

Reviewing of General Polymer Types, Properties and Application in Medical Field

Nuha Salih Mustafa¹, Mohammed A. Ali Omer^{1,2}, Mohamed E. M. Garlnabi¹, Hamed A. Ismail³

¹College of Medical Radiologic Science & Technology-Department of Radiotherapy & Nuclear Medicine-Sudan University of Science & Technology- Khartoum –Sudan.

²College of Applied Medical Science-Department of Radiologic Technology- Qassim University – Buraidah – KSA

³College of Applied Medical Science-Department of Radiologic Science – Najran University – Najran – KSA

Abstract: Multiple biological, synthetic and hybrid polymers are used for multiple medical applications. A wide range of different polymers is available, and they have further the advantage to be tunable in physical, chemical and biological properties in a wide range to match the requirements of specific applications. This review gives a brief overview about the introduction, polymer types, properties and developments of polymers in medicine in general, addressing first stable polymers, then polymers with degradability as a first biological function, followed by various other functional and responsive polymers. There is subsequently an overview of the most frequently used polymer classes. The main body of the review then is structured according to the medical applications, where key requirements of the applications and the currently used polymer solutions are indicated.

Keyword: Polymer, Properties, application in Medical Field, Review

1. Introduction

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 (McCrum et al 1997)

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)

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). The trend of the following review is to highlight the general polymer types, Properties and their application in medical field.

2. Literature Review

2.1 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 (1).

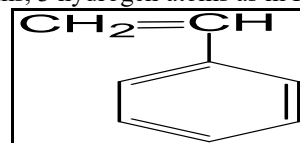


Figure 1: Shows the chemical structure of monomer styrene (M S) (Young, R. J. (1987), Clayden, J. et al 2000)

Polystyrene are made up from the repeating unit each one consists of 4 monomer styrene unit and the structural formula of polystyrene is usually written as shows in Figure (2) or (3).

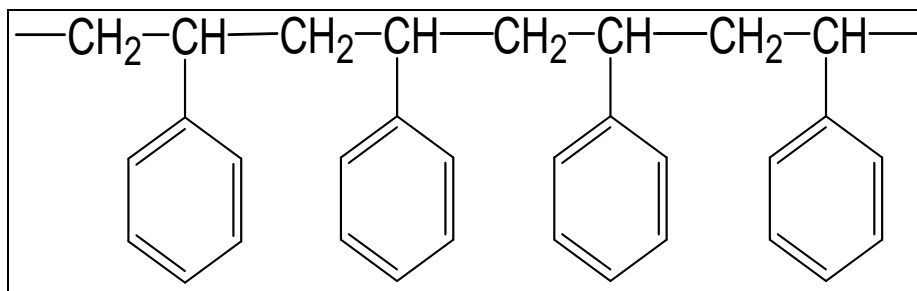


Figure 2: Shows the chemical structure of polystyrene (PS) (Young, R. J. (1987), Clayden, J. et al 2000)

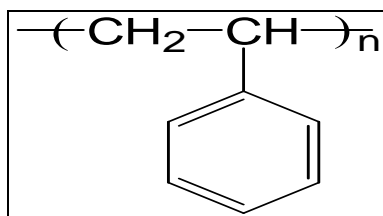


Figure3: Shows the structural formula of polystyrene where n is the number of repeating units in the polymer Young, R. J. (1987), Clayden, J. et al 2000)

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 (4)

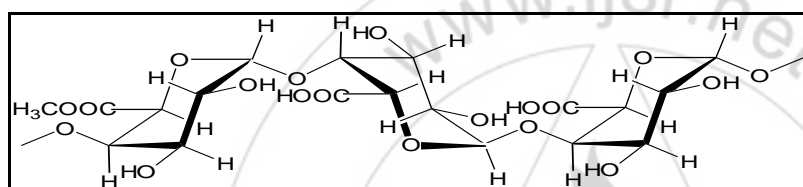


Figure 4: Shows chemical structure of biopolymers (Clayden, J. et al 2000)

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 are presented in table (1).

