Sudan University of Science and Technology

College of Graduate Studies

Management of Polymer Waste Using Gamma Irradiation Technique

معالجة النفايات البوليميرية باستخدام تقنية التشعيع باشعة قاما

A thesis submitted for the fulfillment of the PhD degree in medical physics

By:

Nuha Salih Mustafa Abdalmotalab

M. Sc. in Medical Radiation Physics

B. Sc. in Radiotherapy

Supervisor:

Dr. Mohammed Elfadil Gar Alnabi

Co-Supervisor:

Dr. Mohammed Ahmed Ali Omer

Chapter One

Introduction

The term polymer is refers to high molecular mass of complex molecules formed of small molecular units known as monomers, covalently linked together by polymerization process. Polymers can be found in nature in the form of polysaccharide and cellulose in plant cells, heavy rubber or poly isoprene in latex of certain trees, and proteins and nucleic acids in all living species. (Moad and Solomon, 1995)

Management of solid waste is an important problem, which is becoming progressively worse as a byproduct of continuing economic growth and development. Polymeric materials (plastics and rubbers) comprise a steadily increasing proportion of the municipal and industrial waste going into landfill. Development of technologies for reducing polymeric waste, which are acceptable from the environmental standpoint, and which are cost-effective, has proven to be a difficult challenge due to complexities inherent in the reuse of polymers. Establishing optimal processes for the reuse/recycling of polymeric materials thus remains a worldwide challenge as we enter the new century. Polymeric materials, and the fact that it is applicable to essentially all polymer types, irradiation holds promise for impacting the polymer waste problem. The three main possibilities for use of radiation in this application are enhancing the mechanical properties and performance of recovered materials or material blends, principally through crosslinking, or through surface modification of different phases being combined, treatment causing or enhancing the decomposition of polymers, particularly through chain scission, leading to recovery of either low molecular weight mixtures, or powders, for use as chemical feedstock’s or additives and production of advanced polymeric materials designed for environmental compatibility (Burillo et al, 2001).

Polymers are studied in the fields of biophysics and macromolecular science, and polymer science (which include polymer chemistry and polymer physics). Historically, products arising from the linkage of repeating units by covalent chemical bonds have been the primary focus of polymer science; emerging important areas of the science now focus on non-covalent links. Poly isoprene of latex rubber and the polystyrene of Styrofoam are examples of polymeric natural biological and synthetic polymers, respectively. In biological contexts, essentially all biological macromolecules i.e., proteins (polyamides), nucleic acids (polynucleotides), and polysaccharides are purely polymeric, or are composed in large part of polymeric components e.g., isoprenylated lipid modified glycoproteins, where small lipidic molecule and oligosaccharide modifications occur on the polyamide backbone of the protein.(Ten Feizi et al 2004) It has been reported that polymers can be degraded by acidic hydrolysis (Hasegawa et al., 1993; Bohn and Be Miller, 1995) or enzymatic treatment (Ilyina et al., 2000; Shimokawa et al., 1996). Although these methods are effective in decreasing the molecular weight, they do have certain disadvantages such as high cost, low yield, long processing time, and acidic wastes from the chemical or enzymatic treatment (Jeon and Kim, 2002; Marie et al., 1994).

Gamma irradiation is used for the final biological sterilization (Woods and Pikaev 1994; Hugo, 1995) of materials that can be subsequently used for manufacturing biomedical products. In addition, ionizing radiation leads to the degradation of polysaccharides such as starch, cellulose, and pectin by the cleavage of the glycosides bonds. (Chopping et al., 2003)

The basic advantages of degradation of polymers by radiation include the ability to promote changes reproducibly and quantitatively, without the introduction of chemical reagents and without the need for special equipment setup to control for temperature, environment, and additives Therefore, this technology is simpler and more environmentally friendly than conventional methods. (Charlesby, 1981)

1.1 Problems of the study:

Polymer waste has many problems include high toxicity of the polymers, de-fertilization of earth, hazards for domestic animals when eaten and classic way of managing polymer with burring was wrong because of accompanied toxic products and fumes, so ionizing radiation such as γ-radiation has significant capability to alter chemical structures of materials resulting to wider desirable properties such as polymers and metal nanoparticles.

1. 2. Significant of the Study:

γ-radiation has significant capability to alter chemical structures of materials resulting to wider desirable properties such as polymers and metal nanoparticles, so the researcher need to manage the polymer waste by using gamma irradiation technique. Polymeric materials, and the fact that it is applicable to essentially all polymer types, irradiation holds promise for impacting the polymer waste problem, the advantages of radiation processing of the materials relative to other methods are no metallic catalyst is required; (gives pure product), no oxidizing or reducing agent is required, the process occurred at a solid-state condition, fast method and inexpensive, environmental friendly and controllable acquisitions. This study will establish clear line of polymer waste management by using gamma irradiated.

1.3. General objectives of the study:

The aim of this work was to study the effect of gamma ray doses on the polymer and using gamma irradiation technique to manage polymer waste in Sudan during period from July 2012 to July 2015 to reduce the harmful health and environmental impacts of polymer waste.

1.4 Specific Objectives of the study:

- To reduce toxic hazard of managing polymer waste.
- To identify new technique of polymer managing.
- To decompose the polymer composites materials into beneficial molecules.
- To find the effect of gamma radiation doses on polymer waste.
- To correlate between the change of polymer waste property and the amount of gamma radiation dose.

1.5 Thesis outline:

The backbone of the following thesis will be formed of five chapters. Chapter one will deal with the general introduction about the research, scope of the study, problem statement and the objectives of the study. Chapter Two will deal with literatures review cover the theoretical background and previous studies. Chapter Three will deal with the methodology of the study, including materials, samples preparation, equipment and measurement. Chapter four will cover the results. And chapter Five will cover discussion, conclusion, recommendations, and references.

Chapter Two

Theoretical Background

2.1. Background of Polymers:

A polymer is a large molecule, or macromolecule, composed of many repeated subunits. Because of their broad range of properties, (Painter et al 1997) both synthetic and natural polymers play an essential and ubiquitous role in everyday life. Polymers range from familiar synthetic plastics such as polystyrene to natural biopolymers such as DNA and proteins that are fundamental to biological structure and function. Polymers, both natural and synthetic, are created via polymerization of many small molecules, known as monomers. Their consequently large molecular mass relative to small molecule compounds produces unique physical properties, including toughness, viscoelasticity, and a tendency to form glasses and semi crystalline structures rather than crystals.(Mc Crum et al 1997)

2.1.1 History of polymers:

The term was coined in 1833 by Jöns Jacob Berzelius, though with a definition distinct from the modern IUPAC definition (Jensen et al, 2008). The modern concept of polymers as covalently bonded macromolecular structures was proposed in 1920 by Hermann Staudinger, who spent the next decade finding experimental evidence for this hypothesis. (Allcock et al, 2003)

In the table 2.1, some major dates which marked the important stages in the history of polymers are shown.

Table 2.1 Shown some major dates which marked the important stages in the history of polymers

1838	A. Payen identifies a compound of formula (C6H10O5)N that is extracted from wood which he names cellulose.
1844	CH. Goodyear carries out the vulcanization of natural rubber by using sulfur.
1846	C. Schonbein prepare the first “artificial” polymer, nitrocellulose, by esterification of cellulose by means of a nitrosulphuric acid mixture.
1866	Discovery of polystyrene by M. Berthelot.
1883	“Artificial silk” is obtained per H. de CHARDONNET, by spinning a concentrated nitrocellulose solution
1907	First synthetic rubbers by polymerization of conjugated polymerization, A. Hoffmann
1910	Industrialization of the process of production of first synthetic polymer, by L. Baekeland; the phenol-formol resins are produced under the name of “bakelite”.
1919	H. Staudinger proposes the macromolecular theory, thus opening the way for the science and the technology of polymers.
1925	Confirmation of the macromolecular theory by Th. Svedberg; He succeeds in measuring the molar mass of a polymer by ultracentrifugation.
1928	K. Meyer and H. Mark establish the link between molecular structure and crystallographic structure of polymers.
1933	Radical polymerization of ethylene under high pressure, by E. Fawcett and R. Gibson (I.C.I.).
1938	First synthetic polyamides (“nylons”) produced by W. Carothers (Of DuPont de Nemours).
1942	P. Flory and M. Huggins propose the first theory on the behavior of polymers in solution.
1943	The family of polyurethanes is discovered by O. Bayer.
1947	T. Alfrey and C. Price propose the theory of chain.
1953	F. Crick and J. Watson (Nobel Prize of medicine 1962) propose the double helix structure of the DNA.
1953	K. Ziegler polymerizes ethylene under low pressure.
1954	G. Natta discovers isotactic polypropene.
1955	Establishment of a relation between the relaxation time of polymer chains and the

	variation at the glass transition temperature by M. Williams, R. Landel and J. Ferry.
1956	Discovery of “living” polymerization by M. Szwarc.
1957	First polymeric monocrystals obtained by A. Keller.
1959	Development of the size exclusion chromatography by J. Moore.
1960	Discovery of thermoplastic elastomers starting from block copolymers.
1970-1980	Development of the laws of scale and concept of reptation of polymeric chains in the molten state, by P-G. de Gennes.
1974	Development of aromatic polyamides by the firm DuPont de Nemours.
1980	W. Kaminsky and H. Sinn use the combination aluminoxanes/metallocenes for the polymerization of olefins.
1982	T. Otsu introduces the concept of controlled radical polymerization.
1986	The first dendrimers are synthesized by D. Tomalia.
1994:	The controlled radical polymerization by atom transfer, is developed by Mr. Sawamoto and K Matyjaszewski
2000	H. Shirakawa, A.J. Heeger and A.G. McDiarmid obtain the Nobel Prize of Chemistry for their work on intrinsic conducting polymers.
2005	Nobel Prize of Chemistry awarded to Y. Chauvin, R. Grubbs and R. Schrock, for their work on the reaction of metathesis and its application to polymers.

2.1.2 Polymer Composite:

Polymers are large molecules that are buildup of a number of repeating units called monomers. The name of the polymers is often based on their repeating units as example from the monomer styrene which is consists of 7 backbones of Carbone atoms, 3 hydrogen atoms as in figure (2.1).

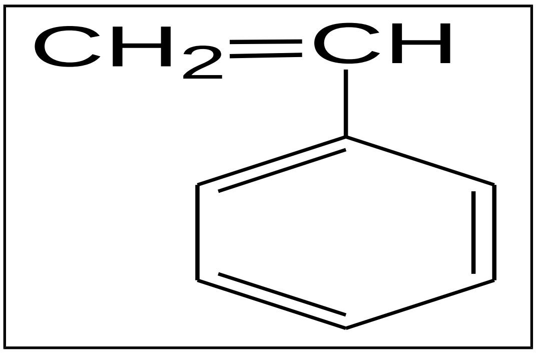


Figure 2.1 shows the chemical structure of monomer styrene (M S) (Young, R. J. (1987), (Clayden, J. et al 2000)

Polystyrene are made up from the repeating unit each one consists of 4 monomer styrene unit as in figure (2.2).

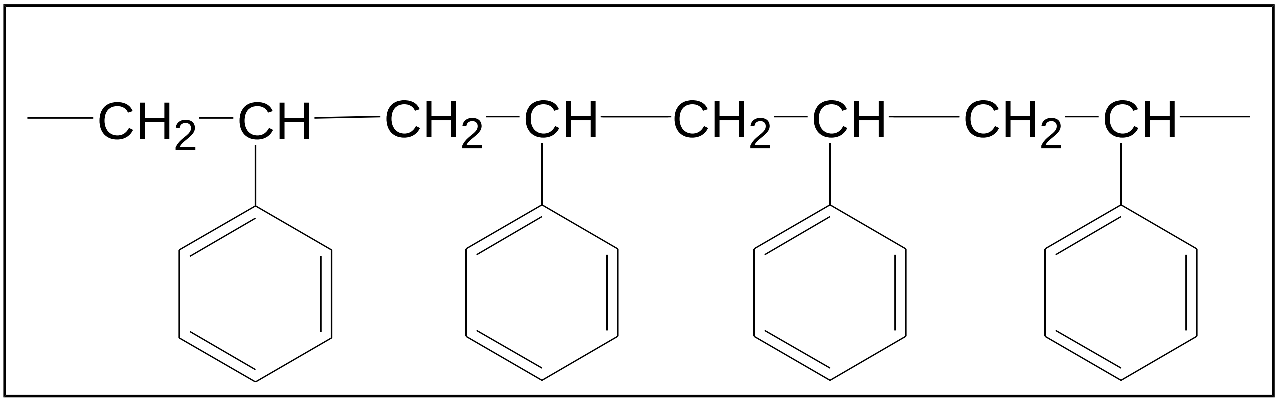


Figure 2.2 Shows the chemical structure of polystyrene (PS) (Young, R. J. (1987), Clayden, J. et al 2000)

The structural formula of polystyrene is usually written as shows in figure 2.3

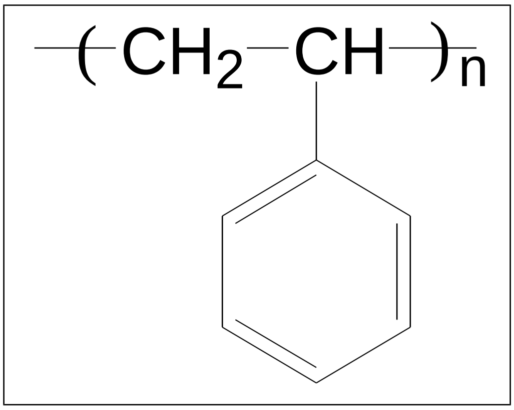


Figure 2.3 shows the structural formula of polystyrene where n is the number of repeating units in the polymer (Clayden, J. et al 2000)

The above polymers and many others are usually made by synthesis from their monomers. However, one can also make polymers from natural sources. These polymers are called biopolymers. Some examples of biopolymers are cellulose derivatives, gelatin, pectin, chitosan and alginate. These polymers often have a complex molecular structure as in figure 2.4

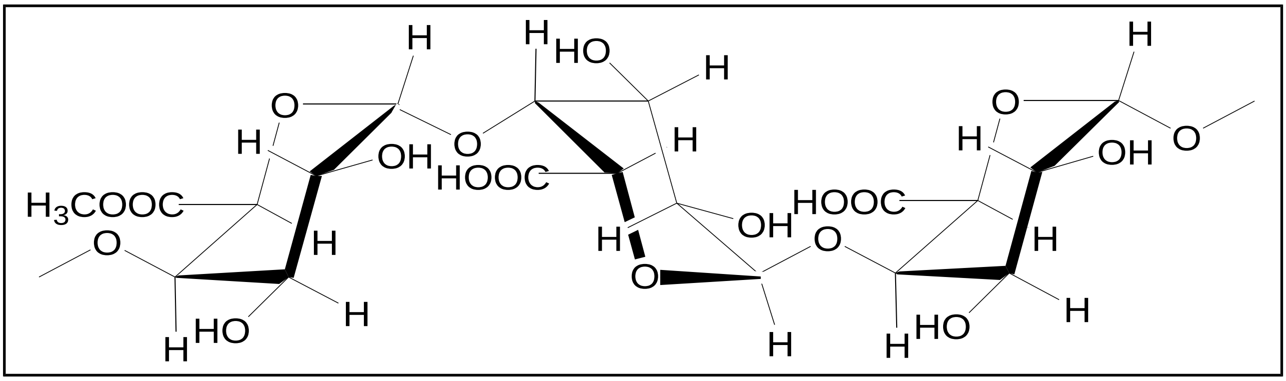


Figure2.4 shows chemical structure of biopolymers (Clayden, J. et al 2000)

Many polymeric materials having chain-like structures similar to polyethylene are known. Polymers formed by a straightforward linking together of monomer units, with no loss or gain of material, are called addition polymers or chain-growth polymers. A listing of some important addition polymers and their monomer precursors is presented in table 2.2.

Table 2.2 show some common addition polymers

Name(s)	Formula	Monomer	Properties	Uses
Polyethylene low density (LDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	soft, waxy solid	film wrap, plastic bags
Polyethylene high density (HDPE)	$–(CH_2\text{-}CH_2)_n–$	ethylene $CH_2=CH_2$	rigid, translucent solid	electrical insulation bottles, toys
Polypropylene (PP) different grades	$–[CH_2\text{-}CH(CH_3)]_n–$	propylene $CH_2=CHCH_3$	atactic: soft, elastic solid isotactic: hard, strong solid	similar to LDPE carpet, upholstery
Poly(vinyl chloride) (PVC)	$–(CH_2\text{-}CHCl)_n–$	vinyl chloride $CH_2=CHCl$	strong rigid solid	pipes, siding, flooring
Poly(vinylidene chloride) (Saran A)	$–(CH_2\text{-}CCl_2)_n–$	vinylidene chloride $CH_2=CCl_2$	dense, high-melting solid	seat covers, films
Polystyrene (PS)	$–[CH_2\text{-}CH(C_6H_5)]_n–$	styrene $CH_2=CHC_6H_5$	hard, rigid, clear solid soluble in organic solvents	toys, cabinets packaging (foamed)
Polyacrylonitrile (PAN, Orlon, Acrilan)	$–(CH_2\text{-}CHCN)_n–$	acrylonitrile $CH_2=CHCN$	high-melting solid soluble in organic solvents	rugs, blankets clothing
Polytetrafluoroethylene (PTFE, Teflon)	$–(CF_2\text{-}CF_2)_n–$	etrafluoroethylene $CF_2=CF_2$	resistant, smooth solid	non-stick surfaces electrical insulation
Poly(methyl methacrylate) (PMMA, Lucite, Plexiglas)	$–[CH_2\text{-}C(CH_3)CO_2CH_3]_n–$	methyl methacrylate $CH_2=C(CH_3)CO_2CH_3$	hard, transparent solid	lighting covers, signs skylights
Poly(vinyl acetate) (PVAc)	$–(CH_2\text{-}CHOCOCH_3)_n–$	vinyl acetate $CH_2=CHOCOCH_3$	soft, sticky solid	latex paints, adhesives
cis-Polyisoprene natural rubber	$–[CH_2\text{-}CH=C(CH_3)\text{-}CH_2]_n–$	isoprene $CH_2=CH\text{-}C(CH_3)=CH_2$	soft, sticky solid	requires vulcanization for practical use
Polychloroprene (cis + trans) (Neoprene)	$–[CH_2\text{-}CH=CCl\text{-}CH_2]_n–$	chloroprene $CH_2=CH\text{-}CCl=CH_2$	tough, rubbery solid	synthetic rubber oil resistant

2.1.3 Molecular architecture:

The shape of the polymer molecule is important for many of its properties as show in figure 2.5.

