

**The Effect Of Aging Dental Composites In Biologically-Relevant Conditions On Their
Mechanical Properties**

BY

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THESIS

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Summary

Dental composites have become the primary choice for dental restorations. Composites consist of a mixture of solid filler particles bound by polymers which are cured in place following placement in the prepared tooth preparation. It is critical to the long-term performance of the restoration that the material properties do not deteriorate during the life of the restoration. However, there is increasing evidence that dental composites deteriorate following placement, leading to failure of the restoration, usually due to secondary dental caries. The conditions in the oral cavity contribute to the break-down of the composites.

This degradation is likely caused by four main types of processes: physical material degradation (e.g. fatigue due to cyclic loading during mastication), abiotic chemical degradation due to wetting/drying cycles, aqueous dissolution (particularly under acidic conditions as occurs with tooth enamel), and biodegradation of the organic components of the composite. Recent research has clearly indicated that the latter process, biodegradation of the polymer can be catalyzed by enzymes in the oral cavity, both human derived and bacterial in origin. These studies have typically been performed in vitro with only the polymer component of the dental composite (no filler). While such studies provide a mechanistic understanding of the process, they do not help clarify if these processes are just a decrease in strength or an interaction between the oral environment and the restoration.

To address these concerns, a study was undertaken to measure the strength of composites (diametral stress strength and Young's modulus) following aging under various environmental conditions relevant to the oral cavity; air, artificial saliva (AS), acidified artificial saliva, and artificial saliva with esterase enzyme. A large number of replicates was performed to ensure

statistical validity and control for composite curing variability. The aging periods were performed for longer periods of time than is frequently cited in the literature based on an analysis of the maximum amount of time necessary for diffusion penetration of the composite test specimens.

The results demonstrate that air incubated samples had the highest strength, followed by a statistically significant reduction in strength in the AS incubated samples. Acidification of AS media (~50 mM free acid) did not result in any statistically significant reduction in strength compared to AS incubations. In contrast, incubation in the presence of esterase enzymes resulted in a marked, statistically significant reduction in strength. Taken together, these results showed that demineralization/dissolution of the composite under acidic conditions did not result in a significant decrease in strength, while exposure to esterase enzyme resulted in a significant deterioration in material properties. These results further show that composites are susceptible to significant deterioration in material strength under conditions relevant to the oral cavity.

1. INTRODUCTION

1.1 Background

The strong preference for tooth-colored restorations by patients and the growing demand for esthetic dentistry, coupled with concern about the environmental and toxic hazards of mercury-base dental amalgam, has resulted in the widespread use of resin based dental composites in restorative dentistry. [1, 2]

The provision of affordable and effective long-lasting restorations is important for many reasons. First and foremost, placement of a restoration undoubtedly results in enlargement of the tooth cavity which weakens the tooth and may cause pulpal injury. Second, it leads to reduction of the dental treatment costs in the long run. [3] Moreover, studies show that patients are more satisfied when the restoration has the same color as their teeth or when their damaged teeth are preserved. [4] Therefore, dental composites have become a primary component of modern aesthetic dentistry. [5]

Even though composites outperform amalgam and other restorative materials in some clinical studies, they tend to have a shorter lifetime. [6] The main reason for this shorter lifespan is believed to be due to the fact that composites are more prone to secondary caries (SC), which is the recurrence of caries at the interface of the tooth and the restoration. [7-9] Secondary caries are often referred to as the primary cause of restoration failures, and are estimated to account for approximately 50% of restoration replacements. This is supported by a large

number of studies over 25 years showing secondary caries were reported as the cause of the failure regardless of the type of the restorative material used. [10-23]

The increased demand for the dental composites has attracted the attention of dental material scientists, and has resulted in the numerous efforts to find the reasons of their failures and also improve their properties. [24] These approaches have investigated the changes in filler size and shape, increases in the volume of the filler material, changes in the composition of the matrix of the composites, and enhancement in the methods of polymerization to improve material strength and longevity. [25] Various dental composites have been introduced by manufacturers; all with varying claims of superior mechanical and esthetical properties, as well as increased biocompatibility. These enhanced properties include improved physical properties, increased flexure strength, lower wear rates, improved biocompatibility and tissue response, increased fracture toughness, reduced polymerization shrinkage, higher curing rates and lower tendencies to discolor. [24, 25] Currently, significant improvements in the mechanical properties of the composite resins, and thereby longer service life span, has led to them being used for both anterior and posterior tooth restorations. [26-29] Thus, it is clear that the greater the longevity of the restoration, the more successful the restorative procedure. [30]

1.2 aging environments

Dental composites are continuously exposed to innumerable materials and environments when they are placed in the mouth. The oral environment includes saliva, microbes, enzymes, as well as myriad food particles; and is therefore a very complex environment both chemically and mechanically. These conditions include some harsh and extreme chemical environments and/or

mechanical conditions that could severely affect the degradation of the dental restorative materials and cause physiochemical alterations. [26] Material degradation that decreases the load-bearing capacity of the composite can occur in these environments due to both bio/chemical processes, as well as physical degradation through the application of the mechanical loads, such as mastication. Several studies have been conducted on measuring the mastication and bite force in humans and they mainly agree that these forces are in the range of 10 - 1000 N. [31-34] Even though the biting and chewing forces are typically not high, it is the repetitive nature of mastication that causes fatigue. The situation may become progressively worse and lead to eventual initiation and growth of some cracks, finally causing failure of the matrix and/or filler deterioration. [35]

1. 3 Thesis Objectives

The objective of this study was to examine the impact of aging on the diametral compressive strength and modulus of elasticity (or young's modulus) of light-cured dental composite resins under biomimetic conditions simulating those in the mouth. This was achieved by aging composites in four different environments: air, artificial saliva, a mixture of artificial saliva and acetic acid, and mixture of artificial saliva and enzyme. The latter two conditions were selected to investigate the abiotic impact of conditions thought to occur under the dental caries process.

The specific objectives of this research are to:

- 1) Determine the effect of aging dental composites in various aging solutions on material strength.
- 2) Compare the damaging effects of the substances in each environment on the dental composites.

- 3) Identify and measure potential elements leached out from the composites into the aging solutions.

First examined was the diametral compressive strength followed by the identification of elements that may have leached out from the composites during the aging process. Finally, the implications of these results on our understanding of the longevity of dental composites were discussed.

2. LITERATURE REVIEW

2.1 Resin based dental composites

Composite materials are made from two or more constituent materials with inter-atomic interactions. These components usually have significantly different physical or chemical properties. However, they produce a material with preferred (and usually superior) characteristics that can be very different from the properties of the individual components. To name but a few, these superior properties can include increased strength, decreased weight or lower cost when compared to their individual parent materials. Dental composites have become the favored restorative material in recent years due to their vastly superior properties in many clinical aspects, such as their aesthetic appearance and clinical versatility. [6] Dental composites are composed of four main components: a resin matrix, filler particles, coupling agents and an initiator/inhibitor polymerization system. [10] These composites are comprised of an organic matrix/ceramic aggregate composites consisting of synthetic resins with filler particles (usually glass, quartz or a ceramic material such as oxides) that are used as restorative material or adhesives. Synthetic resins evolved as restorative materials because of their superb properties such as insolubility, aesthetic and insensitivity to dehydration. In addition, they are easy to manipulate and reasonably inexpensive. [27] The resin matrix of the dental composites is a polymeric matrix that usually has a methacrylate base, including Bis-GMA and other dimethacrylate monomers (such as TEGMA, UDMA, HDDMA). Some examples of the commonly used monomers are illustrated in Fig 2.1.

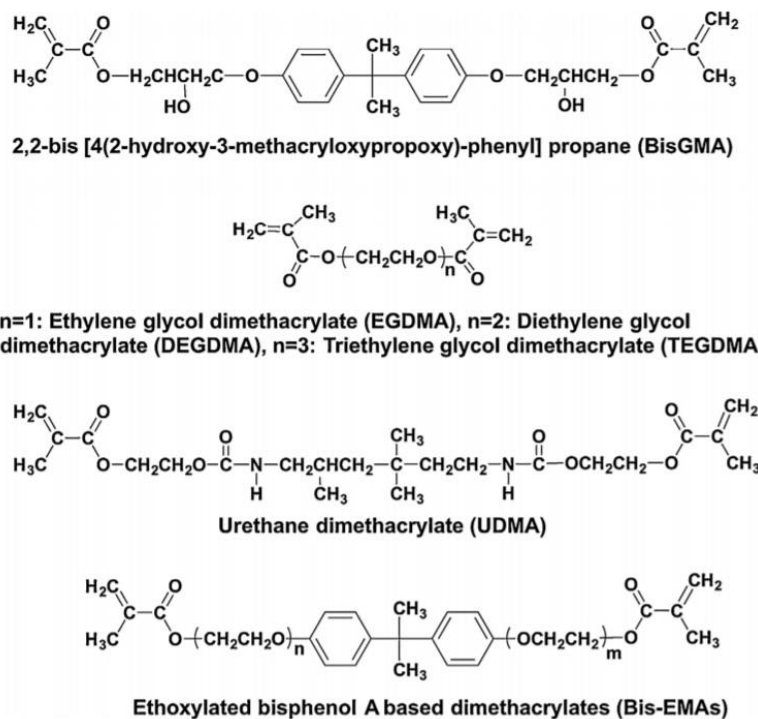


Figure 2.1 - Common methacrylate based di-vinyl monomers used in dental resin materials, Figure from reference [36].

