Pulse-delay Curing: Influence of Initial Irradiance and Delay Time on Shrinkage Stress and Microhardness of Restorative Composites

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Clinical Relevance

New photoactivation protocols need to be tested before being recommended for clinical use. This study suggests that pulse-delay curing may be an efficient way to reduce polymerization shrinkage stress without compromising degree of conversion or polymer network structure.

SUMMARY

Objectives: Evaluate the influence of pulse-delay curing on shrinkage stress and microhardness of 2 restorative composites (Herculite XRV and Tetric Ceram). Methods: Two pulse irradiances (500 and 100 mW/cm²) were applied for 1 or 5 seconds, respectively (radiant exposure = 0.5 J/cm²). In both cases, photoactivation was completed applying 500 mW/cm² for 39 seconds after a delay time of 0, 1 or 3 minutes. Shrinkage stress was monitored for 10 minutes in specimens 5-mm in diameter by 1-mm in height. Knoop hardness (KHN) was used to estimate the degree of conversion 10 minutes after photoactivation and after 48 hours of storage in distilled water (37°C) in specimens with similar geometry and dimensions. Additional KHN readings after 48 hours of storage in ethanol (37°C) were used to estimate polymer structure. The results were evaluated using ANOVA/Tukey test and Student *t*-test (α=0.05). Results: For Tetric Ceram, 3-minute delay led to stress reduction compared to continuous curing at 500 mW/cm² (4.7±0.6 MPa and 7.0±1.3 MPa, respectively). At 100 mW/cm², 1 minute delay was enough to cause significant stress reduction (5.2±0.5 MPa). For Herculite, the pulse with 3 minute delay led to stress reduction compared to no delay for both irradiances (100 mW/cm²: 6.3±0.5 MPa and 7.8±0.8 MPa, respectively; 500 mW/cm²: 6.4±0.3 MPa and 7.8±0.7 MPa, respectively). At 10 minutes, only small differences in microhardness were observed for both materials. No differences were found after water and ethanol storage (*p*>0.05). Conclusions: The composites behaved differently when subjected to pulse curing. Stress reduction was influenced by delay time but not by pulse irradiance. KHN results suggest that similar degrees of conversion and polymer structure were achieved with the photoactivation methods tested.

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INTRODUCTION

As resin composites undergo polymerization, restriction imposed by adhesion to the cavity walls results in shrinkage stresses that may be transferred to the tooth/restoration interface.[1-2] Depending on the magnitude of such stresses and the bond strength between the adhesive system and tooth substrate, problems, such as debonding, cusp deflection or cracks in enamel, may occur.[3-6]

In the early stages of the reaction, volumetric contraction may be compensated for by viscous flow of the composite.[7-8] However, at very low degrees of conversion (around 1%), development of a crosslinked network (gel point) reduces flow capacity and contraction stresses become apparent.[9-10] After gelation, a certain amount of stress relief is still possible through chain relaxation. However, as the reaction continues and the material reaches the vitrification point, stress relief is no longer possible and internal stress increases significantly.[11] Since viscous flow and chain relaxation are time-dependent phenomena, the longer the material stays in the pre-gel and pre-vitrification stages, the lower the shrinkage stresses will be.[11-12]

Such arguments have been used in the development of photoactivation protocols, which serve as alternatives to high irradiance continuous curing.[3,5] Generally speaking, these methods lead to the formation of a reduced number of polymer growth centers, reducing the reaction rate and increasing the opportunity for flow before the vitrification stage.[13]

Among the photoactivation protocols suggested, those using an initial pulse with radiant exposure up to 1 J/cm^2 seem to be the most efficient in reducing shrinkage stress.[13-16] Several authors have tested initial irradiances between 100 and 650 mW/cm^2 when evaluating the influence of pulse-delay curing on shrinkage stress and other properties of composites.[5,13-14,17] Previous studies have reported a decrease in microleakage[5] and shrinkage stress[13-14] without compromising the degree of conversion. Recently, other studies have reported a trend toward higher softening in ethanol for polymers formed by pulse-delay curing, suggesting that a polymer with a more linear structure and reduced crosslinking density was formed.[17-18] This could compromise the longevity of the restoration.

