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Polymers Degradation

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Abstract: Degradation is usually an unwanted process. But, in some cases, controlled polymer degradation is useful. As it can improve the processability of the polymer or it can be used in the recycling or natural decomposition of waste polymer. Polymeric degradation is a physico-chemical process, that involves physical and chemical phenomena. This differs from the metallic corrosion reactions which are electrochemical.

Keywords: *Polymers, physico-chemical failure, degradation, biodegradation.*

Introduction

Generally, degradation is the act of reducing something or someone to a less respected state. Degradation in polymer science is “a complex process by which a polymeric material exposed to the environment and workload loses its original properties”. Degradation occurs by the action of heat, stress, radiation, oxidation, hydrolysis or chemical and biological agents to an extent that alter the material’s properties and compromise its function. In most of the cases, the cleavage of macromolecules is a basic part of the polymer degradation. Therefore, the breakage macromolecules into fragments of several structures and sizes is often referred to as polymer degradation. However, if monomer(s) are the final product, then the process is called depolymerization, since it is the opposite of polymerization ^{1,2}. Biodegradation is the change in the polymer’s physical and chemical properties induced by organisms, isolated enzymes or by the action of the oral environment ².

Degradation Mechanism of Polymers

Several polymer networks are known to have a moderately high chemical and thermal stability due to its large insoluble structures. Despite of this, these networks have the ability of absorbing water and chemicals from the environment, resulting in the dissolution of these networks. The occurrences of sorption and solubility act as forerunners to chemical and physical changes that has a permanent negative effect on the the structure and function of the polymers, in addition it shows some biological concerns. As a results, vol-

umetric changes such as swelling, physical changes such as plasticization and softening, and chemical changes such as oxidation and hydrolysis may occur, which compromise the function of these polymers. ³

a. Sorption

1. Quantity

Dimethacrylate monomers form a dental polymer network that has the ability to absorb aqueous solvents to certain percentage of their total weight. Water sorption is proved to follow Fickian diffusion kinetics. Sorption was found to be greater in ethanol/water solutions than that of water. However, water sorption was lower in materials which highly filled, with a rate of uptake and time to reach saturation almost equal to those unfilled. When

comparing the water sorption of resin-modified glass ionomers, compomer and composite after 9 months in artificial saliva, the results revealed that the resin-modified glass ionomers showed the higher water sorption of 7.0%, followed by compomer 1.2% and composite showed the least by 0.17%. The process of water uptake of composites and resin cements may continue up to 6 months, however most materials reach the saturation level after 7–60 days. As a conclusion, water sorption depends mainly on the chemistry and nature of the monomers. Therefore, water sorption was greater for Bis-GMA-based resins compared to ethoxylated Bis-GMA (Bis-EMA) resins that showed the lowest due to the absence of the hydroxyl groups of Bis-GMA. Additionally, higher concentrations of TEGMDA in Bis-GMA resins lead to higher water uptake due to the hydrophilic ether linkages of TEGDMA.⁷

2. Swelling

This type of degradation occurs when the polymers are subjected to liquids. The liquid starts to diffuse and be absorbed into the polymer. Swelling occurs when the polymer is partially soluble in the solvent, whereas dissolution is the complete dissolution process, or in other words the swelling continuation. The small liquid molecules squeeze themselves between the polymer molecules, that force the macromolecules to be pushed apart. That leads to the expansion or the swelling of the polymer.³ Nevertheless, the presence of porosity and free volume between chains, especially in the region near crosslinks within the polymer network, may lead to the absorption of water without volumetric change theoretically. However, decrease in volumetric change may occur as a result of the leaching out of unreacted components. Therefore, the dimensional changes depend on the material's structure.⁷ In addition, the polymer becomes softer and more ductile due to the increase in the chain separation that decreased the secondary intermolecular bond. The solute also influences the glass transition temperature of the polymer to the extent that it can change a once strong polymer into a rubbery and weak especially when placed at a temperature lower than its ambient temperature.⁷

Factors that affect swelling and dissolution:

a. The chemical structure:

