THE INFLUENCE OF DELAYED LIGHT CURING ON THE

POLYMERIZATION CONTRACTION STRESS AND

DEGREE OF CONVERSION IN DUAL-CURED

RESIN LUTING AGENTS

by

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DEDICATION

To my wife, Maha,

whose love and support make all things possible.

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INTRODUCTION

Recently, resin luting agents have become the preferred choice for many clinical applications because of their superior properties in comparison with other types of luting agents.[1] They are characterized by their wide range of use because of their excellent esthetic shade-matching potential and better physical and mechanical properties compared with many other types of dental cements.[2] Furthermore; the adhesive nature of the resin cements results in superior retention and fracture resistance in ceramic restorarions.[3, 4] Composite luting agents can be classified according to their initiation mode as chemically activated, photo-activated, or dual-activated materials.[5] Chemically-cured resin luting agents are mostly used for metallic restorations. They require a long setting time and have an uncontrollable working time. In contrast, light-cured resin luting agents allow better control and manipulation. Nevertheless, incomplete polymerization could be a possible outcome due to several factors such as type, thickness and shade of the restoration, exposure time, light intensity and photo-activation method. Therefore, dual-cured resin luting agents afford better control during the cementation procedure and can be hardened in deep areas where it is difficult for the curing light to penetrate.[1, 6]

Polymerization shrinkage is one of the main concerns related to composite resin luting agents when monomers start to form long and entangled polymer chains accompanied by a closer packing of molecules that, in turn, leads to a reduction in the bulk volume.[7-9] This reduction in volume has been termed polymerization shrinkage or curing contraction. Upon bonding of the resin to the more rigid tooth structure, stresses will develop within the material as a result of shrinkage under constraints, and these

stresses render the polymerization shrinkage to be clinically significant.[10-13] Adhesive failure and consequently microleakage are possible outcomes if the developed stresses exceed the adhesive bond strength.[14-16] It has been reported that light-cured resin luting agents generate higher polymerization contraction stress than chemically cured resins.[17, 18] It is also reported that chemically cured resins have an extended setting time with a longer pre-gel phase that enables the flow to reduce polymerization contraction stress, while the stress reduction is limited in light-cured resins due to a rapid polymerization process and shorter pre-gel phase. Based on these findings in dental resin materials, soft-start polymerization has been suggested as a clinical technique to reduce contraction stress.[17, 19, 20] Soft-start polymerization is a technique in which the polymerization process starts with a light curing of low intensity and then finishes with a high intensity light curing. Ramp and pulse-delay are variations of this technique that have been shown, in many studies, to have significantly less contraction stress compared with continuous exposure.[21-25] Marginal adaptation has been reported to be significantly improved by Uno and Asmussen[19] with this curing technique. Feilzer et al.[17] hypothesized that lowering the contraction stress can be achieved by using low light intensity that extends the visco-elastic stage of the setting resin. Many major concerns have been reported with the soft start technique despite the promising results.[26] Degree of conversion (DC) is the percentage of double bonds that have been converted to single bonds to form the cross-linked polymeric resin. Rasmussen and Peutzfeldt[27] reported that this technique generates a linear polymer structure with fewer cross-links that is significantly more susceptible to softening in ethanol compared with resin cured with standard curing. Yap et al.[28] reported that resin samples of 2 -mm thickness have

significantly lower hardness and degree of conversion at the bottom of the samples when cured with the soft start and the pulse delayed technique compared with full intensity curing. In another study, Lu et al.[29] reported that soft-start curing results in significantly less contraction stress and degree of conversion (DC). In their study they measured contraction stress and DC simultaneously in the same specimens. Contraction stress was measured with a tens meter developed by the American Dental Association Health Foundation for the sole purpose of measuring contraction stress in dental composites.[30, 31] DC was determined with near infrared (NIR) spectroscopy. It was concluded that the lower conversion values were the main reason for the reduction in stress. It has been speculated in a different study that a delay in the photo-activation of dual-cured materials would be beneficial in enhancing their DC.[32] The rationale behind this idea was that the immediate exposure to light and formation of cross-linked polymer chains could interfere with the chemical curing by entrapping polymerization promoters and unreached monomers in the network, therefore interfering with the self-cure mechanism. However, this effect is not yet recognized and warrants investigation since in the majority of studies, thick specimens were used to evaluate the polymerization of looting agents, and different results might be found if a clinically relevant thin film was tested.[32] Braga and Ferracane[33] studied the effect of increasing the concentration of inhibitor in the resin system as an alternative method to slow the rate of polymerization. They reported that increasing inhibitor concentration lowers the curing rate that in turn leads to significantly less contraction stress without any compromise in conversion. However, it was stated that there is a tendency to decrease DC with increasing the concentration of inhibitor. The degree of monomer conversion is considered a critical factor in performance of

resins. Incomplete polymerization may increase residual monomer that could compromise biocompatibility and result in a resin with inferior mechanical and physical properties.[34-38]

The objective of this study was to investigate:

1. The influence of delayed light curing on the polymerization contraction stress and degree of conversion (DC) of dual-cured resin cements.

2. The influence of eliminating the photo-activation in dual-cured resin cements on the polymerization contraction stresses and the degree of conversion.

3. The amount of delay in photo-initiation of the dual-cured resin cements that can achieve a reduced contraction stress value with the highest possible degree of conversion.

CLINICAL SIGNIFICANCE

The shrinkage associated with resin composite polymerization has significant clinical concerns and is believed to be the cause of many undesired effects such as cohesive failures within material or dental structure, marginal failures, micro leakage and recurrent decay.[14, 39 40-42] On the other hand mechanical properties and biocompatibility are highly affected by the percentage of unreached monomers, which explains the importance of increasing the double bond conversion in the resin. Decreasing the extent of unreached monomers in the system reduces the plasticizing effect of these monomers and increases the cross-linking that increases the strength of the polymer.[26]

Currently, development of new dental composite materials is substantially influenced by the belief that contraction stresses and the degree of conversion of resins are related to their clinical performance. Many modifications of resin composition and

clinical manipulation have been proposed for the reduction of contraction stress and achieving maximum degree of conversion.[26]

This project should help in filling a gap in knowledge and should provide new information that would hopefully lead to the development of a new clinical strategy in the dual-cured resin cement application that can achieve reduced polymerization contraction stresses along with the highest possible degree of conversion.

HYPOTHESES

1. There will be a significant decrease in the amount of polymerization contraction stress associated with delayed photo-activation of a dual-cured resin looting agent compared with immediate photo-activation of a dual-cured resin looting agent.

2. There will be a significant increase in DC associated with delayed photo-activation of a dual-cured resin looting agent compared with immediate photo-activation.

NULL HYPOTHESES

1. No difference in the amount of polymerization contraction stresses will be seen between the delayed photo-activation of a dual-cured resin looting agent and immediate photo-activation of a dual-cured resin looting agent.

2. No difference in the amount of DC will be seen between the delayed photo-activation of a dual-cured resin looting agent and immediate photo-activation.

REVIEW OF LITERATURE

LUTING AGENTS

Unfilled resins were first introduced in 1937. They were polymers based on

methyl methacrylate and broadly called acrylic resins. They are prepared by a process in

which covalent bonds are formed between molecules to form larger molecules, this

process of preparation is called polymerization. Poly(methyl methacrylate) (PMMA) still

has the form of two basic components that are powder and liquid. The powder is

composed of small particles of PMMA with benzoyl peroxide as an initiator. The liquid

is methyl methacrylate with an amine as an activator. When these two components mix

together the polymerization process starts and longer molecule chains are formed to

provide the acrylic resin its final shape.[26] Methyl methacrylate polymerization is

accompanied by a 21 percent reduction in volume. However, continued development in

the dental industry has been able to drastically reduce this reduction in volume.

Nevertheless, even with this reduction in volume, it is still considered a disadvantage

associated with many clinical problems seen with composite restorative materials and

resin luting agents that may eventually lead to failure.[26] Filler content and resin matrix

composition dictate the amount of volumetric shrinkage and elastic modulus values of the

material.[43] In 1962, a major advancement in esthetic dentistry was made by Bowen[44] as

he developed a new type of composite with a resin based on bisphenol A glycidyl

methacrylate (Bis-GMA) and inorganic filler particles that were chemically bonded to

resin matrix through an organic silane coupling agent. Bis-GMA has a high molecular

weight and it is extremely viscous, which makes it difficult to mix with large filler

loadings. Triethylene glycol dimethacrylate (TEGDMA) having a lower molecular

weight, is therefore used to dilute the highly viscous Bis-GMA and enhances its flowability.