The major component (both by mass and volume) of commercial dental composites is the reinforcing filler particles. [37] That is the constituent that provides the composite with mechanical properties. [10] The nature and size of the filler particles have significantly improved since first being introduced. [38]

Besides an organic resin matrix and inorganic filler particles such as silica, dental composites have several other essential components in common. All have a coupling agent (such as silanes) that chemically bonds the filler particles and the resin matrix. The inhibitor is used to prevent the polymer from polymerizing too early and has a profound effect on the setting behavior of the composites. [37] Moreover, an initiator or accelerator/terminator is required to activate the polymerization process when exposed to light. [39] Other components are added in small

amounts to provide some properties such as UV absorbing, color stabilizing and preventing the composite from premature polymerization. In most recent compositions, dimethylglyoxime is also usually added to achieve certain physical properties such as flowability. [40, 41]

Numerous different types of filler materials have been used for composites. [42] Past research suggests that filler particle size has had the greatest impact on the development of composites. [43] In early composites, relatively large inorganic filler particles were used (also known as macrofilled composites) which caused rough surfaces in the finished composite. [44]

Subsequently, microfilled composites were used which had lower filler content and therefore lower mechanical strength but better surface and handling. [43] This was one of the most significant improvements in filler particle development, which allowed for an even distribution of filler particles within the composite matrix, with smaller particle-to-particle separation as a result. [37] Hybrid composites were introduced later, which were radio-opaque and had smoother finished surfaces compared to conventional composites. More recently, nanotechnology has found applications in many fields of science and technology including dental composite manufacture. [44, 45] Nanofilled composites consist of sub-100 nm particles. Several manufacturers now produce nanofilled dental composites such as Filtek Supreme® (3M, ESPE, USA), Grandio and Grandio Flow® (Voco, Guxhaven, Germany), TPH spectra® (Universal composite restorative, USA) and Tetric EvoCeram Bulk Fill® (Ivoclar Vivadent AG, Schaan, Liechtenstein). Conventional restorative materials have traditionally been used for single purpose applications; some were suitable for esthetics, while others were developed for increased stress-bearing capacity in areas that undergo pressure during mastication. However, these nanocomposites are claimed to have superior properties including excellent optical

properties, high flexural strength and elastic modulus, low abrasion, low thermal expansion coefficient and low polymerization shrinkage so that they can be used for both applications. [46, 47] They also reduce the heat caused during polymerization and reduce the amount of water sorption by the resin matrix. [37] These superb properties are due to the higher filling loading which is made possible by inserting the nanoscale particles with a uniform distribution. [48]

2.2 Biomimetic aging environments to mimic *in vivo* conditions

Human saliva comprises 99.5% water, with biological, organic and inorganic substances dissolved or suspended in the aqueous medium. These dissolved and suspended constituents include electrolytes, mucus, white blood cells, epithelial cells, glycoproteins, various enzymes (such as digestive enzymes like amylase and lipase) and antimicrobial agents. Many of these constituents also impact the development of dental carries. Dental carries or cavities are breakdown of the teeth due to many reasons such as production of acids by bacteria in the oral environment. [49] Constituents that do not have pure salivary origin (such as urea, glucose and fluoride), can bind with other materials present in the mouth such as hydrogen ions, creating environmental conditions that are beneficial or antagonistic to the development of dental caries, or even directly attach the tooth. Such substances usually come from dietary intake, and therefore can vary widely from person-to-person. [50]

Saliva has several important functions in dental health, such as acting as a cleansing and antimicrobial agent. Moreover, saliva serves as lubricant in the mouth by wetting food, washing

away and moving the food particles from teeth towards the throat, permitting the initiation of swallowing and protecting the teeth from desiccation. [51]

In order to study the effect and process of aging conditions on the stability of dental composites, these materials have been exposed to various fluids such as water, artificial saliva, alcohol and acidic or basic solvents. [52] For many years, distilled water was the most used aging solution for in *in vitro* studies in the field of odontology. This was mainly due to the very small size and weight of the water molecules that facilitate their diffusion and penetration into dental materials. [53] It was observed that water plays an important role in the chemical degradation of the composites. [54] This degradation was due to swelling of the material and hydrolytic reactions. [55-57] Recent studies, however, highlight the influences and effects of aging in saliva in comparison with distilled water. [58-60] Due to the abovementioned variations in the composition of the human saliva, many researchers have used artificial saliva in their studies to provide a consistent comparison between studies. This is in spite of considering the fact that artificial saliva does not usually consists of organic and/or biological components that are present in human saliva. Numerous artificial saliva recipes have been used in published research in this field. From a biophysical point of view, saliva is a viscoelastic fluid, but there have been very few studies that take this fact into consideration. The variations of the saliva recipes are mainly in their composition and concentration. [3, 26, 58, 61-72] In the research, the recipe for artificial saliva was a mixture of 0.400 g/L NaCl, 0.400 g/L KCl, 0.795 g/L $\text{CaCl}_2 \cdot \text{H}_2\text{O}$, 0.690 g/L $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$, 0.005 g/L $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 1.000 g/L $\text{CO}(\text{NH}_2)_2$. [26, 66-69]

Another aging environment that has been used frequently in studies of potentially cariogenic environments is the use of acidic solutions of hydrochloric acid, lactic acid or acetic acid. [73-80] A mixture of ethanol and distilled water is also another common aging solution for *in vitro* studies, with several studies showing that aging in presence of ethanol caused significant decreases in mechanical properties such as fracture toughness. [61, 63, 81-86]

2.3 Previous studies of enzyme activity

Loss of material from dental composites does not result from mechanical forces such as wear and fatigue alone. It has been suggested that biochemical degradation of the composites can also occur in the oral environment. Moreover, saliva and the salivary constituents can soften the surface of the composites and make them more susceptible to mechanical degradation. In addition, as mentioned earlier, dental composites have a resin matrix which undergoes polymerization after it is placed in the oral environment. This curing process usually happens by photolytic curing directly of the dental composite *in situ*. The resin material experiences a volumetric shrinkage or contraction during this polymerization process. [87] This volumetric contraction can have some major destructive impacts such as tooth distortion and gap formation at the interface of the restoration material and tooth structure. As a result of this gap, saliva and other salivary fluids can leak and may cause some problems such as the formation of secondary caries. [10] Human saliva is a complex mixture of dissolved and particulate matter which originate from several various sources. One class of these components are esterase enzymes, which are believed to play a role in the direct biodegradation of the dental composites. [88, 89]

In addition to the activity of saliva and salivary agents, there are a number of mechanisms that can lead to the degradation of resin composites. These mechanisms include degradation and dissolution due to salivary agents, mechanical wear and fatigue caused by mastication and finally, the interaction between the foods, drugs, enzymes and the bacteria present in the oral environment. [39, 90] Some of the enzymes found in saliva are essential in beginning the digestion process. They protect the teeth from bacterial decays breaking down food particles that are entrapped within dental crevices.. [50]

On the other hand, there have been several studies that demonstrated the adverse effects of some of these enzymes. Most studies have focused on the effect inflammatory cholesterol esterases (CE) and salivary pseudo-cholinesterase (PCE) have on the polymer matrix of dental composites. [38] These studies have shown that almost all of the resin composites, regardless of their chemical composition and manufacturer, are likely to biodegrade to some extent in the presence of enzymes. [7, 88-103] The type of enzymes catalyzing the biodegradation that was used in these studies are various type of hydrolases present in human saliva. One study showed that cholesterol esterase (CE) can degrade dental composites (especially Bis-GMA/TEGDMA-based composite) by hydrolyzing the synthetic matrix of the composite resin system. [91] Other studies have investigated the degradation of composites in presence of porcine liver esterase. [93, 94, 96, 97, 101, 103, 104]

2.4 Polymerization shrinkage and water sorption by dental adhesive resins

Ideally, polymers that are used in dentistry, especially as restorative materials, are expected to be insoluble and have relatively high chemical and thermal stability. [87] However, most of the

commercial dental composites can absorb water and other chemicals from their surrounding environment and release some components in return. [52] In addition, movement of water and other solutions can promote plasticization resulting in weakening of the polymers. [105, 106] Hence, both water sorption and water solubility can have detrimental effects on the stability, structure and function of the restorative dental materials. [107] Moreover, filler particles help reduce the amount of shrinkage in the composites. The clinically significant effect of the shrinkage is formation of a marginal gap on the interface of the enamel and composite which can promote microleakage. [37] The quality, nature and hydrophilicity of the resin matrix are some of the main determining factors in selecting the molecules that can be taken up from the environment and in dictating how much swelling can occur when the composite is exposed to a solution. [52] Dental restorative materials in the oral environment are exposed to saliva which contains various substances and molecules such as enzyme systems and bacteria and they might have interactions with each other. [108] Moreover, there are some other exogenous substances that may be present in the oral environment that cover a variety of chemicals like acids, bases, alcohols etc. [25] In conclusion, the chemical, structural and topological features of the composite (precisely speaking, the resin matrix) along with the duration of the exposure are important factors that have effect on the type of the influence that a substance can have on the restorative material. [109]

2.5 Previous studies of the impact of bacteria on composite integrity

One of the inherent drawbacks of dental composites compared to amalgam fillings is that they may undergo biodegradation in the oral environment. There have been some studies on the

accumulation of the dental plaque (dental biofilm) on the surface of the composites in the human mouth. [6] This study demonstrated that plaques are more likely to accumulate on the surface of the composite compared to other restorative materials or even the tooth enamel itself (the hard smooth outer surface of the teeth). One reason could be the lack of antibacterial or buffering properties of the composites. [110] Another reason could be the release of compounds from the composite that stimulates the accumulation of bacteria. Some studies have shown that specific surface properties of the composite, such as surface roughness and topography, could also be the reason for formation of the biofilm. [111] It has been well established that increasing the roughness of the surface will further promote bacterial accumulation and cause higher bacterial retention on the composites as a result. Upon the degradation of margin interfaces, *Streptococci mutans* spp. (SM), *Lactobacilli* spp. and other acidogenic bacteria are able to infiltrate the margins by accumulating in the marginal gap. [10, 13] These accumulations can promote the demineralization of the tooth interface and further progress secondary caries. [7] The presence of a biofilm is vital for the development of the caries. Oral biofilms cannot continue to exist in the oral cavity if the oral detachment forces such as the exerted force by tooth brushing overcome them. [112, 113]

Moreover, *S. mutans* spp. and *Lactobacilli* spp. (also known as cariogenic oral bacteria) exist in the dental biofilm. *S. mutans* are known as the major etiological agent responsible for dental caries. According to some studies, they are also the primary inhabitants present at the marginal interface (between tooth and restoration). [10, 114, 115] *Lactobacilli* cause existing carious lesions to progress. However, they prevent streptococcal pathogens from inducing dental decay. These bacteria are categorized as acid-producing bacteria and they are capable of

degrading the resin matrix of composites by their esterase activity [116] and also by producing acids and therefore create a low-pH environment [117]. In addition, they increase surface roughness by degrading the resin matrix. [118]

S. sobrinus, which is a closely related species to SM, enhances formation of caries within teeth and is thought to be more implicated as the causative agent of dental caries than is SM. The biofilm consists of a mixture of polysaccharides and plaque that creates a suitable environment for *S. sobrinus* to grow. Optimal growth of *S. Sobrinus* occurs at body temperature (37°C) and slightly acidic conditions (pH of 6.3). This bacterium has difficulty surviving outside of the human oral cavity. [10, 119]

