, Effect of sputtering parameters on optical and electrical properties of ITO films on PET substrates. Applied Surface Science.* ***285****: p. 157-166.*
26. *Kumar, V., et al., Carbon ion beam induced modifications of optical, structural and chemical properties in PADC and PET polymers. Radiation Physics and Chemistry.* ***81****(6): p. 652-658.*
27. *Engineers, N., Disposable Products Manufacturing Handbook, NIIR Project Consultancy Services.*
28. *Cobbs Jr, W.H. and R.L. Burton, Crystallization of polyethylene terephthalate. Journal of Polymer Science, 1953.* ***10****(3): p. 275-290.*
29. *Liu, Q., et al., Influence of pore size and pore shape on thermoâ€sensitive properties of poly [(ethylene terephthalate)â€graftâ€(Nâ€isopropylacrylamide)] track membranes. Polymer International, 2009.* ***58****(9): p. 1078-1083.*
30. *Choi, M.-C., Y. Kim, and C.-S. Ha, Polymers for flexible displays: From material selection to device applications. Progress in polymer science, 2008.* ***33****(6): p. 581-630.*
31. *Ryu, G.S., et al., Fabrication of organic thin film transistors on Polyethylene Terephthalate (PET) fabric substrates. Organic Electronics.* ***15****(7): p. 1672-1677.*
32. *Bower, D.I., An introduction to polymer physics. 2003, AAPT.*
33. *Kumar, V., et al., Study of chemical, optical and structural properties of 120 MeV Ni 11 ions beam irradiated poly (ethylene terephthalate) film.*
34. *Li, G., et al., The effect of microwave irradiation on the crystallization behavior of PET/PEN blends. Journal of Macromolecular Science, Part B: Physics, 2007.* ***46****(6): p. 1139-1149.*
35. *Achilias, D.S., et al., Aminolytic depolymerization of poly (ethylene terephthalate) waste in a microwave reactor. Polymer International.* ***60****(3): p. 500-506.*
36. *Li, J.Y., et al. Effect of Microwave treatment on the properties of PET Fiber. in Advanced Materials Research: Trans Tech Publ.*
37. *Qu, B., et al., Enhancement of mechanical properties of buckypapers/polyethylene composites by microwave irradiation. Composites Science and Technology.* ***164****: p. 313-318.*