The resin-based luting agents are commonly preferred in the application of various types of indirect restorations because of their superior properties in comparison with other types of luting agents.[1, 45] They are characterized by a wide range of clinical use including cementation of ceramic veneers, posts, nonmetallic inlays, onlays, crowns, and fixed partial prostheses.[46-48] Resin luting agents have excellent esthetic shade-matching potential and better physical and mechanical properties compared with many other dental cements.[2] In terms of shear and tensile bond strength, resin luting agents are stronger than other types of cement such as glass ionomer cement and zinc phosphate cement, and were preferred in various clinical situations.[49, 50] Furthermore, the adhesive nature of the resin cements results in superior retention and fracture resistance in ceramic restorations.[3, 4] Resin luting agents can be classified according to their initiation mode as chemically activated, photo-activated, or dual-activated materials.[5] They differ chemically in terms of initiators and activators. Chemically-cured resin luting agents, which are mostly used for metallic restorations, require a long setting time and have uncontrollable working times. In contrast, light-cured resin luting agents allow better control and manipulation, but the thickness of the ceramics and the tooth structure can lead to incomplete polymerization. It is necessary for adequate light energy to reach the luting material in order to obtain high bond strengths after the luting procedure.[51] Clinically, depending on the type, location, color and thickness of the restoration, light will be partially attenuated by scattering and or absorbing while crossing the material and the luting agent layers. Thus, polymerization decreases, which results in a lower level of

conversion under these restorations. Dual-cure luting resins were developed in an attempt to combine the desirable properties of chemical and light polymerizing materials, providing an adequate degree of conversion beneath various restorations where it is difficult for the curing light to penetrate.[45]

Previous studies have assessed the hardness of light-activated luting materials, and have usually observed that luting materials with a low degree of conversion record lower hardness values when compared with luting materials with higher conversions.[52-55]

POLYMERIZATION
CONTRACTION STRESS

The measurement and characterization of polymerization contraction stresses has been the center of attention since the 1950s because of their significant impact on the performance and longevity of dental restorations.[56] The conversion of monomers into long and entangled polymer chains is accompanied by a closer packing of molecules, which leads to bulk contraction, this reduction in volume has been termed polymerization shrinkage or curing contraction. This volumetric shrinkage ranges between 1.5 percent and 5 percent.[18, 57-59] The contraction values reported should be considered approximate because they are completely dependent upon the extent of the polymerization reaction. This makes comparison of contraction data from different studies a tenuous proposition, as it is not typical for authors to measure degree of conversion along with contraction, except in rare cases.[33, 43] Development of stresses in the contracted resin composites is a result of several factors. During the polymerization process, as the polymer chains lengthen, entangle, and cross-link, the volumetric contraction will start to occur simultaneously with the material developing rigidity. A resin material will pass through

several changes during the polymerization process; from a viscous paste into a visco-elastic solid, and finally will become an almost fully elastic solid. During polymerization, there is a stage called the gel point, which is defined as the point at which the system loses fluidity,[60] when the composite elastic limit reaches a point that does not allow further plastic deformation or flow to compensate for the volumetric reduction. At this point shrinkage forces will start to build-up, resulting in stresses on the bond between the composite and the tooth structure. Prior to this point, the polymer chains slip and reorient into new positions, which enables viscous flow of the resin without jeopardizing the internal structure of the material or the adhesive bond. Beyond the gelation point, shrinkage of resins starts to result in stress development. The higher the rate of monomer conversion, the faster the gel point is reached, and the lower is the flow capacity of the material. The higher the rate of conversion, the higher is the final shrinkage of the composite and its elastic modulus, both of which contribute to producing higher stresses.[33, 61-63]

Polymerization shrinkage is clinically significant when resin is being bonded to the more rigid tooth structure. In these situations, stresses will develop within the material as a result of shrinkage under constraints. These internal stresses are transferred to the tooth/resin interface as tensile and shear forces.[10-13] Plastic flow from free surfaces and localized interfacial debonding will provide an amount of stress relief in the contracting composite.[64-67] Adhesive failure and subsequent microleakage are possible consequences if the contraction stress exceeds the adhesive bond strength.[14-16, 68] This phenomenon was first described by Bowen[69] when he discussed the influence of the confinement of setting materials as the main factor associated with contraction stresses.

Davidsonet al.[64] and Feilzer et al.[70] studied this phenomenon in depth and mentioned that the amount of contraction stress developed depends on the outline form of cavity preparation or the test specimens as well as composition and curing modalities of the composite where the tensometer is the most frequent method of measuring it. Recently, one study verified that the volume of the shrinking composite also influences the stress values.[71] Two chemically-cured composites were investigated by Davidson and de Gee.[64] Contraction stresses and stress relaxation by flow were calculated theoretically and experimentally. It was reported that the experimental contraction stress values were lower than the theoretical values and the investigators related this difference in stresses to the ability of resins to flow before gelation. It was concluded that pre-gelation polymerization contraction of resins was not clinically relevant because it was compensated by flow. On the other hand, it was emphasized that post gel contraction may result in debonding of the resin/tooth interface.

Light-cured composites have been reported to generate higher polymerization contraction stresses than chemically cured composites.[18, 61] The contraction stress of resin cements has been measured by Bragaet al.[72] where the contraction stress in dual-cure mode was 4.5 MPa to 6.4 MPa, which was higher than that in self-cure mode (3.4 MPa to 4.0 MPa).

Over the years, different approaches have been proposed to reduce the magnitude and the effects of the contraction stresses in dental composites. The soft-start polymerization technique and the incremental placement technique are the most common techniques that have been introduced.[19, 23, 25, 73-75]

Soft-start polymerization is based on the belief that extending the flow time of resins before reaching the gel point will extend the time of stress relief, and that can be achieved by slowing the rate of polymerization. In this technique, the polymerization process starts with a low intensity light curing and then finishes with a high intensity light curing.[19, 23, 24] Ramp and delayed cure are different techniques that have also been introduced as variants to the soft-start polymerization technique. The ramp technique starts with light of low intensity that increases gradually in a stepwise mode. In the delayed curing technique, the curing process of the resin restoration starts with light of low intensity for a few seconds followed by a relaxation period of two to three min before completion of the resin curing at high intensity.[21, 22, 28] The relationship between curing light energy, degree of conversion, and post-gel polymerization contraction have been evaluated in a study by Sakaguchi and Berge.[23] It was reported that by using the soft start curing technique, a significant reduction of contraction stresses was recorded compared with the full intensity cure. In addition, there was no significant difference in degree of conversion recorded between the two groups. They suggested that soft start curing decreased the contraction strain rate that allowed further relaxation of stresses to occur, which resulted in reduction of polymerization stress values.

Watts and Al Hindi[25] investigated the contraction strain of four commercial resin composites when using the soft start curing technique. The results showed that using full intensity curing resulted in an immediate increase in contraction strain. On the other hand, lower strain values were shown for a short period of about 0.2 minute during polymerization when soft start curing was used. Nevertheless, no significant difference in final strain values was recorded for any of the resins. The authors suggested that the

low strain values during the critical early moments of the polymerization process might be beneficial for the adhesive bond to tooth structure. Many major concerns have been reported with the soft start curing technique despite the promising results reported.

Asmussen and Peutzfeldt[27] reported that resins cured with this technique have higher susceptibility to softening in ethanol and that could decrease the polymer resistance to softening substances in the oral environment such as food or enzymes. Yap et al.[28] reported that lower values of hardness and degree of conversion were recorded at the bottom of 2 -mm thickness resin samples cured with soft start and pulse delayed techniques compared with full intensity curing. Sahafi et al.[76] reported that there is no improvement in marginal adaptation with the soft start curing compared with the conventional full intensity polymerization.

The ratio of bonded surfaces to unbonded free surfaces is called configuration factor (C-factor). Increasing the C-factor for a restoration would significantly increase shrinkage stress due to a decrease in flow capacity.

In a study by Lutz et al.[74] it was concluded that the C-factor is key in reducing residual stresses and consequently obtaining better marginal adaptation. Feilzer et al.[77] investigated wall-to-wall contraction of thin layers of a chemically activated and a light activated resin composite. They found that decreased wall-to-wall distance resulted in increased contraction stresses and a value of three times the linear contraction was reached. Also lower stresses were recorded for the chemically-cured composite in comparison with the light-cured resin. In another study by the same group in 1993[39] it was concluded that light-cure composites generate higher polymerization stresses than chemical-cure resins due to limited flow with the rapid setting materials. In a study by

Kinomoto et al.[18] it was concluded that the higher velocity of polymerization in the light

cure composite compared with the chemical cure composite; resulted in larger stress

values in the light-cured material.

DEGREE OF CONVERSION

Degree of conversion (DC) is the percentage of double bonds that have been

converted to single bonds to form the cross-linked polymeric resin. Degree of conversion

is believed to have a high impact on the performance of resins. Mechanical properties

and biocompatibility are highly affected by the percentage of unreacted monomers, which

explains the importance of increasing the double bond conversion in the resin.

