The effect of curing light source on polymerization contraction stress and degree of conversion over time in an orthodontic adhesive

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ABSTRACT

Objective: The purpose of this study was to determine the effect of two different curing light sources on contraction stress and degree of conversion (DC) over time in an orthodontic adhesive.

Methods: Contraction stress was determined with a contraction stress measurement (CSM) device in which the orthodontic adhesive, Transbond XT (3M Unitek), was placed between a glass plate and steel rod. The steel rod passed through a washer load cell. A halogen (Ortholux XT, 3M Unitek) and an LED (Ortholux LED, 3M Unitek) were the curing light sources tested. Light was introduced from the bottom of the glass plate and loads developed within the adhesive were transferred to the load cell. Contraction force was recorded for four different time intervals: 5 minutes, 10 minutes, 1 hour, and 24 hours. Degree of conversion of each specimen at the four time points was measured with FTIR. Data were analyzed with two-way ANOVA and Bonferroni's post-hoc testing at the 0.05 level of significance. Regression analysis was also performed between contraction stress and DC.

Results: With equal light energy density the LED led to significantly greater contraction stress within the adhesive than the halogen unit ($p<0.05$). Contraction stress and DC values were significantly ($p<0.05$) greater after 24 hours compared to all other time points after initial light exposure. Irradiation condition did not significantly affect degree of conversion. The relationship between stress and DC was non-linear ($r^2 = 0.91$).

Significance: Spectral irradiance may play a significant role in polymerization efficiency. Greater contraction stress obtained with the LED, without a significant increase in DC, may adversely affect bond strength. Furthermore, other developing

properties of the composite contribute to stress build-up – such as cross-linking and modulus development – and further research is needed to determine their possible clinical effect on bond strength.

PREFACE

The organization of this thesis is as follows:

A comprehensive literature review precedes a stand alone manuscript prepared for submission for consideration of publication. A summary of the discussion and the main conclusions drawn from the study follow the manuscript and conclude the thesis. Due to the format with a complete manuscript for publication found within the body of the thesis, some of the material presented is duplicated.

LITERATURE REVIEW

The use of adhesive resins to bond orthodontic brackets to teeth was first introduced in 1964 (Newman, 1964). The original self-curing adhesives have increasingly been replaced by light-cure adhesive systems – revolutionizing the field of orthodontics by allowing the clinician ample time to accurately position brackets prior to polymerization of the adhesive. However, when bonding brackets with conventional halogen lamps, a polymerization time of at least twenty seconds is necessary to achieve sufficient bond strength due to the relatively low power density of the lights (Wang and Meng, 1992). A considerable amount of clinical time is thus required in full mouth bonding. In an effort to reduce curing time, modern lights with increased intensity have been developed – argon lasers, plasma arc lights and high-intensity halogen units all offer a reduction in cure time (Marvropoulos *et al.*, 2005). The desire to further improve curing light efficiency has led to the most recent development in curing light technology – a new generation of high-intensity blue light emitting diodes (LEDs). The LEDs convert electric current into a characteristic light with a specific narrow spectral distribution. Their high intensity and efficient emission spectrum may allow LEDs to reduce the required cure time without compromising bonding efficiency.

The light-curing process begins with activation of a photoinitiator. Most visible light-activated resin systems utilize camphoroquinone (CPQ) as the diketone absorber. CPQ has an absorption maximum in the blue region of the visible light spectrum at a wavelength of 470 nm (Althoff and Hartung, 2000). When CPQ is activated by blue

light, free radicals are created which initiate the polymerization process (Stahl *et al.*, 2000).

Halogen-based LCUs (Figure 1) have been the most popular method of delivering blue light to polymerize dental composites (Mills *et al.*, 1999). The bulbs generate light when an electric current is passed through extremely thin tungsten-quartz filaments heating them to high temperatures (3000°C). Most of the energy put into the halogen light system is converted into heat, but a small portion of light is also generated (Althoff and Hartung, 2000). Selective filters are then required to screen the other wavelengths – narrowing the spectra of white light so only blue light is emitted (Stahl *et al.*, 2000).

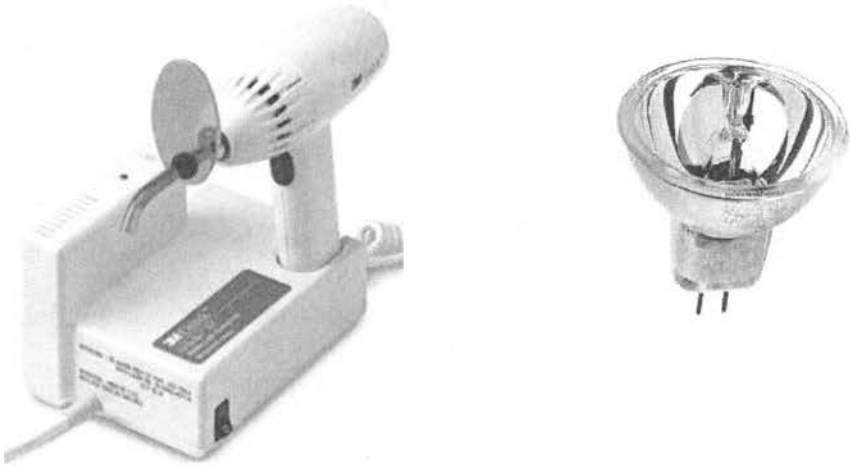

Figure 1 Halogen light curing unit and bulb.

The halogen light system is inherently inefficient and possesses a number of shortcomings. The light power output is less than 1 percent of the consumed electrical power (Althoff and Hartung, 2000). Moreover, the high heat generated degrades the bulb's components over time (Mills *et al.*, 1999), resulting in a limited effective lifetime of about 100 hours (Rueggeberg *et al.*, 1996).

LED light-curing units (Figure 2) have been developed to overcome many of these drawbacks associated with halogen curing lights. To generate light, LEDs utilize junctions of doped semiconductors. One layer is doped with electrons (n-doped) and the other is doped with 'holes' (p-doped), or lack of electrons. When a voltage is applied to the terminals, electrons are injected from the n-region into the p-region. As the holes and electrons recombine at the LED's p-n junction, photons of a specific wavelength range are emitted – generating a narrow bandwidth of light (Smith, 2000). Ideally, for efficient polymerization, the irradiance spectrum of the curing light should match the absorbance spectrum of the photoinitiator (Stahl *et al.*, 2000). The extent to which the light emitted by curing units is absorbed by photoinitiators and free radicals are formed defines polymerization efficiency (Neumann *et al.*, 2005). In the case of gallium nitride LEDs, the spectral output falls within the absorption spectrum of the CPQ photoinitiator (400-500 nm) present in the light-cure adhesive – eliminating the need for filters (Stahl *et al.*, 2000). Furthermore, the LED's peak emission is 465nm which closely matches CPQ's maximum absorption of 470nm. The halogen lights, however, emit a broader bandwidth with a peak emission (497nm) falling outside of CPQ's absorption curve (Figure 3). The good correlation between the absorption spectrum of CPQ and the emission spectrum of the LEDs may increase curing efficiency (Jandt *et al.*, 2000)

Figure 2 LED light curing unit.

and allow the LED required cure times to be less than that of the halogen lamps – decreasing the overall bond time. LEDs are also resistant to shock and vibration and consume little power during operation (Dunn and Bush, 2002). Furthermore, their expected lifetime is several thousand hours without significant degradation of light intensity over time (Haitz *et al.*, 1995).

