

Optimizing light-cured composite through variations in camphorquinone and butylhydroxytoluene concentrations

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Abstract: The use of a free-radical polymerization inhibitor, butylhydroxytoluene (BHT), and a common photo-initiator, camphorquinone (CQ), to reduce polymerization stress in dental composite was investigated in this study. Samples were prepared by mixing Bis-GMA, UDMA, and TEGDMA at a 1:1:1 ratio (wt%), and silanized borosilicate glass fillers at 70 wt% were added to form the composite. Sixteen groups of resin composite were prepared using combinations of four CQ (0.1%, 0.5%, 1.0%, and 1.5%) and four BHT (0.0%, 0.5%, 1.0%, and 1.5%) concentrations. For each group, six properties were tested, including flexural strength (FS), flexural modulus (FM), degree of conversion (DC), contraction stress (CS), stress rate, and gel point (GP). The effects of CQ and BHT combinations on each of these properties were evaluated using two-way analysis of variance (ANOVA) and Fisher's Protected Least Significant Differences test at the 5% significance level. Groups with low CQ and BHT showed moderate values for FS, FM, and CS with a 70% DC. Increasing the BHT concentration caused a decrease in CS and DC with an increase in GP values. Increasing the CQ content led to a steady increase in values for FS and FM. High CQ and BHT combinations showed the most promising values for mechanical properties with low stress values.

Keywords: Composite Resins; Photoinitiators, Dental; Light-Curing of Dental Adhesives.

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Introduction

Polymerization shrinkage is an inherent property in resin composite and occurs when the monomer is converted into a polymer. This phenomenon is still considered a drawback of composite resin because it has a major impact on its clinical performance.¹ Many research studies have investigated this issue. Systematic investigation into the interplay of the various components in the initiator system provides a starting point for the understanding of the impact of the initiator system on the polymerization kinetics of the polymer. An example is the work by Pfeifer et al.,² where changing the concentration of photo-initiators or co-initiators in the unfilled resins was shown to reduce the polymerization rate while keeping the final degree of conversion. However, attempts aimed at reducing polymerization stress were usually complicated by a marked increase in the susceptibility to liquids, such as ethanol,³ and decreased mechanical properties.⁴

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To prevent premature polymerization, small amounts of butylhydroxytoluene (BHT; approximately 0.01% by weight) are usually used as an inhibitor.⁵ This ingredient is also important for increasing the shelf life of the resin during its storage and transportation. Changing the concentration of the inhibitor can modulate the curing and mechanical properties of the resin composite. Al-Shammari⁶ showed that modifying the initiator and inhibitor levels can lead to slow polymerization shrinkage with lower contraction stress and does not affect the degree of conversion in a model composite formulated with 1% camphorquinone (CQ) by weight and BHT levels from 0.01 to 0.8% by weight. A significant decrease in the degree of conversion was found at a BHT concentration of 1.4%. Increasing the amount of BHT from 0.01 to 1.4% resulted in the reduction of polymerization stress. In addition, flexural strength and flexural modulus were not affected by BHT levels up to 1.2%; however, they were significantly decreased at 1.4%.⁶

In the literature, little attention has been given to testing the effect of different combinations of initiators and inhibitors. The main objective of this study was to investigate the effects of CQ and BHT combinations on

the curing and mechanical properties of light-cured resin composite. Further, we hypothesize that at a specific CQ/BHT combination, polymerization shrinkage stress can be effectively reduced without sacrificing the mechanical properties of the resin.