Table 1: Show some common addition polymers and their relevant monomers names and chemical structure

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

Molecular Architecture

The shape of the polymer molecule is important for many of its properties as show in Figure (5).

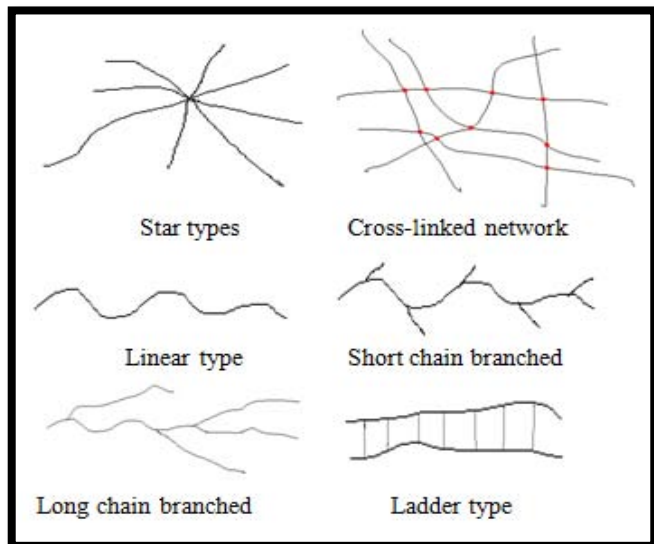


Figure 5: Show the polymer architecture (a) linear b.Short-chain branched (c) long chain branched (d) ladder (e) star branched (f) cross linked network (Clayden, J. et al 2000)

2.2 Polymers Classification

Polymers are classified in different types on different basis as in the following enumeration, Classification based on the source of origin, which is classified in three types:

- **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.

- **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.

- **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.

The classifications based on the structure are three types of polymers as follows:

- **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.

- **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 $-\text{CH}_3$), amylopectin and glycogen.

- **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.

The classifications based on polymerization process are two types as follows:

- **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.

- **Condensation polymers:**

They are formed by the combination of two monomers by removal of small molecules like water, alcohol or NH_3 . 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.

The 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.

- 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) **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.

- 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.

- 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.

The classification based on the homogeneity of Polymers:

Pectin Homopolymers and copolymers; Homopolymers consists of only one type of repeating unit, e.g. polymer (A) copolymers are polymers consisting of more than one type of repeating unit as in Figure (6).

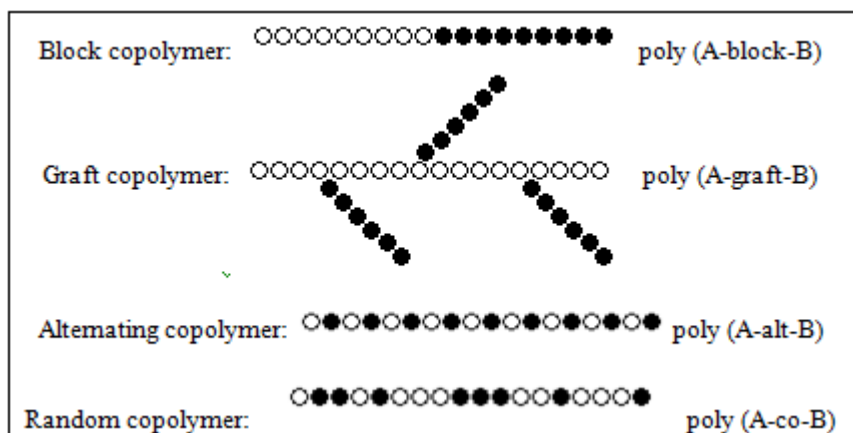


Figure 6: Shows the types of common copolymers chemical structures (Clayden, J. et al 2000)

The classification based on growth polymerization, implies two types:

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. polyethylene

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 NH₃, H₂O and HCl. It is possible when the monomer have more than one functional group. It proceeds through the formation of dimer, trimer, tetramer, etc. e.g. Dacron. U

2.3 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 (Baeurle, 2009).