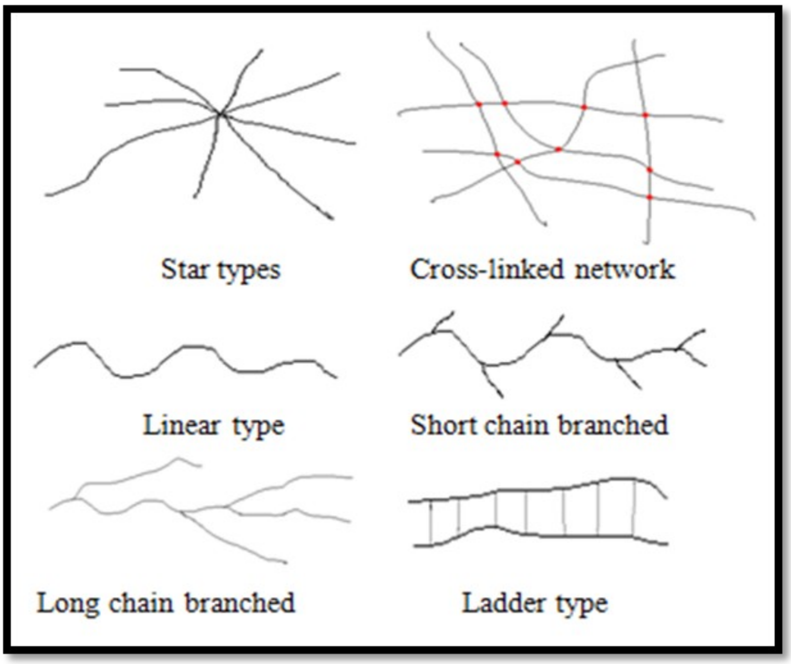


Figure 2.5 show the polymer architecture (a) linear b. Short-chain branched (c) long chin branch (d) ladder (e) star branch (f) cross linked network (Clayden, J. et al 2000)

2.1.4 Polymers Classification:

Polymers are classified in different types on different basis.

2.1.4.1 Classification based on source is classified in three types:

2.1.4.1.1 Natural polymers:

Polymers either obtained from plants or animal are called natural polymers. They are called plant and animal polymers. Ex. Cellulose, Jute, Lihen, Silk, Wool, Leather, RNA, DNA, Natural rubber.

2.1.4.1.2 Semisynthetic polymers:

The polymers obtained by simple chemical treatment of natural fibers to improve their physical properties like lastrus nature, tensile strength are called semisynthetic fibers. e g. Acetate rayon, cupra ammonium silk, viscous rayon.

2.1.4.1. 3 Synthetic fibers:

The fibers obtained by polymerization of simple chemical molecules in laboratory are synthetic fibers. e g. Nylon, terylene, polyethene, polystyrene, synthetic rubber, nylon, pvc, backlite, Teflon, Orion etc.

2.1.4.2 Classification based on the structure of polymers:

Polymer is classified by structure in three types

2.1.4.2.1 Linear polymers:

In these polymers monomers are linked with each other and form a long straight chain. These chains have no any side chains. e g. Polyethene, PVC, Nylons, polyesters etc. Their molecules are closely packed and have high density, tensile strength, and melting point.

2.1.4.2.2 Branched polymers:

They have a straight long chain with different side chains. Their molecules are irregularly packed hence they have low density, tensile strength and melting point, e g. polypropylene (side chain —CH3), amylopectin and glycogen.

2.1.4.2.3 Network or cross linked polymers:

In these monomeric units are linked together to constitute a three dimensional network. The links involved are called cross links. They are hard, rigid .and brittle due to their network structure, e g. Bakelite, Maia mine, formaldehyde resins, vulcanized rubber etc.

2.1.4.3 Classification based on polymerization process:

On this basis they are classified in two types.

2.1.4.3.1 Addition polymers:

The polymers formed by the addition of monomers repeatedly without removal of by products are called addition polymers. These polymers contain all the atoms of monomers hence they are integral multiple of monomer unit, e g. Orion, Teflon, polyethene, polypropylene, PVC. The monomeric units are generally alkenes and its derivatives.

2.1.4.3.2 Condensation polymers:

They are formed by the combination of two monomers by removal of small molecules like water, alcohol or NH3. They have ester and amide linkage in their molecules. Their molecular mass is not the integral multiple of monomer units, e g. Polyamides (Nylons), polyesters, polyurethanes.

2.1.4.4 Classification based on molecular forces:

Mechanical properties of polymers like tensile strength, toughness, elasticity depends upon intermolecular forces like van-der Waals forces and hydrogen bonding. On the basis of these forces they are classified as.

2.1.4.4.1 Elastomers:

These are the polymers in which polymer chains are held up by weakest attractive forces. They contains randomly coiled molecular chains having few cross links. As the stain is applied polymer get stretched and as the force is released polymer regain its original position. These polymers are elastic and called elastomers, e.g. Neoprene, and vulcanized rubber.

2.1.4.4.2 Fibers:

They have high intermolecular attractive force like H-bonding. They have high tensile strength and used in textile industries, e g. Nylon-6, Nylon-66, and Terylene.

2.1.4.4.3 Thermoplastic polymers:

These are the polymers having intermolecular forces between elastomers and fibers. They are easily molded in desired shapes by heating and subsequent cooling at room temperature. They may be linear or branched chain polymers. They are soft in hot and hard on coding, e g. Polythene, polystyrene, PVC.

2.1.4.4.4 Thermosetting polymers:

This polymer is hard and infusible on heating. These are not soft on heating under pressure and they are not remolded. These are cross linked polymers and are not reused, e g. Bakelite.

2.1.4.5 Classification Based on the Homogeneity of Polymers:

Pectin Homopolymers and copolymers; Homopolymers consists of only one type of repeating unit, e.g. ○○○○○○○○○○○○○○○○○○ poly(A) Copolymers are polymers consisting of more than one type of repeating unit. Types of co polymers as show in figure 2.6.

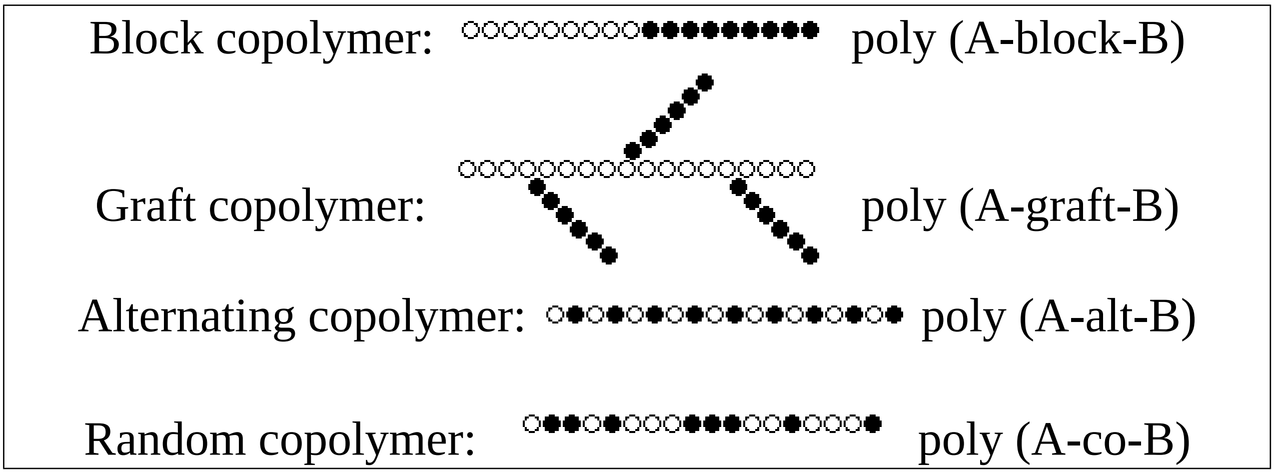


Figure 2.6 Shows the Type of copolymers

2.1.4.6 Classification based on Growth polymerization:

On this basis the polymers are classified in two types

2.1.4.6.1 Chain growth polymerization:

This polymerization process involves the addition of molecules at the reactive end of the growing chain across the double bond. Many alkenes and its derivatives undergo growth chain polymerization, e g. polyethene

2.1.4.6.2 Step growth polymerization:

This type of polymerization involves the step wise intermolecular condensation through a series of independent reaction. This process involves loss of simple molecules like NH_3, H_20 and HC1. It is possible when the monomer have more than one functional group. It proceeds through the formation of dimer, trimmer, tetramer, etc. e g. Dacron. U

2.1.5 Polymer properties:

Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents. (S.A. Baeurle, 2009)

2.1.5.1 Polymerization:

Radiation polymerization is a process in which the free radicals interact with the unsaturated molecules of a low molecular unit known as monomer to form high molecular mass polymer or even with different monomers to produce crosslink polymer as show in figure 2.7

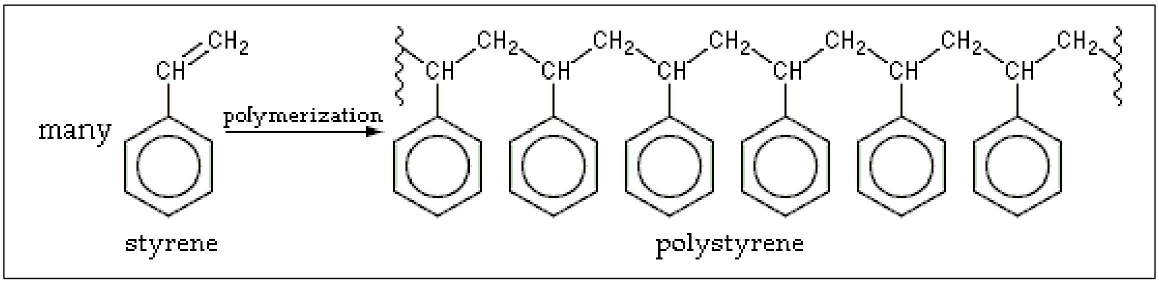


Fig 2.7 show an example of alkene polymerization, in which each styrene monomer's double bond reforms as a single bond plus a bond to another styrene monomer. The product is polystyrene (Jenkins, A. D et al 1996)

The formed polymer can be in different forms called homo polymer and copolymer depending on the monomer compositions link together. Radiation-induced polymerization process can be achieved in different media whether it is liquid or solid unlike the chemical polymerization which can only accomplished in aqueous media. It is also temperature independent. Radiation polymerization often continues even after removing away from the radiation source. Such condition is known as post-polymerization ((Jenkins, A. D et al, 1996).

Since radiation initiation is temperature independent, polymer can be polymerized in the frozen state around aqueous crystals. The mechanism of the radiation induced polymerization is concerning the kinetics of diffusion-controlled reactions and consists of several stages: addition of hydroxyl radicals and hydrogen atoms to carbon-carbon double bond of monomer with subsequent formation of monomer radicals; addition of hydrated electrons to carbonyl groups and formation of radical anion of a very high rate constant and the decay of radicals with parallel addition of monomer to the growing chain.

2.1.5.2 Chemical properties:

The attractive forces between polymer chains play a large part in determining polymer's properties. Because polymer chains are so long, these inter chain forces are amplified far beyond the attractions between conventional molecules. Different side groups on the polymer can lend the polymer to [ionic bonding] or [hydrogen bonding] between its own chains. These stronger forces typically result in higher tensile strength and higher crystalline melting points.

The intermolecular forces in polymers can be affected by [dipole]s in the monomer units. Polymers containing [amide] or [carbonyl] groups can form [hydrogen bond]s between adjacent chains; the partially positively charged hydrogen atoms in N-H groups of one chain are strongly attracted to the partially negatively charged oxygen atoms in C=O groups on another. These strong hydrogen bonds, for example, result in the high tensile strength and melting point of polymers containing [Carbamate urethane] or urea linkages. [Polyester]s have[intermolecular force. Dipole-dipole interactions |dipole-dipole bonding] between the oxygen atoms in C=O groups and the hydrogen atoms in H-C groups. Dipole bonding is not as strong as hydrogen bonding, so a polyester's melting point and strength are lower than [Kevlar]'s ([Twaron]), but polyesters have greater flexibility.

Ethene, however, has no permanent dipole. The attractive forces between polyethylene chains arise from weak [van der Waals force]s. Molecules can be thought of as being surrounded by a cloud of negative electrons. As two polymer chains approach, their electron clouds repel one another. This has the effect of lowering the electron density on one side of a polymer chain, creating a slight positive dipole on this side. This charge is enough to attract the second polymer chain. Van der Waals forces are quite weak, however, so polyethylene can have a lower melting temperature compared to other polymers. (F. J. Duarte 2003)

2.1.5.3 Optical properties:

Polymers such as PMMA and HEMA: MMA are used as matrices in the gain medium of solid-state dye lasers that are also known as polymer lasers. These polymers have a high surface quality and are also highly transparent so that the laser properties are dominated by the laser dye used to dope the polymer matrix. These type of lasers, that also belong to the class of organic lasers, are known to yield very narrow line widths which is useful for spectroscopy and analytical applications (F. J, 1999). An important optical parameter in the polymer used in laser applications is the change in refractive index with temperature also known as dn/dT. (F. J. Duarte 2003)

2.1.5.4 Thermal properties:

A true workhorse for polymer characterization is thermal analysis, particularly Differential scanning calorimetry. Changes in the compositional and structural parameters of the material usually affect its melting transitions or glass transitions and these in turn can be linked to many performance parameters. For semi crystalline polymers it is an important method to measure crystallinity. Thermo gravimetric analysis can also give an indication of polymer thermal stability and the effects of additives such as flame retardants. Other thermal analysis techniques are typically combinations of the basic techniques and include differential thermal analysis, thermo mechanical analysis, dynamic mechanical thermal analysis, and dielectric thermal analysis. Dynamic mechanical spectroscopy and Dielectric spectroscopy are essentially extensions of thermal analysis that can reveal more subtle transitions with temperature as they affect the complex modulus or the dielectric function of the material, (Campbell, D. et al 1989).

2.1.5.5 Mechanical Properties:

The characterization of mechanical properties in polymers typically refers to a measure of the strength of a polymer. The tensile strength and Young's modulus of elasticity are of particular interest for describing the stress-strain properties of polymer. Dynamic mechanical analysis is the most common technique used to characterize this viscoelastic behavior. Other techniques include viscometry, rheometry, and pendulum hardness, the description of stress-strain behavior is similar to that of metals. (Campbell, D. et al 1989)

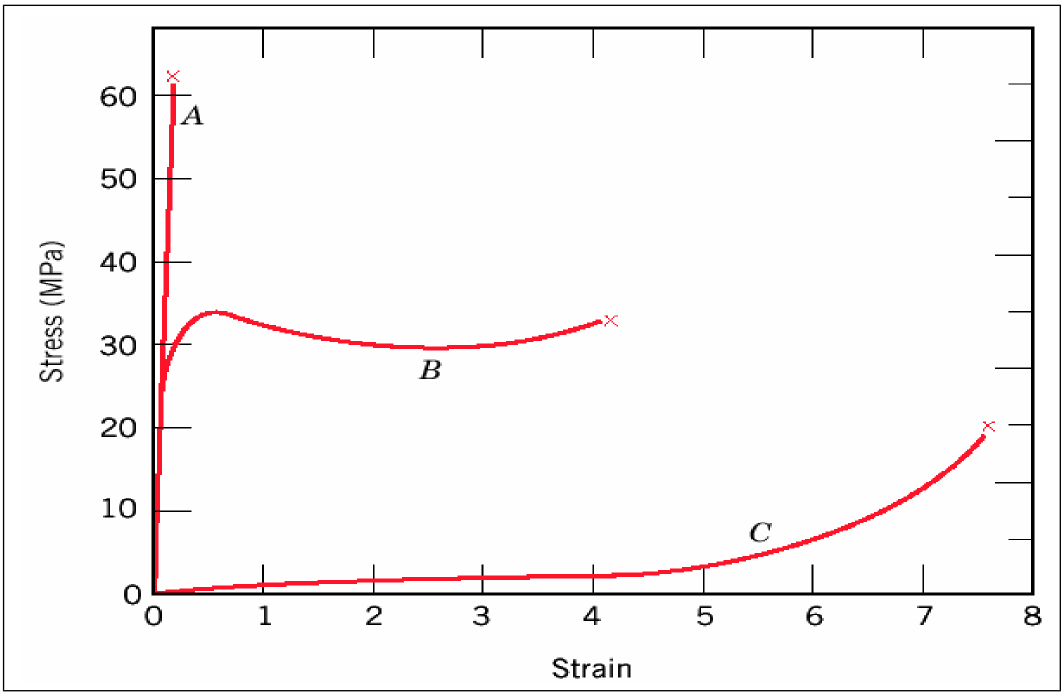


Figure 2.8 shows Polymers can be brittle (A), plastic (B), or highly elastic (C). Deformation shown by curve C is totally elastic (rubber-like elasticity, large recoverable strain at low stress levels).

