COMPOSITE CURE AND POST-GEL SHRINKAGE
WITH DIFFERENT HALOGEN AND LED CURING
LIGHTS

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The objective of this research study was to determine the curing efficiency of different LED (light-emitting diodes) and halogen curing lights through various selected properties such as the thermal emission, effectiveness of cure at various cure depths, depth of cure, polymerization shrinkage and degree of conversion. Two LED (Elipar FreeLight [FL], 3M-ESPE; GC e-Light [EL], GC), a high intensity (Elipar TriLight [TL], 3M-ESPE) and a very high intensity (Astralis 10 [AS], Ivoclar Vivadent) halogen lights were selected for this study. The results obtained for the various properties for these lights were compared to a conventional (Max [MX] (control), Dentsply-Caulk) halogen light. Ten different light curing regimens including pulse (EL1), continuous (FL1, EL2, TL1), turbo (EL3, AS1) and soft-start (FL2, EL4, TL2) modes of various lights were also investigated.

Thermal emission of the light curing units (LCUs) when used in various curing modes was assessed using a K-type thermocouple and a digital thermometer at distances of 3 and 6 mm. The temperature profiles and mean maximum temperature change (n = 7) generated by each LCU were obtained. The effectiveness of cure of the different modes was determined by measuring the top and bottom surface hardness (KHN) of 2 mm, 3 mm and 4 mm thick composite (Z100, [3M-ESPE]) specimens using a digital microhardness tester (n = 5, load = 500 g; dwell time = 15 seconds). Depth of cure with the different modes was determined by penetration, scraping and micro-indentation techniques. A strain-monitoring device and test configuration was used to measure the linear
polymerization shrinkage of a composite restorative during and post light polymerization up to 60 minutes when cured with the different modes. Five specimens were made for each cure mode. Micro-Raman spectroscopy was used to determine the degree of conversion at the top and bottom surfaces of a composite restorative at 60 minutes post light polymerization. Five specimens were made for each cure mode. Results obtained were analyzed using ANOVA/Scheffe’s post-hoc test and Independent Samples t-tests at significance level 0.05.

At 3 mm, temperature rise observed with LED lights ranged from 4.1 to 12.9 ºC while that of halogen lights was 17.4 to 46.4 ºC. At 6 mm, temperature rise ranged from 2.4 to 7.5 ºC and 12.7 to 25.5 ºC for LED and halogen lights respectively. Thermal emission of LED lights was significantly lower than halogen lights. Significant differences in temperature rise were observed between different curing modes for the same light and between different LED/halogen lights. For all lights, effectiveness of cure was found to decrease with increase cavity depths. The mean hardness ratio (KHN bottom/ KHN top) for all curing lights at a depth of 2 mm was found to be greater than 0.80 (the accepted minimum standard). At 3 mm, all halogen lights produced hardness ratio greater than 0.80 but some LED light regimens did not; and at a depth of 4 mm, mean hardness ratio observed with all curing lights was found to be less than 0.80. Significant differences in top and bottom KHN values were observed between different curing regimens for the same light, and between LED and halogen lights. While curing with most modes of EL resulted in significantly lower top and bottom KHN values than the control (MX) at all depths, the standard mode of FL
resulted in significantly higher top and bottom KHN at depths of 3 and 4 mm. All specimens cured by the different light curing regimens met the ISO depth of cure requirement of 1.5 mm except most modes of EL determined by the micro-indentation technique. Curing with most modes of EL resulted in significantly lower depth of cure than the control, no significant difference was observed for the different modes of FL and greater depth of cure was observed in TL. Scraping and penetration techniques were found to correlate well but tend to overestimate depth of composite cure. Thus, the effectiveness and depth of cure was found to be light units and modes dependent.

Shrinkage associated with the various modes of EL were found to be significantly lower than MX immediately after light polymerization and at 1 minute post light polymerization. No significant difference between MX and the various lights / cure modes were observed at 10, 30 and 60 minutes post light polymerization. At all time intervals, post-gel shrinkage associated with continuous light curing mode was found to be significantly higher than the soft-start light curing mode for FL and TL. Degree of conversion ranged from $55.98 \pm 2.50 \%$ to $59.00 \pm 2.76 \%$ for the top surface and $51.90 \pm 3.36 \%$ to $57.28 \pm 1.56 \%$ for the bottom surface. No significant difference in degree of conversion was observed for the ten light curing regimens when compared to MX (control). The curing efficiency of LED lights was comparable to that of halogen lights regardless of curing modes for the degree of conversion.
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Sections of the results/related research in this thesis have been presented, published, accepted for publication or are submitted.