The other main groups of bacteria are non-mutans streptococci. Unlike mutans streptococci that are present in the plaque covering spots, non-mutans streptococci are mainly found in white spots. Furthermore, mutans streptococci are more acidogenic and aciduric in comparison with the non-mutans streptococci. SM is also more competitive under severely acidic conditions. [120-123] Actinomyces are normally present in the gums and they are the most common cause of infections in dental procedures and oral abscesses. [124, 125]

In spite of the large body of literature on the role bacteria play in primary caries in human teeth, relatively little is known with regard to the mechanism of the bacterial biodegradation of composites in the oral environment. It remains unclear to which extent surface of the composite can be degraded by acidic metabolites caused by the oral bacteria and enzymatic activity. [6, 126]

2.6 Previous studies on the mechanical properties of composites in the oral environment

Degradation of composites in the oral cavity is challenging to study *in vivo*. Many studies incubate or expose the composites to various aging environments to mimic conditions in the oral cavity. This exposure could be intermittent, such as during ingestion and mastication of food or drinks. Continuous exposure is also probable when food particle, chemicals, etc. adhere to the restorative material in the oral environment. [127] A large number of such studies have been conducted in an effort to understand and evaluate the mechanical behavior of dental composites in conditions designed to simulate the oral environment. [82, 128-133] In many instances, the applied stress to teeth and restorations is low and repetitive rather than consisting of a continuous high stress. [134] In materials science, this phenomenon is called fatigue, which is the weakening of the material as a result of repeated applied loads. This localized cyclic progressive loading can cause structural damage at values much less than the nominal maximum stress value (ultimate tensile stress limit or yield stress limit). [135]

Mechanical properties and parameters that are used to describe the properties and behavior of most materials, such as dental materials, include elastic modulus (also known as Young's modulus or modulus of elasticity), dynamic Young's modulus, shear modulus, flexibility, resilience and Poisson's ratio. [40] Tensile testing (especially uniaxial tensile testing) is one of the most common and fundamental materials science tests for obtaining these mechanical characteristics.

An elastic modulus is a number that measures the resistance of the material to being deformed elastically (i.e., non-permanently or plastically) under an applied stress. In other words, it

describes the relative stiffness or rigidity of the component. Because stiffness is relative, in the case of dental prostheses it can increase by increasing its thickness. But the elastic modulus of the material, which is the slope of its stress-strain curve in elastic deformation region, is a constant value and does not change. [136]

In order to determine tensile strength, the specimen (usually a rod, wire, or dumbbell-shaped specimen) is subjected to tensile loading. For this test, which is also referred to as uniaxial tension test, the specimen needs to have two shoulders and a gage in between. The shoulders should be large enough so they can be readily gripped, whereas the gage section has a smaller cross-section so that the deformation (typically necking) and failure occurs in this area. [137] This test works perfectly for most materials (especially metals and metallic alloys) but it is not suitable for brittle materials (such as ceramics, composites, amalgams and cements). Most dental materials are quite brittle and thus are highly susceptible to crack initiation in the presence of surface flaws when a tensile stress is applied to them. These materials exhibit elastic deformation primarily and have little or no plastic deformation potential (straight line on the stress-strain plot). In addition, tensile strength of the brittle materials is noticeably lower than their corresponding compressive strength. This is due to their inability to plastically deform and reduce the tensile stress at flaw tips. Moreover, a tensile test is quite difficult to perform for brittle materials because of alignment and gripping problems. Therefore, diametral compression test, also referred to as the indirect tension test or the Brazilian disk test, is used extensively to determine the fracture properties for brittle materials. [138-140] In this method, the specimen is a short cylinder and the compressive load is placed by a flat plate against the side of the specimen (Fig 2.2). Tensile stress is produced by vertical compressive force along the

side of the cylinder, which is perpendicular to the vertical plane passing through the center of the specimen. In this test, fracture occurs along the vertical plane and tensile stress is directly proportional to the applied compressive load. [40, 61]

The diametral stress is calculated by the following formula:

$$\text{Tensile Stress} = 2F / \pi Dt \quad (2.1)$$

Where: F = applied force (N), D = cylinder diameter (m) and t = cylinder thickness (m).

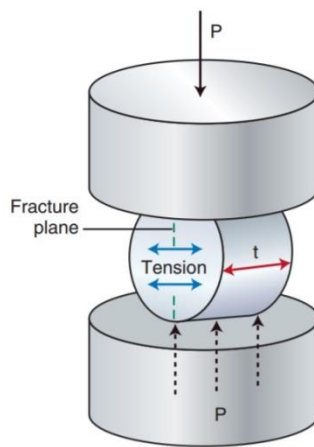


Figure 2.2 - Diametral compression test. A tensile fracture is produced, even though the applied force at the side of the specimen is a compressive force. Figure from reference [40].

The simplicity of the diametral compression test along with reproducibility of its results have all led to its widespread use. However, it is worth mentioning that this test cannot be conducted on all kind of materials. One particular instance is materials with high toughness that undergo an extensive plastic deformation and energy absorption before fracture. [135] Most metals in all temperatures and some other materials, such as polymers, at high temperature exhibit such behavior which can result in unreasonably high tensile strength values. The ideal expected

fracture result in this test is fragmentation of the specimen into two segments. The results cannot be really reliable if it fractures into several pieces. [40]

As mentioned above, the filler particles are the components of the composite matrix that likely determine the overall compressive strength, Young's modulus (or modulus of elasticity), thermal expansion coefficient, the amount of polymerization shrinkage and water absorption. [87] It has been reported by some researchers that the fatigue caused by the cyclic mastication forces is responsible for wear, chipping and failure of dental restorative materials. [141, 142] Moreover, microleakage of saliva and salivary fluids render the composites more prone to mechanical wear and damage during mastication. [62] These fluids soften the surface layer of the composites and as a result of wear, the outermost layer of the composite is removed. Thus it creates an ongoing cycle of exposing the underlying layers to chemical and biological degradation. [96] When water and other liquid molecules reach the gap at the interface of the tooth and composite, this destructive process may be promoted and/or accelerated. [7, 10, 92, 143] Degradation of composites and their mechanical properties impose limitations on usage of these composites. A combination of factors leads to degradation of composites, thereby decreasing their mechanical properties. [144] One major factor is the applied stress on the composites due to volumetric contraction of the matrix during polymerization. [58] This shrinkage in the volume happens as a result of the transforming from van der Waals to covalent bonds between the monomers. Therefore, the amount of shrinkage depends on the amount and kind of the polymer that the matrix of the composite is composed of. Microcracks form as a consequence of this volumetric shrinkage which provides pathways for penetration of the saliva and salivary agents. [57, 145] Another key factor in degradation of the restorative materials is

the temperature and duration of aging process. [57, 146] The aging time varies between the studies in this field. Some researchers, such as Soederholm et al. and Drummond et al, [128, 147] studied the effect of aging composites in air and water for six months. They reported significant decrease in the tensile strength [128], fracture toughness and flexural strength [147] of the samples stored in water. This is in contrast with the results of the dry samples (aged in air), which displayed minimum changes in these mechanical properties. [147]

2.7 Summary and Conclusions

Dental composites have become the primary choice for dental restorations. Composites consist of a mixture of solid filler particles bound by polymers which are cured in place following emplacement. It is critical to the long-term performance of the restoration that the material properties do not deteriorate during the life of the restoration. However, there is increasing evidence that dental composites deteriorate following placement, and the prevalence of secondary dental caries has increased. These suggest the conditions in the oral cavity contribute to the break-down of the composites.

This degradation is likely to be caused by four main types of processes: physical material degradation (e.g. fatigue due to cyclic loading during mastication), abiotic chemical degradation due to wetting/drying cycles, aqueous dissolution (particularly under acidic conditions as occurs with tooth enamel), and biological degradation due to the biodegradation of the organic components of the composite such as the binding polymer. Recent research has clearly indicated that the latter process, biodegradation of the polymer can be catalyzed by enzymes in the oral cavity, both human derived and bacterial in origin. These studies have typically been

performed in vitro with pure polymer. While such studies provide a mechanistic understanding of the process, they do not help us understand if these processes occur in the cured composite, or whether any such degradation results in decreased material strength.

3. THE EFFECTS OF LONG TERM AGING IN VARIOUS AQUEOUS ENVIRONMENTS ON DENTAL COMPOSITE STRENGTH

3.1 Introduction

Numerous studies have investigated the degradation of dental composites in the oral environment. The majority of early studies were focused mainly on material loss due to fatigue and wear caused by mechanical forces. [3, 61, 81, 148-155] More recent research focused on investigating the effect of various fillers and additives to the dental resin composite on their overall material properties like compressive strength and durability. [156-159] Most recently, researchers became more interested in investigating the chemical breakdown of dental restorative materials, with a particular focus on the organic polymers within the resin. The genesis for this new focus was early studies suggesting that oral cavity enzymes might have a role in degradation of the dental composites. [93, 155] Studies focusing on the degradation of resin composites have been performed in the presence of saliva (both artificial and human-derived) and in the presence of salivary-like enzymes in environments designed to mimic those found in the oral cavity. [26, 90, 91, 94] Specific studies include investigating the biodegradation of resin composites and adhesives by oral bacteria and enzymes, as well as studying the biological effects of these by-products on oral bacteria and cells in the oral cavity. [7, 10, 87, 116, 160] Many of these studies have been influenced by the large body of research on dental caries, and the ecological theory of dental caries whereby cariogenic bacteria create acidogenic conditions that attack tooth enamel. Although cariogenic bacteria create acidic conditions through their fermentative breakdown of sugars, tooth enamel itself is known to

abiotically dissolve under highly acidic conditions. Thus, dental caries is at least partially due to an abiotic dissolution, as abiotic incubations of teeth and enamel in organic acid solutions have clearly demonstrated. In contrast, relatively few studies have investigated this abiotic dissolution mechanism with composites, although the very different chemical formulation of composites compared to enamel suggest that acidic dissolution may be relatively minor.

While studies to date have investigated the specific biodegradation of simplified components of the dental composite (such as resin polymer) by enzymes and bacteria, they do not address whether the material properties of the entire composite are like-wise affected by the breakdown of the organic constituents of the composite. The composite includes many inorganic particle additives that comprise the bulk of the composite mass, as well as representing the primary component of compressive strength. Further, the composite is a complex solid, and incubations of individual components of the composite solid do not necessarily extend to the matrix as a whole. For example, diffusion of extra-cellular enzymes and other dissolved constituents into the composite matrix is a slow process, and this time effect has not been addressed in many studies.

