DENTAL MATERIALS 37 (2021) 1772–1782

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Thermal shrinkage reveals the feasibility of pulse-delay photocuring technique

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ARTICLE INFO

Article history:
Accepted 13 September 2021

Keywords:
Polymerization stress
Thermal shrinkage
Radiant exposure
Exposure reciprocity law
Additive manufacturing

ABSTRACT

Objectives. To resolve the feasibility of the pulse-delay photocuring technique as a clinical strategy for reducing the detrimental polymerization stress induced in dental composites during the photocuring process.

Methods. Model dental composites with high and low-filler contents were cured with the pulse-delay photocuring technique using different combinations of photocuring variables (irradiance, exposure time, and delay time). Irradiance used ranged from 0.1 W/cm^2 to 4 W/cm^2. The exposure time of the first pulse varied from 0.2 s to 27.2 s and the delay times ranged from 10 s to 120 s. The radiant exposure was varied from 4 J/cm^2 to 20 J/cm^2. A cantilever-beam based instrument (NIST Standards Reference Instrument 6005) was used to implement the photocuring technique for the measurement of the polymerization properties (the degree of monomer conversion, polymerization stress induced due to shrinkage, and temperature change due to the reaction exotherm and curing light absorbance) simultaneously in real-time. These properties were compared with those obtained using the conventional photocuring technique (i.e., using a constant irradiance for a fixed exposure time, a uniform exposure).

Results. There exists a minimum radiant exposure, such that a reduction in the polymerization stress can be achieved without sacrificing the degree of monomer conversion by using the pulse-delay over the conventional photocuring technique. More specifically, stress reductions of up to 19% and 32% was observed with the pulse-delay when compared with the conventional photocuring technique at an irradiance of 0.5 W/cm^2 and 4 W/cm^2, respectively. The reduction occurred when the exposure time of the first pulse was greater than, but closer to, the gelation time (i.e., lower than the vitrification time) of the composite, regardless of the delay time used. Lower thermal shrinkage (contraction) during the post-curing time, rather than the stress relaxation during the delay time or lower degree of monomer conversion as claimed in the literature, is the cause of the reduction in the polymerization stress.

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https://doi.org/10.1016/j.dental.2021.09.007
0109-5641/Published by Elsevier Inc. on behalf of The Academy of Dental Materials.

Significance. The study clarifies a long-standing confusion and controversy on the applicability of the pulse-delay photocuring technique for reducing the polymerization stress and promotes its potential clinical success for dental restorative composites.

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1. Introduction

In restorative dentistry, the conventional photocuring technique for photocurable composites involves continuous exposure to a light-curing unit of a fixed irradiance for a given amount of time [1–3]. Shrinkage due to the conversion of monomer to polymer, often reported as the degree of monomer conversion (DC), during the photocuring process results in the undesired polymerization stress (PS) [4–6]. Several studies have shown that a slow photocuring process provides time for sufficient stress relaxation in the composite and consequently achieves an overall reduction in the PS without jeopardizing the DC [7–9]. Accordingly, several alternative photocuring techniques, sometimes collectively termed as soft-start techniques, have been proposed [8,10,11]. Of these techniques, the pulse-delay photocuring technique has been discussed intensively due to its potential ease of clinical adoption, as it does not necessarily require a special curing light with varying irradiance. This technique involves applying a first pulse of light with low radiant exposure (=irradiance × exposure time) followed by a delay time (light-curing unit off), then applying a second pulse of light with high radiant exposure [5,6,11–17]. It is claimed that the composite undergoes a stress relaxation (decrease in stress) during the delay time resulting in an overall reduction in the PS when compared with the conventional photocuring technique [4,5]. However, other studies refute this claim [13,18,19]. For instance, Lu et al. [18] simultaneously measured the DC and PS of a model composite having low-filler content and claimed that the PS reduction is due to a lower resultant DC, not the stress relaxation. Later, in a separate study by the same authors [20], they showed that the stress relaxation in the composite is minimal over the time scale (the delay time in the pulse-delay photocuring technique) involved in the clinical practice. Thus, different and conflicting claims on the pulse-delay photocuring technology have stirred up confusion and controversy for whether it can be properly used in response to the detrimental effect of polymerization stress on the performance of dental composites. The objective of this study is to resolve these controversies through scrutinizing the underlying mechanism for reducing the polymerization stress and advocate a better understanding of the pulse-delay photocuring technique.

In the current study, model composites comprised of a blend of traditional dimethacrylate monomers, bisphenol A glycidyl methacrylate and triethyleneglycol dimethacrylate, and commercial silanized micro-sized glass fillers with two different level of filler contents (high-filler and low-filler) were used to fulfil the objective. The composites contained a mixture of camphorquinone and ethyl 4-dimethylaminobenzoate as their visible-light initiator system. A highly sensitive cantilever beam-based instrument (NIST SRI 6005) [21,22] coupled with near-infrared spectroscopy and a microprobe thermocouple was used to examine the photocuring techniques. The instrument also has an integrated LED light-curing unit providing variations in the photocuring variables (irradiance and exposure time) for the conventional and the pulse-delay techniques. Our results indicate, irrespective of the photocuring technique used (conventional or pulse-delay), that a minimum radiant exposure (a prerequisite) is indeed needed to achieve an adequate polymerization (i.e., any further increase in the radiant exposure beyond the minimum will produce no significant increase in the DC). This prerequisite affirms the applicability of the exposure reciprocity law to dental composites [23], and at such radiant exposures only a meaningful comparison between the pulse-delay and conventional techniques can be made. Accordingly, a significant reduction in PS was observed for high-filler composites, which are clinically relevant, using the pulse-delay technique when compared with the conventional technique. This reduction in PS is not due to the stress relaxation during the delay time or a lower DC in the pulse-delay technique as reported in the literature, but due to a reduced thermal shrinkage (contraction) during the post-cure (i.e., post-irradiation, when the light-curing unit is turned off at the end of second pulse). The thermal contraction is incurred when the exothermic and the light absorbing heat dissipate to the surrounding tooth structure and atmosphere. For the low-filler composite (clinically irrelevant), a lower PS can be achieved with the pulse-delay comparing with the conventional technique, but the DC is sacrificed even when the prerequisite for the exposure reciprocity law is satisfied. Also, this reduction is due to not only a lower DC, but also a relatively lower thermal contraction when compared with conventional technique.