Decreasing the extent of unreacted monomers in the system reduces the plasticizing

effect of these monomers and increases the cross-linking, which increases the strength of

the polymer.[26]

Dimethacrylate monomer has two vinyl groups. The degree of conversion for

dimethacrylate has been shown to be in the range of 55 percent to 75 percent, which

implies that 55 percent to 75 percent of vinyl groups have reacted and been converted

from double bonds to single bonds.[78-80] Activation mode, type, and concentration of

initiators regulate reaction kinetics and degree of conversion.[43]

There is a sharp increase in rate of polymerization of dimethacrylate as the

conversion of monomer increases. This phenomenon is known as auto-acceleration or

the Trommsdorff-Norish effect. This phenomenon leads to the formation of long and

entangled polymer chains, which results in increased viscosity of the material.[81] Auto-

acceleration is a direct result of an increase in viscosity of the reaction medium. This

increase in viscosity significantly hinders the active chains to meet and terminate. This

limited mobility results in low final conversions despite the presence of initiators and unreacted double bonds.[82, 83] Consequently, the increased viscosity of the high molecular weight base monomers will result in a high concentration of unreacted double bonds after polymerization.[35, 78, 80]

Degradation and erosion of dental composites are believed to be an outcome of incomplete polymerization. The degree of degradation in resins is influenced by many factors, such as the chemical composition of the resin, the degree of cross-linking the degree of conversion and, in addition, the oral environment.[84-87]

In a study byTarumi,[88] he concluded that high degree of conversion is desired to minimize the amount of eluted monomers to the oral environment. This study was in agreement with Ferracane[37] when he investigated the effect of degree of conversion on elution of components in dental composites. The results showed a significant increase in the degree of conversion when the curing time was doubled. Also, a significant reduction in elution was shown for a 60 second light-curing time compared with 30 seconds. Ferracane concluded that percentage of elution and degree of conversion are inversely related. Light initiation of composite resins carries the risk of a lower degree of conversion due to the influence of many variables including light intensity, spectral distribution, curing time, and increment thickness.[89-92]

It has been speculated that a delay in the photo-activation of dual-cured materials would be beneficial in enhancing their DC.[32] The rationale behind this idea is that the immediate exposure to light and formation of cross-linked polymer chains could interfere with the reaction by entrapping polymerization promoters and unreacted monomers in the network, therefore interfering with the self-cure mechanism. However, this effect is not

yet recognized and warrants investigation since, in the majority of studies, thick specimens have been used to evaluate the polymerization of luting agents, and different results might be found if a clinically-relevant thin film were tested.[32, 93]

Many methods have been used to assess degree of conversion in dental composites. Physical determination of surface hardness is one of the widely used methods. In this method, degree of conversion is evaluated indirectly by measuring the amount of cure at a certain depth and comparing hardness of the bottom to the top surface.[34, 36] Higher hardness values indicate more resin polymerization.[94] Results of at least 80 percent are generally accepted since it indicates a uniform and adequate polymerization through a given sample.[94]

FTIR (Fourier Transform Infrared) spectroscopy is another widely-used method to determine degree of conversion by direct measurement. It detects the C=C stretching vibrations directly before and after curing of materials.[91, 95, 96] FTIR spectroscopy has also been used to monitor the progress of polymerization by measuring real-time conversion.

In the Mid-IR technique, the intensities of the aliphatic C=C absorbance peak at 1638.6 cm^{-1} and the aromatic C$^{..}$C reference peak at 1609.4 cm^{-1} are measured. The ratio of the absorbance intensities of C=C to C$^{..}$C is compared before and after polymerization to determine the percentage of unreacted carbon double bonds. The degree of conversion is obtained by subtracting this percentage from 100.[91, 95]

One of the strengths of IR spectroscopy is its ability as an analytical technique to obtain spectra from a wide range of solids, liquids and gases. However, in many cases some form of sample preparation is required in order to obtain a good quality spectrum. The technique of Attenuated Total Reflectance (ATR) has in recent years revolutionized

solid and liquid sample analyses because it combats the most challenging aspects of infrared analyses, namely sample preparation and spectral reproducibility. ATR is used for analysis of the surface of materials and operates by measuring the changes that occur in a totally internally reflected infrared beam when the beam comes into contact with a sample (Figure 1). An infrared beam is directed onto an optically dense crystal with a high refractive index at a certain angle. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample held in contact with the crystal. The attenuated energy from each evanescent wave is passed back to the IR beam, which then exits the opposite end of the crystal and is passed to the detector in the IR spectrometer. The system then generates an infrared spectrum.

MATERIALS AND METHODS

The resin luting agent used in this study was Illusion Dual-cured (BISCO, Inc., Schaumburg, IL). This dual-cured system consisted of a clear base paste and a clear catalyst paste that are mixed together in equal proportions.

POLYMERIZATION CONTRACTION
STRESS MEASUREMENT

A tensometer (ADA Health Foundation NIST, Gaithersburg, MD) (Figure 1) was used to measure polymerization contraction stress for each resin cement sample. This device was based on basic cantilever beam theory.[30, 31] The tensile force generated by the bonded shrinking composite sample deflected a cantilever beam. The deflection of the beam was measured with a linear variable differential transformer (LVDT) (Model: 050-HR-000, Component Distributors Inc., Ft. Lauderdale, FL). The contraction stress was obtained by dividing the measured tensile force by the cross-sectional area of the sample. The tensometer consists 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. Each composite sample was placed between two quartz rods positioned vertically in the tensometer. The top rod was connected to the cantilever beam at a distance of 12.50 cm from the beam holder. The bottom quartz rod was used to complete the sample assembly to the tensometer and to guide irradiation from the curing unit to the sample. The LVDT (Component Distributors Inc.) was positioned 23 cm from the sample assembly at the free end of the cantilever beam.

Before each stress measurement, two pieces of quartz rod (6mm in diameter) were flattened and polished with 600 grit wet silicon carbide paper. Two layers of silane agent were applied to one end of each rod. The upper rod was mounted first with the silanized end pointing down. The bottom quartz rod was then aligned vertically with the upper rod and mounted with the silanized end pointing up. The distance between the two silanized ends was fixed at 1 mm for all samples. Thus, each composite sample was a disk of 6mm in diameter and 1 mm in height corresponding to a C-factor of 3 (diameter/2height).

A polytetrafluorethylene (PTFE) sleeve was placed around the gap between the two rods to keep the composite sample in place. Two holes were drilled on opposite sides of the sleeve. The first hole (1.5 mm diameter) was utilized for the injection of the composite. The second one (0.5 mm diameter) was used for air escape during sample injection.

Equal volumes of base and catalyst of the dual-cured cement samples were mixed for 15 seconds and injected into the sample holder to fill the space between the silanized ends. Then glycerin gel was applied on the sleeve holes to avoid oxygen inhibition during the curing process. After the mixing and injecting procedure, the samples were shielded from ambient light.

Seven groups of dual-cured resin cement (A, B, C, D, E, F and G) were tested. Polymerization contraction stress kinetics was measured for 30 min immediately after the mixing and injecting procedure of the sample Groups A through F with data collected every second. Polymerization contraction stress kinetics was measured for 60 min immediately after the mixing and injecting procedure of sample Group G with data collected every second.

The cement was light-cured for 60 seconds through the bottom quartz rod according to the delayed photo-activation schedule (Table I). The dual-cured control group (A) was defined by 0 min photo-activation delay, while dual-cured control group (G) was defined by no photo-activation applied.

Elipar Highlight curing unit was used (ESPE, Dental-Medizin Gmbh. Seefeld, Germany). The light intensity at the end of the quartz rods was 618 ± 21 mW/cm^2 measured with a Cure Rite radiometer (Dentsply Caulk, Milford, DE). The light intensity was checked between groups and the lamp was changed when needed.

Contraction stress was determined by dividing the measured tensile force by the cross-sectional area of the sample.

Five samples for each group were tested. All experiments were conducted at room temperature (23 ± 1 °C).[26]

DEGREE OF CONVERSION MEASUREMENT

Degree of conversion was determined with Attenuated Total Reflectance (ATR) spectroscopic technique. To collect the uncured spectra, equal volumes of cement base and catalyst were mixed for 15 seconds and then placed in a standard FTIR sample holder with a 5 mm diameter opening. The ATR spectra of the uncured resin were collected with a Jasco FTIR spectrometer (Model: 4100, Jasco Corp., Tokyo, Japan) (Figure 2). The ATR spectra were acquired in absorbance mode from 16 scans at 4 wave number resolution. Prior to running the samples, the background spectra were collected through an empty mold with one glass slide to avoid internal reflectance patterns.

Table I shows the seven groups of dual-cured resin cement that were tested (labeled Groups A through G). The dual-cured control group defined by 0 min photo-

activation delay was Group A, while the dual-cured control group defined by no photo-activation applied was Group G.

Equal volumes of base and catalyst of the dual-cured cement samples were mixed for 15 seconds on a Mylar strip sheet over a glass slab and then covered by another Mylar strip sheet and pressed firmly with a glass slide against the glass slab to achieve thin film thickness samples.

Samples in Groups A through F were stored for 30 min while Group G was stored for 60 min before testing. Samples of all groups were shielded from ambient light during the storage period.

Samples in Groups A through F were cured for 60 seconds each during the storage period with a light curing unit (L.E. Demetron 1, SDS Kerr, Orange, CA) according to the scheduled photo-activation delaying period (Table I). The specimens were placed inside the FTIR chamber and the cured spectra were collected as described above.

In ATR spectroscopy, the calculation of conversion relies on the methacrylate = C - H2 peak between 6102 cm^{-1} and 6233 cm^{-1} with absorption maximum at 6165 cm^{-1}, since the intensity of this peak decreases after polymerization. The degree of conversion (DC) was obtained directly from the decrease in the integrated intensity after being normalized for thickness using the following equation:

$$DC = (1 - \frac{peak\ area\ cured}{peak\ area\ uncured}) \times 100$$

The peak area cured and the peak area uncured are illustrated in Figures 3 and 4.

Five samples for each group were tested.