Ideal irradiance of the initial pulse remains a controversial matter among authors. Lower initial irradiance would be expected to favor reduced reaction rates, leading to more significant stress reduction.[19] Indeed, a previous study verified that higher polymerization stress reduction (between 12% and 27% when compared to the high irradiance continuous mode) was obtained with irradiances as low as 60 mW/cm^2 and exposure times of 5 seconds for the initial pulse.[15]

Another important parameter is delay time between irradiances. During the dark period, polymerization reaction still occurs, but at a reduced rate.[15] Therefore, longer delay periods between pulses would increase the possibility for viscous flow and chain relaxation. Significant reductions in shrinkage stress and microleakage have been reported for pulse-delay methods, with dark periods varying from 1 to 5 minutes.[5,15] Nevertheless, some authors believe that the period required for significant relaxation to occur is longer than that usually employed for pulse-delay photoactivation, suggesting that shrinkage stress reduction obtained with these methods is reduced due to a lower degree of conversion and, consequently, lower shrinkage.[11] However, similar degrees of conversion and polymerization shrinkage have been shown for certain composites using pulse-delay and continuous cure with the same total radiant exposure.[15]

Since stress reduction provided by pulse-delay curing should not be accomplished at the expense of either the degree of conversion or polymer structure, it is important to evaluate the effect of the photoactivation mode on the quality of the polymer formed. Therefore, this study evaluated the influence of irradiance of the initial pulse and delay between pulses on the shrinkage stress and microhardness of 2 commercially available composites. Microhardness was used to indirectly evaluate the degree of conversion 10 minutes after photoactivation and after 48 hour storage in distilled water. Also, crosslinking density was indirectly assessed by comparing microhardness values before and after an additional 48 hours of storage in ethanol.

METHODS AND MATERIALS

Table 1 describes the composition of the 2 microhybrid composites tested (Tetric Ceram/Ivoclar-Vivadent, Schaan, Lichtenstein and Herculite XRV/SDS-Kerr, Orange, CA, USA). For each material, 6 experimental groups were defined according to initial pulse irradiance (100 mW/cm^2 x 5 seconds or 500 mW/cm^2 x 1 second) and delay between pulses (0, 1 or 3 minutes). In all groups, a second irradiation of 500 mW/cm^2 x 39 seconds was applied, so that the total radiant exposure (energy dose) was approximately 20 J/cm^2.

Table 1: *Materials Used in This Study (information provided by the manufacturer)*			
Material	**Manufacturer**	**Composition**	**Batch #**
Tetric Ceram	Ivoclar Vivadent Schaan, Lichtenstein	Bis-GMA, UDMA and TEGDMA; filler (0.04–3 µm; 60% vol)	F57791
Herculite XRV	Kerr Corporation Orange, CA, USA	Bis-GMA and TEGDMA; filler (59% vol)	301240

Shrinkage Stress Test

The flat ends of glass rods 5-mm in diameter and 13-mm in length were sandblasted with alumina (250 µm), silanated (3M ESPE, St Paul, MN, USA), then coated with 1 layer of unfilled resin (SBMP Plus, bottle 3; 3M ESPE) and photoactivated for 30 seconds. One of the glass rods had its lateral surface protected by Scotch tape; it was then attached to a chuck connected to the load cell of a universal testing machine (Instron model 5565, Canton, MA, USA). The other rod was attached to a steel fixture that was connected to the other end of the testing machine; the steel fixture allowed the tip of the light curing unit (VIP, BISCO Inc) to be kept in contact with the opposing side of the glass rod. The composite was placed on the prepared surfaces between 2 rods, using a 1-mm fixed distance (Figure 1). Output irradiance was increased by 100 mW/cm^2 to ensure that irradiance, reaching the composite through the glass, matched the values described above. Irradiance was periodically checked using a radiometer (Model 100, Demetron Res Corp Danbury, CT, USA). An extensometer (Instron, Canton, MA, USA) was attached directly to the glass rods in order to keep the specimen height constant, simulating a low compliance situation. System compliance was estimated to be 7.9 x 10^{-6} mm/N.[20] Maximum contraction force was recorded after 10 minutes. Maximum stress was obtained by dividing maximal force by the cross-sectional area of the glass rod. Five specimens were tested for each experimental group.