2.1.6 Applications of polymers in Medical field:

A variety of polymers have been used for medical care including preventive medicine, clinical inspections, and surgical treatments of diseases. Among the polymers employed for such medical purposes, a specified group of polymers are called polymeric biomaterials when they are used in direct contact with living cells of our body. Typical applications of biomaterials in medicine are for disposable products (e. g. syringe, blood bag, and catheter), materials supporting surgical operation (e. g. suture, adhesive, and sealant), prostheses for tissue replacements (e. g. intraocular lens, dental implant, and breast implant), and artificial organs for temporary or permanent assist (e. g. artificial kidney, artificial heart, and vascular graft). These biomaterials are quite different from other non-medical. (Maitz, 2015) The main polymer type used in medicine:

2.1.6.1 polyolefins

The polyolefins polyethylene (PE) and polypropylene (PP) are very inert and hydrophobic materials which do not degrade in vivo. Its main applications are sliding surfaces of artificial joints as show in Figure 2.9. (Breitbart et al, 2007)

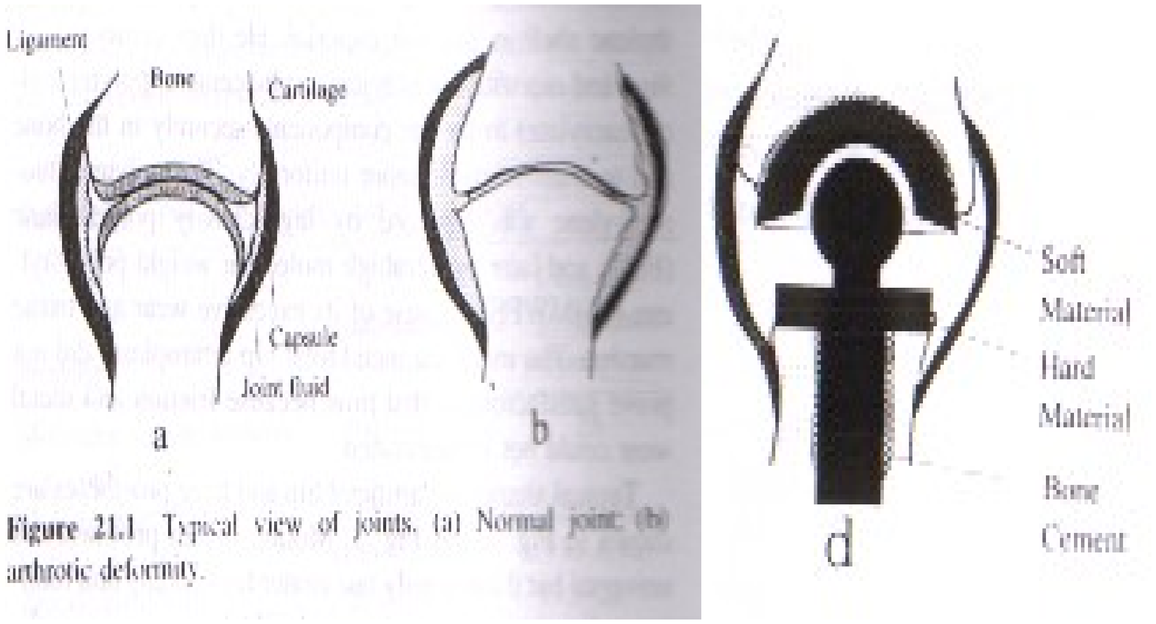


Figure: 2.9 show (a) Normal joint Figure (b) replacement of the joint is required (d) artificial joint has a sliding interface using a combination of a hard material against a soft material

The artificial joint has a sliding interface using a combination of hard material Metallic femoral head, Soft material Polytetrafluoroethylene (PTFE) shell Cement material: cold-curing acrylic cement poly methyl methacrylate) to fix the components and to transfer the stress more uniformly as show in Figure 2.10

Figure: 2.10 show artificial joint has a sliding interface

2.1.6.2 Polytetrafluoroethylene (PTFE):

PTFE(Teflons) has an ethylene backbone with four covalently bound fluorine molecules. It is a highly hydro phobic non-degradable material. It’s mainly applied as vascular graft as show in Figure 2.11. (Breitbart et al, 2007)

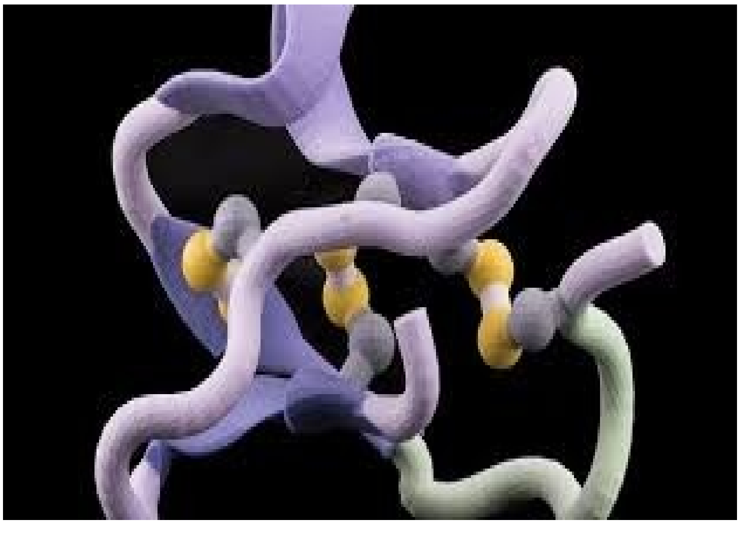


Figure: 2.11 show the artificial vascular veins

2.1.6..3 Polyvinylchloride (PVC):

PVC has an ethylene backbonewith one covalently bound chlorine. Its fabrication and application requires stabilizers and plasticizers, which are the main reason for medical concerns against this polymer. Plasticizers, most frequently phthalates, turn the rigid PVC to a soft polymer, which is used for extra corporeal tubing or blood storage bags. (Folarin et al, 2011)

2.1.6.4 Silicone:

Silicones consist of an –Si–O– backbone with different chain lengths and cross links, which determine mechanical properties from liquid oil via a gel structure to rubber elastomer. The biological response differs for various applications. There is high tolerance in ophthalmologic applications (.Mackenzie, 2007), fibrous capsule formation at breast implants. (Wong et al, 2006)

2.1.6.5 Methacrylates:

Methyl methacrylates polymerize to very rigid polymers (PMMA) by radical polymerization and therefore find application in dentistry and in orthopedics. They are used for application with polymerization in situ. Due to the optical properties (Plexiglasss) and inertness in the eye, they are also used as intraocular lenses as shown in figure 2.12.

Figure: 2.12 show the artificial lenses

2.1.6..6 Polyesters:e

Biostable and biodegradable polyesters are used in biomedicine. Biostable polyesters containing aromatic groups are poly carbonates (PC), poly (ethylene terephthalate) (PET, dacron). They are used inform of membranes, filaments and meshes. (Hofmann, 1996)

2.1.6.7 Polyethers:

Ether bondings are bio stable. Poly ether ether ketone (PEEK) as hard material for orthopedic applications and polyether sulfone(PES) for dialysis membranes are main representatives of this polymer class in biomedicine(Krieter et al, 2011)

2.1.6.8 Polyamides:

Naturally, all proteins consist of units liked by amide bonds and highly repetitive proteins like collagen or silk fibroin can be classified here. The most important synthetic polyamide with clinical application is nylon. For its high tensile strength it is used for suture materials. (Pruitt et al, 2009)

2.1.6..9 Polyurethanes:

Poly urethanes are synthesized with multiple chemistries and properties. Polyester-polyether-, and polycarbonate- based polyurethanes with aromatic or aliphatic components are in medical use, where aromatic formulations have the better bio stability. Poly ether based poly urethanes, especially aliphatic formulations show rapid softening in the body, making them more comfortable for the patient. (Neil et al, 2010) as shown in figure 2.13.

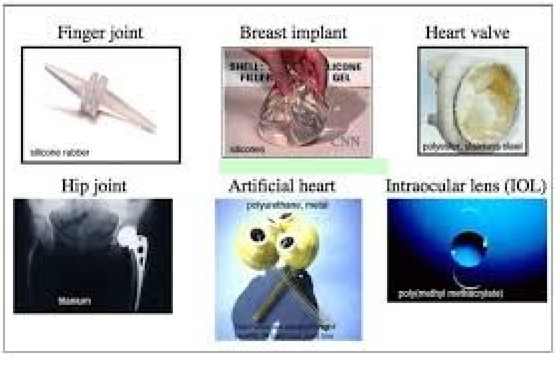


Figure: 2.13 show the various applications of polymer in medical use

1.2 Polymer waste management (PWM):

Waste management is all those activities and action required to manage waste from its inception to its final disposal. This includes amongst other things, collection, transport, treatment and disposal of waste together with monitoring and regulation. It also encompasses the legal and regulatory framework that relates to waste management encompassing guidance on recycling etc. Effective and efficient management of polymer waste including application of 3R Reduce, Reuse and Recycle is an essential element for promoting sustainable patterns of consumption and production. (Waste Management, 2013)

1.2.1 Landfill:

Is a site for the disposal of waste materials by burial and is the oldest form of waste treatment. Historically, landfills have been the most common method of organized waste disposal and remain so in many places around the world. Some landfills are also used for waste management purposes, such as the temporary storage, consolidation and transfer, or processing of waste material (sorting, treatment, or recycling) (Merriam-Webster, 18 May 2014).

Typically operation, in non-hazardous waste landfills, in order to meet predefined specifications, techniques are applied by which the wastes are include confined to as small an area as possible, compacted to reduce their volume, and covered (usually daily) with layers of soil.

During landfill operations the waste collection vehicles are weighed at a scale or weighbridge on arrival and their load is inspected for wastes that do not accord with the landfill’s waste acceptance criteria. Afterward, the waste collection vehicles use the existing road network on their way to the tipping face or working front where they unload their contents. After loads are deposited, compactors or bulldozers are used to spread and compact the waste on the working face. Before leaving the landfill boundaries, the waste collection vehicles pass through a wheel cleaning facility. If necessary, they return to the weighbridge in order to be weighed without their load. Through the weighing process, the daily incoming waste tonnage can be calculated and listed in databases for record keeping. In addition to trucks, some landfills may be equipped to handle railroad containers. The use of 'rail-haul' permits landfills to be located at more remote sites, without the problems associated with many truck trips.

Typically, in the working face, the compacted waste is covered with soil or alternative materials daily. Alternative waste-cover materials are chipped wood or other "green waste", several sprayed-on foam products, chemically 'fixed' bio-solids and temporary blankets. Blankets can be lifted into place at night then removed the following day prior to waste placement. The space that is occupied daily by the compacted waste and the cover material is called a daily cell. Waste compaction is critical to extending the life of the landfill. Factors such as waste compressibility, waste layer thickness and the number of passes of the compactor over the waste affect the waste densities. (ADC, 2012)

Advantages to using landfills were often the most cost-efficient way to dispose of waste, especially in countries like the United States with large open spaces. While resource recovery and incineration both require extensive investments in infrastructure, and material recovery also requires extensive manpower to maintain, landfills have fewer fixed or ongoing costs, allowing them to compete favorably. In addition, landfill gas can be upgraded to natural gas landfill gas utilization—which is a potential revenue stream. (LFG Energy Projects, 2015)

Poorly managed landfills have the potential of causing a number of issues. Infrastructure disruption, such as damage to access roads by heavy vehicles, may occur. Pollution of the local environment, such as contamination of groundwater or aquifers or soil contamination may occur, as well. Pollution of local roads and water courses from wheels on vehicles when they leave the landfill can be significant and can be mitigated by wheel washing systems. Methane is naturally generated by decaying organic wastes in a landfill. It is a potent greenhouse gas, and can itself be a danger because it is flammable and potentially explosive. In properly managed landfills, gas is collected and utilized. This could range from simple flaring to landfill gas utilization. Poorly run landfills may become nuisances because of vectors such as rats and flies which can cause infectious diseases. The occurrence of such vectors can be mitigated through the use of daily cover. Other potential issues include wildlife disruption, dust, odor, noise pollution, and reduced local property values.

1.2.2 Incineration

Incineration is a disposal method in which solid organic wastes are subjected to combustion so as to convert them into residue and gaseous products. This method is useful for disposal of residue of both solid waste management and solid residue from waste water management. This process reduces the volumes of solid waste to 20 to 30 percent of the original volume. Incineration and other high temperature waste treatment systems are sometimes described as "thermal treatment". Incinerators convert waste materials into heat, gas, steam, and ash.

Incineration is carried out both on a small scale by individuals and on a large scale by industry. It is used to dispose of solid, liquid and gaseous waste. It is recognized as a practical method of disposing of certain hazardous waste materials (such as biological medical waste). Incineration is a controversial method of waste disposal, due to issues such as emission of gaseous pollutants.

Incineration is common in countries such as Japan where land is scarcer, as these facilities generally do not require as much area as landfills. Waste-to-energy (WtE) or energy-from-waste (EfW) is broad terms for facilities that burn waste in a furnace or boiler to generate heat, steam or electricity. Combustion in an incinerator is not always perfect and there have been concerns about pollutants in gaseous emissions from incinerator stacks. Particular concern has focused on some very persistent organic compounds such as dioxins, furans, and PAHs, which may be created and which may have serious environmental consequences.

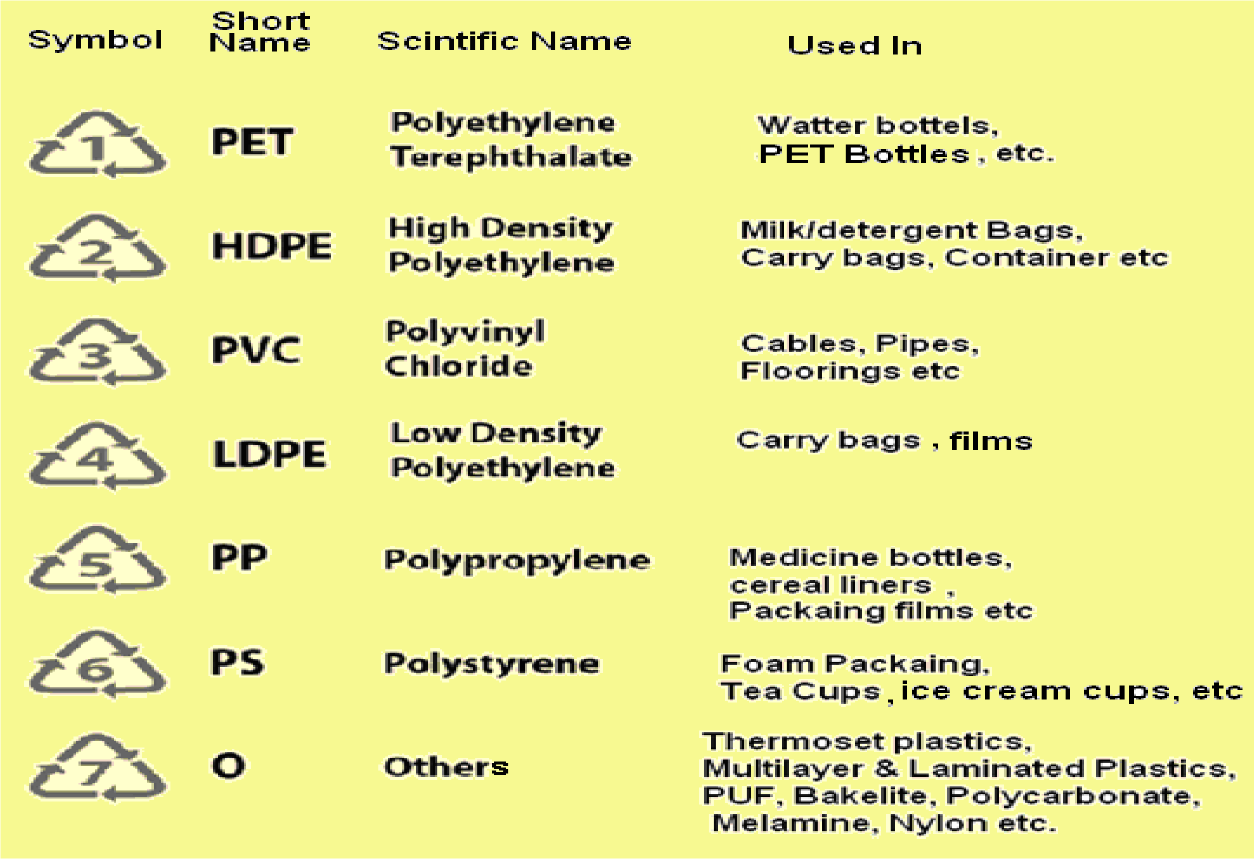
1.2.3 Recycling:

Recycling is a process to convert waste materials into reusable material to prevent waste of potentially useful materials, reduce the consumption of fresh raw materials, reduce energy usage, and reduce air pollution from incineration and water pollution from landfilling by reducing the need for "conventional" waste disposal and lower greenhouse gas emissions as compared to plastic production. Recycling is a key component of modern waste reduction and is the third component of the 3R "Reduce, Reuse and Recycle" waste hierarchy.(PM's,2006)

There are some ISO standards related to recycling such as ISO 15270:2008 for plastics waste and ISO 14001:2004 for environmental management control of recycling practice.

Recyclable materials include many kinds of glass, paper, metal, plastic, tires, textiles and electronics. The composting or other reuse of biodegradable waste such as food or garden waste is also considered recycling. Materials to be recycled are brought to a collection Centre or picked up from the curbside, then sorted, cleaned and reprocessed into new materials destined for manufacturing.

The main category of plastics includes; A. Recyclable Plastics (Thermoplastics) include PET, HDPE, LDPE, PP, PVC, PS, etc., and B. Non-Recyclable Plastics (Thermoset & others) like Multilayer & Laminated Plastics, PUF, Bakelite, Polycarbonate, Melamine, Nylon etc. As per BIS Codification as notified in Rule 8 (b) of the Plastic Waste (Management and Handling) (Amendment) Rules, 2011, there are seven categories of plastics:



Symbol	Short Name	Scintific Name	Used In
1	PET	Polyethylene Terephthalate	Watter bottels, PET Bottles , etc.
2	HDPE	High Density Polyethylene	Milk/detergent Bags, Carry bags, Container etc
3	PVC	Polyvinyl Chloride	Cables, Pipes, Floorings etc
4	LDPE	Low Density Polyethylene	Carry bags , films
5	PP	Polypropylene	Medicine bottles, cereal liners , Packaing films etc
6	PS	Polystyrene	Foam Packaing, Tea Cups , ice cream cups, etc
7	O	Others	Thermoset plastics, Multilayer & Laminated Plastics, PUF, Bakelite, Polycarbonate, Melamine, Nylon etc.

Figure 2.14 shows the recyclable plastic

In the strictest sense, recycling of a material would produce a fresh supply of the same material for example; used office paper would be converted into new office paper, or used polystyrene foam into new polystyrene. However, this is often difficult or too expensive compared with producing the same product from raw materials or other sources, so "recycling" of many products or materials involves their reuse in producing different materials (for example, paperboard) instead. Another form of recycling is the salvage of certain materials from complex products, either due to their intrinsic value (such as lead from car batteries, or gold from circuit boards), or due to their hazardous nature (e.g., removal and reuse of mercury from thermometers and thermostats).

