

Title Page:

The influence of delayed light curing on the degree of conversion and polymerization contraction stress in dual-cured resin luting agents.

Authors:

Nawaf Labban,^a Mounir Iskandar,^b Jeffrey A. Platt,^b Carl J. Andres,^b John A. Levon,^b

Suteera Hovijitra,^b David T. Brown^b

Nawaf Labban,^a labbanny@yahoo.com

Mounir Iskandar,^b hathhala81@gmail.com

Jeffrey A. Platt,^b ksacademics2@gmail.com

Carl J. Andres,^b ksacademics1@gmail.com

John A. Levon,^b academicksa2@gmail.com

Suteera Hovijitra,^b professionals114@gmail.com

David T. Brown^b mmalidr1@gmail.com

Affiliations:

a. Department of Prosthetic Dental Sciences, King Saud University, College of Dentistry, Riyadh, KSU

b. Department of Restorative Dentistry, Indiana University School of Dentistry, Indianapolis, IN.

Correspondence:

Nawaf Labban

King Saud University, College of Dentistry, Department of Prosthetic Dental Sciences (SDS)

Building 23, room 2A/79, P.O. Box 60169, Riyadh 11545, Kingdom of Saudi Arabia

Phone: +9661467-9015, E-mail: labbanny@yahoo.com

Running title: Effect of delay in photo-initiation on resin luting agents

Keywords: Delayed light curing; polymerization contraction stress; degree of conversion; dual-cured resin; luting agents

Funding: Self-Funded

Conflict of interest: None declared

This is the author's manuscript of the article published in final edited form as:

Labban, N., Iskandar, M., Platt, J. A., Andres, C. J., Levon, J. A., Hovijitra, S., & Brown, D. T. (2018). The influence of delayed light curing on the degree of conversion and polymerization contraction stress in dual-cured resin luting agents. *Journal of Adhesion Science and Technology*, 32(5), 516–526. <https://doi.org/10.1080/01694243.2017.1370165>

Abstract

The aim of the study was to assess the effect of delayed photo-initiation on the polymerization contraction stress (PCS) and degree of conversion (DC) of a dual-cure resin-luting agent. Thirty-five disk (6mmx1mm) samples (n=10 each group) of dual cure resin luting agent for PCS assessment were fabricated and polymerized using two illuminated quartz rods. Based on the delay in photo-initiation, 30 disks were divided among six groups [group A-0 minutes (min) delay, group B-2 min, group C-4 min, group D-6 min, group E-8 min and group F-10 min]. A non-photoinitiated group (group G-chemical cure- n=5) was included as control. The PCS for all specimens was assessed using a Tensometer. For DC evaluation thirty-five specimens were divided into seven groups with delays in photo-initiation (group H-0 min, group I-2 min, group J-4 min, group K-6 min, group L-8 min and group M-10 min, group N-chemical cure). DC was assessed using Attenuated Total Reflectance (ATR) spectroscopic technique. Statistical comparison among groups was performed using analysis of variance ($\alpha=0.05$). The maximum and minimum PCS and DC values with delayed photo-initiation was observed in group-C (3.34 MPa) & group-F (2.44 MPa); and group-M (0.78 MPa) and group-H (0.55 MPa) respectively. Chemically cured samples showed the least PCS (group-G, 1.94) and DC (group-N, 0.53) values in their respective categories. PCS significantly decreased with delayed photo-initiation. A significant increase in DC was noticed when photo-initiation was delayed in the dual cure resin luting agent.

Key words: delayed light curing; polymerization contraction stress; degree of conversion; dual-cured resin; luting agents

1. Introduction

Resin luting agents have become a popular choice for multiple clinical applications in dentistry due to their unique properties in comparison to acid based luting agents [1]. Adhesive ceramic restorations with complete and partial coverage (inlays, onlays and crowns) mandate the use of adhesive resin cements to enhance strength, augment retention and improve esthetics.[2]. In particular, dual activated resin cements are preferably employed in clinical procedures to allow for controlled setting during clinical procedures along with potential for better conversion rate of monomers to polymers. [3]

Polymerization shrinkage is a concern for resin luting agents and occurs when monomers form long and entangled polymer chains with closer packing of molecules causing reduction in the bulk volume [4-6]. On bonding the resin to the more rigid tooth structure, stresses develop within the material as a result of shrinkage under constraints that potentially render the polymerization shrinkage to be clinically significant [7-10]. Adhesive failure and consequent microleakage are possible outcomes if the developed stresses exceed the adhesive bond strength [11-13]. Due to a rapid polymerization process and a shorter pre-gel phase of photoinitiated resins, the generation of higher polymerization contraction stresses (PCS) than for chemically cured resins has been reported [14, 15]. Chemically cured resins have an extended setting time with a longer pre-gel phase that enables chain rearrangement and a reduction in PCS. With this understanding, soft start polymerization has been suggested as a clinical technique to reduce contraction stress [14, 16, 17]. Feilzer et al., hypothesized that lowering the contraction stress can be achieved by using low light intensity that extends the viscoelastic stage of the polymerizing resin [14]. Soft start polymerization is a technique, which includes initial illumination with low intensity light followed by high intensity illumination. In addition, ramp and pulse-delay are variations of this technique, which

have shown to generate significantly less contraction stress compared to continuous exposure [18-22].

