THE EFFECT OF INHIBITOR AND INITIATOR CONCENTRATION ON DEGREE OF CONVERSION, FLEXURAL STRENGTH AND POLYMERIZATION SHRINKAGE STRESS ON RESIN-MATRIX COMPOSITE

by

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DEDICATION

This thesis is dedicated to my family, for all the emotional and continuous moral support they gave me.

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TABLE OF CONTENTS

Introduction……………………………………………………………..…...... 1

Review of Literature…………………………………………………...… 7

Materials and Methods……………………………………………........ 26

Results………………………………………………….…………….…... 35

Tables and Figures…………………………………………………….…. 42

Discussion…………………………………………………….……….. 68

Summary and Conclusions……………………………………….....… 76

References…………………………………………………………..……. 79

Abstract…………………………………………………………......…. 88

Curriculum Vitae

LIST OF ILLUSTRATIONS

TABLE I Formulation of test groups…... 43

TABLE II Mean flexural strength and standard deviation (SD)……….. 44

TABLE III Mean flexural modulus and standard deviation………………………………………………. 45

TABLE IV Mean degree of conversion and standard deviation (SD)…………………………………………………… 46

TABLE V Mean depth of cure and standard deviation (SD)…….…..... 47

TABLE VI Mean contraction stress and standard deviation (SD)…………………………………………………… 48

TABLE VII Mean stress rate and standard deviation (SD)…………………………………………………… 49

TABLE VIII Mean gel time and standard deviation (SD)…………………………………………………… 50

TABLE IX Degree of conversion, depth of cure, flexural strength and flexural modulus for all groups……………………......... 51

TABLE X Contraction stress, stress rate, and gel point for all groups……………………... 52

FIGURE 1 Bisphenol A glycidyl methacrylate (Bis-GMA)………… 53

FIGURE 2 Urethane dimethacrylate (UDMA)……………………..... 53

FIGURE 3 Triethylene glycol dimethacrylate………………………. 54

FIGURE 4 Camphorquinone (CQ)…………………………………. 54

FIGURE 5 N,N-dimethylaminoethyl methacrylate (DMAEMA) 2-hydroxyethyl methacrylate……………………………… 55

FIGURE 6 Butyl hydroxytoluene (BHT)... 55

FIGURE 7 A three-point bend test apparatus...……………………… 56

FIGURE 8 Stainless steel split mold for flexural strength specimen preparation……………………... 57

FIGURE 9 ADA tensometer………………………………………… 58

FIGURE 10 Diagram of the ADA tensometer …………….………… 59

FIGURE 11 Fourier transform infrared spectroscopy (FTIR)………. 60

FIGURE 12 Mean flexural strength and standard deviation ………… 61

FIGURE 13 Mean flexural modulus and standard deviation…………. 62

FIGURE 14 Mean degree of conversion and standard deviation……. 63

FIGURE 15 Mean depth of cure and standard deviation……………... 64

FIGURE 16 Mean contraction stress and standard deviation…………. 65

FIGURE 17 Mean stress rate and standard deviation…………………. 66

FIGURE 18 Mean gel point and standard deviation…………………. 67

INTRODUCTION

Worldwide, and for more than a century, amalgam was the material of choice for restoring class I and II cavities. This is mainly due to its high strength, good wear resistance, low cost, and adaptivity in restoring small, medium, and large lesions with a high success rate. In early 1980, a decline began in the acceptance of amalgam by both patients and clinicians and the desire for options has been a topic in the dental literature for several years.[1]

In recent years the use of a resin-matrix composite restoration in posterior teeth has increased significantly. This increase is mainly because of patients demanding esthetic, metal-free restorations, although they are more technique-sensitive to place and more costly.[2, 3]

Light-polymerized composite is most frequently used in clinical practice, and in most cases, the photopolymerization is done by using a high-intensity light that converts the monomer or the oligomer into a polymer and produces a transformation from a viscous paste into a final solid product. Following light irradiation, free-radical polymerization of the monomer is initiated and is accompanied by the cross-linking of the molecule, which results in polymerization shrinkage. The shrinkage brings forth contraction stress in the resin-matrix composite leading to debonding in certain areas of the adhesive joint and adversely affecting the bond strength. Above the gel point (the point at which the polymer acquires a higher modulus and can transfer the polymerization stress to various interfaces), further polymerization will result in a transfer of the stress to the composite boundaries (the tooth itself).[4-6]

In order to release some stresses that are produced as a result of the polymerization shrinkage, the resin-matrix composite will tend to plastically flow from the free surface resulting in additional areas of weakness.[7] If the contraction stresses exceed the bond (between the resin and the tooth), adhesive failure and microleakage will result.[8] The polymerization shrinkage and associated stress can result in poor marginal adaptation, postoperative pain, and recurrent caries.[9]

The amount of this shrinkage stress is related to many factors, such as the ratio of the bonded to unbonded areas (C-factor); the higher the C-factor, the less free surface; the composite will be less likely flaw to accommodate the change in the volume. Also, shrinkage is related to other factors such as the nature of the matrix of the material, filler loading, and the material compliance of the substrate.[10-12]

The polymerization shrinkage in the currently used resin-matrix composite is between 2 and 6 percent. A direct relation exists between the polymerization shrinkage and the degree of conversion, so that we can say that if the final degree of conversion is reduced, this will reduce the shrinkage and the associated stress. However, this will also lower the mechanical properties. As an alternative approach to control this shrinkage stress, researchers have explored controlling the curing rate.[13] Examples of such a strategy include soft-start polymerization and pulse-delay curing. Soft start polymerization uses low power intensity of light followed by high power intensity. Pulse delay curing initiates the polymerization by a short flash of light followed by a waiting time of minutes before the final curing. These techniques are reported to result in lower stress as a result of the prolonged pre-gel state of the chain. This results in the relaxation of a portion of shrinkage stress while the resin reaches its final hardening.[14-16]

However, these methods of curing are associated with the development of a polymer with an increased susceptibility to softening in ethanol, mainly due to the reduction in cross-linking.[15]

Several attempts were done to reduce the polymerization shrinkage, and silorane was introduced to represent a monomer containing both siloxane and oxirane; it undergoes ring-opening polymerization with volume expansion and is claimed to have less shrinkage and shrinkage stress than the methacrylates with an improvement in the marginal integrity and microleakage.[17, 18] It was recognized that the ring-opening polymerization of the silorane is cationic reaction and that no oxygen inhibitor layer exists on the surface of the composite after polymerization in air. This oxygen inhibitor layer plays a very important role in adhesion between successive resin layers by the formation of covalent bonds within an interpenetrating network; therefore, the bond between the layers depends on the reactivity of the component. A decrease was found in shear bond strength between the layers in the silorane composite and an increase in the adhesive failure was associated when the time of placement between the successive layers increased.[19]

In an attempt to find an alternative method to control and retard the polymerization, researchers are looking into the effects of inhibitor concentration.[20] Inhibitors are antioxidant molecules added to the resin to scavenge free radical that originates from prematurely reacted initiators preventing the premature, spontaneous initiation and propagation of the free-radical polymerization. The most commonly used inhibitors in adhesives are butylated hydroxytoluene, also butylhydroxytoluene (BHT), and monomethyl ether hydroquinone (MEHQ). BHT has been used as an inhibitor in resin-matrix composite in concentration around 0.01 % by weight. [7, 21]

Braga and Ferracane reported that increasing the inhibitor concentration results in a lower curing rate and a decrease in contraction stress without any compromise in conversion. However, they found a tendency toward a decrease in degree of conversion with an increase in the inhibitor concentration. However, the effects of inhibitors on mechanical properties were not evaluated in these studies.[13]

Recently, Al-Shammari showed promising results in varying the concentration of the inhibitors on the polymerization characteristics of light-cured resin-matrix composite. The research concluded that fine-tuning the inhibitor levels can be an effective method in slowing down polymerization and reducing contraction stress without compromising the degree of conversion.[20]

In Al-Shammari’s research thesis, the author proposed that the mechanism for the observed phenomena is that the optimized inhibitor level allows for a polymerization rate slow enough to reduce the shrinkage stress, yet fast enough in achieving a conversion that does not jeopardize the mechanical property of the composite. Though the approach was novel and exciting, the experiment was conducted at one, single initiator level. Since the polymerization kinetic is governed synergistically by initiator and inhibitor, it is imperative that we do a full-range investigation on appropriate initiator-inhibitor combinations to see if further reduction in polymerization shrinkage can be achieved.

NULL HYPOTHESIS

1. Varying initiator-inhibitor concentrations will not have a significant effect on polymerization shrinkage stress.

2. Varying initiator-inhibitor concentrations will not have a significant effect on flexural strength.

3. Varying initiator-inhibitor concentrations will not have a significant effect on degree of conversion.

ALTERNATIVE HYPOTHESIS

1. Varying initiator-inhibitor concentrations will have a significant effect on polymerization shrinkage stress.

2. Varying initiator-inhibitor concentrations will have a significant effect on flexural strength.

3. Varying initiator-inhibitor concentrations will have a significant effect on degree of conversion.

REVIEW OF LITERATURE

RESIN-MATRIX COMPOSITE

The first tooth-colored restorative material, silicate cement, was introduced in 1870. It was the only esthetic tooth-colored restorative material available for restoring the anterior teeth. For almost 70 years, these cements were composed of acid-soluble silicate glass with fluoride flux powder and a phosphoric acid liquid. When mixed-acid- base reaction occurs; the major advantage of these cements is the anticariogenic property due to the fluoride content. On the other hand, the drawbacks of these cements are that they are brittle, undergo dissolution in oral fluid, lose their translucency, exhibit surface crazing, and lack adequate mechanical properties.[22]

The development of the first polymeric tooth-colored composite in dentistry was in 1940; it was based on poly (meth methacrylate) powder, methylmethacrylate monomer, benzyl peroxide, and n,n- dimethylparatoluidine. Upon mixing, polymerization will occur, by which covalent bonds are formed between the molecules to form a large molecule and to form the continuous phase. The amine in the liquid reacts with the peroxide in the powder to form a pair of benzoate free radicals; this radical attacks a carbon atom with acrylic double bond creating unpaired electrons that attack another double bond, and the resulting radical will continue to attack other double bonds.[22, 23]

During the mid 1950s, the chemically cured methacrylate restorations were considered esthetic, initially, but had a variety of problems associated with an increase in discoloration, lack of color stability, recurrent tooth decay, and pulp reactions; these problems are mainly attributed to the polymerization shrinkage, a large coefficient of thermal expansion, and monomer leaching.[24]

The inherent problems of the unfilled resin led to the development of a filled acrylic resin in the 1960s. Improvements in the formulation of the resin were achieved in the following years by adding the filler particles and coupling agents. The resulting composites have better mechanical properties and wear resistance but still have the polymerization shrinkage and lack of bonding to the tooth, which limit their use.[23, 25, 26]

The improvements in filler technology resulted in a resin-matrix composite restoration more resistant to the wear and decreased the failure and replacement of the resin restorations. The mechanical properties of the resin-matrix composite depends on many factors, the most important of which is the microstructure involving the distribution and morphology of the filler particles.[27]

Quartz fillers were added to polymethyl methacrylate to make a composite structure, which is by definition a three-dimensional combination of at least two, chemically different materials with a distinct interface between them. These fillers had a low coefficient of thermal expansion, reduced polymerization shrinkage, and water sorption, mainly as a result of the reduced incorporation of resin.[22, 28]

Some mechanical properties, such as strength and wear resistance, can be maximized by increasing the filler content.[29] The effect of filler in the resin-matrix composite depends on many factors, such as the type, size, shape, and amount of fillers used in the formulation, and on the existence of efficient coupling between the filler and the resin.[30]

Shortly after these developments, researchers started looking at ways of introducing an organic silane coupling agent as a chemical agent that would bond the fillers, such as inorganic silica, to the organic matrix. The bond is polymeric in nature; the organic silane coupling agent plays a very important role in the transfer of stresses from the weaker resin matrix to the strong filler particles. The resulting bond produces an increase in tensile, compressive, transverse, and impact strength. The resulted resin-matrix composites with the silanated fillers also have lower coefficient of thermal expansion values than composites with unsilanated fillers and unfilled resins.[22, 31]

Bis-GMA is a reaction product of bisphenol A and glycidyl ester methacrylate. The advantages of Bis-GMA over other monomers are less shrinkage, higher modulus, and reduced toxicity due to its lower volatility and diffusivity into tissues.[32]

The concern with Bis-GMA is that it is highly viscous with high molecular weight, making it difficult to add the fillers to the monomer and to mix the chemically cured composite. For this reason, dilute monomers like triethylene glycol dimethacrylate (TEGDMA) are added to act as a viscosity controller, and to make it easier to add the filler component,[32-36] even though its inclusion increases the amount of water sorption and the resin polymerization shrinkage.[37]

Urethane dimethacrylate (UDMA), which is an oligomer added to some resins, has a reduced viscosity and greater toughness due to the flexibility of the urethane linkages.[38]