STATISTICAL METHODS

Comparisons were performed using one-way analysis of variance (ANOVA). Pair-wise comparisons between groups were performed if the overall p-value for the group effect was less than 0.05. A 5-percent significance level was used for each test. The distributions of the degree of conversion and amount of polymerization contraction stresses were checked and found to satisfy the assumptions required for the ANOVA. In addition, because the relationship of delay time with the outcomes generally appeared to be linear, a regression analysis was performed to estimate the changes in the outcomes per minute of delay time.

RESULTS

CONTRACTION STRESS

Chemical-cure had significantly lower contraction stress than all of the light cure groups. For the light-cure groups, a 4-min delay had higher contraction stress than 0-min, 2-min, 6-min, 8-min, and 10-min delay; 0-min and 2-min delay had higher contraction stress than 6-min, 8-min, and 10-min delay; and 6-min delay had higher contraction stress than 8-min and 10-min delay. Contraction stress decreased 0.086 MPa per minute delay (Tables II and III).

DEGREE OF CONVERSION BY PEAK AREA

Chemical-cure had significantly lower degree of conversion by peak area than 2-min, 4-min, 6-min, 8-min, and 10-min delaylight-cure. For the light-cure groups, 0-min delayhad a lower degree of conversion by peak area than 2-min, 4-min, 6-min, 8-min, and 10-min delay; 2-min delay had a lower degree of conversion by peak area than 4-min, 6-min, 8-min, and 10-min delay; 4-min and 6-min delay had a lower degree of conversion by peak area than 8-min and 10-min delay; and 8-min delay had a lower degree of conversion by peak area than 10-min delay. Degree of conversion increased 0.021 per minute delay (Tables IV and V).

TABLES AND FIGURES

TABLE I

Photo-activation delaying period

Delayed period before photo-activation in min.	0 min	2 min	4 min	6 min	8 min	10 min	No photo-activation
Group	A	B	C	D	E	F	G

TABLE II

Contraction stress (MPa) by group

Group	N	Mean	SD	SE	Min	Max
Group A: **0 min delay**	5	3.216	0.081	0.036	3.112	3.286
Group B: **2 min delay**	5	3.152	0.083	0.037	3.046	3.259
Group C: **4 min delay**	5	3.348	0.080	0.036	3.212	3.408
Group D: **6 min delay**	5	3.032	0.070	0.032	2.949	3.101
Group E: **8 min delay**	5	2.526	0.069	0.031	2.434	2.608
Group F: **10 min delay**	5	2.444	0.079	0.036	2.359	2.552
Group G: **Chemical cure**	5	1.944	0.083	0.037	1.875	2.068

TABLE III

Comparison of contraction stress (MPa)
by group showing p-value

Comparison			p-value	
0 min delay	vs.	2 min delay	0.2075	
0 min delay	vs.	4 min delay	0.0127	0 min delay < 4 min delay
0 min delay	vs.	6 min delay	0.0009	0 min delay > 6 min delay
0 min delay	vs.	8 min delay	<0.0001	0 min delay > 8 min delay
0 min delay	vs.	10 min delay	<0.0001	0 min delay > 10 min delay
0 min delay	vs.	Chemical cure	<0.0001	0 min delay > Chemical cure
2 min delay	vs.	4 min delay	0.0005	2 min delay < 4 min delay
2 min delay	vs.	6 min delay	0.0215	2 min delay > 6 min delay
2 min delay	vs.	8 min delay	<0.0001	2 min delay > 8 min delay
2 min delay	vs.	10 min delay	<0.0001	2 min delay > 10 min delay
2 min delay	vs.	Chemical cure	<0.0001	2 min delay > Chemical cure
4 min delay	vs.	6 min delay	<0.0001	4 min delay > 6 min delay
4 min delay	vs.	8 min delay	<0.0001	4 min delay > 8 min delay
4 min delay	vs.	10 min delay	<0.0001	4 min delay > 10 min delay
4 min delay	vs.	Chemical cure	<0.0001	4 min delay > Chemical cure
6 min delay	vs.	8 min delay	<0.0001	6 min delay > 8 min delay

(continued)

TABLE III (continued)

6 min delay	vs.	10 min delay	<0.0001	6 min delay > 10 min delay
6 min delay	vs.	Chemical cure	<0.0001	6 min delay > Chemical cure
8 min delay	vs.	10 min delay	0.1084	
8 min delay	vs.	Chemical cure	<0.0001	8 min delay > Chemical cure
10 min delay	vs.	Chemical cure	<0.0001	10 min delay > Chemical cure

TABLE IV

Degree of conversion by peak area

Group	N	Mean	SD	SE	Min	Max
Group A: **0 min delay**	5	0.553	0.015	0.007	0.538	0.571
Group B: **2 min delay**	5	0.648	0.015	0.007	0.632	0.666
Group C: **4 min delay**	5	0.688	0.022	0.010	0.656	0.712
Group D: **6 min delay**	5	0.687	0.031	0.014	0.655	0.724
Group E: **8 min delay**	5	0.741	0.017	0.007	0.719	0.766
Group F: **10 min delay**	5	0.788	0.022	0.010	0.766	0.819
Group G: **Chemical cure**	5	0.538	0.019	0.009	0.508	0.557

TABLE V

Comparison of peak area by p-value

Comparison			p-value	
0 min delay	vs.	2 min delay	<0.0001	0 min delay > 2 min delay
0 min delay	vs.	4 min delay	<0.0001	0 min delay > 4 min delay
0 min delay	vs.	6 min delay	<0.0001	0 min delay > 6 min delay
0 min delay	vs.	8 min delay	<0.0001	0 min delay > 8 min delay
0 min delay	vs.	10 min delay	<0.0001	0 min delay > 10 min delay
0 min delay	vs.	Chemical cure	0.3491	
2 min delay	vs.	4 min delay	0.0176	2 min delay > 4 min delay
2 min delay	vs.	6 min delay	0.0203	2 min delay > 6 min delay
2 min delay	vs.	8 min delay	<0.0001	2 min delay > 8 min delay
2 min delay	vs.	10 min delay	<0.0001	2 min delay > 10 min delay
2 min delay	vs.	Chemical cure	<0.0001	2 min delay < Chemical cure
4 min delay	vs.	6 min delay	0.9518	
4 min delay	vs.	8 min delay	0.0021	4 min delay > 8 min delay
4 min delay	vs.	10 min delay	<0.0001	4 min delay > 10 min delay
4 min delay	vs.	Chemical cure	<0.0001	4 min delay < Chemical cure
6 min delay	vs.	8 min delay	0.0018	6 min delay > 8 min delay

(continued)

TABLE V (continued

| 6 min delay	vs.	10 min delay	<0.0001	6 min delay > 10 min delay
6 min delay	vs.	Chemical cure	<0.0001	6 min delay < Chemical cure
8 min delay	vs.	10 min delay	0.0056	8 min delay > 10 min delay
8 min delay	vs.	Chemical cure	<0.0001	8 min delay < Chemical cure
10 min delay	vs.	Chemical cure	<0.0001	10 min delay < Chemical cure
0 min delay	vs.	Uncured	<0.0001	0 min delay < Uncured
2 min delay	vs.	Uncured	<0.0001	2 min delay < Uncured
4 min delay	vs.	Uncured	<0.0001	4 min delay < Uncured
6 min delay	vs.	Uncured	<0.0001	6 min delay < Uncured
8 min delay	vs.	Uncured	<0.0001	8 min delay < Uncured
10 min delay	vs.	Uncured	<0.0001	10 min delay < Uncured
Chemical cure	vs.	Uncured	<0.0001	Chemical cure < Uncured
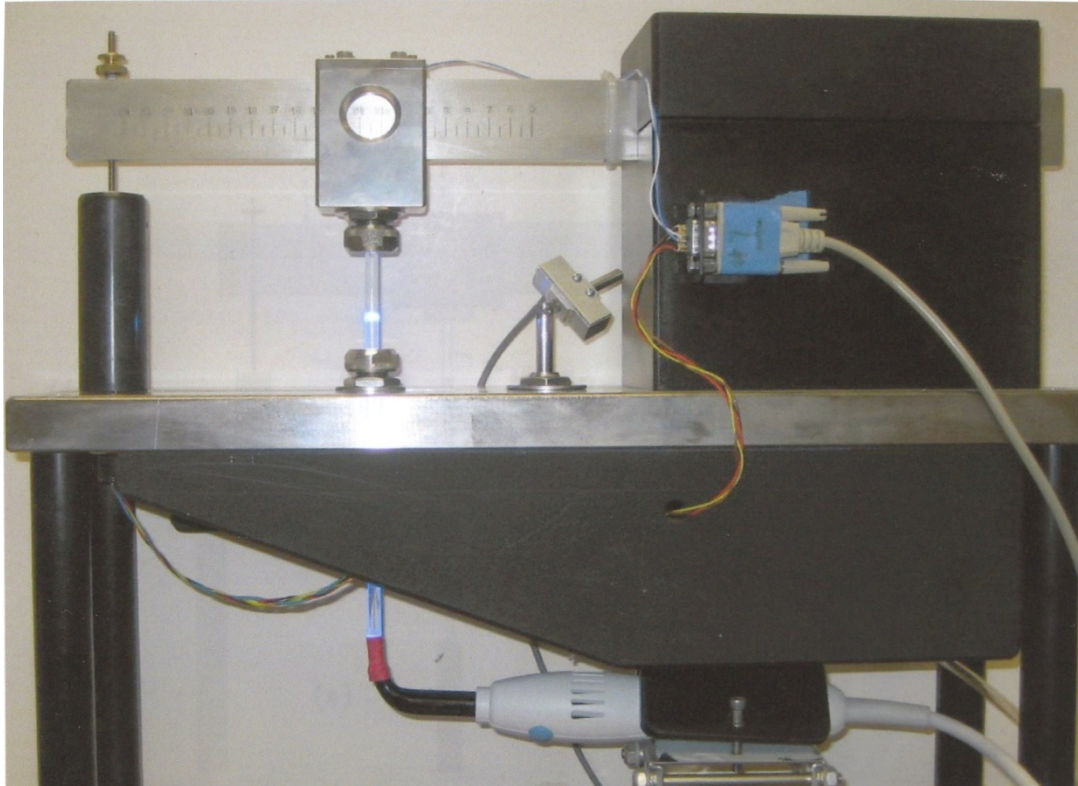
FIGURE 1.   The ADA tensometer.