The more the polymers and solvent chemical structures are similar to each other, the more it is expected for this polymer to swell and/or dissolve.

b. Temperature & molecular structure:

As the molecular weight increases, the degree of crosslinking and crystallinity increases and therefore the resulting degradation will be decreased as the temperature is lowered. For example, in a study that compared the volumetric change after water storage after 2 months between composite core material and resin-modified and glass ionomers, revealed that composite core showed an increase in volume by 0.4–1.0% which was less than resin-modified and glass ionomers which showed 5 or 8% increase. In another study, also showed an increase in volume after 2 years in water by 0.5% in dental composite when compared to composite cement and compomer, 1.1% and 2.26% respectively. This volumetric expansion may lead to the development of stresses on the interfacial bonds with the cavity wall in rigid material, that may eventually lead to the falling of the restoration from the cavity.⁷

3. Plasticization

The solvent effect on the polymer network is known as plasticizing. The solvent molecule acts as a space occupier, which prevents the formation of primary bonds between the chains and decreases the interchain interactions such as entanglements and secondary bonding. As a result, separation of the chains will occur, leading to the decrease of hardness and other properties. The effect of softening will begin at the surface, which will significantly affect the hardness and wear and will then progress into the bulk networks at the slower rate affecting the bulk properties. The rate of softening depends on the rate of solvent uptake, which starts immediately, and it might take up to one to two months to reach the maximum when the polymer network is completely saturated.⁷

b. Solubility

1. Species

The dimethacrylate monomers form a crosslinked polymer network through free radical polymerization, yet unreacted monomers such as polymerization promoters and oligomers exist. Also, ions from the filler particles may be leached out in filled polymers. These unreacted monomers and ion can be degraded from the network and cause a biological drawback. Examples of leachable by-products from dental resin are methacrylic acid, formaldehyde, and specific methacrylate molecules. Therefore, as a conclusion any set material such as composite and adhesive resin can undergo degradation and elution of its components such as the photo-initiators. They can undergo degradation in alcohol or organic solvents and water; however, water shows lower values of leached components. Also, it was found that monomers and plasticizers were released from uncross-linked polymers such in denture base, reline, soft liner and tissue conditioning materials. ⁷

2. Quantity

As the unreacted methacrylate groups is reacted on one end of dimethacrylate molecules, which is covalently bonded to the main polymer chain in dental restorative resins, sealants, and adhesives, therefore they will not leach out in aqueous environments. However, unreacted monomer and small chain polymer was found significantly leached. Amounts of released components vary from 0.05% to 2.0% of the weight of the specimen and even higher when placed in alcohol and other organic solvents, 2–6%. Other studies also revealed higher percentages of elution up to 10% of the unreacted monomer in dental composite. The leaching out process is rapid for most species that may take 1–3 days to be completed from set resins. On the other hand, leaching of very small concentrations may take 1 week as in case of Bis-GMA. The rate of elution depends on the surface area and the light-curing process. However, the monomer elution does not continue for a long period due to presences of small concentrations and the rapid rate of release. ⁷

Polymer Erosion

Polymer erosion indicates the loss of material due to the release of the monomers and oligomers from the polymer. The erosion of a degradable polymer is considered a complicated process, as it depends on several processes, such as degradation, swelling, the dissolution and diffusion of oligomers and monomers, in addition to morphological changes. However, degradation is considered the most important process of erosion. Molecular weight loss, weight loss and geometric changes all are indication of erosion. Therefore, the mechanism of erosion degradable polymers should be understood to be able to use these materials successfully, such as in tissue engineering and drug delivery. ⁵

Types of erosion:

1. Surface (or heterogeneous) erosion

This occurs when the degradation of the polymer bonds is faster than the diffusion of water, it will be consumed by the hydrolysis of bonds on the polymer surface, preventing diffusion into the bulk. ^{4,5} In this type of erosion, the polymers get smaller due to the loss of the surface material only, while maintain its original geometric shape. ⁵ Erosion occurs at a constant rate throughout the process. ^{4,5} One of its advantages is that the erosion process is predictable. Therefore, this can be useful in case of drug delivery, where the rate of erosion can indicate release of drugs. ⁵