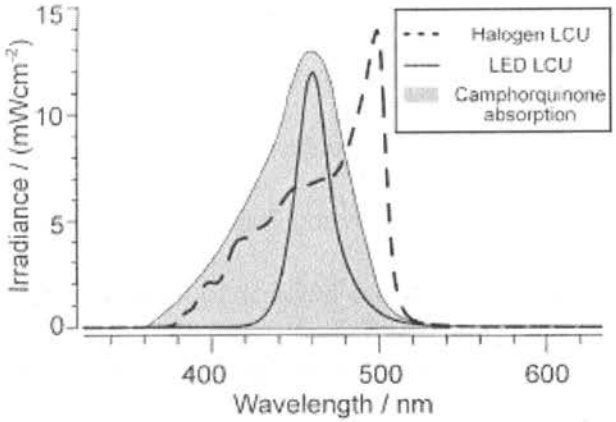

Figure 3 Sample spectral irradiance of a halogen unit and an LED superimposed over the absorption spectrum of CPQ (Stahl *et al.*, 2000).

The first commercially available LED units had lower light intensities than the halogen lamps. However, studies have shown that when used with the same exposure times, those LEDs are able to bond orthodontic brackets to teeth just as well as the halogen-based curing lights (Dunn and Taloumis, 2002; Bishara *et al.*, 2003). Moreover, previous research has also shown that when adjusted to the same irradiance, LEDs perform as well as halogen lights in regard to depth of cure (Mills *et al.*, 1999). Recently, LED technology has advanced significantly – leading to the construction of LED light curing units (LCUs) with higher power and similar irradiances to conventional halogen LCUs (Mills and Jandt, 2001). A study on a high power LED prototype found its polymerization technology to reach comparable

performance levels of hardness and compressive strength to a halogen LCU (Mills *et al.*, 2002). Research on the first generation LED curing lights and the few studies on the high intensity LEDs suggest these lights as good alternatives to conventional polymerization techniques. However, the clinical use of LCUs with different spectral intensities and irradiance values has raised questions about their effect on cure rate and thus on the final mechanical properties of the dental resins.

The degree of conversion (DC) of a composite material is considered key in establishing the resins' physical and mechanical properties (Ferracane and Greener, 1986). A high degree of double bond conversion translates into high mechanical strength as well as low amounts of residual monomer (Althoff and Hartung, 2000). However, DC is closely related to undesirable shrinkage stresses that develop in light-cured composites (Silikas *et al.*, 2000). During the polymerization process, dental composites have the intrinsic problem of volumetric shrinkage. Dilatometry, a common method used to measure shrinkage, yields a range of 1.034-5.63% volumetric shrinkage for restorative composites (Lai and Johnson, 1993; Oberholzer *et al.*, 2002; Rosin *et al.*, 2002; Kleverlaan and Feilzer, 2005). This shrinkage has been shown to create contraction stresses within the composite, which can adversely affect the dimensional stability of the material leading to mechanical failure or the formation of marginal gaps (Katona and Winkler, 1994). Moreover, these polymerization contraction stresses have been shown to increase with an increasing ratio of bonded to unbonded surfaces – defined as the C-factor (C = radius/height of the composite specimen; Feilzer *et al.*, 1987). The free composite surfaces are more likely to allow for flow, decreasing shrinkage restriction and thus reducing stress. In

orthodontic bracket bonding the configuration ratio is quite high due to the high proportion of bonded composite surface. Therefore, polymerization shrinkage may significantly increase residual stress within the adhesive and influence the durability of the bracket bond. Studies have found an increase in DC to be associated with an increase in shrinkage strain (Silikas, 2000). Therefore, less shrinkage and thus less contraction stress can be found with a reduction in the final DC – which ultimately may compromise some of the physical and mechanical properties of the composite material (Ferracane and Greener, 1986). This reduction in DC and mechanical strength of the composite may also adversely affect the orthodontic bond.

Minimizing polymerization shrinkage is clinically desirable – however, not at the expense of the degree of polymerization or stability of the composite. One method of controlling this shrinkage – possibly without affecting the final DC – is through the rate of cure. Polymerization stress values have been shown to increase with an increase in rate of cure (Emami and Soderholm, 2005). Developing a polymer network at a slower rate may allow for plastic flow and molecular rearrangements – delaying stress-build-up (Feilzer *et al.*, 1990). Studies have shown that shrinkage strain occurring prior to gelation may not significantly contribute to stress, since flow is viscous but unrestricted (Versluis *et al.*, 1998). Therefore, by decreasing the rate of elastic modulus development and increasing the composite's time in a non-rigid state during curing, stress-relaxation in the pre-gelation phase may result in a composite with less overall internal contraction stress.

The rate of polymerization and thus contraction stress can be controlled with varying light intensity. High intensity lights have been shown to produce higher contraction strain rates (Sakaguchi and Berge, 1997). It has also been demonstrated that by reducing light intensity and increasing the cure time, a reduction in polymerization contraction strain can be achieved without significantly altering the final degree of conversion (Sakaguchi and Berge, 1998). A recent study also demonstrated that it is possible to achieve a high final DC by using a soft-start curing method – an initial low irradiance is followed by a higher irradiance ultimately decreasing the polymerization rate (Emami and Soderholm, 2005).

Higher intensity light curing units, such as the LED, are recommended for their minimal irradiation time and ability to produce sufficient curing depth and mechanical properties. However, possible negative influences such as higher polymerization contraction stress due to a faster rate of cure may significantly affect the stability of composite adhesives and bond strength. Few studies have simultaneously analyzed the degree of conversion and polymerization shrinkage stresses that develop in orthodontic adhesive resins cured by different light systems. Furthermore, no research has been done evaluating the possible effect of these polymerization stresses on bracket to enamel bond strength over time.

MANUSCRIPT FOR SUBMISSION

Abstract:

Objective: The purpose of this study was to determine the effect of two different curing light sources on contraction stress and degree of conversion (DC) over time in an orthodontic adhesive.