FIGURE 2. The MIR spectra of the uncured resin were collected with a
Jasco FTIR spectrometer (Model: 4100, Jasco Corp.,
Tokyo, Japan)
http://www.jascoinc.com/products/images/im_ftir4100.jpg .
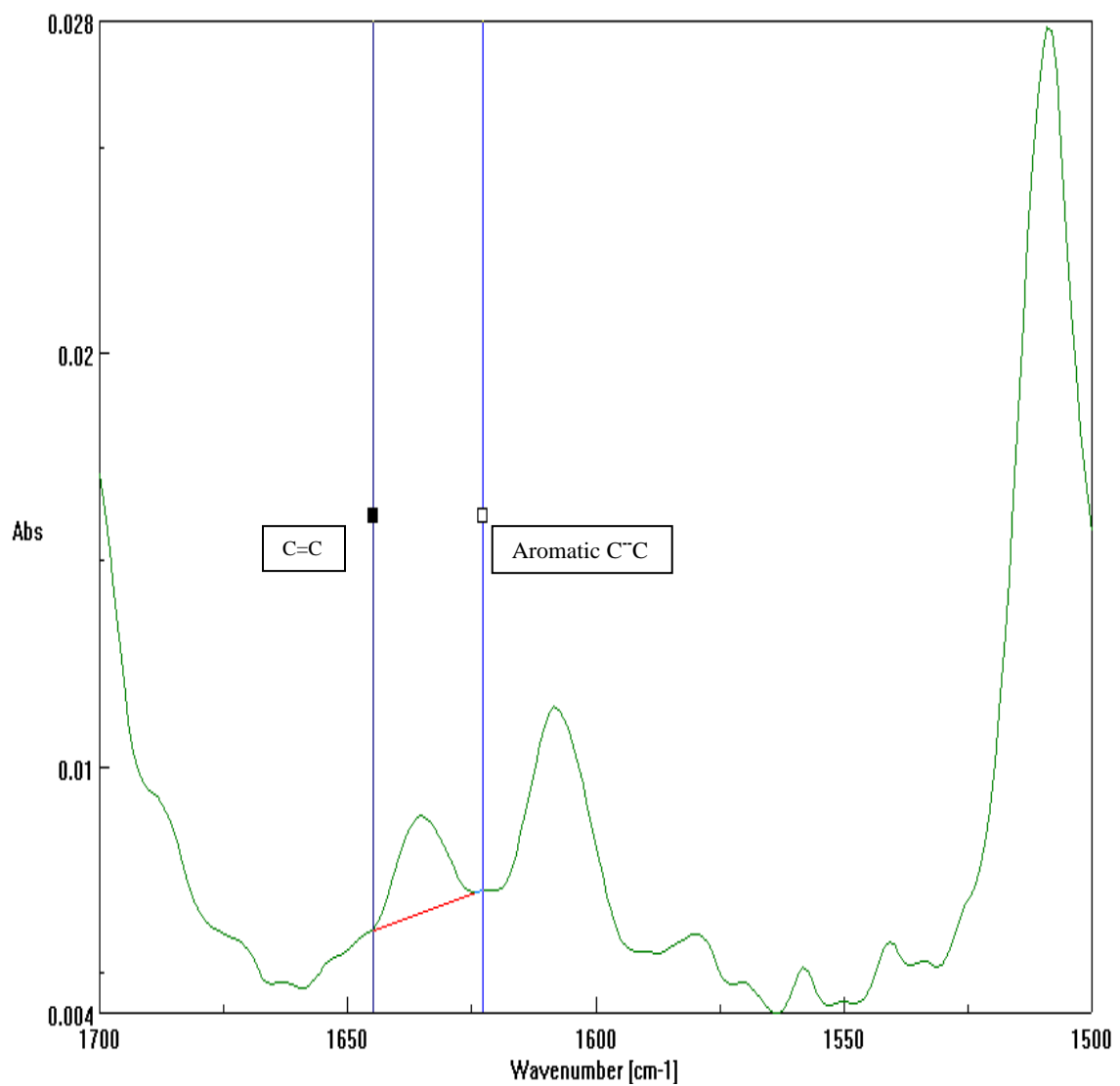
FIGURE 3.   Graph showing ATR spectra of light-activated luting resin.
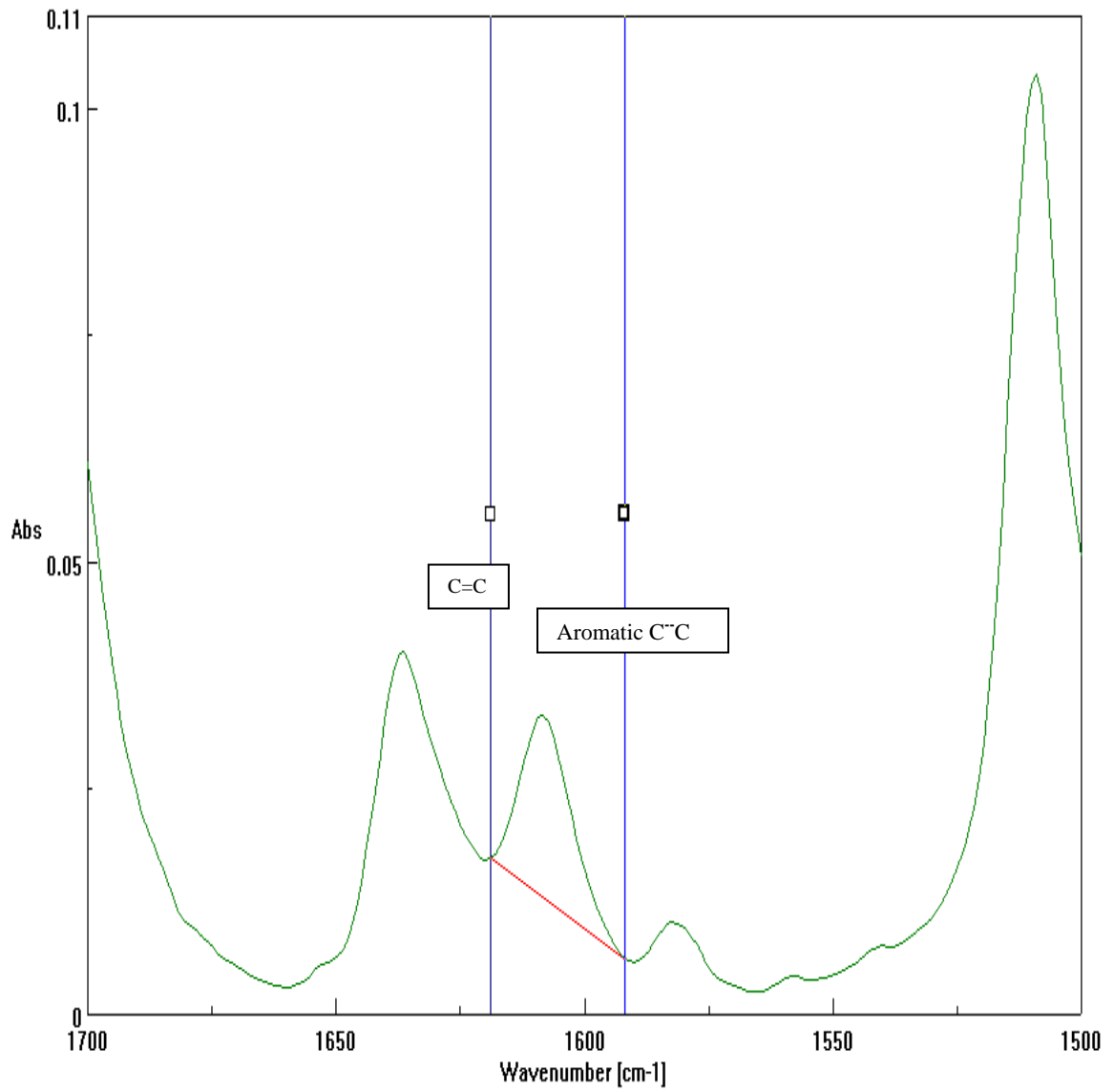
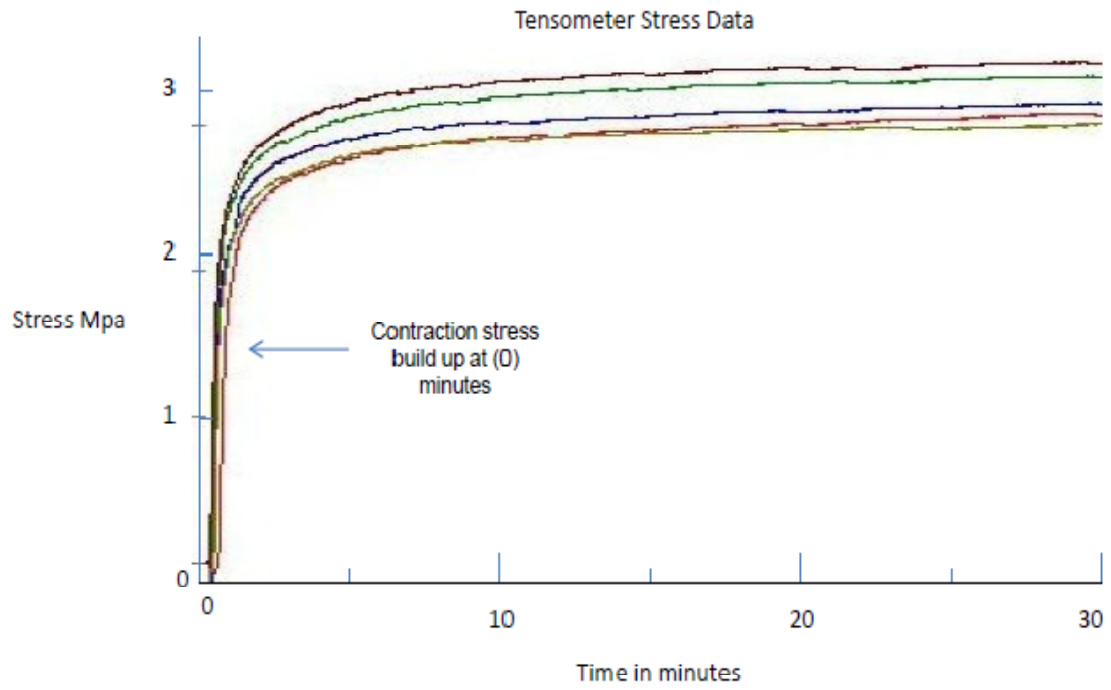FIGURE 4.   Graph showing ATR spectra of uncured luting resin.