2. Bulk (or homogeneous) erosion

This occurs when the diffusion of water into the polymer is faster than the degradation of polymer bonds, as the degradation is not restricted to the polymer surface. ^{4,5} In bulk erosion, the polymers erosion is not just limited to the surface. As a result, the size will not change for a significant period during its application. The situation is more changeling for bulk eroding polymers since their erosion velocity is not constant. ⁵

Morphological changes during erosion

The morphological changes during erosion were first limited on the surface of the polymer, revealing cracks and surface roughness. As the erosion process continues, the polymers become a more porous structure. There are two types of pores: macropores with a diameter of approximately 100 μm which originate because of the crack formation and micropores with a diameter of approximately 0.1 μm which originate because of polymer bulk erosion was observed in poly(anhydrides). The crystallinity of the polymer has an effect on the rate of erosion. Where, the crystalline skeleton of an eroded spherulitic skeleton shows regions of erosion at the amorphous parts of the spherulite and the crystalline skeleton is still retained.⁵

Types of polymer degradation

Polymers start to degrade when active centres are formed in it. The dominant active centres of degradation are radicals that are created in a polymer thermally, photochemically, mechanochemically or by any oxidation process. Therefore, the type of initiation is used as an adjective denoting the type of polymer degradation². Polymers may show two types of degradation, either (i) hygroscopic degradation by absorption of a liquid solvent followed by dimensional changes, or (ii) covalent bond rupture induced by heat, electromagnetic radiation (mainly ultraviolet), chemical dissolution into a solvent (hydrolytic) or oxidation reactions⁶. In hydrolytic degradation, there are two principal ways by which polymer bonds can be cleaved: passively by hydrolysis or actively by enzymatic reaction⁴. Enzymatic degradation is only available for naturally occurring biopolymers like polysaccharides, proteins (gelatin and collagen) where appropriate enzymes are available⁵. Passive hydrolysis is the most important mode of degradation for most artificial polymers⁵.

i. Hygroscopic degradation

Regarding water diffusion in polymers, two main models have been discussed. The first one is the free volume theory which assumes that water penetrates resin matrix through nanopores and remains as unbound water between the chains without any chemical reaction. The second model is the interaction theory which suggests that water diffuses through the material and binds to hydrophilic groups by Vander Waals or hydrogen bonds. The absorbed water is found as bound water, which is attached to polymer chains^{3,6}. The water uptake and swelling is encouraged by the presence of hydrophilic groups such as (ether linkages in TEGDMA, hydroxyl groups in Bis-GMA, urethane linkages in UDMA, and the presence of ester groups in all)³.

Consequences of hygroscopic degradation

1. Plasticization because water molecules penetrate into the spaced between chains and the macromolecules are forced apart reducing secondary intermolecular bonding forces and entanglements, therefore, the polymer becomes softer and more ductile. This, in turn, increases the probability of polymer fatigue failure because crack growth becomes easier³.
2. Extrinsic discoloration and aesthetic failure due to ingress of stains with water molecules³.
3. Changes on the physical and mechanical properties such as decreasing the glass transition temperature, flexure strength, hardness and fatigue limit³.
4. Dimensional changes (usually swelling) accompany water sorption. This results in stress build-up at the bond interface between denture base resin and relining materials decreasing the bond strength between them³.

N.B: The dimensional change of a polymer network in a solvent is difficult to predict, and is very material dependent because: i. The polymer network contains porosity and free volume between chains, so, it is theoretically possible for water to be absorbed without creating a change in volume. ii. Water uptake is accompanied by a loss of unreacted components that would cause a reduction in volume⁷.