In summary, our understanding of the mechanisms for the breakdown of individual components of dental composites suggests that bacterial and/or oral enzymatic activity plays a role in their breakdown. However, these past studies do not allow us to understand what mechanism(s) accounts for breakdown of the tooth or restorative material, whether this biodegradation will occur on the composite solid itself, or how this biodegradation will impact the overall material properties of the composite. The overall objective of the research was to

address some of the gaps in knowledge in the literature with a focus on the entire composite.

The strategy to achieve this objective was to test the effects of various environments on material properties of whole composites under long-term aging. The environments included various aqueous solutions designed to mimic and isolate biotic and abiotic processes in the oral cavity, with comparisons made to aging in air as a reference state.

3.2 Materials and Methods

3.2.1 Overview

This study investigated the material properties of dental composites aged under various environmental conditions. In each set of experiments, 20 specimens were aged in air and various aqueous solutions. The large number of sample replicates (20) was chosen to control for the effects of variability in composite preparation on material properties.

The dental composite used in this study was a direct nano-filled composite (FiltekTM Supreme Plus[®], 3M ESPE, St. Paul, MN, USA). These composites are comprised of triethyleneglycol dimethacrylate, urethane dimethacrylate and bis-EMA resins. The composite filler is comprised primarily of zirconia-silica microfiller (0.6-1.4 μ m) and silica nanofiller 5-20 nm.

3.2.2 Fabrication of composite specimens

The composite samples were prepared in cylinders with diameter of 6.311 ± 0.024 mm and thickness of 5.058 ± 0.039 mm. The cylindrical test specimens were prepared by placing approximately 0.3 g of composite material into an open-ended epoxy rings (NEMA Grade G-10/FR4 glass epoxy laminate, Gund Co., Inc., St. Louis, MO). The samples were photopolymerized (40 sec) on each side of the epoxy ring by exposure to an Optilux 501 curing

light (Kerr Corp., Orange, CA). After curing, sets of 10 specimens were put into high density polyethylene plastic bottles (250 mL, Nalgene®, City, State) to be aged in their respective environments. The incubation bottles were placed in an incubator at 37 °C (human body temperature) and aged for >163 d. Aging environments included air (AIR), artificial saliva (AS), a 50/50 by volume solution of artificial saliva and acetic acid (AS+HAc) and a solution of artificial saliva and enzyme (AS+ENZ).

3.2.3 Artificial saliva solution

A commonly used recipe for artificial saliva reported in the literature [26] was used in the present study as shown in Table 3.1.

Table 3.1. Composition of artificial saliva solution.

Constituent	Concentration (g/L)	Role(s)
NaCl	0.400	Electrolyte, osmotic balance
KCl	0.400	Electrolyte, osmotic balance
CaCl ₂ ·H ₂ O	0.795	Calcium source, divalent cation hardness
NaH ₂ PO ₄ ·H ₂ O	0.690	Phosphorus source, buffer
Na ₂ S·9H ₂ O	0.005	Sulfide source, reducing agent
CO(NH ₂) ₂	1.000	Carbon/nitrogen source, amine

3.2.4 Acetic acid incubations

Experiments were performed by incubating the composites in an acidic solution to determine if dissolution of composite components occurs as has been observed in dental enamel, and if so whether it may weaken the composite strength. Literature studies have shown [75], that a free acid (FA) concentration of 50 mM (i.e. [FA] = 5×10^{-2} M) is necessary for enamel to dissolve,

and thus was the target starting FA concentration for this study. Low pH experiments (4-5.5) had FA concentrations that were most similar to those reported *in vivo* [161, 162]. This would be an upper boundary value representing a lesion-producing environment.

To achieve this condition, AS+HAc was made from a 0.1 M (100 mM) concentration of sodium acetate in artificial saliva (AS), and then titrated with 6 N HCl to pH = 4.7. These calculations were performed assuming the carbonate system was in equilibrium with the atmosphere (i.e. $[H_2CO_3] \sim 10^{-5}$ M), and was thus not significant in the charge and proton balances.

Relevant equations:

Mass balances (assume complete dissolution of Na-Acetate salt):

$$C_{t,Na} = [Na^+] = 10^{-1} \text{ mM} \quad (3.1)$$

$$C_{t,Ac} = [Ac^-] + [HAc] = 10^{-1} \text{ mM} \quad (3.2)$$

Other equations:

$$C_{t,Cl} = \text{number of moles of HCl titrant added} = [Cl^-] = \text{unknown} \quad (3.3)$$

$$K_a = 10^{-4.7} = [H^+][Ac^-]/[HAc] \quad (3.4)$$

$$K_w = 10^{-14} = [H^+][OH^-] \quad (3.5)$$

Charge balance:

$$[Ac^-] + [OH^-] + [Cl^-] = [Na^+] + [H^+] \quad (3.6)$$

Using equations 3.1-3.6 and knowing the final pH = 4.7, we can calculate how many equivalents of HCl to add: $[Ac^-] = [HAc] = [Na^+]/2 = 5 \times 10^{-2}$ mM (from equations 3.1-3.2, and 3.4).

Thus equation 6 has one unknown:

$$[\text{Cl}^-] = 10^{-1} + 10^{-4.7} - 5 \times 10^{-2} - 10^{-9.3} \sim 5 \times 10^{-2} \text{ mM} \quad (3.7)$$

Confirm by checking this with the Proton Condition:

Proton Reference Level (PRL): Ac^- , HCl and H_2O . Species with fewer protons than the PRL = OH^- and Cl^- ; and species with more protons than the PRL = H^+ and HAc . Thus the Proton Condition (PC) is satisfied by: $[\text{HAc}] + [\text{H}^+] = [\text{OH}^-] + [\text{Cl}^-]$.

Plugging in: $5 \times 10^{-2} + 10^{-4.7} = 10^{-9.3} + 5 \times 10^{-2}$, which is consistent with slightly less than 50 meq of HCl ($5 \times 10^{-2} \text{ mM}$) to be added.

Thus we need to add $\sim 8 \text{ mL/L}$ of 6 N HCl to a $5 \times 10^{-2} \text{ mM}$ solution of HAc : $(6 \text{ meq/mL})(X \text{ mL}) = 50 \text{ meq}$; $X = 50/6 \sim 8 \text{ mL}$.

3.2.5 Enzyme incubations

AS+ENZ was made using lyophilized esterase from porcine liver (Sigma-Aldrich Inc., St. Louis, MO, USA). Porcine liver esterase has been used in similar studies as a standardized model oral cavity esterase. [93, 94, 96-98, 101, 104] For this experiment, AS+ENZ specimens were aged in AS solution prepared as described above, to which was added 30 U/mL porcine liver esterase (initial activity). [101]

3.2.6 Testing of compressive strength

After aging, the samples were removed from the solutions and the cylindrical samples were extruded from their epoxy tubes and their compressive strength was determined by destructive testing using the diametral compression test. Both the force necessary to extrude the

composites from the epoxy sheath (the “push-out” test) and the load necessary to achieve compressive failure were measured using an Instron 1125[®] material testing system (Instron Corp. Canton, MA) with a 500 kg load cell at a loading rate of 2.0 mm/min. The 500 kg load cell was controlled by MTS digital controller (MTS, City, State). Load to failure was applied to the length of the specimens as shown (Fig. 2.2, Section 2.6, above) from the top through a cross head running at a loading rate of 2.0 mm/min. The tensile stress was then calculated from the diametral stress equation 2.1.

3.2.7 Determination of aging time scale

There is a wide disparity in the duration of aging experiments in the dental materials literature. There have been studies that had aging time as little as hours to days. [131] On the other hand, some studies stored the samples in aging solutions for three to six months or even longer periods of time. [54, 128, 147]

We decided to determine an appropriate aging period based on the assumption that solutes should have sufficient time to diffuse completely through the composite polymer matrix to allow exposure of the matrix solids to the reacting solute (the “exposure time”). A typical aging time period from the literature (the “reaction time”) would then be added to allow for both “exposure” and “reaction” for the overall aging time. The diffusion time was determined assuming simple 1D Fickian diffusion in a cylinder with closed sides. The equation for Fickian diffusion in one dimension is expressed as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial y^2} \quad (3.8)$$

Where C denote the concentration of the diffusing species at time t .

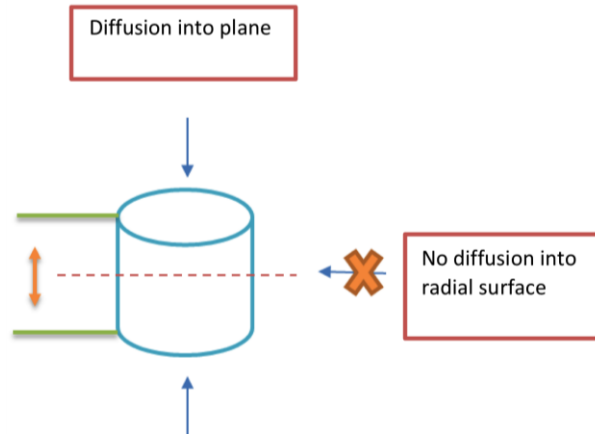


Figure 3.1 - Schematic of diffusion into the cylindrical specimens (a finite slab).

In our case, diffusion is into the cylindrical specimen. However, the walls of the cylinder are covered by the epoxy sleeve and thus precluding radial diffusion. We thus model diffusion into the sample as being only from the ends, which is equivalent to a 1D diffusion into a finite slab. This is only true when one dimension has a very large value in comparison with the other two dimensions, so that those two are negligible. This condition is shown in Fig. 3.1.

The boundary and initial conditions for the 1D finite slab case are as follows:

Initial conditions:

$$t \leq 0, 0 \leq y \leq L; C_i = C_0 \text{ (}\emptyset \text{ in this case)} \quad (3.9)$$

Boundary conditions:

$$\text{At center: } t \geq 0, y = 0; \frac{\partial C_i}{\partial y} = 0 \quad (3.10)$$

$$\text{At boundary: } t \geq 0, y = L; C_i = C_1 \quad (3.11)$$

Equation 3.8 can be solved for the IC and BC by substituting for dimensionless concentration, distance, and time as follows:

$$\theta = \frac{C_i - C_0}{C_1 - C_0} \quad (3.12)$$

$$\eta = \frac{y}{L} \quad (3.13)$$

$$\tau = \frac{t D}{L^2} \quad (3.14)$$

Where: C_i , C_1 and C_0 = the concentration in the cylinder at the location of interest i , the cylinder surface, and in the cylinder at time $t = 0$, respectively; η is the dimensionless cylinder thickness, L is the half cylinder thickness (diffusion occurs from both sides and is thus symmetrical about the middle), and τ is dimensionless time of diffusion. In this case at $t = 0$, $C_0 = 0$ because concentration in the cylinder was zero before aging started.