1.2.3.1 Technological Challenges of Polymer Recycling:

1.2.3.1.1 Compatibility:

There are many types of polymers. Except in rare cases, different polymer types are not compatible that is, they are not mutually soluble. When an attempt is made to mold a mixture of two or more polymer types, the different materials form separate phases, and the overall material sample typically has very poor mechanical properties and poor integrity. Even small amounts of an “impurity” polymer can have a negative effect on properties. Given that there are numerous different polymer types, this implies that either the waste stream must be very efficiently sorted into its different components (a time consuming process), or that a way must be found to compatibilized the two phases through some sort of surfactant or coupling agent at the interface. (C. P. Rader et al 1995)

1.2.3.1.2 Contamination:

By their nature, polymers can absorb low molecular weight compounds, which dissolve and migrate into the bulk of the material. Thus, compounds causing discoloration, odor, or toxicity maybe incorporated into the material. The remolding process would not be expected to result in destruction of dissolved contaminants; discoloration by impurities may become worse as a result of the thermal treatment. Thus, remolded material may not be usable for the original function, but may need to be employed in a less demanding (typically lower value) application. For example, reuse of materials in food applications is probably impossible. No company would be willing to manufacture plastic milk jugs using a waste stream consisting of recycled plastic milk containers. If one such container had been used for storage of a foreign substance prior to recycling (such as insecticide), and that foreign substance showed up in the remade milk containers even in small amount, the resulting lawsuits and public reaction would , almost undoubtedly put the company out of business. (C. P. Rader et al 1995)

1.2.3.1.3 Crosslinking:

Thermoset polymers, which were cross-linked as a part of their initial processing to enhance properties, are particularly problematic for recycling. Remelting and reforming is not possible. Fortunately, most of the common (inexpensive) engineering plastics are not cross-linked. Rubber tires, however, are an example of a highly cross linked product which exists in large quantities. (Roughly half the world's rubber production goes into tires. (C. P. Rader et al 1995)

1.2.4 Using Radiation in Polymer Recycling:

Radiation may potentially provide major benefit either for material recycling or for chemical recycling. A success in material recycling could constitute a major breakthrough in demonstrating an energy-efficient and economically attractive recycling technology. Because of its ability to penetrate solid materials, including opaque materials, and to effect chemistry in the solid phase, radiation may be uniquely suited to this purpose. Because radiation can result in degradation of materials, depending on polymer type and environmental conditions, it may likewise be of utility in reducing energy costs by pretreatment of polymers to promote chemical recycling. These methods were originally developed for use in processing new non-recycled) polymers.

Ionizing radiation offers unique possibilities for application to the problem of recycling polymers, due to its ability to cause crosslinking or scission of a wide range of materials. Scission or crosslinking can be made to occur in the interior of bulk materials in the "as received" condition, without the necessity of dissolving the material or having some chemical initiator incorporated in the material matrix. Adhesion between particulate of different material types, or with fillers/fibers, can be promoted by coating of the particles with a radiation-activated crosslinking monomer prior to mixing and remolding of the recovered material. It would appear that crosslinking of recovered scrap polymer by radiation shows much more promise when a reactive monomer is added to the mixture, and it is recommended that this approach be more widely explored. A broad range of possibilities should be pursued using various combinations of recovered scrap of one or more materials, reactive additive, and inexpensive filler additives, in an effort to create a useful structural engineering material.

2.2.5 Radiation grafting:

Radiation grafting is a process in which active radical sites are formed on or near the surface of an exciting polymer, followed by polymerization of monomer on these sites. Grafting is accompanied by homopolymerization of the monomer; the material to which the monomer is grafted is described as the backbone, trunk or support. Radiation grafting is used to modify the polymers texture such as film, fibers, fabrics and molding powders.

The process of grafting can be expressed as follow; suppose the polymer A is exposed to γ-rays, thus the active free radical sites A^* created randomly along the polymer backbone chain, this free radical initiate a free radical on the monomer B then undergoes grafting polymerization at that active sites. The extension of the attached monomer B upon the base polymer A is termed as the degree of grafting DOG which refers to the mass of the grafted polymer as a percentage of the mass of the original base polymer. Such process can be expressed in schematic Figure 2.9.

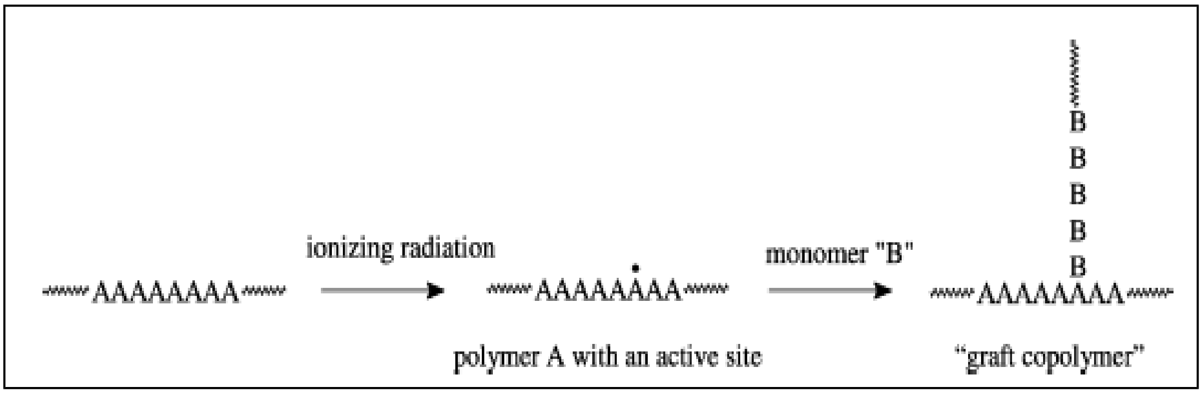


Figure 2.15 shows the schemes for grafting process for polymer A with monomer B using γ-radiation.

2.2.6 Effects of Ionizing Radiation on Polymers:

Ionizing radiation can affect the polymers' structure both positively and negatively depending on the dose rate, the presence of oxygen, the structure and the compounding of polymers. Polymers are organic molecules containing C-C, C-H, C-O bonds and these bonds are susceptible to radiation (Charles E, 2007). Ionizing radiation excites these bonds. Excited bonds result in bond cleavage and radicals formation. Formed radicals cause reactions in polymer matrix. As a result of these reactions, the polymer chain is affected by virtue of the ionizing radiation. These effects are classified as constructive (crosslinking) and destructive (degradation) (Charles E, 2008). Reactions caused by ionizing radiation on polymers are classified in to six parts Recombination Reactions; not observed any significant effects in the polymers' structural and mechanical properties. (Charles E, 2007; Charles E , 2008)

Cross-linking: Results in increase in strength, molecular weight, glass transition temperature and decrease in elongation (Classified as constructive). Chain Scission: Results in decrease in strength, elongation, glass transition temperature and molecular weight (Classified as destructive). Formation of volatile products: Mainly hydrogen gas evolution or side-chain deterioration (Classified as destructive). Formation of peroxy radicals in presence of oxygen: Classified as destructive. Unsaturation production or deterioration: Classified as both constructive and destructive. Crosslinking and chain scission occur in the structure of the polymers at the same time via radiation. These reactions are classified as primary reactions. On the other hand, one of these reactions dominates numerically in the structure and this domination designates whether or not the polymer is cross linkable or degradable under ionizing radiation.

Table 2.3 shows some polymers which are classified as crosslinking or degradable under radiation. (Vs Ivanov, 1988; Charles E, 2007)

Table 2.3 Classification of polymers behavior under ionizing radiation (Charles E, 2007)

Cross linkable Polymers	**Degradable Polymer**
Polyethylene	Polyisobutylene
Polystyrene	Poly(-methylstyrene)
Polyacrylates	Polymethacrylates
Polyacrylamide	Polymethacrylamide
Polyvinyl chloride	Poly(vinylidiene chloride)
Poly(ethylene-vinyl acetate)	Cellulose
Polyamides	Polytetrafluoroethylene
Polyesters	Polytrifluorochloroethylene
Polysiloxanes	Polypropylene
Polyvinyl alcohol	Polybutene
Ethylene Propylene Diene Terpolymers	Polyether
Ethylene Propylene Copolymers	
Conjugated diene butyl rubber	

In cross linkable polymers, scission reactions occur often as crosslinking reactions in the main chain. However, these scission reactions take place in the C-H bonds. Hydrogen in C-H bonds is ruptured by the effect of radiation. (J. Davenas et al, 2002)

After rupturing, newly formed radicals are connected to each other at their radical sites. On the other hand, in degradable polymers, scission reactions take place not only in the C-H bonds but also in the main chain (i.e. C-C bond cleavage). Therefore, in degradable polymers, molecular weight decreases and depletion in the mechanical and the chemical properties are observed (Davenas et al, 2002). Additionally, there are several effects apart from crosslinking and chain scission in the polymer structure by virtue of radiation. These effects are called secondary effects (Charles E, 2007). These secondary effects result in the formation of gas and peroxy radicals in the presence of oxygen. Moreover, ionizing radiation decreases crystallinity to some extent in crystalline polymers (IAEA, 2009).

In addition to Table 2.5, to predict whether a polymer is cross linkable or degradable under ionizing radiation, it is important to know the structure and the compounding of the polymer, the substituents in the main chain, the bond types and bond energies. The types of additives and their quantity are important in the radiation stability of polymer. Some additives like antioxidants, reinforcement agents, and peroxides show a protective influence against ionizing radiation to some extent (Holmes et al, 2004). The presence of π bonds in the main chain and the existence of a substituent in the structure are important parameters in predicting the polymers' behavior under radiation. Including π bonds in the main chain causes the polymer to degrade. This is due to the difference in the values of bond dissociation energies. In π bonds, less overlapping is observed between the component p-orbitals due to their parallel orientation. Less overlapping results in weakness in the π bonds. For this reason, the dissociation energy value of π bonds is smaller than σ bonds (Hornback J.M, 2006). Therefore, the minimum required dose to excite the π bonds becomes smaller. Formation of unstable radicals is accelerated in polymers containing π bonds in the main chain. As a result, polymers including π bonds in the main chain are classified as degradable. Moreover, if a polymer's main chain includes substituted groups, the polymer's resistivity to radiation decreases as substituted groups in polymer chain increase. Polymers which have quaternary carbon atom have low resistance to ionizing radiation. Quaternary carbons do not have C-H bonds due to the tetra substitution; C-C bonds are ruptured by virtue of the radiation (Carraher C.E etal, 2007). Therefore, cleavage of C-C bonds causes degradation of the polymers. Figure 2.10

shows the monomer types which are classified as cross linkable or degradable under ionizing radiation. (Davenas et al, 2002)

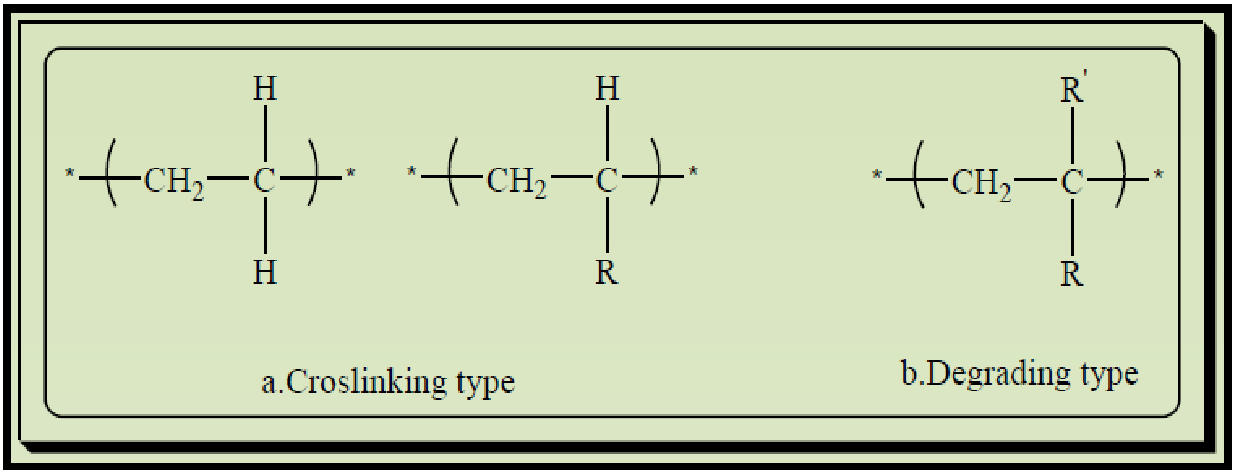


Fig.2.16 Degrading and crosslinking type of monomers (Davenas et al, 2002)

2.2.7 Polymer degradation:

Polymer degradation is a change in the properties tensile strength, color, shape, etc. of a polymer or polymer-based product under the influence of one or more environmental factors such as heat, light or chemicals such as acids, alkalis and some salts. These changes are usually undesirable, such as cracking and chemical disintegration of products or, more rarely, desirable, as in biodegradation, or deliberately lowering the molecular weight of a polymer for recycling. The changes in properties are often termed "aging".

Polymer degradation is the common name given to various processes deteriorating polymers’ properties.(Kelen Tibor, 1983) Effects of degradation are discernible in the reactor where polymer is synthesized, in the extruder where it is fabricated, during its service life when it gives its useful performance, and after its failure when it is either recycled or discharged to the environment. (Fried J.R, 2003)

2.2.7.1 Types of chemical degradation can be listed as:

- Thermal degradation
- Photo-oxidative degradation
- Hydrolytic degradation
- Environmental stress cracking
- Chemical degradation
- Mechanochemical degradation
- Radiation induced degradation
- Biodegradation
- Degradation due to weather
- Degradation during storage

2.2.7.2 Effects of degradation on polymers may be assessed from the following items:

1. Changes in chemical structure: Weathering leading to oxidative degradation generally produces conjugated double bonds, carbonyl groups and hydroxyl groups
2. Changes on the surface
3. Loss in mechanical properties
4. Embrittlement
5. Changes in molecular weight
6. Generation of free radicals
7. Toxicity of products formed due to thermal degradation, pyrolysis or combustion of polymers
8. Loss of additives and plasticizers
9. Discoloration

Examples of polymers those are particularly susceptible to attack of naturally occurring and or man-made agents are listed in Table 2.4 (Fried J.R, 2003)

Table 2.4 shows effects of environmental agents on polymers. (Fried J.R, 2003)

Agent	Susceptible polymer	Example
Biodegradation	Short-chin polymers, Nitrogen-containing polymers, polyesters	Polyurethanes, polyether-polyurethane
Ionizing radiation	Aliphatic polymers having quaternary carbon	PMMA, Polyisobutylene
Moisture	Heterochain polymers	Polyesters, polyamides polyurethanes
Organic liquid and vapors	Amorphous polymers	Polystyrene, PMMA
Ozone	Unsaturated elastomers	Polyisoprene, polybutadiene
Sunlight	Photosensitive polymers	Polyacetals, polycarbonate

Multiple exposures, such as a combination of moisture and heat or oxygen and light (photo oxidation), can result in accelerated deterioration. Deterioration of plastics to normal environmental conditions is called weathering. Factors that contribute to weathering include radiation UV, visible, and near-infrared, moisture, temperature cycling and wind. (Fried J.R, 2003)

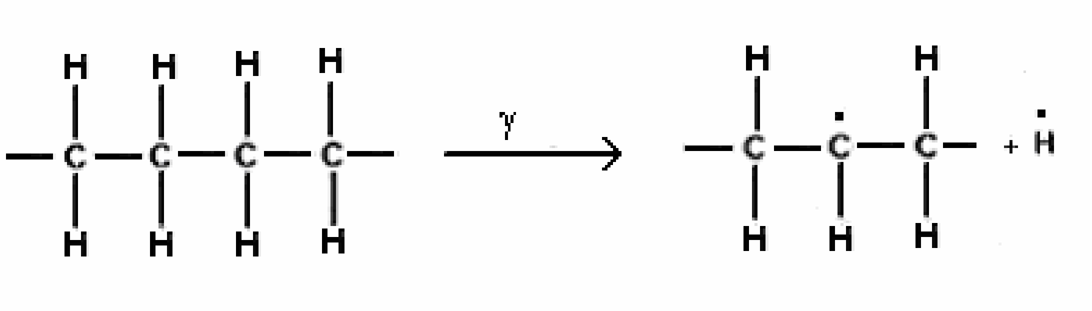
During degradation, chain scission can occur by one of three mechanisms. These include (1) random degradation, where the chain is broken at random sites, (2) de polymerization, where monomer units are released at an active chain end and (3) weak-link degradation where the chain breaks at the lowest energy bonds. In addition to thermal energy, degradation may be initiated by photochemical action, irradiation or mechanical action. Non-chain scission reactions; one example of a common non-chain scission reaction is de hydro halogenation, which results from the breakage of a carbon-halogen bond and the subsequent liberation of hydrogen halide. The most important example of a polymer that degrades by de hydro halogenation is polyvinyl chloride (PVC). (Fried J.R, 2003).

2.2.7.3 Elementary Radiolysis Processes in Polymers:

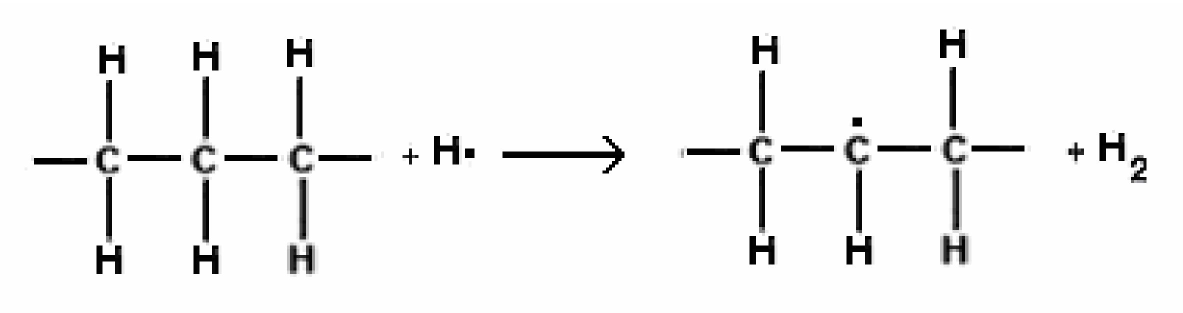
Primary radiation reactions can be observed at very low temperatures in the absence of oxygen, where other ways of energy conversion such as molecular movements or formation of oxidized species are blocked. Polyethylene illustrates the different modifications resulting at the molecular level from the energy transferred upon irradiations. It must be pointed out that radiolysis leads to the scission of the chemical bonds (C– H) whereas (C–C) bonds appear less affected. Partridge has attributed this behavior to excitation energy transfers along the macromolecular chain preventing main chain scission, whereas C–H bond scission is favored by the localization of the excitation (Davenas J.,et al,2002). The reactions of the radiolysis of polyethylene are given below.

Reaction I: Hydrogen abstraction

The free radical (H.) released in the initial radiolysis reaction has enough kinetic energy to eject another hydrogen atom to produce a hydrogen molecule.

