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# Recent Advances endodontic sealers

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**Abstract:** Bioceramic-based endodontic sealers were utilized as a root canal sealer due to their great biocompatibility and idleness. Later era of bioceramic- based endodontic sealers has risen as a novel fabric with a bioactivity potential grants an impermeable seal to the root canal framework that stands out compared with customary root canal sealers.

**Keywords:** Bioceramics; endodontic sealers

Preparations based on bioceramics have recently been introduced to the market due to their interesting physical, chemical and biological properties compared to traditional endodontics. Several bioceramic-based sealants are being introduced to the market.

Unlike traditional endodontic sealants, bioceramic sealants are hydraulic and hygroscopic and have a unique healing process. In addition, it had an excellent property due to its biocompatibility, antimicrobial activity and bioactivity, which affected mineral deposition during treatment, promoting a chemical bond with the tooth walls in the biological environment, which improves their sealing ability.

The high alkalinity of the bioceramic endodontic seal increases the mineralization process and induces its antimicrobial effect. However, the stability of these dimensions remains controversial. Some studies have found no shrinkage of bioceramic endodontic sealants during healing, while other studies have found slight expansion during healing.

The composition of bioceramic-based endodontic sealants mainly consists of some or all of the following components; calcium silicates, calcium phosphate, calcium, hydroxide, zirconium oxide, fillers and thickeners. Bioceramics is a term that refers to a class of biomaterials that contain ceramics.

Bioceramics are primarily designed for medical and dental applications to be truly biocompatible. Therefore, bioceramics can be defined as biocompatible ceramic materials or metal oxides that include silica, alumina, zirconium, bioactive glasses, ceramics, calcium silicates, hydroxyapatite, and calcium phosphate.

There are two main advantages of using bioceramic endodontic sealants. First, their excellent biocompatibility avoids side effects of the surrounding tissues, allowing clinical success in cases where there is a high risk of compression of the material into the periodontium, such as internal resorption over an open apex and root or iatrogenic instruments.

Second, the bioactivity of bioceramic endodontic sealants, which is related to the calcium phosphate component, which improves the chemical bond between the crystalline structure of the tooth and the bioceramic sealants by depositing a layer of apatite on the interface, forming the so-called. monobloc" concept and then achieving an airtight seal and creating strong chemical bonds between dentin and core filling materials.

Although bioceramic endodontics vendors have shown promising results as endodontics. Further studies are necessary to determine the clinical results associated with the use of these concentrations.

Controversy regarding the difficulty in removing them from the root canal during rehabilitation is a significant issue among clinicians. In addition, research has revealed that changes in the water content of the environment negatively affect the healing time of bioceramic sealants.

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# Effect and Future Trends of Erosive Conditions on Tooth-Colored Restorative Materials: a review

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**Abstract:** Acidic environment is one of the causes for aggressive destruction of teeth and tooth-colored restorations leading to the dissolution of tooth structure and deterioration in the restorations' properties. Several attempts are found in the literature to resist these erosive conditions rendering the restorations to withstand the harsh chemical and acidic attacks.

**Keywords:** erosion, wear, tooth-colored restorations, acidic degradation.

Oral cavity is one of the harshest environments of the human body. Hence, teeth & dental restorations are regularly subjected to food & beverages that produce large variations in the oral pH and temperature. Dental restorations must be able to withstand these effects in a comparable or even better way than enamel. Dental erosion is a chemical process characterized by acid dissolution of dental hard tissue not involving acids of bacterial origin. It is also called 'biocorrosion': as it encompasses not only endogenous and exogenous acidic impacts, but also proteolytic degradation of the teeth induced by proteases from the gastric fluid (1).

## 1. Classification of wear (2):

Wear is the process by which material is displaced or removed by the interfacial forces which are generated as two surfaces rub together. Types of wear that occur in the oral environment are as follows:

a. **Erosive wear:** degradation of material due to impact of particles travelling with significant velocity.

b. **Abrasive wear:**

When two surfaces rub together, the harder of the two materials may indent, produce grooves in or cut away material from the other surface. This direct contact wear is known as two-body abrasion and occurs in the mouth whenever there is direct tooth-to-tooth contact. Abrasive wear may also occur when there is an abrasive slurry interposed between two surfaces such that the two solid surfaces are not actually in contact. This is called three-body abrasion, and occurs in the mouth during mastication, with food acting as the abrasive agent. Toothpastes also act as abrasive slurries between the toothbrush and the tooth.

c. **Corrosive wear:**

Occurs when a chemical reaction between the worn material and corroding medium leads to a loss of material on the worn surface.

d. **Fatigue wear:**

The repeated loading of teeth produces cyclic stresses that can lead in time to the growth of fatigue cracks. These cracks often form below the surface, and initially grow parallel to it before veering towards the surface or coalescing with other cracks.

## 2. Etiology of erosion (1):

a. Endogenous sources as stomach acid, gastroesophageal reflux disease (GERD) and eating disorders as bulimia or anorexia.
b. Exogenous sources from dietary habits like acidic beverages or food, lifestyle, occupational hazards (chemical industries) or acidic medications and patients with low salivary flow; xerostomia.

The most frequent type of dental erosions are dietary erosions that could be caused among other things by frequent intake of acidic beverages (e.g. fruit juices, or carbonated soft drinks). Their consumption leads to significant decrease of pH in oral cavity up to 15 minutes. However, these acids act not only on hard dental tissues, but also on all restorations materials found in the mouth (3).

## 3. Process of tooth erosion:

Early clinical signs of dental erosion are characterized by initial softening of the enamel surface with subsequent and/or progressive loss of volume, with a softened layer (i.e., less surface hardness) remaining at the mineralized tooth surface, loss of enamel texture, a silky glossy appearance and sometimes a dulling of the surface gloss, referred to as the “whipped clay effect”, cupping of cusps on the occlusal surfaces and flattening of the occlusal structures. In later stages, occlusal morphology can completely disappear with hollowed out surfaces and restorations “standing proud” above adjacent tooth structures as shown in figure 1-3.

Figs. 1–3: Composite restorations in a patient still suffering from bulimia after intra-oral service of one year only. The restorations showed clear visible signs of marginal disintegration with loss of restoration fragments. Figs. 4 and 5: Occlusal view of upper posterior composite restorations after 5.5 years in service.

## 4. Consequences of erosive tooth wear

Once in contact with enamel, the acid with hydrogen ion (H3+) or its chelating capacity (from the anions in organic acids) begins to dissolve the hydroxyapatite crystal and release the minerals, figure 6 (1).

The critical pH at which enamel becomes susceptible to erosion is estimated to be 5.5. Hence, when an acidic material whose pH is at or below this level comes into contact with enamel frequently and for a prolonged period of time, enamel erosion occurs. In prismatic enamel, acid attacks lead to its demineralization. This is due to the dissolution of either the prism cores or the inter-prismatic areas. The eroded prismatic enamel may also have a microscopic honeycomb appearance. This is because the prismatic enamel is dissolved by acid, while the inter-prismatic enamel remains extended above the surface. In aprismatic enamel, the dissolution pattern is more irregular, with various degrees of mineral loss, figure 6 (4).

Dentine is more susceptible to erosion than enamel, and it can be eroded at a relatively high pH (6.0) due to the carbonate content of dentine is greater than that of enamel (6% versus 3%), and the crystals in dentine are much smaller than those of enamel. The latter structure makes more surface area of dentine available for an acid attack (4).

**Two actions are responsible for the erosively induced tooth wear observed in the oral cavity (1):**
1. Dissolution and loss of dental hard tissue & destabilization of collagen network which is directly induced by the acid attack.

2. Wear of the softened surface by mechanical impacts, such as toothbrushing, tooth-to-tooth contacts.

**Recently the term “erosive tooth wear” was coined for this two-step chemical–mechanical process.**

In severe situations, as in gastroesophageal reflux disease (GERD), A significant loss of tooth structure, vertical dimension, and/or function, hypersensitivity, esthetically unacceptable defects, and pulp exposure could occur (1).

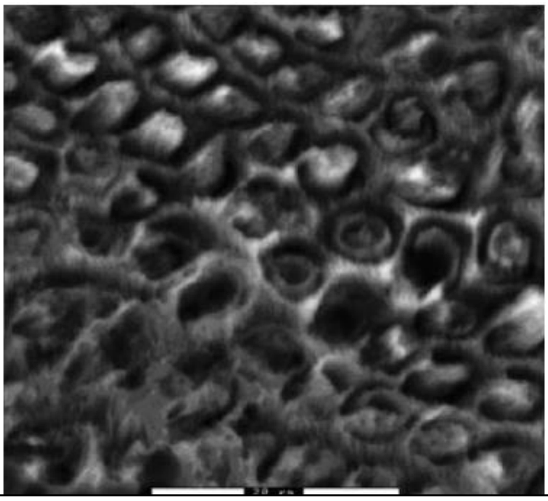

Figure 6. Prismatic structure of the enamel is clearly visible, and different etching patterns can be seen in different regions of the image. Protruding prisms can be seen in the top left of the image, protruding prism boundaries in the middle right and aprismatic enamel can be seen in the bottom left.

## 5. Role of Saliva:

Saliva is considered an important biological factor influencing dental erosion due to its ability to dilute, neutralizes, buffers acids, form acquired dental pellicle and remineralize eroded dental hard tissues. These protective mechanisms can be potentially reduced in patients with low salivary flow rate and/or low buffering capacity (5).

## 6. Treatment of teeth with erosions:

In the past, patients were left untreated, or the rehabilitation was performed with extensive crown and bridge work. However, as a result of the improvements in adhesive materials, it has become possible to rehabilitate eroded teeth in a less invasive manner to protect it using direct restorative material (RM) such as composite resins and glass ionomer cement (GIC). These materials are capable of reestablishing the function and esthetics of tooth structure as well as controlling the hypersensitivity. Before restoration of the teeth, abolishment of the causative erosive factors has to be achieved. Thus, nutrition control and/or medical and psychological treatment should be applied, and patients have to be instructed about measures how to prevent erosion using anti-erosive strategies and change of behavior.

Thus, for restoring and protection of the worn dentition, composite restorative materials and ceramic restorations are preferably used. Also, dentin sealants or desensitizers might be applied to protect and seal exposed dentin areas. These procedures might be beneficial at initial stages of hard tissue loss or when final restorations are not yet applicable (6).

### Definitive treatment protocol (additive):

Once the etiology has been established and risk factors controlled, restorative management can be considered. When there is no compromise to the existing tooth structure, resin sealants, or bonding agents can be applied over the dentin. This may not only reduce sensitivity for a limited time period but may also slow down the progression of ETW. Restorations should be conservative and additive in nature, especially in mild and moderate lesions. Additive procedures can involve both direct resin composite and indirect ceramic partial coverage restorations. In advanced lesions where loss of occlusal vertical dimension may have occurred, more aggressive therapy to restore esthetics and function may be indicated. This includes full coverage crowns as part of an extensive oral rehabilitation. Regular monitoring and evaluation of ETW management should be done during recall visits (6).

**Resin composite restorations, glass ionomer cement and ceramic restorations are usually used as treatment options to rehabilitate patients with erosion:**

- Minimal Loss of Vertical Dimension <0.5 mm: surface Sealant or direct flowable Resin Composite. The sealing procedures must be repeated periodically; fortunately, to ensure stability of the new sealant.
- Loss of Vertical Dimension <2 mm: Direct Reconstruction with Composite Materials or glass ionomer restoration.
- Loss of Vertical Dimension >2 mm: Rehabilitation with indirect Ceramic Veneers and Overlays.
- Loss of Vertical Dimension >4 mm: Rehabilitation with indirect Ceramic restorations as crowns and bridges (7).

**Although restorative materials are less susceptible to erosion compared to enamel, the erosive attack can induce, at least to some extent, the degradation of the matrix and fillers of restorative materials.**

## 7. Effect of erosive conditions on different tooth-colored restorative materials

### a. Effect of erosion on composite restorative materials:

Using composite for direct restorations allows for a minimally invasive treatment, only replacing the dental hard tissue lost under the erosive conditions. Additionally, using direct restorations might be regarded as an expectative approach allowing to render the patient familiar with the new vertical dimension. Composition of composite materials has a certain effect on the erosion of the surface of composites. Mechanism of erosion is the hydrolysis of ester radicals present in dimethacrylate monomers, i.e. BisGMA, UDMA and TEGDMA.