The study manifests one less discussed important feature that the thermal shrinkage induced from the heat dissipation plays an equally crucial role as the autogenous shrinkage induced from the double bond conversion in the development of the polymerization stress (PS). This is because that significant heat dissipation occurs near the end of conventional photocuring process, where the elastic modulus of composite reaches its highest value. Thus, the study promotes a better understanding of the PS development mechanism and clarifies discrepancies between those two photocuring techniques reported in the literature. Also, it provides basis to quantify the photocuring variables (the exposure time of the first pulse and the delay time) used in the pulse-delay technique, such that the thermal shrinkage can be manipulated and consequently the benefit of the pulse-delay technique can be significantly achieved. This benefit could become even more considerable when nanofillers and fibers [24] are intro-

duced in dental composites for enhancing their mechanical properties.

2. Materials and methods[†]

2.1. Materials

Two experimental composites were prepared to contain a 7:3 mass ratio of the conventional dental resins, namely, bisphenol A glycidyl dimethacrylate (BisGMA) and triethylene glycol dimethacrylate (TEGDMA) acquired from Esstech Inc., Essington, PA, USA. Camphorquinone (CQ, Sigma-Aldrich, Milwaukee, WI, USA) and ethyl 4-dimethylaminobenzoate (4E/EDAB, Sigma-Aldrich, Milwaukee, WI, USA) were used at 0.2% and 0.8% relative to resin mass, respectively, as the photoinitiation system. Silanated barium alumino borosilicate glass (BABG, mean particle size of 1 μm, donated by Dentsply-Caulk, Milford, DE, USA) was added in two proportions, 30% by mass (~18% by volume) and 75% mass (~52% by volume) relative to the net weight of composite. Fillers were blended with the resins using a centrifugal mixer (DAC 150FVZ, Flack-Tek Inc., Landrum, SC, USA) to ensure adequate mixing. The two composites will be abbreviated as 7B3T-30F (low-filler) and 7B3T-75F (high-filler) in this study here forth. Data collected were subjected to one-way analysis of variance; pairwise comparisons were done using the Holm-Sidak method. Statistical significance was accepted at $p \leq 0.05$. The analyses were performed using SigmaPlot version 14.0 (Systat Software Inc., San Jose, CA, USA).

2.2. Instrumentation

Composite specimens of disk shape (2.5 mm diameter, 2 mm height, C-factor = 0.625) were prepared. The polymerization properties (i.e., the degree of monomer conversion (DC), the polymerization stress (PS), and the temperature change (TC)) of the composites were measured using the NIST-developed cantilever-beam based standard reference instrument (NIST SRI 6005, Polymerization Stress Tensometer, design based on ANSI/ADA Technical Specification No. 150). The design of the instrument, compared with its previous version [25,26], follows the first principle of mechanics that provides much higher sensitivity and accuracy to the presence of shrinkage induced during polymerization [21]. The instrument is coupled with an in situ near-infrared spectrometer (NIRQuest512-2.2, Ocean Optics, Inc., Dunedin, FL, USA) in transmission mode and a microprobe thermocouple (0.1 mm diameter, Physitemp Instruments, Clifton, NJ, USA). As a result, DC, PS, and TC can be measured simultaneously in real-time unprecedently for clinically relevant dental composites. A more detailed description of the testing mechanics and instrument setup has been reported in our previous studies [21,22,27]. The composite specimens were placed at a location along the cantilever-beam at which the instrumental compliance was 0.33 μm/N to mimic the compliance of tooth cavities reported in the literature [28,29]. An LED curing light (blue light, peak at 460 nm wavelength, LZ1-10DB00, LED Engin, Mouser Electronics, Mansfield, TX, USA) system including a controller (6340 ComboSource, Arroyo Instruments LLC, San Luis Obispo, CA, USA) integrated into the instrument allows the precise delivery of irradiance for a specified amount of time.

After the measurement of the polymerization properties using the aforementioned cantilever-beam based instrument, the Vickers hardness test was carried out on composite samples. Prior to the test, the samples were stored in a dark dry environment under vacuum for two weeks, then they were polished under a sequence of SiC papers (Struers Inc., Westlake, OH, USA) of decreasing abrasiveness (P800, P1200, P2400, and P4000) under continuous water cooling. Afterward, the samples were rinsed and dried with compressed air, followed by storage under a dark dry vacuum environment for 24 h before the hardness test. The microhardness machine (Tukon 1202, Wilson Hardness, Norwood, MA, US) with an indentation load of 2.94 N (300 gf) was used for the measurement. The dwell time at a peak load of 15 s was used, and the indentation size was measured with a 50× objective.

2.3. Photocuring conditions

Fig. 1a and 1 b show schematics of light irradiation used and polymerization properties (the degree of monomer conversion, DC; the polymerization stress, PS; and the temperature change, TC) measured in the conventional and pulse-delay photocuring techniques, respectively, for dental composites. Primarily, two irradiances ($I_0 = 0.5$ W/cm^2 and 4 W/cm^2) were used, the exposure time of the first pulse (t_1) varied from 0.2 s to 27.2 s, the delay times (t_d) ranged from 10 s to 120 s; thus, the radiant exposure (RE) ranged from 4 J/cm^2 to 20 J/cm^2. For each combination at least three replicates were conducted. All the measurements and sample preparations were performed under a yellow light environment to minimize premature photopolymerization and at room temperature (~ 21 °C). Also, all measurements were recorded from 20 s before and 10 min after the initiation of the photocuring process.