Substituting equations 3.12-3.14 into equation 3.8 gives:

$$\frac{\partial \theta}{\partial \tau} = D \frac{\partial^2 \theta}{\partial \eta^2} \quad (3.15)$$

The new initial and boundary conditions for equation 3.15 are as follows:

Initial conditions:

$$\tau \leq 0, 0 \leq \eta \leq 1.0; \theta = 0 \quad (3.16)$$

Boundary conditions:

$$\text{At center: } \tau \geq 0, \eta = 0; \frac{\partial \theta}{\partial \eta} = 0 \quad (3.17)$$

$$\text{At boundary: } \tau \geq 0, \eta = 1; \theta = 1 \quad (3.18)$$

Solving equation 3.15 for the initial and boundary conditions gives:

$$\frac{C - C_0}{C_1 - C_0} = 1 - \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp\{-D (2n+1)^2 \pi^2 t / 4l^2\} \cos \frac{(2n+1)\pi x}{2l} \quad (3.19)$$

This solution is plotted in Fig. 3.2. From the graph, we can see that when $\tau \cong 2$, the term

$$\frac{C_t - C_0}{C_1 - C_0} \sim 1.0 \text{ and diffusion has reached approximately steady state.}$$

Malacarne et al. (2006) had measured the diffusion coefficients for four different commercial adhesives with values of 10^{-8} to $10^{-7} \text{ cm}^2/\text{s}$. [107]

After inserting these diffusivities into equation 3.11 together with the known geometry of the composite cylinders, we can get the approximate time needed for diffusion equilibrium to occur as follows:

$$\tau = 2 = \frac{t D}{L^2} \quad (3.13)$$

$$t_{ss} = \frac{2L^2}{D} = \frac{(2)(0.25\text{cm})^2}{10^{-8}\text{cm}^2/\text{s}} = 1.25 \times 10^7 \text{s} \quad (3.14)$$

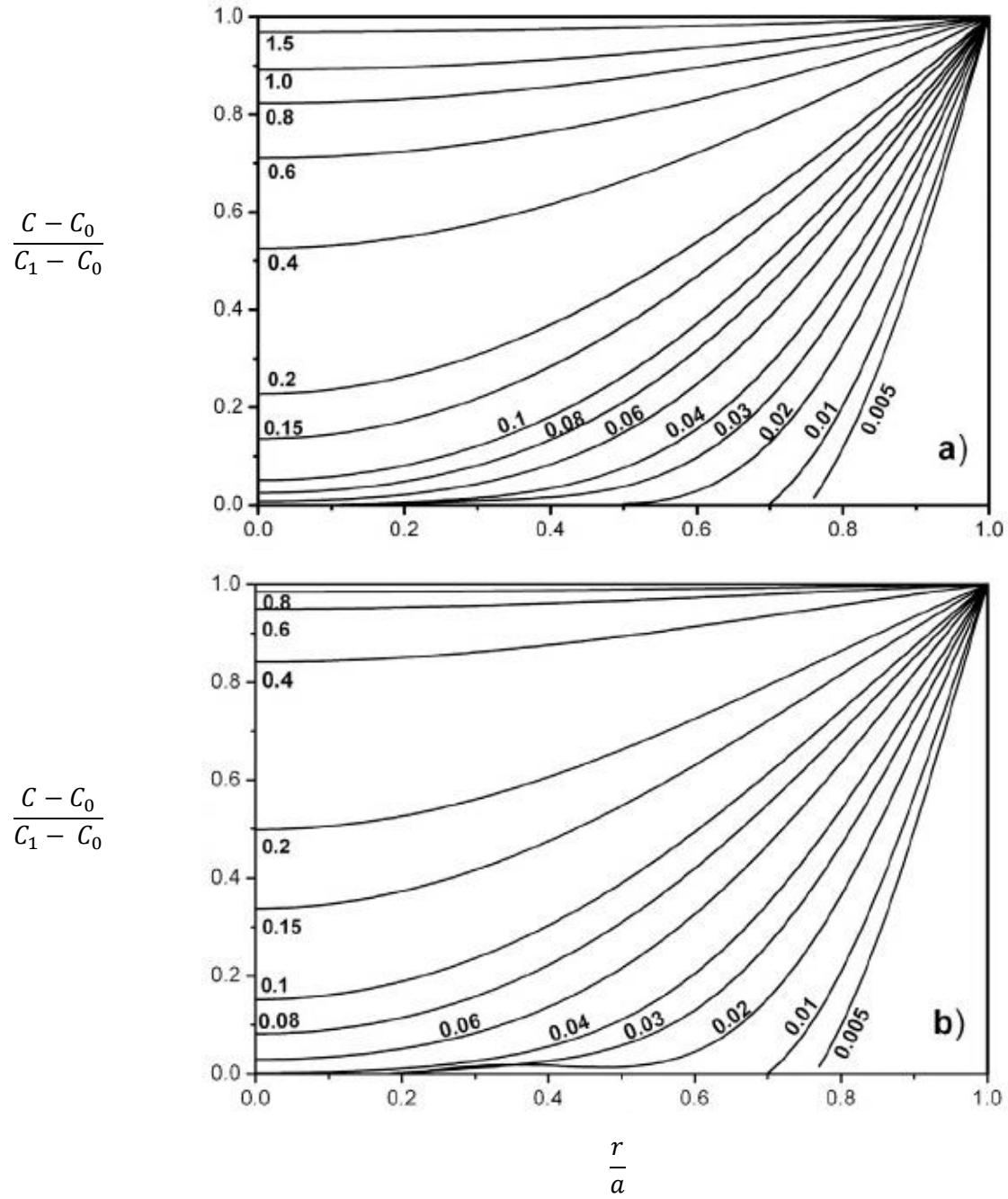


Fig 3.2. Concentration distributions at various times for a) a plane sheet $-l < x < l$ (numbers on curves are values of $t' = tD/RI^2$); and for b) a solid cylinder of radius a (numbers on curves are values of $\tau = tD/Ra^2$). (Modified from Crank [163]).

$$\frac{1.25 \times 10^7 s}{(3600 s/hr \times 24 hr/1 d)} = 140 \text{ d upper limit} \quad (3.15)$$

$$\frac{1.25 \times 10^6 s}{(3600 s/hour \times 24 hour/1 day)} = 14 \text{ d lower limit} \quad (3.16)$$

Based on these calculations, diffusion exposure time should be complete after a maximum of ~140 d. Adding to this a typical three week reaction time from literature values, we find an aging period in excess of 160 d for complete exposure plus reaction time.

3.2.8 Analysis of leaching

After aging, the samples were removed from the solutions and their compressive strength was tested as described in section 3.2.6. Aliquots (10 mL) of the aging solutions (AS, AS+HAc, AS+ENZ) were sent to an independent laboratory (Perkin Elmer Technical Center, Downers Grove, IL) for the measurement of inorganic leachants (Si, Zr and other elements) by inductively coupled plasma/mass spectroscopy (ICP/MS, NexION 2000, Perkin Elmer Inc., Waltham, MA) in full elemental scan mode.

3.2.9 Statistical analysis

There were 20 specimens in each set of experiments. Statistical parameters for each set of data were performed by the statistical analysis software package SYSTAT (v13, SYSTAT Inc., San Jose, CA). Inspection of the linearity of probability plots of all data in each data set, together with the quantitative measures of kurtosis and skewness, confirmed that the data were largely normally distributed. Comparisons between means for each data set for statistical significance was by ANOVA of non-paired data.

3.3 Results and Discussion

This study included one dependent variable i.e., the tensile strength of the composite, which was evaluated with respect several independent variables, including mass, diameter, thickness, exposed surface area, media and load magnitude.

The results of this study are presented in terms of mean diametral tensile strength of each tested group, followed by statistical analysis.

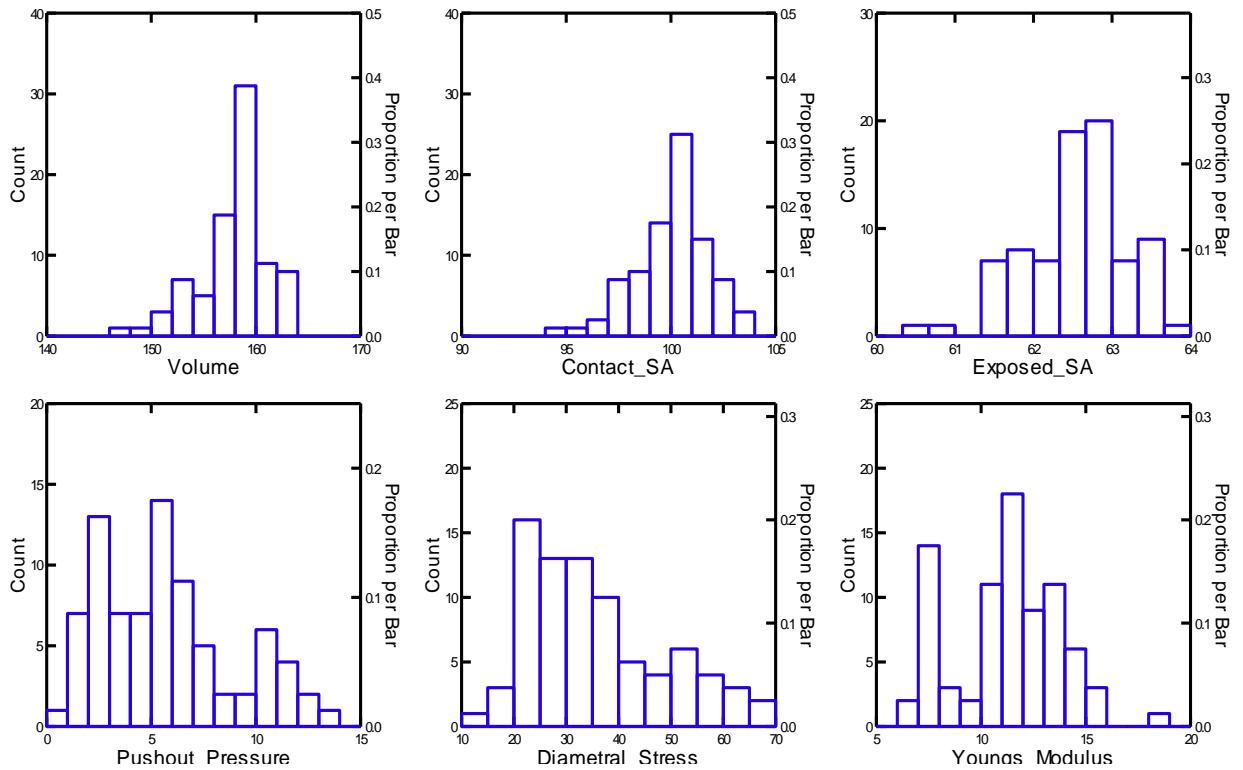


Figure 3.3. Histogram of A-C) geometric and D-F) strength parameters for all data. Note that most data sets are largely normally distributed with some skewness in diametral stress.