FIGURE 5.   Graph showing contraction stress (MPa) of the immediate
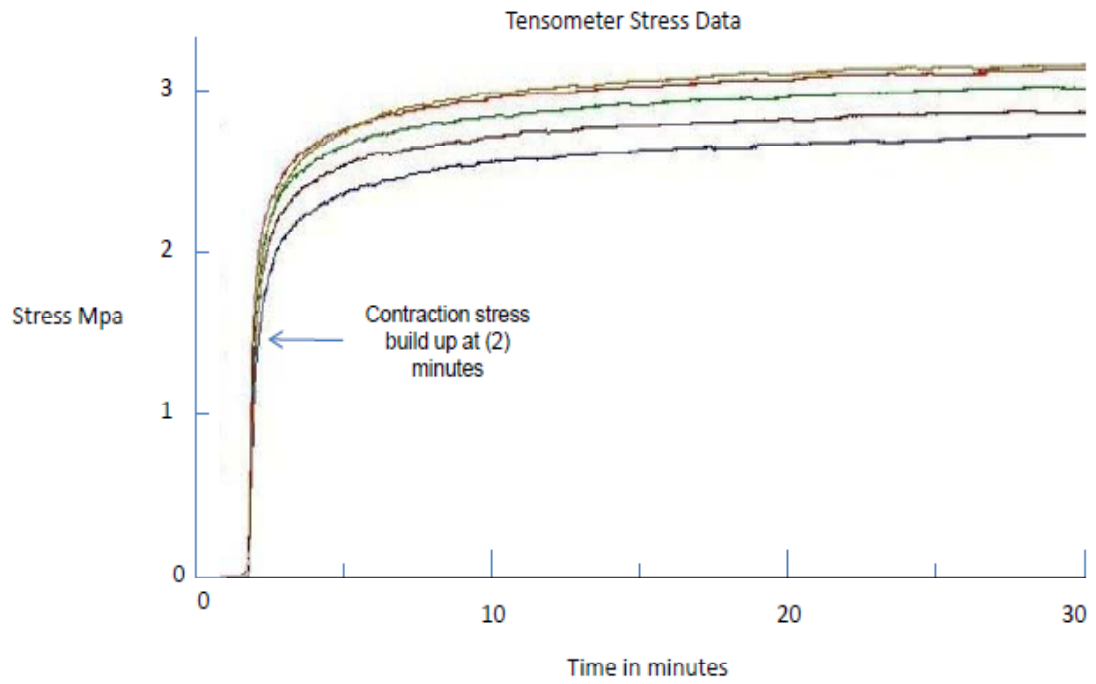light-cured group (Group A).

FIGURE 6.   Graph showing contraction stress (MPa) of the 2-min delayed-cure group (Group B).

FIGURE 7. Graph showing contraction stress (MPa) of the 4-min delayed-cure group (Group C).

FIGURE 8.　Graph showing contraction stress (MPa) of the 6-min delayed-cure group (Group D).

Tensometer Stress Data

Stress Mpa

Contraction stress
build up at (8)
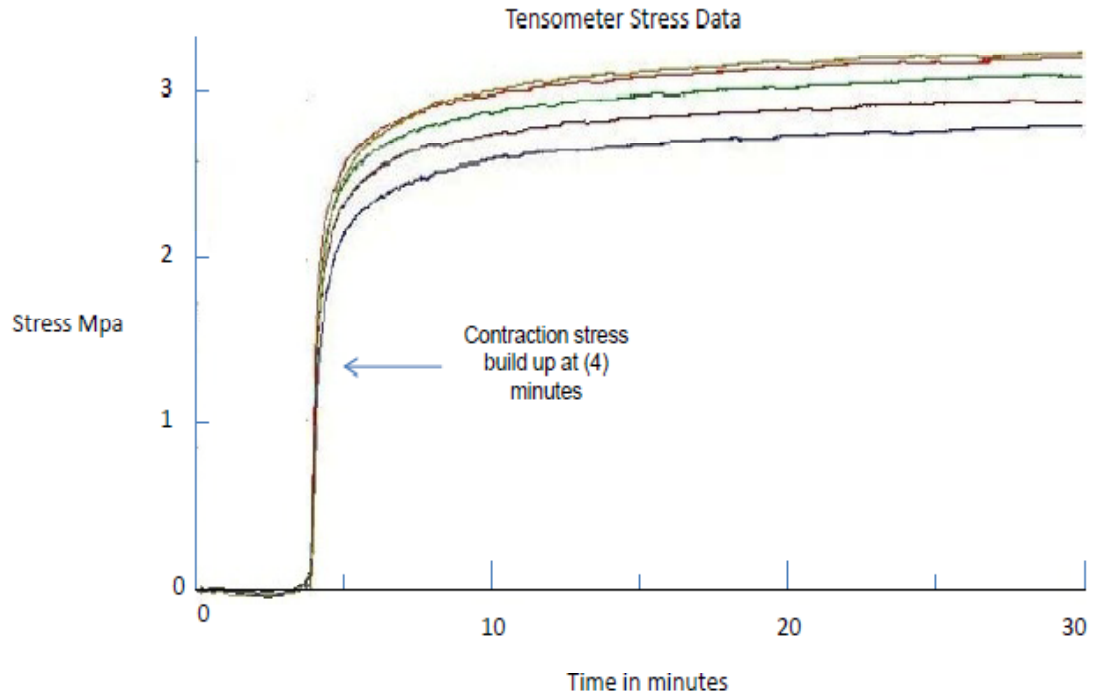minutes