In the early 1980s, the classification of the resin-matrix composites was based on some factors such as filler chemical composition, particle size, manufacturing technique, surface roughness, and Young’s modulus.[39, 40] Composites can also be classified according to filler particle size, number of particles, and the area occupied by the particles.[41]

The first composites were called traditional or macrofilled composite; they were made with large quartz fillers. These fillers were produced by grinding large chunks of quartz into irregular particles ranging in size from 0.1 µm to 100 µm with an average size of 20 µm to 40 µm. The advantages of the quartz fillers that they are readily available and have an excellent optical property matching the polymer resin. However, these large quartz particles created some inherent problems: hardness, making it difficult to produce finer particles and therefore more difficult to polish; a lack of radiopacity, and abrasion to the enamel. Thus, these large particles could become easily dislodged from the restoration and produce a rough or dull surface of the final restoration, because of the difference in the hardness between the inorganic fillers and the resin matrix, compromising the esthetics and polishability of the restoration. As a result, this will increase the plaque accumulation and gingival irritation, and create restorations that are sensitive for staining. [42-44]

In the following years, modification in the morphology, size, and components of the fillers affected the development of the composite; barium glass has been added for an opacity purpose; silica has been added to improve the handling, and ytterbium, for an esthetic effect.[44] Microfill composite was also introduced. It contains amorphous silica with a submicroscopic (average particle size of 0.04 µm in diameter). Although these microfilled composites produce a restoration with an excellent esthetic and polishability, the lower filler content may compromise the materials’ mechanical and physical properties. They have lower tensile strength and surface hardness and absorb more water compared with the conventional composite, making these materials contraindicated in stress-bearing areas.[28, 44]

Hybrid resin-matrix composite was developed in order to produce a material having the advantages of both macrofilled and microfilled resin-matrix composites without inheriting their problems. Hybrids contain a small blend of submicron particles (0.04 µm) and small particles (1 µm to 4 µm). This combination of different sizes of filler particles allows the highest level of filler loading with improved physical properties. They produce a smooth surface and can be polished to high luster, making them the material of choice for class III and class IV restorations.[28]

Resin-matrix composite can also be found as flowable with lower filler content and greater proportion of monomer; the filler content is 20 percent to 25 percent less than that of the universal composite materials. They are easy to place and more adaptable to the internal cavity walls compared with the conventional composite, but showed a high polymerization shrinkage and inferior mechanical properties due to the lower filler content. These limitations confine their use to low-stress bearing areas, and to use as liners, fissure sealants, and filling of small cavities. They show a wide range of placement properties; some materials did not flow any more than the conventional composite controls, and the rate of flow in others was difficult to control.[45-47]

Packable composites were introduced into the market as an amalgam alternative,[48] to overcome the non-packable property in the conventional composite. Some researchers claimed that in order to have good proximal contact, the ideal composite should be stiff enough to facilitate the placement without adhering to the instruments used. Furthermore, it was claimed that this packable composite had minimal polymerization shrinkage and an increased depth of cure or degree of conversion of up to 5 mm. However, there is little scientific documentation regarding polymerization shrinkage and degree of conversion for these materials.[49] The packable composite has higher filler loading, and improved filler technology compared to the hybrid composite.[48] As a result of the high viscosity of these materials, they tend to have poor adaptation to the cavity wall, poor margins, and voids in the final restoration.[22]

Inhibitors and initiators are two important molecules in the resin-matrix composite that play an important role in the initiation and termination of the polymerization reaction.[22]

In order to understand the importance of inhibitors and initiators in the polymerization of resin-matrix composite, it is important to understand the polymerization reaction. In dental resin, both the chemical and the light-cured composite involve addition reaction that involve the covalent bonding between two or more identical molecules and result in the formation of a large molecule, and unlike the condensation reaction does not form a by-product.[22]

The reactions occur through a chain process; the presence of an activator is important for the formation of initiator species; the reactive initiator molecules activate the monomer molecules. For example, when the ethylene molecule becomes activated by the initiators, the double bond opens up to form an activated ethylene unit. The activated units continue to grow into larger ethylene molecules, and the reaction continues to the propagation of the reactive center. The growth of the chain stops when the reactive center is destroyed, which can occur by one of many termination reactions, such as the interaction of the ends of two chains, the reaction of an active chain with an initiator radical, by the transfer of the active center to another initiator or monomer, and finally, through the interaction of impurities or inhibitors.[7, 22]

The American Dental Association and Federation Dentaire International define two types of resin-matrix composites: Type 1, chemically cured material and resin-matrix composite; Type 2, external energy-activated material.[50]

In dentistry, the most commonly used method to initiate polymerization in resin-matrix composite is either chemical or light activation. Chemical polymerization of vinyl-based resins is usually done via a free-radical polymerization mechanism at ambient temperature; this is usually achieved by using a binary, redox-curing system consisting of peroxide and an aromatic, tertiary amine.[51] This would generate free radicals that initiate the reaction at a fast rate, not allowing sufficient working time; for this reason, inhibitors are added to the initiators containing paste, to retard the reaction and to extend the working time for the clinician.[22]

The chemically activated composite has some disadvantages that may compromise the mechanical properties, such as the possibility of incorporation of bubbles into the restoration. Furthermore the incorporation of bubbles during the mixing can inhibit the polymerization reaction.

On the other hand, light-activated polymerization is achieved via the generation of free radicals from the activation of a photoiniator, usually α-diketone, to its excited triplet state. This activation is followed by the reduction of the activated photoinitiator by an amine accelerator to form an intermediate excited complex (exciplex), which is followed by the release of the free radicals on dissociation.[51]

The light-cured composite is most commonly used because of the improved storage stability and extended working time. The extended working time gives the clinician the opportunity to control the placement and reduce air porosities caused by mixing, which enhances the physical properties.[52, 53 54]

The earlier system used to initiate the polymerization reaction was ultraviolet light (300 nm to 400 nm),with benzoine methyl ether added to the resin to absorb the UV light and produce free radical, but the problem with this method was the long activation time and limited depth of cure. This method was discontinued and visible light curing was adopted as a method.[22]

INITIATORS AND INHIBITORS

Inhibitors are molecules added to the resin-matrix composite to prevent premature polymerization when the material is exposed to the room light during the dental procedure. Materials such as hydroquinone, eugenol, and oxygen all serve to inhibit or slow the polymerization reaction rate if used in large amount; for this reason, a small amount of hydroquinone is used to prevent the premature polymerization of the methacrylate and to extend the half-life of the monomer. BHT (butylhydroxytoluene) is most commonly used as an inhibitor in a concentration of 0.01 % by weight.[7, 55]

They mainly inhibit the polymerization reaction by reacting with the initiating and propagating radicals and converting them to either non-radical species or a very low reactivity to undergo the propagation reaction. This inhibitory action occurs mainly due to the hydrogen transfer to the reactive radical, producing a free radical with a delocalized unpaired electron, making it unable to initiate the polymerization reaction (unable to open the double bond). When the inhibitors are present, the polymerization rate will be negligible until their concentration is substantially reduced. When the concentration of the inhibitors become low, the polymerization and propagation become competitive with the inhibition reaction. In order for the inhibitors to be effective, they must react with the free radical at a faster rate than that of the radical with the monomer.[7, 56]

On the other hand, initiators are molecules added to the light-cure resin-matrix composite to absorb the light and initiate the free-radical addition polymerization reaction. The most commonly used photointiator in the resin formulation is camphorquinone (CQ) a light-activated free-radical photo initiator with an absorbance range between 400 nm and 500 nm and requiring the presence of tertiary aliphatic amine reducing agent (an electron donor), usually DMAEME for an efficient polymerization. It is composed of di-2, 3-diketo-1, 7, 7-trimethylnorcamphane and has a molecular weight of 166.[57-59]

The CQ abstracts a hydrogen atom from the tertiary amine (added as an accelerator) resulting in free-radical generation. There is evidence that a higher concentration of photointiators improves the degree of conversion and the mechanical properties of the resin, but unfortunately if the photointiators are added above a certain threshold or limit, no benefits are observed. The esthetic result is affected due to the CQ’s yellow color. The photoinitiator phenylpropanedione (PPD) showed quite promising results; it had less “yellowing” effect on the restoration; also PPD produces a lower rate of polymerization without affecting the final degree of conversion compared with CQ and results in less stress within the material and at the tooth-resin interface.[60]

POLYMERIZATION SHRINKAGE

Polymerization shrinkage is considered an inherent property of all dimethacrylate-based resin-matrix composites and is a critical limitation of dental resin-matrix composite. This shrinkage occurs mainly as a result of the conversion of the monomer into polymer; volumetric reduction occurs as a result of the covalent bonds that are created, and intermolecular distance and free volume are reduced, which results in a shrinkage of the resin-matrix composite.[4, 61-64]

As a result of the polymerization reaction, gelation is produced, in which the resin transforms from a viscous-plastic to a rigid elastic phase. The transition between these two phases is referred to as the "gel point" when the material can no longer provide a viscous flow to keep up with the curing contraction. At the early stage of the reaction, the molecule can slip into new positions and orientations; on the other hand at a later stage, the contraction decreases; the material gains strength and is less able to yield. When the gel point reaches polymerization, the composite is rigid enough to prevent plastic flow.[63]

In-vitro measurements have shown that polymerization contraction of resin-matrix composite ranges from 0.2 percent to 2 percent linear shrinkage and from 1.7-percent to 5.7-percent volumetric shrinkage. This polymerization shrinkage results in a stress of 2 MPa to 6 MPa as measured in model systems.[65] This shrinkage is associated with debonding at the adhesive interface resulting in gap formation, microleakage, postoperative pain, marginal discoloration, recurrent caries, and loss of the restoration.[66-68] In most cases, this shrinkage is associated with a polymerization shrinkage stress, resulting in movement of the cusp, debonding or enamel crack, microleakage and postoperative pain.[67, 69]

Feilzer et al. investigated wall-to-wall contraction of thin layers of chemically and light-activated resin-matrix composite. It was found that the chemically cured composite showed lower stresses than light-cured composite, and this is attributed mainly to the presence of porosity due to hand mixing which increased the free surface and thus the flaw capacity of the resin. They also showed that contraction stresses increased with decreased wall-to-wall distance and reached a value of three times the linear shrinkage.[70] The stress from the polymerization shrinkage is affected by many factors, such as the restorative technique used, modulus of elasticity of the resin, and the polymerization rate.[71]

Incremental filling technique reduces the stresses at the tooth-restoration interface, which can be attributed mainly to the reduced volume of resin-matrix composite at placement that decreases the overall contraction by reducing the bulk of material cured at one time and the C-factor. Incremental techniques are associated with higher resin bond strength and less cuspal deflection, compared with the bulk placement technique.[72]

Another method to reduce shrinkage, as discussed earlier, is controlling the curing rate. The problem with this method is that the resin has an increased susceptibility to soften in ethanol.

Studies show that varying the concentration of some components of the resin-matrix composite can affect the polymerization. A recent study found that higher TEGDMA/BisGMA ratios in experimental composites resulted in increased volumetric shrinkage and higher contraction stress values as a result of enhanced conversion.[73]

Recently, Al-Shammari showed promising results in varying the concentration of the inhibitors on the polymerization characteristics of light-cured composite. The research concluded that fine-tuning the inhibitor levels can be an effective method in slowing down polymerization and reducing contraction stress without compromising the degree of conversion.[20]

DEGREE OF CONVERSION

During polymerization of the methacrylate based resin, the viscous liquid undergoes a gradual transformation into a rigid material by radical polymerization that involve the C=C of the methacrylate group. The extent of the transformation from double to single bond is known as “degree of conversion.” In fact, maximizing the degree of conversion and minimizing the polymerization shrinkage are antagonistic goals. This polymerization results in volume shrinkage that happens in three origins: chemical contraction due to the changes in the interatomic spacing between the molecules; thermal contraction during the cooling, because the curing reaction is exothermic, overheating the resin to contract and return to room temperature; and finally, the post-contraction that occurs up to 24 hours as a result of verification of the system that results in a freezing of the radical in the cross-linked structure and a cessation of further reaction.[74]

Studies show that up to 6 percent residual monomer remains in BISGMA/TEGDMA resin after curing; this monomer can leach into the body. Thus we can say that the higher the degree of conversion, the greater the biocompatibility, because of the reduced amount of the residual monomer that leaches into the oral cavity.[75]

Several studies showed that there is a strong correlation between the degree of conversion and the physical and biological properties; they showed that the higher the degree of conversion, the higher the contraction stress, which leads to bond failure. Mechanical properties of resin-matrix composite are influenced by the network formation and cross-linking taking place during the setting reaction.[76, 77]

Fourier transformation infrared spectroscopy (FTIR) is the most commonly used method to detect the C=C stretching vibration before and after curing of the tested material. McCabe reported that differential thermal analysis (DTA) by using split fiber optic light source is a valuable and convenient method easily performed for investigating the curing performance of light-cured resin-matrix composite.[78] The ratio of absorbance intensities of aliphatic C=C (peak at 1638 cm $^{-1}$) against an internal standard before and after curing of the specimen is usually used to evaluate the percentage of unreacted carbon-carbon double bonds. The aromatic C· · ·C (1608 cm^{-1}) and carbonyl group (>C=O, 1720 cm^{-1}) absorbance is used as an internal standards for Bis-GMA and BTDMA-based composites, respectively.[79]

A study was done by Imazato et al. to measure the degree of conversion of experimental composite using both FTIR and DTA. Their result showed that by both FTIR and DTA, the degree of conversion of experimental composites increased as the proportion of TEGDMA increased, although DTA showed 3±10 percent greater values than FTIR. For proprietary composites that contain hybrid filler, the values by DTA were not significantly different from those by FTIR at 20 sec exposure. Longer irradiation time resulted in greater degree of conversion for both methods, and DTA showed 5±7 percent greater values than FTIR. However, the degree of conversion of the composites containing prepolymerized resin filler was 30 percent less by FTIR than by DTA, possibly due to the influence of unpolymerized species in the filler.[78]

Fernanda et al. showed that a high energy level, degree of conversion had a tendency to level off earlier than contraction stress, and they concluded that using a high-energy density may increase the stress value without increasing the conversion.[76]

Another study was done by Leonardo et al. to investigate the effect of four light-curing methods on the degree of conversion, contraction stress, and stress rate developed by a resin-based composite at two C-factor levels. They concluded that the higher the C-factor level, the higher the amount of stress generated, and the faster the stress development. C-factor was proven to have no effect on the degree of conversion of the restorative composite.[11]

Thus, there is a direct relation between the degree of conversion and contraction stress, and many studies have been done to evaluate the effect of the degree of conversion on the stress.