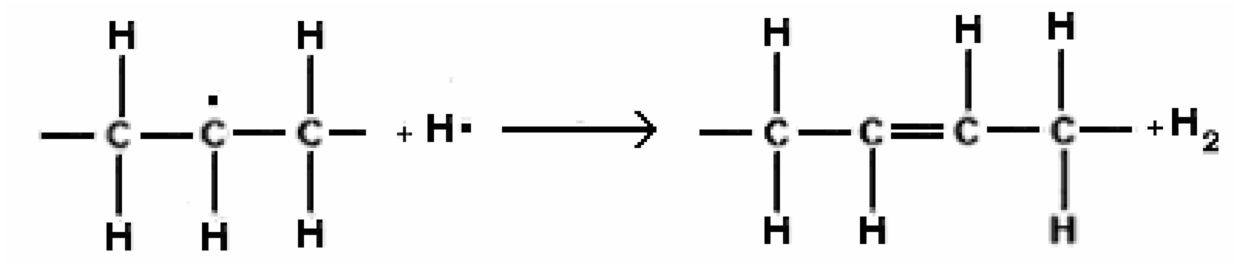


Reaction II: Formation of molecular hydrogen

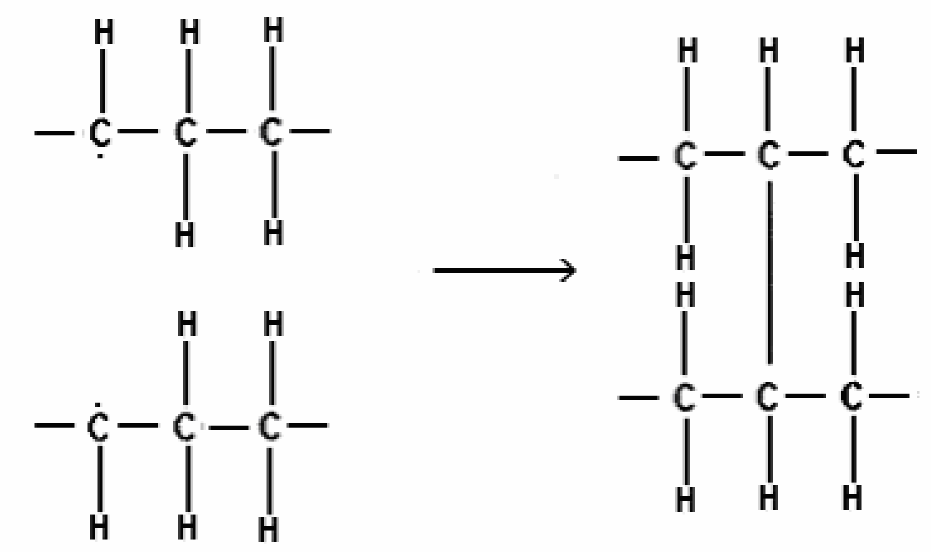


Different recombination pathways follow the irreversible loss of hydrogen molecule:

Reaction III: double bond formation results from two events occurring on the same chain



Reaction IV: Recombination leading to crosslinking



Hydrogen evolution – formation of unsaturated bonds and cross-linking are the main changes induced at the molecular level in PE. In addition to these elementary modifications other polymers may also show scissions on the main chain inducing degradation.

Reaction V: Main chain scission

The radiochemical yield for chain scission becomes significant when four carbons surround a carbon of the main chain. The presence of bulky side groups in particular inhibits the restoration of main chain scissions. The empirical rule of quaternary carbon allows the distinction between polymers whose evolution is controlled by cross-linking or degradation.

2.3 Ionizing radiation:

Ionizing radiation is a broad energetic spectrum of electromagnetic waves or high velocity atomic or subatomic particles. The radiation can be categorized according to their ability to ionize the media. Non-ionizing radiation is electromagnetic radiation that does not have sufficient energy to remove an electron of the atom. The various types of non-ionizing radiation are ultra violet (UV), visible light, infrared (IR), microwaves (radio and television), and extremely low frequency (ELF, or as they called EMF or ELF-EMF). Ionizing radiation is electromagnetic radiations, such as X-rays, γ-rays and charged particles (electrons, α-particles and β-particles) which possess sufficient energy to ionize an atom by removing at least an orbital electron. According to the 1996 European Guideline of the European Atomic Energy Community (EURATOM), electromagnetic radiation with a wavelength of 100 nm or less is considered as ionizing radiation which is corresponds to ionizing potential of 12.4 eV or more. The ionization potential is dependent on the electronic structure of the target materials and generally in the order of 4 – 25 eV. (Smith, 2000)

The International Commission of Radiation Units (ICRU) has subdivided the ionizing radiation into direct and indirect ionizing radiation, based on the mechanisms by which they ionized the atom. Direct ionizing radiations are fast charged particles, such as alpha particles, electrons, beta particles, protons, heavy ions, and charged mesons, which transfer their energy to the orbital electron directly and ionize the atom by means of Columbic force interactions along their track. Indirect ionizing radiations are uncharged quantum, such as electromagnetic radiations (X-rays and γ-rays), neutrons, and uncharged mesons, which undergo interactions with matter by indirectly releasing the secondary charged particles which then take turn to transfer energy directly to orbital electrons and ionize the atom. Some properties of ionizing radiation are shown in Table 2.5

Table 2.5 shows the properties of different ionizing radiation (Smith, 2000)

Characteristics	Alpha	Proton	Beta or electron	Photon	Neutron
Symbol	${}^{4}_{2}\alpha$or He^{+2}	${}^{1}_{1}p$ or H^{+}	${}_{-1}e$ or β	γ- or X-rays	${}^{1}_{0}n$
Charge	+2	+1	-1	Neutral	Neutral
Ionization	Direct	Direct	Direct	Indirect	Indirect
Mass (amu)	4.00277	1.007276	0.000548	-	1.008665
Velocity (m/s)	6.944 x10^{6}	1.38 x10^{7}	2.82 x10^{8}	2.998 x10^{8}	1.38 x10^{7}
Speed of light	2.3%	4.6%	94%	100%	4.6%
Range in air	0.56 cm	1.81 cm	319 cm	820 m	39.25 cm

1 atomic mass unit (amu) = 1.6 x 10^{-27} kg.

Speed of light c = 3.0 x 10^{8} m/sec.

2.3.1 Radiation sources:

The sources of ionizing radiation can be divided into two categories namely as natural and man-made sources. The first natural sources are cosmic radiation which is the radiation coming from outside our solar system as positively charged ions (protons, alpha, heavy nuclei) and interact with atmosphere to produce secondary radiations such as x-rays, muons, protons, alpha particles, pions, electrons and neutrons. The second natural sources are external terrestrial sources which represent the radioactive materials found naturally in the earth crust, rocks, water, air and vegetation. The major radionuclides found in the earth crust are Potassium-40, Uranium-235, and Thorium-210.The main sources of man-made radiations that expose the public are in the form of medical diagnostic X-ray, radiation therapy, nuclear medicine and sterilization. The common radioactive sources are ^{131}I, ^{99m}Tc, ^{60}Co, ^{192}Ir, ^{90}St and ^{137}Cs. Other man-made sources exemplar in occupational and consumption products that originated in mines, combustible fuel (gas, coal), ophthalmic glasses, televisions, luminous, watch’s dial (tritium), X-rays at the airport (scanner), smoke detectors (Americium-241) and fluorescent lamp starters, nuclear fuels, nuclear accidents and nuclear weapons. The yield of artificial sources is represented either as quantum in X-rays and γ- rays or as high energy particles such as beta particles (β), alpha particles (α), neutrons and electrons (Smith, 2000). Most of the types of radiation source discussed above are used in medicine, industry, and research. Today the most common radiation sources used is ^{60}Co, which is an artificial source of γ radiation and linear accelerators for photon and electron beams having potential energy ranging from 0.3-10 MeV to 20 MeV. Table 2.6 shows the radiation sources commonly used in industry and research.

Table 2.6 shows the radiation sources commonly used in industry and research. (Smith, 2000)

Category	Source
Nuclear power	^{235}U fission products, ^{90}Sr, ^{137}Cs
Occupational exposure	X-ray, isotopes for γ- rays
Weapons tests	^{235}U,^{239}Pu, fission products
Every day sources	Coal, Tobacco and Air-travel
Medical tests & treatment	X-ray, γ-rays & electrons
Cosmic rays	Protons, electrons, neutrons
Food	^{40}K, ^{137}Cs, ^{14}C and ^{131}I
Rocks & building	^{235}U, ^{238}U, and ^{232}Th
Atmosphere	^{222}Rn and ^{137}Cs

2.3.2 Gamma radiation sources:

Gamma radiations are produced by the nuclear transitions that occur within the nuclei of radioactive elements. The emitted photons are mono-energetic with specific energy to the isotope from which they originate. By far the most commonly employed radioactive isotope for γ-rays is cobalt-60 (Co^{60}), an isotope with a half-life of 5.272 years. Co^{60} emits two γ-photons of equal intensity at 1.17 and 1.33 MeV. It is produced in nuclear reactors by a neutron-capture reaction involving Co^{59}. Due to the long half-life, high penetrating power and ease of production, Co^{60} sources have become sources of choice in both industrial and research institutions. The activity of the sources prepared in nuclear reactors can be made high up to 40 Ci/g (1.5 TBq/g), however sources with activity from 1 to 5 Ci/g are typically common for use. Over 80% of the Co^{60} produced world-wide is manufactured by the Canadian company, Ontario Hydro and marketed by another Canadian company, MDS Nordion.

Co^{60} radioisotope decays to stable nickel-60 by a nuclear transition (β-decay) in which a neutron is converted into a proton via the emission of a β-particle with energy of 312 keV and two γ-photons, one of 1.17 MeV and another of 1.33 MeV. The decay scheme of this isotope is illustrated in Figure 2.9 (Choppin et al., 1995; Attix, 1986)

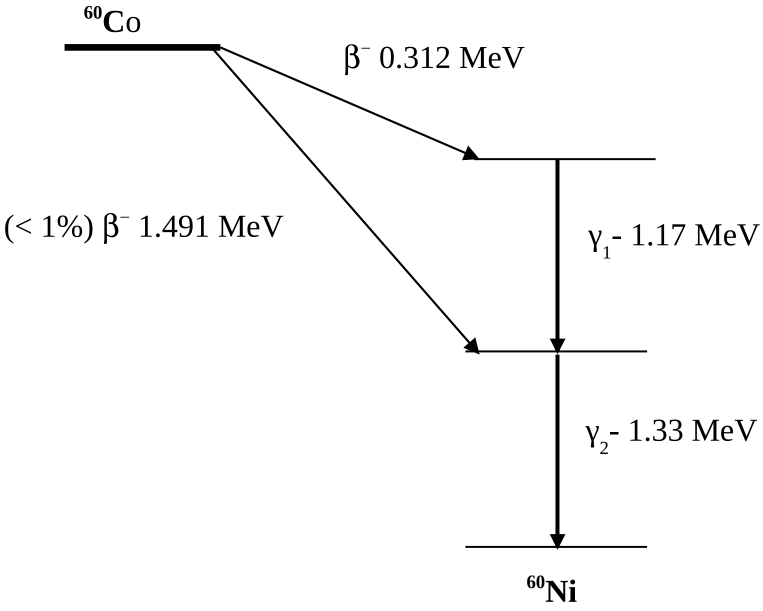


Figure 2.17 Decay scheme of Co^{60} radioisotope which ends by Nicle-60 stable.

Another frequently used γ-ray source is cesium-137, a fission product from nuclear reactors. The energy of the emitted photon is 662 keV and the half-life is 30.17 years. Nuclear reactors themselves are potential sources of γ-rays.

2.3.3 Gamma radiation interaction with matter:

When photons of γ-radiation interact with matter, they undergo attenuation and hence lose their energy and intensity by the process of photoelectric absorption, Compton inelastic scattering, pair production, and Rayleigh elastic scattering (Evan, 1952).

2.3.3.1 Photoelectric absorption:

Absorption of γ-rays occurs when the γ-ray photon is absorbed by an electron resulting in ejection of the electron from the inner shell of the atom and ionization of atom take place. Subsequently, the ionized atom returns to the neutral state with the emission of characteristic X-ray of the atom shown in Figure 2.10. This subsequent emission of lower energy photons is generally absorbed and does not contribute to (or hinder) to the secondary ionization. Photoelectron absorption is the dominant process for γ-ray absorption up to energies of about 500 keV. The photoelectric absorption process predominates for photons in the low energy range between 10 keV and 200 keV. This is the phenomenon explained by Einstein in 1905, in which an incident photon gives up all its energy $h\upsilon$ to a bound electron, usually K shell (90%), where subsequently part of the energy is used to overcome the electron binding energy E_{B} and the extra energy is converted as kinetic energy K_{E} of the photoelectron. This can be expressed in equation (1.1).

$$h\upsilon = K_E + E_{\mathrm{B}} \tag{2.1}$$

The atom that is left in an excited state will emit fluorescent x-rays or Auger electrons. The characteristic X-rays may escape especially for high-energy photons and high atomic number of absorbing material unless the absorber is thick enough to stop the γ-rays. The ranges of the Auger electrons are short and locally absorbed. The cross-section for photoelectric effect in K shell of an atom with atomic number Z for photon energy $h\upsilon$ is given by equation (2.2), from which we could deduce that the photoelectron absorption is dominant for atoms of high atomic numbers and for photon of low energy.

$$\sigma_K = \varphi_0 4\sqrt{2}\left(\frac{m_0c^2}{h\upsilon}\right)^{7/2}\frac{Z^5}{137^4} \qquad (2.2)$$

Where $\varphi_0 = \pi r_0^{\ 2}$ and $r_0 = e^2 / m_0 c^2 = 2.818 \times 10^{-15} m$ is the classical electron radius, m_0 is the rest mass of electron and c is the speed of light. m_0c^2 is the rest energy of the recoil electron, according to mass-energy equation proposed by Einstein in 1905 in the relativity theory.

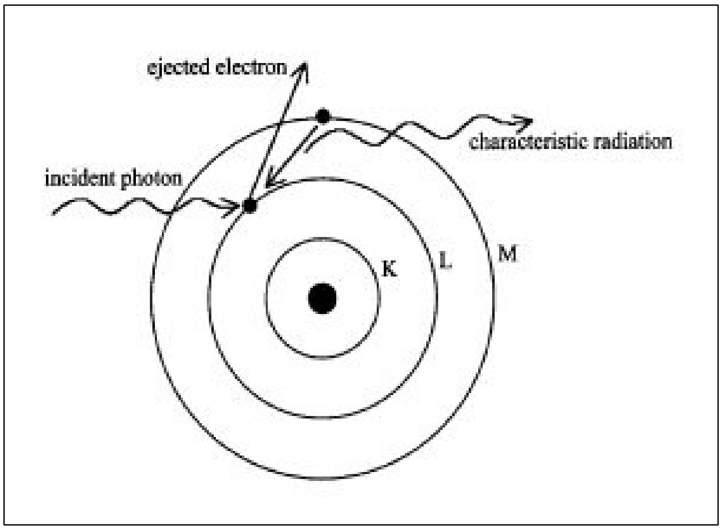


Figure 2.18 Schematic diagram of photoelectric absorption of γ-radiation resulting in ejection of orbital electron from L shell leading to ionization process of an atom.

2.3.3.2 Compton Scattering:

Compton scattering process also known as an incoherent scattering, occurs when the incident photon ejects free or weakly bonded electron from an atom and a photon of lower energy is scattered from the atom. Relativistic energy and momentum are conserved in this process and the scattered γ-ray photon has less energy and therefore greater wavelength than the incident photon shown in Figure 2.11. Compton scattering is important for low atomic number specimens. At energies of 100 keV - 10 MeV the absorption of radiation is mainly due to the

Compton effects. The change in wavelength of the scattered photon is given by equation (2.3) (Mc Gervey, 1983)

$$\frac{c}{v'} - \frac{c}{v_o} = \lambda' - \lambda_o = \frac{h}{mc(1-\cos\theta)} \qquad (2.3)$$

Where λ is the wavelength of the incident photon, λ_0 the wavelength of the scattered photon, m is the mass of the electron and θ the angle of scattering for the photon. On rearranging, the above equation we got the following equation (1.4)

$$hv = \frac{h}{1+\alpha(1-\cos\theta)} \qquad (2.4)$$

Where α is the ratio of the energy of the photon to the rest energy of the electron i.e. $\alpha = hv/m_0c^2$. The kinetic energy *T* for the recoil electron is given by equation (1.5).

$$T = hv\frac{\alpha(1-\cos\theta)}{1+\alpha(1-\cos\theta)} \qquad (2.5)$$

And the scattering angle of the electron is given by equation (1.6)

$$\cot\phi = (1+\alpha)\tan\frac{1}{2}\theta \qquad (2.6)$$

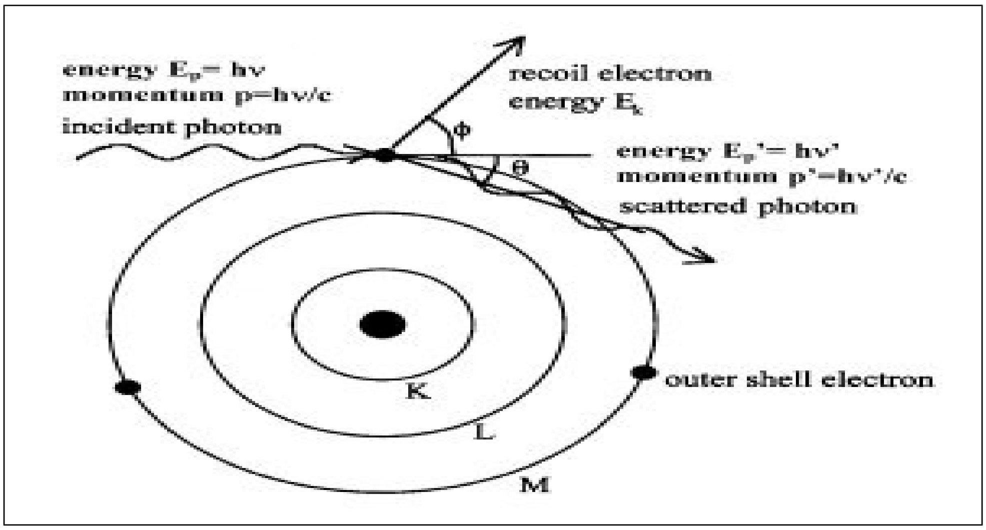


Figure 2.19 Schematic diagram of Compton scattering for γ-radiation resulting in ionization and scattering of the incident photon with less energy

2.3.3.3 Pair Production:

The production of a positive and negative electron pair (pair production) is a process that can take place in the vicinity of the nucleus field of an atom or an electron field. Absorption of photons through the mechanism of pair production can occur when the energy of an incident photon is greater than twice the rest mass of an electron, i.e. $2m_0c^2$ = 1.022 MeV (Johns and Cunningham, 1983). During pair production interactions, a photon has its energy converted to an electron–positron pair. The positron so produced interacts with matter by ionizing and exciting atoms through the same processes as electrons, thus losing energy and being brought to rest. At this point, the positron combines with an electron in an annihilation process producing two photons with energy equal to 0.511 MeV as shown in Figure 2.12.