Organic acids dissolve Bis-GMA polymers more easily causing leaching of the diluent agents such as TEGDMA. The softening and hydrolysis of the resin matrix could promote displacement of the filler particles, contributing to the formation of a rough surface and protrusion of fillers as a result of matrix degradation.

Under persisting acidic and erosive conditions using dietary acids, hybrid and nano-hybrid composite restorative materials have been shown to be resistant to acidic attacks compared to glass-ionomer restoratives. However, the erosive challenges degrade the resin matrix or the silane coupling agent, resulting in the loss of filler particles. There is a linear relationship between wear resistance by acids and the filler volume (8).

Biodegradation phenomenon is a complex process that may lead the composite polymer matrix to collapse, causing several problems such as filler-polymer matrix debonding, release of residual monomers, wear and erosion caused by food, chewing and bacterial activity. This process may deteriorate the mechanical properties of the material and reduce the clinical life of composite resin restorations. Furthermore, surface disintegration of composite resins may increase wear and plaque retention, thus decreasing the longevity of the restoration, and potentially increasing the risk of secondary caries.

**Effect of erosive conditions on microhardness and surface roughness of resin composite restorations(9):**

- Nanocomposites are the most stable under erosive conditions with higher wear resistance and microhardness values. This is due to nano-sized regular particles, which allow the incorporation of a large volume of inorganic fillers.
- Surface roughness values of nanocomposites after erosive challenges are lower than hybrid composites due to homogeneous composition and their particles are less prominent on the surface.
- Resin materials that have larger filler particles presented greater surface micromorphology changes when submitted to acidulated phosphate fluoride (APF) gel, i.e., Fluoride ions causes depolymerization reaction of the coupling agent so that weakening the interface between the filler and matrix, resulting in the release of the filler particles, causing the filler particles to project out thereby increasing surface roughness.
- APF typical dissociation reaction in the solution results in H+ & F ions that forms hydrofluoric acid (HF) a known glass etchant which dissolves glass particles , dissolves composite filler particles and fluorosilicate glass particles that contribute to decrease in surface hardness. Organic esters in the methylmethacrylate matrix undergo hydrolytic cleavage of the ester group in low pH.
- Fluoride ion has been implicated in depolymerization reaction of the matrix filler interface. Possible mechanisms may explain the interaction pathway of fluoride which are hydrolysis of the organosilicon ester group and disorganization of the siloxane network formed from the condensation of intramolecular silanol group which stabilizes the interface (10).

**Effect of erosive conditions on adhesive bonding strength and microleakage of resin composite restorations (11) :**

- Composite specimens subjected to erosive attacks showed microleakage and decreased bond strength of etch- and-rinse and self-etching adhesives.

- The effects on bonding are more pronounced on enamel than on dentin because erosion primarily affects the inorganic part of the tooth and bonding to enamel is mainly achieved by a micromechanical interlocking of resin into microporosities of the acid-etched surface. However, in case of GERD, the gastric protease (pepsin) leads to organic matrix degradation and progression of erosive lesions in dentin.

**Influence of fluoride releasing restorations in inhibiting erosion of adjacent enamel(12):**

Inability of the fluoride-containing restorative materials to prevent erosion in the vicinity of the restorations. Due to the low levels of fluoride released by the materials and/or the high aggressiveness of the erosion when compared to caries.

**Influence of topical fluoride varnishes in inhibiting erosion of adjacent enamel(13):**

However, topical fluoride varnishes with high concentrations are shown to be effective in increasing enamel microhardness thus reducing erosion, since varnishes creates a calcium fluoride ($CaF2$) layer acting as a physical barrier hampering the contact of the acid with the underlying enamel or to act as a mineral reservoir which is attacked by the erosive challenge. Thereafter, released calcium and fluoride might increase the saturation level with respect to dental hard tissue in the liquid adjacent to the surface, thus promoting remineralization.

The protective effect of fluoride varnishes is mainly related to the mechanical rather than to the chemical protection and the anti-erosive effect of conventional fluorides requires a very intensive fluoridation regime.

**-Recent trends to overcome erosions using resin composites**

1. CAD/CAM designed ultrathin composite occlusal veneers yielded a decreased risk of failure as compared to lithium disilicate ultrathin occlusal veneers. The use of ultrathin occlusal veneers might be regarded as a conservative approach to treat erosive lesions, with the aim to save as much dental hard tissue as possible.

2. CAD/CAM composite restorations (hybrid ceramics or nano-composite compositions) behave similarly or even better than human enamel with respect to two-body wear and toothbrushing wear.

3. Incorporation of bioactive components into composite resins may be an advantageous alternative for restorations in patients frequently exposed to erosive challenges, due to the release of ions that could play a relevant role in the erosive tooth wear process by promoting tooth remineralization E.g., dicalcium phosphate dihydrate particles(14).

4. Application of Surface penetrating sealants are unfilled/nanofilled low-viscosity resins polymerized on surface of resin composite to preserve or improve its properties. It is applied to fill the cracks, decrease the porosity, increase the wear resistance, and maintain the marginal integrity of restorations (15).

5. Giomer's technology was developed to enhance material properties, providing wear resistance associated to fluoride release. Surface Pre-Reacted Glass-ionomer (S-PRG) fillers (fluoro-boro-aluminosilicate glass and a polyacrylic

acid solution) release multiple ions including F− Sr2+, Na+, BO33- , Al3+, and SiO3 which results in the buffering action and prevents enamel demineralization around the material (16).

### b. Effect of erosion on glass ionomer restorations:

Compared to resin composite, glass ionomer cement is more unstable and experiences a decrease in hardness values and an increase in surface loss under erosive conditions. This is due to the dissolution of the silicate-glass hydro-gel network peripheral to the glass particles. Conventional glass ionomer (GI) restoration shows lowest micro-hardness and highest surface degradation compared to resin modified glass ionomer (RMGI). Moreover, conventional GI does not provide enough protection against erosion for the surrounding enamel and dentin because it shows more marginal than bulk degradation. Therefore, it is preferable to use them in a closed sandwich restoration rather than leave them exposed directly to this environment. Then if any leakage of acid occurs, some protection against demineralization may be provided to the adjacent tooth structure by the GIC (17).

Release of ions such as fluoride, sodium, phosphate and silicate have also been found to increase at lower pH values due to the presence of higher amounts of H+ ions and these attack the cement matrix, causing release of ions and consequently dissolution (18). This may be accompanied by an increase in the pH of the acid solution, because of the glass ionomer buffering effect is likely to be beneficial in protecting the teeth from the occurrence and evolution of dental erosion(19).

RMGI is less susceptible to acidic degradation compared to conventional GIC, due to the presence of reinforcing and higher acid resistance resin matrix. Therefore, RMGI provides protection against erosion for the surrounding enamel and dentin and can be considered material of choice among fluoride releasing materials for restoring erosive lesions in patients at higher risk for erosion in contrast to the conventional GI (14).

However, the increase in the surface roughness of RMGI is due to the matrix dissolution peripheral to the glass particles, which could be the result of dissolution of the siliceous hydrogel layer (20).

### c. Effect of erosion on dental ceramics surface roughness and hardness:

Although dental ceramics are chemically inert, their chemical stability is influenced by the elemental composition, microstructure, and chemical character of the erosive agent, and changes in oral temperature and exposure time.

It is important to understand the two phases present in a ceramic, i.e., a crystalline phase and a glass phase. When a low pH solution (acidic in nature) comes in contact with ceramic, it attacks the glass phase, causing its breakdown and release of crystals into solution, which affects the kinetics of ion release and ultimately leads to dissolution and a roughened ceramic surface.

In an acidic environment, there is anion exchange between the protons present in erosive solutions and network modifiers (Ca, Zn, Li) in ceramic bulk.

The risk of acidic environment lies in its chelating effect that can cau se degradation, ionic dissolution and leaching out of alkaline lithium and aluminum ions, which are less stable in the glassy phase than in the crystalline phases, and results in the dissolution of the ceramic silicate network leading to crack propagation, roughening, plaque accumulation, discoloration, and weakening of ceramic structure (21) (22).

Strong acids such as HCl from gastric regurgitate (GERD) can etch the surface of glass-based ceramics, resulting in increased surface roughness and a decrease in the hardness values of the ceramic restorations. Local hydrolysis in ceramic cracks is accelerated in acidic pH, as GERD, leading to crack propagation and, hence, ceramic corrosion. The subsequent increase in surface roughness can increase the accumulation of bacterial plaque on the ceramic restorations (23).

Strong acidic compounds, such as hydrofluoric acid and acidulated phosphate fluorides (APFs) are able to etch the surface of both glass and feldspathic based ceramic materials. This detrimental effect of APF gels is already existent after a 4 min exposure of metal-ceramic and all-ceramic glass-based materials. APF gels are used for either fluoridation regimes but may also be used for pre-treatment of glass-based ceramics in repairing protocols. In the case of hydrofluoric acid, its etching property is used in the pre-treatment of glass-based and feldspathic ceramic restorations before adhesive luting to dental hard tissues(1).

When dental ceramic restorations are exposed to erosive beverages they produce surface degradation, subsequently leading to crack propagation within the ceramic structure. This phenomenon is a result of leaching out of the alkali ions, which tend to be less stable in the glass phase in comparison to the crystalline phase. As a consequence of such degradation, the exposed ceramic surface will eventually be roughened, thereby promoting greater plaque accumulation, discoloration, and weakening of ceramic structure as well as resulting in the wearing of antagonist natural teeth and restorations (24).

Zirconia is the most resistant material against acid attack. This may be due to their polycrystalline microstructure that provides strength and fracture resistance. Additionally, the absence of a glass phase makes the polycrystalline ceramics more resistant to acid attack.

Lithium disilicate has a different microstructure than zirconia that render it more prone to acid attacks. It contains approximately 70% of the volume of needle-like crystals in a glassy matrix, making it more prone to corrosive acid compared to zirconia. Acids might cause a disruption to the silica phase of lithium disilicate through leaching out of alkaline ions such as Al, Si, and Zr (25).

Figure 7. Emax occlusal overlay with 0.5-0.6mm thickness for restoring vertical dimension lost due to erosion using e-max press ingots.

Figure 8. Anterior porcelain palatal veneers restoring eroded incisal edges.

**Example of acid attacks effect on microstructure of restorative materials (26):**

Scanning electronic micrographs visualize the conventional GIC group that the acid episodes caused cracks in the microstructure of this material, which increased in number and size with the following episodes, figures 9. Similar images were obtained for RMGIC, however, this material showed a smaller amount of cracks, which were only more evident after one month of immersion, figures 10.

The direct resins showed similar results regarding to degradation, which was proved by the images showing, as time went by, a degradation of the polymeric matrix with consequent increasing of roughness and decreasing of microhardness (Figure 11). The images of the ceramic showed that this material, although suffering a degradation as the immersion time went by, underwent a smaller degradation than the other materials. It can be seen in the images the maintenance of the surface during the first two readings, and the presence of bubbles and grooves on the surface of the material, suggesting a slight degradation, figures 12.

SEM images of all materials tested at the different phases of evaluation of the samples (initial, 7 days and 30 days), at x 10,000 magnification, figures 9,10,11 and 12:

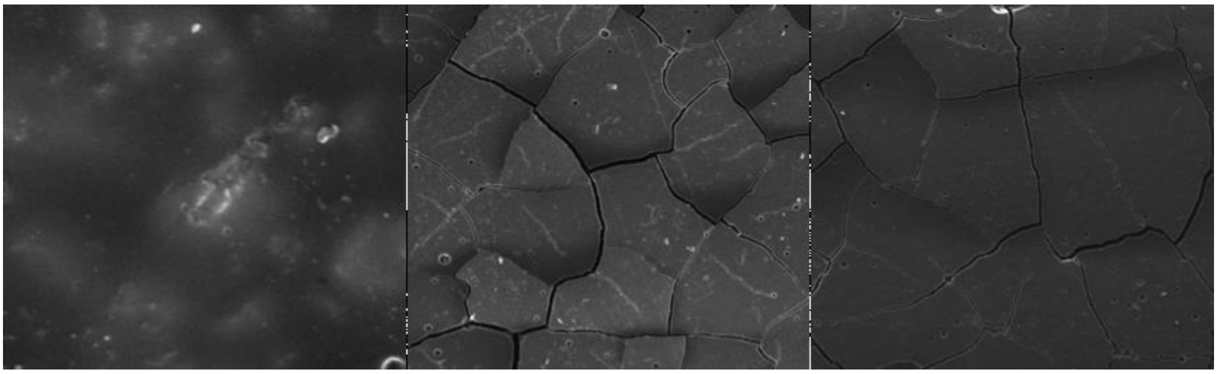

Figure 9. Photomicrography; Glass Ionomer Cement (Vidrion): a) initial reading; b) second reading; c) third reading.