3. Results

Fig. 2 shows the degree of monomer conversion (DC), obtained using the conventional photocuring technique for composite, ranging from 48.89% to 62.57% as the radiant exposure was varied from 4 J/cm^2 to 20 J/cm^2 at two irradiances ($I = 0.5$ W/cm^2 and 4 W/cm^2). Unless otherwise mentioned, all the results discussed here pertain to the high-filler composite (7B3T-75F). No statistically significant differences were observed between the DC with the two irradiances if the radiant exposure is greater than 12 J/cm^2. Also from the result, an adequate degree of conversion obtained using the conventional photocuring technique, denoted by DC_{CPT}, was determined. An adequate degree of conversion is defined here as a DC achieved with the conventional technique such that any further increase in

[†] Certain commercial materials, equipment, and software are identified in this manuscript in order to specify adequately the experimental and analysis procedures. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology (NIST) nor does it imply that they are necessarily the best available for the purpose.

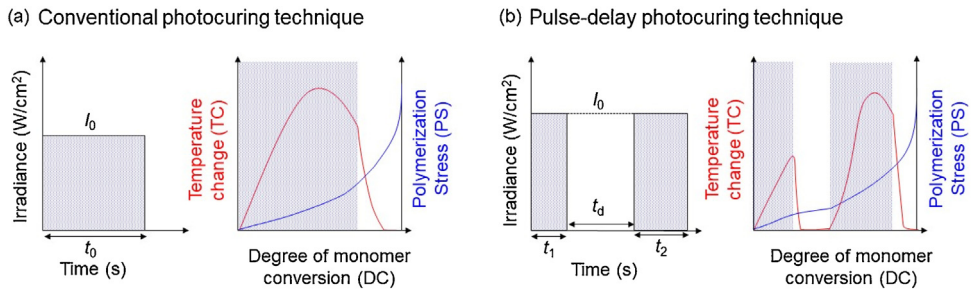

Fig. 1 – Schematics of light radiation and measured polymerization properties (i.e., DC, PS, and TC) for conventional (a) and pulse-delay (b) photocuring techniques. The shaded area corresponds to light curing unit being on. The radiant exposure (RE), =irradiance × exposure time, used in the conventional and the pulse-delay techniques are always the same, i.e., $RE = I_0t_0 = I_0t_1 + I_0t_2$, unless otherwise mentioned in the study. t_0 is the exposure time for the conventional technique. t_1, t_2 are the exposure times of the first and second pulse respectively for the pulse-delay technique. t_d is the delay time (during which the light-curing unit is off) between the first and second pulse of photo-cure. I_0 stands for the irradiation (in W/cm²) used in the photocuring techniques. Note: The irradiance of the first and second pulses for the pulse delay technique in (b) can in theory be different.

Table 1 – Vickers hardness of the bottom side, the side away from the light source, of the cylindrical composites after being cured with the conventional and pulse-delay photocuring technique for the 7B3T – 75F composite.

Irradiance, $I = 0.5$ W/cm²		Irradiance, $I = 4$ W/cm²	
Exposure time of first pulse, t_1 (s)	Hardness (GPa)[1]	Exposure time of first pulse, t_1 (s)	Hardness (GPa)[1]
40¶	0.83 ± 0.03^a	5¶	0.73 ± 0.02^a
1.6#	0.81 ± 0.03^a	0.2#	0.75 ± 0.01^a
3.2#	0.84 ± 0.02^a	0.4#	0.72 ± 0.02^a
6.4#	0.83 ± 0.01^a	0.8#	0.72 ± 0.03^a

¶ Represent conventional photocuring technique, thus, $t_0 = t_1$ (refer Fig. 1).
# Delay time (t_d) = 120 s was used for the pulse-delay photocuring technique.
[1] Values represent mean ± one standard deviation. Same small letter superscripts in each column represent statistical similarity ($p > 0.05$).

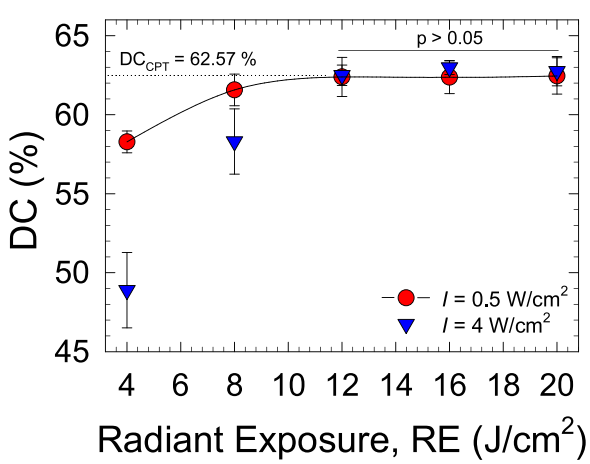

Fig. 2 – Degree of monomer conversion (DC) values obtained from the conventional photocuring technique as the radiant exposure (RE) was varied. Horizontal bar over data points represents no statistical significance ($p > 0.05$). DC_{CPT} is the plateaued value obtained by averaging the DC obtained with both the irradiances at RE of 12 J/cm², 16 J/cm², and 20 J/cm². Vertical bars shown represent one standard deviation and some of them may be smaller than the symbols used.

the radiant exposure will produce no significant increase in the conversion. The DC_{CPT} will be used as a benchmark when comparing the pulse-delay with conventional technique. The result shown in Fig. 3 indicates no statistically significant difference exists on the DC (i.e., $DC/DC_{CPT} \approx 1$) between the pulse delay and the conventional techniques as the exposure time of the first pulse (t_1) and the delay time (t_d) were varied at a fixed RE of 20 J/cm². For $I = 0.5$ W/cm², the t_1 ranged from 0.8 s to 27.2 s, and t_d ranged from 10 s to 120 s (Fig. 3a and 3 c). For $I = 4$ W/cm², the t_1 ranged from 0.2 s to 3.4 s, and t_d ranged from 10 s to 120 s (Fig. 3b and 3 d). Also, the Vickers hardness of the composites listed in Table 1, which generally correlates with the DC and the elastic modulus, further confirmed that no significant difference between the composite photocured with two photocuring techniques. However, if a lower RE (i.e. less than 12 J/cm²) was used for both the photocuring techniques, then the DC achieved was significantly lower than DC_{CPT}, unlike Fig. 3. This can be noticed from the result shown in Fig. 4. As the radiant exposure was increased from 4 J/cm² to 20 J/cm² for both the photocuring techniques, the DC was increased and leveled off to DC_{CPT}.