Methods: Contraction stress was determined with a contraction stress measurement (CSM) device in which the orthodontic adhesive, Transbond XT (3M Unitek), was placed between a glass plate and steel rod. The steel rod passed through a washer load cell. A halogen (Ortholux XT, 3M Unitek) and an LED (Ortholux LED, 3M Unitek) were the curing light sources tested. Light was introduced from the bottom of the glass plate and loads developed within the adhesive were transferred to the load cell. Contraction force was recorded for four different time intervals: 5 minutes, 10 minutes, 1 hour, and 24 hours. Degree of conversion of each specimen at the four time points was measured with FTIR. Data were analyzed with two-way ANOVA and Bonferroni's post-hoc testing at the 0.05 level of significance. Regression analysis was also performed between contraction stress and DC.

Results: With equal light energy density the LED led to significantly greater contraction stress within the adhesive than the halogen unit ($p<0.05$). Contraction stress and DC values were significantly ($p<0.05$) greater after 24 hours compared to all other time points after initial light exposure. Irradiation condition did not significantly affect degree of conversion. The relationship between stress and DC was non-linear ($r^2 = 0.91$).

Significance: Spectral irradiance may play a significant role in polymerization efficiency. Greater contraction stress obtained with the LED, without a significant increase in DC, may adversely affect bond strength. Furthermore, other developing properties of the composite

contribute to stress build-up – such as cross-linking and modulus development – and further research is needed to determine their possible clinical effect on bond strength.

Introduction:

Advances in technology come with the desire for more efficient patient care. There is also a corresponding need for clinicians to critically analyze new products and techniques to ensure complete understanding and proper application. Recent development of light sources has led to possibly the most efficient curing light to date for photo-activated orthodontic adhesives – the high-intensity blue LED. Studies have suggested LEDs as good alternatives to the halogen curing units. However, the question remains, "When curing a light-activated orthodontic adhesive, does an LED light provide superior properties when compared to halogen?"

A number of conflicting issues arise when attempting to define the "optimal" composite cure. Degree of conversion (Ferracane and Greener, 1986), depth of cure (Jandt *et al.*, 2000), and degree of polymerization (Yap *et al.*, 2004) are all factors that have been used to signify the quality of composite cure. Mechanical properties such as elastic modulus (Sakaguchi and Ferracane, 2001), bond strength (Silta *et al.*, 2005) and residual stress (Park and Ferracane, 2005) have also been analyzed and used as indicators of composite quality. This study evaluated the effects of different irradiation conditions on specific properties of a common orthodontic adhesive – in an attempt to shed light on achieving the "optimal" orthodontic bond.

Ideally, for efficient polymerization, the irradiance spectrum of the curing light should match the absorbance spectrum of the photoinitiator (Stahl *et al.*, 2000). The extent to which the light emitted by curing units is absorbed by photoinitiators and free radicals are formed defines polymerization efficiency (Neumann *et al.*, 2005). In the case of gallium nitride light emitting diodes (LEDs), the spectral output falls

within the absorption spectrum of the camphorquinone (CPQ) photoinitiator (400-500 nm) present in the light-cure adhesive – eliminating the need for filters (Stahl *et al.*, 2000). Furthermore, the LED's peak emission is 465nm which closely matches CPQ's maximum absorption of 470nm. The halogen lights, however, emit a broader bandwidth with a peak emission (497nm) falling outside of CPQ's absorption curve (Figure 1). The good correlation between the absorption spectrum of CPQ and the emission spectrum of the LEDs may increase curing efficiency (Jandt *et al.*, 2000) and allow the LED required cure times to be less than that of the halogen lamps – decreasing the overall bond time.

The first commercially available LED units had lower light intensities than the halogen lamps. However, studies have shown that when used with the same exposure times, those LEDs are able to bond orthodontic brackets to teeth just as well as the halogen-based curing lights (Dunn and Taloumis, 2002; Bishara *et al.*, 2003). Moreover, previous research has also shown that when adjusted to the same irradiance, LEDs perform as well as halogen lights in regard to depth of cure (Mills *et al.*, 1999). Recently, LED technology has advanced significantly – leading to the construction of LED light curing units (LCUs) with higher power and similar irradiances to conventional halogen LCUs (Mills and Jandt, 2001). A study on a high power LED prototype found its polymerization technology to reach comparable performance levels of hardness and compressive strength to a halogen LCU (Mills *et al.*, 2002). Research on the first generation LED curing lights and the few studies on the high intensity LEDs suggest these lights as good alternatives to conventional polymerization techniques. However, the clinical use of LCUs with different spectral

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The purpose of this study was to investigate the effect of two different curing light sources, an LED and a halogen unit, on the polymerization contraction stress and degree of conversion of an orthodontic adhesive over time. The hypotheses were:

H1: Polymerization contraction stresses at 1 hour and 24 hours after initial light exposure would be greater with the LED than with the halogen.

- The larger overlap of the LED's emission spectra with camphorquinone compared to the halogen's would lead to increased photon absorption, free radical formation, and polymerization activation with a more developed polymer network and increased residual stress.

H2: Polymerization contraction stresses for both the LED and halogen would be greater at 24 hours than at 1 hour following initial light exposure.

- Post-irradiation polymerization would yield a more developed polymer network over time with a corresponding increase in stress.

H3: Degree of conversion at 1 hour and 24 hours after initial light exposure would not be significantly different between the LED and halogen at equal light energy densities.

- Adjusting the lights to deliver equal light energy density with similar irradiation and cure time would result in similar degree of conversion values obtained with each curing unit.

H4: Degree of conversion for both the LED and halogen would be greater at 24 hours than at 1 hour following initial light exposure.

- The polymer network and other properties of the composite would continue to develop after light exposure had ceased leading to an increase in DC over time.

Materials and Methods:

The curing light sources used in the experiments were a conventional halogen curing light (Ortholux XT, 3M Unitek) and a high intensity LED unit (Ortholux LED, 3M Unitek). The Ortholux XT halogen light has a reported irradiance by the manufacturer of 550 mW/cm^2. The Ortholux LED reportedly emits light exclusively in the 430-480 nm range at a constant intensity of 1000 mW/cm^2 without significant degradation of light emission over time. The irradiance of both light sources was measured initially with a lab-grade power meter (PowerMax 5200, Molectron Detector, Inc., Portland, OR; Table 1) and periodically throughout the experiments to ensure the light intensity of each source remained consistent. The adhesive evaluated in this study, Transbond XT (3M Unitek; Table 2), is a commonly used orthodontic adhesive with CPQ as the main photoinitiator.