Methodology

Composite resin preparation

Resin composite material was prepared by mixing bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), and tetraethylene glycol dimethacrylate (TEGDMA; Sigma-Aldrich, St. Louis, USA) at a ratio of 1:1:1 by weight. The ingredients were placed in a container and stirred for 48 hours. BHT (Sigma-Aldrich) was added as an inhibitor at four concentrations (0.0%, 0.5%, 1.0%, and 1.5%). CQ (Sigma-Aldrich) and dimethylaminoethyl methacrylate (DMAEMA, Sigma-Aldrich) were used as the initiator and co-initiator, respectively, and were added in a dark room. Four concentrations of CQ (0.1%, 0.5%, 1.0%, and 1.5%) were used. Sixteen groups of resin composite with different concentration combinations of BHT and CQ (Table) resulted. Silanized

Table. Mean and standard deviation of the parameters tested with different camphorquinone (CQ) and butylhydroxytoluene (BHT) combinations, grouped based on CQ level.

CQ (wt%)	BHT (wt%)	Flexural Strength*	Flexural Modulus	Degree of Conversion (%)	Contraction Stress	Stress	Gel
		(MPa)	(GPa)		(MPa)	Rate (MPa/min)	Point (s)
		n = 10	n = 10	n = 9	n = 5	n = 5	n = 5
0.1	0.0	77.9 (16.7) ^a	6.29 (0.65) ^a	69.2 (2.9) ^a	2.92 (0.08) ^a	5.96 (0.30) ^a	4.9 (1.4) ^a
	0.5	53.9 (9.5) ^b	3.75 (0.43) ^b	67.9 (2.2) ^a	1.71 (0.06) ^b	1.51 (0.12) ^b	12.0 (0.7) ^b
	1.0	63.8 (9.2) ^{a,b}	3.86 (0.43) ^b	47.6 (1.4) ^b	1.55 (0.09) ^b	1.29 (0.07) ^b	12.5 (2.1) ^b
	1.5	66.5 (10.8) ^{a,b}	3.59 (0.25) ^b	42.7 (3.1) ^c	1.51 (0.05) ^b	1.48 (0.14) ^b	13.0 (3.2) ^b
0.5	0.0	93.6 (16.3) ^a	9.06 (0.74) ^a	69.3 (2.4) ^a	3.48 (0.16) ^a	11.13 (0.77) ^a	4.6 (1.7) ^a
	0.5	94.0 (21.2) ^a	7.92 (0.64) ^b	65.2 (3.2) ^b	3.02 (0.23) ^b	6.33 (0.46) ^b	5.5 (1.6) ^a
	1.0	84.8 (23.1) ^a	8.06 (1.48) ^b	64.8 (2.2) ^b	2.94 (0.05) ^b	4.45 (0.20) ^c	9.1 (1.1) ^b
	1.5	94.2 (23.9) ^a	7.58 (0.5) ^b	64.0 (1.3) ^b	2.82 (0.05) ^b	3.49 (0.16) ^d	8.4 (1.7) ^b
1.0	0.0	109.1 (13.2) ^a	8.73 (0.43) ^a	64.9 (1.9) ^a	3.67 (0.31) ^a	12.24 (1.35) ^a	5.2 (2.4) ^a
	0.5	92.5 (15.2) ^a	8.68 (0.69) ^a	59.9 (3.8) ^b	3.41 (0.14) ^b	7.10 (0.44) ^b	6.2 (0.8) ^a
	1.0	108.2 (13.6) ^a	8.94 (0.53) ^a	59.9 (1.8) ^b	3.34 (0.25) ^b	6.52 (0.67) ^b	7.0 (1.4) ^a
	1.5	100.1 (20.4) ^a	8.12 (0.8) ^a	66.1 (2.1) ^a	3.17 (0.07) ^b	4.70 (0.30) ^c	7.4 (0.3) ^a
1.5	0.0	99.9 (11.1) ^a	9.37 (1.13) ^a	72.6 (2.5) ^a	4.02 (0.16) ^a	12.23 (0.84) ^a	7.4 (2.0) ^a
	0.5	103.6 (29.1) ^a	10.33 (1.12) ^b	72.5 (2.6) ^a	3.70 (0.36) ^b	8.11 (0.79) ^b	5.4 (1.9) ^a
	1.0	114.1 (21.1) ^a	8.73 (0.55) ^{a,c}	66.2 (2.2) ^b	3.83 (0.18) ^{a,b}	7.46 (0.45) ^b	6.2 (1.6) ^a
	1.5	113.4 (19.2) ^a	8.42 (0.84) ^c	67.9 (2.0) ^b	3.30 (0.18) ^c	4.93 (0.63) ^c	7.4 (3.0) ^a