Microhardness Test

Specimens 5-mm in diameter and 1-mm in height (n=3) were built by placing a plastic mold between 2 Mylar strips, then placing this set between 1-mm glass slabs. A total of 10 Knoop indentations (200 g x 10 seconds; HMV-2T, Shimadzu Co, Kyoto, Japan) were performed on the irradiated surface 10 minutes after photoactivation. Two other series of indentations were carried out on the same specimens after immersion in distilled water for 48 hours at 37°C and after a second 48 hour storage period in 99.3% ethanol at 37°C (Labsynt Ltda, Diadema, SP, Brazil).

Statistical Analysis

The materials were analyzed separately. Shrinkage stress data were analyzed separately by 1-way ANOVA/Tukey test for each pulse irradiance. Differences in irradiance of the initial pulse for each delay time were evaluated using Student's *t*-test. Microhardness data were analyzed separately for each storage period using 2-way ANOVA/Tukey test. In all cases, a global significance level of 5% was used.

RESULTS

Preliminary analyses of stress data using 2-way ANOVA revealed that irradiance of the initial pulse was not significant (*p*=0.443). Therefore, in order to avoid unnecessary comparisons, 1-way ANOVA and Student's *t*-test were used. For Tetric Ceram (Table 2), when 100 mW/cm^2 was used, the specimens which were photoactivated with no delay between pulses (6.4 ± 0.8 MPa) presented higher stress values compared to those cured with either 1- or 3-minute delay (5.2 ± 0.5 and 4.9 ± 0.3 MPa, respectively). For 500 mW/cm^2 pulse, the stress values obtained with the continuous method (7.0 ± 1.3 MPa) were statistically higher than those obtained by the 3-minute delay specimens (4.7 ± 0.6 MPa), while 1-minute delay resulted in stress values similar to both (5.6 ± 0.7 MPa). For Herculite (Table 3), when 100
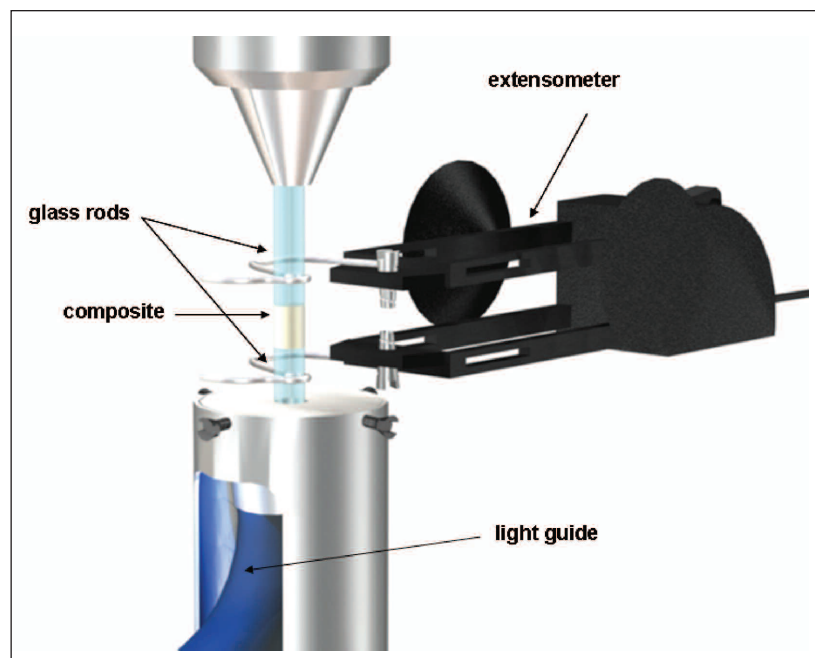

Figure 1. *Shrinkage stress test apparatus.*

Table 2: *Shrinkage Stress Averages and Standard Deviations (MPa) for Tetric Ceram Under Different Curing Protocols*

Initial Irradiance	Delay Between Pulses		
	No Interval	1 Minute	3 Minutes
500 mW/cm² x 1 second	7.0 (1.3) Aa	5.6 (0.7) ABa	4.7 (0.6) Ba
100 mW/cm² x 5 seconds	6.4 (0.8) Aa	5.2 (0.5) Ba	4.9 (0.3) Ba