Contraction stress was determined with the use of a contraction stress measurement (CSM) device as used and described in a previous study (Sakaguchi *et al.*, 2004; Figure 2). A rigid steel load frame housed the curing light sources, a washer load cell (ELW-D1, Entran, Fairfield, NJ, USA) and a steel piston. The piston passed coaxially through the load cell. Composite adhesive was placed directly below the piston and load cell, and was supported by a 5mm thick glass plate which was secured above the light sources. Custom polyvinylsiloxane molds were fabricated for each light guide to properly position them within the device so they were flush with the glass slide and directly below the adhesive specimens. Custom acrylic holders for the bases of the curing units were also fabricated to ensure consistent positioning of the curing light units in the same orientation for each trial. A ball of composite was placed on the piston and flattened as the piston was forced to a preset distance of 0.25 mm from the

glass slide with a pre-load force of 7.15 lbs. Excess flash was removed with a sharp explorer producing a composite specimen 5.0 mm in diameter and 0.25 mm in thickness. The specimens were 91% constrained with a c-factor of 10.0. Light curing was triggered 20 seconds following the start of data collection and was introduced from the bottom of the glass plate. Loads developed by the composite during polymerization were transferred to the load cell and recorded at 10 measurements per second with 12 bit resolution. Data points were collected by a Model 6100 Scanner (Vishay Measurement Group, Inc., Raleigh, NC, USA).

Three different groups of irradiation conditions were tested. In two of the groups the composite specimens were cured with the two light sources according to the manufacturers respective recommended times: 20 seconds total with the halogen light and 10 seconds total with the LED unit. The third group of samples was cured with the LED through a neutral density filter (Thorlabs, Inc., Newton, NJ, USA; ND 0.1 = 80% transmission) such that the irradiance value was equal to that of the halogen. Cure time was increased with the filtered LED to equal that of the halogen, thus providing similar light energy density (irradiance x exposure duration) between the two curing units and eliminating a possible significant influence of the combination of power density and exposure duration. The irradiation conditions tested are shown in Table 1.

Contraction force was monitored for time periods of 5 minutes, 10 minutes, 1 hour, and 24 hours. Studies have shown most polymerization after light exposure is complete within 24 hours (Leung *et al.*, 1983). The appropriate sample size (p=0.05)

was determined by running a power analysis on pilot study data collected prior to experimentation. Seven specimens were tested for each irradiation condition at 5 minutes, 10 minutes and 1 hour. Six specimens were tested with the halogen and filtered LED unit and four with the unfiltered LED at the 24-hour time period.

In order to reduce variability and help to directly correlate the data from the two separate experiments, the degree of conversion was measured on the same specimens from and immediately following the shrinkage stress tests. The degree of conversion of the orthodontic adhesives was analyzed by micro-Fourier Transform infrared (FT-IR) spectroscopy (DS-20/XAD, Analect Instruments, Irvine, CA, USA). The two frequency method and tangent baseline technique were used to estimate the degree of conversion of each sample on a relative percentage basis (Rueggeberg *et al.*, 1990). Immediately following stress measurements at the four different time periods, samples of approximately 100 μm long and 50 μm thick were removed with a scalpel from the specimens cured in the CSM. The absorbance of aliphatic and aromatic C=C were measured using a transmission technique through the samples placed on a KCl window. Five spectra were also acquired and averaged from specimens of uncured adhesive to serve as a reference.

Statistical Analysis:

Descriptive statistics including the mean and standard deviation of stress and degree of conversion at the four time points were calculated for each of the irradiation conditions tested. A two-way analysis of variance (ANOVA) was used to identify significant differences in mean stress and degree of conversion values with respect to irradiation condition and time after initial light exposure. The Bonferroni post-hoc test was used to determine which groups were significantly different. Pair-wise comparisons were also conducted with unpaired t-tests to determine significant differences in stress and DC with respect to all of the different combinations of irradiation condition and time after initial light exposure. Pearson's correlation analysis was performed to analyze relationships between stress and degree of conversion. All statistical analyses were performed at the 0.05 level of significance.

Results:

Irradiance values measured with the power meter are given in Table 1. The halogen and filtered LED had similar irradiance values (722 mW/cm^2 and 733 mW/cm^2 respectively) when measured through the glass plate and were used with a 20 second cure time to deliver similar light energy density (14440 mJ/cm^2 and 14660 mJ/cm^2 respectively). The unfiltered LED had a greater irradiance through the glass plate (986 mW/cm^2) than the halogen and filtered LED. However, the unfiltered LED was used with a 10 second cure time to deliver 32% less light energy density (9860mJ/cm^2) than the halogen and filtered LED.

Mean contraction stress values for each irradiation condition are given in Table 3. Two-way ANOVA found the main effects of time after initial light exposure and irradiation condition to both be significant ($p<0.001$) for the dependent variable stress (Table 4). Interaction was not significant ($p=0.56$). The results of Bonferroni post-hoc tests and pair-wise comparisons are summarized in Table 5. As shown in Figure 3, stress values obtained with the filtered LED were significantly greater ($p<0.05$) compared to the halogen at all time points at equal light energy densities. With regard to time after initial light exposure, stress values were not significantly different within each irradiation condition between the 5 minute, 10 minute, and 1 hour time points (Figure 4). However, all irradiation conditions showed significantly greater stress values at 24 hours compared to all other time points ($p<0.05$).

Mean degree of conversion values for each irradiation condition are given in Table 6. Two-way ANOVA (Table 7) showed a non-significant interaction between the main

factors ($p=0.90$). The main effect of irradiation condition was also found to be non-significant ($p=0.27$). However, degree of conversion was significantly affected by time after initial light exposure ($p<0.0001$). Bonferroni post-hoc tests and pair-wise comparison results are summarized in Table 8. Degree of conversion values were not significantly different between irradiation conditions at each time point ($p=0.65$, $p=0.39$, $p=0.41$, and $p=0.13$, respectively; Figure 5). With regard to time after initial light exposure, all irradiation conditions showed significantly greater degree of conversion values at the 24 hour time point compared to all other time points ($p<0.05$; Figure 6).

Pearson's correlation analysis revealed a non-linear relationship between stress and degree of conversion (Figure 7).

Discussion:

With equal light energy density, stress values obtained with the filtered LED were significantly greater ($p<0.05$) compared to the halogen at all time points. Stress values obtained with the unfiltered LED (10 second exposure) were not significantly different than the halogen (20 second exposure) at all time points, despite emitting 32% less light energy density. This suggests that polymerization efficiency is not solely dependent on light energy density. The wavelength, of light has also been shown to affect polymerization (Nomoto, 1997). The only wavelengths effective in activating the polymerization reaction are those absorbed by the photoinitiator (Cook, 1982) with the most efficient wavelength band for activation of CPQ reported to be centered around 470 nm (Nomoto, 1997). Therefore, spectral irradiance likely plays a significant role in the kinetics and quality of composite polymerization. In the 450-470 nm range, the irradiance of the LED is up to twice that of the halogen (Stahl *et al.*, 2000). A study quantifying free radical formation found an LED with $1/3^{rd}$ to $1/5^{th}$ the irradiance of halogen lights to produce 1.5-1.7 times as many primary radicals as the halogen source (Teshima *et al.*, 2003). Therefore, the spectral irradiance specific for CPQ is greater with the LED, potentially leading to greater free radical formation and greater curing efficiency. Faster polymerization at higher intensity was shown to produce more cross-linked polymers whereas slower polymerization at low intensity yielded longer molecular chains with increased flow capacity (Miyazaki *et al.*, 1996). With more efficient polymerization and possibly a faster rate of cure, the LED may be producing greater cross-link density as well as elastic modulus, resulting in greater residual stress.