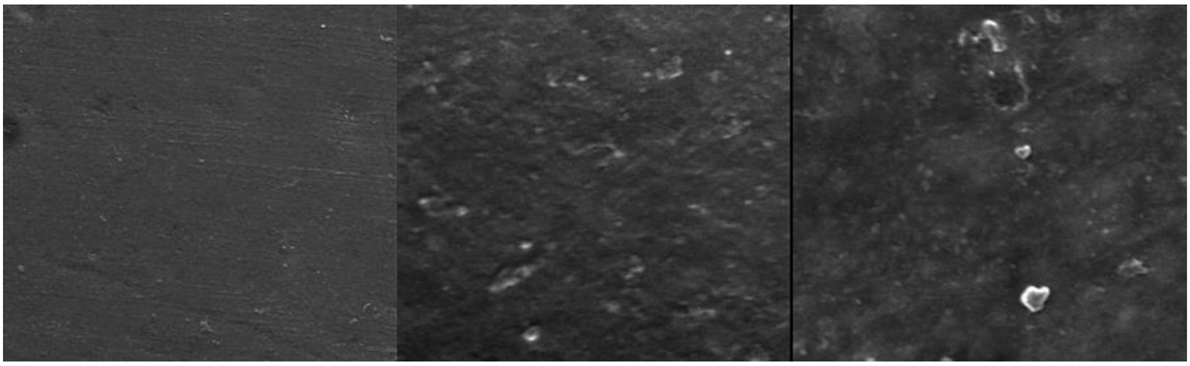

Figure 10. Photomicrography - Direct Resin (Z350): a) initial reading; b) second reading; c)third reading.

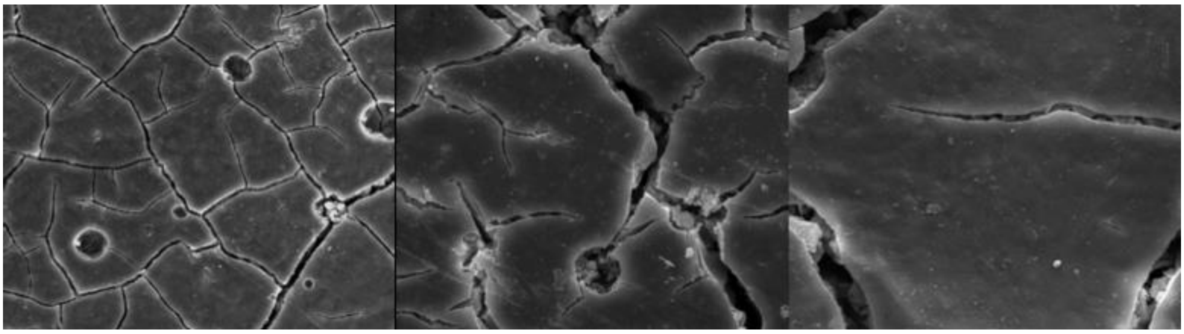

Figure 11. Photomicrography - Resin-modified Glass Ionomer Cement (Vitremer): a) initial reading; b) second reading; c) third reading.

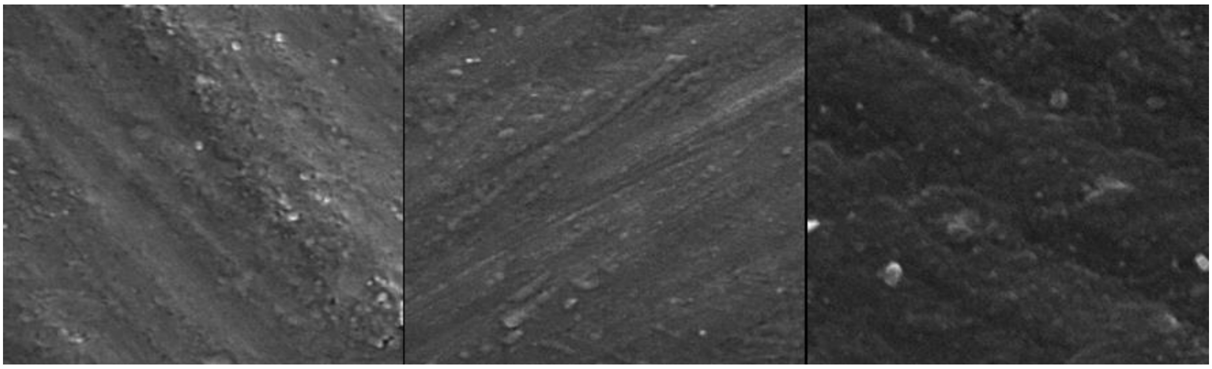

Figure 12. Photomicrography Ceramic (Empress II): a) initial reading b) second reading; c) third reading.

## Conclusion:

Under acidic conditions all restorative materials show degradation over time (surface roughness, decrease of surface hardness, substance loss). However, ceramic materials and resin composites present much better durability than conventional glass-ionomer cements and resin-modified glass-ionomer cements and that the latter materials should not be used in erosion patients.

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# Basic Concept of Bone Cements

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**Abstract:** Every year numerous patients in the world undergo bone replacement and reconstruction treatment due to severe trauma, tumor resection, systemic and periodontal diseases, abnormal skeletal development of genetic disorders and bone defects caused by fracture, all represent major causes of disability and a loss of quality of life which urge the need for replacement .

**Keywords:** : *Bone cment, calcium sulfate cement, calcium phosphate cement*

Every year numerous patients in the world undergo bone replacement and reconstruction treatment due to severe trauma, tumor resection, systemic and periodontal diseases, abnormal skeletal development of genetic disorders and bone defects caused by fracture, all represent major causes of disability and a loss of quality of life which urge the need for replacement (1).

## I. Bone Replacement Material:

Currently, autograft is the gold standard for the treatment of bone defects and bone regeneration, where bone tissue harvested from and implanted in the same individual (a patient's own tissue), it can be obtained from intraoral sites from the same individual, such as the mandibular symphysis, mandibular ramus, external oblique ridge due to being good sources of cortical and cancellous bone. However, its main disadvantages include morbidity at the donor site and the need for two operative procedures, donor-site injury, chronic post-operative pain and infection. Allograft is an alternative method, where bone tissues are harvested from a compatible living individual implanted in another one of the same species (from a donor). Allografts exhibit good histocompatibility and are found available in various forms, from whole bone segments, cortico-cancellous, and cortical pieces to chips, powder, and demineralized bone matrix (DBM). It has many postoperative complications such as rejection of the donor tissue by the recipient’s immune system and concerns with disease transmission such as HIV and hepatitis. To overcome potential immunogenicity and morbidity at donor sites, artificial synthetic bone substitute materials are generated to closely mimic the biological properties of natural bone and are promising alternative for the repair and replacement of bone defects(1,2).

Bone cements are bone substitute and bone filling materials, can be defined as biomaterials obtained by mixing powder and liquid phases, forming a plastic paste, which can be moulded and implanted as a paste. They have the ability to self-set once have implanted in the body, ensuring perfect fit at the implant site and good bone–material contact as well. The term “cement” is a misnomer since the term cement is used to represent a substance that bonds two things together. However, bone cements have no inherent intrinsic adhesive properties, but instead, they depend on the close mechanical interlock between the irregular bone surface and the prosthesis. They are widely used in various orthopedic and dental implant fixation and of great significance for filling and repairing the irregular trauma site and bone defects(3).

## II. Characteristic of an ideal bone substitute material:

The main function of bone cement is to provide mechanical support and stimulate osteo-regeneration, with the goal of bone replacement. The four fundamental biological properties of osseointegration, osteogenesis, osteoconduction, and osteoinduction, are paramount in performing this role effectively. **Osseointegration** is the ability of a grafting material to chemically bond to the surface of the bone in the absence of an intervening fibrous tissue layer. **Osteoconduction** refers to the ability of a bone grafting material to generate a bioactive scaffold on which host cells can grow. This structure enables vessels, osteoblasts, and host progenitor cells to migrate into the interconnected osteomatrix. **Osteoinduction** is the recruitment and activation of host mesenchymal stem cells into the grafting site, where local proteins (BMPs) and other factors induce the differentiation of stem cells into osteoblasts. **Osteogenesis** is the formation of new bone via osteoblasts or progenitor cells present within the grafting material. These four fundamental properties enable new bone formation which occurs in parallel to direct osseous interconnection. Additionally, various properties influence the success rate as biocompatibility, bioresorbability, sterility, structural integrity, adequate porosity for vascular ingrowth, plasticity, ease of handling, and compressive strength(2).

## III. Classification of bone cements:

Bone cements materials currently in clinical use can be classified into: polymethylmethacrylate (PMMA), calcium sulfate-based bone cements (CSCs), calcium phosphate ceramics, the most used in bone tissue engineering are hydroxyapaptite (HA), tricalcium phosphate (TCP) or combination of the two, known as biphasic calcium phosphate (BCP), calcium phosphate cements (CPCs) and organic-inorganic composite bone cements.

To date, the most used biodegradable bone cements mainly include calcium phosphate-based cements (CPCs), calcium sulfate cements and composite bone cements. The biggest advantage of biodegradable bone cements is that they gradually degraded by chemical dissolution and cell absorption after implantation in the bone defect and finally replaced by newly formed bone (1).

### 1. Acrylic bone cements (ABC):

The term ‘bone cement’ was initially applied to acrylic bone cements (ABCs), widely used since the 1960s for anchorage of implants in orthopaedic surgeries, and bone defect. ABCs are based on polymethylmethacrylate (PMMA) which is an acrylic polymer that is formed by mixing two sterile components a liquid MMA monomer and a powered MMA-styrene co-polymer. When the two components are mixed, the liquid monomer polymerizes around the pre-polymerized powder particles to form hardened PMMA. It is accepted as a biocompatible polymer when cured.

PMMA bone cement has some favorable properties such as ease of handling and application, significant mechanical strength (used for high and medium load-bearing applications), suitable curing time and economical. The major reason for its limited application in the oral environment can be attributed to its very low biodegradability, it is bio-inert and lacks bioactivity, the poor interfacial integration between the host bone tissue and the cement brings a major challenge in the clinical practice and may cause interfacial loosening, with no functions of bone conduction or induction, tissue necrosis resulting from the exothermic setting reaction, the heat generated during curing may reach up to 110°C which can cause thermal necrosis of surrounding bone cells and extensive bone damage since collagen denatures with prolonged exposure to temperatures in excess of 56°C, as well chemical necrosis can occur due to unreacted monomer release , monomer toxicity, degradation of fragments causes irritation and inflammation at the implanted site(4,5).

## 2. Calcium Sulfate Cements:

Calcium sulfate also referred to as gypsum, it is the first synthetic scaffold used for bone regeneration. The advantage of calcium sulfate cement is biocompatiblility, low cost, osteoconducitivty, safe as the degradative products even cause no tissue inflammatory reaction when implanted in the body. Major drawback is it lacks bioactivity and the rapid degradation of calcium sulfate which exceeds the rate of new bone formation, (too rapid to be replaced by new bone invivo) , resulting in significant loss of mechanical properties at the defect site, limiting its clinical application. It is reported that calcium sulfate cement generally takes 4–6 weeks to completely degrade under the condition of good blood vessels. However, the degradation time of calcium sulfate was prolonged to 6–10 weeks in the poorly vascularized bone defect(1).

## 3. Calcium phosphate ceramics:

The synthetic mineral salts, HA and b-TCP are calcium phosphate–based ceramics. Ceramics are inorganic solids, that require high temperature and high-pressure processing to produce dense, highly crystalline, bioinert ceramics. They are produced in a highly thermal process known as “sintering,” where they are heated between 700°C and 1300°C to form their crystalline structure, this allows for improved strength but slower resorption.

### 3.1. Hydroxyapatite (HA):

The chemical composition of HA closely resembles that of the inorganic component of bone, enables it to be used as a bone grafting material and as a defect filler. It is classified as bioactive, referring to its support towards the formation of hard tissue and osseoconduction and as well osteointegrative. However, synthetic HA do not contain trace amounts of $Na^+$, $Mg^{2+}$, $K^+$ and $Sr^+$, which are found in naturally derived HA and influences various biomechanical reactions. Synthetic HA does not possess a microporous structure, as seen in bovine-derived.