Pair production is an absorption process in which a photon in the field of nucleus produces an electron-positron pair, where the total kinetic energy is equal to the energy of photon minus the rest energy of the two particles, which have been created as shown in equation (2.7), thus the photon energy must be greater than 1.02 MeV for the interaction to take place. The electron and positron do not necessarily receive equal energy, but their average energy is given by equation (2.8).

$$h\upsilon = (m_0c^2 + T_-) + (m_0c^2 + T_+) \qquad (2.7)$$

$$\bar{T} = \frac{h\upsilon - 1.022}{2}\ \text{MeV} \qquad (2.8)$$

The cross-section of the pair production in the field of nucleus is given by equation (2.9)

$$\sigma_{PP} = \frac{1}{137} r_0^{\,2} Z^2 \left[\frac{28}{9} \ln\left(\frac{2h\upsilon}{m_0c^2} \right) - \frac{218}{27} \right] \qquad (2.9)$$

The triplet production process is similar but the interaction takes place with one of the atomic electrons which receives sufficient energy to be set free. It occurs when the incident photon have an energy of $4m_0c^2$, i.e. it implies both the pair production at the nucleus level plus triplet production. The total kinetic energy is equal to the energy of photon minus the rest energy of the three ejected particles as given by equation (2.10), from which the average kinetic energy can be deduced by equation (2.11) (Motz *et al.*, 1969)

$$hv = \left(m_0c^2 + T_-\right) + \left(m_0c^2 + T_+\right) + \left(m_0c^2 + T_*\right) \qquad (2.10)$$

$$\bar{T} = \frac{hv - m_0c^2}{2} \text{ MeV} \qquad (2.11)$$

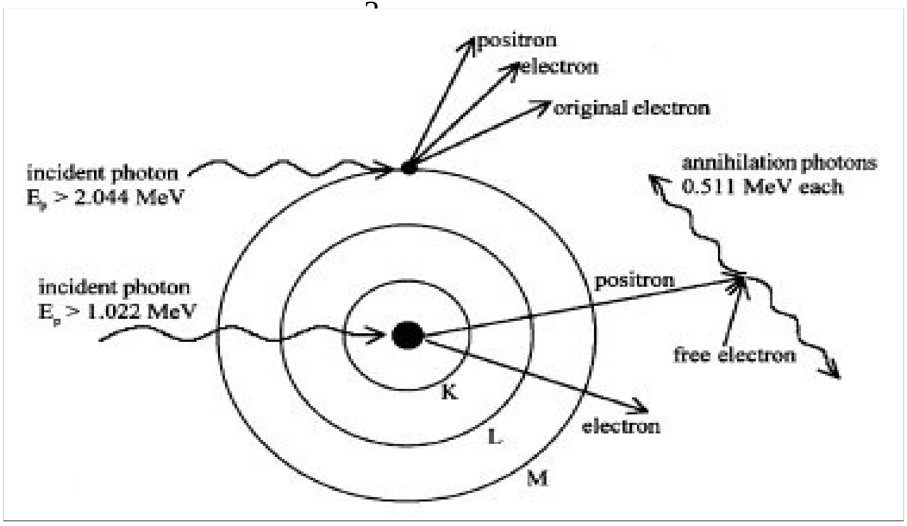


Figure 2.20 Schematic diagram of Pair Production process for γ-radiation being interfered in the nucleus field and orbital electron to produce triplet particles.

2.3.3.4 Raleigh scattering:

The coherent Rayleigh scattering by an atom is predominant for photons at low energy range from 1 keV to 100 keV. The Rayleigh scattering is a process in which a photon is deflected by a bounded electron of the atom and photon going off in different directions with no loss in energy. The atomic system may recoil as a whole under impact without the atom being ionized or excited. The probability of this process is large only for low energy photons and high atomic number material.

The differential cross-section of the coherent scattering of photon at deflection angle θ by a bounded electron is given by equation (2.12)

$$d\sigma_{coh} = \frac{1}{2} r_0^{\,2} \left(1 + \cos^2 \theta\right) \left[\frac{F(\alpha, \theta, Z)^2}{Z} \right] d\Omega \qquad (2.12)$$

Where $F(\alpha, \theta, Z)$ is the atomic form function which varies from zero at large angle to Z at the smaller angle.

2.3.3.5 Gamma ray attenuation coefficients:

In general the characteristic of radiation interaction with matter is that each individual photon is absorbed or scattered from the incident beam in a single event. The photon number removed ΔI is proportional to the thickness traveled through µx and the initial photon number I_0, i.e. $\Delta I = -\mu I_o \Delta x$, where, μ is a constant proportionality called the attenuation coefficient. In this case, upon integrating, we have the following equation (2.13)

$$I = I_o e^{-\mu x} \qquad (2.13)$$

The attenuation coefficient is related to the probability of interaction per atom, i.e. the atomic cross section σ_a is given by equation (2.14)

$$\mu = \frac{\sigma_a N_A \rho}{A} \qquad (2.14)$$

Where A is the mass number and N_A the Avogadro's number (6.022 x 10^{23}mol/1), Table 2.7 briefly summarized the entire γ-radiation photon interactions with their possible energies required to initiate the reactions (Smith, 2000; Siegbahn, 1965).

Table 2.7 the different types of γ-radiation interactions with mater. (Siegbahn, 1965)

Process	**Type of interaction**	**Other names**	**Approximate *E* of Maximum importance.**	**Z dependence**
Photoelectric	With bonded electrons, all *E* given to electron		Dominant at low *E* (1-500) KeV, cross section decrease as *E* increase	Z^3
Scattering from electrons coherent	With bond atomic electron, with free electrons	Rayleigh electron, resonance scattering, Thomson scattering	<1MeV and greatest at small angles. Independent of energy	Z^2, Z^3 Z Z
Incoherent	With bond atomic electron, with free electrons	Compton scattering	<1MeV least at small angle. Dominate in region of 1 MeV, decreases as *E* increase	Z Z^2
Pair Production	In Coulomb field of Nucleus	Elastic Pair production	Threshold ~1MeV, *E*> 5MeV. Increase as *E* increase.	Z
Pair production Delbruk scattering	In coulomb field of electron & nucleus	Triplet production inelastic pair production. Nuclear potential scattering	Threshold at 2 MeV increases as *E* increases. Real Max > imaginary, below 3 MeV(both	Z^4

			increase as *E* increases)	

2.3.4 Gamma radiation interaction with molecules:

The essence of **γ** -radiation interaction with molecules and change the physical and chemical characteristics of the formed compound is ascribed to the amount of energy being transferred, which will create ion, free radicals and excited molecule. Such interaction process is termed ionization and excitation of the molecules, which can cause chemical changes to the irradiated molecule. This is due to the fact that all binding energy for organic compound in the range of 10 – 15 eV. In case of low transferred energy by photon, the molecule undergoes excitation state before returning to the rest state by emitting X-ray photons or break down to release free radicals which in turn undergoes polymerization.

The ejected electron from the irradiated molecule (A^+) is subjected to the strong electric field of the formed positive charge. Therefore the recombination is a frequently occur, either during irradiation or after the end of irradiation to create energetic molecule (A^{**}). Such highly energetic excited molecule will break down into free radicals and new molecule (Denaro, 1972). The fundamental of this reaction can be shown in the following scheme Figure 2.13.

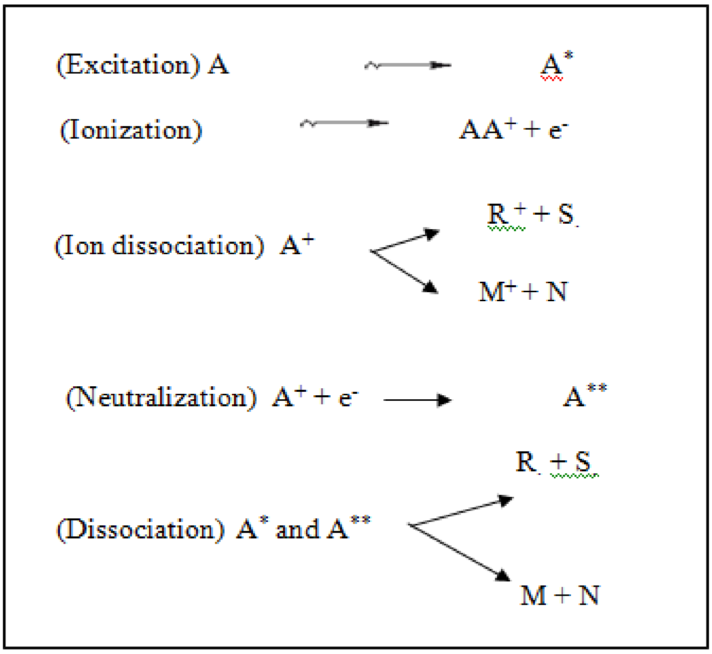


Figure 2.21 shows the expected irradiation results of the organic molecules, where R. and S. are free radicals and M and N are molecular products.

2.5 Literature Review:

Various studies related to the gamma irradiation of polymer are available in literature. Some of these studies focused on radiation induced crosslinking and vulcanization; some of these focused on the stability and the degradation of polymer. Some researches related with management of polymer via radiation are summarized below:

JoaÄo et al (2000) studied the interest on recycled materials from post-consumer polymers present in discarded commercial packaging has gained increasing attention. The development of new engineering materials based on degraded polymers is an interesting possibility. Blends of low cost plastics such as polyolesns, polystyrene, poly(vinyl chloride), discarded in urban waste are of particular interest. The Instituted macromolecules had developed a two-step process for recovering plastic residues which allows obtaining materials with good properties. One of these materials may be used as plastic lumber and consists of a recycled 75/25 LDPE/HDPE partially degraded blend. The exposure of this blend to low doses of Co60 gamma radiation improves its mechanical properties due to

partial cross-linking. Differential scanning calorimetry, gel permeation chromatography, infrared spectroscopy and X-ray diffraction have been used to investigate the effects of gamma irradiation on the thermal behavior of polymer material. Typical DSC curves obtained from the blend samples, before and after irradiation, The influence of radiation dose in the thermal parameters, melting temperature, crystallization temperature and cristallinity of the recycled PE blend.
The melting and crystallization temperatures were found to decrease as the radiation dose increases, showing a tendency to stabilization at higher values. The correlation of the degradation process, melting heat and molecular weight distribution is discussed. (JoaÄo et al ,2000)

Rosiak et al (2000) they said that in the recent years, an important factor stimulating research on radiation-induced reactions of polymers in aqueous solution is the application of this technique for synthesizing new materials or modifying the properties of polymers. Hydrogels are probably the most prominent examples of water-borne products obtained by radiation technology. Radiation techniques have proved to be particularly suitable for producing hydrogels for biomedical use. The main factors that contribute to the success of these technologies are: water as a human-and environment-friendly solvent, lack of any potentially harmful chemicals (monomers, initiators, crosslinking agents, etc.)
simple production schemes, parallel synthesis and sterilization of the products in the sealed, final packages, valuable medical properties of the products, broad range of applications, and the possibility of manufacturing “smart” gels reacting to temperature, pH, light, etc. However, there is only limited number of successfully commercialized technologies most of these products belong to the one category synthetic wound dressings. The technology invented in Poland has been transferred to other member countries of the IAEA, e.g. Brazil, Egypt, Philippines, Syrian Arab Republic, Vietnam, etc. The other examples of polymers biomaterials

produced using ionizing radiation have been presented. It includes drug delivery systems; new intelligent polymer support for cells cultivation, materials designed for implants as well as radiation methods for the production of nanogels polymeric systems with intra molecular crosslinking. The results of basic studies on transformation of polymers in aqueous solution are good foundations to achieve the new technologies and biomaterials. (Rosiak et al, 2000)

Kassem et al. (2002) studied the Irradiation of polymeric materials with ionizing radiations (e.g. γ-rays) produces ionization and excitation in them. This irradiation leads to the formation of very reactive intermediates, free radicals, ions and excited states. These intermediates can follow several reaction paths, which result in disproportion, hydrogen abstraction, arrangements and/or the formation of new bonds. The degree of these transformations depends on the structure of the polymer and the conditions of treatment before, during and immediately after or even days, weeks, or months after irradiation. This transformation often lead to resultant physical changes such as embrittlement, strength, discoloration, odor generation, stiffening, softening, increase or decrease in melting point, enhancement or reduction of resistance to chemical attacks and chemical changes such as molecular weight, chain length, entanglement, branching, pendant functionality, chain termination.(Kassem et al, 2002)

M. Sen et al (2003) studied the effect of gamma irradiation conditions on the radiation induced degradation of un cross linked, commercial isobutylene isoprene rubbers has been investigated in this study. Influence of dose rate and irradiation atmosphere on the degradation of butyl rubber has been followed by viscosimetric and chromatographic analyses. Limiting viscosity number of all butyl rubbers decreased sharply up to 100 kGy and leveled off at around the same molecular weight independent of dose rate. Slightly higher decrease in viscosity was observed for samples irradiated in air than in nitrogen especially at low dose rate irradiation. Cross-linking GðXÞ, and chain scission GðSÞ yields of butyl rubbers were calculated by using weight- and number-average molecular weights of irradiated rubber determined by Size Exclusion Chromatography analyses. G-value results showed that chain scission reactions in isobutylene–isoprene rubber in air atmosphere are more favorable than in nitrogen atmosphere, and that lower dose rate enhances chain scission over cross-linking. (M. Sen et al, 2003)

Cleland et al (2003) demonstrated that high power; high energy X-ray (bremsstrahlung) generators are suitable sources of ionizing radiation for processing bulk materials. The basic physical, chemical and biological effects of irradiating materials with this form of energy are essentially the same as the effects obtained with gamma rays and accelerated electrons. The choice of energy source for a particular application depends on practical aspects of the irradiation process, such as material thickness, throughput rate, dose uniformity ratio and economics. X-ray photons are emitted when energetic electrons strike any material. The intensity increases with the energy of the incident electrons and with the atomic number of the target material. With electron energies greater than 1 MeV, the angular distribution of the emitted radiation is concentrated in the direction of the electron beam. The broad energy spectrum of bremsstrahlung (braking radiation) extends up to the maximum energy of the incident electrons. Although the most probable photon energy is only about 0.3 MeV, the penetration is significantly greater than gamma rays from large area cobalt-60 sources. The penetration of high energy X- rays allows large loads of high density materials to be irradiated with low dose uniformity ratios. The narrow X-ray beam allows pallet-sized loads to be irradiated singly, thus shortening the irradiation time. This facilitates changing the processing conditions for different materials. In contrast to the emission of gamma rays from radioactive sources, X-ray generators can be switched off when not needed for production. This saves energy and simplifies maintenance procedures. High power, high energy electron accelerators are now available, with electron beam power ratings of 300 kW and 500 kW at 5 MeV and up to 700 kW at 7 MeV. Several industrial X-ray processing facilities have already been built in Japan, North America and Europe. X-ray processing is now a practicable and economically competitive technique. X-ray processing is a relatively new irradiation method that can be used for various applications, such as sterilizing medical devices, preserving foods, curing composite structures and improving the properties of bulk materials. (Cleland et al, 2003)

CZVIKOVSZKY (2003) studied that temporary engineering materials became gradually more and more complex in their composition and structure. The multiple functions required today in our machine parts and other applications demand this complex structure, consisting of different components, all contributing with their best features. This multicomponent approach is dominant in the polymer engineering field in systems such as copolymers, compounds, blends and alloy, composites, and recycling of multicomponent materials. Radiation processing may help to overcome theoretical and technological difficulties, in the way of creating new multicomponent polymeric systems. In the present work, we focused on solving the major obstacle, the inherent thermo dynamical incompatibility of partners in polymer blends, alloys, composites and recycled products. Radiation-assisted compatibilization may promote the common use of synthetic and natural polymers in multicomponent engineering polymers. This type of compatibilized material multicomponent may easily be processed by the plastics machinery of today. It certainly will gain importance when renewable natural products of the biomass should participate at an accelerated rate in saving the fossil (petroleum) resources. Radiation treatment applying reactive additives may broaden the field of radiation cross-linking of polymers, which are non-cross-linkable without reactive additives. Radiation-assisted compatibilization of multicomponent, recycled polymer systems may turn the recycling procedures of our day which are rather directed toward down-cycling, into an upgrading procedure up cycling. Radiation initiated bonds of the interface between reinforcement and matrix offer a superior quality in high-tech composite systems.

Eui et al (2008) evaluated the effect of gamma irradiation on the physical and structural properties of b-glucan. b-Glucan solution (10%, w/v) was exposed to a cobalt-60 source (10, 30, and 50 kGy). Gel permeation chromatography data showed that the average molecular weight of irradiated b-glucan significantly decreased as the irradiation dose increased, in addition, gamma irradiation improved the solubility and decreased the viscosity of b-glucan by the radiolysis of the glycosidic bonds, and this effect was dependent upon the absorbed dose.
Fourier transform infrared spectroscopy results showed that the functional groups of b-glucan were not significantly affected by gamma irradiation and scanning electron microscopy results showed that the irradiated b-glucan was deformed into smaller granules . Therefore, gamma irradiation could be used in commercial processes as an effective method to resolve the physical problems involved in the use of b-glucan with high viscosity and low solubility (Eui et al, 2008)

Placek et al. (2009) performed a study to determine the EPDM rubbers life time in nuclear power plants. EPDM rubbers having two different thicknesses were irradiated up to 90 kGy which was the total dose simulating 10 years' service for the initial dose rate of 1 Gy/h. After irradiation, mechanical, gas leakage and compression set (CS) tests were carried out. In the determination of service time, compression set were used as reference. CS endpoint criterion was set for the tested samples at 85%. According to the results; compression set of 85 % was reached for 7 mm thick EPDM at simulation equivalent to 2 years' service. On the other hand, CS of 85 % was not reached for EPDM with a 14 mm thickness equivalent to 4 years of service.(Placek et al. 2009)

Abiona et al (2010) considered the effects of γ-irradiation on the physic chemical stability and mechanical properties of commercial polypropylene (PP) have been investigated using X-ray diffraction analysis, Raman spectroscopy, ultraviolent visible spectroscopy and tensile test. Found that the γ -irradiation of polypropylene led to remarkable changes in the physic chemical properties of the material due to chain scission, oxygen effects and cross-linking activities. These changes result in the production of degraded products such as water vapor, carbon monoxide from hydroxyl and carbonyl groups as confirmed by Raman and Ultraviolent visible spectroscopic analyses. It was observed that the melting temperature and crystallinity reduce as radiation doses increases likewise; there were losses in mechanical properties of the polymer as indicated by reduction in elongation to fracture and reduction in tensile strength of the materials as dose increases. (Abiona et al, 2010)

FIRAT (2010) investigated degradation of ethylene propylene diene terpolymer (EPDM) via gamma radiation and possible use of EPDM in radioactive waste management were. In estimation of radiation stability and possible use of EPDM in radioactive waste management, dose rate (both high and low), irradiation environment (in water and in air), additives (carbon black, zinc oxide, plasticizer) used in formulation, peroxide type (either aliphatic or aromatic) and content were parameters which were analyzed. Three EPDM samples having different peroxides were irradiated in water and in air with two different dose rates (993 Gy/h, 54 Gy/h) to 2163 kGy (for high dose rate) and 1178 kGy (for low dose rate). Irradiation periods for low dose rate were 2.5 years (last sample) which have not been observed in literature. Characterization of irradiated EPDM samples were done by mechanical (tensile, hardness, compression), dynamic mechanical (DMA), thermal (TGA-FTIR) and morphological (ATR-FTIR, XRD, SEM) tests. High dose rate irradiations were done in predicting how far EPDM resist to radiation and which dose rate emitted waste can be immobilized and stored in EPDM for 300 years. Low dose rate irradiations were carried out in determining.