Baraga et al. showed that the longer the curing time, the higher conversion, the stress, and the shrinkage. They also showed that a significant stress reduction was verified (approximately 29 percent) in material that contained 0.5-percent BHT and 1.0-percent BHT. However, no difference in stress was found among material that contained 0.05-percent BHT, 0.2-percent BHT, and 0.5-percent BHT. No significant difference was found in the degree of conversion. They concluded that the maximum stress rate and shrinkage were reduced with a higher inhibitor concentration. Reduction in reaction speed occurs as a result of the chemical inhibition by the free radicals that are terminated by reacting with the phenolic hydrogen of the BHT molecule ($C_{15}H_{24}O$). The phenoxy radicals may then inactivate another free radical by C-C or C-O coupling or by the loss of another hydrogen atom to form a quinone, which may react further. Therefore, each inhibitor molecule can terminate two or even more polymer chains; the conversion proceeds at a reduced rate until the inhibitor is completely consumed. This results in an extension of what is known as a “pre-gel phase,” at which the shrinkage forces can be dissipated before the cross-linking reaches a certain point where the molecular displacement becomes impossible. After that, the shrinkage is very likely to generate contraction stress. The tendency for lower degree of conversion with higher BHT levels indicates that, in concentrations above 1 percent, the final conversion may be compromised.[13]

Another method to assess the degree of conversion is by an indirect test that involves the physical determination of surface hardness.[80]

FLEXURAL STRENGTH AND FLEXURAL MODULUS

One of the major problems associated with resin-matrix composite that leads to failure of posterior restorations is fracture within the body of the restoration. This is related to many factors, such as the elasticity, fracture toughness, and marginal degradation of the material under stress, which is usually evaluated by testing flexural strength and flexural modulus.[81]

Flexural strength is a meaningful mechanical property to assess brittle materials such as resin-matrix composite; flexural strength is the force required to break a material and can be defined as the failure stress of a material as measured in bending. Modulus of elasticity is a measure of the material stiffness to elastic deformation and is defined mathematically as the slope of the stress strain curve within the proportional limit. The higher the elastic modulus, the stiffer the material to elastic deformation.[22, 82-84]

Clinically, composite restorations are subjected to flexural stresses in the anterior and posterior teeth, making the flexural strength and flexural modulus important to both the clinicians and material scientists.[83]

Therefore, a higher modulus of elasticity means that the force of attraction between the atoms of the material is high, and greater force will be required to produce elastic deformation. In areas of high stresses, material with low modulus will deform under masticatory stress leading to failure of the material. Thus, higher flexural strength is desired for materials that are subjected to high masticatory load.[85] The most commonly used method to test the flexural strength is by using large specimens (25 × 2 × 2 mm^3) as dictated by ISO 4049.[85, 86]

Studies showed, as mentioned previously, that the mechanical properties of the resin-matrix composite depend on many factors, mainly the composition and the microstructure of the material. The microstructure includes many factors, such as morphology of the filler particles, their distribution in the bulk of the material, and the presence of pre-existing cracks and voids.[27, 87]

The most appropriate modulus of elasticity for a resin-matrix composite should be comparable or preferably higher than that of dentin; the value of 60-percent inorganic filler content (volume percentage) is considered as the minimum level for restoring posterior teeth with resin-matrix composite.[86]

Studies showed that microfilled composites with lower filler volume had lower stiffness, fracture toughness, and lower fatigue strength compared with heavily filled composite.[83]

Other components of the resin-matrix composite such as inhibitors or initiators have not been studied in detail to evaluate their effect on mechanical properties.

A recent study has looked at the effect of varying the concentration of BHT on mechanical properties. It showed that the flexural strength and the flexural modulus were not affected by increasing the BHT level up to 1.2 percent, but it also showed a significant decrease when the concentration reached 1.4 percent.[20]

Another study showed that increasing the inhibitor concentration reduces the flexural strength and flexural modulus, and this was attributed to the lower weight chain and fewer cross-links that were found. They concluded the lower degree of conversion was responsible for the reduction in mechanical properties.[88]

DEPTH OF CURE

Studies on resin-matrix composite showed that many physical properties such as hardness, creep, flexural modulus, and tensile and compressive strength depend upon the degree of polymerization.[89] Also, studies show that the presence of uncured or partially polymerized material in the final restoration may reduce the mechanical properties and can result in a reduced biocompatibility and the release of uncured monomer harmful to the oral mucosa and pulp.[90-92]

The depth of the cure depends on many factors, such as the composite, which includes the impact of shade, particle size, and load distribution; and light-related factors, which include light intensity, spectral distribution, and exposure time. The more intense the light source, the more the photons are absorbed by the photo initiators. Further, the more the camphorquinone is raised to the excited stage, the more it will react with amine and form free radical.[58, 59] In this fashion, the depth of cure is affected by resin type, resin shade, filler level, spectral distribution of the activation light, and exposure time.[90, 93]

Many methods were used to evaluate the depth of cure of the light-cured resin-matrix composite. These methods can be evaluated directly by using the Knoop or Barcol hardness test, [77] or by scraping away the uncured material and measuring the length of the remaining material.[94]

The objective of this project was to investigate the effect of varying the inhibitor and initiator concentrations on the polymerization shrinkage of light-cured resin-matrix composite. The specific aims are:

1. To determine the effect of various levels of inhibitors and initiators on the polymerization contraction stress kinetics.

2. To examine the effect of various levels of inhibitors and initiators on the degree of conversion.

3. To investigate the effect of various levels of inhibitors and initiators on the flexural strength and modulus of elasticity.

4. To investigate the effect of various levels of inhibitors and initiators on the depth of cure of light-cured resin-matrix composite.

MATERIALS AND METHODS

RESIN-MATRIX COMPOSITE

The resin for this study was prepared from Bis-GMA, UDMA, and TEGDMA (Sigma-Aldrich, St Louis, MO) at a 1:1:1 ratio. Bis-GMA was left in the incubator for 24 h. The resin was used as received. Sixteen grams of each resin were added to the bottles and stirred; then, we left the bottles in a controlled-temperature room followed by storage at 5◦C.

Camphorquinone (CQ, Sigma-Aldrich) and dimethylaminoethyl methacrylate (DMAEMA, Sigma-Aldrich) were used as the initiator and the co-initiator, and BHT was used as an inhibitor. Sixteen combinations of initiators and inhibitors were investigated. The concentrations of BHT were 0 percent, 2.0 percent, 6.0 percent, and 20 percent. The concentrations of CQ were 2.0 percent, 6.0 percent, 20 percent, and 60 percent. The concentration levels included a wide range of formulation concentrations to allow us to explore the full range of effects of initiators and inhibitors.

The BHT was grounded using a mortar and pestle to obtain a powder consistency. A large batch was grounded at the beginning to be used for all groups to ensure that the consistency was the same across all samples, and then BHT was added to the resin with continuous stirring to obtain a homogenous mix. The DMAEMA and CQ were added in a dark room to prevent light from initiating the reaction.

The addition of the 0.7-um borosilicate glass filler (Pentron Technologies, Wallingford, CT) was performed with continuous mixing under vacuum so as not to incorporate air bubbles. The total amount of glass filler was 70 percent of the total weight. (See Table I for the formulations of the test groups, and Figures 1 through 6 for diagrams of the individual structures incorporated into the fabrication of the resin-matrix composite.)

FLEXURAL STRENGTH AND FLEXURAL MODULUS

Flexural strength and flexural modulus were determined by using the three-point bending test as specified by the ISO specification 4049.[22]

A total of 16 groups were used, with four levels of inhibitors (BHT: 2%, 6%, 20% 60%) and initiators (CQ: 2%, 6%, 20 %, 60%); 10 samples per group were used. The flexural test specimens were fabricated according to ISO 4049 specifications (25 mm length × 2 mm width× 2 mm height) using stainless steel split molds.

A glass slide and a Mylar strip were placed beneath the mold, and then the resin-matrix composite was placed in the mold by using a plastic spatula. The resin was overfilled, and then a second Mylar strip and a glass slide were placed on top of the mold. Gentle pressure was applied to extrude the excess material from the mold and to prevent the formation of air bubbles within the specimens.

The top and bottom surfaces of the specimens were light-cured with three overlapping irradiation cycles of 40 seconds with a light-curing unit (L.E. Demetron, SDS/Kerr). Periodic measurements of the light cure were to be taken with a Cure Rite radiometer (Dentsply Caulk, Milford, DE) to check if the bulb or mirror needed cleaning or replacement between different groups.

The specimens were then removed from the mold, and the excess of the material was removed. Polishing was done with SiC paper (230-grit, 400-grit, and 600-grit) to achieve smooth edges. Then, the specimens were stored for seven (7) days.

After one week and before the test was carried out, each specimen's thickness and width were measured with a digital micrometer. Three measurements for the width and thickness from various areas of the beam were taken, and the mean of these measurements was recorded.

The test was done using a universal testing machine (Sintech Renew 1121, Instron Engineering Corp., Canton, MA) (Figure 7 and Figure 8). A standard three-point bending jig was attached to the machine and connected to a computer with a specifically designed program (Test-Works 3.0 MTS Systems Co., Eden Prairie, MN). This software controls the testing machine and records the breakage load and beam deflection. Then, the specimens were placed on the jig and the test carried out using a span length of 15 mm and a crosshead speed of 1 mm/min.

FLEXURAL STRENGTH

Flexural strength σ_b was calculated using the following equation:

$$\sigma_b = \frac{3PL}{2bh^2}$$

Where

P = maximum breakage load (N);

L = supporting span (15 mm);

b = specimen width (mm);

h = specimen height (mm).

MODULUS OF ELASTICITY

The maximum deflection of the beam in the elastic zone was also calculated using the following equation:

$$E_b = \frac{P'L^3}{4Ybh^3}$$

Where:

P' = load below elastic limit (N);

L = supporting span (15 mm);

b = specimen width (mm);

h = specimen height (mm);

Y = beam deflection at P’.

POLYMERIZATION SHRINKAGE STRESS MEASUREMENT

A tensometer was used to measure the polymerization shrinkage stress, contraction stress rate, and gel time for each resin. It depends on the deflection of the cantilever beam, which was measured with a linear variable deferential transformer (LVDT) positioned 23 cm from the sample assembly at the free end of the cantilever beam. The measured tensile force was divided by a cross-sectional area of the sample to obtain the contraction stress (Figure 9 and Figure 10).

This tensometer consisted of a rectangular beam (10 mm in width and 40 mm in height) clamped horizontally on the beam holder. The beam was made of stainless steel with a Young’s modulus of 193 GPa.

The top of each composite was connected to the cantilever beam at a distance of 12.50 cm from the beam holder. Quartz rods were used to complete the assembly to the tensometer, and to guide the irradiation from the curing unit to the sample.

The two pieces of quartz rod were flattened and polished with 600-grit wet silicon carbide paper. Each rod was about 6 mm in diameter. Two layers of silane agent were applied to one end of each rod. The two rods were aligned manually; the upper rod was mounted first with the silanized end pointing down. The bottom quartz rod was aligned vertically with the upper rod and then mounted with the silanized end pointing up. In order to keep the composite sample in place, polytetrafluoroethylene (PTFE) sleeves were placed around the gap between the two rods. Two holes were drilled in the sleeve; the first hole was 1.5 mm in diameter for the injection of the composite, and the other hole was 0.5 mm in diameter for air escaping during a sample injection.