*For each experimental property, values with the same superscript letters indicate non-significant difference ($p < 0.05$) across each CQ level.

borosilicate glass filler (0.7 μm ; Pentron Technologies, Wallingford, USA) was added with continuous mixing and constituted 70% of the total weight of the resin.

Flexural strength and modulus

Rectangular beam specimens were fabricated from all groups ($2 \times 2 \times 25$ mm; $n = 10$) utilizing a stainless steel split mold. After placing the resin into the mold, a Mylar strip was placed, and gentle pressure was applied to extrude the excess material from the mold. The top and bottom surfaces of the specimens were light cured with 3 overlapping irradiation cycles of 40 seconds each using a light curing unit (L.E. Demetron, SDS/Kerr). Periodic measurements of the intensity of the curing light were performed using a cure rate radiometer (Dentsply Caulk, Milford, USA). After curing, the specimens were removed from the mold and polished with a silicon carbide paper with different grit sizes (240- and 400-grit) and stored in water overnight within an incubator at 37°C.

Each specimen's width and thickness was measured at three different locations on the beam using a digital micrometer, and average values were recorded. Flexural strength (FS) and flexural modulus (FM) were tested using a universal testing machine (Sintech Renew 1121, Instron Engineering Corp., Canton, USA). A standard 3 point bending jig was attached to the machine and connected to a computer with specifically designed software (Test-Works 3.0 MTS Systems Co., Eden Prairie, USA). Specimens were placed on the jig, and the test was carried out using a span length of 15 mm and a crosshead speed of 1 mm/min until the specimen was fractured. Failure load and beam deflection were recorded by the computer, and FS and FM were calculated using the following equations:

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

where σ_b = flexural strength (MPa), P = maximum failure load (N), L = supporting span (15 mm), b = specimen average width (mm), and h = specimen average height (mm).

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

where E_b = flexural modulus (MPa), P' = load below elastic limit (N), L = supporting span (15 mm),

b = specimen average width (mm), h = specimen average height (mm), and Y = beam deflection at P' .

Degree of conversion

Degree of conversion (DC) was determined using Fourier transform infrared spectroscopy (FT/IR-4100, Jasco, Tokyo, Japan). A small amount of uncured resin was placed onto the 5 mm diameter sample holder of the FTIR machine, and the samples were scanned ($n = 3$) and analyzed. Cured specimens were prepared by placing a small amount of resin between two sheets of Mylar. The specimen was placed between two glass slabs, and firm pressure was applied to obtain a thin specimen. A stainless steel jig with a 7 mm opening was placed on top of the specimen and light cured for 40 seconds using the light curing unit. After curing, the specimen was obtained using a sharp scalpel and transferred to the FTIR for scanning. Three specimens were made for each group, and three scans were obtained for each specimen for a total of nine scans per group.

During analysis, the peak area under the wave length of 1638 cm^{-1} represented the aromatic $\text{C} = \text{C}$ coming from Bis-GMA and was assigned as P1. The peak area under the wave length of 1608 cm^{-1} was assigned as P2 and represented the vinyl $\text{C} = \text{C}$. DC was calculated using the following equation:

$$DC = 1 - \frac{\text{cured } [P1/P2]}{\text{uncured } [P1/P2]}$$

Polymerization shrinkage stress

A tensometer was used to measure the polymerization contraction stress (CS), stress rate (SR), and gel point (GP) for each resin group. This test is based on the deflection of a cantilever beam, which was measured with a linear variable differential transformer (LVDT) and was positioned 23 cm from the sample assembly at the free end of the cantilever beam. The measured tensile force was divided by the cross sectional area of the sample to obtain the CS.