When evaluating the effect of time after initial light exposure, stress values were not significantly different within each irradiation condition between the 5 minute, 10 minute, and 1 hour time points. However, all irradiation conditions showed significantly greater stress values at the 24 hour time point compared to all other time points. Other studies have also shown contraction stress to increase over time (Park and Ferracane, 2005). The polymerization reaction of light-activated composites continues even after light exposure has ceased (Leung *et al.*, 1983). The results of this study suggest as the polymer network continues to develop over time, the composite's flow capacity becomes limited and residual stress increases (Braga and Ferracane, 2002). Additional cross-linking and modulus development of the composite network post-irradiation may have contributed to the increased residual stress at 24 hours (Park and Ferracane, 2005).

The stress values found in this study were low compared to those obtained in other studies testing restorative composites (Condon and Ferracane, 2000; Braga and Ferracane, 2002; Watts *et al.*, 2003). The adhesive composition and thickness, irradiation conditions, as well as the device used to measure stress and its compliance were different in this study compared to others. Stress values measured by load cells as the composite contracts are influenced by elongation of parts of the testing device, also called the compliance of the assembly. As the compliance of the system increases, the stress values measured will decrease. The CSM device used in this study had an intermediate compliance compared to other mechanical testing devices reported in the literature (Lim *et al.*, 2002; Watts *et al.*, 2003). The MTS closed loop servohydraulic testing instrument provides a near zero compliance system by using an

eddy current feed back mechanism (Lim *et al.*, 2002), resulting in relatively higher stress values registered by the load cell. The *Bioman* shrinkage-stress instrument (Watts *et al.*, 2003) represents the other end of the compliance spectrum utilizing a cantilever load cell to measure stress. Correction factors have been used with this device to mimic the compliance of a tooth, increasing the 'raw' stress values. Regardless of the system's compliance, the CSM device used in this study resulted in data with low variance and thus was internally reliable. This allowed for comparison of stress values between the different groups of irradiation conditions. Furthermore, stress values derived from contraction force rates of composites tested using the same measurement device are comparable to those found in this study (Sakaguchi *et al.*, 2004).

The relationship between polymerization shrinkage stress and the degree of conversion is not well understood. Measuring stress without performing degree of conversion tests or measuring DC at widely varying times or on entirely different samples has led to conflicting results (Lu *et al.*, 2004). Therefore, DC was measured on the same specimens tested in the contraction stress measurement device. The range of DC values found in this study (43 – 62%) is similar to those found in previous studies on the same orthodontic adhesive (Bang *et al.*, 2004; Kauppi and Combe, 2003). Degree of conversion values were not significantly different between irradiation conditions at each time point. Good correlation between light energy density and DC has been shown (Emami and Soderholm, 2003). The results of the present study are similar to others that also found photoactivation methods do not affect DC when the total light energy density delivered with each irradiation

condition was equal (Witzel *et al.*, 2005; Lim *et al.*, 2002). However, a lower DC may have been expected with the unfiltered LED which emitted 32% less light energy density compared to the filtered LED and halogen units. A possible explanation for not seeing a difference in DC may be due to saturation of camphorquinone. With saturation of the photoinitiator, the maximum reaction rate may have been reached. A significant increase in conversion is not expected above a certain light energy density (Calheiros *et al.*, 2004). It is possible that the light energy density levels tested in this study were all greater than the "threshold" level, resulting in similar DC values between irradiation conditions. Additional runs with varying light energy density could help to elucidate the relationship between light energy density and DC, thus determining the level at which DC levels off.

With respect to time after initial light exposure, degree of conversion values were significantly greater after 24 hours compared to all other time points. The restorative literature shows conflicting results where some studies found a significant increase in DC at 24 hours (Leung *et al.*, 1983; Tarumi *et al.*, 1999) while others found DC to level off (Lu *et al.*, 2004), with no difference at 24 hours (Calheiros *et al.*, 2006). The orthodontic literature is more consistent with studies showing bond strength to significantly increase at 24 hours (25%), possibly due to polymerization progression after light exposure has ceased (Wendl and Droschl, 2004). The significant increase in DC at 24 hours found in this study also suggests a continuation of post-cure polymerization over time.

Light energy density affects degree of cure and mechanical properties of resin composites (Rueggeberg *et al.*, 1994). Studies on the effect of different combinations of irradiance and exposure duration are limited and have shown conflicting results (Nomoto *et al.*, 1994; Miyazaki *et al.*, 1996; Musanje and Darvell, 2003; Peutzfeldt and Asmussen, 2005). Reducing the irradiance of the LED with the neutral density filter and increasing the recommended clinical cure time to equal those conditions with the halogen allowed for direct comparison between the lights. By eliminating the variables of irradiance and exposure duration, any significant differences found between stress values and DC could be attributed to inherent differences between the halogen and the LED curing units.

The relationship between stress and degree of conversion was found to be non-linear with small increases in DC leading to larger increases in stress. The non-linear relationship is consistent with other reports in the literature (Braga and Ferracane, 2002; Calheiros *et al.*, 2004) and suggests that other developing properties of the composite are contributing to stress build-up – such as cross-link density and modulus development. As cross-linking and modulus increase, the capacity for flow decreases and the composite becomes unable to yield to shrinkage forces. This leads to an exponential increase in stress with small increases in DC (Braga and Ferracane, 2002).

The present study was designed and conducted to simulate a clinical situation as much as possible. However, as is the case with other well-controlled *in vitro* studies, the effort to reduce variables limited the clinical simulation. The thickness of the

glass slide used in measuring stress decreased the irradiance reaching the composite. The drop in light intensity with distance is exponential (Oyama *et al.*, 2004). However, in an orthodontic bonding scenario the tip of the light source is not flush with the adhesive, thus also reducing the irradiance of the light reaching the composite. Therefore, curing through the 5mm thick glass plate may be comparable to conditions present when curing under an orthodontic bracket. Another potential limitation of this study is that although a multi-axial stress state develops as a composite shrinks (Laughlin *et al.*, 2002), the testing device used measured the stress developing only in the long axis of the adhesive. Furthermore, stress was measured using adhesion to a glass substrate and a metal piston – not an orthodontic bracket bonded to a tooth; light exposure was from the bottom of sample through glass – not from the side as in a clinical situation; and all experiments were conducted dry and at room temperature. The oral environment is likely to induce a number of other variables that may affect the mechanical and physical properties of the composite. Some of the internal stresses may equilibrate with oral fluids and relax over time. However, orthodontic and masticatory loading conditions are very complex and may exacerbate internal material defects present immediately following light exposure, possibly increasing crack propagation and decreasing fracture resistance.