Figure 3.3 shows the geometric and strength parameters for all data. A notable trend is that all of the geometric properties (Fig. 3.3.A to 3.3.C: Volume, Contact Surface Area and Exposed

Surface Area) data have almost formed bell-shaped curves. This means that they have been normally distributed. This can be confirmed according to the Table 3.2. In statistics, Standard Deviation is a quantified measurement of the amount of variation or dispersion of a data set. It is a way of grouping data where the majority of the data is around the mean. This becomes more evident when the sample size is larger. [164] As shown in Table 3.2, the mean and the median of geometric data are very similar and the standard deviation is relatively low. This indicates that the data points tend to be close to the mean and therefore they are normally distributed. The trend is almost the same for figure 3.3F. However, pushout pressure and diametral stress are a little right skewed as shown by figure 3.3D and E.

Descriptive statistics are used to describe the basic features of the data and they present quantitative descriptions in a manageable form. In a research study, when there are lots of measurements, descriptive statistics help us to simplify large amounts of data in a sensible way. They provide simple summaries about the test samples and the measurements. [165]

Figure 3.4 shows the probability plots for three strength parameters (Diametral Stress, Pushout Pressure and Young's Modulus). Each color represents one of the aging environments in the experiments. Figure 3.4.A shows the diametral stress values for each of the incubation conditions. In order to have a normal distribution, the observations should fall as closely as possible to the line. It can be observed that most of the observations in AS + HAc and AS + ENZ fall near the line. There are also some in the tails, but overall they are normally distributed. For Air and AS, a fair number of the observations fall closely to the line but certainly they are not perfectly on the line. So it can be concluded that all of the datasets are normally distributed.

Table 3.2. Summary statistics for the material strength properties of dental composites aged in Air, AS, AS+HAc and AS+ENZ.

Statistic	Push Out Force (N)				Push Out Pressure (MPa)				Diametral Stress (GPa)				Young's Modulus (GPa)			
	Air	AS	AS+HAc	AS+ENZ	Air	AS	AS+HAc	AS+ENZ	Air	AS	AS+HAc	AS+ENZ	Air	AS	AS+HAc	AS+ENZ
Mean	236	735	722	601	2.42	7.25	7.19	5.98	54.0	31.4	34.3	22.5	14.02	11.26	11.91	7.66
Standard Error	16.6	45.3	85	62	0.17	0.45	0.85	0.61	1.6	1.3	1.2	0.7	0.32	0.19	0.26	0.14
Median	235	659	600	518	2.42	6.48	5.96	5.17	53.8	30.7	34.2	22.9	13.8	11.3	11.67	7.59
Mode	#N/A	#N/A	188	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	#N/A	11.4	13.10	#N/A
Standard Deviation	74.4	202.8	378	277	0.75	2.00	3.81	2.74	7	6	5	3.18	1.44	0.87	1.18	0.61
Sample Variance	5529	41130	143225	76731	0.57	3.98	14.51	7.51	51	34	28	10.10	2.06	0.75	1.39	0.37
Kurtosis	0.61	0.01	-1.37	-0.50	0.61	0.12	-1.37	-0.53	-0.69	0.09	-0.34	0.70	5.12	2.78	-0.56	0.28
Skewness	0.39	1.01	0.30	0.56	0.32	1.02	0.31	0.53	0.02	0.40	0.12	-0.58	1.88	0.08	0.48	0.43
Range	308	693	1117	961	3.12	7.03	11.37	9.48	24	24	20	12.97	6.47	4.41	4.03	2.45
Minimum	82	504	188	145	0.83	4.88	1.83	1.44	41	21	25	14.53	12	9.10	10.30	6.57
Maximum	390	1197	1305	1106	3.95	11.91	13.19	10.9	66	45	45	27.50	19	14	14.33	9.01
Sum	4729	14705	14431	12014	48	145	143.77	120	1080	629	687	451	280	225	238	153
Count	20	20	20	20	20	20	20.00	20.0	20	20	20	20.00	20	20	20.00	20.00
Confidence Level(95.0%)	34.80	94.92	177.12	129.64	0.35	0.93	1.78	1.28	3.34	2.74	2.47	1.49	0.67	0.41	0.55	0.29

It should be noted that there were 20 observations in each environment which is an adequate number of replicants from scientific point of view. However, the general rule of thumb in statistical analysis is that the more data that we have, the closer we expect the observations to be to the diagonal line. That is, of course, if the data has been normally distributed.

Moreover, when these observations in Figure 3.4.A are compared to each other, we can see that diametral stress values are much higher for AIR aged samples than other environments. There is a significant decrease in the diametral stress in all other conditions, especially in AS + ENZ. There is not a statistically significant difference in this parameter for AS and AS + HAc. This suggests that acid does not solely affect the strength of the material against compressive force. Whereas enzymatic activities have shown more deteriorative influence on the diametral stress.

Figure 3.4.B shows the pressure that was needed to detach and push each of the composite specimens out of their epoxy ring. It can be observed that the push out pressure values are not statistically significantly different for all the specimens that were aged in a solution. However, AIR aged samples needed less force to detach from their epoxy rings. Another observation from this figure is that the data for the AIR dried samples are more normally distributed than the other environments. This could have a couple of reasons that will be discussed later in this section.

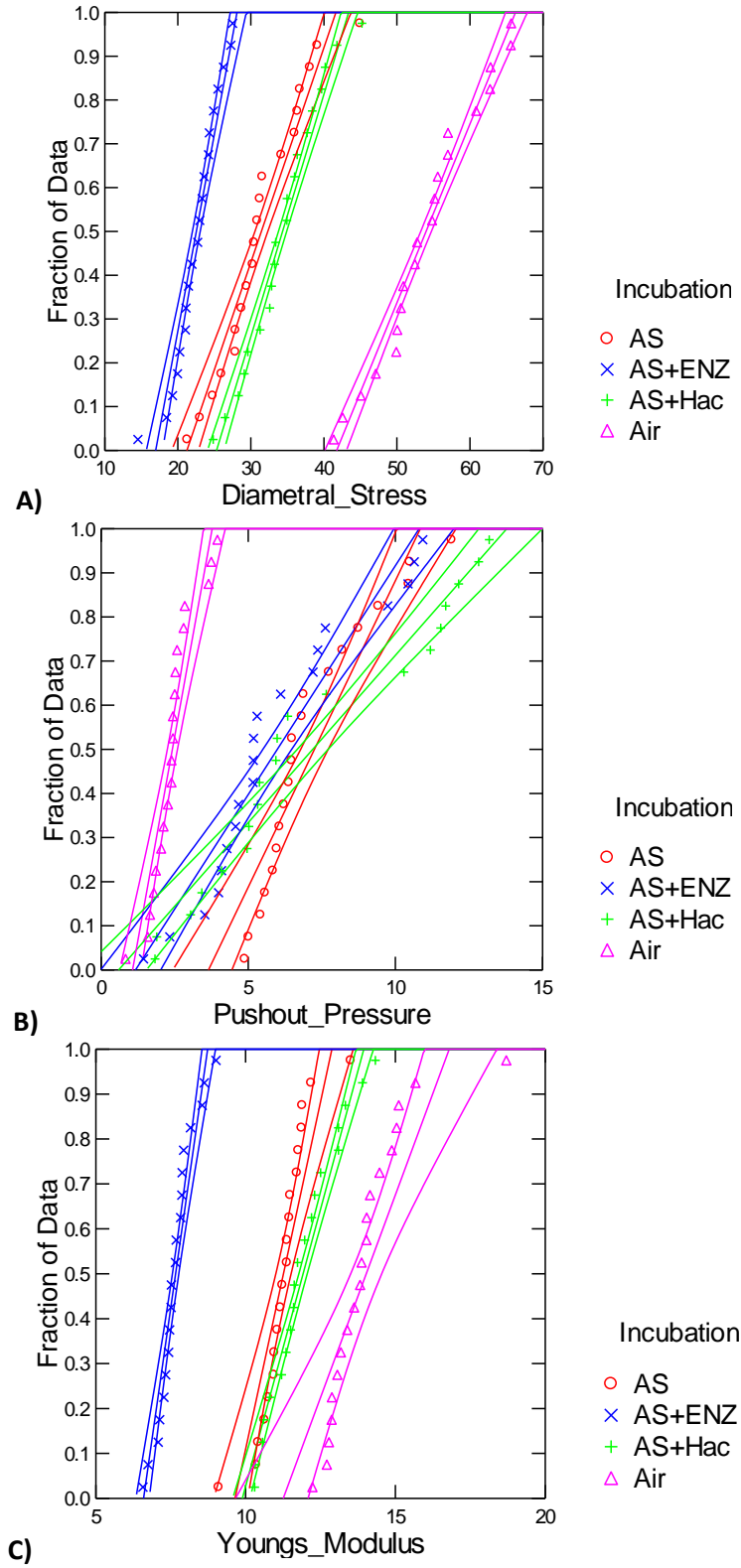


Figure 3.4. Fractional distribution plots for A) diametral stress, B) pushout pressure and C) Young's modulus arranged by incubation condition. Shown are 95% CI for linear regression through distribution.

Figure 3.4.C demonstrates the young's modulus values for the tested specimens. Except for the samples in the AIR that have some stronger deviations than what we had before, all of the other observations seem to be perfectly normally distributed. Similar to the diametral stress (Figure 3.4.A), this figure also shows that modulus of elasticity has much higher values in the dry samples. It also shows that the lowest observations were made on the AS + ENZ specimens. This means that these specimens are less stiff and more flexible than the rest of them.