2.3.1 Polymerization

Polymerization is a process in which 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 (7).

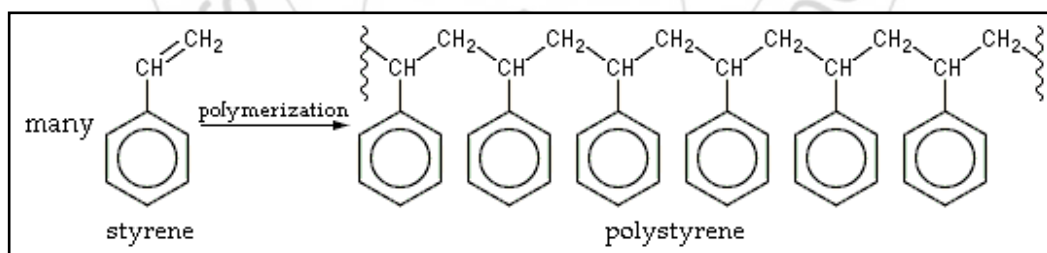


Figure 7: Show an example of alkene polymerization, in which each styrene monomer's double bond reforms as a single bond plus a bond to another styrene monomer. The product is polystyrene (Jenkins, A. D et al 1996)

The polymerization could be achieved by different methods or techniques each have its own advantages and disadvantages and the formed polymer can be in different forms called homo polymer and copolymer depending on the monomer compositions link together.

• **Physical polymerization**

The physical polymerization implies two types, which are commonly applicable in experimental and industries fields:

Ionizing Radiation polymerization:

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. The good

example for such technique is the study presented by Rosiak et al, 2000, and Kassem et al, 2002.

Non ionizing radiation polymerization (Ultraviolet radiation):

Non ionizing radiation polymerization reactions are chain-growth polymerizations which are initiated by the absorption of visible or ultraviolet light. The light may be absorbed either directly by the reactant monomer (direct photo polymerization), or else by a photosensitizer which absorbs the light and then transfers energy to the monomer. In general only the initiation step differs from that of the ordinary thermal polymerization of the same monomer; subsequent propagation, termination and chain transfer steps are unchanged. (Allcock et al, 2003)

In step-growth photo polymerization, absorption of light triggers an addition (or condensation) reaction between two comonomers that do not react without light. A propagation cycle is not initiated because each growth step requires the assistance of light. Photopolymerization can be used as a photographic or printing process, because polymerization only occurs in regions which have been exposed to light. Unreacted monomer can be removed from unexposed regions, leaving a relief polymeric image. Several forms of 3D printing, including layer by layer stereolithography and two-photon absorption 3D photopolymerization, use photopolymerization. (Soto et al, 2014).

• Chemical polymerization:

The chemical mechanism that cells use to make and break polymers are basically the same in all cases, Monomers are connected by a reaction in which two molecules are covalently bonded to each other through loss of a water molecule; this is called a condensation polymerization because the lost molecule is water. When a bond forms between two monomers, each monomer contributes part of the water molecule that is lost; one molecule provides a hydroxyl group, while the other provides hydrogen. To make a polymer, this reaction is repeated as monomers are added to the chain one by one.

Polymers are disassembled to monomers by hydrolysis, a process that is essentially the reverse of the dehydration reaction. 'Hydrolysis,' from Greek, means to 'break with

water.' Bonds between monomers are broken by the addition of water molecules, a hydrogen from the water attaching to one monomer and a hydroxyl attaching to the adjacent monomer. The process of digestion in our bodies is an example of hydrolysis. The bulk of the organic material in our food is in the form of polymers that are much too large to enter our cells. Hydrolysis helps to break these polymers into absorbable bits within the digestive tract.