Composite was injected into the sample holder to fill the space between the silanized ends, and then the composite was light-cured through the bottom quartz rod with an Elipar Highlight curing unit (ESPE, Dental-Medizin Gmbh, Seefeld, Germany) for 60 s through the lower glass rod. The contraction force was measured for 30 min.

These composite samples were disks 6 mm in diameter and 2.25 mm in height corresponding to a C-factor of 1.33 (diameter/(2)height). Three samples were made for each group.

The polymerization contraction stress was measured for 30 min from the start of photoinitiation with data collected every second. The contraction stress was determined by dividing the measured tensile force by a cross-section area of the sample. The stress rate was determined for each specimen by taking the first derivative of the stress vs. time curve. The gel point was determined from the first data point with a significant non-zero slope.

DEGREE OF CONVERSION MEASUREMENT

The degree of conversion was determined with infrared (IR) spectroscopic technique. First, the peak areas were determined for the uncured resin-matrix composite. Three samples from each group were taken; the sample was placed in the FTIR sample holder with a 5-mm diameter opening, and one reading of the peak area was taken for each sample. Then, resin-matrix composite was placed between two Mylar strips, with a glass slab beneath and on the top to avoid air entrapment. A stainless jig with a 7-mm opening was placed above the assembly, and the curing was done through the jig opening for 20 seconds using a light curing unit (L.E.Demetron, SDS/Kerr).

Specimens of 0.15-mm thickness and 6 mm in diameter were used. Three samples from each group were done, and three measurements of the peak areas for each sample were taken.

The specimens were placed in a standard FTIR sample holder; the infrared radiation was absorbed by the sample and then converted to thermal energy. This was followed by the diffusion of heat to the surface of the specimen, which generated sound pressure waves, and these waves were captured by a high-sensitivity microphone. The detected signal was then converted to a conventional IR spectrum[76] (Figure 11).

The IR spectra acquired an absorbance mode wave of 1500 cm^{-1} to 1700 cm^{-1}. The area under the peak 1608 was assigned to the aromatic C=C coming from BIS-GMA and used as the internal standard. The area under the peak 1638 was assigned to the vinyl C=C and was be used to evaluate the degree of conversion. Degree of conversion was obtained directly from the decrease in the 1638 peak intensity using the following equation:

$$
\begin{aligned}
&\text{Degree of conversion}\\
&= \frac{\#\text{ of converted } C = C}{\text{Total }\#\text{ of } C = C}\\
&= \frac{\text{Total }\#\text{ of } C = C \text{ - Remaining }\#\text{ of } C = C}{\text{Total }\#\text{ of } C = C}\\
&= 1 - \frac{\text{Remaining }\#\text{ of } C = C}{\text{Total }\#\text{ of } C = C}\\
&= 1 - \frac{\text{Cured(area under 1638/area under 1608)}}{\text{Uncure(area under 1638/area under 1608)}}
\end{aligned}
$$

DEPTH OF CURE

A scraping technique had been used to evaluate the depth of cure according to the ISO standards for dental resin 4049.[94] Three specimens from each group were condensed into a Teflon mold; each specimen was of 4 mm in diameter and 6 mm in depth. Above the Teflon mold, a 1-mm metal spacer was placed to hold the tip of the light-curing unit 1 mm from the surface of the resin. The specimens were light-cured with a light-curing unit (L.E.Demetron, SDS/Kerr) for 40 seconds. A radiometer was used to check the consistency between the specimens.

After the light curing, the specimens were removed from the mold, and the soft, uncured resin-matrix composite was scraped with a plastic spatula. The height of each specimen was measured using a digital micrometer in three different areas, and the average of the three measurements was recorded. The value was divided by two in order to obtain the ISO 4049 depth of cure.

STATISTICAL METHODS

The effects of inhibitor (BHT) and initiator (CQ) concentrations on stress rate, gel point, contraction stress, depth of cure, flexural strength, and flexural modulus were assessed using two-way analysis of variance (ANOVA) models. The effects of inhibitor and initiator concentrations on DC were assessed using ANOVA that included random effects to account for repeated measurements from the same sample. Plots (3-D and contour) were used to visually depict the results. The tests for interaction between the inhibitor and the initiator were considered to be significant if the p-value was less than 0.10. A 5-percent significance level was used for all group comparisons. When the interaction effect was significant, pair-wise comparisons of the treatment combinations were examined for significance using the Fisher's Protected Least Significant Differences Method. When the interaction effect was not significant, the main effects were examined for significance. When the main effects were significant, pair-wise comparisons between the levels within each factor were examined using the Fisher's method.

RESULTS

FLEXURAL STRENGTH AND MODULUS

Mean flexural strength and modulus values and standard deviations are shown in Table II and III and Figure 12 and 13. The flexural strength for all CQ-BHT combination is shown in table IX.

Groups L, M, N, O and P were not cured with the three overlapping irradiation cycles of 40 seconds, so that these groups were not tested for the flexural strength.

For group H, only two samples out of the 10 broke. The flexural strength was 23.67 MPa for No. 2 and 13.83 MPa for No. 10. The rest of the samples were only bent and did not break under load.

For Group I, the middle of the specimens was soft and not fully cured. After the one-week storage, some of the specimens opened at both edges; only six specimens out of the 10 were testable; three out of the six specimens broke under load; their flexural strengths were 34.64 MPa, 14.23 MPa, and 11.05 MPa. Two samples were bent but did not break under load, and one sample was discarded due to the load cell that was moving down after breaking of the specimen. For group J, all the specimens were very soft and not fully cured in the middle, and they opened at the edges after one week storage; three specimens out of the 10 were testable; samples No. 1 and No. 3 were bent, but did not break; sample No. 2 broke under load, and the flexural strength was 5.77 MPa.

For group K, all the specimens were very soft, fully cured in the middle, and opened after the one-week storage period. Only one sample was tested; the rest of the bars were non-testable. The flexural strength of the tested specimen was 2.17 MPa.

The interaction between inhibitor and initiator was significant (p = 0.0492). For CQ = 2.0 percent, the samples with 20-percent BHT had significantly lower flexural strength than those with 0.0-percent BHT, 2.0-percent BHT, and 6.0-percent BHT.

For CQ = 6.0 percent, the samples with 20-percent BHT had significantly lower flexural strength than those with 0.0-percent BHT, 2.0-percent BHT, and 6.0-percent BHT. Six–percent BHT had significantly lower flexural strength than those with 2.0-percent BHT.

For BHT = 0.0 percent, 2.0 percent, and 6.0 percent, the samples with 2.0-percent CQ had significantly lower flexural strength than those with 6.0-percent CQ; however, for BHT = 20 percent, the CQ had no significant effect (p = 0.57) on flexural strength.

Elastic modulus values for each resin group are summarized in Table III. The interaction between inhibitor and initiator was significant (p = 0.0001). For CQ = 2.0 percent, the samples with 20-percent BHT had significantly lower flexural modulus than those with 0.0-percent BHT, 2.0-percent BHT, and 6.0-percent BHT. The samples with 6.0-percent BHT had significantly lower flexural modulus than those with 0.0 percent BHT and 2.0-percent BHT.

For CQ = 6.0 percent, the samples with 2.0-percent BHT had significantly lower flexural modulus than those with 0.0-percent BHT; and samples with 2.0-percent BHT and 6.0-percent BHT had significantly lower flexural modulus than those with 0.0-percent BHT.

For BHT = 0.0 percent, 2.0 percent, and 6.0 percent, the samples with 2.0-percent CQ had significantly lower flexural modulus than those with 6.0-percent CQ; however, for BHT = 20 percent, the samples with 6-percent CQ had significantly lower flexural modulus than those with 2.0-percent CQ.

DEGREE OF CONVERSION

Conversion values obtained from the FTIR are shown in Table IV and Figure 14. The degree of conversion for all CQ-BHT combination is shown in Table IX.

The interaction between inhibitor and initiator was significant (p = 0.0001). For CQ = 2.0 percent, the samples with 20-percent BHT had significantly lower DC than the samples with 0.00-percent BHT, 2.0-percent BHT, and 6.0-percent BHT; and samples with 6.0-percent BHT had significantly lower DC than 2.0-percent BHT and 0.0-percent BHT.

For CQ = 6.0 percent, the samples with 20-percent BHT had significantly lower DC than samples with 0.0-percent BHT, 2.0-percent BHT, and 6.0-percent BHT. The samples with 2.0-percent BHT and 6.0-percent BHT had significantly lower DC than those with 0.0-percent BHT.

For CQ = 20 percent, the samples with 20-percent BHT had significantly lower DC than samples with 0.0 percent-BHT, 2.0-percent BHT, and 6.0-percent BHT. The samples with 0.0-percent BHT and 6.0-percent BHT had significantly lower DC than 2.0-percent BHT.

For CQ = 60 percent, the groups with 20-percent BHT had significantly lower DC than samples with 0.0-percent BHT and 2.0-percent BHT. The samples with 6.0-percent BHT had significantly lower DC than those with 2.0-percent BHT.

For BHT = 0.0 percent and 20 percent, the samples with 60-percent CQ had significantly lower DC than those with 2.0-percent, 6.0-percent, and 20-percent CQ. The samples with 20-percent CQ had significantly lower DC than 2.0-percent CQ and 6.0-percent CQ.

For BHT = 2.0 percent, the samples with 60-percent CQ had significantly lower DC than the samples with 2.0 percent CQ, 6.0-percent CQ, and 20-percent CQ. The samples with 6.0-percent CQ had significantly lower DC than 2.0-percent CQ and 20-percent CQ.

For BHT = 20 percent, the samples with 60-percent CQ had significantly lower DC than samples with 2.0-percent CQ, 6.0-percent CQ, and 20-percent CQ. The samples with 2.0-percent CQ and 6.0-percent CQ had significantly lower DC than samples with 20-percent CQ.

DEPTH OF CURE

Depths of cure measurements are shown in Table V and Figure 15. The depth of cure for all CQ-BHT combination is shown in Table IX.

The interaction between inhibitor and initiator was significant (p = 0.0001). For CQ = 2.0-percent, the samples with 0.0-percent BHT had a greater depth of cure than samples with 2.0-percent BHT, 6.0-percent BHT, and 20-percent BHT. The samples with 2.0-percent BHT had a greater depth of cure than the samples with 6.0-percent BHT and 20-percent BHT. The samples with 6.0-percent BHT had a greater depth of cure than samples with 20-percent BHT.

For 6.0-percent CQ, the samples with 20-percent BHT had a shallower depth of cure than samples with 0.0-percent BHT, and 2.0-percent BHT. The samples with 6.0-percent BHT had a shallower depth of cure than samples with 0.0-percent BHT. The 2.0-percent CQ had a significantly greater depth of cure than samples with 6.0-percent CQ regardless of BHT level; however, the difference between 2.0-percent CQ and 6.0-percent CQ was larger for lower levels of BHT.

POLYMERIZATION SHRINKAGE STRESS

In this study, the only groups that were tested were A, B, C, E, F and G; the rest of the groups were not cured in the curing time so that they were not tested. The contraction stress, stress rate and gel time for all CQ-BHT combination is shown in Table X.

Mean and standard deviations of maximum contraction stress are given in Table VI and Figure 16. The interaction between inhibitor and initiator was not significant ($p = 0.16$). Six-percent BHT had significantly lower contraction stress than samples with 0.0-percent BHT and 2.0-percent BHT. Two-percent CQ had significantly higher contraction stress than samples with 6.0-percent CQ.

Mean and standard deviations of maximum contraction stress rate are summarized in Table VII and Figure 17. The interaction between inhibitor and initiator was significant ($p = 0.0684$). For CQ = 2.0 percent, the samples with 0.0-percent BHT had significantly higher stress rates than samples with 2.0-percent BHT and 6.0-percent BHT. The samples with 2.0-percent BHT had significantly higher stress rates than those with 6.0-percent BHT; however, for CQ = 6.0 percent, the BHT had no significant effect ($p = 0.12$) on stress rate.

For BHT = 0.0 percent, the samples with 2.0-percent CQ had higher stress rates than those with 6.0-percent CQ; however, for BHT = 2.0 percent and 6.0 percent, the CQ had no significant effect ($p = 0.31$ and $p = 0.87$, respectively) on stress rate.

Gel times for the experimental resins are presented in Table VIII and Figure 18. The interaction between inhibitor and initiator was significant (p = 0.0008). For CQ = 2.0 percent, samples with 6.0-percent BHT had significantly higher gel points than those with 0.0-percent BHT and 2.0-percent BHT; however, for CQ = 6.0 percent, the values for samples with 6.0-percent BHT were significantly higher than for those with 0.0-percent BHT.