5. Biological failure due to leaching out of unreacted components and residual monomers that may elicit inflammatory reactions, chemical irritation to the oral mucosa, labial oedema, ulcerations or burning mouth syndrome and denture stomatitis ⁶.

ii. Covalent bond rupture (Scission)

Chain scission is a term used in polymer chemistry describing the degradation of a polymer main chain. It is often caused by thermal stress (heat) or ionizing radiation (e.g. light, UV radiation or gamma radiation), hydrolysis or enzymes. During chain cleavage, the polymer chain is broken at a random point in the backbone to form two highly molecular fragments to some extent ⁸.

Mechanisms of Covalent bond rupture ⁸

1. β -chain scission:

It is the rupture of the carbon-carbon bond at a molecular chain end and accompanied by free radical release.

2. α -chain scission:

It is the breakage of the bond between a carbon and a functional group along the chain backbone.

3. Oxidation:

It is the breakage of the double bond along the polymer chain.

N.B: The mechanism of chain attack or bond rupture depends on several factors as; presence of impurities which may be catalyst, solvent or any incorporation during the polymerization reaction. Or a result of physical or chemical treatment.

Consequences of covalent bond rupture

1. Reduction in the molecular weight due to chain separation at the point of bond breakage, subsequently, decreases the mechanical strength and resistance to chemical attack (because many polymer properties depend on the molecular weight of polymer chain) ^{3,8}.
2. Oxidative degradation by ultraviolet rays may cause chain crosslinking and embrittlement ³.
3. Change in polymer properties for specific use, such as hardening and rigidity of soft liners and tissue conditioning materials due to leaching out of plasticizers from denture base (clinical failure) ^{3,7}.
4. Intrinsic discoloration and aesthetic failure.

There are many types of degradation by covalent bond breakage depending on the cause or the initiating factor, which are:

1. Thermal degradation.
2. Chemical degradation.
3. Mechanochemical degradation.
4. Photo-chemical/photo-oxidative degradation.
5. Enzymatic (biological) degradation.

ii.1. Thermal degradation

Thermal degradation corresponds to the scission of molecular chains at elevated temperatures³. The increase in temperature amplifies intramolecular vibrations and accelerates cleavage of macromolecules. The intra-chain chemical bonds that are sufficiently stressed by these motions dissociate giving rise to polymer fragments of lower molecular weight². The way in which a polymer degrades under the influence of thermal energy in an inert atmosphere is determined, on the one hand, by the chemical structure of the polymer itself, on the other hand by the presence of traces of unstable structures (impurities or additions)⁹. Thermal degradation does not occur until the temperature is so high that primary chemical bonds are separated. It begins typically at temperatures around 150–200 °C and the rate of degradation increases as the temperature increases⁹. Thermal stability is related primarily to the magnitude of the bonding energies between the various atomic constituents of the polymer: higher bonding energies result in more thermally stable materials³. For example, the magnitude of the C–F bond is greater than that of the C–H bond, which in turn is greater than that of the C–Cl bond³. The fluorocarbons, having C–F bonds, are among the most thermally resistant polymeric materials and may be used at relatively high temperatures. However, because of the weak C–Cl bond, when polyvinyl chloride is heated to 200 °C for even a few minutes it discolours and gives off large amounts of HCl³.

Types of thermal degradation

There are three types of thermal decomposition: chain depolymerisation, random degradation and degradation by substituents reactions.

1. Chain depolymerization⁹

Chain depolymerisation is the successive release of monomer units from a chain end or at a weak link. It is the reverse of chain polymerisation; it is often called depropagation or unzipping. A “weak link” may be a chain defect, such as an initiator fragment, a peroxide or an ether linkage arising as impurities from polymerisation. Depolymerisation is characterised by:

- a) the major product is monomer
- b) the decrease of degree of polymerisation is initially negligible, and accordingly the mechanical properties do not deteriorate fast.

Example is liberation of monomer from polymethyl methacrylate when a sample is held close to a burning candle.

2. Random degradation⁹

Occurs by chain rupture at random points along the chain, giving a disperse mixture of fragments which are usually large compared with the monomer unit. The probabilities of breaking any bond in the polymer chain are equal. Random scission is characterised by a) the major products are typically fragments with molecular weights up to several hundred (monomers, dimers, trimers, etc.), b) the decrease of molecular weight is initially significant; therefore, the mechanical properties decrease fast and c) the rate of degradation is initially rapid and gradually decrease (when reaching a maximum).