Some common polymers in life are:

- Disaccharides and polysaccharides like maltose, sucrose, and glycogen.
- All protein made from amino acid.
- Nucleic acid, like DNA and RNA made from a nucleotide.

Some common commercial condensation polymers are:

- Polyurethane.
- Polyethylene terephthalate (polyester).
- Nylon 6,6.

2.3.2 Polymers Properties

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) in the monomer units. Polymers containing (amide) or (carbonyl) groups can form (hydrogen bonds) 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 (Duarte, 2003), which could be ascertained by polymerization interaction i.e. increasing of molecular weight as for instance as show in Figure (8).

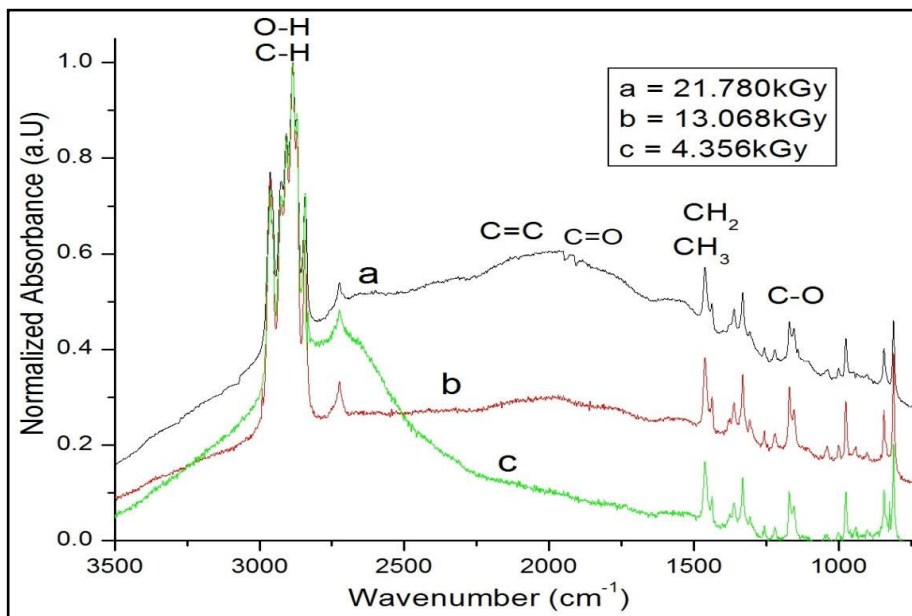


Figure 8: Raman spectra showing the effects of irradiation on iPP

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 types of lasers that also belong to

the class of organic lasers are known to yield very narrow line widths which are useful for spectroscopy and analytical applications. An important optical parameter in the polymer used in laser applications is the change in refractive index with temperature (Duarte, 2003). The optical properties were studied by UV-Vis Spectroscopy as shown in Figure (9).