Figures 3.5.A to C are the notched box plots showing the strength parameters of all test specimens in the four various environments. A very brief explanation of the notched box plots will be provided here before getting into the details of the observations in this study. In descriptive statistics, a box plot is a relatively simple method for graphically looking at the distribution of numerical data through their quartiles. As shown in Fig 3.5, box plots have lines extending vertically from the boxes (whiskers), which indicate the variability of the observations outside the upper and lower quartiles. Outliers may also be plotted as individual points. Box plots are non-parametric which means that they are not based on parameterized families of probability distributions. In other words, they display variations of a statistical observation without making assumptions about their statistical distribution. Figure 3.6 displays a typical notched box plot in details. [166, 167]

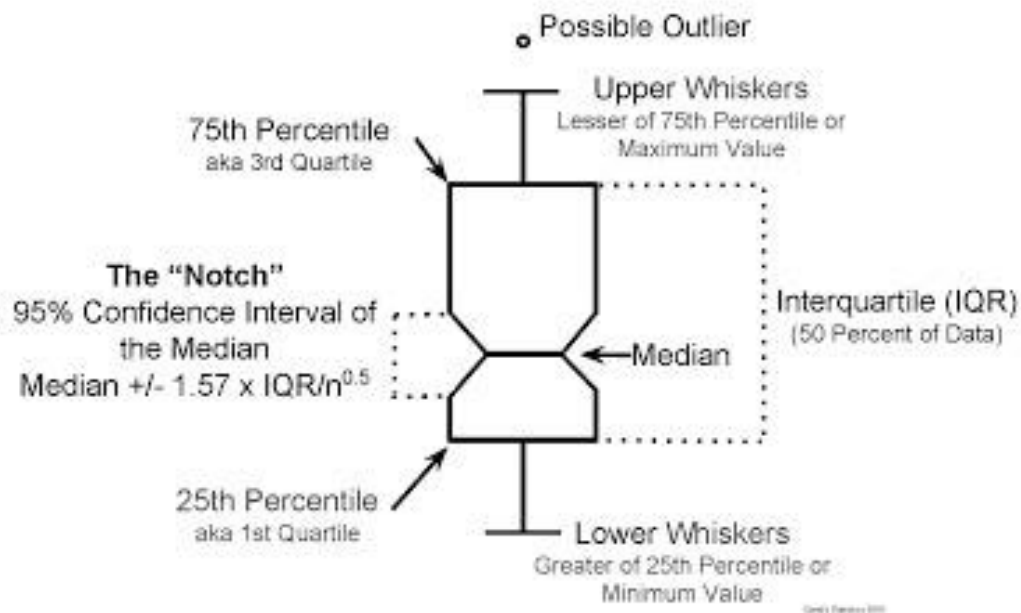


Figure 3.5 - A typical notched box plot.

Figure 3.6 shows the distribution of the strength parameters with the box plots in the four aging environments. It can be observed from figure 3.6.A that the pushout pressure is not varied for AIR aged samples. It can be observed that this figure is almost symmetrical and therefore it is pretty much normally distributed. However, there is a large variation in pushout pressure values in other incubation conditions, especially AS + HAc. This difference has been also observed in previous plots.

Diametral stress, which is plotted in figure 3.6.B shows interesting results. For AS and AS + HAc, the box plots are statistically significantly similar to each other. This agrees with the results of fractional distribution plots. In addition, there is no specific skewness observed in figure 3.6.B, Q1 and Q3 are approximately the same distance from the median and the whiskers have the same length. Therefore, it can be concluded that these data are normally distributed.

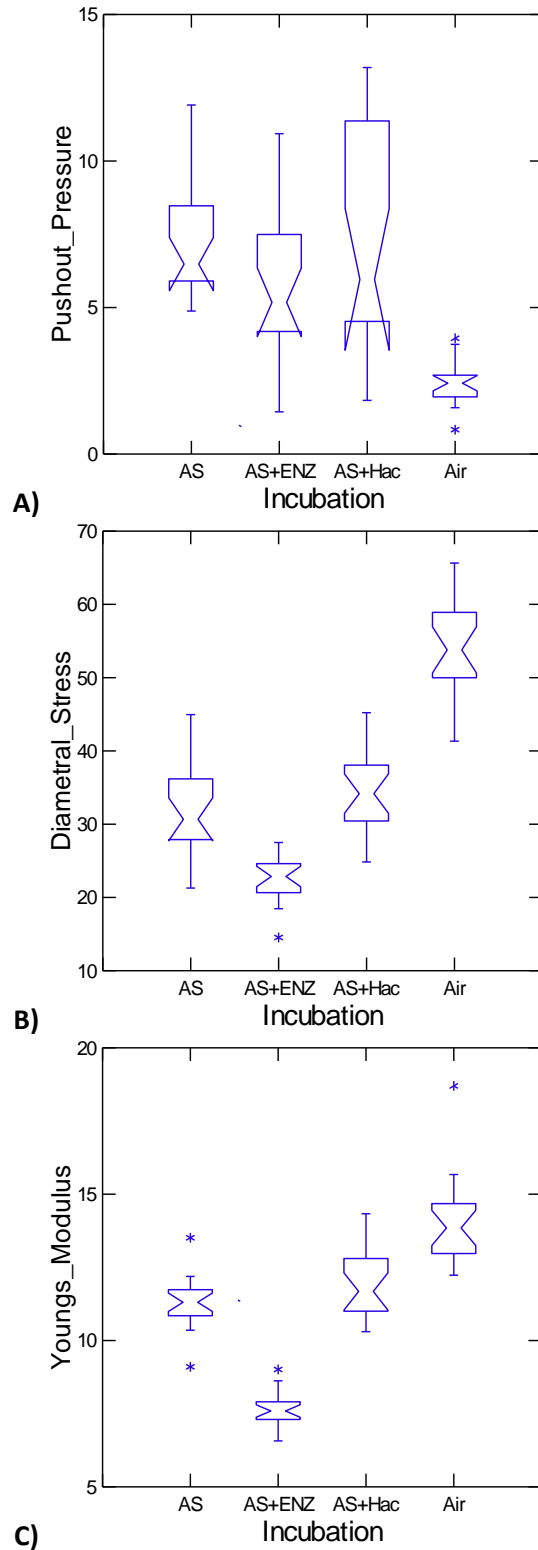


Figure3.6 Notched box plots showing the A) push out pressure, B) diametral stress, and C) modulus of elasticity of all test specimens aged in AS, AS+ENZ, AS+Hac and Air.

Figure 3.6.C is a boxplot of the Young's modulus of the composites incubated under different experimental conditions. This plot shows a slight positive skewness for AS + HAc data. Although there are four potential outliers in this dataset, they are not highly deviated from the outer fence, representing 1.5 interquartile ranges from the median.

Figure 3.7 shows the results of a two sample t-tests comparing all of the aging environments with AS. The t-test quantitatively determines the difference between two means, providing quantitative statistical proof that the differences are statistically significantly different. It can be easily observed that the AS and AS + HAc datasets (Figure 3.7.B) are similar and are not statistically significantly different. The greatest statistically significant difference is between AS and Air (Figure 3.7.A), with the specimens aged in Air showing higher strength values. Figure 3.7.C also shows the composite strength was statistically significantly lower (CI 95%, $p < 0.05$) when incubated in the presence of enzyme than when incubated in AS, providing further proof the presence of esterase significantly weakened the composite.

Figure 3.8 is the scatterplot matrix of linear correlations comparing most important strength and geometry parameters by incubation in this study. Regression analysis is used to better understand the relation between independent and dependent variables and to explore the forms of these relationships. Almost all of the important strength and geometry parameters were discussed above. Even though specimens were made by an individual rather than a system or a machine, it can be observed that all geometric data are nearly normally distributed.

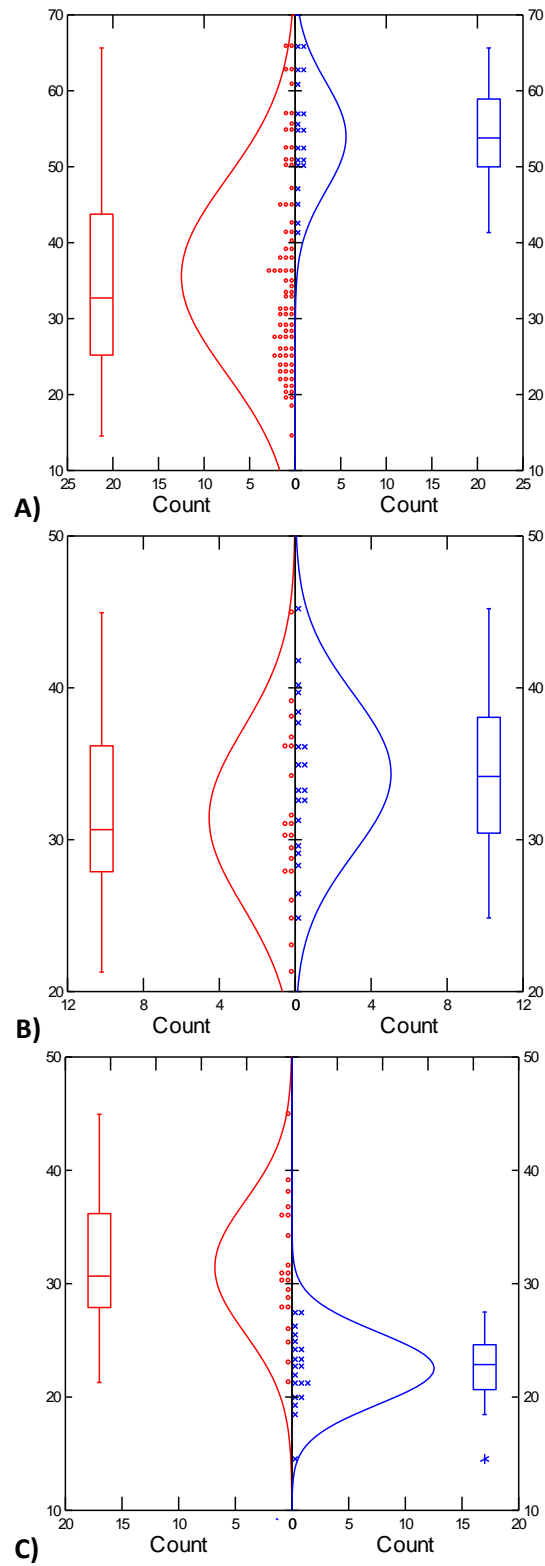


Figure 3.7. Two sample t-tests for comparison of means between A) AS and Air, B) AS and AS+HAc, and C) AS and AS+ENZ.