This tensometer consisted of a rectangular beam (10 mm in width and 40 mm in height) clamped horizontally on a beam holder. The beam was made of stainless steel with a Young's modulus of 193 GPa. The top of each composite was connected to the cantilever beam at a distance of 12.5 cm from the

beam holder. Quartz rods were used to complete the assembly to the tensometer and also to guide the irradiation from the curing unit to the sample. The two pieces of quartz rod were flattened and polished with 600-grit wet silicon carbide paper. Two layers of silane coupling agent were applied to the rod ends facing the specimens. The two rods were aligned manually, and the upper rod was mounted first with the silanized end pointing down. The bottom quartz rod was aligned vertically with the upper rod and then mounted with the silanized end facing up. Polytetrafluoroethylene sleeves were placed around the gap between the two rods, and two holes were drilled in the sleeve, the first one to inject the resin into the assembly and the other to vent the excess. Composite was injected into the sample holder to fill the space between the silanized ends, and then the composite was light cured through the bottom quartz rod using an Elipar Highlight curing unit (ESPE, Dental-Medizin GmbH, Seefeld, Germany) for 60 seconds.

The resultant composite samples were disks of 6 mm in diameter and 2.25 mm in height, corresponding to a C-factor of 1.33 (diameter/2(height)). Five samples were made for each group, and the CS was measured for 30 minutes from the start of photo-initiation with data collected every second. The CS was determined by dividing the measured tensile force by a cross section area of the sample. SR was determined for each specimen by taking the first derivative of the stress vs. time curve. Data from the first data point with a significant non-zero slope was considered as GP of the resin.

Statistical tests

The effects of BHT and CQ concentrations on SR, GP, CS, DC, FS, and FM were assessed using two-way analysis of variance (ANOVA) models. Plots (3-D and/or contour plot) were used to visually depict the results. The tests for interaction between the inhibitor and initiator were considered to be significant if the p-value was less than 0.05. When the interaction effect was significant, pair-wise comparisons of the treatment combinations were examined for significance using the Fisher's Protected Least Significant Differences Method. When the interaction effect was not significant,

the main effects were examined for significance. When the main effects were significant, pair-wise comparisons between the levels within each factor were examined using the Fisher's Protected Least Significant Differences Method.

Results

For easier visualization of the data, we used 3D iso-contour map plots (Figure 1). For FS and FM, groups with low CQ and BHT showed moderate values. Increasing the BHT concentration caused minor changes in the mechanical properties (Figure 1a and 1b). At high levels of both CQ and BHT, a clear improvement of mechanical properties was noted, although the increase in FM was less pronounced. The highest FS value was recorded at CQ = 1.5% and BHT = 1.0%, whereas for FM, the highest reading was obtained at CQ = 1.5% and BHT = 0.5%

A 70% conversion was obtained at low CQ and BHT values (Figure 1c). This percentage was reduced sharply as BHT concentrations increased. This was compensated for with the increase in CQ content up to 1.0% (DC = 65%). Subsequently, DC values remained relatively unchanged, even with further increase in CQ content. On the other hand, keeping BHT low and increasing CQ was associated with a slight reduction in DC values. However, further increase in CQ elevated DC values to near 75%.

Regarding GP, the fastest reaction time (GP = 5 s) was observed with CQ = 0.1% and BHT = 0.0% (Figure 1d). Increasing BHT dramatically slows the reaction (GP approximately 12 s), while increasing CQ causes a slight reduction in GP followed by a moderate increase up to 7 seconds. A similar trend was observed in high CQ and BHT groups. Regarding polymerization stress, data show moderate values for SR and CS at low CQ and BHT concentrations (Figure 1e and 1f). Increasing BHT content of the resin is accompanied by a decrease in both SR and CS, while increasing CQ leads to the highest values for these parameters. In groups with high CQ and BHT, SR and CS values are comparable to baseline. Table shows means and standard deviations of the tested properties at each concentration of CQ in relation to increasing BHT concentrations.