HA has a delayed and low resorption rate due to its relatively high Ca/P ratio, high stability and crystallinity. HA ceramic is a valid alternative to autogenous graft without donor morbidity, it can be used as a structural bone substitute to correct and fill bone defects due to its good mechanical strength.

The application of HA in dentistry is usually coating on surface of metallic implants, to improve osteoblast activity or to increase the contact area of bone implants, improving the biological fixation, biocompatibility, and bioactivity of implants(2,6).

**Recent advances** have investigated producing nano-sized HA, enhances biomechanical properties that more closely mimics the composition of natural bone, with a much closer resemblance to bone extracellular matrix; enhanced delivery and controlled release of bioactive molecules, such as growth factors, allowing for enhanced osteo-regenerative properties. Nanocrystalline HA exhibits improved biological performance and dissolution compared with its conventional forms of HA, with a larger surface to volume ratio, promoting more effective adhesion, proliferation, and differentiation of osteogenic progenitor cells, resulting in improved fracture toughness and mechanical properties(2).

### 3.2. Tricalcium Phosphates (TCP)

TCP possesses two crystallographic forms, α-TCP, and β-TCP. The α-TCP only exists at very high temperatures (around 1500 ◦C). TCP are bioactive, biocompatible, osteoinductive, and bioresorbable materials that allow and promote bone tissue regeneration. β-TCP is formed at a temperature of 900–1100 °C. β-TCP has a more stable structure and lower biodegradation rate than α-TCP, therefore, β-TCP preserves the structural stability for a longer time and has more uses in clinical applications comparatively, in bone regeneration and as a bone substitute material, and can also used in developing monophasic/biphasic bioceramics. β-TCP is less stable than HA, exhibits faster biodegradation and higher solubility compared with HA due to its lower Ca/P ratio(2,6).

In dentistry, α-TCP is used primarily as a fine powder to prepare calcium phosphate cements due to its high solubility and reactivity, which makes it ideally used as injectable biodegradable cements. However, the main drawbacks that limit the use of α-TCP in its pure form in biomedical applications are its rapid resorption rate which is faster than the formation of a new bone, and its limited mechanical properties.

Pure phasic β-TCP possesses many desirable properties, such as its ease of handling, radiopacity allowing monitoring of healing, good osteoconductivity due to macroporosity, has excellent cell adhesion and biomineralization promoting fibrovascular ingrowth, proliferation of osteoblasts cells osteogenic, good resorbability, and low immunogenicity and risk of disease transmission. Whilst the interconnected porous structure of β-TCP allows for improved vascularization, it also results in the material's poor mechanical strength under compression. This results in β-TCP being unsuitable as a bone substitute however it is suitable for use as a filler in bony defects and repair at morphological sites. It is commonly used to repair marginal periodontal and periapical defects; it considered useful in supporting the growth of bones after surgery. However, the mechanical properties and brittleness of this material limit its use to non-load bearing applications(7).

### 3.3 Biphasic Calcium Phosphate Ceramics (HA and β-TCP Ceramic)

**Advancements** have attempted to develop a material combining two phases, ideally mimicking the extracellular matrix properties of the respective tissues, which are tightly connected to each other without additional adhesive components. Some of the strands of one material are extended into the part of the other material to realize an interlocking of both parts. Phases of incompatible calcium phosphates, such as the more stable HA and the more soluble β -TCP, to harness both the resorbability of β-TCP as well as the osteoconductive potential of HA. This results in more rapid and higher bone regeneration rates seen compared with the use of HA alone, and the greater mechanical properties than β-TCP present the major benefits of using biphasic. Thus, BCP material possesses superior bioactivity, biodegradability, osteoinductivity, and mechanical properties than HAP or β-TCP alone and has greater ability to stimulate osteogenic differentiation of BMSCs(2,6).

Despite the improvements in mechanical strength compared with β-TCP alone, biphasic CP ceramics still possess compressive strengths lower than that of cortical bone. The use of biphasic CP ceramics has been indicated as bone grafts, bone substitute in periapical surgery and has shown predictable clinical outcomes and complete alveolar bone healing over a two-year period. Hence, this material has shown the potential for bone healing via osteoconduction and osteoinduction processes(2).

### 4- Calcium phosphate cements (CPCs)

CPCs belong to the group of bioactive synthetic materials, they occupy a particular position due to their resemblance to the chemical components and structures of natural bone tissue, they can directly be injected into the bone defect and allowed to set in situ. When used for in vivo applications, it is prepared by mixing a calcium phosphate salt (powder component commonly containing sintered CP materials such as α-TCP and HA) with water or with an aqueous solution to form a workable paste that reacts at room or body temperature. The calcium phosphate cement dissolves and precipitates into a less soluble calcium phosphate.; and self-set as hydroxyapatite when moistened. During precipitation, the calcium phosphate crystals increase in size, giving rise to a precipitate containing one or more calcium phosphates and gets interlocked, thus the entanglement of the precipitated crystals is responsible for hardening and providing structural rigidity to the cement(8).

These cements are great candidates for various clinical applications. CPCs are considered as the most suitable injectable biomaterials to accommodate narrow and irregular dental bone defects, and used as bone fillers and can be injected to form a bioactive scaffold for tissue engineering, Moreover, since the calcium phosphate cements are fabricated at room or at body temperatures, also they can be used as drug delivery vehicle for antibiotics, antitumor drugs and to deliver bioactive agents.

The major reason for CPCs' wide uses in oral environment are their unique combination of osteoconductivity, bioactivity that favors their combination with growth factors, drugs, polymers, capacity to directly bond to bone, thus establishing a uniquely strong interface, biocompatibility, biodegradability, injectability, moldability, and negligible shrinkage. In addition, CaPs do not cause an antigenic response in the body and can be easily customized to its intended application. Another advantage of calcium phosphate cement is their ability to set at physiological temperature, replicate the structure and composition of bone in a repeatable manner to form hydroxyapatite that resembles biological apatites without the addition of any additives, during the setting reaction only a small amount of heat is released (nonexothermic setting) as compared to polymethylmethacrylate cements and also the volume of calcium phosphate cement remains constant during the setting reaction. As well the porosity and microstructure of CPCs can be altered by adjusting the process parameters, such as the liquid-to-powder ratio and the particle size of the powder phase (5,6).

However, calcium phosphate cements are brittle materials with low mechanical strength and fracture toughness. It cannot be used in load bearing regions of bone due to the possibility of collapse under physiological conditions, and weak mechanical properties that cannot match the strength of human cortical bone (4,9)

According to CPCs end product of reaction, they can be classified into three groups: apatite (HA, $Ca_5(PO_4)_3OH$), brushite (DCPD, $CaHPO_4 \cdot 2H_2O$) and monetite (DCPA, $CaHPO_4$) (1).

### 4.1. Apatite Cements

There are two different reaction paths for the setting of apatite cements. The first is an acid–base reaction, one acidic and one alkaline calcium phosphate source react to form a neutral product. Tetracalcium phosphate (TTCP) is the most frequently applied alkaline calcium phosphate source. The mixture of TTCP with an acidic calcium phosphate source (DCPA or DCPD) produces the precipitation of HA. Apatite formation occurs at pH > 4.2.

$$2\ CaHPO_4 + 2\ Ca_4(PO_4)_2O \rightarrow Ca_{10}(PO_4)_6(OH)_2$$

The second type of reaction is a simple hydration reaction. Calcium-deficient HA (CDHA) is prepared via the hydrolysis of a single CaP compound such as $\alpha\text{-}Ca_3(PO_4)_2$ (α-TCP), which is applied in most clinical products.

$$3\ \alpha\text{-}Ca_3(PO_4)_2 + H_2O \rightarrow Ca_9(HPO_4)(PO_4)_5(OH)$$

Apatite cements generally degraded through chemical dissolution and active degradation mediated by cellular activity (osteoclast activity) and the active degradation is dominant. Due to the limited degradation of cellular activity, HA is the least soluble and most stable of the different CPCs. Many experiments indicated that apatite cements showed only slight degradation and new bone regeneration after being implanted in vivo for several months or even years. The slow degradation of apatite not only hinders the regeneration of new bone, but also severely limits its clinical application. Apatite cements have better mechanical strength than brushite cements.

### 4.2. Brushite Cements (dicalcium phosphate dihydrate)

Brushite cements are prepared using an acid–base reaction composed of acidic phosphorus source and basic calcium source. The most applied formulation is monocalcium phosphate monohydrate (MCPM) and β-tricalcium phosphate (β-TCP). It precipitates at more acidic conditions of the paste at $pH < 4.2$.

$$Ca(H_2PO_4)_2 \cdot H_2O + \beta\text{-}Ca_3(PO_4)_2 + 7\ H_2O \rightarrow 4\ CaHPO_4 \cdot 2\ H_2O$$

Brushite-based biomaterials are characterized by good bioactivity, bioresorbability and biocompatibility. Under physiological conditions, the dissolution rate of brushite cements is almost three times that of HA cements. Ideally, the biodegradation rate of brushite cements should be in line with the newly formed bone to allow the newly formed bone to gradually restore its mechanical properties. However, compared with the regeneration rate of bone, the degradation rate of brushite cements is still slightly slower. There are several methods to improve the degradation rate of brushite cements to be in line with rate of bone formation, while retaining its osteogenic ability and biocompatibility by: (i) reducing the powder-to-liquid ratio of CPCs increases its injectability (ii) improving porosity, by introducing different pore sizes into bone cement to improve the local metabolism and the promote degradation rate of cement, (iii) inhibiting phase conversion by preventing brushite cements from recrystallizing to form apatite ( e.g.by incorporation of $Mg^{2+}$ into the brushite cement to prevent phase conversion). Brushite (dicalcium phosphate dihydrate) cement is a promising bone substitute material. It is degraded by simple chemical dissolution; therefore, they are of special interest for applications where replacement of the cement by newly forming bone is desired.

### 4.3 Monetite Cements

Monetite is the anhydrous form of brushite, can be obtained by adjusting the reaction conditions of brushite cements. For example, setting brushite cements in excessively low pH conditions, in water-deficient environments, or in the presence of metallic ions, favoring monetite formation Another way of fabricating monetite cements is via the thermal dehydration of already-set brushite cements.

$$CaHPO_4 \cdot 2\ H_2O \rightarrow CaHPO_4 + 2\ H_2O$$

Monetite cement is an excellent calcium phosphate cement, its resorption can offer a good balance between implant degradation and new bone regeneration thus, maintaining mechanical stability, an advantage that separated monetite from brushite and HA. Compared with brushite cements, it was found that monetite cements resorb at a faster rate in vivo, as monetite is not transformed, not recrystallize into apatite as readily as brushite.

## 5- Organic-Inorganic Composites

To further improve the properties of bone cement in various aspects, researchers often add organic components to the inorganic phase. The organic components added in composite bone cement can be divided into natural polymers and synthetic polymers. Natural polymers mainly include gelatin, sodium alginate and chitosan; the synthetic polymer is mainly composed of Polycaprolactone (PCL), Poly (Lactic Acid) (PLA), PLGA. These polymers are often added into bone cement in different ways (polymer chain, microspheres) to regulate the degradation rate to meet the corresponding clinical needs. Poly-lactic acid (PLA) has been defined as a biomaterial with potential clinical applications in many studies due to its slow degradation properties and reliable biocompatibility. However, the drawback of pure polymer scaffolds is the lack of osteogenic inducement, which is also the main reason why researchers were chosen to explore composite materials. The addition of polymers enriches the types of biodegradable bone cement and improves its degradability and provides a good method for the clinical customization of personalized biodegradable bone cement and are suitable for the repair of critical bone defects as they possess sufficient mechanical properties(1).