Another important aspect of composite resins is its degree of conversion (DC), which is defined as the percentage of polymerizable units that have been utilized in the formation of a cross-linked polymeric resin. Incomplete polymerization may increase residual monomer that could compromise biocompatibility and result in a resin with inferior mechanical and physical properties [23-27]. Yap et al., reported that resin samples of 2 mm thickness have significantly lower hardness and degree of conversion at the bottom of the samples when initiated with the soft start and the pulse delayed technique compared to full intensity initiation [28]. In another study, Lu et al., reported that soft-start initiation results in significantly less PCS and DC [29]. Unlike photoinitiated resins, Pegoraro et al., speculated that a delay in the photoinitiation of dual-initiated materials would be beneficial in enhancing their DC [30]. The rationale being that the immediate exposure to light and formation of cross-linked polymer chains could interfere with the chemical initiation by entrapping polymerization promoters and unreacted monomers, causing compromised self-initiation mechanism. Therefore, it is hypothesized that a delay in photo-initiation of a dual cure resin luting agent would positively impact its DC and PCS. Consequently, the aim of the study was to assess the influence of delayed photo-initiation on the polymerization contraction stress and degree of conversion (DC) of a dual-cure resin-luting agent.

2. Materials and Methods

In this in-vitro experiment PCS and DC of a dual cure resin luting agent (Illusion Dual-cured, BISCO Inc., IL, USA. Batch No. 0800013231) was assessed using Tensometer and Attenuated Total Reflectance (ATR) spectroscopic techniques respectively.

2.1 Polymerization Contraction Stress Measurement

Two quartz rod (6 mm 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 with the silanized end pointing down. The lower quartz rod was 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 6 mm in diameter and 1 mm in height corresponding to a C-factor of 3 [diameter/ 2(height)]. A polytetrafluorethylene sleeve with two holes was placed around the gap. Equal volumes of base and catalyst of the luting agent (Variolink II, Ivoclar Vivadent AG FL-9494 Schaan / Liechtenstein) were mixed for 15 seconds and injected into the sleeve to fill the space between the silanized ends. (Fig 1) 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 were tested with five samples in each group. For six groups, photoinitiation occurred for 60 seconds [(Manufacturers recommendation, 20 sec for initial tac and 40 sec curing time, (Ivoclar Vivadent AG FL-9494 Schaan / Liechtenstein))] through the bottom quartz rod according to the delayed photoinitiation periods. Delayed photo-initiaton

resulted in six groups, these are, group A-0 minutes (min), group B-2 min, group C-4 min, group D-6 min, group E-8 min and group F-10 min. Five samples were included in the non-photoinitiated group (group G) which was chemically cured. A Tensometer (American Dental Association Health Foundation. NIST. Gaithersburg, MD) was used to measure PCS for each sample (Fig 1). 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. A LVDT (linear variable differential transformer) (Model: 050-HR-000, Component Distributors Incorporation, Ft. Lauderdale, FL) was positioned 23 cm from the sample assembly at the free end of the cantilever beam.

PCS kinetics was measured every second for 30 minutes immediately after the mixing and injecting procedure for all photoinitiated groups (groups A to F). For the non-photoinitiated group (group G- chemical cure), the stress curves had not reached a plateau after 30 minutes and measurements were collected for 60 minutes. An LEDemetron I (SDS/Kerr, Orange, CA, USA) was used for all photo-initiation. Power density was determined to be 955 mW/cm^2 using a spectrophotometer with a FOIS-1 integrating sphere (USB2000, Ocean Optics Inc, FL, USA) and monitored at the end of the quartz rods to be $\geq 615 \text{ mW/cm}^2$ as measured with a Cure Rite radiometer (Dentsply Caulk, Milford, DE, USA). The light intensity was verified before measurements were obtained for each group.

Contraction stress was determined by dividing the measured tensile force by the cross-sectional area of the sample. All experiments were conducted at room temperature (23 ± 1 °C).[31]

2.2 Degree of Conversion

DC was determined using an FT-IR Spectrometer Frontier (Model: 4100, Jasco Corporation, Tokyo, Japan) with an attenuated total reflectance (ATR) accessory 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 (Fourier transform infrared spectroscopy) spectrometer 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. Equal volumes of base and catalyst of the luting agent 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.

Similar to the PCS test, seven groups (Groups H to N) with five samples per group were tested. The photoinitiated groups were stored for 30 minutes while the non-photoinitiated group was stored for 60 minutes before testing. Samples of all groups were shielded from ambient light during the storage period. The photoinitiated groups were exposed to polymerization light for 60 seconds according to the scheduled periods as

indicated in Tables 1 and 2. The specimens were placed inside the FTIR chamber and cured spectra were collected as described above.