Fig. 5a and 5 b show the polymerization stress (PS) and temperature change (TC) as a function of the DC for both the photocuring techniques, respectively. The result shown in Fig. 5a indicates that no considerable stress relaxation occurs during the delay time (i.e., at DC ~ 37%), while a notable PS

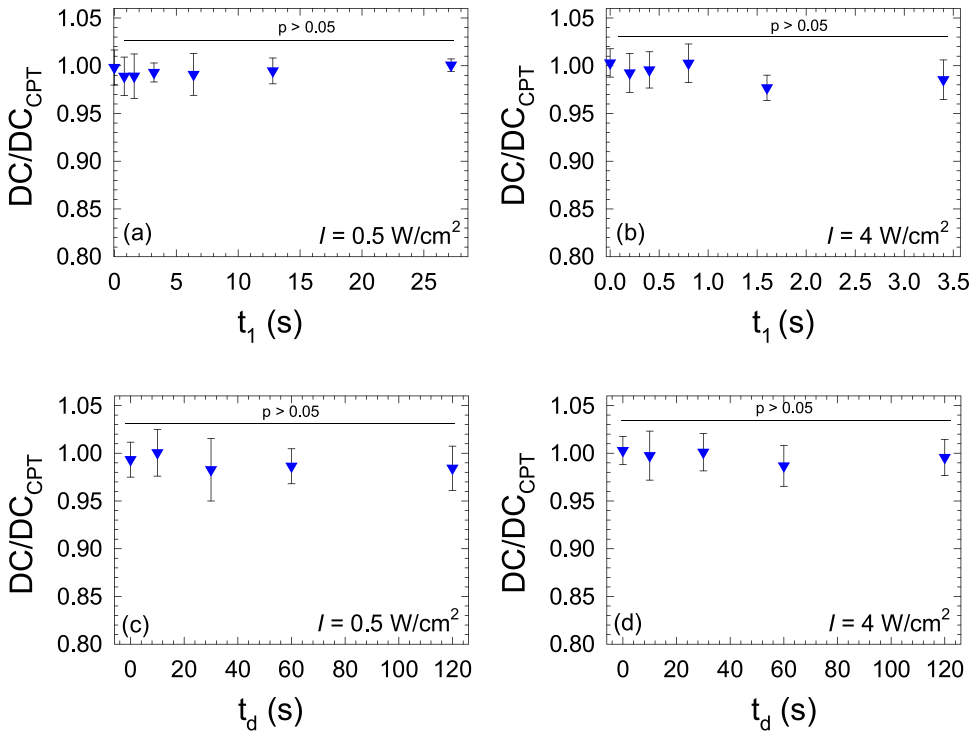

Fig. 3 – Normalized degree of monomer conversion (DC) obtained from the pulse-delay technique as the first exposure time (t_1) and delay time (t_d) were varied for the 7B3T-75F composite. The DC is normalized with the DC_{CPT} (=62.57%) value noted in Fig. 2. The radiant exposure (RE) was 20 J/cm^2 in all the figures. t_d of 120 s was used in (a) and (b). t_1 was 1.6 s for (c) and 0.2 s for (d), both being equivalent to the same radiant exposure of the first pulse (0.8 J/cm^2). Horizontal bar over data points represents no statistical significance ($p > 0.05$). Vertical bars shown represent one standard deviation and some of them may be smaller than the symbols used.

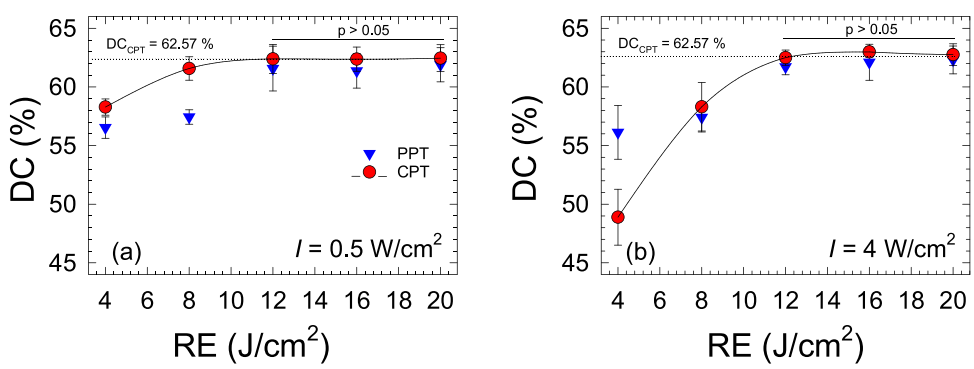

Fig. 4 – Degree of monomer conversion (DC) for the pulse-delay and the conventional photocuring technique as the radiant exposure (RE) was varied for the 7B3T–75F composite. Exposure time of first pulse (t_1, refer Fig. 1) equal to 1.6 s and 0.2 s were used in (a) and (b), respectively, both being equivalent to the same radiant exposure of the first pulse (0.8 J/cm^2). Delay time (t_d, refer Fig. 1), of 120 s was used for the pulse-delay photocuring technique at each RE in (a) and (b). DC_{CPT} is the plateaued value of DC with the conventional photocuring technique, Fig. 2. Horizontal bar over data points represents no statistical significance ($p > 0.05$). Vertical bars shown represent one standard deviation and some of them may be smaller than the symbols used.

reduction occurs at the late stage of polymerization in the pulse-delay comparing with conventional photocuring technique. This reduction is due to a much less temperature change (TC) produced in the pulse-delay technique, which significantly reduces the thermal shrinkage associated with the cooling during the post-cure (i.e., starting at DC∼ 50% shown in Fig. 5b). From Fig. 5c, one can clearly notice that PS induced in the pulse-delay photocuring technique is indistinguishable from that in the conventional photocuring technique until the TC of the pulse-delay photocuring technique diminishes to near zero (marked as 'X' in the figure). Afterwards, the PS of pulse-delay photocuring technique deviates to much lower values compared with that of conventional photocuring technique.