Despite the potential limitations of the study, the results provide some clinical implication. Based on the observed increase in DC over time, delaying archwire insertion for severely displaced teeth may be recommended. Furthermore, greater contraction stress values obtained with the LED may adversely affect clinical bond strength. Residual stresses within the composite may increase susceptibility to

microcracks and internal damage, ultimately decreasing bond strength. However, the increase in stress might also be associated with higher stiffness and improved mechanical properties. The question becomes, "What are the optimal mechanical properties of the composite, low residual stress or high elastic modulus?" Further studies are needed to determine the effect of contraction stress on bond strength over time. In addition, analyzing the development of other properties such as elastic modulus and cross-link density of the orthodontic adhesive could help to explain the observed increase in DC and stress and help to determine how these properties relate to the "optimal" orthodontic bond.

Conclusions:

- With equal light energy density the LED led to greater contraction stress within the orthodontic adhesive than the halogen unit.
- At the manufacturers recommended cure times stress values obtained with the halogen were not significantly different than those with the LED.
- Contraction stress and DC values were greater after 24 hours compared to all other time points after initial light exposure.
- With similar light energy density, the halogen and LED irradiation conditions did not significantly affect DC.
- The relationship between stress and DC was non-linear, with stress increasing exponentially with increasing DC.

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Tables:

Table 1 Curing lights and irradiation conditions tested

Curing Light	Irradiance (mW/cm^2) Reported by Manufacturer	Irradiance* (mW/cm^2)	Irradiance (mW/cm^2) With glass plate	Cure Time (s)	Light Energy Density (mJ/cm^2) With glass plate
Halogen Ortholux XT (3M Unitek, Monrovia, CA)	550	986	722	20	14440
LED Ortholux LED (3M Unitek, Monrovia, CA)	1000	1488	986	10	9860
LEDf**		1302	733	20	14660

*Irradiance measured with lab-grade power meter (PowerMax 5200, Molectron Detector, Inc., Portland, OR)
**LEDf = Ortholux LED with neutral density filter (ND=0.1, 0.65mm thick)

Table 2 Transbond XT Composition

	% by Volume
Bis GMA	14%
Bis EMA	9%
Fillers silylated quartz submicron silica	77%
Curatives Camphorquinone	<1%
Others	<1%

Table 3 Descriptive statistics of stress values (MPa): mean ± SD

Halogen		Stress (MPa)	Sample Size
	5 min	1.25 ± 0.07	7
	10 min	1.35 ± 0.17	7
	1 hr	1.38 ± 0.20	7
	24 hr	1.86 ± 0.17	6
LEDf			
	5 min	1.49 ± 0.14	7
	10 min	1.58 ± 0.13	7
	1 hr	1.59 ± 0.14	7
	24 hr	2.25 ± 0.21	6
LED			
	5 min	1.41 ± 0.15	7
	10 min	1.50 ± 0.19	7
	1 hr	1.67 ± 0.16	7
	24 hr	1.98 ± 0.19	4

Table 4 Two-way ANOVA: Outcome Variable Stress

Source of Variation	df	Sum of squares	Mean Square	F	Significance
Interaction	6	0.1243	0.02072	0.8118	ns
Time after initial light exposure	3	4.254	1.418	55.56	***
Irradiation Condition	2	0.98	0.49	19.2	***

ns = no significance *p<0.05 **p<0.01 ***p<0.001

Table 5 Pair-wise comparison of stress values

Irradiation Condidtion		5 min			10 min			1 hr			24 hr		
		Halogen	LED	LEDf	Halogen	LED	LEDf	Halogen	LED	LEDf	Halogen	LED	LEDf
5 min	Halogen		ns	*	ns	*†	***†	ns	***†	***†	***	***†	***†
	LED			ns	ns†	ns	*†	ns†	ns	*†	***†	***	***†
	LEDf				ns†	ns†	ns	ns†	ns†	ns	**†	***†	***
10 min	Halogen					ns	*	ns	*†	*	***	***†	***†
	LED						ns	ns†	ns	ns†	**†	***	***†
	LEDf							*†	ns†	ns	**†	**†	***
1 hr	Halogen								ns	ns	***	***†	***†
	LED									ns	*†	***	***†
	LEDf										**†	**†	***
24 hr	Halogen											ns	***
	LED												*
	LEDf												

p-values from Bonferroni posttests ns = no significance *p<0.05 **p<0.01 ***p<0.001

† p-values from unpaired t tests

Table 6 Descriptive statistics of degree of conversion values (%): mean ± SD

Halogen		DC (%)	Sample Size
	5 min	44.26 ± 6.09	7
	10 min	47.05 ± 5.95	7
	1 hr	48.61 ± 7.29	7
	24 hr	60.05 ± 1.68	6
LEDf			
	5 min	43.00 ± 3.67	7
	10 min	50.56 ± 8.60	7
	1 hr	52.57 ± 9.97	7
	24 hr	62.37 ± 3.00	6
LED			
	5 min	46.43 ± 5.54	7
	10 min	50.27 ± 2.61	7
	1 hr	51.22 ± 2.00	7
	24 hr	61.24 ± 2.21	4

Table 7 Two-way ANOVA: Outcome Variable Degree of Conversion

Source of Variation	df	Sum of squares	Mean Square	F	Significance
Interaction	6	73.45	12.24	0.3628	ns
Time after initial light exposure	3	2534	844.6	25.03	***
Irradiation Condition	2	91.01	45.5	1.349	ns

ns = no significance *p<0.05 **p<0.01 ***p<0.001

Table 8 Pair-wise comparison of degree of conversion values

Irradiation Condidtion		5 min			10 min			1 hr			24 hr		
		Halogen	LED	LEDf	Halogen	LED	LEDf	Halogen	LED	LEDf	Halogen	LED	LEDf
5 min	Halogen		ns	ns	ns	ns†	ns†	ns	**†	ns†	***	***†	***†
	LED			ns	ns†	ns	ns†	ns†	ns	ns†	***†	***	***†
	LEDf				ns†	**†	ns	ns†	***†	**	***†	***†	***
10 min	Halogen					ns	ns	ns	ns†	ns†	***	**†	***†
	LED						ns	ns†	ns	ns†	***†	*	***†
	LEDf							ns†	ns†	ns	*†	*†	**
1 hr	Halogen								ns	ns	**	**†	**†
	LED									ns	***†	*	***†
	LEDf										ns†	ns†	*
24 hr	Halogen											ns	ns
	LED												ns
	LEDf												

p-values from Bonferroni posttests ns = no significance *p<0.05 **p<0.01 ***p<0.001

† p-values from unpaired t tests

List of Figures:

1. Sample spectral irradiance of a halogen unit and an LED superimposed over the absorption spectrum of CPQ (Stahl *et al.*, 2000).

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3. The effect of irradiation condition on contraction stress over time. Mean contraction stress values shown with SD bars.

4. The effect of time after initial light exposure on contraction stress. Mean contraction stress values shown with SD bars.