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

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

2.3 Statistical analysis

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 < 0.05. 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.

3. Results

3.1 Polymerization Contraction Stress

The specimens in non-photoinitiated group (group G) had significantly less (p<0.05) polymerization contraction stresses than specimens in photoinitiated groups (group A to F). For the photoinitiated groups, specimens in group C (4-minute delay) showed the highest PCS compared to groups A (0 min), B (2 min), D (6 min), E (8 min)

and F (10 min). Figure 2 presents a comparison of mean PCS among study groups, showing gradual decrease in PCS with increasing photo-initiation delay. Figure 3 shows a sudden increase in PCS at 4 minute photo initiation reaching nearly 2Mpa, followed by a minimal but steady PCS rise upto 30 minutes. By contrast, specimens in group F showed a gradual PCS rise (from 6 to 10 min) prior to photo initiation, however a sudden PCS rise was seen at 10 min photo initiation (Fig. 4). In addition, specimens with groups A and B had significantly higher ($p < 0.05$) PCS than specimens in groups D (6 min), E (8 min) and F (10-min). With an exception to group C (4 min delay), an inverse relation was observed with increasing delay in photo-initiation and PCS among all photoinitiated groups i.e. increasing photo-initiation delay caused a reduction in PCS. On average, PCS decreased 0.086 MPa per minute delay (Table 1).

3.2 Degree of Conversion by Peak Area

The specimens in non-photoinitiated group (group N) had significantly lower ($p < 0.05$) DC by peak area than specimens in photoinitiated groups (groups H to N). Among the photoinitiated specimens, 0 minute delay (group H) in photo-initiation showed significantly lower ($p < 0.05$) DC than specimens in groups I (2 min), J (4 min), K (6 min), L (8 min) and M (10 min). A direct relationship was observed with increasing delay in photo-initiation and DC by peak area i.e. DC improved with increased delay of photo-initiation. The maximum DC was observed among specimens in group M (10 min delay). The degree of conversion increased 0.021 per minute delay in photo-initiation. (Table 2) Figure 5 presents a comparison of mean DC among groups, showing linear improvement with increasing delay in photo-initiation. It reveals a reduction in DC for chemical cured

specimens as compared to photoinitiated specimens, DC falling lower than the specimens receiving photoinitiation immediately, (group H- 0 min)

4. Discussion

The aim of the present study was to investigate the impact of time delay in photoinitiation of dual-cure resin luting agent on PCS and DC. It was hypothesized that a delay in photo-initiation of a dual cure resin-luting agent would positively impact its DC and PCS. It was observed that a delay in photo-initiation resulted in reduction of contraction stresses and increase degree of monomer conversion.

Different approaches of soft start polymerization have been proposed in previous studies to reduce the magnitude and the effects of PCS in dental composites [32-34]. It has been believed that extending the flow time of resins before reaching the gel point will extend the time of stress relief, and this can be achieved by slowing the rate of polymerization [16, 18-20, 22, 28, 32-34]. In the present study, photo-initiation was applied immediately and at two-minute intervals (up to 10 min) after mixing. These time intervals were selected to see the overall influence of delaying photo initiation on PCS and DC of dual cured resins, as well its possible clinically application. While the results showed that the 4-minute delay in photo initiation had the highest contraction stress among all groups, contraction stress showed a decrease in value in the rest of the groups with an increase in delay period. This observation could be related to very early onset of chemical-initiation followed by a cage effect on the initiator, slowing its availability to contribute to

initiation and causing a decrease in the rate of polymerization. However, further investigations are required to validate this hypothesis.

Interestingly, in the present study, 2 and 4 minute delay groups showed no increase in contraction stress before photo-initiation occurred. The 6-minute delay group showed a small but perceptible increase in rate of stress development between 4 and 6-minute groups. This phenomenon became increasingly evident for the longer delay groups. For the 0, 2, 4, and 6-minute delay groups, contraction stress curves increased after photo-initiation, which was in a period at or before the gel point. The material at this stage was a viscous paste in which the polymer chains slip and reorient into new positions representing viscous flow. Final contraction stress had less value when photo-initiation was delayed although the stress curves on the graph showed no changes prior to the gel point. The 8 and 10 minute delay groups showed a gradual stress build up corresponding to the beginning of gelation due to the chemical-initiation process. Initial evidence of this began after 4 to 5 minutes. A sharp increase in stress build up was noticed upon light application in all group samples until it reached a polymerization stress plateau. This was consistent with several studies showing that resin composite reaches a degree of rigidity that severely inhibits further plastic deformation or flow that results in stress accumulation with ongoing volumetric reduction [35-39]. However further studies are recommended to assess the correlation of PCS and DC for dental resin composites.