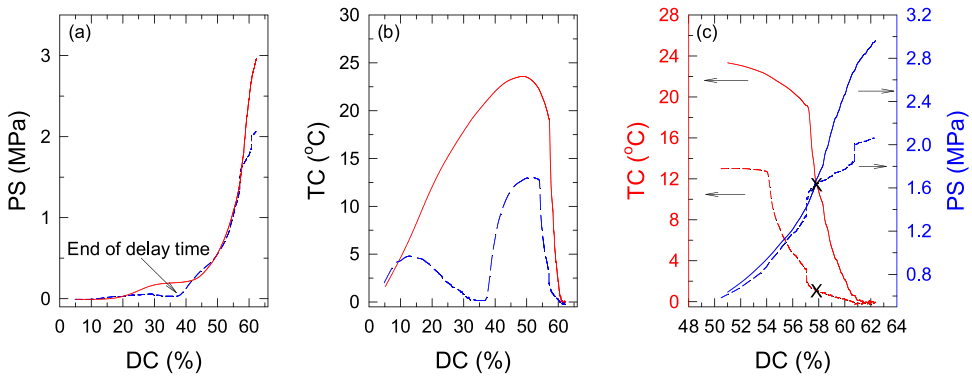

Fig. 5 – Polymerization stress (PS) and temperature change (TC) as a function of the degree of monomer conversion (DC) for the conventional and the pulse-delay photocuring techniques in (a) and (b), respectively, for the 7B3T-75F model composite. A subsection of (a) and (b), the PS and TC above DC of 50%, is plotted in (c). 'X' marks the point where the PS between the two photocuring techniques started to deviate significantly. For both the techniques, an irradiance of 4 W/cm^2 and a radiant exposure of 20 J/cm^2 were used. The exposure time of the first pulse (t_1) and the delay time (t_d) were 0.2 s and 120 s respectively for the pulse-delay photocuring technique. The curves shown here are mean values of three different experimental runs for each photocuring technique.

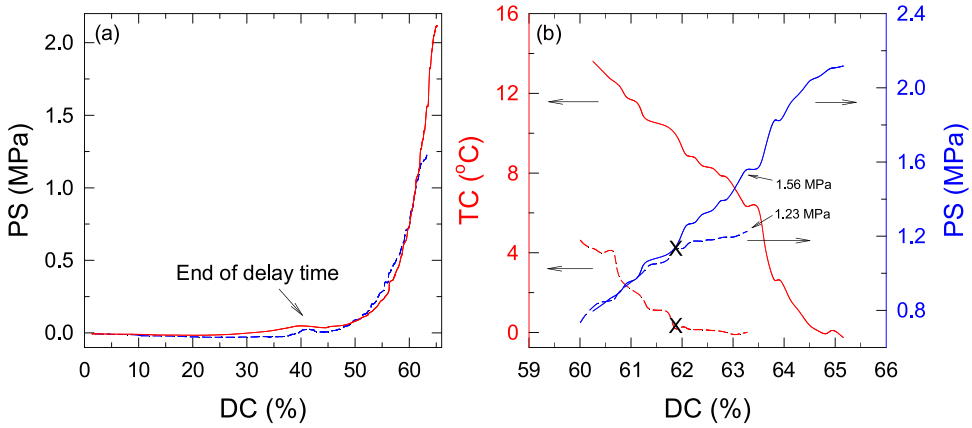

Fig. 6 – Solid and dashed curve represents polymerization stress (PS) with degree of monomer conversion (DC) for the conventional and pulse-delay photocuring technique (refer Table 2) respectively in (a) and (b) for the 7B3T-30F model composite. The PS and temperature change (TC) above DC of 60%, is plotted in (b). 'X' marks the point where the PS between the two photocuring techniques started to deviate significantly in (b). The curves shown here are mean values of three different experimental runs for each photocuring technique.

Table 2 – Degree of monomer conversion (DC), and polymerization stress (PS), peak temperature change (TC) values when the 7B3T-30F composite was cured with the conventional and the pulse-delay photocuring technique.

Photocuring Condition[1]	DC (%)[2]	PS (MPa)[2]	Peak TC (°C)[2,3]
0.45 W/cm^2 × 60 s	64.98 ± 0.57^a	2.13 ± 0.11^a	29.57 ± 1.70^a
0.1 W/cm^2 × 5 s, 120 s delay time, 0.45 × 60 s	62.83 ± 0.72^b	1.23 ± 0.05^b	14.21 ± 2.87^b

[1] The radiant exposure of the pulse-delay photocuring technique is greater than conventional photocuring technique by ~2%. These photocuring conditions are similar to what were used in Lu et al. [18].
[2] Values represent mean ± one standard deviation. Same small letter superscripts in each column represent statistical similarity ($p > 0.05$).
[3] Temperature change above the room temperature (~ 21 °C).