5. The effect of irradiation condition on degree of conversion over time. Mean DC values shown with SD bars.

6. The effect of time after initial light exposure on degree of conversion. Mean DC values shown with SD bars.

7. Regression curve between contraction stress and degree of conversion. Mean values shown with SD bars.

Figures:

Figure 1.

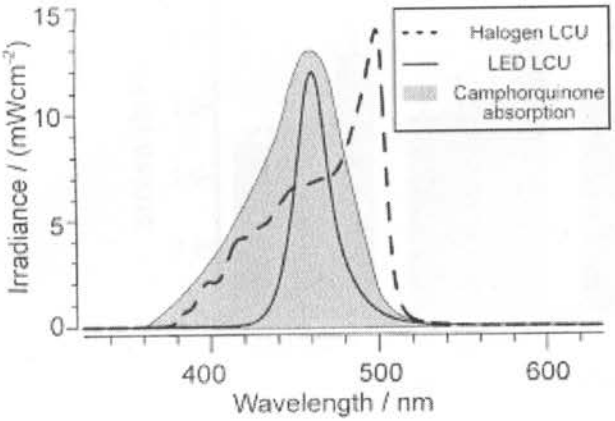
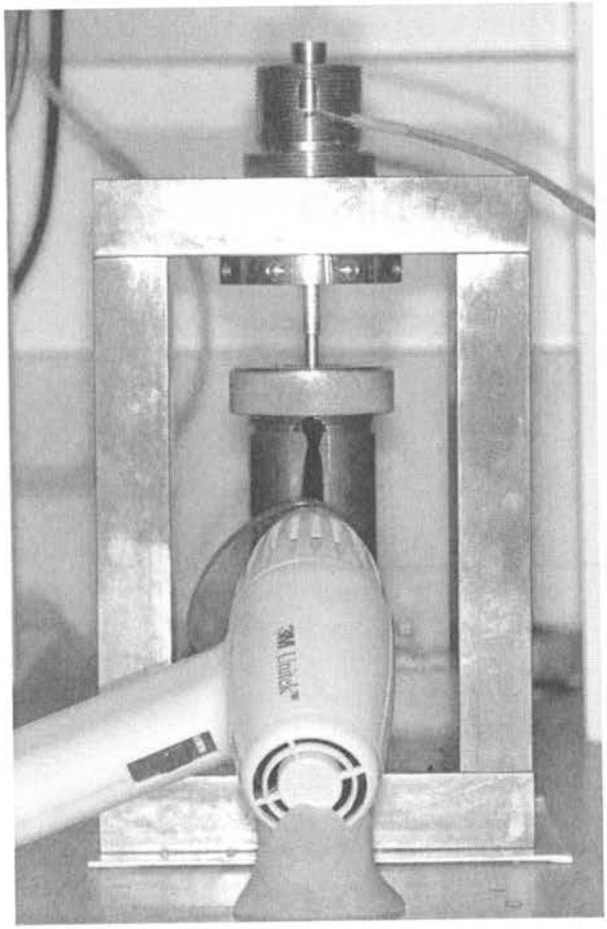


Figure 2.

A.



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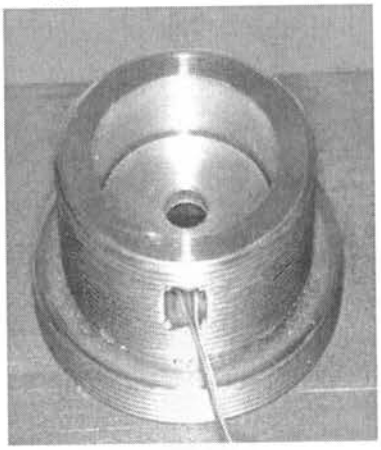

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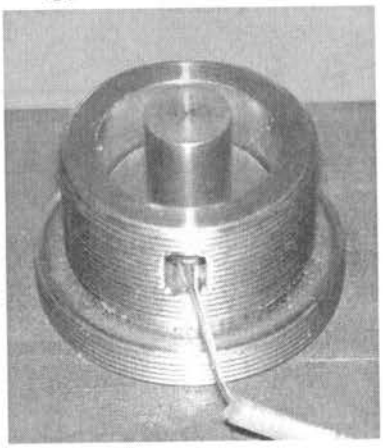

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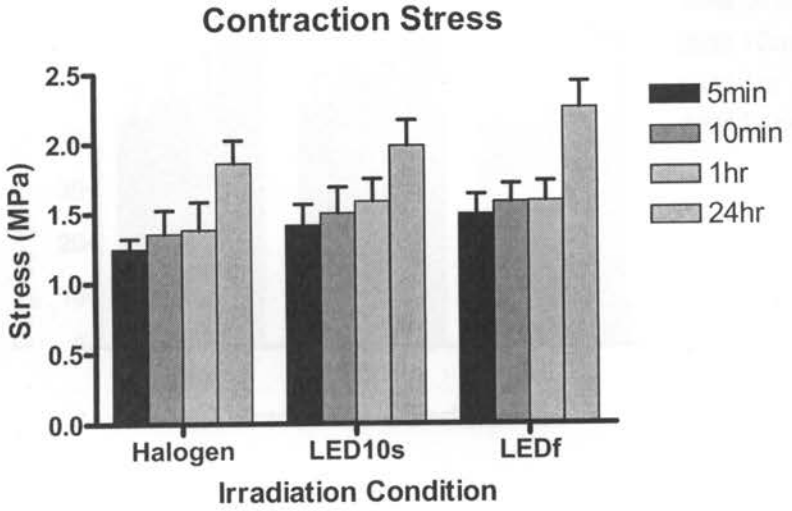


Figure 4.

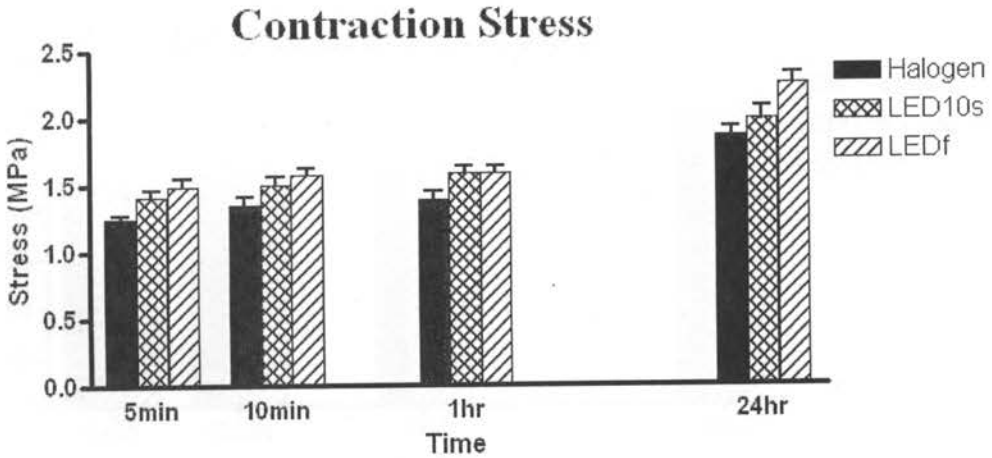


Figure 5.