A high DC is considered a desired outcome for dental restorative resins. Mechanical properties and biocompatibility are highly affected by the percentage of unreacted polymerizable groups, which explains the importance of increasing the double bond

conversion in methacrylate-based resins. Increasing the DC in the system reduces the plasticizing effect of unreacted monomers and increases crosslinking which improves the strength of the polymer [31]. DC was tested using the same light activation intervals described for testing PCS. Significant increases in value were seen with every delay period and the non-photoinitiated group had the lowest DC value. It is the author's opinion that the extension of the flow time of resin (delay in photo-initiation) increases the amount of monomer involved in the entire reaction through the chemical and photo-initiated polymerization that consequently increases the degree of conversion of the resin luting agent. In the present study ATR (attenuated total reflection)-FTIR was used for the assessment of DC. A standard FTIR requires pulverizing the cured resin, which generates heat resulting, is promotion of polymerization, hence influencing the accuracy of DC measurement. In addition, in order to simulate clinical condition, the resin specimens had 1mm thickness in contrast to previous studies. [30]

The results of this study showed a significant decrease in contraction stress and significant increase in degree of conversion with delayed photo activation of the resin luting agent. From a clinical point of view, delaying photoinitiation would help in improving the physical and chemical properties of the luting agent. In addition, it would improve the overall performance of the restoration by minimizing adhesive failure and microleakage in addition to enhancing the mechanical properties and biocompatibility of the luting agent. However the association between improvement of DC and PCS due to photo initiation delay and physical and mechanical properties of resin composite in-vitro and in-vivo need to be investigated. It has been reported that a 10 minutes delay in

polymerization in light cured resin resulted in a significant reduction of bond strength values. [40] It is noteworthy, that in the present study dual cured resin was employed. In addition, a 10-minute delay resulted in comparatively high DC and low PCS, however implementing such a time interval is not clinically pragmatic and its effects in-vitro and in-vivo are not known. In addition, studies comparing the influence of different time intervals of photo initiation on the properties of the material are recommended. Therefore, although it is suggested to delay photo-initiation of dual-cured resin luting agents as a clinical strategy, further investigations are warranted to identify a clinically feasible duration of interval, to achieve highest possible degree of conversion with minimal polymerization contraction stress and adequate physical and mechanical properties of resin composite.

5. Conclusion

Extending the stress relief period of a dual cured luting agent by delaying photo-initiation has a positive effect on PCS and DC values. The findings suggest delaying photo-initiation of dual-cured resin luting agents as a clinical strategy, to achieve highest possible degree of conversion with minimal polymerization contraction stress.

6. Acknowledgements

The authors gratefully acknowledge the statistical assistance provided by George Eckert and the technical assistance provided by Meaghan MacPherson.

7. References

1. Lee IB, An W, Chang J, Um CM. Influence of ceramic thickness and curing mode on the polymerization shrinkage kinetics of dual-cured resin cements. *Dent Mater.* 2008; 24:1141-7.
2. Piwowarczyk A, Lauer HC. Mechanical properties of luting cements after water storage. *Oper Dent.* 2003;28:535-42.
3. Peumans M, Van Meerbeek B, Lambrechts P, Vanherle G. Porcelain veneers: a review of the literature. *J Dent.* 2000;28:163-77.
4. Cook WD, Beech DR, Tyas MJ. Structure and properties of methacrylate based dental restorative materials. *Biomaterials.* 1985; 6:362-8.
5. Stansbury JW. Curing dental resins and composites by photopolymerization. *J Esthet Dent.* 2000; 12: 300-8.
6. Venhoven BA, de Gee AJ, Davidson CL. Polymerization contraction and conversion of light-curing BisGMA-based methacrylate resins. *Biomaterials.* 1993; 14:871-5.
7. Katona TR, Winkler MM. Stress analysis of a bulk-filled Class V light-cured composite restoration. *J Dent Res.* 1994; 73:1470-7.
8. Versluis A, Tantbirojn D, Douglas WH. Do dental composites always shrink toward the light? *J Dent Res.* 1998;77: 1435-45.
9. Winkler MM, Katona TR, Paydar NH. Finite element stress analysis of three filling techniques for class V light-cured composite restorations. *J Dent Res.* 1996; 75:1477-83.

10. Kinomoto Y, Torii M. Photoelastic analysis of polymerization contraction stresses in resin composite restorations. *J Dent.* 1998; 26:165-71.
11. Bausch JR, de Lange K, Davidson CL, Peters A, de Gee AJ. Clinical significance of polymerization shrinkage of composite resins. *J Prosthet Dent.* 1982; 48:59-67.
12. Davidson CL, de Gee AJ, Feilzer A. The competition between the composite-dentin bond strength and the polymerization contraction stress. *J Dent Res.* 1984;63: 1396-9.
13. Palin WM, Fleming GJ, Nathwani H, Burke FJ, Randall RC. In vitro cuspal deflection and microleakage of maxillary premolars restored with novel low-shrink dental composites. *Dent Mater.* 2005; 21: 324-35.
14. Feilzer AJ, Dooren LH, de Gee AJ, Davidson CL. Influence of light intensity on polymerization shrinkage and integrity of restoration-cavity interface. *Eur J Oral Sci.* 1995;103:322-6.
15. Petrovic LM, Drobac MR, Stojanac ILj, Atanackovic TM. A method of improving marginal adaptation by elimination of singular stress point in composite restorations during resin photo-polymerization. *Dent Mater.* 2010;26:449-55.
16. Yamamoto T, Nakamura Y, Nishide A, Kubota Y, Momoi Y. Contraction stresses in direct and indirect composite restorations compared by crack analysis. *J Adhes Dent.* 2013; 15:47-54.
17. Puckett AD, Fitchie JG, Kirk PC, Gamblin J. Direct composite restorative materials. *Dent Clin North Am.* 2007;51: 659-75.