Upper case letters refer to comparisons within the same row (1-way ANOVA/Tukey test). Lower case letters refer to comparisons within the same column (Student's t-test). Values followed by the same letter are not statistically different (p>0.05).

mW/cm² initial irradiance was used, the stress values obtained by specimens photoactivated with no delay between pulses (7.8 ± 0.8 MPa) were statistically higher than those cured using a 3-minute delay (6.3 ± 0.5 MPa), while 1-minute delay resulted in stress values similar to both (7.2 ± 0.5 MPa). The same trend was observed with 500 mW/cm² initial irradiance, where no delay specimens presented higher stress compared to the 3-minute delay group (7.8 ± 0.7 and 6.4 ± 0.3 MPa, respectively), while 1-minute delay resulted in stress values similar to both (6.9 ± 1.2).

Knoop hardness observed at 10 minutes showed that for Tetric Ceram, the interaction between initial pulse irradiance and delay time was significant ($p=0.026$), as was the delay time ($p=0.003$) (Table 4). The interaction was significant because of the lower hardness values obtained by the specimens photoactivated with the high irradiance pulse and 1-minute delay (24.7 ± 1.6) when compared to the same irradiance without delay (29.0 ± 1.4). For Herculite (Table 5), at 10 minutes, only the delay time was significant ($p=0.017$). The higher hardness values were observed for the continuous method (38.3 ± 1.7) when compared to the pulse-delay method (1 minute: 35.3 ± 1.1 and 3 minutes: 35.0 ± 2.5).

There was no statistical difference among the experimental groups of either composite after 48 hours of storage in distilled water ($p>0.05$). After an additional 48 hours of storage in ethanol, there was also no statistical difference among groups for Tetric Ceram ($p>0.05$). As for Herculite, ANOVA showed significance for delay time ($p=0.03$), although the Tukey test was not able to detect any difference.

DISCUSSION

For both materials used in this study, pulse-delay curing led to a reduction in shrinkage stress values when compared to continuous light-curing methods. Other authors reported similar results, attributing this to a prolonged pre-gel phase that would allow the material to flow in order to accommodate the volumetric reduction.[13,15] More recently, other authors argued that the observed stress relief would more appropriately be related to chain relaxation than to viscous flow.[11]

Tetric Ceram presented higher stress relief with use of the pulse-delay protocol when compared to Herculite. When 500 mW/cm² initial irradiance was used, 34% stress reduction was observed for Tetric Ceram between no delay and a 3-minute delay, while a reduction of only 19% was observed for Herculite. For 100 mW/cm² initial irradiance, a significant 19% relief was achieved by Tetric Ceram with 1 minute delay, while the same percentage could only be noticed for Herculite when the 3-minute delay was used. This might be due to either a higher degree of conversion or to a higher elastic modulus for Herculite. The percentage of stress

Table 3: *Shrinkage Stress Average and Standard Deviation (MPa) for Herculite Under Different Curing Protocols*

Initial Irradiance	Delay Between Pulses		
	No Interval	1 Minute	3 Minutes
500 mW/cm² x 1 second	7.8 (0.7) Aa	6.9 (1.2) ABa	6.4 (0.3) Ba
100 mW/cm² x 5 seconds	7.8 (0.8) Aa	7.2 (0.5) ABa	6.3 (0.5) Ba

Upper case letters refer to comparisons within the same row (1-way ANOVA/Tukey test). Lower case letters refer to comparisons within the same column (Student's t-test). Values followed by the same letter are not statistically different (p>0.05).