A promising xenograft material currently being researched is chitosan, a naturally occurring polymer. Chitosan can stimulate bone regeneration by providing a structural scaffold that supports osteoblastic activity, the formation of mineralized bone matrix and inducing differentiation of MSCs into osteoblasts. Due to the poor mechanical properties of chitosan, it is often combined with other materials such as gelatin, calcium phosphates and bioglass to provide more desirable properties, by mixing chitosan with gelatin and hydroxyapatite (HA) produces a porous scaffold with desirable properties, as decreased degradability and an open pore structure conducive to cell attachment and vascularization.Recent studies in dental field reported successful use of chitosan-based materials as a membrane for GBR, guided tissue regeneration, coating implant surfaces, restoring alveolar bone height(2)

**Recently** the fabrication of high toughness, biocompatible and resorbable organic–inorganic composite bone cements consisting of brushite, gypsum, and polyglactin fibers was investigated.  Brushite has fast in vivo resorption rates and tend to transform into the insoluble hydroxyapatite phase after implantation, which impairs their in vivo resorption and limits their clinical application. Adding gypsum and functionalized polyglactin fibers composed of poly (lactic-co-glycolic acid), PLGA, fibers have been used as a reinforcing agent with calcium phosphate cements because of their resorbability and biocompatibility, have great potential for bone regeneration and tensile strength and it further increased the toughness of the material due to the chemical interactions between the functionalized fibers and the cements. Combining brushite and gypsum can prevent hydroxyapatite precipitation, thus increased their in vitro resorbability and produce a biocompatible composite with a resorption rate closely matching the new bone formation (10).

For brushite-gypsum composite, brushite and gypsum initial powders were mixed at 5 different weight ratios (table 1). The control groups were prepared using either pure brushite powders (100/0) or pure gypsum powder (0/ 100), (10).

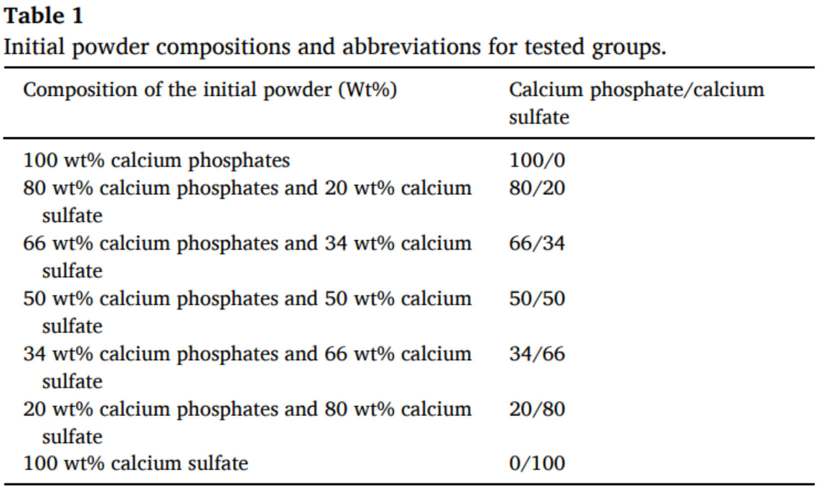

**Table 1**

Initial powder compositions and abbreviations for tested groups.

| Composition of the initial powder (Wt%) | Calcium phosphate/calcium sulfate |
|---|---|
| 100 wt% calcium phosphates | 100/0 |
| 80 wt% calcium phosphates and 20 wt% calcium sulfate | 80/20 |
| 66 wt% calcium phosphates and 34 wt% calcium sulfate | 66/34 |
| 50 wt% calcium phosphates and 50 wt% calcium sulfate | 50/50 |
| 34 wt% calcium phosphates and 66 wt% calcium sulfate | 34/66 |
| 20 wt% calcium phosphates and 80 wt% calcium sulfate | 20/80 |
| 100 wt% calcium sulfate | 0/100 |

Since fracture toughness of cement materials is inversely correlated to their porosity, the porosity of brushite-gypsum composites was measured using a helium pycnometer. Results revealed that adding gypsum to brushite cements decreased the porosity of the hardened composite and thus increases the fracture toughness of the cement. Composites with a brushite-gypsum ratio of 34/66, showed the highest fracture toughness, had the lowest porosity (20%), which was 41% lower than the porosity of pure brushite cement (100/0) ($P < 0.05$). On the other hand, the cements with higher porosity such as the pure brushite and pure gypsum cements, presented lower fracture toughness (10).

## IV. **Dental Applications of bone cements** (2,8,11,12):

1. Calcium phosphates are used in the form of injectable cements or as coatings on titanium and titanium alloy implants to combine the bioactivity of the calcium phosphates and the strength of the metal.
2. Bone-filling material is of great significance for repairing bone defect site.
3. Bone cement can be used to improve stability of implant, especially in patients with insufficient cortical bone, bone cement can be used as the bone graft material, for dental implant fixations.
4. Calcium phosphate cements can be successfully used in different oral applications, including repair of periodontal defects and periodontal regeneration, alveolar ridge augmentation, sinus lifting graft.
5. the application of HA in dentistry is generally limited to the coating on surface of metallic implants.
6. β-TCP has wide applications in periodontics due to its chemical similarity with the cancellous bone, showing improved integration into the natural bone and quick resorption. It is commonly used to repair periodontal defects, followed by alveolar bone and periapical defects around the dental implant.
7. Synthesis of calcium phosphate scaffolds in tissue engineering for bone or dentin regeneration.
8. Bone cements can carry drugs directly to the bone without causing adverse effects on healthy tissues, since systemic drug delivery to the bone is difficult as human bone has limited perfusion. Growth

factors in addition to anti-inflammatory, anticancer, analgesic, and antibiotic reagents are just a few of the medicinal chemicals that may be added into bone cements for various treatments.

Growth factors (GFs) have been widely utilized in bone repair for their bone remodeling functions. Bone morphogenetic proteins (BMPs), are effective osteogenic proteins that promote bone regeneration and bone formation, have ability to recruit and signal to mesenchymal progenitor cells to differentiate toward a bone-forming cells, regulating bone balance by controlling the differentiation of osteoblasts and osteoclasts. Among them, BMP-2 and BMP-7 are the most effective factors for skeletal development including proliferation and formation of bone and cartilage cells for clinical use.

Mixing of growth factors can alter the osteoinductive properties of CaP materials, hence promoting bone repair and formation. It is widely accepted that in the regeneration of lost bone and periodontal tissues, growth factors play a vital role in the complex cascade of tissue regeneration process (potent osteoinductive activity)(6).

BMP has been incorporated into several scaffold systems to localize the delivery of BMP to the defect area whilst minimizing protein diffusion, to increase effectiveness. Porous β-TCP have a high affinity used as potential carriers and delivery systems for loading of bone morphogenetic protein-2 (BMP-2). Scaffold were briefly etched with citric acid in order to increase surface area and thus protein adsorption and loading, The incorporation of BMP-2 was sufficient to induce bone within the scaffolds pores and resulted in an amount of newly formed bone that was 1.3 times higher than with unloaded scaffolds(13,14).

In a comparative study, some commercial biomaterials, such as β-tricalcium phosphate, calcium phosphate cement, and polylactic/polyglycolic acid, incorporated with BMPs, were assessed. The highest bone regeneration was observed in β-tricalcium phosphate kind. Most of calcium phosphate cement remained because of its low degradability. In the polylactic/polyglycolic acid, although the materials wholly degraded, the remained polymer fragments created inflammatory response besides bone regeneration.

9. Human Demineralized bone matrix can be used to regenerate mineralized bone filling in extraction sockets in an attempt to minimize post-extraction atrophy and help to preserve and restore dimensions of the alveolar ridge(bone height and thickness) following tooth extraction for implant placement. DBM can be as used as a bone repair matrix and a carrier for delivering bioactive agents.

DBM is an allograft derivative, which is acid-treated to remove the mineral mesh. This demineralization process results in exposure, of the underlying inner bone matrix rich in growth factors and bone morphogenetic proteins, collagen (mainly type I and type IV), a small amount of calcium phosphate, and cell debris. DBM is relatively easy to handle with minimal immunological rejection due to the elimination of the antigenic surface structure of the bone during acid-treatment; good bone conduction ability, they also exhibit the conventional benefits of allograft materials and demonstrated to be an osteoconductive and osteoinductive substitute. DBM provides a lack of structural support due to the loss of many inorganic components and thus possesses poor mechanical properties, thus it is not suitable for the repair of bone defects in load-bearing areas. The use of DBM is only limited to filling bone defects and is generally used in combination with other allografts, BMPs or composite bone substitute material(15).

DBM cannot fullfil the role of scaffold owing to lack of calcium/phosphate and causing rapid resorption before new bone formation occurs. To improve DBM's ability for bone-graft material, mixing DBM with calcium phosphate enriched material may be a key. One of the most used forms of calcium phosphate for synthetic bones is β-tricalcium phosphate (TCP), widely studied in the field of tissue regeneration due to its osteoconductivity, biocompatibility, and bio-resorption. The mixture of DBM and TCP exhibited excellent bone formation by a synergistic effect, since TCP has a suitable rate of degradation, it can promote the release of calcium and phosphorus ions to induce bone formation(15)

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# Recent Advances and Modifications in Bone Cements

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**Abstract:** The current review describe the state of the art of the modification of bone cement formulations, mainly biomimetic functionalized scaffolds, ion doped materials, the potential of decellularized extracellular matrix scaffolds and 3D printing scafoolds, and the reasons for the development of modifications.

**Keywords:** : *bone cement, biomimetic functionalized scaffolds, ion doped materials,* 3D printing scafoolds

## 1- Biomimetic Functionalized scaffolds:

Bone tissue may be subjected to trauma or other degenerative diseases during lifetime. The regeneration of impaired bone tissue is still a largely unmet clinical need, particularly when it comes to the treatment of critical size and load-bearing bone defects. Material scientists have been expending efforts to find effective technological solutions, based on the use of scaffolds, to develop materials and devices that exhibit high biomimetic character. Biomimetics is the ability of a scaffold to reproduce and mimic both the compositional and three-dimensional structural features of the host natural bone tissues and recreate its features in synthetic scaffolds., i.e., capable of exhibiting bioactivityy instructing cells by virtue of their chemical and structural similarity with the target tissue. Biomimetics have great promises and is a potentially fruitful direction of injectable bone repair material (16).

### 1.1 Ion doped materials:

In general, bone tissue is poorly vascularized, treating bone diseases and defects, with general drug administration, is a challenge. The issue becomes more severe when this vascularization is disrupted by trauma or during a surgical process. The mentioned problems are the main reason to encourage scientist to utilize implants containing biological agents and compensate for the shortage. **Several trace inorganic ions** have been discovered to be conducive to bone tissue regeneration. Recently, research has focused on improving the properties of CPC by doping in calcium phosphates, hydroxyapatite (HA), or another natural or polymeric material, with various trace elements essential for bone metabolisms, such as magnesium (Mg), zinc (Zn), strontium (Sr) and silicon (Si), copper which would effectively mimic the mineralization process of natural bone, further promote the biological performance of CPCs by improving bone metabolism and hence promote osteoinduction and osteointegration. It has been widely investigated and proved to be beneficial to the osteogenic differentiation of osteoblastic cells. The introduction of these trace elements into calcium phosphate-based ceramics or cements could stimulate the responses of bone repair-related cells and influence the physicochemical properties (such as strength and degradation). Thus, the repairing effect of bone defects could be enhanced if the osteogenic capacity of CPC is enhanced(2).

Among the different bioactive metal ions tested, strontium has been extensively investigated in the context of bone repair materials due to its structural and physicochemical similarity to calcium, promoting bone regeneration and inhibiting bone resorption.

A recent approach to advance the properties of CPCs is the combination of CaP containing cements with **bioactive glasses (BGs),** BG is characterized for its ability to support bone growth by chemically bonding to bone, and release of silica ions from BG surface, which is followed by the formation of an amorphous calcium phosphate precipitation. Precipitated amorphous calcium phosphate leads to the formation of a hydroxyapatite (HAp) layer on the surface of the material, which further activates cell migration to trigger new bone formation. The desirable properties of bioglass include relatively easy handling and adaptability to the defect site, good biocompatibility, osteoconductivity, antimicrobial activity, and a porous structure promoting vascularization(16).

They have been successfully used in periodontal surgery to stimulate bone regeneration. However, BAG can be brittle and possess low mechanical strength and poor fracture resistance. Thus, their use in dentistry is limited to low stress bearing area or in combination with other grafting materials. Bioglass materials have been successfully used in periodontal osseous defects and preserve alveolar bone following tooth extractions in orthodontic patients.

### 1.2 The Potential of decellularized extracellular matrix scaffolds:

The field of acellular biomaterials is progressing and is becoming a practical alternative to cell-based therapies. Previously, acellular materials only were regarded as fillers for the tissue defects, but now are able to be engineered into scaffolds that can interact with surrounding cells and tissues to alter the traditional recovery processes from disease or trauma or bone defect(16).