18. Hofmann N, Denner W, Hugo B, Klaiber B. The influence of plasma arc vs. halogen standard or soft-start irradiation on polymerization shrinkage kinetics of polymer matrix composites. *J Dent.* 2003; 31: 383-93.
19. Lim BS, Ferracane JL, Sakaguchi RL, Condon JR. Reduction of polymerization contraction stress for dental composites by two-step light-activation. *Dent Mater.* 2002; 18: 436-44.
20. Vandewalle KS, Roberts HW, Andrus JL, Dunn WJ. Effect of light dispersion of LED curing lights on resin composite polymerization. *J Esthet Restor Dent.* 2005;17:244-54;
21. Silikas N, Eliades G, Watts DC. Light intensity effects on resin-composite degree of conversion and shrinkage strain. *Dent Mater.* 2000; 16: 292-6.
22. Watts DC, al Hindi A. Intrinsic 'soft-start' polymerisation shrinkage-kinetics in an acrylate-based resin-composite. *Dent Mater.* 1999; 15: 39-45.
23. Asmussen E. Restorative resins: hardness and strength vs. quantity of remaining double bonds. *Scand J Dent Res.* 1982; 90: 484-9.
24. Santini A. Current status of visible light activation units and the curing of light-activated resin-based composite materials. *Dent Update.* 2010 ;37:214-6, 218-20, 223-7.
25. Gajewski VE, Pfeifer CS, Fróes-Salgado NR, Boaro LC, Braga RR. Monomers used in resin composites: degree of conversion, mechanical properties and water sorption/solubility. *Braz Dent J.* 2012;23:508-14.

26. Ferracane, J.L., Elution of leachable components from composites. *J Oral Rehabil.* 1994; 21: 441-52.
27. Kloukos D, Pandis N, Eliades T. Bisphenol-A and residual monomer leaching from orthodontic adhesive resins and polycarbonate brackets: a systematic review. *Am J Orthod Dentofacial Orthop.* 2013;143:S104-12.
28. Yap AU, MS Soh, Siow KS. Effectiveness of composite cure with pulse activation and soft-start polymerization. *Oper Dent.* 2002; 27: 44-9.
29. Lu H, Stansbury JW, Bowman CN. Impact of curing protocol on conversion and shrinkage stress. *J Dent Res.* 2005; 84: 822-6.
30. Pegoraro TA, da Silva NR, Carvalho RM. Cements for use in esthetic dentistry. *Dent Clin North Am.* 2007;51: 453-71.
31. AL-Shammari MS. The effect of inhibitor concentration on polymerization characteristics of light-cured resin composites. May, 2007, Indiana University School Of Dentistry: Indianapolis. 148.
32. Causton BE, Miller B, Sefton J. The deformation of cusps by bonded posterior composite restorations: an in vitro study. *Br Dent J.* 1985; 159: 397-400.
33. Lutz F, Krejci I, Barbakow F. Quality and durability of marginal adaptation in bonded composite restorations. *Dent Mater.* 1991; 7: 107-13.
34. McCulloch AJ, Smith BG. In vitro studies of cuspal movement produced by adhesive restorative materials. *Br Dent J.* 1986; 161: 405-9.
35. Feilzer AJ, de Gee AJ, Davidson CL. Setting stresses in composites for two different curing modes. *Dent Mater.* 1993; 9: 2-5.

36. Braga RR, Ferracane JL. Contraction stress related to degree of conversion and reaction kinetics. *J Dent Res.* 2002; 81: 114-8.
37. Labella R, Lambrechts P, Van Meerbeek B, Vanherle G. Polymerization shrinkage and elasticity of flowable composites and filled adhesives. *Dent Mater.* 1999; 15:128-37.
38. Venhoven BA, de Gee AJ, Davidson CL. Light initiation of dental resins: dynamics of the polymerization. *Biomaterials.* 1996; 17: 2313-8.
39. Odian G. *Principles of Polymerization. Step Polymerization.* Fourth edition. 2004: John Wiley.
40. Tay FR, King NM, Suh BI, Pashley DH. Effect of delayed activation of light-cured resin composites on bonding of all-in-one adhesives. *J Adhes Dent.* 2001;3:207-25.

Figure Legends

Figure 1: Assembly for assessment of polymerization contraction stress (PCS). A, aligned quartz rods- B, Resin material- C, Light source - D, Tensometer assembly, A rectangular beam - E, LVDT (linear variable differential transformer) - F, Data Cable.