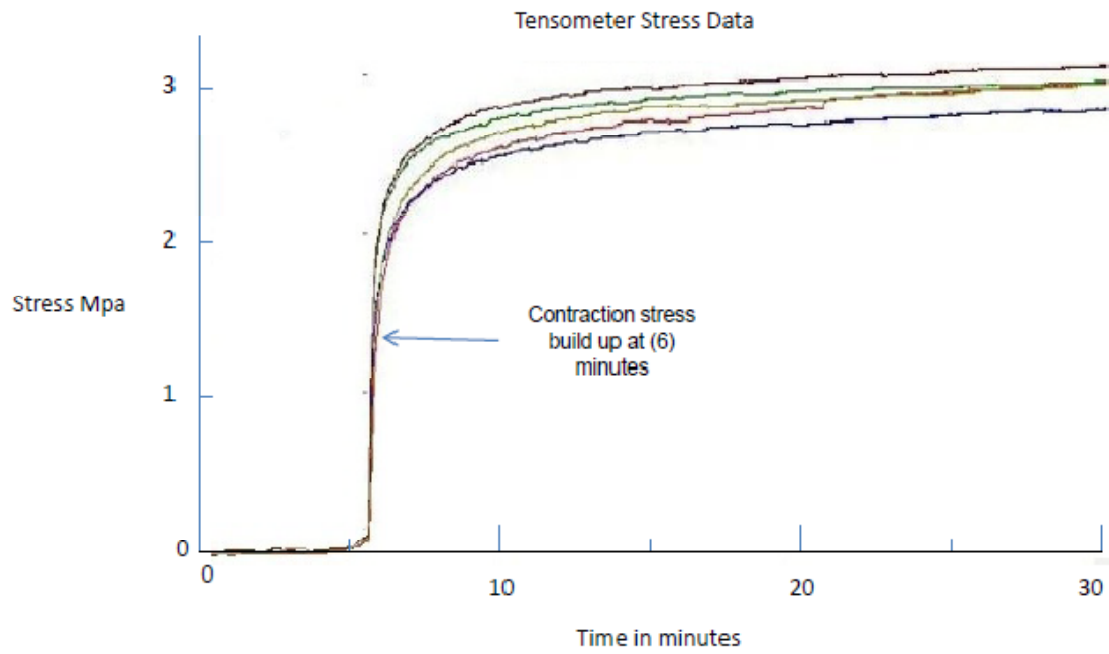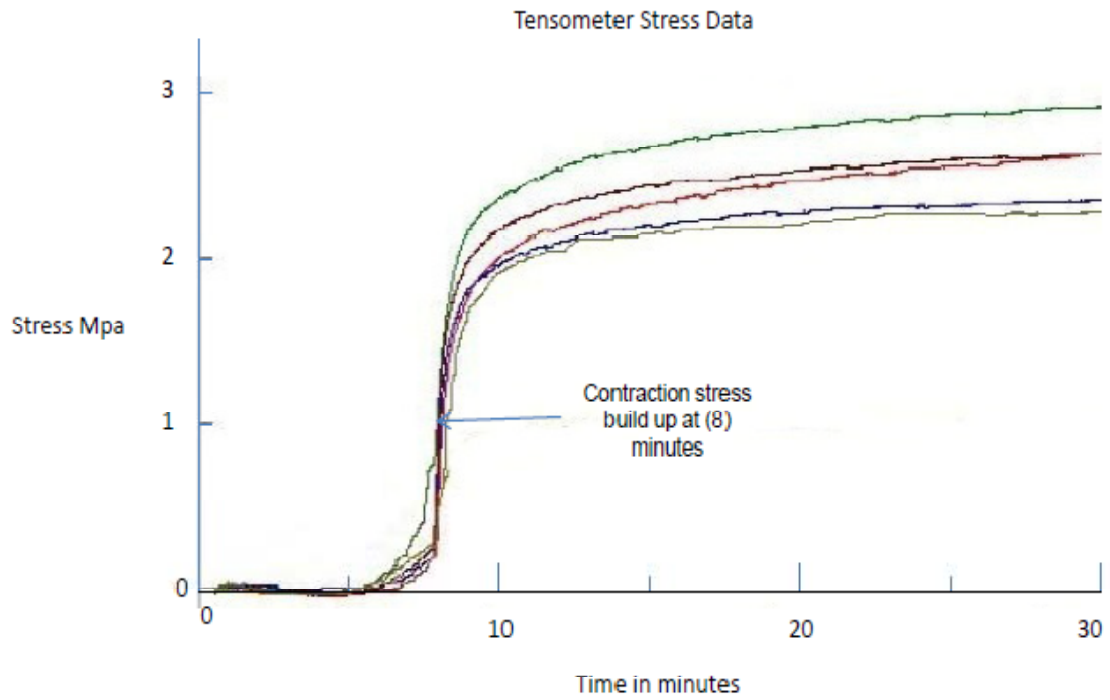Time in minutes

FIGURE 9.   Graph showing contraction stress (MPa) of the 8-min
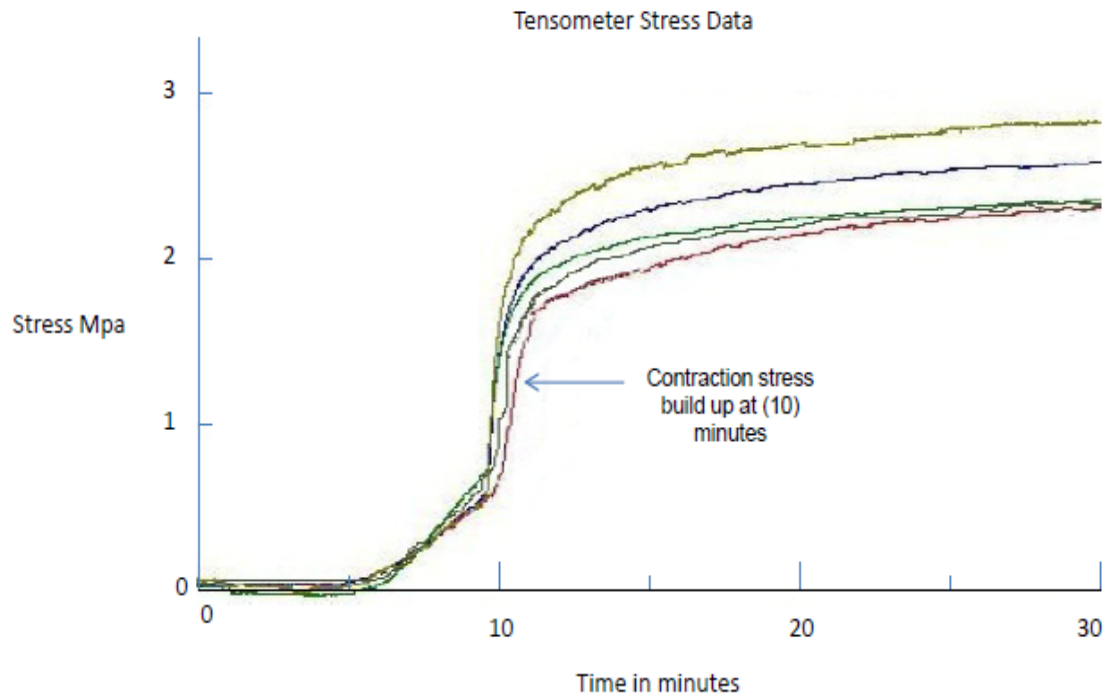   delayed-cure group (Group E).
.

FIGURE 10.   Graph showing contraction stress (MPa) of the 10-min
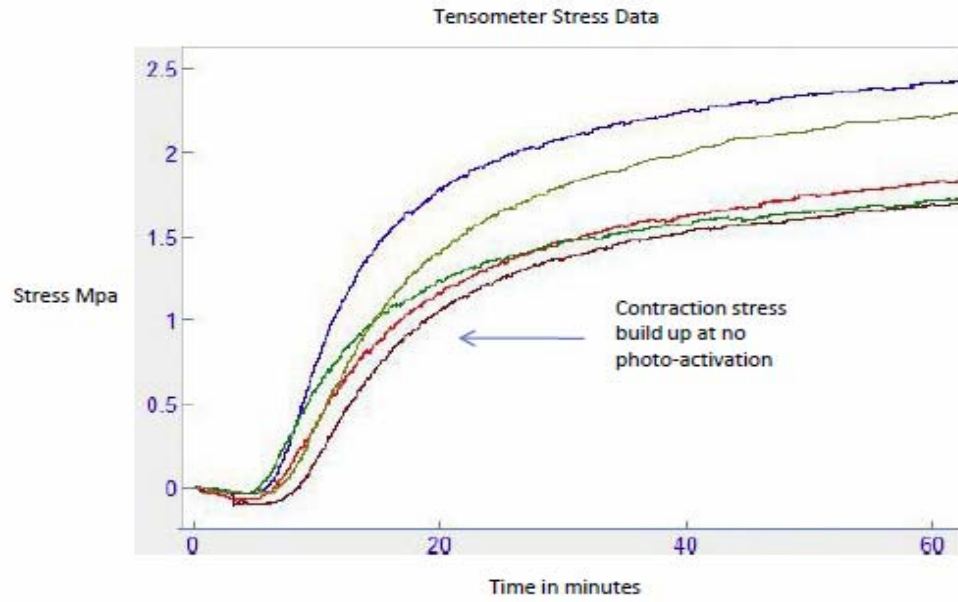delayed-cure group (Group F).

FIGURE 11.   Graph showing contraction stress (MPa) of the group
receiving no photo-activation (Group G).

DISCUSSION

Different approaches to soft-start polymerization have been proposed in previous studies to reduce the magnitude and the effects of the contraction stresses in dental composites. It is believed that extending the flow time of resins before reaching the gel point will extend the time of stress relief, which can be achieved by slowing the rate of polymerization.[19, 21-23, 25, 28, 73-75] Achieving maximum degree of conversion was always a major concern. Mechanical properties and biocompatibility are highly affected by the percentage of unreacted monomers, which explains the importance of increasing the double bond conversion in the resin. Decreasing the extent of unreacted monomers in the system reduces the plasticizing effect of these monomers and increases the cross-linking, which increases the strength of the polymer.[26]

The specific aim of this study was to investigate the influence of delayed light curing on the polymerization contraction stress and degree of conversion in dual-cured resin luting agents.