Omer et al (2011) studied that for the wider interested applications of polymer hybridized metal nanoparticles composites, poly vinyl-alcohol /silver nanoparticles composites in a form of a film was prepared by in situ irradiation doping technique up to 50 kGy. The effect of radiation upon the composites resulted in reducing the silver ions into black metallic silver, so the general film color changed from white to golden-yellow then black color at 50 kGy. The UV-visible spectroscopy revealed an absorbance band peaking at 425 nm which was increased exponentially with dose increment. The study of UV-spectrogram revealed that the maximum absorbance Amax increased following the particles radius. Scanning electron Microscopy (SEM) revealed shiny nanoparticles of silver cored in Polyvinyl-alcohol PVA with homogeneous distribution and having an average size of 30 nm as well as the XRD spectrum that shows cubic center face of silver nanoparticles in the film and a crystalline peak for PVA reduced by radiation to amorphous phase Gamma Radiation Synthesis and Characterization of Polyvinyl Alcohol/ Silv Nano Composites Film. (Omer et al, 2011)

Raman deep et al (2012) Polypropylene films were irradiated with C5þ (70 MeV) and Ni11þ (150 MeV) ions of varying fluence. The ion induced optical, chemical and structural changes were investigated using UV-Vis and Fourier Transform Infrared (FTIR) spectroscopy and X-ray diffractometry (XRD). UV-Vis data showed an increase of optical absorbance and a shift of the absorption edge towards the red end of the spectrum when the ion fluence was increased. This shift may be attributed to the greater degree of conjugation. FTIR analysis revealed the formation of alcoholic and ketonic groups. Significant loss of crystallinity occurred with increasing ion fluence. UV-Vis analysis Ultraviolet-Visible (UV-Vis) spectroscopy is an important tool to investigate the optical band gap energy (Eg).The absorption of light. (Raman deep et al, 2012)

Fırat Hacıoğlu (2013) studies the changes in the properties of ethylene propylene diene terpolymer (EPDM) irradiated with different dose rates in ambient atmosphere and aqueous environment were investigated. Irradiations were carried out both with low dose and high dose rate irradiation sources. EPDM samples which were differentiated from each other by peroxide type and 5-ethylidene 2-norbornene (ENB) contents were used. Long term low dose rate irradiations were carried out for the duration of up to 2.5 years (total dose of 1178 kGy) in two different irradiation environments. Dose rates (both high and low), irradiation environments (in aquatic and open to atmosphere), and peroxide types (aliphatic or aromatic) were the parameters studied. Characterization of irradiated EPDM samples were performed by hardness, compression, tensile, dynamic mechanical analysis (DMA), TGA–FTIR, ATR-FTIR, XRD and SEM tests. It was observed that the irradiation in water environment led to a lower degree of degradation when compared to that of irradiation open to atmosphere for the same irradiation dose. In addition, irradiation environment, peroxide type and dose rate had effects on the extent of change in the properties of EPDM. It was observed that EPDM is relatively radiation resistant and a candidate polymer for usage in radioactive waste management. (Fırat Hacıoğlu, 2013)

Chapter Three

Materials and Method

3.1 Study Design:

Prospective experimental study conducted in Khartoum-Sudan during period from 2012 to 2016 to manage polymer waste by using Gamma irradiation technique.

3.2 Materials:

The plastic waste would be collected randomly from the environmental and differentiated according to color, then packed and compressed to be in a bulk form with a diameter of 5*5 cm and thickness of 6 cm.

3.3 Methods:

The plastic waste would be collected randomly from the environmental and differentiated according to color only then packed and compressed to be in a bulk form with a diameter of 5*5 cm and thickness of 6 cm and sand witched between 0.5cm of buildup material, then the samples were irradiated at different doses in range of 0 – 800 kGy at room temperature using Co^{60} gamma cell model 220 with dose rate of 6.05Gy/min, then the sample was characterized using Hounsfield

Tensometer ASTM D412, compression set machine Zwick Roell E Type, Hardness machine Zwick Roell Type A Durometer.

3.4 Equipment:

3.4.1 Gamma irradiation:

Co^{60} gamma cell model 220 with dose rate of 6.05Gy/s, manufactured by atomic Energy of Canada Ltd the Co^{60} produces two mains γ-rays of 1.17 and 1.33 MeV, which give the average energy of 1.25 MeV. The dose rate on December 17, 2004 was 6.05Gy/s. The new dose rate was calculated based on the half-life, $T_{1/2}$, of the source, i.e. the elapsed time in which the activity of the source reduced by half, is equal to 5.27 years by the equation (3.1)

$$\dot{D} = \dot{D}_0 \exp(-\ln 2\ t / T_{1/2}) \qquad (3.1)$$

Where $\dot{D}_0$ is the dose rate at time $t = 0$. In May 2005, the dose rate of the source was calibrated using Ferrous Sulphate dosimeter. Fricke dosimeter was then irradiated in the calibrated beam to the doses that the solution is well characterized. The dosimeter was read using UV-Vis spectrophotometer to measure the absorbance of $FeSO_4$ at the wavelength of 304 nm. The deviation of the current value to standard value is of main interest for chamber stability and is maintained to within ± 1%. The deviation was calculated using the following equation (3.2).

$$Deviation = \frac{2.75 \times 10^2 \times \Delta A}{1 + 0.007(T - 25^0 C)} \qquad (3.2)$$

Where ΔA is the changing absorbance, T is the temperature in Celsius. Response of Fricke dosimeter was compared to the secondary standard chamber and the consistencies of by these methods were maintained to be less than ± 3%. The solution was then sent for standardization using gamma chamber and also for calibration of routine dosimeter. The routine check source measurements were performed every three months in order to assess the long term stability of the reference standard chamber, as shown in Figure (3.1).

Figure 3.1 γ-irradiation cell models 220 at the national atomic energy research center- Khartoum

3.4.2 Tensile Tests

Hounsfield Tensometer with a crosshead displacement rate of 500 mm/min was used for tensile tests. Tests were carried out in accordance with ASTM D412. Maximum stress at break, elastic modulus, elongation at break and tensile strength results were noted from the machine readings.

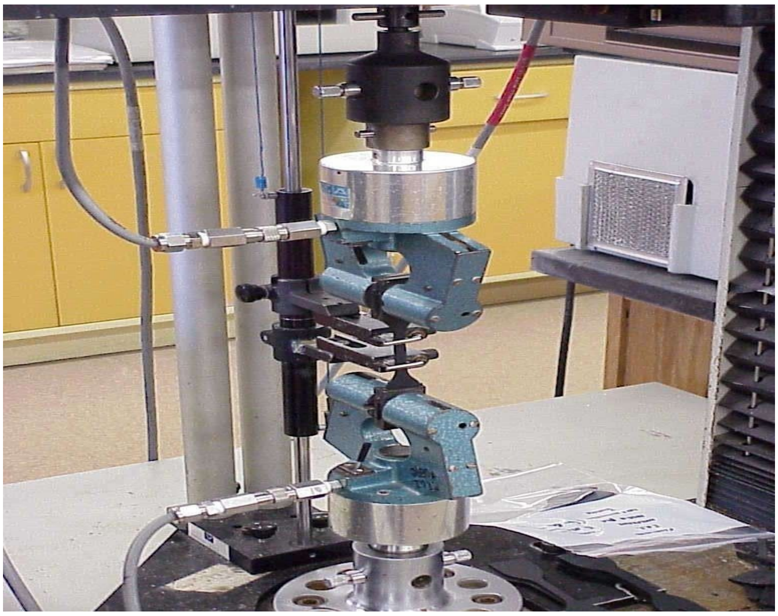


Figure3.2 Show Tensile Tests of polymer ASTM D412

3.4.3 Compression Set:

E Type Universal Testing Machine Zwick Roell E Type Universal Testing machine was used to determine the Load Deflection of polymer samples.

Fig 3.3 show E Type Universal Testing Machine used to determine the Load Deflection of polymer samples

3.4.4 Hardness

A Durometer Type Zwick Roell was used to determine the Hardness of irradiated polymer samples.

Fig 3.4 Zwick Roell Type A Durometer used to determine the Hardness of irradiated polymer samples.

Chapter Four

Results

The following chapter deals with highlighting of investigation the effect of high gamma irradiation doses in polymer waste an important advantage of using after completion of irradiations, the mechanical tests were carried out and the results were obtained. Results for the compression set, elongation at break, hardness, elastic modulus and strength are given below.

1.1 Compression Set:

Compression set (CS) test quantify the permanent deformation of a material after it is loaded to compressive forces for a determined time period

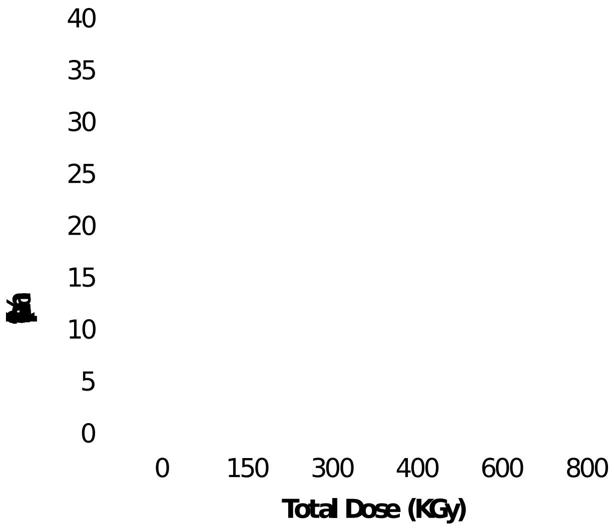


Fig 4.1 Compression set values of polymer sample which were irradiated

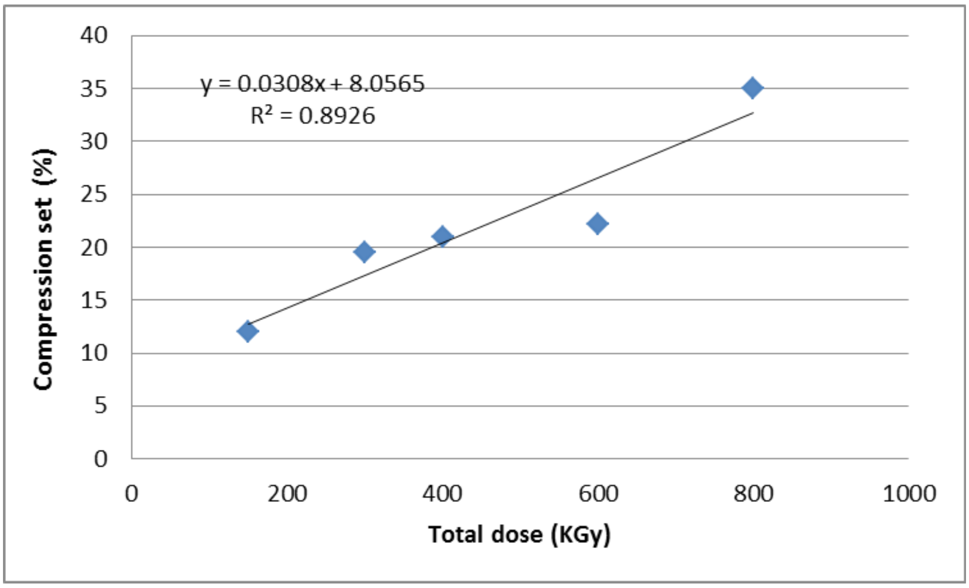


Figure 4.2 Shows linear change in compression set values of sample after 150 kGy

1.2 Elongation at Break:

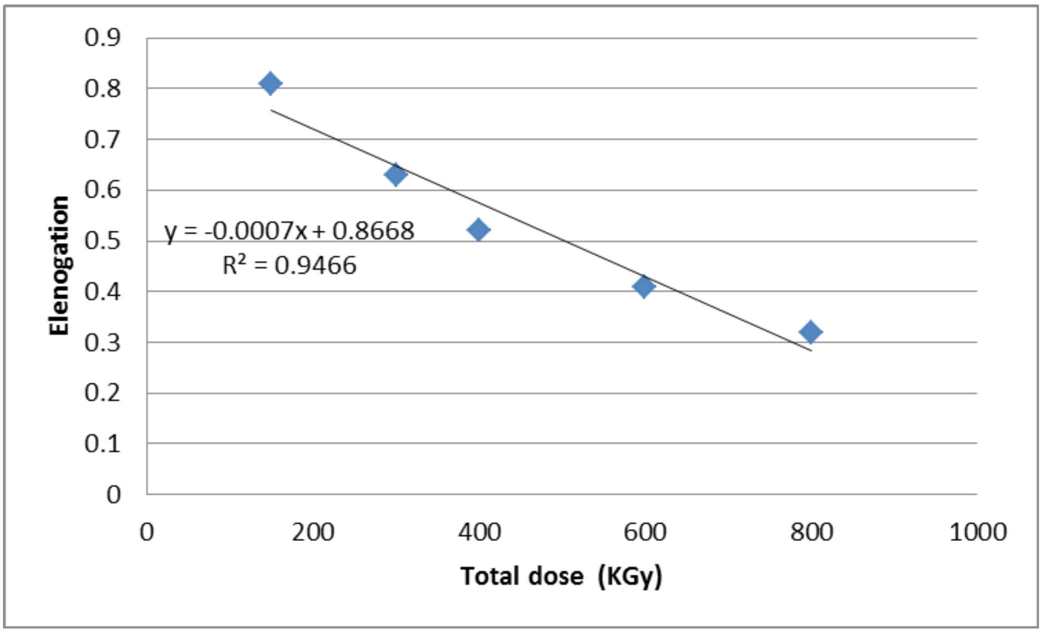


Figure 4.3 shows the correlation between the total irradiation dose in KGy and elongation at break results of polymer sample

1.3 Hardness:

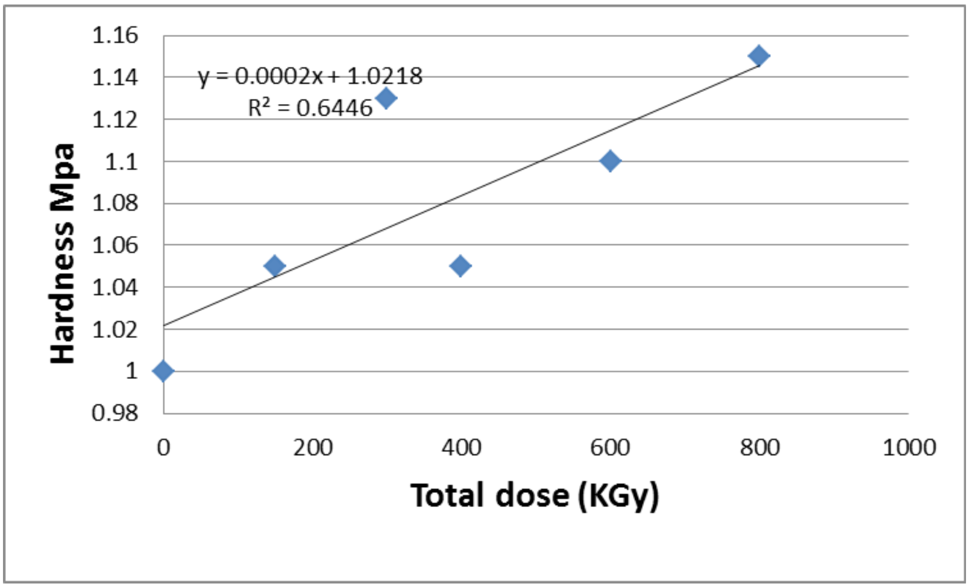


Figure 4.4 shows the correlation between the total irradiation dose in KGy and Hardness results of polymer samples

4.4 Elastic Modulus:

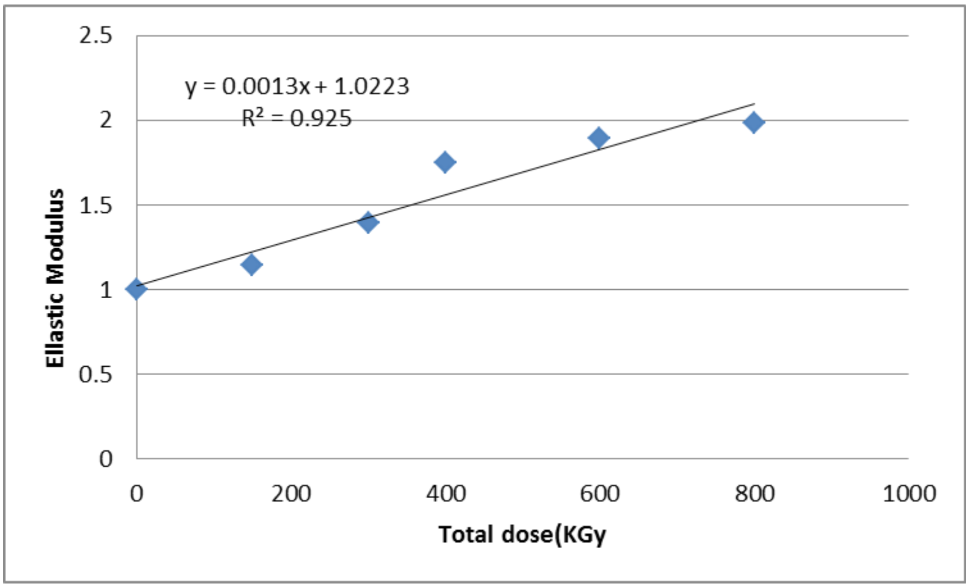


Figure 4.5 shows the correlation between the total irradiation dose in KGy and elastic modulus results of polymer sample