3. Degradation by substituent reactions⁹

Occurs by modification or elimination of substituents attached to the polymer backbone. Volatile products are not monomers. Example is hydrogen chloride elimination in the case of Polyvinyl chloride. This polymer undergoes degradation reactions, where it loses HCl quite easily, due to polymer backbones with conjugated double bonds.

ii.2. Chemical (hydrolytic) degradation

Water is responsible for the chemical hydrolysis of polymers. Normally hydrolysis proceeds slowly in the neutral conditions of the oral cavity, however, it may be catalysed by acids, bases, or enzymes³. Polymer dissolution is directly proportional to the similarity of chemical structure between the solvent and polymer³. For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids as gasoline. On the other hand, hydrofluoric acid (HF) that corrode many metals and dissolve glass, is stored in plastic bottles³.

ii.3. Mechano-chemical degradation

A linear polymer macromolecule can be mechanically broken to two fragments if sufficient mechanical work is applied to it under flow shear stress². Mechano-chemical degradation is only possible on long molecules. Accordingly, the mid-chain cleavage mode is typical of this degradation². Shear degradation is desired in preparation of rubber mixtures before vulcanization. Where some rubbers contain large portions of macromolecules with the relative molecular weight (more than one million). So, cleavage significantly reduces the viscosity of the vulcanization mixture, thus achieving faster and better homogenization of the mixture².

N.B: Combined corrosive environment (as water) and mechanical stresses lead to stress corrosion cracking (SCC). SCC often progresses rapidly and can lead to sudden failure of polymer³.

ii.4. photo-chemical/photo-oxidative degradation

It is well known that all existing organic polymers degrade if they are subjected to ionising radiation (as ultraviolet radiation) with high dose³. In photochemical degradation, depending on the photon energy, radiation may excite and activate reactive groups in the polymer, or dissociate some of its bonds to radicals². One of its reactions is ionization, in which the radiation removes an orbital electron from a specific atom, converting that atom into a positively charged ion. Consequently, one of the covalent bonds associated with the specific atom is broken and there is a rearrangement of atoms or groups of atoms at that point. This bond breaking leads to either chain scission or crosslinking at the ionization site, depending on the chemical structure of the polymer and the dose of radiation³. Crosslinking may result in limiting chain mobility, increased embrittlement of the polymer and microcracks formation. The greatest radiation damage to polymers is caused by UV irradiation. After prolonged exposure, most polymer films become brittle, discolour, crack, and fail. For example, camping tents begin to tear and plastic windows become cloudy³. Not all consequences of radiation exposure are deleterious. Crosslinking may be induced by irradiation to improve the mechanical behaviour and degradation characteristics. For example, γ -radiation is used commercially to crosslink polyethylene to enhance its resistance to softening and flow at elevated temperatures³. When it occurs in air, photochemical initiation is followed by oxidation of the polymer and the overall complex process is called photooxidative degradation².

ii.5. Biological (enzymatic) degradation¹⁰

Polymeric materials can be degraded by microorganisms in the environment by their secreted enzymes. Enzymatic attacks on the polymer side chains results in, reduces hardness and wear resistance of the polymer and producing harmful by-products. The extent of the enzymatic degradation is related to the extent of cure of the resin, because ester groups may be more available for attack in more loosely crosslinked networks. However, the composition of the monomers producing the network is of primary importance in determining the extent of degradation, TEGDMA has been shown to be more susceptible to enzymatic hydrolysis than Bis-GMA or Bis-EMA^{11, 12}.