Figure 2: Comparison of mean PCS after photoinitiation, showing gradual decrease with increasing photo-initiation delay.

Figure 3: Polymerization contraction stress data distribution at 4 minutes curing delay for individual specimens (group C)

Figure 4: Polymerization contraction stress data distribution at 10 minutes curing delay for individual specimens (group F)

Figure 5: Comparison of mean DC, showing linear improvement with increasing delay in photo-initiation.

Table 1: Comparison among study groups for Polymerization Contraction Stress (PCS) (MPa)

Groups	Polymerization Parameters	N	Mean	SD	SE	Min	Max
A	0 min delay	10	3.216 ^a	0.081	0.036	3.112	3.286
B	2 min delay	10	3.152 ^{ab}	0.083	0.037	3.046	3.259
C	4 min delay	10	3.348 ^c	0.080	0.036	3.212	3.408
D	6 min delay	10	3.032 ^d	0.070	0.032	2.949	3.101
E	8 min delay	10	2.526 ^e	0.069	0.031	2.434	2.608
F	10 min delay	10	2.444 ^{ef}	0.079	0.036	2.359	2.552
G	Chemical cure	10	1.944 ^g	0.083	0.037	1.875	2.068

The same superscript letters indicate no statistical differences ($p > 0.05$).

Table 2: Comparison among study groups for Degree of Conversion by Peak Area

Groups	Polymerization Parameters	N	Mean	SD	SE	Min	Max
H	0 min delay	10	0.553 ^a	0.015	0.007	0.538	0.571
I	2 min delay	10	0.648 ^b	0.015	0.007	0.632	0.666
J	4 min delay	10	0.688 ^c	0.022	0.010	0.656	0.712
K	6 min delay	10	0.687 ^{cd}	0.031	0.014	0.655	0.724
L	8 min delay	10	0.741 ^e	0.017	0.007	0.719	0.766
M	10 min delay	10	0.788 ^f	0.022	0.010	0.766	0.819
N	Chemical cure	10	0.538 ^{ag}	0.019	0.009	0.508	0.557

The same superscript letters indicate no statistical differences ($p > 0.05$).