For BHT = 0.0 percent, 2.0 percent, and 6.0 percent, the samples with 6.0-percent CQ had significantly higher gel points than those for 2.0-percent CQ; however, for BHT = 6.0 percent, the CQ had no significant effect (p = 0.61) on stress rate.

TABLES AND FIGURES

TABLE I

Formulation of test groups

Group	**Monomer** **BisGMA:UDMA:TEGDMA**	**Initiator CQ Wt%**	**Co-initiator DMAEMA Wt%**	**Inhibitor BHT Wt%**	**Filler Borosilicate Wt%**
A	1:1:1	2 %	1%	0%	70%
B	1:1:1	2 %	1%	2%	70%
C	1:1:1	2%	1%	6%	70%
D	1:1:1	2%	1%	20%	70%
E	1:1:1	6%	3%	0%	70%
F	1:1:1	6%	3%	2%	70%
G	1:1:1	6%	3%	6%	70%
H	1:1:1	6%	3%	20%	70%
I	1:1:1	20%	10%	0%	70%
J	1:1:1	20%	10%	2%	70%
K	1:1:1	20%	10%	6%	70%
L	1:1:1	20%	10%	20%	70%
M	1:1:1	60%	30%	0%	70%
N	1:1:1	60%	30%	2%	70%
O	1:1:1	60%	30%	6%	70%
P	1:1:1	60%	30%	20%	70%

TABLE II

Mean flexural strength and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0.0%	2%	10	54.27	103.45	76.97 (15.85)
B	2%	2%	10	53.44	101.29	77.42 (13.29)
C	6%	2%	10	52.56	85.69	69.91 (10.78)
D	20%	2%	10	15.40	45.70	26.08 (9.61)
E	0%	6%	10	55.86	135.84	99.94 (27.66)
F	2%	6%	10	75.85	133.57	112.04 (16.61)
G	6%	6%	10	65.89	108.65	89.91 (15.73)
H	20%	6%	2	13.84	23.67	18.76 (6.95)

TABLE III

Mean elastic modulus and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	10	1679	2986	2336 (423)
B	2%	2%	10	1638	2571	2043 (317)
C	6%	2%	10	1282	2332	1714 (347)
D	20%	2%	10	251	1115	671 (264)
E	0%	6%	10	2768	3986	3522 (356)
F	2%	6%	10	1898	3797	3017 (504)
G	6%	6%	10	2003	3303	2772 (461)
H	20%	6%	10	184	342	247 (52)

TABLE IV

Mean degree of conversion and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	3	0.72	0.82	0.77 (0.03)
B	2%	2%	3	0.62	0.85	0.79 (0.05)
C	6%	2%	3	0.64	0.79	0.69 (0.02)
D	20%	2%	3	0.52	0.66	0.60 (0.03)
E	0%	6%	3	0.73	0.88	0.79 (0.05)
F	2%	6%	3	0.59	0.76	0.69 (0.04)
G	6%	6%	3	0.65	0.73	0.70 (0.03)
H	20%	6%	3	0.47	0.66	0.62 (0.04)
I	0%	20%	3	0.67	0.78	0.73 (0.04)
J	2%	20%	3	0.76	0.82	0.81 (0.01)
K	6%	20%	3	0.73	0.77	0.75 (0.01)
L	20%	20%	3	0.52	0.57	0.56 (0.02)
M	0%	60%	3	0.37	0.42	0.39 (0.02)
N	2%	60%	3	0.34	0.45	0.41 (0.02)
O	6%	60%	3	0.32	0.39	0.36 (0.02)
P	20%	60%	3	0.28	0.36	0.33 (0.01)

TABLE V

Mean depth of cure and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	3	2.45	2.74	2.60 (0.15)
B	2%	2%	3	1.85	2.01	1.93 (0.08)
C	6%	2%	3	1.20	1.32	1.26 (0.06)
D	20%	2%	3	0.95	1.00	0.98 (0.03)
E	0%	6%	3	1.01	1.41	1.27 (0.23)
F	2%	6%	3	1.10	1.14	1.11 (0.02)
G	6%	6%	3	0.94	1.01	0.97 (0.04)
H	20%	6%	3	0.44	0.52	0.47 (0.04)

TABLE VI

Mean contraction stress and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	4	3.17	4.27	3.56 (0.51)
B	2%	2%	5	3.05	3.75	3.43 (0.27)
C	6%	2%	6	0.76	2.19	1.53 (0.56)
E	20%	2%	3	2.50	3.31	3.00 (0.44)
F	0%	6%	4	1.18	3.03	2.10 (0.86)
G	2%	6%	3	0.90	1.44	1.20 (0.27)

TABLE VII

Mean stress rate and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	4	3.66	8.54	5.55 (2.19)
B	2%	2%	5	2.83	4.15	3.39 (0.60)
C	6%	2%	6	0.06	1.76	1.15 (0.68)
E	20%	2%	3	2.57	3.50	3.00 (0.47)
F	0%	6%	4	1.91	3.33	2.66 (0.59)
G	2%	6%	3	0.55	2.05	1.27 (0.75)

TABLE VIII

Mean gel time and standard deviation (SD)

Group	BHT	CQ	N	Min	Max	Mean (SD)
A	0%	2%	4	7.36	24.68	15.58 (7.18)
B	2%	2%	5	18.38	24.89	21.68 (2.71)
C	6%	2%	6	41.62	55.41	48.18 (4.84)
E	20%	2%	3	31.62	41.60	36.45 (5.00)
F	0%	6%	4	37.18	45.86	42.53 (3.84)
G	2%	6%	3	45.26	53.77	49.91 (4.31)

TABLE IX

Degree of conversion, depth of cure, flexural strength and flexural modulus for all groups

BHT

	2%	6%	20%	60%
20 %	**D** DC =60% DOC= 0.98 FS= 26.08 MPa FM = 0.671 GPa	**H** DC=62% DOC= 0.47 FS = 18.76 FM = 0.247 GPa	**L** DC= 55% Soft	**P** DC=33% Soft
6 %	**C** DC=69% DOC= 1.26 FS=69.91 MPa FM = 1.714 GPa	**G** DC=70% DOC = 0.97 FS= 89.91 MPa FM= 2.772 GPa	**K** DC=75% Soft	**O** DC=35% Soft
2 %	**B** DC=79% DOC= 1.26 FS = 77.42 MPa FM = 2.043 GPa	**F** DC=69% DOC= 1.11 FS= 112.04 MPa FM = 3.017 GPa	**J** DC=80% Thin	**N** DC=41% Soft
0 %	**A** DC=77% DOC = 2.60 FS= 76.97 MPa FM = 2.336GPa	**E** DC=79% DOC = 1.27 FS= 99.94 MPa FM = 3.522 GPa	**I** DC=62% Thin	**M** DC=39% Soft

CQ

DC: degree of conversion.
DOC: depth of cure (mm).
FS: flexural strength (Mpa).
FM: flexural modulus (GPa).

TABLE X

Contraction stress, stress rate, and gel point for all groups

BHT

	2%	6%	20%	60%
20%	**D** Not tested	**H** Not tested	**L** Not tested	**P** Not tested
6 %	**C** CS= 1.53 Mpa SR=1.15Mpa/ min GP=48.18 seconds	**G** CS=1.20 Mpa SR=1.27Mpa/ min GP=49.91 seconds	**K** Not tested	**O** Not tested
2 %	**B** CS= 3.34 Mpa SR=3.39Mpa/ min GP=21.68 seconds	**F** CS= 2.10 Mpa SR=2.66Mpa/ min GP=42.53 seconds	**J** Not tested	**N** Not tested
0 %	**A** CS=3.56 Mpa SR=5.55Mpa/ min GP=15.58 seconds	**E** CS=3.00 Mpa SR=3.00Mpa/ min GP=36.45 seconds	**I** Not tested	**M** Not tested

CQ

CS: contraction stress (Mpa).
SR: stress rate (Mpa/ min).
GP: gel point (seconds).

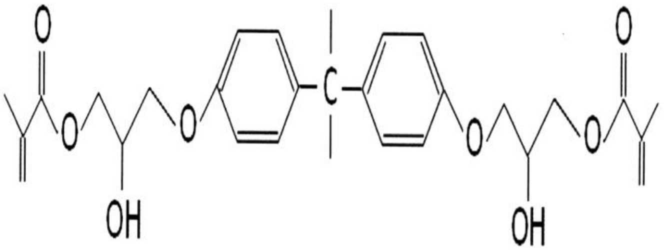

FIGURE 1. Bisphenol A glycidyl methacrylate (Bis-GMA).

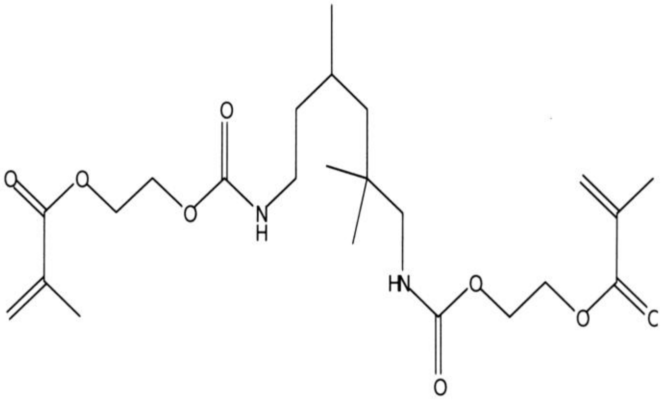

FIGURE 2. Urethane dimethacrylate (UDMA).

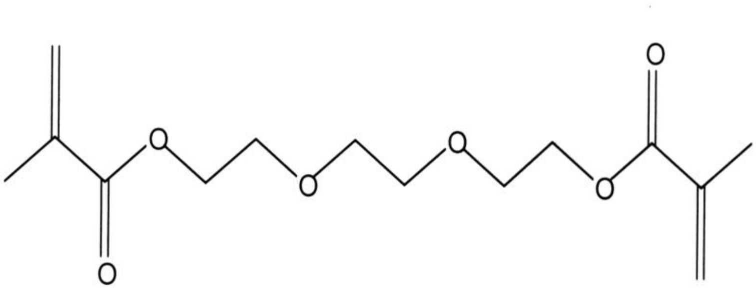

FIGURE 3. Triethylene glycol dimethacrylate.

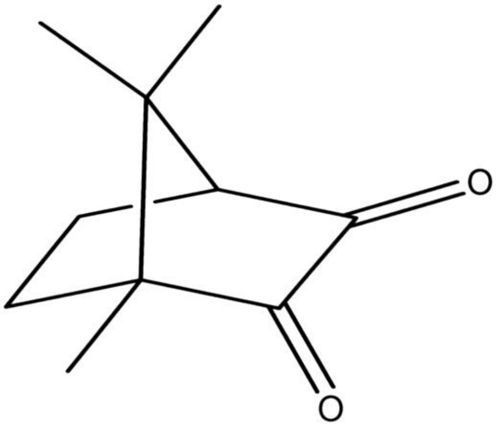

FIGURE 4. Camphorquinone (CQ).

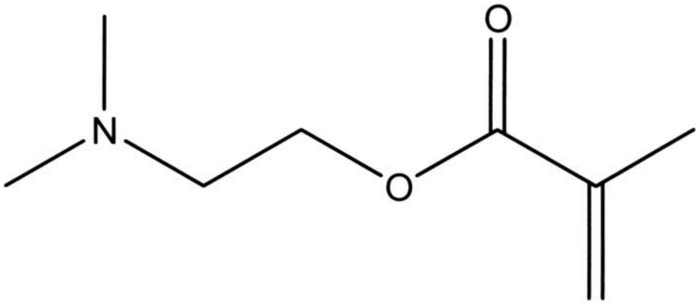

FIGURE 5. N,N-dimethylaminoethyl methacrylate (DMAEMA).

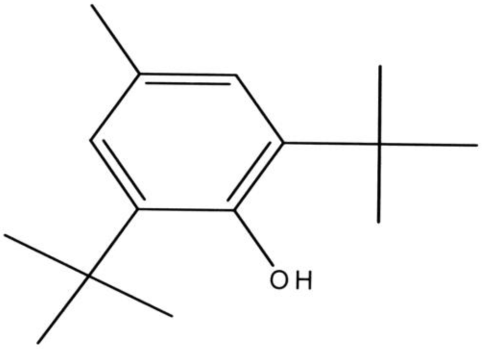

FIGURE 6. Butyl hydroxytoluene (BHT).