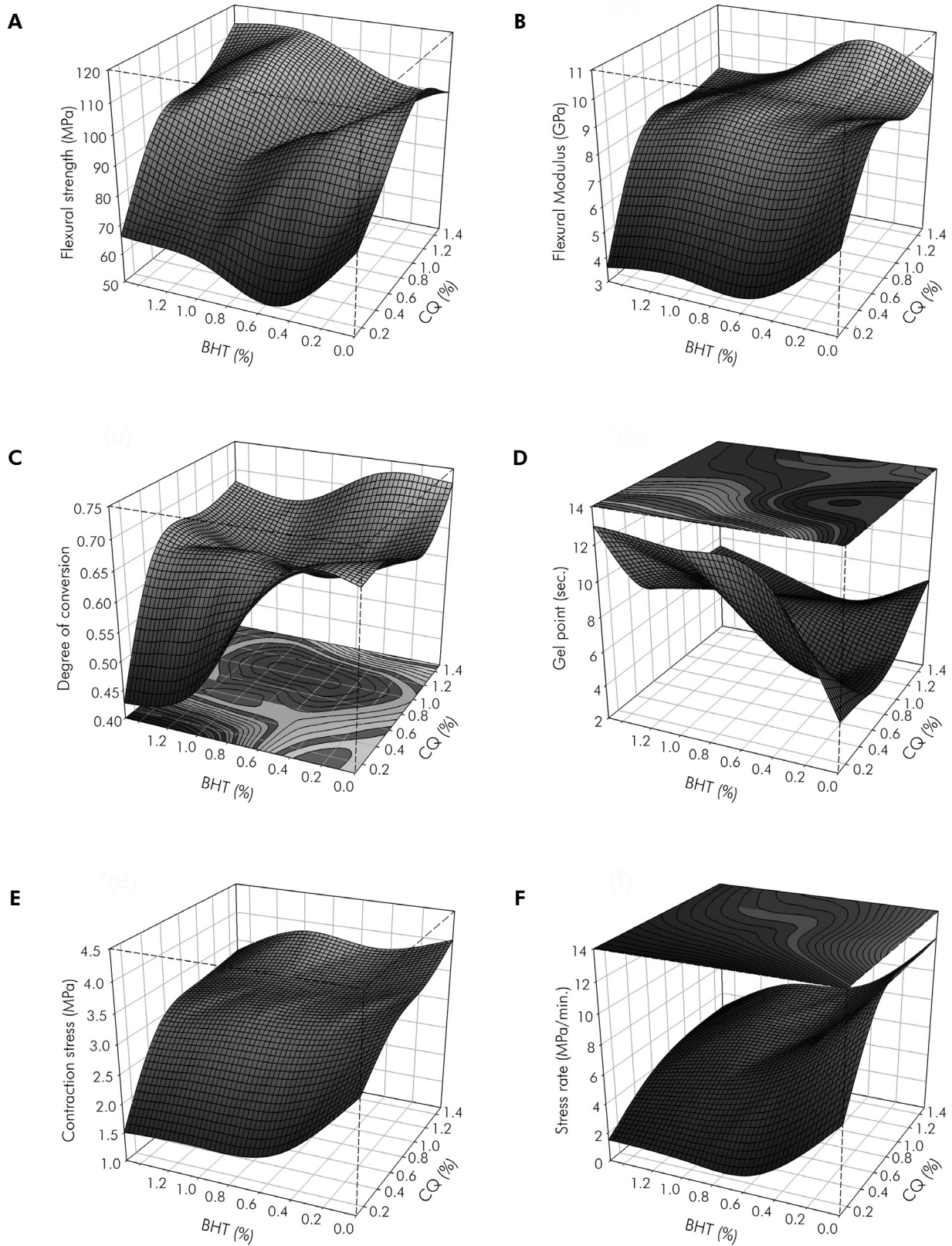


Figure 1. Iso-contour 3D map plots showing the interaction of different camphorquinone (CQ) and butylhydroxytoluene (BHT) combinations on the values of (a) flexural strength, (b) flexural modulus, (c) degree of conversion, (d) gel point, (e) contraction stress, and (f) stress rate.