Another biomimicry target is the extracellular matrix (ECM), a complex network of polysaccharides and proteins secreted and regulated by cells that provides biochemical signals for the modulation of cell activities and as a bridge for connecting cells and materials. Bone ECM has both inorganic and organic constituents. The inorganic part, consisting of calcium phosphate, mainly in the form of hydroxyapatite (HA), is the source of bone strength, while the organic part, composed mostly of type I collagen, provides the tissue and cell with flexibility and adhesion, respectively.

Decellularized bone refers to biomaterials formed by human or animal organs/tissues with the removal of immunogenic cellular components via decellularized technologies, it is frequently used as a special scaffold material in bone tissue engineering, due to its ability to eliminate cellular components and antigenicity while its osteogenic and biomechanical properties as well as its physiological are similar to the bone matrix.

dECM scaffolds mainly consist of extracellular matrix (ECM) is a three-dimensional (3D) framework containing extracellular macromolecules such as collagen, elastin, fibronectin, laminin proteins, Meanwhile, the physicochemical signals and biological performance of dECM can be remained after decellularization, which provides a substrate for mechanical supporting and a biological 3D carrier for subsequent cell seeding , thus mimic an optimal non-immune environment with native three-dimensional structures and various bioactive components.

A recent study prepared decellularized extracellular matrix (dECM) deposited on a biphasic calcium phosphate (BCP) scaffold. Rat derived bone marrow messencymal stem cells RBMSCs were chosen as a source of ECM (MSCs can create ECM that mimics various tissues depending on culture conditions), isolated from femur and were cultured on porous BCP scaffolds under osteogenic condition to generate bone-like ECM on the surface of scaffold for 3 weeks, these scaffolds were decellularized by physical or chemical method. decellularized ECM derived from RBMSCs was evaluated whether it could improve the attachment and proliferation of newly seeded cells compared to those directly grown on bare BCP scaffold alone. The results indicated that the BCP scaffold with ECM was effective in promoting the bioactivity of scaffolds, showed increased osteoblastic differentiation as well as offering a stable microenvironment for osteogenesis (16,17).

## 2. 3D printing scaffold

Tissue engineers need to mimic the micro/nano-architecture of natural bone to investigate the means of stimulating effective tissue growth, cell actions such as migration, adhesion, proliferation, as well as differentiation could be regulated, further promoting bone regeneration.

Although injectability is one of the advantages of CPCs, designing of prefabricated biomimetic CaP ceramic scaffolds are often prepared for two reasons: (1) To ensure a complete setting reaction because only fully set CPCs demonstrate excellent tissue responses, when fail to set, they cause inflammatory reactions. Therefore, manufacturing prefabricated CPCs ensures complete setting prior to in vivo prefabricated (2) To facilitate the creation of interconnected macroporous structures into CPCs, that stimulates cell differentiation into osteoblasts and to stimulate cell chemotaxis and new bone matrix deposition. Self-setting CPC scaffolds without any modification are microporous but not macroporous and have limited pore interconnections. Variations in surface roughness, fiber alignment, especially interconnected pore structures, could be prepared by 3D printing technology that is able to produce sophisticated architectures with 3D features. Recently research has aimed to develop three-dimensional (3D) printing, has rapidly developed to allow the fabrication of pre-set 3D-printed CPC scaffolds(16).

**Recent research** has aimed to develop 3D prefabricated pre-set CPC scaffolds. 3D printing is an additive manufacturing process in which geometrical data are used to produce 3D structures by depositing (incremental addition) of materials layer by layer, they are favored to meet the specific needs of each patient defect and can accurately shape internal structures and external contour.

These printers utilize inkjet cartridges that are identical to those found in common desktop printers. 3D artificial bone tissue can be easily created using biological ink, these ink cartridges can be opened, cleaned, and refilled with the binder solution or bioactive inks, which exists in the form of a viscous fluid.

The benefits for clinical applications include easy adaptation and fixation, reduced surgical time, favorable esthetic results, and minimal waste products. For CPC scaffolds**, binder jetting** is the most employed 3D printing technique. Binder jetting operates using ceramic powders and polymeric binders. The powders form the final ceramic structure, while the binder acts as temporary material to hold each layer together before sinterization.

One or several print heads spray a binder solution, from inkjets (for example, an aqueous solution) precisely onto a bed layer of CPC powder phase which is most often a CaP, such as hydroxyapatite or tricalcium phosphate (TCP), α-TCP is most used than β-TCP, which is more thermodynamically unstable (and thus more soluble) than b-TCP. For HA or TCP powder mixed with the binder used in the 3D printing process to form a 3D object (referred to as the "green part", green strength which is not suitable for end-use and are then subjected to a post-process such as sintering or infiltration to achieve desirable mechanical properties), the binding solution is usually a polymer in solvent liquid ( which is pyrolyzed during sintering after printing) , or an aqueous solution, CaP powders such as TCP typically require aqueous binding solutions, such as dilute phosphoric acid (in a concentration range of 5–30 wt.%). The acidic binder initiates a dissolution-precipitation reaction, which yields brushite. The acidic binder solutions applied to CaP powders, locally joins and unify adjacent powder particles together to fuse the particles and hardens the wetted areas and enable low temperature binding of the particles in a dissolution-precipitation reaction.

The process repeats by spreading another layer of powder and ejecting binders according to design by the computer. As the build progresses, the layers of the print are bonded together, resulting in a box of powder with binder arranged in the 3D shape. This continues until the complete 3D structure is formed with desired geometry. Once the printing step is complete, some binder jet technologies require a post-cure to dry the binder, the binder may be then removed by post-processing to cure or set the binder if needed, such as high-temperature sintering or by chemical dissolution. Eventual removal of the binder will weaken mechanical stability; however, the structural drying and sintering process will help rebuild its integrity(17–19) .

After curing, the green parts have enough strength to be handled and moved to the densification furnace. At this critical step of powder-based 3D printing, the removal of the loose powder inside the pores of the printed scaffold after printing is done by a process known as depowdering, where the printed part(s) may be removed from the powder bed . Depowdering is especially challenging when the pores and pore interconnections are small and found in the innermost parts of the scaffolds with large dimensions (17–19) .

Bone tissue engineering scaffolds require interconnected 3D pore structures that permit cell infiltration as well as allowing nutrient access and waste removal. The printability of the material is related to many parameters such as particle size and size distribution, morphology and surface area of the powder, roughness and flowability of the powders, the solubility/wettability/ reactivity of the powder with the binder, and binder drop size. A study investigating beta-tricalcium phosphate powder suggested that 3D printing was not feasible with particles either too small (with a mean particle size of 7 μm) or too large (with a mean particle size of 51 μm), while mean particle sizes in the range of 20–35 μm resulted in good printing accuracy and considered optimal. Small particles tend to agglomerate under the influence of van der Waals forces. Very fine or porous particles exhibit low flowability and high surface roughness. Therefore, these factors greatly affect the smoothness and homogeneity of the powder bed. However, although large particles have better flowability, the powder flows easily but does not pack sufficiently, they tend to yield layer displacements due to low powder bed stability causing interlayer instability that compromises binding and geometrical accuracy, because the resolution is at least twice the particle size (17,19).

Main advantages of binder jetting are the ability to print pure CaP scaffolds, simultaneous printing of bioinks (drugs or growth factors) in ink cartridges, the shaping process occurs at room temperature and atmosphere, avoiding issues related to oxidation, residual stress, and phase changes, making the powder around the parts in the build box (the area where the powder bed is ready for printing) highly recyclable and is great for larger, porous ceramic structures. While drawbacks include the designed pores are limited to ~ 500 μm, brittle and limited mechanical properties, inability to directly print cells, (19).

**Organic/ inorganic scaffolds by 3D printing:**

3D printing has become a widely used technique to fabricate composite scaffolds in regenerative medicine. One of the main problems associated with the use of biodegradable polymers in the development of biomimetic scaffolds, such as PLA, PLGA, and PCL is their degradation problems that could affect overall osteointegration process. Highly viscous nature of polymers can lead to inhomogeneous infiltration, inappropriate pore interconnectivity, as well as a significant reduction in the overall porosity which may hinder vascularization of the resulting composite material and affect the final mechanical performance. The incorporation of natural polymers, as collagen results in an ideal strategy in the development of bioactive organic/inorganic composite scaffolds. Further introduction of polyethylene glycol (PEG) has been addressed to increase hydrophilicity and the resulting cell adhesion, proliferation, and differentiation on the scaffold surface. Even though these polymeric components do not reproduce the biological features of natural polymers, such as collagen, their use can help in modulating the rheologic properties of bio-inks yielding scaffolds with complex shape and geometry.

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# Time Dependents Properties Viscoelasticity Models

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**Abstract:** The mechanical properties of many dental materials depend on the rate of loading. They show a behavior intermediate to that of a rigid solid and a viscous liquid. This behavior is called viscoelastic behavior.

**Keywords:** : *Viscoelasticity, viscoelastic materials*

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## 1. Introduction

The mechanical properties of many dental materials depend on the rate of loading. They show a behavior intermediate to that of a rigid solid and a viscous liquid. This behavior is called viscoelastic behavior. (1)

Viscoelastic materials are materials showing viscous and elastic behaviors simultaneously. These materials exhibit both properties and a time-dependent strain behavior. *Elastic strain* typically results from stretching but not breakage of atomic or molecular bonds in an ordered solid. The *viscous* component of viscoelastic strain results from the rearrangement of atoms or molecules within amorphous materials. The elastic portion (which stores energy) behaves according to Hooke's law. The viscous portion (which dissipates energy) behaves according to Newton's law. Viscoelastic materials show time-dependent and delayed response when load is applied and removed.(2,3)

Examples of such materials in dentistry are elastomeric and hydrocolloid impression materials, amalgam, waxes, polymers, and orthodontic elastics. Dentin, oral mucosa, and periodontal ligaments also exhibit viscoelastic behavior. (4)

All polymers exhibit viscoelastic properties. The polymer chains exhibit elastic behavior, chains uncoil but they do not slip past one another because of crystalline regions, entanglements, or crosslinks. Thus, they recoil completely when unloaded (i.e. they store the energy used in displacing them). They also exhibit viscous behavior when chains stretch, uncoil, and slip past one another. This produce plastic, irreversible, permanent distortion and partial recovery when unloaded (Figure 1). Friction between the chains causes a net loss of energy after they return to their original positions. (3)

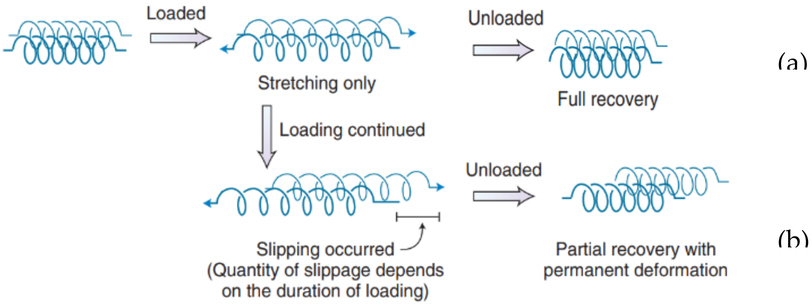


**Figure 1:** (a) Elastic and (b) viscoelastic recovery of polymers.

## 2. The ideal elastic behavior

An ideal elastic material responds instantaneously to applied stress and maintain that strain as long as the load is applied. When this stress is removed, the sample recovers its original dimensions completely and instantaneously (Figure 2). Ideal elastic materials obey ***Hooke's law***, where the stress is directly proportional to the strain independent of the rate at which the body is deformed:

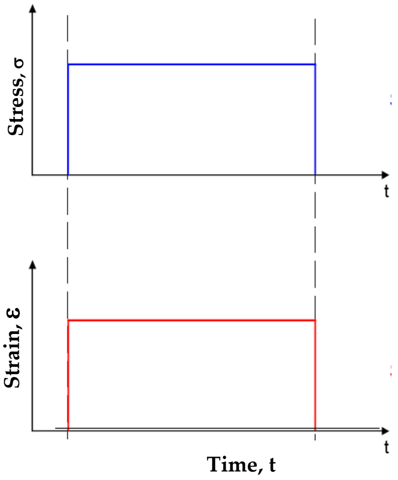


**Figure 2:** Ideally elastic solid response.

$$\sigma = E\,\varepsilon$$

Where σ is the stress, E is the modulus of elasticity and ε is the strain.(2)

## 3. The ideal viscous behavior

An ideal viscous material obeys **Newton's law of viscosity**, where the stress is directly proportional to a strain-rate:

$$\dot{\varepsilon} = \frac{\sigma}{\eta}$$

Where $\dot{\varepsilon} = \frac{d\varepsilon}{dt}$ is the strain rate, σ is the stress and η is the viscosity coefficient.