Table 4: *Knoop Microhardness and Standard Deviations Observed for Tetric Ceram*

Initial Irradiance	Delay Between Pulses	10 Minutes	48 Hours/ Water	+48 Hours/ Ethanol	Reduction %
500mW/cm² x 1 second	No delay	29.0 (1.4)a	36.5 (1.7)a	22.4 (2.2)a	39a
	1 minute	24.7 (1.6)c	36.5 (1.8)a	23.8 (1.1)a	35a
	3 minutes	26.2 (0.8)a,b,c	34.9 (0.9)a	22.5 (2.8)a	36a
100mW/cm² x 5 seconds	No delay	28.0 (0.6)a,b	38.7 (2.4)a	24.4 (0.3)a	37a
	1 minute	27.4 (1.1)a,b,c	37.0 (0.9)a	24.2 (0.8)a	35a
	3 minutes	26.0 (0.8)b,c	34.8 (3.1)a	22.1 (1.3)a	36a

Values followed by the same letter for the same storage period are statistically similar (p>0.05).

Table 5: *Knoop Microhardness and Standard Deviations Observed for Herculite XRV*

Initial Irradiance	Delay Between Pulses	10 Minutes	48 Hours/ Water	+48 Hours/ Ethanol	Reduction %
500mW/cm² x 1 second	No delay	39.0 a (1.7)	47.4 (1.9)a	31.8 a (2.1)	33a
	1 minute	35.6 (1.2)a,b	44.7 (1.9)a	29.3 (1.2)a	35a
	3 minutes	34.0 (2.8)b	45.6 (2.8)a	30.5 (1.7)a	33a
100mW/cm² x 5 seconds	No delay	37.5 (1.6)a,b	48.6 (1.7)a	33.2 (1.5)a	32a
	1 minute	35.0 (1.1)a,b	46.8 (2.8)a	30.2 (1.2)a	35a
	3 minutes	36.0 (2.2)a,b	45.9 (1.3)a	31.2 (1.5)a	31a

Values followed by the same letter for the same storage period are statistically similar (p>0.05).

relief observed in this study was comparable to the 26% reduction described in a previous study that used a similar test set-up, with an initial irradiance of 0.3 J/cm² and a delay time of 2 minutes.[15] The different behaviors presented by the 2 composites may suggest that the stress relief effectiveness of different pulse-delay protocols might be influenced by material composition. Since this could be due to a number of different factors, such as monomer blending, photoinitiator concentrations or filler content, the development of a universal "soft-start" curing protocol, which would cause significant stress relief for most commercial composites, is a challenging task.

Shrinkage stress results were not influenced by initial irradiance, most probably because radiant exposure was similar in both cases (0.5 J/cm²), which would lead to the formation of a similar number of initiation sites.[21] On the other hand, because the rate of reaction (the amount of conversion that takes place as a function of time) is directly related to irradiance,[19] the higher initial irradiance would be expected to result in higher stress values.[15] In all likelihood, the difference between the irradiances used in this study would have to be higher to evidence the effect of the curing rate of the initial pulse on stress development.

For both composites, at least a trend towards a reduction in microhardness was observed at 10 minutes for the pulse-delay groups. Considering that the degree of conversion and microhardness are well correlated for a given composite,[22-23] the lower stress values observed for these groups may be explained by lower conversion at 10 minutes. However, after being stored in distilled water for 48 hours, all groups of both composites showed similar microhardness, suggesting that the curing protocol did not influence the extent of polymerization that occurred during storage ("dark cure").[24] It is

not possible to predict, however, whether stress values for pulse-delay cure would match those obtained for continuous cure a few hours after photoactivation. Similar degrees of conversion were expected, since previous studies have verified that physical properties and degree of conversion of resin materials are related to total radiant exposure.[25-26]

Ethanol storage for 48 hours caused a reduction in microhardness for both composites, regardless of curing mode. This reduction in hardness has been described previously and is likely due to the plasticizing effect of ethanol on the crosslinked polymer structure.[27] After ethanol storage, microhardness values were similar for all groups (continuous or pulsated) for both composites, indicating that the polymer structure was not affected by the photoactivation method. However, other authors have reported that pulse-delay curing leads to the formation of polymer networks that are more prone to solubility in ethanol.[17,28] This difference might be explained by different monomer blending, photoinitiator and photoinhibitor concentrations or filler content that may have influenced the behavior of the composite.[29-32]

CONCLUSIONS

Pulse-delay curing. associated with a 3-minute delay between irradiances, resulted in lower shrinkage stress without compromising conversion or susceptibility to softening in ethanol for 2 different dental composites. However, the percentage of stress reduction seems to be related to compositional characteristics of the resin composite.

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