One of the plots that seem the most interesting, as shown in figure 3.9, is the relation of the diametral stress and young's modulus. Each color in the figure 3.8 represents one of the incubation conditions and it can be observed that all of the data for each aging environment is in one place and their data is not scattered in the whole plot. It also shows that AS and AS + HAC has very similar values (red and green colors). AS + ENZ has the lowest strength values (blue color) whereas Air aged specimens have the highest strength values (purple color).

Since composites have a polymer (resin) network, they do not dissolve in the aging solutions. This is due to the fact that the forces of attraction between the polymer chains in the network are stronger than the intermolecular forces between the solvent molecules and the components of the dental composites. Therefore, the molecules of the aging solutions and solvents scatter in the network and cause swelling and increasing of the network volume. [52]

Comparing the results for Air-aged and AS aged samples, the latter show better bonding to the epoxy (higher push-out pressure values) but much weaker and lower elastic modulus after aging in AS. AS has a similar effect to AS + HAC on the resin matrix contributing to corrosive wear. It might be due to the fact that AS causes hydrolytic degradation of the adhesive interface between filler particles and resin matrix. This degradation process further results in the loss of a mutually protected surface. {De Gee, 1996 #79}

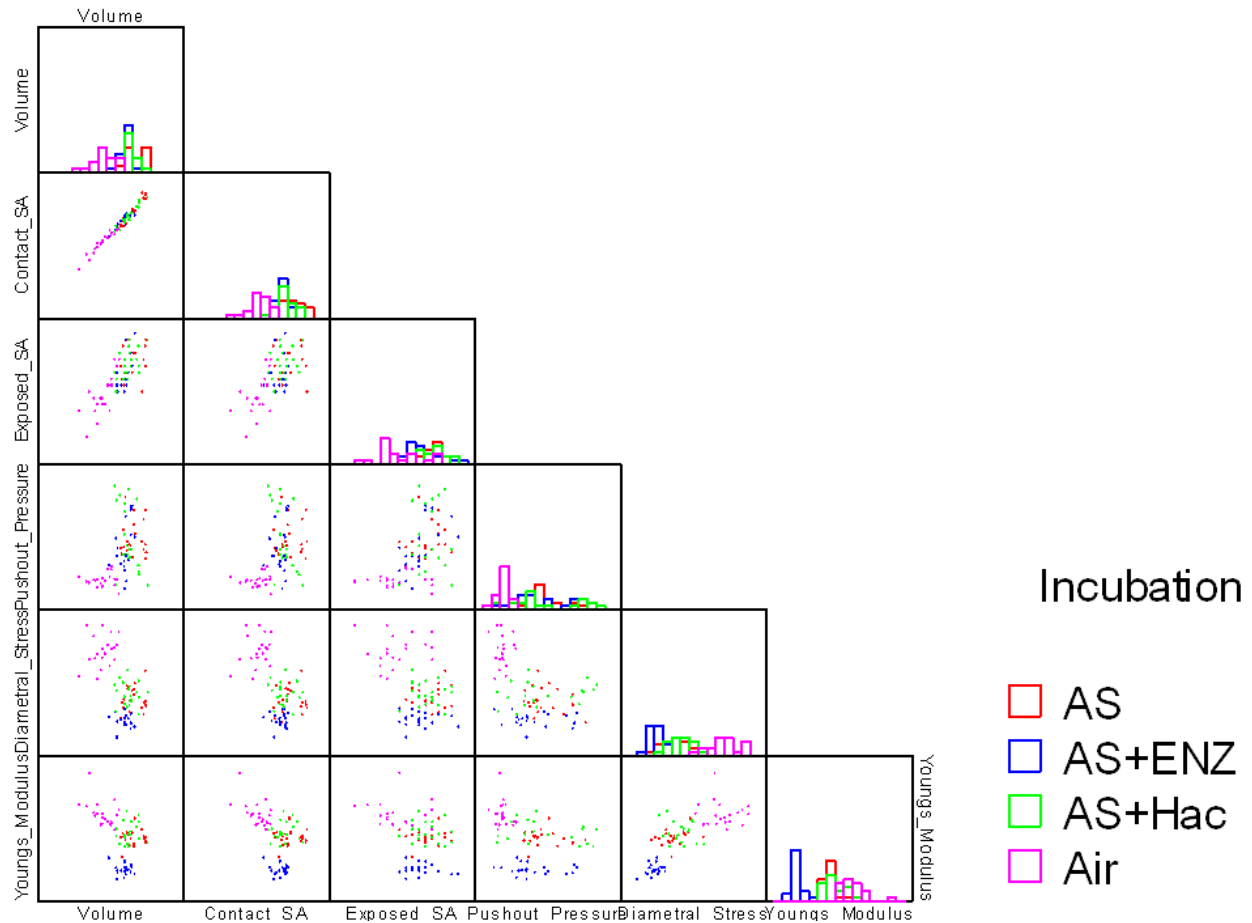


Figure 3.8 - Scatterplot matrix of linear correlations comparing most important strength and geometry parameters by incubation.

One of the very important interactions is in the presence of enzymes that can degrade the polymer network through attacks on the side chains, and therefore deteriorate the properties of the resin network. There is a study suggesting that some harmful by-products may also be produced during enzymatic attack. [6] This agrees with the results of numerous studies that have shown the effect of esterases on dental composites [5, 24, 112, 113]. It also agrees with the data observed in the plots of this study.

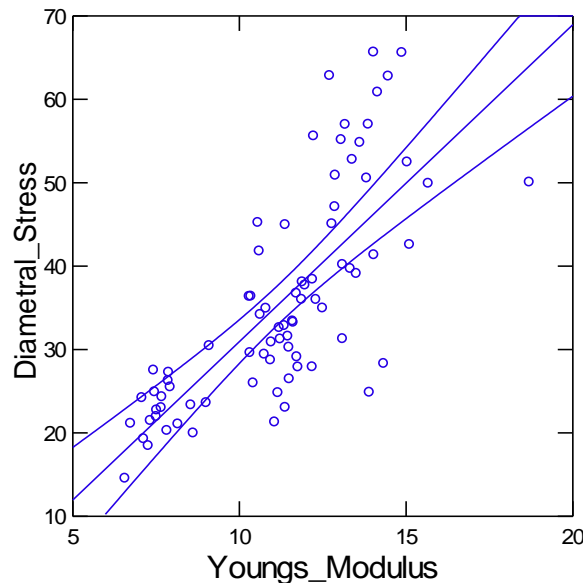


Figure 3.9 – Scatterplot showing linear regression between Young's modulus and diametral stress.

It is worth mentioning that enzymes have relatively large sizes and it limits their mobility in the polymer network. Therefore, it is very unlikely that they can have direct effects in the depth of the network structures. However, as a result of their intense surface effects, composites continue to erode. Consequently, more of the material would be exposed to the aging solution, enzymes in particular, in the long run. [52] It goes without saying that chemistry of the polymer and type of enzyme can both influence the severity of the material degradation. This was evidenced by previous research that investigated the effects of cholesterol esterase on urethane modified bis-GMA/TEGDMA networks and unmodified bis-GMA/TEGDMA networks [110].

These results compare with the air-aged (191 and 199 days), AS aged (183 and 190 days), AS+HAc aged (163 days) and AS+ENZ aged (also 163 days) samples. With respect to the first two

environments (air aged and AS aged), there were no significant differences in any measured property between the two different aging periods under each condition.

The results of the experiments show the following (all tests for significance were at the 95% CI):

1. Composite geometry was normally distributed indicating low sample preparation variability
2. Incubation in AS resulted in a larger composite compared to the air aged samples with significantly stronger (2- to 3-x higher) cohesive strength to the epoxy
3. AS aging results in a significantly weaker composite compared to Air, with peak stress at fracture $\sim 1/2$ that of the air dried samples
4. AS aging results in significantly lower Young's Modulus (95% CI) compared to the air aged samples
5. AS aging was similar to AS + HAc aging, indicating that acidic conditions do not impact composite strength
6. AS + ENZ aging results are highly statistically significantly weaker in all strength parameters, consistent with enzymatic degradation

3.4 Summary and Conclusions

Dental composites are brittle material, which means that they are highly susceptible to surface flaws and internal defects when tensile stresses are present. The reason is that they cannot

plastically deform to reduce stress concentrations, and therefore their tensile strength is far lower than their compressive strengths.

In order to study the effect of storage conditions on the stability of dental composites, the specimens have been exposed to air, artificial saliva, acidic solvent and enzymatic solution in an attempt to study the effects of the aging environments. The effect of these chemicals is varied, but usually involves diffusion of the solution in the composites and elution of unreacted components and some degradative effect on their polymer network.

The present investigation suggests that exposures to acids will not have an immediate effect on the tensile strength of composites. However, it is expected that long term exposure to acids may result in surface softening and diffusion of the chemicals into the resin matrix. With respect to esterase, a direct influence on the tensile strength of the composites was observed. The statistical results showed that enzymatic solution had the most deteriorative effects on the strength properties of the dental composites.

3.5 Limitations

The limitations in this study are:

1. Longer aging times can better show the effect of the aging on the composites.
2. Even though it was shown (section 3.27) that all the aging times were more than the upper limits of the days needed for the diffusion to happen, it would be ideal if they had the same aging time for all the environments for better comparison.

3. Only one loading range was used in this study and cyclic loading effects on intensifying the destructive effects of the solutions were ignored.
4. The artificial saliva that is used for almost all of the *in vitro* investigations (regardless of their recipe) lack the biological and organic components present in the actual human saliva and therefore it is not the exact imitation.
5. In the enzyme containing solution, the enzymatic activity degrades by time and it is not possible to control it or measure it.

3.6 Future Studies

Clinical studies are needed to determine if the *in vivo/ in vitro* studies are replicated under clinical conditions. Also only composite was investigated in this study and it might be interesting to look into the effects of various environments and agents on the bonding between the restorative material and tooth.

In the acidic solution, there was only one acid present in this study. However, that is not the case in the oral environment. Therefore, effects of different acids as well as their mixture might be useful in understanding the detrimental effects of the acids on dental composites.

Moreover, various acid concentrations can have different effects on the material.

Same as above, each enzyme has its unique chemistry and nature and thus will affect the restorative dental materials differently.

Many studies have investigated the role of bacteria in forming dental carries. Even though acids do not seem to have severe effects on mechanical properties of the dental composites, they might act differently in presence of bacteria. Therefore, investigating the mixture of acid and bacteria can be informative in this regard.

Finally, one of the widely used commercial dental composites was investigated in this research. However, there are several other commercial composites that have different nature and chemistry and hence would behave differently under similar circumstances.

Resume

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Fluent
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