Different from a high-filler composite, Fig. 6 and Table 2 present results of the polymerization stress (PS) and temperature change (TC) profiles for a low-filler composite (7B3T-30F) cured with the two photocuring techniques. The material and photocuring technique used are similar to that used in the literature [18]. The result shown in Fig. 6a indicates that no considerable stress relaxation occurs during the delay time either (i.e., at DC ~ 42%), while a notable PS reduction occurs at very final stage of polymerization in the pulse-delay comparing with the conventional photocuring technique. Fig. 6b specifically shows the deviation of the PS profile for the pulse-delay technique after the TC reached close to zero (marked by 'X'). One can observe that the PS are already significantly different (21%) between the two photocuring techniques at the

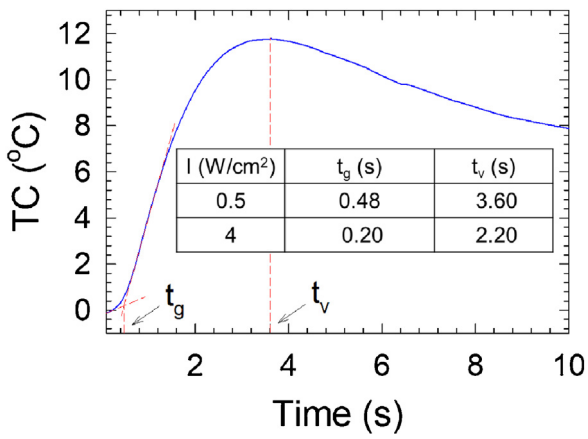

Fig. 7 – A representative curve of the temperature change (TC) as a function of time for the high-filler composite cured using the conventional technique with an irradiance of 0.5 W/cm². t_g and t_v represents the onset of gelation and vitrification time of the composite. Each tabulated value shown in the figure is the mean value derived from three different experimental runs.

same DC value of ~63% (i.e., the final DC value achieved using the pulse-delay technique).

During the photocuring process, early on, the initial viscous liquid state of the composite transitions into a gel like (rubbery) state, often referred to as gelation. Gelation is associated with an onset of rapid network formation in the composite that leads to an accelerated polymerization and exothermic heat generation (measured as temperature change, TC, in this study) [30]. Then, a vitrification state (glassy state) would be followed resulting in a slowdown of the heat generation. The onset of vitrification (t_v) is known to occur at the peak temperature change (i.e., the peak polymerization rate) [31]. Thus, the characterization of the time to gelation (t_g) and vitrification (t_v) is of importance prior to the determination of t_1, such that the heat can be optimally reduced during the delay stage of the curing process. Fig. 7 shows kinetics of the temperature change (TC) during the polymerization process, from which the time to gelation (t_g) and to vitrification (t_v) of the composite were derived. The result indicates that the increase of irradiance in the curing process leads to faster polymerization rates and shorter t_g and t_v (inset in Fig. 7). Figs. 8a and 8 b show the PS reduction for various exposure times of the first pulse (t_1). The results indicate there is a time window of t_1, such that the polymerization stress can be optimally reduced. Different selection of t_1 would induce a different profile of temperature rise during the curing process as shown in Fig. 8c, where the peak TC increases as t_1 increases.

Result in Fig. 9a indicates, in using the pulse-delay technique, that the final PS decreases with the increase of the delay time (t_d) and to a plateaued value when the t_d value is greater than 40 s. The result in Fig. 9b shows that increase of t_1 (from 0.2 s to 1.6 s at $I = 4$ W/cm²) does not alter the plateaued phenomenon observed for $t_d \geq 40$ s. However, for the same t_d, higher t_1 resulted in a lesser reduction in PS. Fig. 9c shows that the peak temperature change (TC) in the specimen decreases during the second pulse as the t_d increases.

4. Discussion

The pulse-delay photocuring technique is one of the approaches in the soft-start techniques advocated to reduce the PS in restorative dental composites. However, the reduction should not compromise the adequate polymerization that would be obtained using the conventional photocuring technique (DC_{CPT}). The result shown in Fig. 2 indicates that DC_{CPT} is 62.57% for a high-filler model dental composite (7B3T-75F, a clinically relevant composite). This DC_{CPT} value is used as a baseline for comparing with the pulse-delay photocuring technique. It has been demonstrated in a previous study [23] that for every dental composite there exists a minimum radiant exposure (RE_m), predominantly depending on the resin viscosity of the composite, for achieving the DC_{CPT} irrespective of the irradiance used. From the result shown in Fig. 2, 20 J/cm² is determined as the RE_m (although the DC_{CPT} occurs at RE ≥ 12 J/cm²). The determination of RE_m is of importance, especially, using a higher irradiance (e.g., 4 W/cm²). There is an increase in the probability of an early bimolecular (radical–radical) termination at a higher irradiance during the initial stages of polymerization, which results in a greater loss of radical growth centers when compared with lower irradiances [13]. Consequently, DC obtained using a higher irradiance is significantly decreased compared with using a lower irradiance for longer time (Fig. 2, lower REs). However, higher REs (e.g., =20 J/cm²) compensates for this greater loss of radical centers, and the DC with the higher irradiance levels off with that achieved with the lower irradiance.

The results shown in Fig. 3 and Fig. 4 together have further demonstrated, similar to what has been reported previously by the authors [23], that the exposure reciprocity law (ERL) is valid only if the radiant exposure is equal to or above the minimum value (≥RE_m) needed for adequate polymerization. The ERL states that for a given radiant exposure, the extent of polymerization (DC) of the composite does not change with 'any combination' of irradiance and exposure time. Note that the application of first and second pulse in the pulse-delay photocuring technique is indeed a format of the 'any combination'. Thus, the main principle that can derived from Fig. 2, Fig. 3 and Fig. 4 is that at a high enough radiant exposure (i.e., RE ≥ RE_m), the conventional and the pulse-delay photocuring technique achieve the adequate DC for the clinically relevant model composite (7B3T-75F, high-filler).

Results of the current study would deliver definitive evidence that the polymerization stress (PS) reduction in the pulse-delay photocuring technique, when compared with the conventional photocuring technique, is due to the reduced thermal shrinkage (contraction during the cooling process of post-cure). Conversely, a lower DC leading to lower polymerization shrinkage or stress relaxation have long been believed for the PS reduction [4,5,18,20]. The polymerization stress (PS) developed in the composite is mainly dependent on, amongst other factors, the polymerization-dependent shrinkage and elastic modulus of composite during the curing process. The shrinkage is a resultant of polymerization shrinkage (autogenous shrinkage due to reduction in physical distance between molecules) and thermal shrinkage (thermal contraction) associated with the cool down process during the post-cure.