Upon loading, the strain generated is not instantaneous and time dependent. The strain keeps on increasing with time on application of the constant load. When the load is removed, the material does not return to its original dimensions (irreversible deformation) (Figure 3).(2)

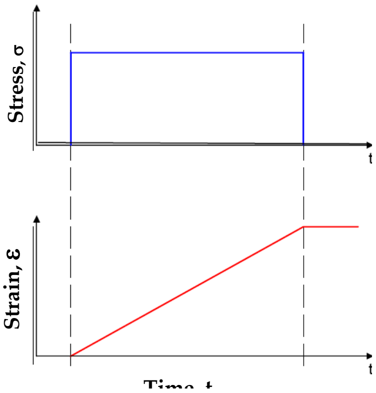


**Figure 3:** Ideally viscous behavior.

## 4. Anelastic behavior

Anelasticity is a time-dependent elastic behavior. When load is applied, a non-linear (gradual) increase in strain with time. When the load is removed, there is a gradual but complete recovery (Figure 4).(5)

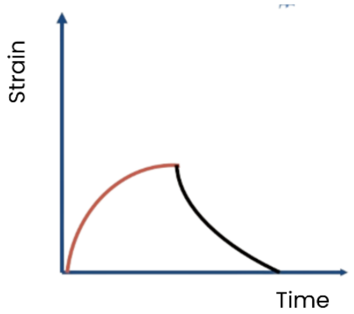


**Figure 4:** Anelastic behavior (delayed elasticity).

## 5. Viscoelastic behavior

This behavior is a combination of ideal elastic, ideal viscous and anelastic. When load is applied, there is an instantaneous elastic strain, followed by a viscous and anelastic time-dependent strain. Upon load removal, there is immediate elastic recovery and gradual anelastic recovery, while the viscous portion will not recover (Figure 5).(5)

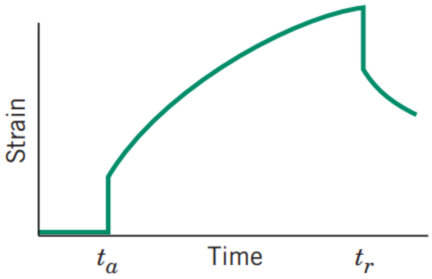


**Figure 5:** Viscoelastic behavior.

## 6. Characteristics of Viscoelastic Materials

There are three main characteristics of viscoelastic materials: *hysteresis, stress relaxation, and creep.*

### a. Hysteresis

Unlike elastic materials which store all the energy due to deformation, viscoelastic materials dissipate some of this energy by internal frictional mechanisms. As a result, there is a difference between the energy provided to the material and the energy recovered. This makes the loading and unloading curves non-equivalent but form a hysteresis loop (Figure 6) .(6)

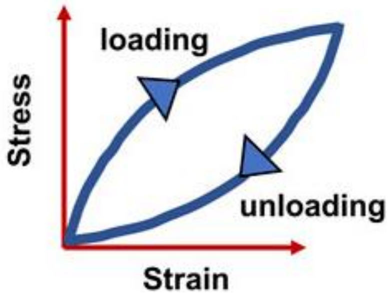


**Figure 6:** Hysteresis.

### b. Stress relaxation

When a viscoelastic material is strained and this strain is kept constant afterwards, the corresponding stresses induced within the material decrease with time (Figure 7). This is due to a re-arrangement of the material on the molecular or micro-scale. (6)

**Figure 7:** Stress relaxation.

### c. Creep

When a viscoelastic material is loaded at a constant stress, holding that stress for some time, the material will show increased deformation (strain) under constant stress (Figure 8). (6)

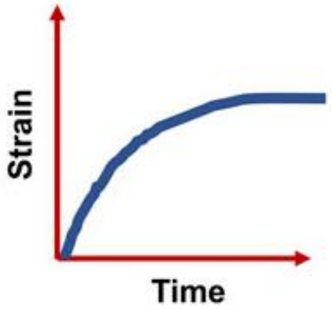


**Figure 8:** Creep.

## 7. Viscoelasticity Models

### The Basic Elements: Spring and Dashpot

### The Spring:

The spring represents the elastic component (Figure 9), The spring has a spring constant (k). Because of this spring constant, there is a maximum deformation that can be reached (under constant force). (2)

**Figure 9:** Spring model to illustrate ideally elastic behavior.

**F = k X**

Where F is the applied force, k is the spring constant and X is the deformation. So spring reaches an equilibrium situation after it gains maximum deformation.(2)

The spring stores all energy the during deformation. This energy is then available to restore the body to its original shape when these forces are removed.(2)

### The Dashpot:

It represents the viscous component (Figure 10). The dashpot responds with a strain-rate proportional to stress according to Newton's law of viscosity. When work is done to a dashpot, energy is not stored, instead heat is generated and lost to the environment due to internal friction.(2)

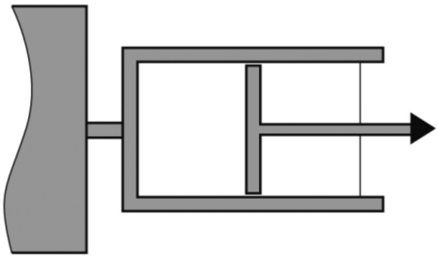


**Figure 10:** The dashpot model to illustrate ideally viscous behavior.

### a. Two-Element Models:

### i. Maxwell Model

The Maxwell model can be represented by a purely viscous dashpot and a purely elastic spring connected ***in series*** (Figure 11). Both components can be deflected independently of each other. (2)

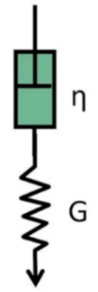


**Figure 11:** Maxwell model.

*Upon loading:* when applying a constant force, only the spring shows immediate deformation until reaching a constant deflection value. Afterwards, the piston of the dashpot begins to move and continue to move as long as the force is applied (Figure 12b).(2)

*Upon load removal:* the spring recoils back elastically (immediately and completely). However, the dashpot remains unchanged. Thus, there is elastic response and a permanent strain but no anelastic recovery (Figure 12b). These kinds of samples remain **partially deformed** due to the viscous portion represented by the Dashpot **(irreversible deformation process)** (Figure 12b).(2)

In Maxwell model, the stress on each element is the same and equal to the imposed stress (called iso-stress model), while the total strain is the sum of the strain in each element.(7)

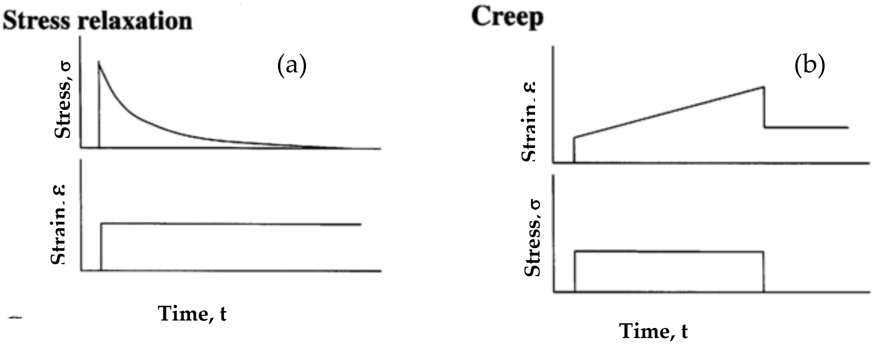


**Figure 12**: (a) Stress relaxation, (b) Creep curves of Maxwell model.

The Maxwell model is **more suitable to explain the stress relaxation of polymer**, as it predicts that stress relax exponentially with time, which is accurate for most polymers (Figure 12a). This model actually represents a **viscoelastic fluid** since it relaxes completely to zero stress and undergoes creep indefinitely. (8)

However, it is **unable to accurately predict creep** as it suggests that strain will increase linearly with time. However, polymers for the most part show the strain rate to be decreasing with time. It is not suitable for modelling materials over long periods of time, as it places no limit upon how much the dashpot can extend. (8)

### ii. Kelvin/Voigt model

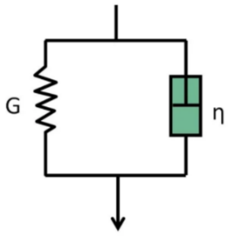


**Figure 13:** Kelvin/Voigt model.

The Kelvin/Voigt model can be represented by a purely viscous dashpot and a purely elastic spring connected ***in parallel***. Both components are connected by a rigid frame (Figure 13). (2)

*Upon loading:* when applying a constant force, deformation is increasing continuously. Since the two components are connected by a rigid frame, they can only be deformed together simultaneously and to the same extent. The spring can not undergo immediate deformation because its motion is slowed down by the dashpot. According to this model, the dashpot will only extend to the extension produced in the spring.(2)

*Upon load removal:* the spring has tendency to immediately recoil back to its original shape, and this is the driving force that will cause both components to return to their initial shape. However, this will occur only after a certain period of time due to the presence of the dashpot. These kinds of samples show **delayed but complete recovery (reversible deformation process).** (2)

In Kelvin/Voigt model, the stain on each element is the same (called iso-strain model), while the total stress is the sum of the stresses in each element.(7)

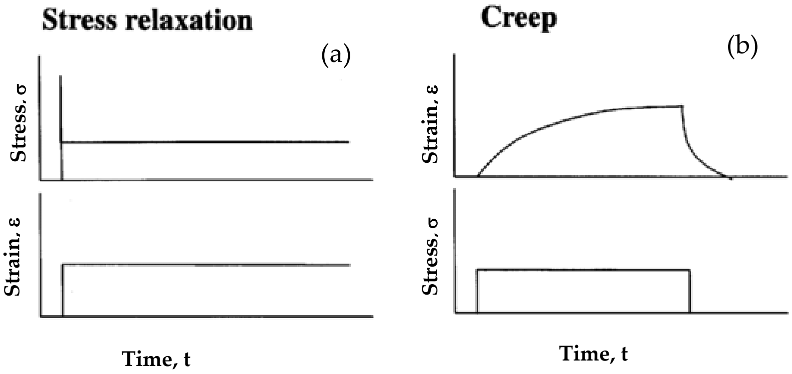


**Figure 14**: (a) Stress relaxation, (b) Creep curves of Kelvin/Voigt model.

This model is suitable for **modelling creep,** because when constant stress is applied, the material deforms at a decreasing rate (It is not linear), i.e. it does not continue to deform as long as stress is applied, rather it reaches an equilibrium deformation (Figure 14b). (8)

However, it is **less accurate in modelling stress**. The stored energy in the spring cannot transfer to the dashpot since the dashpot and spring connect in parallel. So, even though dashpot dissipates its energy, spring cannot dissipate its energy. Thus, the system always has residual stress, and this stress becomes constant after some time (Figure 14a). This model represents a ***viscoelastic solid***.(8)

### b. Three-Element Models:

The Maxwell and Kelvin models are the simplest viscoelastic models. Maxwell model does not describe creep and Kelvin–Voigt model does not describe stress relaxation accurately. (8)

***The Standard Linear Solid Model (SLS) model*** is a more complex model which combines elements of both the Maxwell and Kelvin-Voigt models. SLS is the simplest model that predicts both phenomena. More realistic material responses can be modelled using more elements.(9)

#### i. Zener Models

They describe a material that will react instantaneously to applied strain and fully recover after a load is removed, because the spring connected in parallel will continue to move the piston of the dashpot back to its original position. Thus, Zener models represent **solids** that undergo a **reversible deformation**.(10)

Zener Model type I (Maxwell representation)

It is obtained by adding a spring in parallel to a Maxwell model (Figure 15a). In this system, the dominant model is the Maxwell model. So, this system is more suitable to explain **stress relaxation** behavior of the solid polymer (Figure 15b).(11)

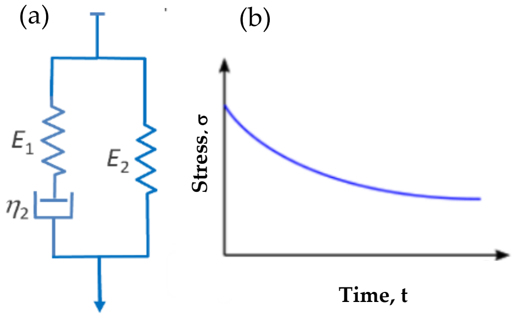


**Figure 15:** SLS Model (a) Zener Model type I, (b) Stress relaxation curve of Zener model.

Zener Model type II (Kelvin–Voigt representation)