Since improvement in the properties was found at high CQ/BHT combinations, we further analyzed the effect of increasing BHT content at 1.5% CQ level in Figure 2. The gradual increase in BHT content from 0.0 to 1.5% showed a significant decrease in SR. This was accompanied by a slight decrease in DC and CS without an effect on FS values.

Discussion

Polymerization shrinkage is still considered a drawback of composite resin because it has a major impact on its clinical performance.¹ This phenomenon is due to the decrease in distance between the monomer molecules caused by the formation of covalent bonds as the polymerization reaction takes place.^{7,8} Manipulation of the initiator system concentrations has been previously reported as a valid method for modulating polymerization shrinkage stress rate and magnitude.⁹ In this study, we hypothesized that different CQ and BHT combinations can modify the curing and mechanical properties of light-cure resin composite based on

their effects on the viscoelastic behavior of the composite during curing, which is directly related to their polymerization shrinkage stress.

This is primarily due to the characterized flow capacity of the resin at the early stages of the polymerization reaction.¹⁰ According to Feilzer et al.,¹¹ the viscous flow of the resin material is a time-dependent process. Slower reactions are associated with periods in which the material is able to yield to polymerization forces through molecular rearrangement, thus producing less contraction stress.

In this study, high conversion values were recorded at high CQ levels. This is expected because high CQ will be associated with more free radicals being produced, leading to a high degree of polymerization. This is associated with high values for mechanical properties, as observed in this study and reported in the literature in association with high DC.^{12,13} However, high CS and faster rates of both gel point transformation and stress rate buildup can also be seen at these levels. This is mainly due to faster transition to the gel phase because at early stages of the polymerization process, resins behave in a viscous manner and then become gradually more elastic as the reaction continues.¹⁴ However, beyond the gel point, more crosslinking starts to develop between the polymer chains, leading to a more elastic behavior of the resin that is associated with higher stiffness and faster contraction stress development. Guimarães et al.¹⁵ reported that the photoinitiator content directly affects the DC more than the bulk mechanical properties and concluded that an overall initiator concentration higher than 1.5 wt% will not add any additional benefit with regard to other resin properties.

On the other hand, high BHT levels have led to a very slow reaction with very low DC, likely due to less available free radicals that are competitively quenched by the inhibitor. Consequently, values for mechanical properties and polymerization stress were very low. A similar trend was reported by Braga and Ferracane,¹ as they found that increasing the concentration of the BHT (from 0.05 to 1.0%) slows both the rate of the reaction and the rate of stress build-up without causing a significant decrease in the final DC.¹ However, in their study, the DC values