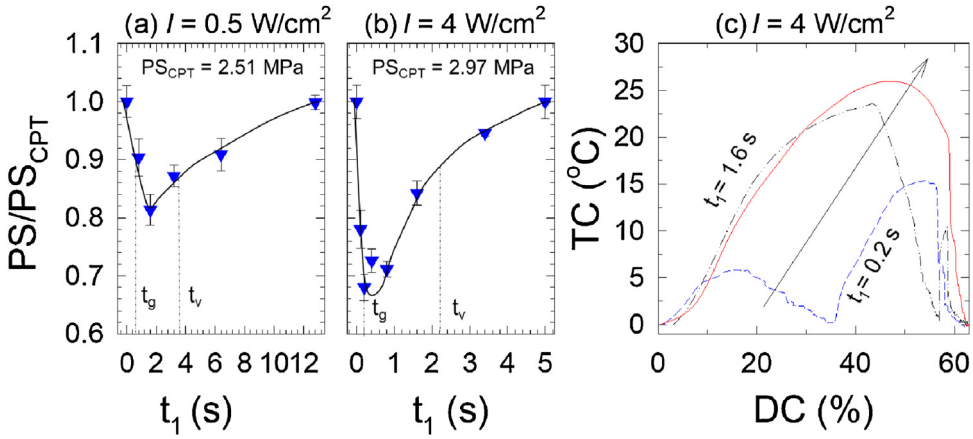

Fig. 8 – Normalized polymerization stress (PS) obtained with the pulse-delay technique as the exposure time of the first pulse (t_1, refer Fig. 1) was varied for the 7B3T-75F composite cured with irradiance of 0.5 W/cm^2 and 4 W/cm^2 in (a) and (b), respectively. PS_{CPT} is the PS obtained using the conventional technique. t_g and t_v represent the time at onset of gelation and vitrification, respectively, determined in Fig. 7. Representative curves of the temperature change, TC, as a function of degree of monomer conversion, DC, for the photocuring techniques as the t_1 is increased (arrow indicates direction of increase) in (c). The solid line in (c) represents the conventional photocuring technique. The radiant exposure (RE) used was 20 J/cm^2 and t_d was fixed at 120 s in all the figures.

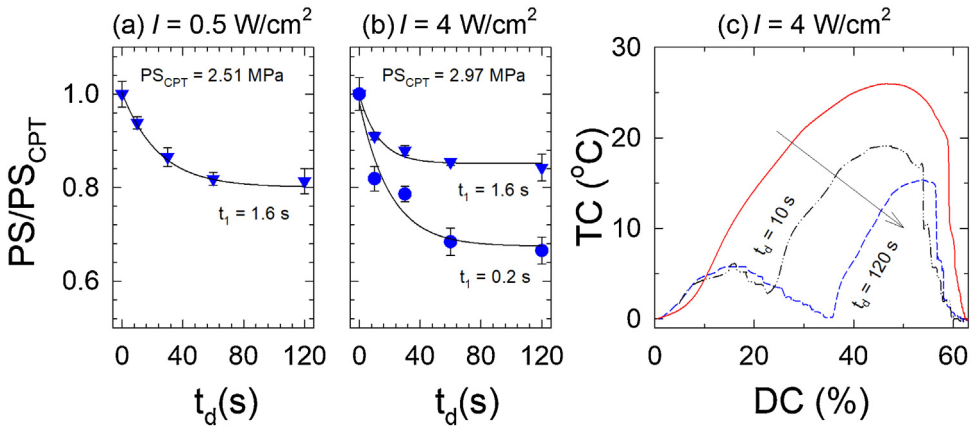

Fig. 9 – Normalized polymerization stress (PS) obtained with the pulse-delay technique as the delay time (t_d, refer Fig. 1) was varied for the high-filler composite in (a) and (b). PS_{CPT} is the PS obtained with the conventional photocuring technique. Representative curves of the temperature change, TC, as a function of degree of monomer conversion, DC, for the photocuring techniques as t_d is increased, while the t_1 is fixed at 0.2 s for an irradiance of 4 W/cm^2 in (c). The solid red line in (c) represents the conventional photocuring technique. The radiant exposure (RE) used was 20 J/cm^2 in all the figures. Vertical bars shown represent one standard deviation and some of them may be smaller than the symbols used. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Certainly, this shrinkage is also slightly compensated by the thermal expansion associated with the reaction exotherm and curing light absorbance during the process. In Fig. 5c, for DC < 58% (i.e., prior to 'X' marked in the figure), a combination of low elastic modulus and dominant polymerization shrinkage (which is similar for both the two photocuring techniques due to the same DC achieved) have resulted in no difference in the PS between the conventional and the pulse-delay photocuring technique (Fig. 5a), while differences in thermal expansion and thermal shrinkage do exist between the two photocuring techniques. For DC > 58%, composites photocured using both the techniques are in the late stage of post-curing process. From the same DC has achieved shown in Fig. 3, it is reasonable to infer that the elastic modulus and polymerization shrinkage obtained from the two photocuring techniques would be similar. Thus, the differences in the late stage PS development from these two techniques, as shown in Fig. 5c, should be due to their difference in the thermal contraction associated with late stage cooling process. This difference attributes to a higher polymerization stress (by ~32%) in the conventional than the pulse-delay photocuring technique. The result shown in Fig. 5 is obtained for a single set of photocuring variables (exposure time of first pulse, t_1, and delay time, t_d) of the pulse-delay photocuring technique; however, similar qualitative observations have been seen for variation in these photocuring variables.