In this study, a different approach to soft-start polymerization has been used, in which light activation of the dual-cured resin luting agents was delayed. Dual-cure luting resins polymerize through chemical and light activation processes combined together. Delayed light activation gives the opportunity for the chemically-activated portion to begin first in which the resin monomer starts to react and create longer polymer chains. Increasing the amount of reacted monomers in the resin prior to reaching the gel point hinders the free movement of chains and is associated with potential increase of stress. Extending the flow time of resins before reaching the gel point by slowing the rate of

polymerization can be achieved by delaying light activation that consequently extends the time of stress relief. Contraction stresses of the dual-cured resin luting agent samples were tested at different stages of the polymerization processes, starting from immediate light activation after mixing and through 10 min. Light activation was applied immediately and at 2-min intervals after mixing in the light activated sample groups (A, B, C, D, E and F) (Figures 5-10). A purely chemically activated sample group was used as a control group (G) (Figure 11). While the results showed that the 4-min delay light-activated group (C) had the highest contraction stress among all samples, contraction stress showed a decrease in value in the rest of the groups with increased periods of delay. The purely chemically-activated group showed the least contraction stress. Graphs in Figures 6, 7 and 8 showed no increase in contraction stress in the first 6 min before light activation had started.

For the groups (A, B, C and D) shown in Figures 5, 6, 7 and 8, contraction stress curves started to increase after light activation at or before the gel point. The material at this stage was in the viscous paste status before turning into the visco-elastic solid in which the polymer chains slip and reorient into new positions enabling viscous flow. Final contraction stress had less value when light activation delayed although the stress curves on the graph showed no changes prior to the gel point. Figure 5 showed immediate increase in contraction stress upon immediate application of curing light. Figures 6, 7 and 8 showed 2-min, 4-min, and 6-min delayed contraction stress build up, respectively. Figures 9 and 10 showed gradual stress build up started after the gel point due to the chemical polymerization process of the dual-cured luting agent. A sharp increase in stress build up was noticed upon light application in all group samples until it

reached the full polymerization process. That was in agreement with several studies showing that composite elastic limit reaches a degree of rigidity that does not allow further plastic deformation or flow to compensate for the volumetric reduction where the shrinkage forces start to build-up, resulting in stress accumulation.[33, 60-63]

Degree of conversion was tested in resin luting agent samples using the same light activation intervals starting from immediate light activation and every 2 min for a 10-minute testing period and one control group that was a purely chemically activated sample. Degree of conversion showed significant increase in value with every delay period with the purely chemically cured sample having the lowest degree of conversion value. Extension of the flow time of resin increases the amount of monomer involved in the entire reaction through the chemical and light activation polymerization processes that consequently increase the degree of conversion of the resin luting agent.

These results indicate that extending the stress relief period of the dual-cured luting agents by delaying light activation has a significant impact on contraction stress and degree of conversion values. There was a significant decrease in contraction stress with delayed light curing of the resin luting agent. Significant increase in degree of conversion was noticed when light activation was delayed in the dual-cured resin luting agent.

From a clinical point of view, these results showed that delayed light activation of the dual-cured luting agent can help in optimizing the physical and chemical properties of the luting agent. This delay will help in maximizing the degree of conversion of the luting agents while keeping the contraction stresses at a reduced level. Delaying the light activation by a practical delaying time can improve the overall performance of the

restoration. It will help in minimizing the adhesive failure and consequently the

microleakage[14-16] in addition to enhancing the mechanical properties and biocompatibility

of the luting agent.

SUMMARY AND CONCLUSIONS

The associated stresses to the resin composite polymerization have significant clinical concerns and are believed to be the cause of many undesired effects. On the other hand mechanical properties and biocompatibility are highly affected by the percentage of unreacted monomers, which explains the importance of increasing the double bond conversion in the resin. Decreasing the extent of unreacted monomers in the system; reduces the plasticizing effect of these monomers and increases the cross-linking that increases the strength of the polymer.

The purpose of this study was to evaluate a clinical technique that can help in optimizing the physical and chemical properties of the dual-cured luting agent by determining the impact of eliminating or delaying the photo-activation procedure on the polymerization contraction stress (PCS) and degree of conversion (DC).

The amount of polymerization contraction stress and degree of conversion of a dual-cured resin luting agent was determined using a tensometer and (ATR) spectroscopic technique respectively. Photo-activation delay in seven tested groups was for 0 min, 2 min, 4 min, 6 min, 8 min, and 10 min, and one group had no photo-activation. Five samples for each group were tested. Polymerization contraction stress was measured for 30 min in the photo-activated groups immediately after the mixing and injecting procedure with data collected every second. The cement was light-cured for 60 seconds through the bottom quartz rod according to the delayed photo-activation schedule. Polymerization contraction stress in the chemically cured groups was measured for 60 min immediately after the mixing and injecting procedure with data

collected every second. Degree of conversion was measured after storing samples for 30 min while chemically cured samples were stored for 60 min before testing. To collect the uncured spectra, equal volumes of cement base and catalyst were mixed and then placed in a standard FT-IR sample holder with a 5-mm diameter opening. The ATR spectra of the uncured resin were collected with a Jasco FT-IR spectrometer. The ATR spectra were acquired in absorbance mode from 16 scans at 4 wave number resolution. Samples were cured for 60 seconds each during the storage period according to the scheduled photo-activation delaying period. The specimens were placed inside the FTIR chamber and the cured spectra were collected as described above.

PCS of the chemical cure luting agent had significantly lower value than all of the light cure groups. For the light cure groups, 4-min delay had higher PCS than 0-min, 2-min, 6-min, 8-min, and 10-min delay, 0-min and 2-min delay had higher PCS than 6-min, 8-min, and 10-min delay; and 6-min delay had higher PCS than 8-min and 10-min delay. PCS decreased 0.086 MPa per minute delay. DC of the chemical cure luting agent had significantly lower value than 2-min, 4-min, 6-min, 8-min, and 10-min delay light cure. For the light cure groups, 0-min delay had lower DC than 2-min, 4-min, 6-min, 8-min, and 10-min delay; 2-min delay had lower DC than 4-min, 6-min, 8-min, and 10-min delay; 4-min and 6-min delay had lower DC than 8-min and 10-min delay; and 8-min delay had a lower degree of conversion by peak area than 10-min delay. DC increased 0.021 per minute delay. These results indicate that extending the stress relief period of the dual-cured luting agents by delaying light activation has a significant impact on contraction stress and degree of conversion values. There was a significant decrease in contraction stress with delayed light curing of the resin luting agent. Significant increase

in degree of conversion was noticed when light activation was delayed in the dual-cured resin luting agent. From a clinical point of view, these results showed that delayed light activation of the dual-cured luting agent can help in optimizing the physical and chemical properties of the luting agent. This delay will help in maximizing the degree of conversion of the luting agents while keeping the contraction stresses at a reduced level. Delaying the light activation by a practical delaying time can improve the overall performance of the restoration in addition to enhancing the mechanical properties and biocompatibility of the luting agent. Due to the limitations of this study, more studies need to be done to evaluate this technique with different geometrical forms that simulate the anatomical form of the oral dentition to measure the contraction stress and degree of conversion.

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ABSTRACT

THE INFLUENCE OF DELAYED LIGHT CURING ON THE

POLYMERIZATION CONTRACTION STRESS AND

DEGREE OF CONVERSION IN DUAL-CURED

RESIN LUTING AGENTS

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The purpose of this study was 1) To determine the impact of eliminating or delaying the photo-activation procedure on the polymerization contraction stress (PCS) and degree of conversion (DC) of a dual-cured resin luting agent, and 2) To determine the amount of delay in photo-initiation of the dual-cured resin cements that can achieve a reduced PCS value with the highest possible DC.

The amount of PCS and DC of a dual-cured resin luting agent was determined using a tensometer and ATR spectroscopic technique, respectively. Photo-activation delay in seven tested groups was 0 min, 2 min, 4 min, 6 min, 8 min, 10 min and no photo-activation. Five samples for each group were tested.

There were two hypotheses for this study: 1) A significant decrease in the amount of PCS associated with delayed photo-activation, and 2) A significant increase in DC associated with delayed photo-activation.

The PCS of the chemical-cure luting agent had significantly lower value than all of the light-cure groups. For the light-cure groups, those with a 4-min delay had higher PCS than those with delays of 0 min, 2 min, 6 min, 8 min, and 10 min. The zero (0)-min and 2-min delay had higher PCS than the 6-min, 8-min, and 10-min delay; and the 6-min delay had higher PCS than the 8-min and 10-min delay. The PCS decreased 0.086 MPa per minute of delay. The DC of the chemical-cure luting agent had significantly lower value than the 2-min, 4-min, 6-min, 8-min, and 10-min delaylight cure. For the light-cure groups, 0-min delay had a lower DC than the 2-min, 4-min, 6-min, 8-min, and 10-min delay; 2-min delay had lower DC than 4-min, 6-min, 8-min, and 10-min delay. The 4-min and 6-min delay had lower DC than the 8-min and 10-min delay; and the 8-min delay had a lower degree of conversion by peak area than the 10- minute delay. The DC increased 0.021 per minute of delay.

Extending the stress relief period of the dual-cured luting agents by delaying light activation has a significant impact on PCS and DC values. There was significant decrease in PCS with the delayed light curing of the resin luting agent. Significant increase in DC was noticed when light activation was delayed in the dual-cured resin luting agents.

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