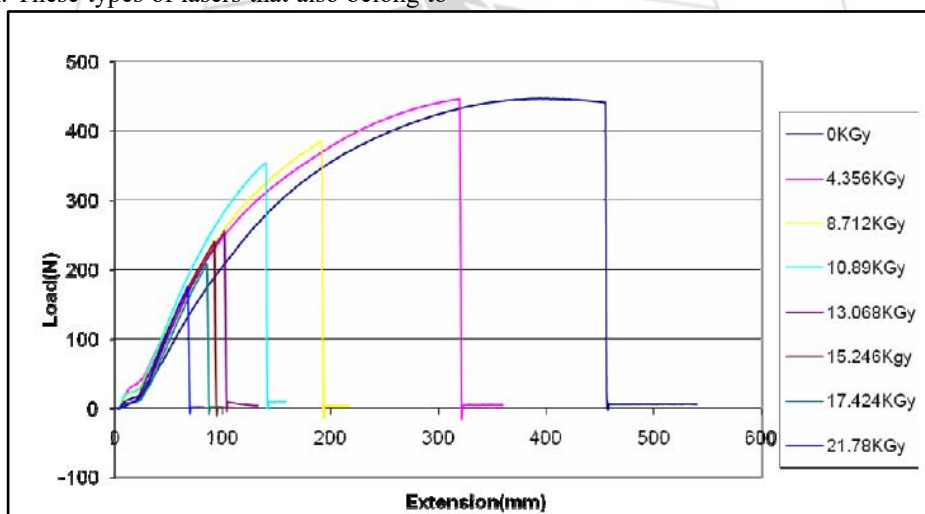


Figure 9: Shows the effect of irradiation on the elongation at fracture of PP (Abiona and Osinkolu, 2010)

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 as show in Figure (10) Or (11)(Campbell et al, 1989).

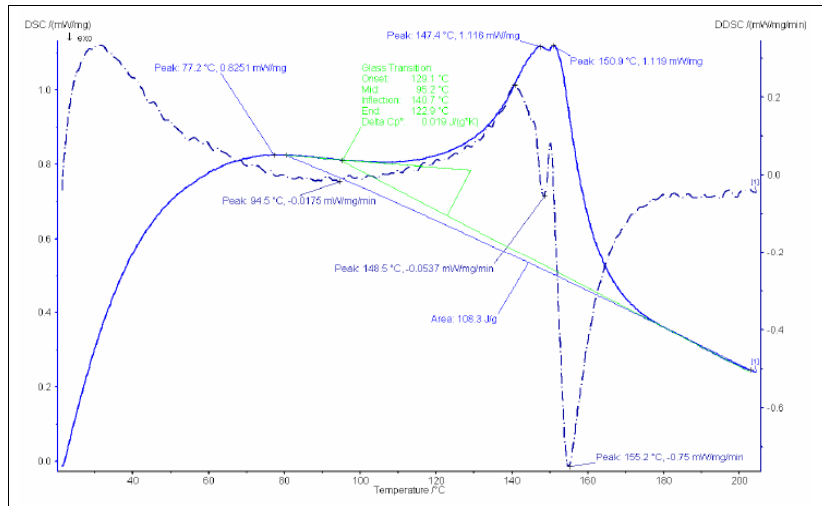


Figure 10: Shows the Differential scanning calorimetric thermogram showing the second emerging peak at 21.780 kGy dose (Lu et al., 2002)