The result presented in the current study strongly indicates that the applicability of the pulse-delay photocuring technique in clinic cannot be inferred from experimental observations or conclusions made for low-filler composites. Lu et al. [18] used a model composite with low-filler content to explore the PS reduction mechanism in the pulse-delay photocuring technique. They claimed the reduction is due to a lower degree of monomer conversion (DC), not stress relaxation as claimed by others [4,5]. Their study has been leading to a broader acceptance of the claim (e.g. [32]). It has been demonstrated in an earlier study that the exposure reciprocity law (ERL) is invalid for low-filler composites with respect to DC (e.g., using a higher irradiance obtains a higher DC than a lower irradiance) while valid for high-filler composites (filler contents > 50% by mass, clinically relevant) [23]. As expected, the resultant DC of a low-filler composite would change, as presented in Ref. [18], with any combination of irradiance and exposure time at the same radiant exposure. In addition to the lower DC, a lower TC with the pulse-delay technique attributes to a lower PS (reaching near to zero as marked by 'X' in Fig. 6b; thus, less contribution to the stress due to the thermal cooling). Further, from the result shown in Fig. 6b and the explanation used for the high-filler composite, one can infer that the lower TC is an equally important factor resulting the lower polymerization stress when the pulse-delay technique is used for the low-filler composite. This is quite different from what was claimed in Ref. [18], where the lower DC alone was claimed. A few differences, however, exist between materials and methods used here in comparison to Ref. [18], such as the curing light spectrum, filler size, instrument sensitivity, etc. Off these differences, the authors believe the sample volume (9.82 mm^3 in this study vs 70.69 mm^3 in Ref. [18]) is the key difference between them that makes a quantitative comparison between the studies inappropriate.

As aforementioned, the main principle behind the pulse-delay photocuring technique for clinically relevant high-filler dental composites is that the radiant exposure (RE) used should be large enough (i.e., $RE \geq RE_m$), such that no sacrifice in polymerization of the composite can be obtained in comparison with the conventional photocuring technique (Fig. 3 and Fig. 4). Once this RE is determined, the strategy to derive the maximum benefit (minimum PS) from the pulse-delay photocuring technique is through minimizing the thermal shrinkage (cooling) during the post-curing process (after the end of second pulse) via an optimal combination of its photocuring variables, namely, the delay time and the exposure time of the first pulse (t_d and t_1, Fig. 1). With the pulse-delay photocuring technique, the reduction in polymerization stress (PS) can be achieved with the exposure time of the first pulse (t_1) that is greater than the gelation time (t_g) but much lower than the vitrification time (t_v), i.e., closer to t_g. For the case of t_1 (the exposure time of first pulse) much less than t_g, no significant polymerization occurs during this time (i.e., before the gelation) and most of the polymerization would take place after the second pulse. For the case of t_1 similar to or greater than t_v, the polymerization is almost accomplished after the first pulse and the cooling process during the delay time happens when the composite has a higher elastic modulus. Thus, for these cases, the resultant polymerization stress (PS) of the pulse-delay technique would not be significantly different from that of the conventional technique (Fig. 8a and 8 b). For t_1 greater than and close to t_g, a significant amount of polymerization occurs prior to the second pulse (i.e., at end of delay time) or during the first pulse itself. This leads to a lower temperature change during the second pulse (for e.g., $t_1 = 0.2$ s in Fig. 8c), and subsequently a lower thermal shrinkage during the post-curing process. Consequently, a low PS relative to the conventional photocuring technique can be achieved (Figs. 8a and 8 b).

Once the material-dependent t_1 is reliably determined by characterizing the gelation and vitrification time of the composite, the exposure time of the second pulse can be easily derived based on the radiant energy and irradiance used in the photocuring process. Also, one can notice that any value of delay-time (i.e., $t_d > 0$) can cause a reduction in PS (Figs. 9a and 9 b). The role of the delay-time in the pulse-delay technique simply is to let the heat, generated in the composite during the first pulse of light, dissipate to a cooler ambient temperature. For the sample configuration and experimental setup used in this study, a thermal equilibrium has reached between the composite and ambient environment when $t_d \approx 40$ s. This means a longer delay time beyond 40 s deems unnecessary; thus, no further reduction in PS when $t_d \geq 40$ s, regardless of t_1 (i.e., $t_1 = 0.2$ s or 1.6 s; Figs. 9a and 9 b). For an optimal stress reduction, using a delay time of 40 s may not be clinically practical. However, for all the cavity classifications (Class I–VI), we believe the thermal insulation provided by the restoration configuration and environment of clinical practice should be much lower than by the specimen configuration and experimental setups of this study [21,22,27]. Thus, in a clinical practice, the delay time, t_d, can be much less than 40 s.

5. Conclusions

The study substantiates the importance of thermal shrinkage (contraction), as a result of cool down process of composite at the post-cure stage, on the overall polymerization (residual) stress developed in the composite. Accordingly, the study shows that the lower thermal shrinkage, not the stress relaxation or lower degree of conversion, should be claimed to attribute the significant reduction in the stress when comparing the pulse-delay with the conventional photocuring technique. Thus, the argument reported in the literature on the mechanism behind the stress reduction of the pulse-delay technique is clarified. A sufficient radiant exposure, such that the exposure reciprocity law is applicable, is a prerequisite for the use of pulse-delay technique not to compromise the degree of monomer conversion as obtained using the conventional technique. Afterwards, the potential benefit of the pulse-delay on the reduction in polymerization stress can be recognized by moderating the thermal contraction through the exposure time of the first pulse (t_1) and the delay time (t_d). This study suggests that the gelation and vitrification times of resin composite are the basis for determining the t_1, while the selection of t_d becomes secondary as long as it is not discordant with clinical practice. Also, the outcome of the study can be extended beyond dentistry into broader applications of photopolymerization, such as additive manufacturing (3D printing), where polymerization shrinkage-associated and/or

thermally induced internal stresses cause problems in manufacturing process. In addition, the success of the pulse-delay photocuring technique would facilitate the advancement of nanotechnology for restorative dentistry by tackling the discouraging issue of polymerization stress rising with enhanced elastic modulus of nanocomposites. Finally, in the design of new class of dental materials, the control of exothermic temperature and its kinetics in monomer reaction can be considered as mechanisms to reduce the risk associated with thermal contraction.

Acknowledgements

The authors are grateful for the financial support provided through the Interagency Agreement between the National Institute of Dental and Craniofacial Research (NIDCR) and NIST [ADE12017-0000].

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