Factors affecting polymers degradation

Polymers used in dentistry in the fabrication of dental composite restorative and prosthetic materials are typically composed of mono- or di-methacrylates. Because their chemical structure is nearly identical, the reaction of prosthetic polymers to an aqueous environment is like that of the composite restoratives. The other commonly used polymeric networks are made from polyacrylic acid and its copolymers, which are used in glass ionomers and adhesives, and from polydimethylsiloxane, which is used in soft denture liners. Dental restorative materials are exposed to a service environment, saliva, containing water and different enzymes and a variety of chemicals, including acids, bases, salts, alcohols and oxygen that enter the oral environment during eating and drinking. The chemistry and duration of exposure are important determinants of polymer network degradation. Several factors relating to the chemistry and structure of the polymer network are important in determining the extent to which the material will be affected by an aqueous environment ^{7, 13}.

1. Polymer structure and composition

1.a. Polymer network characteristics and cross linking

The quality of the network that forms during polymerization will affect the extent to which molecular uptake and swelling occur when a polymer is submerged in a solvent ⁷. Networks with high cross-linking density have reduced solvent uptake and swelling due to the reduced free volume in the network, as well as to the covalent cross-links that maintain the close proximity of the polymer chains ⁷. Generally, highly crosslinked polymers are more resistant to degradative reactions, based on the more limited space and pathways available for solvent molecules to diffuse within the structure ⁷. Arima et al. ¹⁴ has shown a strong correlation between increasing the concentration of cross-linking agents and the reduced degradation of polyethylmethacrylate polymers. However, their study also showed that when the cross-linker contained hydrophilic ether linkages, water sorption increased with cross-linker concentration. Cheng et al. ¹⁵ studied the effect of addition of glutaraldehyde as a cross linking agent on the degradation rate and drug release of gelatin. It was found that the degradation rate and drug release are inversely proportional to the glutaraldehyde concentration.

1.b. Molecular weight

The molecular weight and molecular weight distribution of polymers affects the volume fraction of chain ends and hence the free volume of the polymer and determines the chain mobility and crystallisation. It also determines the number of acidic end groups that can participate in hydrolysis and their possible catalytic effect. Overall, the molecular weight affects both the chemical and physical properties of a polymer and polymer degradation ¹⁶. Zhu et al. ¹⁷ and Park ¹⁸ both correlated the faster degradation of PGA, PLA and their copolymers with decreasing molecular weight. This is attributed to an increase in the free volume and number of acidic reactive end groups.

1.c. Hydrophilicity ⁷

The hydrophilic nature of a polymer is a function of the chemistry of its monomers and its polymerization linkages. The three most common monomers used in dental composites are Bis-GMA, UDMA (urethane dimethacrylate), and TEGDMA (triethyleneglycoldimethacrylate). An examination of the structure of the most popular monomers reveals that they are heteroatom polymers, having carbon and oxygen or nitrogen in their backbones. In addition, their structure shows the presence of hydrolytically susceptible groups, such as ester, urethane, ether linkages and hydroxyl groups. These monomers and their resultant polymers certainly absorb water to a damaging extent. Venz and Dickens ¹⁹ correlated the differences in long term water sorption (6 months) for polymer networks composed of various monomers, showing sorption to be in the following order: TEGDMA>Bis-GMA>UDMA>HMDMA. This difference was explained by the presence of hydrophilic ether linkages in TEGDMA, hydroxyl groups in Bis-GMA, urethane linkages in UDMA, and the presence of ester groups in all, including the HMDMA. Park et al. ²⁰ correlated the relation between the hydrophilicity of amide units in polyesteramide and the degradation rate. It was found that the introduction of amide groups to the aliphatic polyester increased the biodegradability owing to its increased hydrophilicity.

1.d. Fillers effect ⁷

The presence of fillers in a polymer network can affect solvent uptake, dissolution and degradation in direct relation to its percentage as it reduces the overall volume of the absorbing polymer ²¹. Water also serves as a weak acid and may cause the erosion of the surface of filler particles. Composites with pure silica or quartz fillers are inert in water. While, composites containing radiopaque glasses undergo greater dissolution in water and saline solutions ²². The deterioration of the glass is one of the reasons that it is so important to form an organic layer, typically of silane molecules, on the surface of the filler to protect it from the environment ²³. The quality of this interface influences the extent to which the composite material degrades. Poor, nonbonded interface may provide a low energy pathway for solvent molecules and dissolution ²⁴.