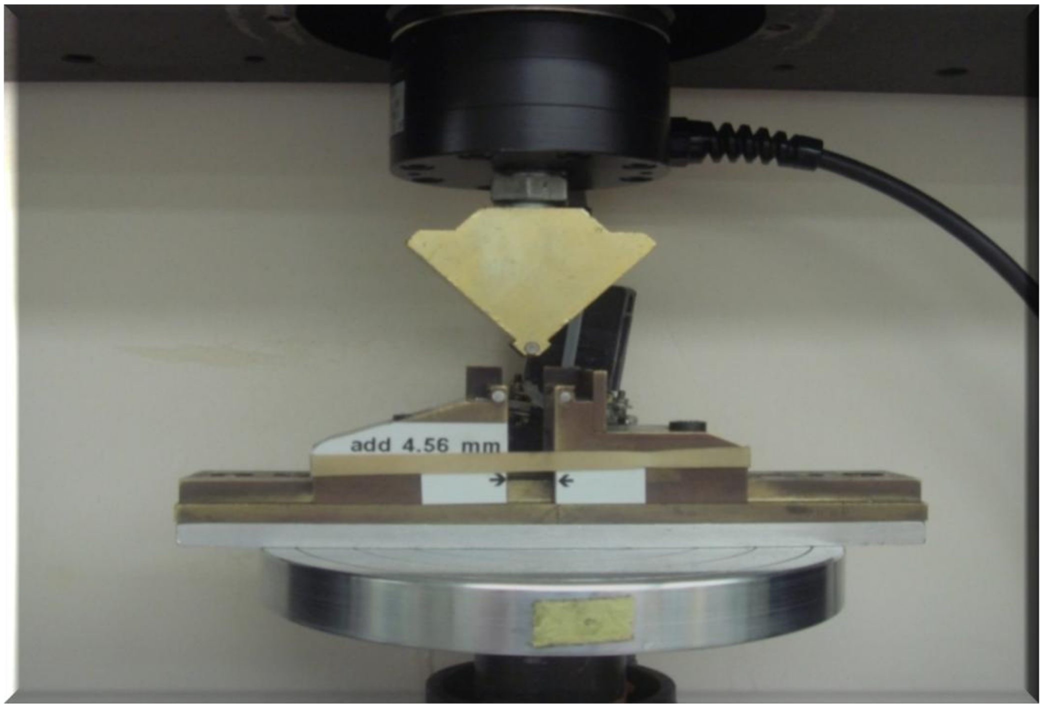

FIGURE 7. A three-point bending apparatus.

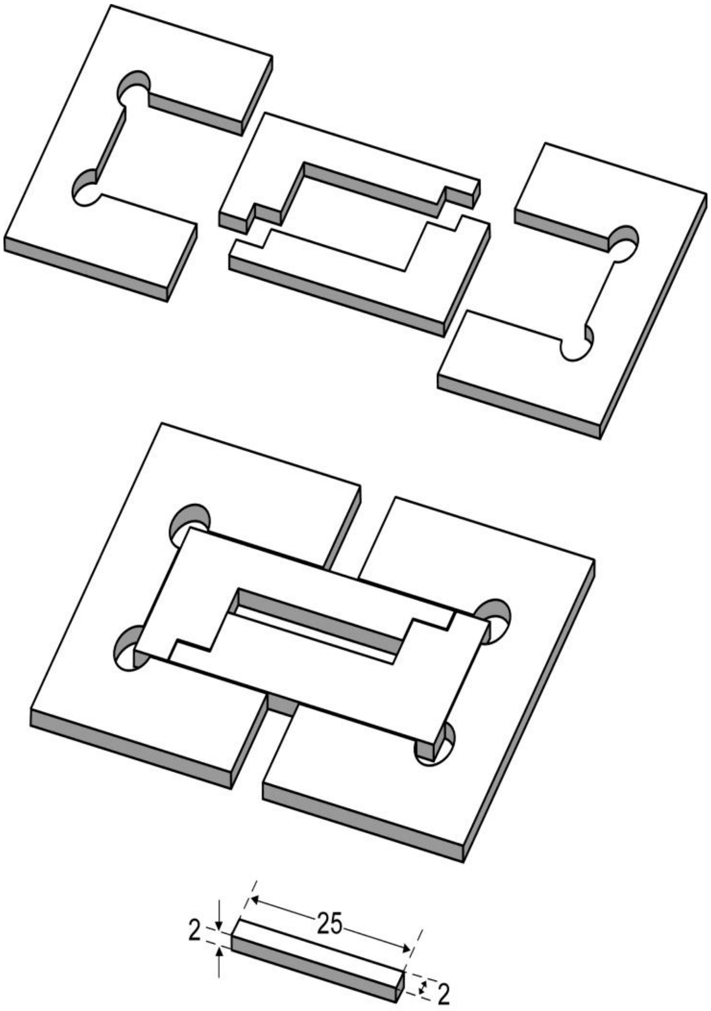

FIGURE 8. Stainless steel split mold for flexural strength specimen preparation.[20]

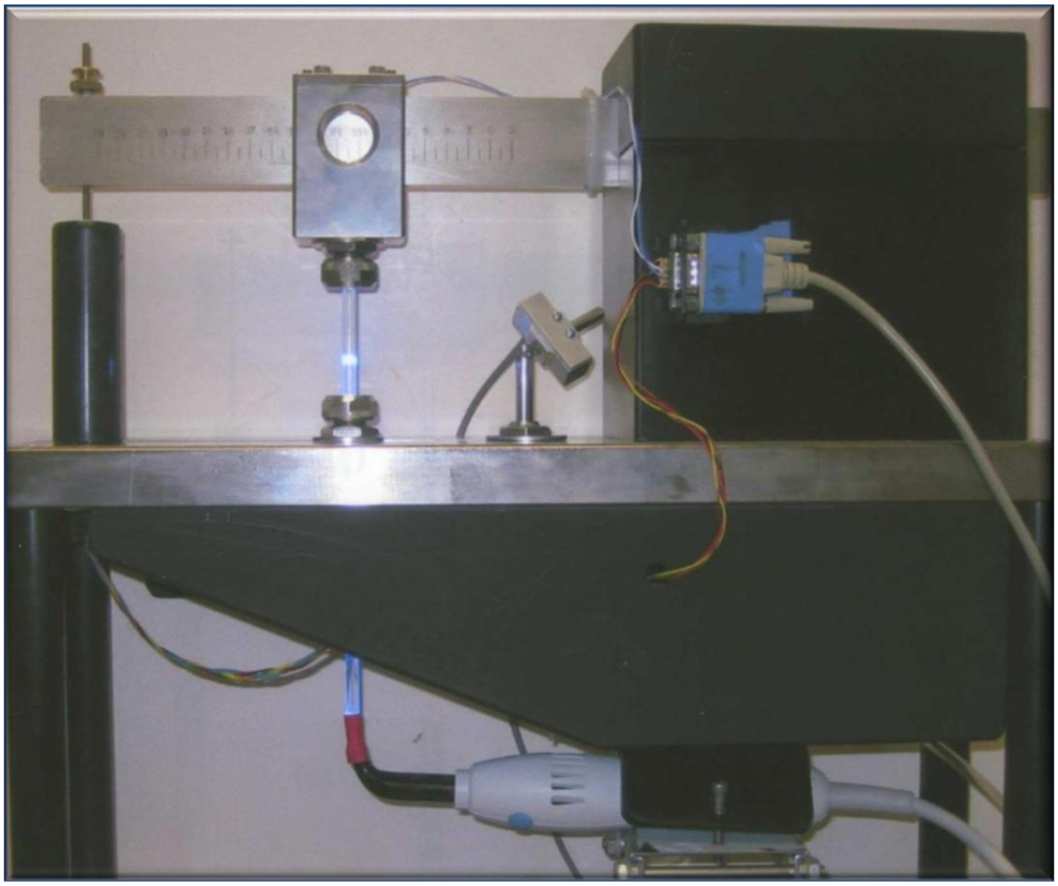

FIGURE 9. ADA tensometer.[20]

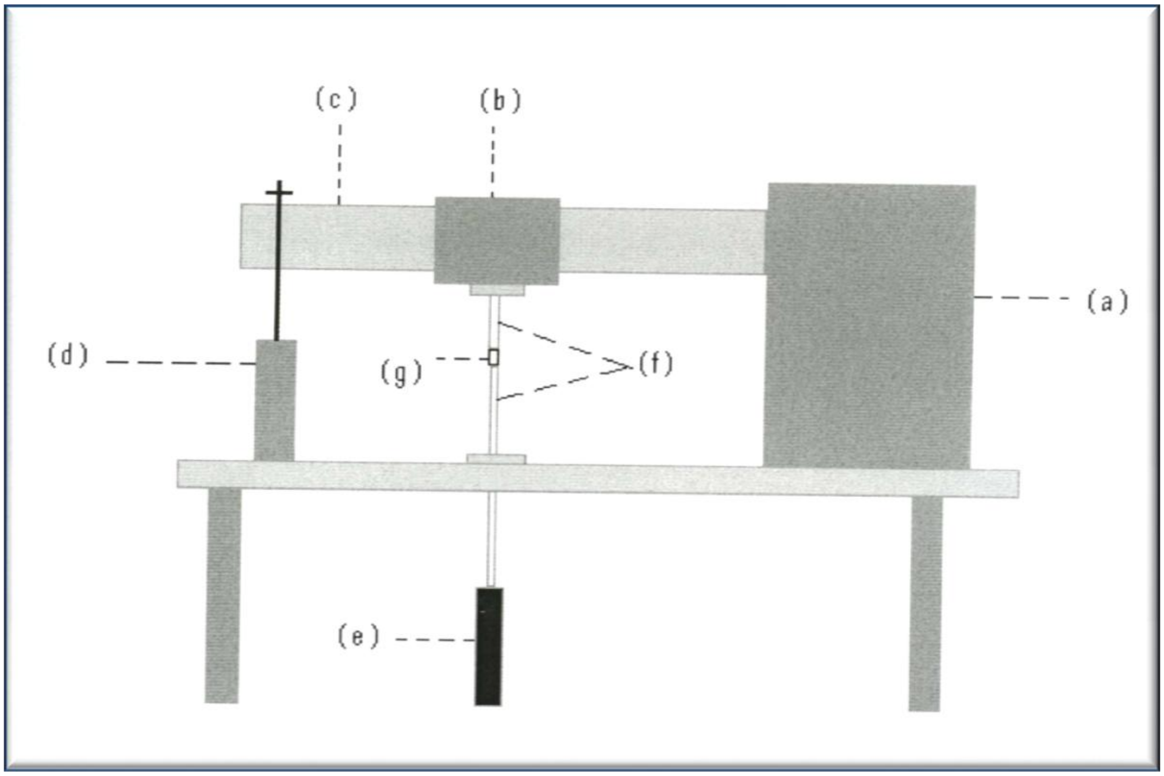

FIGURE 10. Diagram of the ADA tensometer: (a) cantilever beam holder; (b) upper collect holder; (c) cantilever beam; (d) LVDT; (e) curing light guide; (f) quartz rods; (g) resin sample.[20]

FIGURE 11. Fourier transform infrared spectroscopy (FTIR).

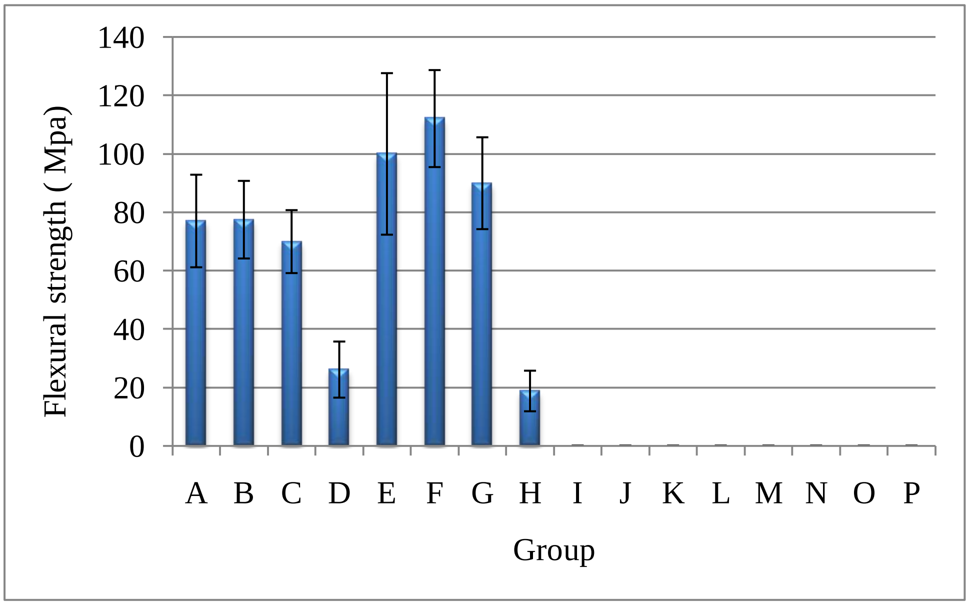

FIGURE 12. Mean and standard deviation of flexural strength.