Figures

Figure 1

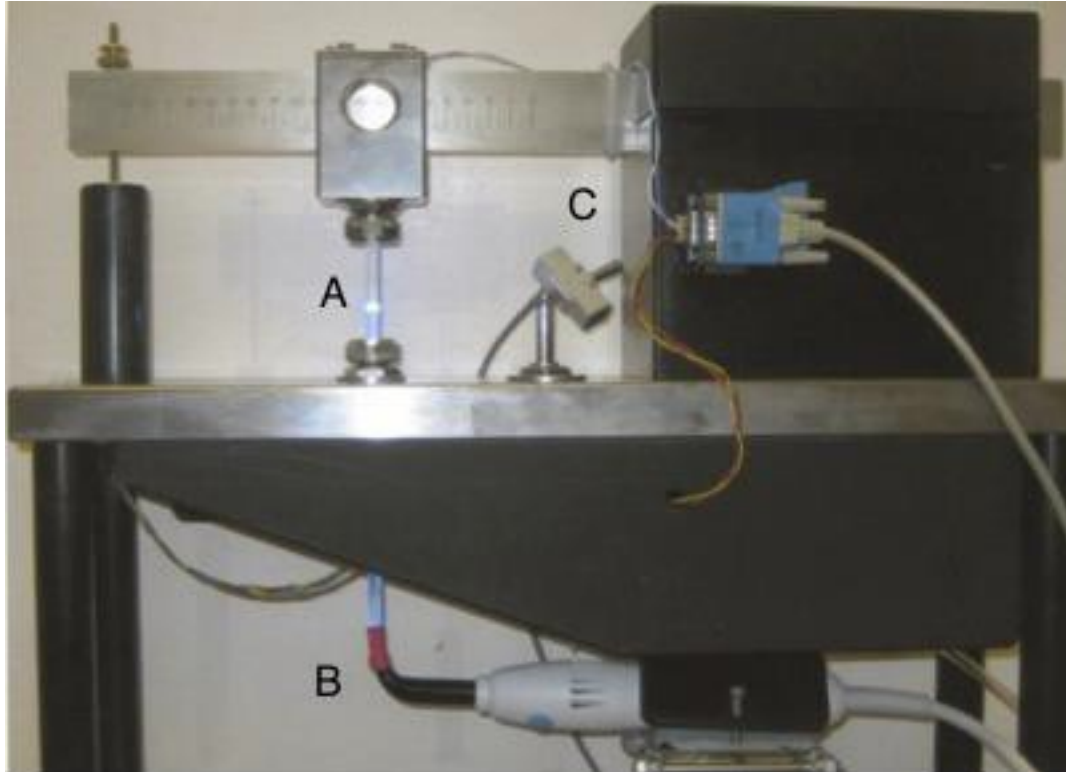


Figure 2

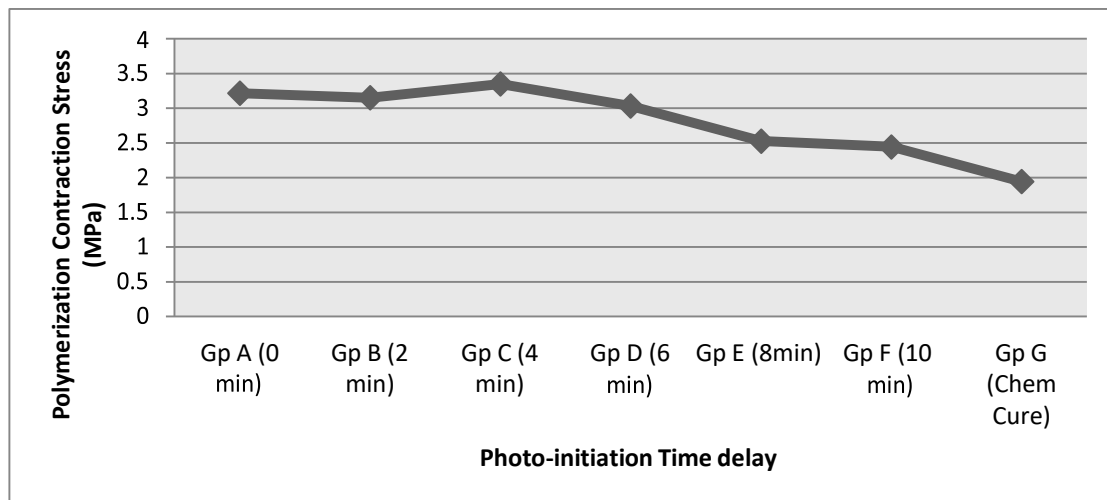
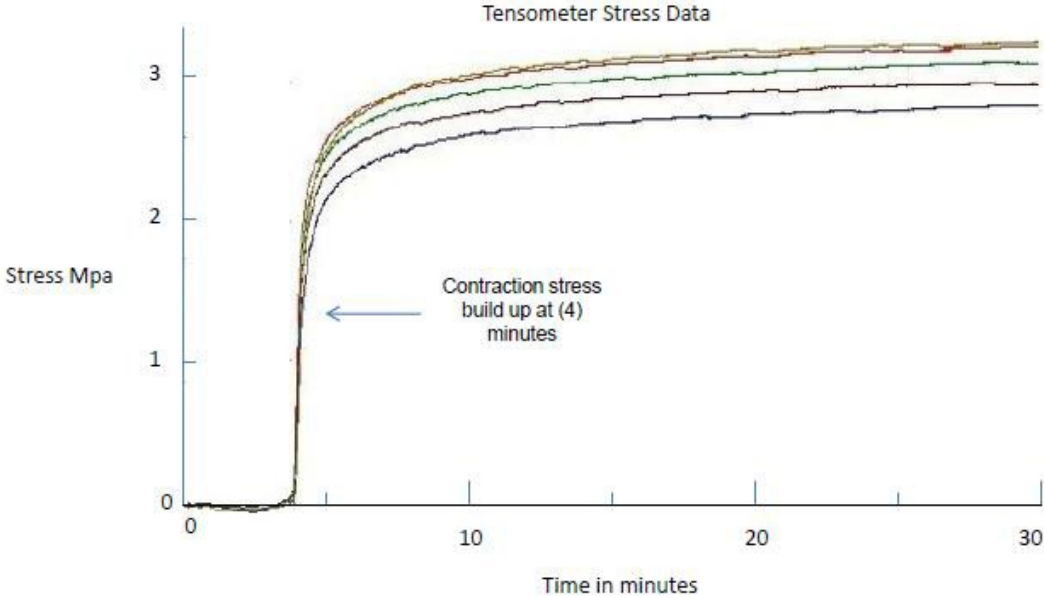
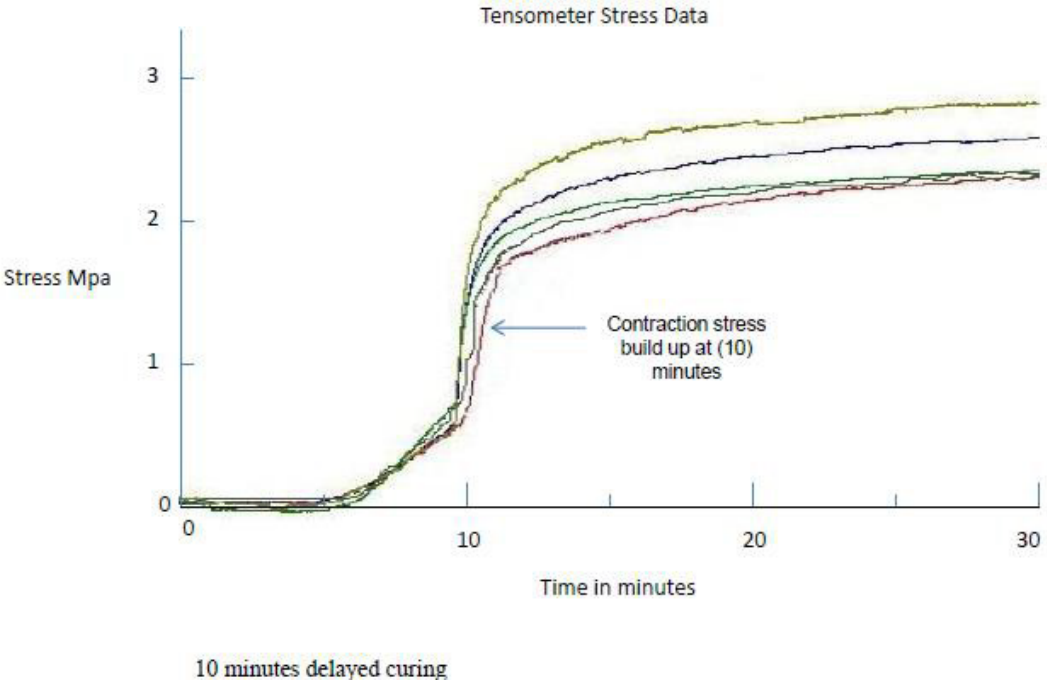