1.e. Porosity ⁷

High level of porosity or microvoids facilitates fluid transport into and out of the polymer, leading to enhanced solvent uptake and degradation.

1.f. Copolymerization ⁵

By introducing a second monomer into the polymer chain, many properties of the original polymer can be influenced, such as crystallinity or glass transition temperature ²⁵. Poly(anhydrides) degradation depends on the copolymer composition. It was shown for poly(1,3-bis-p-carboxyphenoxypropane-co-sebacic acid) (p(CPP-SA)) that degradation depends on the CPP content. Increasing the content of the aromatic monomer from 50 to 100% was reported to increase the time of erosion substantially ²⁶. Other examples are poly(lactic-co-glycolic acid) copolymers, where the decrease of molecular weight during degradation was found to be accelerated with increasing glycolic acid content ²⁷. Other factors that depend on the copolymer composition, such as the glass transition temperature and the crystallinity of a polymer, can have additional indirect effects on degradation rates.

1.g. Polymer Crystallinity ²⁸

Crystallinity has a significant effect on the degradation rate of polyesters because it determines how easily water molecules can access the ester linkages to cause chain cleavage and degradation. Studies by (proton-based nuclear magnetic resonance spectroscopy) suggested that PLA and PLA/PGA copolymers all degrade via the same mechanism but that the GA units on PLA/GA copolymers constitute vulnerable points on the macromolecular chains, so that degradation occurs preferentially on the GA bonds. Hurrell and Cameron ²⁹ reported that removal of amorphous material from the polymer structure would result in a significant loss of mass and degradation. Further analysis using small-angle x-ray diffraction (SAXS) deduced that insertion of secondary crystals within the amorphous region was the cause of the increase in crystallinity and decrease in degradation.

2. Solvents, Enzymes & Saliva components ³⁷

The chemistry of the environment surrounding a polymer network, influences the nature of the interaction between them ⁷. Studies of the effect of storage conditions on the stability of dental polymer networks have exposed the materials to water, artificial saliva, alcohol, and acidic or basic solvents to study the degradation process ⁷. The effect of these chemicals is varied, but typically involves an elution of unreacted components and some degradative effect on the polymer network. Solutions of 50–75% ethyl alcohol in water have been shown to be among the best solvents for dental composite networks ³⁰. Interaction between oral microbes and the polymer network also may occur. Bacteria can colonize on compomer surfaces causing degradative effect as a result of acids produced by the bacteria. Another very important aspect of the interaction between the polymer network and its environment is the presence of enzymes that can degrade the polymer through attacks on the side chains, producing both potentially harmful by-products as well as a deterioration of the properties of the network ³¹.

Numerous studies have shown the effect of esterases on dental composites^{32,33}. These studies have shown a reduction in wear resistance as well as the loss of molecules from the surface of the composite. Due to the large size of the proteins and their limited mobility within a polymer network, it is unlikely that the effects of enzymes would be experienced deep within the structure of the polymer, away from the surface. The chemistry of the polymer will influence the enzymatic degradation of the material, for example, urethane modified bis-GMA/TEGDMA networks have been shown to be more stable in the presence of cholesterol esterase than unmodified bis-GMA/TEGDMA networks³⁴. Water is the most abundant component of saliva and one of the main factors to cause biodegradation. The oral environment necessarily facilitates water sorption from the saliva to the resin. There are two conditions that influence the amount of water diffusion to denture resins. One is the water diffusion coefficient of the material that affects the time needed for its saturation with water. The other one is the amount of residual components that are released for the medium and replaced by water molecules³⁸. Polymeric structures and dental materials may be chemically degraded in saliva through two mechanisms: hydrolysis and enzymatic reaction. Salivary enzymes can degrade polymers through attacks on the side chains, producing by-products as well as a deterioration of the properties of the network³⁸.