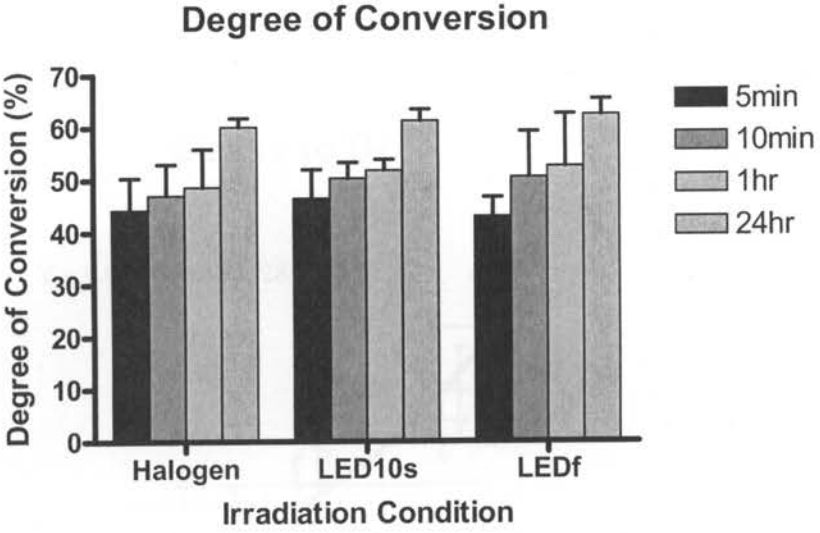


Figure 6.

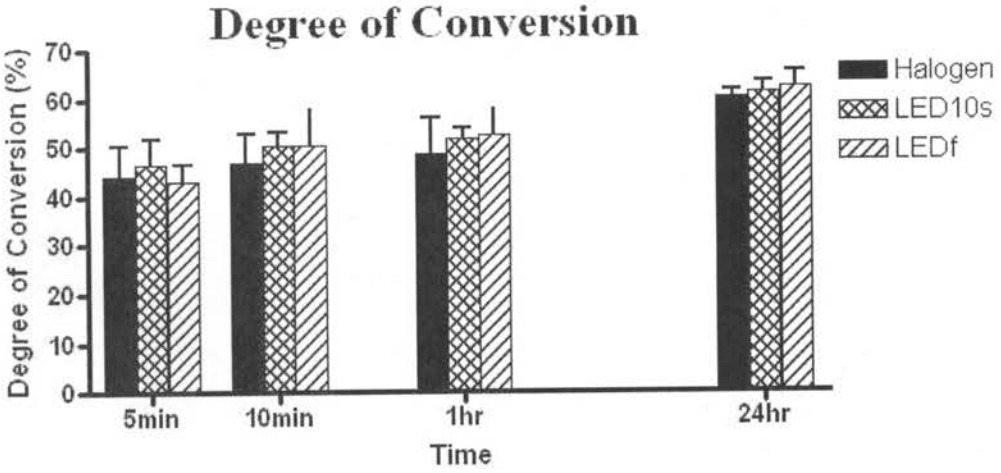
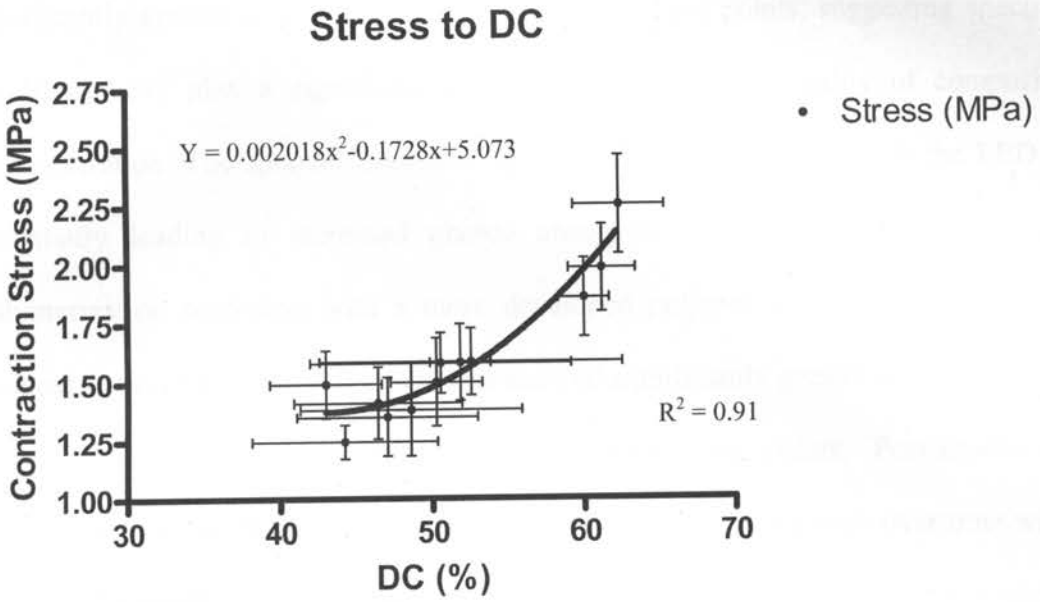


Figure 7.


Stress to DC
Contraction Stress (MPa)
2.75
2.50
2.25
2.00
1.75
1.50
1.25
1.00
30
40
50
60
70
DC (%)
Y = 0.002018x²-0.1728x+5.073
R² = 0.91
Stress (MPa)

CONCLUSIONS

With equal light energy density, stress values obtained with the filtered LED were significantly greater compared to the halogen at all time points, suggesting spectral irradiance may play a significant role in the kinetics and quality of composite polymerization. The spectral irradiance specific for CPQ is greater with the LED – potentially leading to increased photon absorption, free radical formation and polymerization activation with a more developed polymer network and increased residual stress. All irradiation conditions showed significantly greater stress values at the 24 hour time point compared to all other time points. Post-irradiation polymerization may have yielded a more developed polymer network over time with additional cross-linking and modulus development contributing to a corresponding increase in stress at 24 hours.

Degree of conversion values were not significantly different between irradiation conditions at each time point. The light energy density levels tested were possibly greater than the "threshold" level – resulting in saturation of CPQ and similar DC values between irradiation conditions. DC values were significantly greater after 24 hours compared to all other time points, suggesting a continuation of post-cure polymerization over time.

The relationship between stress and degree of conversion was non-linear with small increases in DC leading to larger increases in stress, suggesting that other developing properties of the composite contributed to stress build-up – such as cross-link density and modulus development.