It is obtained by adding a spring in series to a Kelvin–Voigt model (Figure 16a). In this system, the dominant model is the Kelvin–Voigt model. So, this system is more suitable to explain **creep** behavior of the solid polymer (Figure 16b).(11)

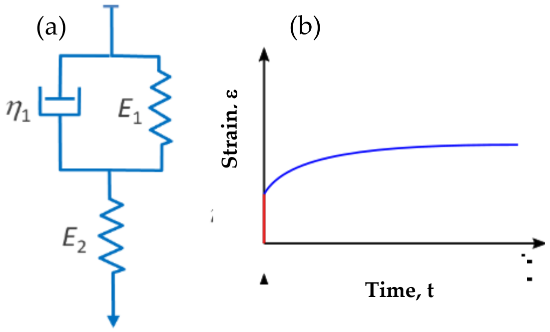


**Figure 16:** SLS Model (a) Zener Model type II, (b) Creep curve of Zener model.

### ii. Jeffreys models (anti-Zener)

Three-Element Models of Standard Linear Fluid *(SLF Model)*

They describe a material that will only **partially recover** after a load is removed because the piston of the dashpot will not move back to its original position when the load is removed. Thus, anti-Zener models represent a **fluid** that undergoes both a **permanent and elastic deformation**.(10)

Jeffreys Model type I (Kelvin–Voigt representation)

It is obtained by adding a dashpot in series to a Kelvin–Voigt model (Figure 17a). In this system dominant model is the Kelvin–Voigt model. Therefore, this system is more suitable to explain **creep** behavior (Figure 17b). (11)

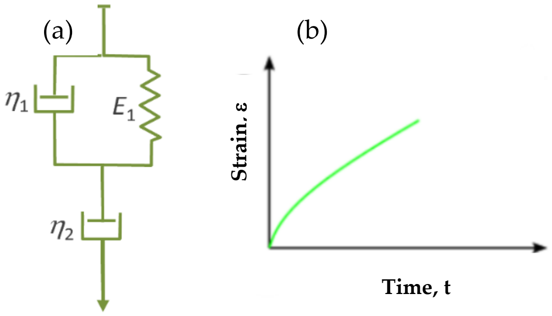


**Figure 17:** SLF Model (a) Jeffreys Model type I (b) Creep curve of Jeffreys model.

Jeffreys Model type II (Maxwell representation)

It is obtained by adding a dashpot in parallel with the Maxwell model (Figure 18a). In this system dominant model is the Maxwell model. Therefore, this system is more suitable to explain **stress relaxation** behavior of molten polymer (Figure 18b). (11)

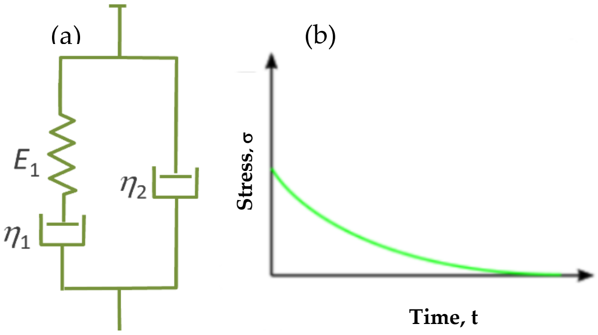


**Figure 18:** SLF Model (a) Jeffreys Model type II (b) Stress relaxation curve Jeffreys model.

### C. Four- Element model (Burgers model)

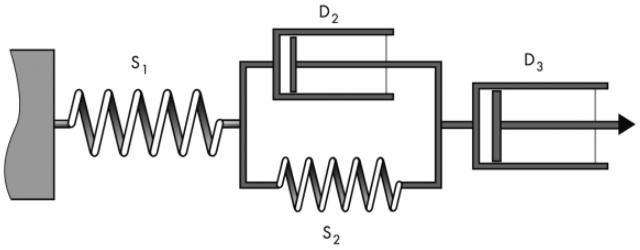


**Figure 19:** Burgers model

It is a combination of the Maxwell model (S1 and D3) and the Kelvin/Voigt model (S2 and D2) joined in series (Figure 19).(2)

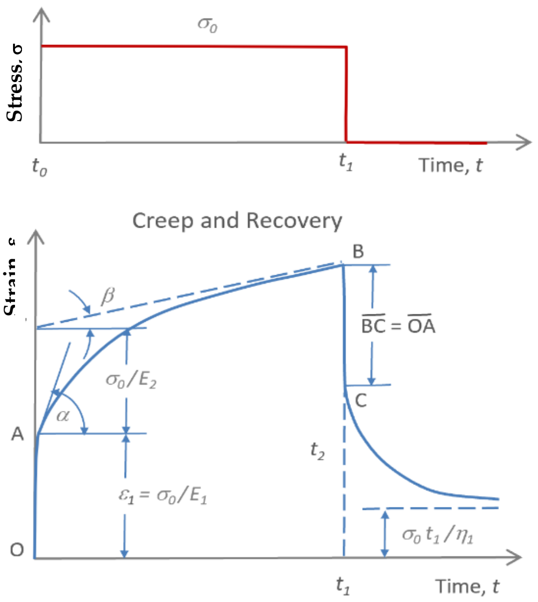


**Figure 20:** Creep and recovery behavior of burgers model.

*Upon loading:* immediate, step-like deformation of spring $S_1$ .Then delayed deformation of spring S2 and dashpot D2 (like the Kelvin/Voigt model), and continuously increasing deformation of dashpot D3 (D3 can show creep indefinitely).(2)

*Upon load removal:* immediate elastic recovery of spring S1. Delayed recovery of spring S2 and dashpot D2 (like the Kelvin/Voigt model). Dashpot D3 remains completely deflected.(2)

The four-parameter model provides a crude qualitative representation of the phenomena generally observed with viscoelastic materials: instantaneous elastic strain, retarded elastic strain, viscous flow, instantaneous elastic recovery, retarded elastic recovery, and plastic deformation (permanent set) (Figure 20).(12)

## 8. Testing of Viscoelastic Materials

The viscoelastic behavior of polymeric materials is dependent on both time and temperature; several experimental techniques may be used to measure and quantify this behavior.

### a. The Creep and Recovery Test

This test involves loading a material at *constant stress*, holding that stress for some length of time and then removing the load. There is an instantaneous elastic strain, followed by increasing strain over time known as ***creep strain***. The creep strain normally would increase with an ever-decreasing strain rate, which eventually leads to a constant-strain steady state. The ratio of total strain to an applied constant stress is **creep compliance $J(t)$:**

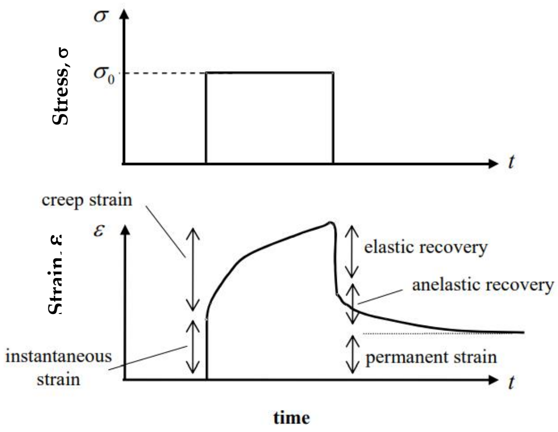
$$J(t) = \frac{\sigma_0}{\varepsilon(t)}$$

where $\sigma_0$ is the constant applied stress and $\varepsilon(t)$ is the time-dependent strain.(7)

In a creep test, the resulting strain for viscoelastic solids increases until it reaches a non-zero equilibrium value, while for viscoelastic fluids the resulting strain increases without bound as time increases.(7)

When unloaded, the elastic strain is recovered immediately. There is then anelastic recovery (strain recovered over time). A permanent strain may then be left in the material (Figure 21).(13)

The creep performance of viscoelastic materials reveals their dimensional stability and capacity to sustain the load in the long run.(14)



their

covery test.

*Dental significance of creep*

For a given load at a given time, the low-copper amalgam has a greater strain compared to high-copper amalgam. The greater creep in the low-copper amalgam makes it more susceptible to strain accumulation and fracture, and also marginal breakdown, which can lead to secondary decay.(4)

### b. Stress Relaxation Test

This test involves straining a material at constant strain and then holding that strain. The stress necessary to maintain this strain is measured as a function of time while temperature is held constant. (5)

In a stress relaxation test, viscoelastic solids gradually relax and reach an equilibrium stress greater than zero, while for viscoelastic fluids the stress vanishes to zero (Figure 22).(7)

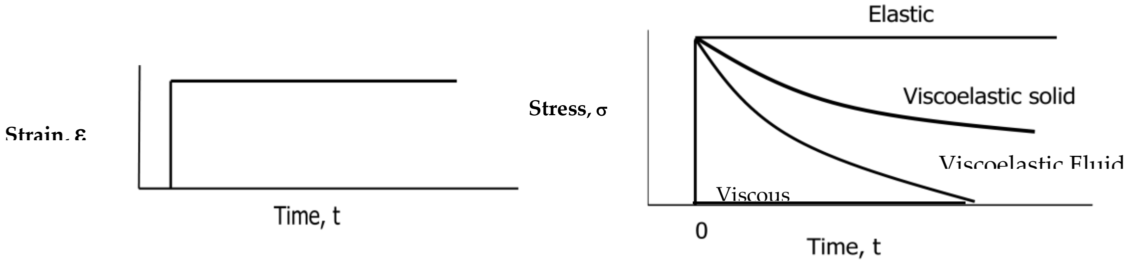


**Figure 22:** Stress relaxation test showing response for an elastic solid, a viscoelastic solid, a viscoelastic liquid and a viscous fluid.

**Relaxation modulus *$E_r(t)$*,** a time-dependent elastic modulus for viscoelastic polymers:

$$E_r(t) = \frac{\sigma(t)}{\varepsilon_0}$$

where $\sigma(t)$ is the measured time-dependent stress and $\varepsilon_0$ is the strain level, which is maintained constant. A constant strain $\varepsilon_0$ acts as "input" to the material from time $t_0$, the resulting time-dependent stress is decreasing until a plateau is reached at some later time. (5)

***Dental significance of stress relaxation***

In the evaluation of orthodontic elastic bands. The initial force was much greater with the plastic band, but the decrease in force with time was much less for the latex band. Therefore, plastic bands are useful for applying high forces, although the force decreases rapidly with time, whereas latex bands apply lower forces, but the force decreases slowly with time in the mouth; latex bands are therefore useful for applying more sustained loads.(4)

Similarly, orthodontic aligners that exhibits rapid stress relaxation may express a decreasing amount of orthodontic force once inserted intraorally. The ideal aligner should exhibit a stress relaxation curve that is fairly flat, representing its capability to exert constant and continuous forces over time. Unfortunately, stress relaxation curves for current aligner materials generally follow a pattern of rapid decay within the first 8 hours of application, then diminish to a plateau thereafter. This highlights the importance of measuring forces exerted by aligners not only during the first hours after tray placement inside the oral cavity but also within the first 24- and 48-hours.(15)

## 9. Dental Significance of Viscoelasticity

In viscoelastic materials, the strain rate can change the stress-strain properties.

### Impression materials

For example, the *tear strength of* ***alginate impression material*****,** is increased about four times when the rate of loading is increased from 2.5 to 25 cm/min. Therefore, alginate impressions should be removed from the mouth quickly to improve its tear resistance. (4)

### Dental amalgam

Another example is the *elastic modulus of* ***dental amalgam***, which is 21 GPa at slow rates of loading and 62 GPa at high rates of loading. Thus, it is particularly important to specify the loading rate with the test results.(4)

### Tissue conditioners

Tissue conditioners also show viscoelastic behavior. An elastic behavior to recover after initial deformation, act as a cushion against the instantaneous cause of pressure, such as biting force. A viscous behavior to allow adaptation to the mucosa, improving the fit of the denture.(16)

### Viscoelastic mucosa.

To get an accurate impression of mucosal tissues in their resting position, patient should not wear the old denture for several hours before taking the impression to allow recovery of the Viscoelastic mucosa. (1)_

## 10. Conclusion

By using these mechanical models, we can predict how the material behaves when a load is applied. In general, the more elements a model has, the more accurate it will be in describing the response of real materials. However, the more complex the model, the more material parameters should be evaluated by experiment. The determination of a large number of material parameters might be a difficult, if not an impossible task.

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