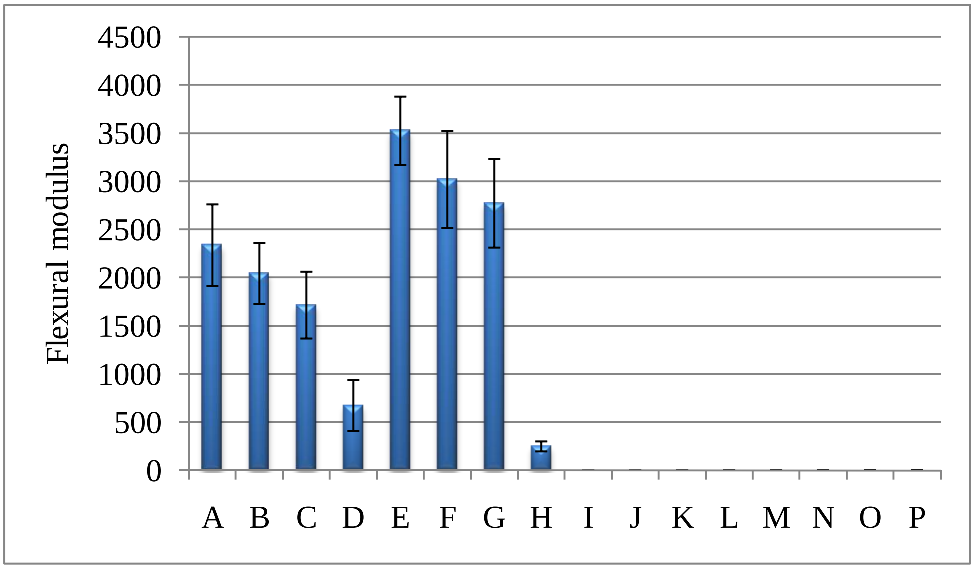

FIGURE 13. Mean and standard deviation of elastic modulus.

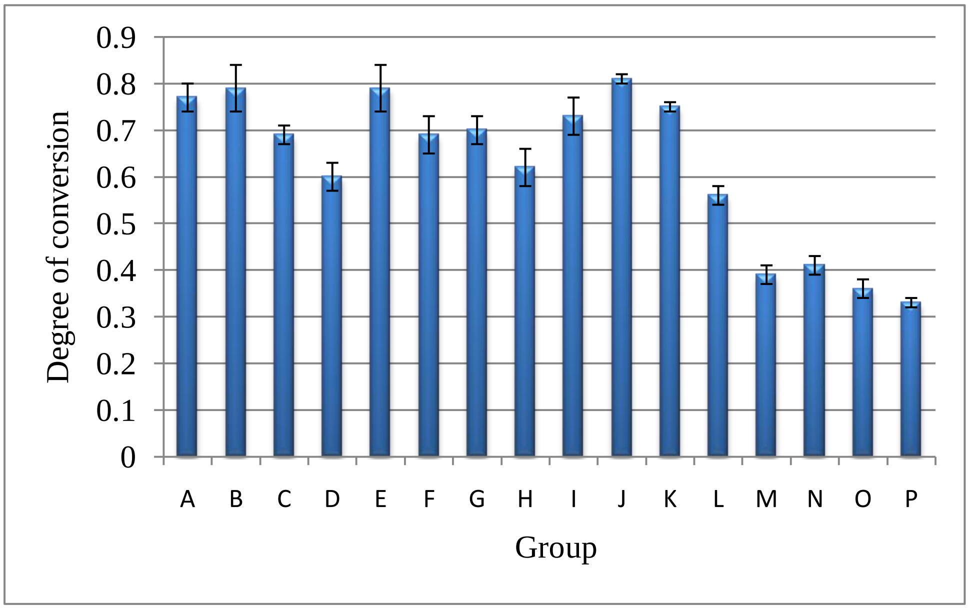

FIGURE 14. Mean and standard deviation of degree of conversion.

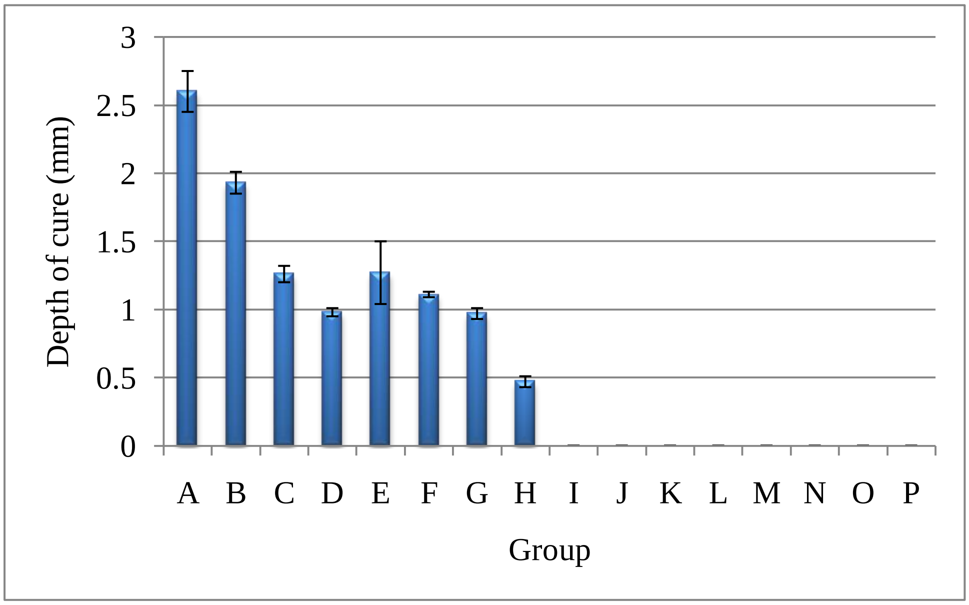

FIGURE 15. Mean and standard deviation depth of cure.

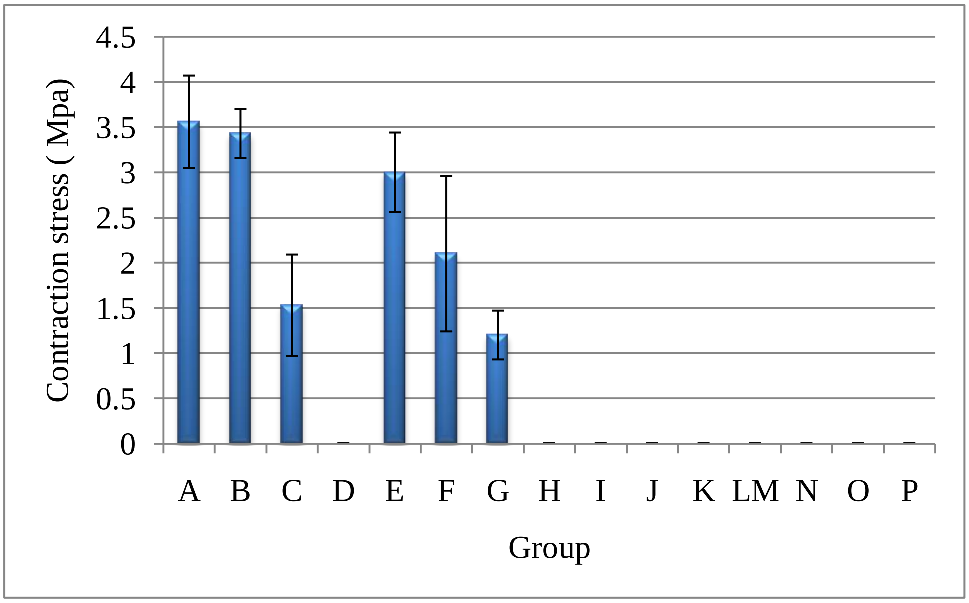

FIGURE 16. Mean and standard deviation of contraction stress.

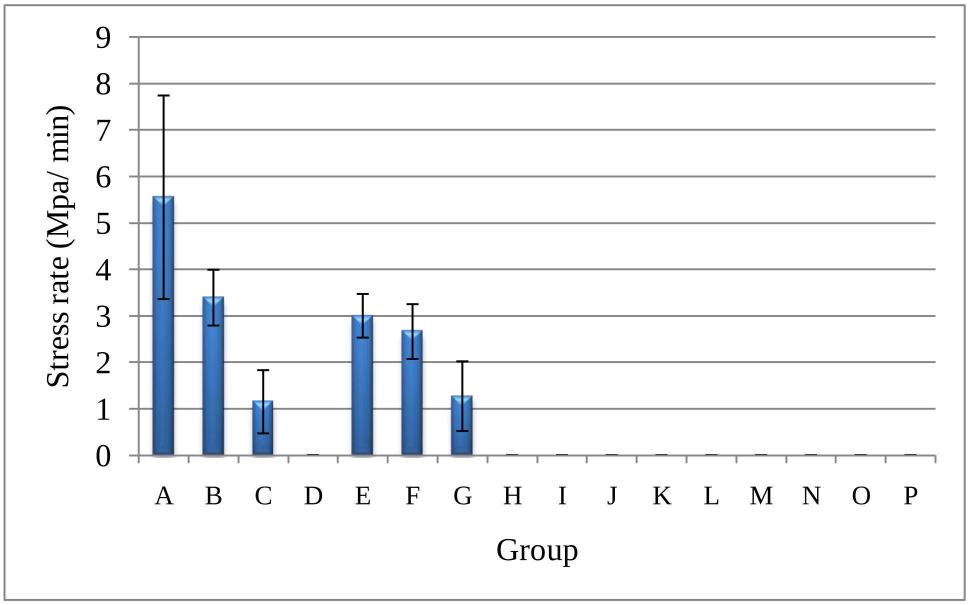

FIGURE 17. Mean and standard deviation of stress rate.

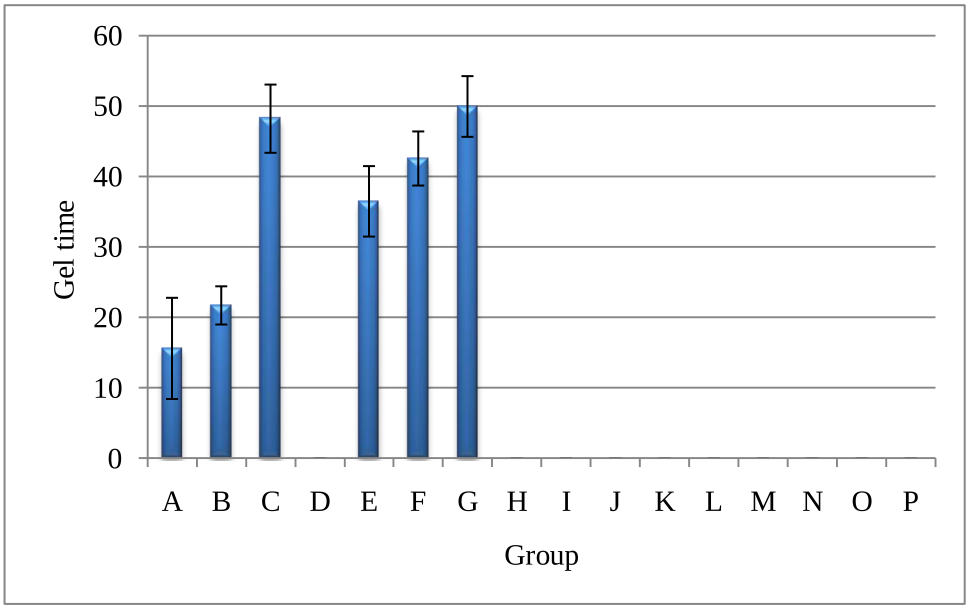

FIGURE 18. Mean and standard deviation gel time.

DISCUSSION

DEGREE OF CONVERSION AND DEPTH OF CURE

Degree of conversion (DC) is considered a very important aspect related to the durability of the restoration and to many physical and biological properties. Low DC can result in uncreated monomers that leach into the oral cavity, reducing the biocompatibility of the resin restoration. Another important reason for studying the DC is its effect on the shrinkage and contraction stresses as the polymerization contraction stress is directly related to the degree of conversion. Thus, we evaluate the DC when comparing the polymerization contraction stress.

At extremely high CQ concentration (60 percent), regardless of BHT level, the degree of conversions are all very low, indicating that the CQ concentration is the dominant factor in the low degree of conversion. From the preparation, we noticed that not all CQ are dissolving, indicating that the CQ concentration has exceeded the solubility limit of CQ in the monomer and that the system is saturated with CQ. The CQ free radicals generated after initiation possibly recombined under this saturated condition and did not allow time for the free radical to react with the vinyl bonds in the monomers. The results suggest that the reactivity between the free radicals is higher than the reactivity between free radicals and the vinyl bonds. By revisiting the degree of conversion values of these groups (M , N, O and P), it was determined that their degrees

Of conversion are less than 55 percent, and that cured samples for these groups are very soft and lack mechanical integrity.