Figure 3



4 minutes delayed curing
Figure 5

Figure 4



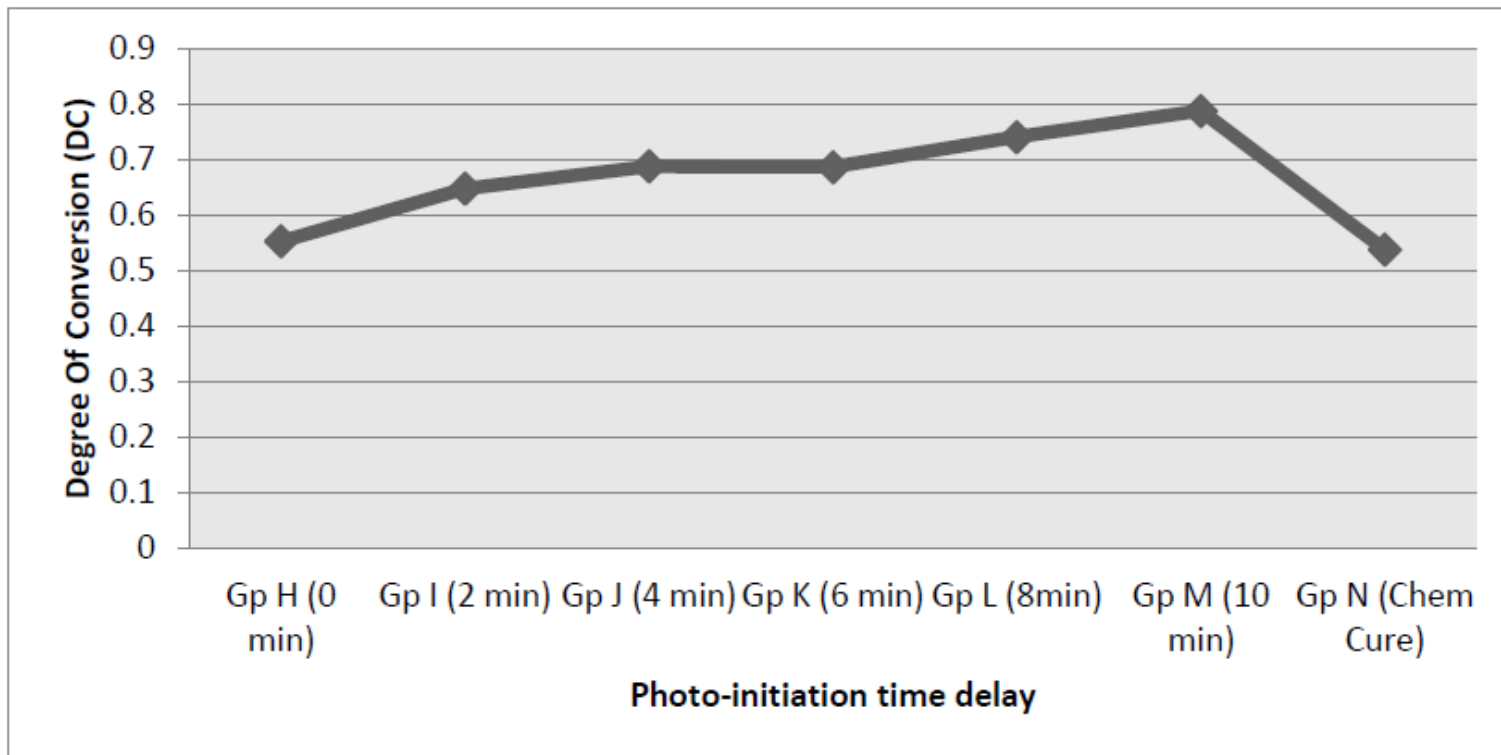


Figure 5