4.5 Strength Test:

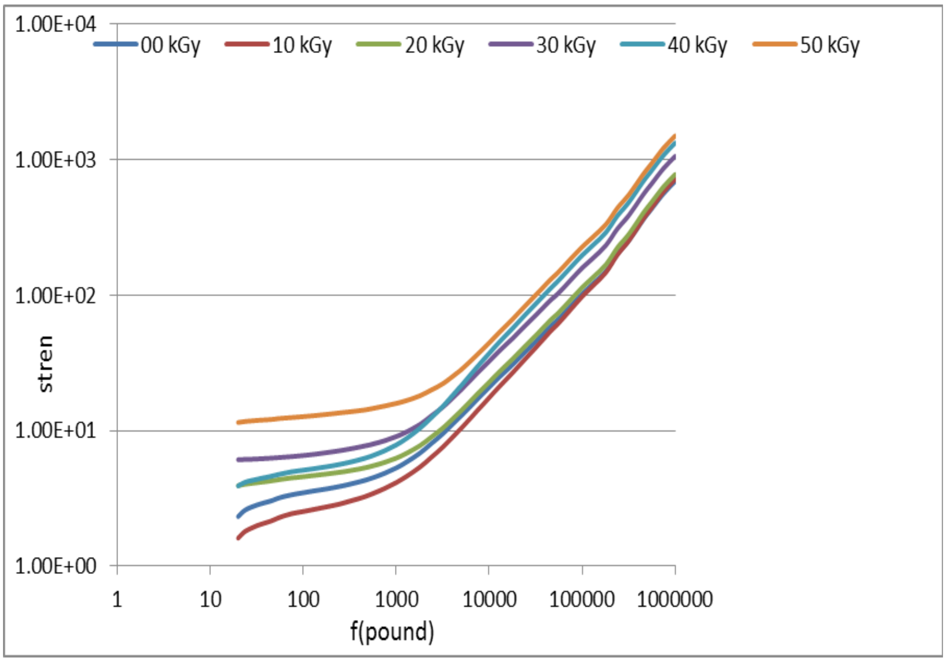


Figure 4.6 shows the change in the polymer waste propriety and the amount of gamma radiation dose

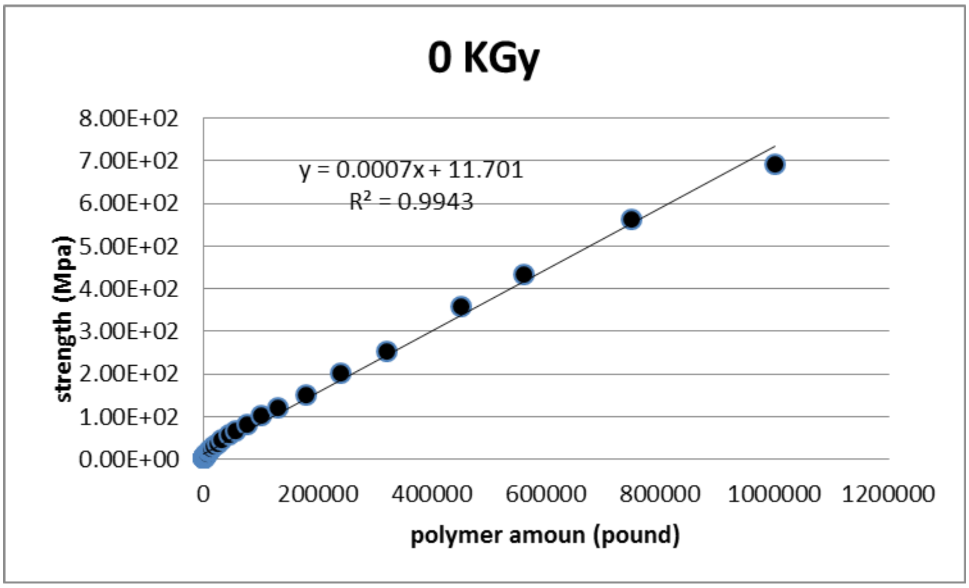


Figure 4.7 shows the correlation between the polymer strength and non-irradiated samples

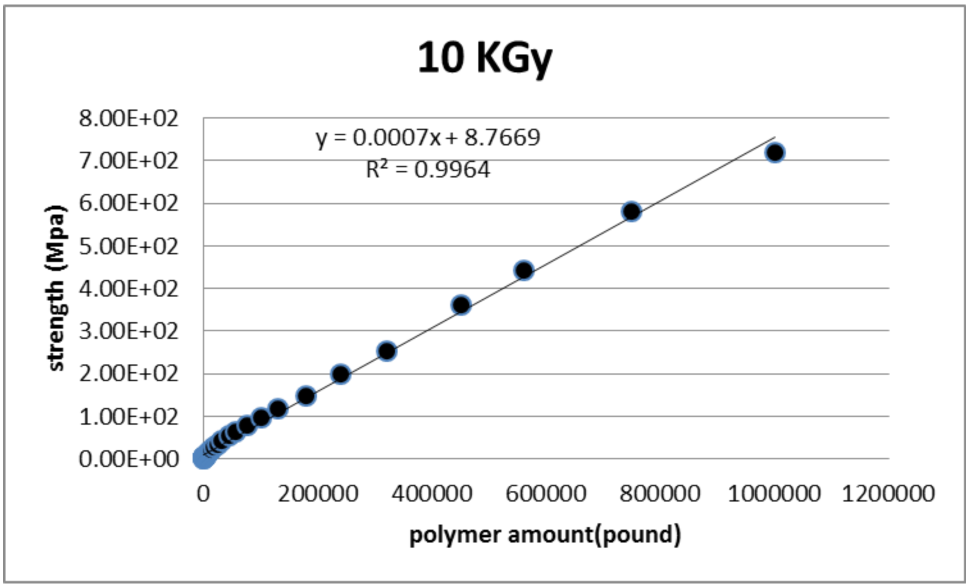


Figure 4.8 shows the correlation between the polymer strength and γ-radiation dose 10 kGy

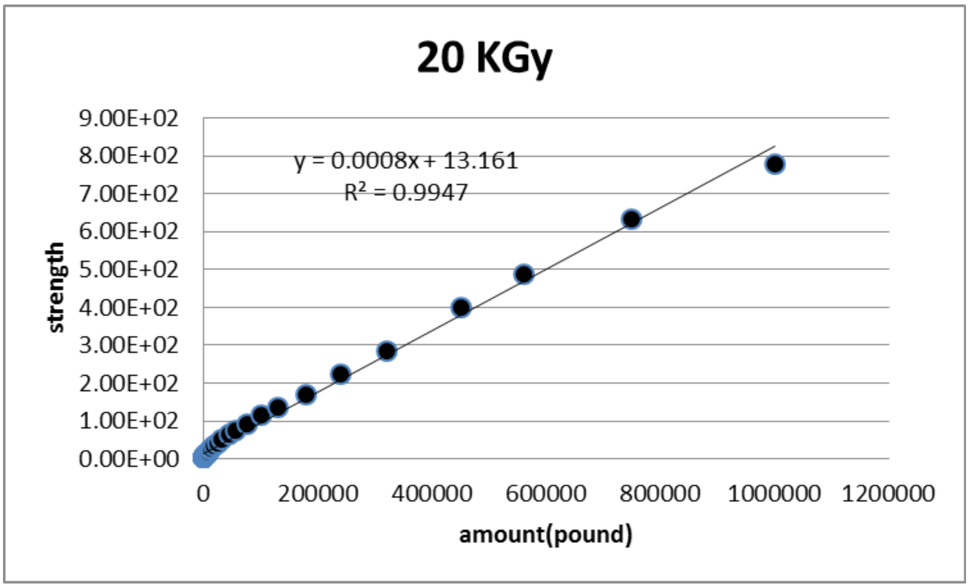


Figure 4.9 shows the correlation between the polymer strength and γ-radiation dose 20 kGy

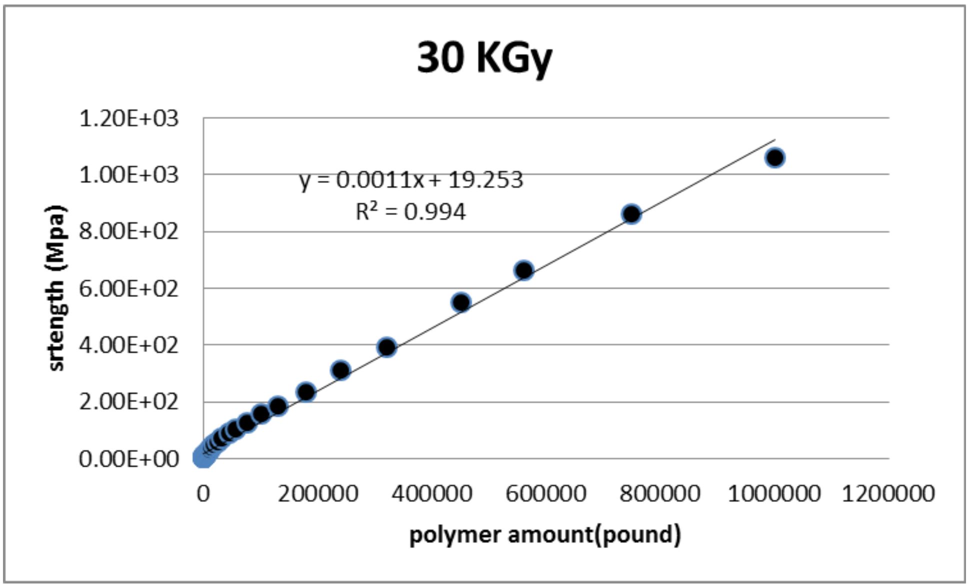


Figure 4.10 shows the correlation between the polymer strength and γ-radiation dose 30 kGy

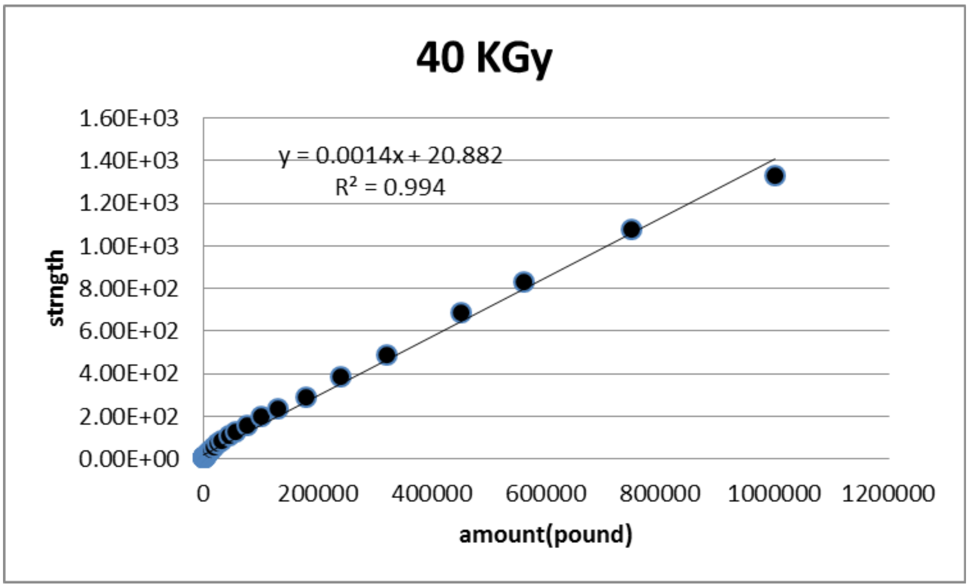


Figure 4.11 shows the correlation between the polymer strength and γ-radiation dose 40 kGy

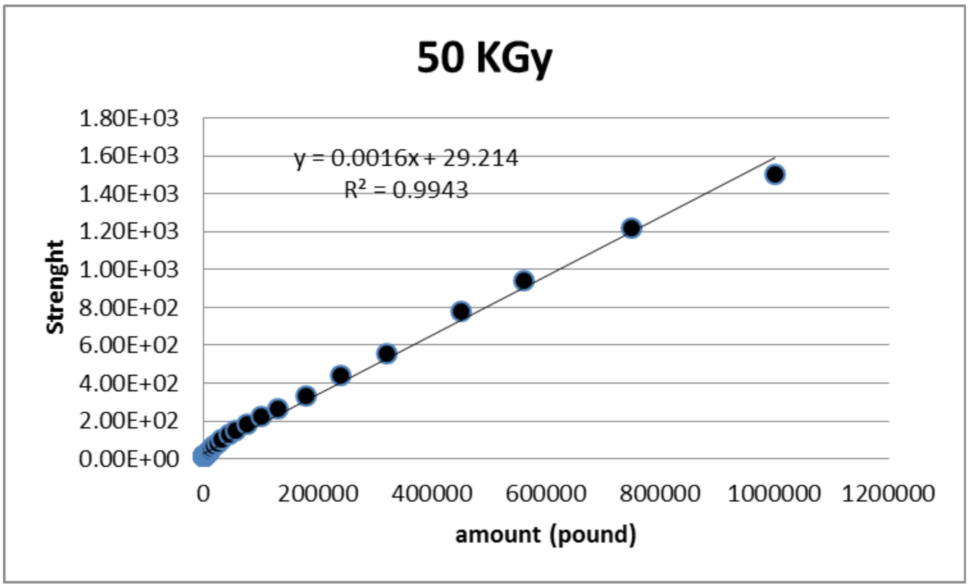


Figure 4.12 shows the correlation between the polymer strength and γ-radiation dose 50 kGy

Chapter five

Discussion, Conclusion and recommendations

5.1 Discussion

The following part is deal with result discussion as appear in chapter four:

The compression set analysis was carried out in order to assess whether polymer keeps its' elastic properties via irradiation, According to the compression set results of irradiated polymer samples, relative compression set values showed a decrease in the early stage of irradiation to total dose of 150 kGy in room temperature. After 150 kGy compression set values increased as total dose increase as shows in Figure (4.1).

The figure 4.2 showed the correlation between the γ-radiation doses 0-800 KGy and the compression set value. It showed that the compression is increase linearly with increasing of absorbed doses based on the following equation y= 0.0301x+8.1281 where y refers to the compression set in (Mpa) and x refers to the dose in KGy with a strongly correlation coefficient 0.94; indicating the increase in compression set results in increase in stiffness in the polymer structure via irradiation, irradiation affected the elastomeric properties of the polymer positively. At high doses CS values indicated that irradiation after 150 kGy increased the stiffness of polymer which became harder so radiation can explain 89.2%of compression. This result also has been reported by Placek et al, 2009.

According to the test results shown in and figure 4.3 increases in the total dose resulted in significant decrease in elongation at break values of the polymer samples. These decreases showed that there is a linear proportional correlation between the two parameters dose in KGy and polymer elongation, decreasing of elongation by 0.007Mpa/KGy, however it was found that relative elongation at break values of 0.41, 0.32 corresponds to 800 kGy, 500 kGy. The corelation of elongation is strong as $R^2 = 0.95$, the correlation could be fitted to the equation of the following form: $y= 0.0007x + 0.8668$. Where y refers to elongation value and x refers to the absorbed dose in KGy this result agree with Abiona et al, 2010.

Figure 4.4 showed the correlation between hardness of the polymer and total absorbed doses, the hardness of the irradiated samples increased up to 300 kGy. After 300 kGy, reduction in the hardness was observed up to 400 kGy. After 400 kGy, the hardness of samples increased up to 800 kGy which was the maximum doses that we applied. Hardness is inversely related with elasticity. Increase in hardness resulted in loss in the elasticity in the polymer structure. Up to 300 kGy, increase in hardness value was probably due to additional crosslinking. After 300 kGy, decrease in hardness was observed. Hardness values at 150 kGy and 400 kGy were the same. This means that between 150 kGy and 400 kGy, constructive (rearrangement of scissed part) and destructive reactions (chain scission) occurred probably to same extent according to the International Atomic Energy Agency reports11180. (IAEA, 2000)

Figure 4.5 shows the correlation between absorbed dose in KGy and the relevant elastic, for irradiated doses in the range of 0-800kGy, It shows that there is a linear proportional correlation between the two parameters (dose in KGy and elastic modulus), The correlation could be fitted to the equation of the following form: $y = 0.0013x + 1.0223$, where y refers to elastic modulus and x refers to the total dose in KGy, 0.96 strong correlation as $R^2= 0.93$.

Figure 4.6 show the change in the polymer waste propriety after irradiation with γ-radiation doses (10-50) kGy. It showed that the irradiated polymer strength have increased when the doses increase with the correlation $R^2 = 0.99$ as shown in figure 4.7, 4.8, 4.9 and 4.12

5.2 Conclusions

According to results of experimental investigation of this study, following conclusions can be revealed:

- Irradiation rate is an important parameter and it is well known that the irradiation rate lead different effects for the same polymer with equal amount of total absorbed dose. If the irradiations are made open to the atmosphere, the diffusion limited oxidation became a critical factor for the radiation-induced effects on the polymers.
- Increase in compression set, hardness, elastic modulus and decrease in elongation at break, maximum stress at break values at higher doses could be also explained.
- Compression set values showed a decrease in the early stage of irradiation to total dose of 150 kGy in room temperature. After 150 kGy compression set values increased as total dose increase.
- Increase in the total dose resulted in significant decrease in elongation at break values of the polymer samples. These decreases showed that there is a linear proportional correlation between the two parameters dose in KGy and polymer elongation.
- The correlation of polymer elongation is strong as $R^2 = 0.95$, the correlation could be fitted to the equation of the following form: $y= 0.0007x + 0.8668$. Where y refers to elongation value and x refers to the absorbed dose in KGy.
- The hardness of the irradiated samples increased up to 300 kGy. After 300 kGy, reduction in the hardness was observed up to 400 kGy. After 400 kGy, the hardness of samples increased up to 800 kGy which was the maximum doses that we applied. Hardness is inversely related with elasticity.

- There is a linear proportional correlation between the two parameters (dose in KGy and elastic modulus), the correlation could be fitted to the equation of the following form: $y = 0.0013\ x + 1.0223$, where y refers to elastic modulus and x refers to the total dose in KGy, 0.96 strong correlation as $R^2 = 0.93$.

5.2 Recommendations

This research could consider an initial study for managing polymer waste by radiation in Sudan, accordingly we recommend by the following recommendations:

- We recommend using modern techniques to synthesize the polymer with suitable uses.
- Further work is needed to support this research especially for changing in propriety of polymer by using gamma irradiation.
- Irradiation holds promise for impacting the polymer waste problem.
- Treatment of polymer waste using gamma irradiation causing or enhancing the decomposition of polymers.
- Production of advanced polymeric materials designed by irradiation for environmental compatibility.
- Gamma irradiation is used for the final biological sterilization of materials that can be subsequently used for manufacturing biomedical products.

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