At 20-percent CQ, a significant increase in the degree of conversion was found in all BHT levels suggesting that the free radicals' recombination is less favorable than reaction with the vinyl bonds. These groups with the 20-percent CQ (I, J, K and L) showed a high degree of conversion values (62%, 80%, 75%, 55% respectively) and very low depth of cure values, suggesting that the reaction may occur fast only in the superficial part of the sample close to the light, which leaves the inside of the sample not completely cured and soft. High levels of CQ react with vinyl bonds and produces many low molecular weight species, as seen from the very low depth of cure and very soft consistency of the cured samples. The groups at 20 percent and 60 percent CQ will not be discussed further. The following discussion is focused on the eight groups with combination of 2-percent CQ and 6-percent CQ and 0%, 2%, 6% and 20% BHT.

For the eight groups with a combination of 2-percent CQ and 6-percent CQ and 0% BHT, 2% BHT, 6% BHT, and 20% BHT, some general trends can be observed. The degree of conversion generally decreases as the concentration of CQ and BHT increases. The same holds for depth of cure. As the concentration of CQ and BHT increases, the depth of cure decreases. At low CQ and low BHT, for example, the group with 2-percent CQ and 0-percent BHT, the high depth of cure may be a combined result of a small amount of initiator to react with the incoming photons and no or low amount of BHT to quench the free radicals. The net results were that more photons traveled deeper and resulted in a greater depth of cure. As CQ level increases, more photons are absorbed, and a lower depth of cure results. As BHT level increases, the free radicals generated are being quenched, which also leads to a shallower depth of cure. The net result from the increase of CQ and BHT leads to a decrease of depth of cure from 2.6 mm to 0.46 mm from Group A to Group H.

The decrease in the DC as the BHT increases was expected and can be explained by the increase in the termination of the polymerization reaction leading to a decrease in the free-radical concentration. At the same time, monomers are able to move freely and meet with active free radicals, resulting in an increase in the propagation reaction and polymerization rate. This continues until the polymerization reaction reaches the maximum, and at a certain point, the viscosity increases. Vitrification of the system occurs, making the movement of the monomer inside the system very difficult, so that the propagation becomes diffusion-controlled, and the rate of polymerization falls to what is known as auto-deceleration. Eventually, the increase in the viscosity with the reaction and the cross-linking of the polymer limit the polymerization resulting in maximum conversion.[20]

The obvious trend is that as the concentration of CQ increases, there will be more light attenuation and an increase in the absorption of the light photon by the CQ, resulting in a decrease in the depth of cure. This condition is worsened by the quenching of the free radicals when we increase the concentration of the BHT.

POLYMERIZATION SHRINKAGE STRESS

Polymerization shrinkage plays a very important role in the failure in bonded resin restorations. As mentioned previously, the stress that is generated by the polymerization shrinkage results in adhesive failure, poor marginal adaptation, recurrent caries, and postoperative pain.[9]

Group C (6-percent BHT, 2-percent CQ) showed the lowest contraction stress and stress rate compared with group A and group B (0.0% BHT, 2% BHT respectively and 2% CQ). The same holds for the 6-percent CQ. Group G with the highest BHT (6%) has the lowest contraction stress and stress rate compared with group E and F. The reduction in the contraction stress rate can be explained by either a decrease in the conversion values or by an increase in the flow of the resin. In the results, group C showed a lower degree of conversion value than A and B, and this may explain the reduction in the contraction stress. The polymerization contraction stress is directly related to the monomer conversion in the resin system. Therefore, it is essential to evaluate the conversion values when comparing the contraction stress of different resin systems.

This also can be explained as the BHT concentration increases. The conversion proceeds at a reduced rate until all the inhibitors are consumed, extending the pre-gel phase. At this stage, the shrinkage force can be dissipated before the molecular displacement is impossible to achieve if the cross-linking reaches a certain point. After that, the shrinkage most likely will generate stresses.[13] The result of this study was in complete agreement with other published studies such as Baraga et al.[13] and Al-Shumari.[20]

In this study, 2-percent CQ, group C, which has the highest BHT concentration, showed a high gel point compared with group A and B, and the gel time became longer with increasing the BHT. The same trend was observed in the groups that have 6-percent CQ. Group G had highest BHT and a higher gel point compared with E with 0.0-percent BHT. This can be explained by the increase in the flow capacity of the resin, increased by extending the gel time, and by reducing the rate of the increase in the modulus of elasticity. Polymerization rate affects the contraction stresses where higher contraction stresses are observed with a higher polymerization rate. Therefore, a faster polymerization rate indicates that the resin-matrix composite reaches the gel point more quickly.

The general trend is that as the concentration of BHT and CQ increases, the contraction stress and stress rate decrease and the gel point increases. The net result from the increase of CQ and BHT leads to a decrease in the contraction stress and stress rate from 3.56 Mpa and 5.55 Mpa/ min respectively, to 1.20 Mpa and 1.27 Mpa/ min from the Group A to Group H, and an increase in the gel time from 15.58 seconds to 49.1 seconds from group A to H.

To recapitulate, we can say that the longer the gel time, the slower the stress rate that can be used as an indirect indicator for the slowing of the polymerization reaction with the increase in inhibitor concentration. Furthermore, we can say that the increase in the resin flow coupled with the decrease in the DC is the main reason for the reduction in the contraction stresses, which is in agreement with Al-Shummari's study.[20]

FLEXURAL STRENGTH AND FLEXURAL MODULUS

In this study, flexural strength testing was based on ISO 4049, which is widely used in dental research. The 2-mm specimen height that is required as the maximum permissible thickness for effective polymerization.[83]

Flexural strength is known to be directly proportional to the filler loading, resin formulation, and degree of conversion. In this study, all the groups had the same amount of filler loading but a different resin formulation. The concentrations of both initiators and inhibitors are different in different groups resulting in different conversion values, and this may have a fundamental effect on mechanical properties.[88]

In general, one would expect that a higher degree of conversion plus a higher depth of cure would mean a stronger mechanical property. However, the groups with similar degrees of conversion and depth of cure did not always have the same mechanical property. For example, group C and group F both have 69-percent degree of conversion and about 2.52 mm and 2.22 mm of depth of cure. But, their mechanical properties were significantly different at 69 MPa and 112 MPa. Groups with a higher degree of conversion and depth of cure did not have higher mechanical properties. For example, Group A and B both have a higher degree of conversion and a higher depth of cure compared with Group F. But, both groups showed a lower mechanical property at 76 Mpa and 77 MPa compared with 112 MPa in group F. The result clearly indicates that degree of conversion and depth of cure are not predictors of mechanical properties in these samples. The group with the highest mechanical property, Group F, actually has an intermediate level of degree of conversion and depth of cure compared with other groups.

Possible explanations to this maybe in the combined effect of CQ and BHT on the final cross-linked polymer network structure. The monomer system of the model composite is composed of three types of monomers, each with different reactivity and different mechanical property characteristics. The monomer mixture is composed of 1:1:1 weight ratio of TEGDMA:UDMA:Bis-GMA. The estimated molar ratio (TEGDMA: UDMA: BIS-GMA) is: 46%: 28 %: 26%. However, as in a multi-component system, not all monomers are incorporated into the final network structure at the equal rate. The reactivity of the monomer determines how much each monomer is incorporated. The degree of conversion only measures the percent of total vinyl bonds consumed in the process, but does not provide information on the final crosslinked structure. For example, that cyclic structure formation may contribute to high degree of conversion when not contributing to a high mechanical property. We suspect that this may be the case we observed in the present study.

Also, the reduction in strength can be explained by the early termination of the propagation reaction and propagating chain that is caused by an excessive amount of inhibitors resulting in a polymer with a short chain and hence a lower molecular weight. Furthermore, these inhibitors may act as external plasticizers as they are not part of the final polymer structure disrupting the intermolecular forces that normally exist in a polymer chain and compromising the strength.[20]

After reviewing the results, the null hypotheses, which proposed that varying initiator and inhibitor concentration will not have a significant effect on polymerization shrinkage stress, degree of conversion, and flexural strength, and modulus were rejected.

Overall, from the collected data, it can be concluded that group F (2-percent BHT and 6-percent CQ) and G (6-percent BHT and 6-percent CQ) provide the most desirable combination of strength (above 80 MPa) and stress (below 3 MPa) and are a potential dose combination range of CQ and BHT.

SUMMARY AND CONCLUSIONS

The objective of this study was to investigate the effect of varying the inhibitor and initiator concentration on degree of conversion, flexural strength, and flexural modulus, and polymerization contraction in light-cured resin-matrix composite. Sixteen groups of light-cured resin-matrix composite were made by varying the concentration of both inhibitors (0.0 wt %, 2 wt %, 6 wt %, 20 wt %), and initiators (2 wt %, 6 wt %, 20 wt %, 60 wt %).

Degree of conversion of the tensometer specimens were measured with near-infrared spectroscopy. Polymerization contraction stress, stress rate, and gel time were determined by using an ADA tensometer. Flexural strength and modulus were determined with three-point bending according to ISO 4049. Depth of cure was determined by a scraping technique according to the ISO standards for dental resin 4049.

From the data collected, the following can be summerized:

1. Resin-matrix composite with 0-percent BHT and 2-percent CQ showed the highest contraction stress and stress rate and the shortest gel time.

2. Resin-matrix composite with the 6-percent BHT and 6-percent CQ showed the lowest contraction stress and stress rate and the longest gel time.

3. At extremely high concentrations of CQ (20% and 60%) and high BHT concentrations (20%) low degree of conversion values were seen (less than 55%). These cured samples were all very soft and did not have any mechanical integrity, even though the groups with high percentages of CQ (20%) showed a high degree of conversion

value. The samples were cured only on the surface leaving a soft, uncured internal surface, suggesting that the high percentage of CQ causes some attenuation of the incoming photons resulting in rapid curing and conversion only on the outer surface, leaving soft samples with no mechanical integrity.

4. Groups with similar degree of conversion and depth of cure did not always have the same mechanical property. Thus, the degree of conversion and depth of cure cannot be used as the only indicator for the mechanical property.

Overall, from the collected data, it seems that group F (2-percent BHT and 6-percent CQ) and G (6-percent BHT and 6-percent CQ) provide the most desirable combination of strength (above 80 MPa) and stress (below 3 MPa) and a potential dose combination range of CQ and BHT.

The effect of inhibitors and initiators appears to change in different resin formulations. It is clearly seen that increasing the level of both the inhibitor and the initiator decreases the polymerization contraction stress and stress rate, but final effects on the conversion are unpredictable. In this study, we saw a decrease in both the conversion value and depth of cure.

Therefore, further studies are needed to investigate the effect of different resin formulations to gain better understanding of the effect of both the initiator and inhibitor on the polymerization kinetics. It is thus important to experimentally define the optimal combination of CQ and BHT to achieve the goal of reducing polymerization contraction stress without compromising the mechanical property.

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ABSTRACT

THE EFFECT OF INHIBITOR AND INITIATOR CONCENTRATION ON DEGREE OF CONVERSION, FLEXURAL STRENGTH AND POLYMERIZATION SHRINKAGE STRESS ON RESIN-MATRIX COMPOSITE

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Polymerization shrinkage is one of the most significant problems associated with resin-matrix composite. Shrinkage results in contraction stress in the resin, leading to possible debonding in certain areas of the adhesive joint and potentially adversely affecting the bond strength. The reduction in the stress may improve the adaptation of the resin restoration, and decrease the problems that are associated with contraction stress, such as postoperative pain and recurrent caries. Recently, it has been found that varying the inhibitor concentration would reduce the polymerization shrinkage without affecting

mechanical properties. In this study, we investigated the effects of varying the initiator and initiator levels on polymerization shrinkage stress, strength, and degree of conversion. An experimental composite was prepared by using a blend of BisGMA: UDMA: TEGMA (1:1:1 weight ratio) with 70 wt% silanated glass fillers. Four levels of inhibitors (BHT 0.0 %, 2%, 6%, 20%) and initiators (CQ 2%, 6%, 20%, 60%) were used (total of 16 combinations). A tensiometer was used to measure the polymerization contraction stress, contraction stress rate and gel time for each resin. FTIR was used to measure the degree of conversion. The flexural strength and flexural modulus were determined using the three-point bending test.

Resin-matrix composite with 0.0-percent BHT and 2.0-percent CQ showed the highest contraction stress and stress rate and the shortest gel time, while resin-matrix composite with the 6.0-percent BHT and 6-percent CQ showed the lowest contraction stress and stress rate and the longest gel time. At an extremely high concentrations of CQ (20 percent and 60 percent) and high BHT concentration (20 percent) low degree of conversion values were observed. Overall, from the collected data, group F (2-percent BHT and 6-percent CQ) and G (6-percent BHT and 6-percent CQ) provide the most desirable combination of strength (above 80 MPa) and stress (below 3 MPa) are present as a potential dose combination range of CQ and BHT.

In conclusion, the effect of inhibitors and initiators appears to change in different resin formulation. Increasing the levels of both the inhibitor and the initiator decrease the polymerization contraction stress and stress rate, and the impact on the conversion is unpredictable. In this study, we found a decrease in both the conversion value and depth of cure.