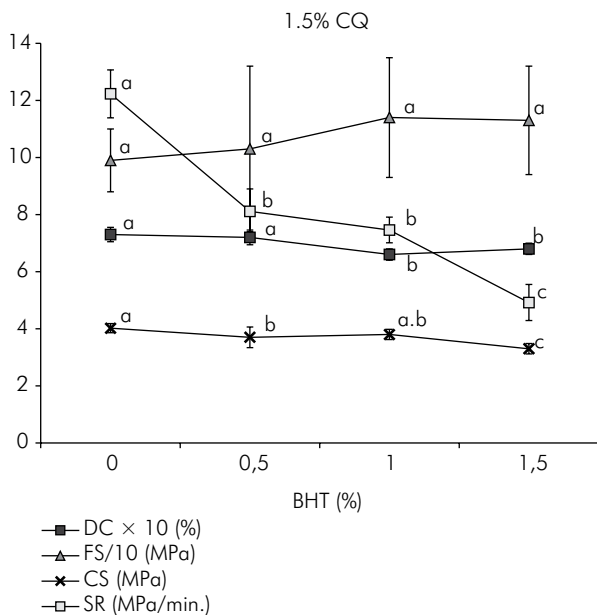


Figure 2. A graph illustrating the effect of increasing butylhydroxytoluene (BHT) concentration on the degree of conversion (DC), flexural strength (FS), contraction stress (CS), and stress rate (SR) of resin composite at the 1.5% camphorquinone (CQ) level. Different letters indicate significant differences within each property ($p < 0.05$).

were lower than what is recorded in the present study, with higher CS and SR values. This could be due to the difference in the matrix composition (no UDMA) and the amount of fillers (40 wt%).

When considering low CQ and BHT levels, a reaction with a high conversion occurred and was associated with moderate values for FS and FM. This could be explained by the cyclization process in which both ends of the polymer chain will react with each another, leading to the termination of chain growth. According to Elliott et al.,¹⁶ cyclization will produce isolated “microgels” without proper cross-linking to the surrounding resin networks. This process will produce higher local conversion that is associated with lower cross-linkage density and thus lower mechanical properties.¹⁷

Contraction stress due to volumetric shrinkage is correlated with the degree of conversion, as reported previously.^{1,18} At the same time, increasing the degree of conversion is associated with higher values of elastic modulus.¹⁹ Although using a material with low DC would yield lower contraction stress and a lower possibility of shrinkage-related complications, this will be at the expense of the mechanical properties of the composite.¹³ Although our findings are in agreement with this concept, we found that this trend was less accentuated as the concentration of BHT increased. At high CQ and BHT, the reaction moved at a moderately slow rate (indirectly suggested via stress rate data), allowing some rearrangement of molecules in the resin that will improve the mechanical properties and maintain the rate of stress development in a range that can be compensated by the viscoelastic capacity of the resin. Low values of CS were also recorded here, as the slow reaction will allow some relaxation of the gel phase of the composite, leading to less overall stress generation.

At CQ = 1.5%, the increase in BHT was associated with a significant decrease in CS and SR. Although the DC decreased from 72 to 68%, FS was not affected. When we consider BHT at 1.5%, increasing the concentration of CQ from 0.1 to 1.5% was accompanied

by a significant increase in CS and SR. However, FS and FM were markedly increased mainly due to the higher DC. However, this is contrary to some investigations that reported an effect on the DC when high CQ levels were used,^{20,21} likely due to the light-shielding effect of the photoinitiator.²²

The reduction in the speed of the reaction by BHT could result from the termination of the free radicals by the active phenol group in the BHT molecule. This process will maintain a slow rate of polymerization and extend the pre-gel phase in which molecular arrangement of the polymer chains will dissipate the stresses formed. After all of the BHT molecules are consumed, the reaction will speed up, and the crosslinking between polymer chains will increase, yielding a more stiff material that is resistant to further plastic deformation.¹ Another widely accepted effect of BHT is its role in preventing premature polymerization and extending the shelf life of the resin, leading to a more stable material. However, this effect can be achieved at much lower amounts than those used in the present study.

Our goal was to identify a CQ/BHT combination that shows lower values for CS and SR while maintaining the mechanical properties of the resin. We successfully found that using a concentration of 1.5 wt% of both the inhibitor and initiator yields a material fulfilling these characteristics. A similar approach was used previously with unfilled resin by Venhoven et al.,⁹ who found that varying the amounts of the initiator and co-initiator can reduce the rate of curing while maintaining the final DC.

Conclusion

In conclusion, we found that the curing and mechanical properties of light-cured resin composite can be tailored using different CQ and BHT combinations. Of particular note, using a high concentration (1.5%) of both of these ingredients will produce a material with relatively high DC and FS while allowing a gradual and slow build-up of contraction stress during polymerization.

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