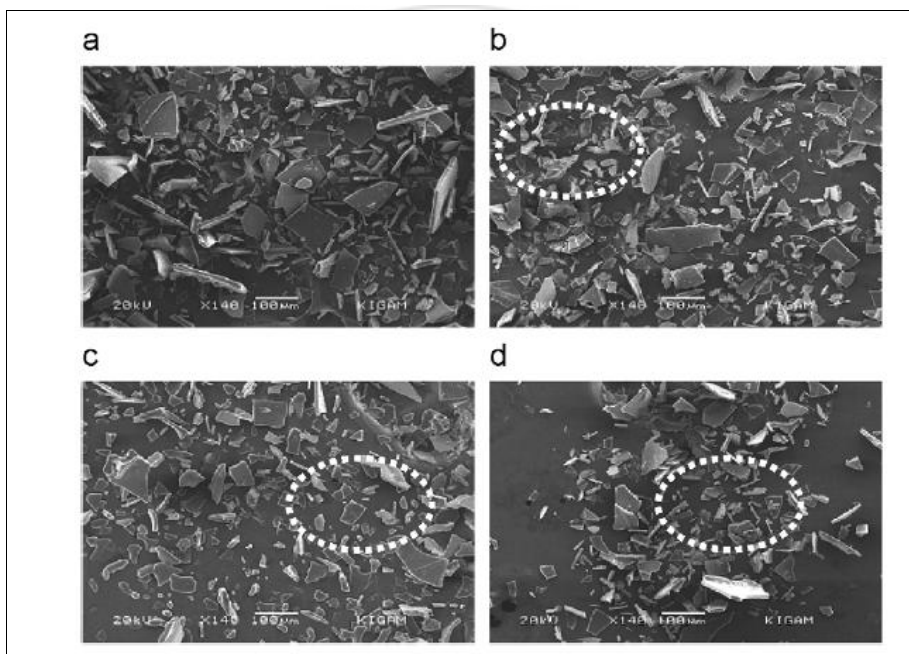


Figure 11: Shows the scanning electron microscopy (SEM) images of b-glucan irradiated at different doses; (a) 0 kGy, (b) 10 kGy, (c) 30 kGy, and (d) 50 kGy. Small particles within oval dots indicate the deformed granules of b-glucan after its exposure to different doses of gamma irradiation. (Eui et al, 2008)

Mechanical Properties:

The characterization of mechanical properties in polymers typically refers to a measure of the strength of a polymer film. The tensile strength and Young's modulus of elasticity are of particular interest for describing the stress-strain properties of polymer films as in figure below. 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 as show in Figure (12). (Campbell et al, 1989)

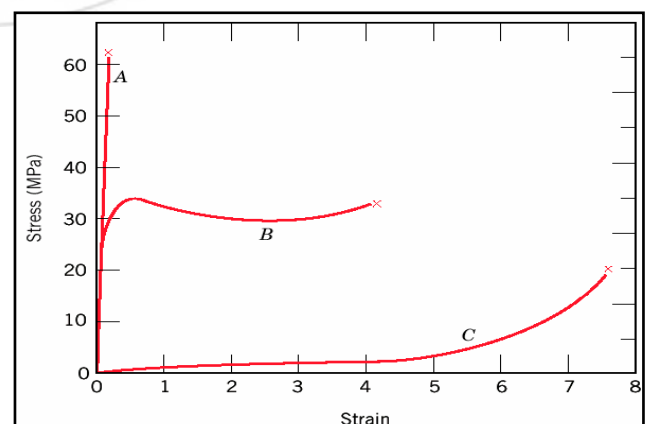


Figure 12: Shows Polymers can be brittle (A), plastic (B), or highly elastic (C). Deformation shown by curve C is totally elastic (rubber-like elasticity, large recoverable strain at low stress levels). These lass of polymers - elastomers

3. 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:

3.1 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 (13). (Breitbart et al, 2007)



Figure 13: (a) Normal joint Figure (b) replacement of the joint is required (c) 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 polymethyl methacrylate) to fix the components and to transfer the stress more uniformly as show in Figure (14).



Figure 14: Show artificial joint has a sliding interface

3.2 Polytetrafluoroethylene (PTFE)

PTFE (Teflons) has an ethylene backbone with four covalently bound fluorine molecules. It is a highly hydrophobic non-degradable material. It's mainly applied as vascular graft as show in Figure (15). (Breitbart et al, 2007)

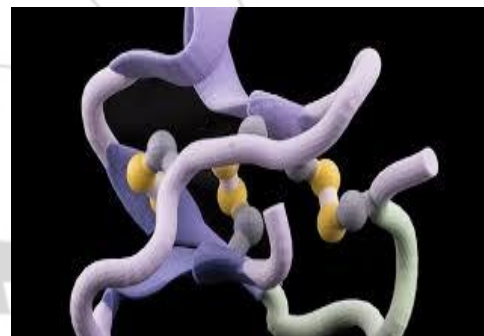


Figure 15: Show the artificial vascular veins

3.3 Polyvinyl chloride (PVC)

PVC has an ethylene backbone with 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. (Folarinet al, 2011)

3.4 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)

3.5 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 (Plexiglass) and inertness in the eye, they are also used as intraocular lenses as shown in figure 16.



Figure 16: Show the artificial lenses

3.6 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 in form of membranes, filaments and meshes. (Hofmann, 1996)

3.7 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)

3.8 Polyamides

Naturally, all proteins consist of units linked 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)

3.9 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)

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