3. Media Ph

Media pH can affect polymer degradation, either directly, by altering the polymer chemistry or indirectly, by interacting with degradation products and affecting degradation kinetics. Chu³⁵ found there was a greater loss in the mechanical properties of PGA sutures in buffered than unbuffered solutions. Also, the presence of buffer ions increases the degradation rate of poly(α -hydroxy acid) copolymers. Ginde and Gupta³⁶ also observed alkaline media (pH 9.2 and 10.6) to have a more severe effect on the degradation and mechanical properties of PGA fibres than acidic or neutral media. This is due to the enhanced removal of degradation products that diffuse out, creating space for water ingress in the structure, thus increasing the degradation kinetics.

4. Chewing forces³⁷

Biodegradation of the materials in the oral cavity can also be induced by fatigue, which is caused by repetitive loads such as chewing force. A continuous application of mechanical and environmental loads leads to progressive degradation and crack initiation and growth, resulting in catastrophic failure of the resins. This process is further assisted by pre-existing voids introduced during the material processing and residual stresses. Chewing can also apply shear and compression forces on denture teeth causing wear^{38,39}.

5. Dietary changes³⁷

Intraoral temperature changes may be induced by routine eating and drinking. These temperature changes affect the polymeric materials as they have a different coefficient of thermal expansion compared to natural tooth. Thermal fluctuations will induce surface stresses that can directly cause crack propagation⁴⁰. Foods and drinks can also affect dental materials by the direct effect of their additives, like ethanol, and their capacity of changing the intraoral pH values⁴¹.

Biodegradable

Biodegradable polymers are a special class of polymer that breaks down after its planned purpose by bacterial decomposition process to result in natural by-products such as gases (CO₂, N₂), water, and inorganic salts⁴². These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and ether functional groups. Biodegradable polymers, have extremely strong carbon backbones that are difficult to break, so the degradation often starts from the end-groups. Since the degradation begins at the end, a high surface area is exposed to chemicals, light, or organisms easily⁴³.

Properties of biodegradable polymers ^{43,44}

1. Biodegradable polymers should be stable and durable enough for use in their particular application, but upon removal they should easily break down.
2. Hydrophilicity, because hydrophobic polymers and end groups will prevent the water-soluble enzymes from interacting with the polymer.
3. Non-toxic, non-irritant, with no inflammatory tissue response.
4. Maintain good mechanical integrity until degraded.
5. Controlled rates of degradation which match that of the healing or regeneration process.

Applications of biodegradable polymers ⁴⁴ One of the most active areas of research in biodegradable polymer is in controlled drug delivery and release and tissue engineering. Also it is used widely in resorbable surgical sutures.

Protection of polymers against degradation ²

Polymer degradation is a complex process by which the polymer loses its original functional properties owing to irreversible changes in its structure. All types of polymer reactions take part in corrosion:

- i. chemical transformation of functional groups.
- ii. cleavage of polymer molecules by oxidation, hydrolysis, photochemical and other chemical reactions, mechano-chemical processes and by depolymerization.
- iii. crosslinking of polymer molecules as well as their fragments.

Crosslinking makes the aged polymer brittle while cleavage processes makes it waxy or sticky. Undesirable degradation processes are significantly reduced by stabilizers admixed into the polymeric material. A single stabilizer is usually not enough; a mixture of a few stabilizers mostly must be used. According to the function, stabilizers are divided to photostabilizers, antioxidants, antiozonants, radical scavengers, peroxide scavengers, acid scavengers, fire retardants and biocides. Because the stabilizer is only admixed into a polymer, not bound to it, its second key property is a good compatibility with the polymer. When the compatibility is poor, the stabilizer is spontaneously displaced to the polymer surface by the thermal motion, from where it is removed by external influences. As a result, the polymer becomes unprotected.

Degradation processes can be reduced also by:

1. Increasing the polymer crosslinking.
2. Decreasing the hydrophilic groups or hydrophilic crosslinking agents in the polymer structure.
3. Increasing the polymer molecular weight.
4. Increasing the fillers content in the polymeric structure.
5. Decreasing the porosity.

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