**International Papers**


4. MS Soh, AUJ Yap and KS Siow, Comparative depths of cure among various curing light types and methods. Operative Dentistry. (Accepted for publications)

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6. MS Soh, AUJ Yap, T Yu and ZX Shen, Analysis of degree of conversion of LED and halogen lights using micro-Raman spectroscopy. Operative Dentistry. (Accepted for publications)

7. AUJ Yap and MS Soh, Post-gel polymerization shrinkage of “Low shrink” composite restoratives. Operative Dentistry. (Accepted for publications)

8. AUJ Yap, MS Soh, VTS Han and KS Siow, Influence of curing lights and modes on crosslink density of dental composites. Operative Dentistry. (Accepted for publications)
9. AUJ Yap, VTS Han, MS Soh and KS Siow, Elution of leachable components from composites after LED and halogen light irradiation. Operative Dentistry. (Submitted for publications)

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1. Soh MS and Yap AUJ, Thermal emission of different light curing units. Paper presented at 1st Scientific NHG Congress, 16-17 August, Singapore.

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1. Literature Review

1.1 Composite Resins

Chemically cured (self or auto curing) composite resins were first developed in the late 1940s as dental restorative materials. They were found to be insoluble, aesthetic, insensitive to dehydration, inexpensive and easy to manipulate. Curing of the composites is initiated by mixing two pastes, which brings together the initiator, benzoyl peroxide, and the activator, an amine such as dihydroxyethyl-p-toluidine (DHEPT), in order to start the polymerization reaction (Ferracane, 1995). However, the materials were found to be only partially successful and are not commonly used today due to inherent weaknesses such as poor activator systems, high polymerization shrinkage, high coefficient of thermal expansion, and lack of wear resistance. These unfavorable physical properties prevent chemically cured composites from being an ideal restorative material. Its poor wear resistance prevents it from maintaining its contour in areas subject to abrasion or attrition. It is not indicated for high-stress areas, since the material has low strength and will flow under load. Its high polymerization shrinkage and coefficient of thermal expansion may cause microleakage and eventual discoloration at the margins as a result of percolation (Sturdevant & others, 1995). In addition, clinical studies have also shown that self-cure composites undergo more darkening than light cured composites over time (Tyas, 1992). Hence, self-cure composites declined in popularity when light-activated composites were developed. Light-activated composites offered a controlled working time and
eliminated time consuming mixing procedures, which incorporated porosities in
the restoration.

The beginning of modern adhesive dentistry was marked by the evolution of Bowen’s Bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane) formulation in the early 1960s (Bowen, 1962;1965). The introduction of this composite-based resin technology to restorative dentistry was one of the most significant contributions to dentistry in the last century. Applications for this new polymer include anterior and posterior composite resin restorations, indirect inlays/onlays, pit and fissure sealants and more wear-resistant denture teeth (Leinfelder, 1997).

Composite materials refer to a compound of two or more distinctly different materials with properties that are superior or intermediate to those of the individuals constituents. Dental composites are complex, tooth-colored filling materials composed of synthetic polymers, particulate ceramic reinforcing fillers, molecules which promote or modify the polymerization reaction that produces the cross-linked polymer matrix from the dimethacrylate resin monomers, and silane coupling agents which bond the reinforcing fillers to the polymer matrix. Each component of the composite is critical to the success of the final dental restoration (Ferracane, 1995).

Eighty to ninety percent of commercial dental composites utilize Bis-GMA monomer as their matrix-forming resin (Ruyter & Øysæd, 1987). Other base monomers used in present commercial composites include urethane
dimethacrylate (UDMA), ethoxylated bisphenol-A-dimethacrylate (BisEMA), bis(methacryloxyloxymethyl) tricyclocdecane and urethanetetramethacrylate (UTMA). Bis-GMA has a very high viscosity because of the hydrogen bonding interactions that occur between the hydroxyl groups on the monomer molecules. As a consequence, Bis-GMA must be diluted with a more fluid resin in order to be useful for dental composites (Ferracane, 1995). Triethyleneglycol dimethacrylate (TEGDMA) has excellent viscosity and copolymerization characteristics and is often used as the diluent monomer for BisGMA-based composites to produce a fluid resin that can be maximally filled with inorganic filler particles. TEGDMA has, however, been replaced with UDMA and BisEMA in several products to reduce shrinkage, aging and environmental effects (Yap, Low & Ong, 2000). Both these resins have higher molecular weights than TEGDMA and therefore have fewer double bonds per unit of weight.

The most significant developments in the evolution of commercial composites to date have been a direct result of modifications to the filler component. Change of size and filler-loading has improved the wear resistance of the early composite resins. Modern composite systems contain filler such as quartz, colloidal silica, silica glass containing barium, strontium and others. This filler increases strength and modulus of elasticity and reduces the polymerization shrinkage, the coefficient of thermal expansion and water sorption (Dogon, 1990).

Despite vast improvements in composite materials, present day composite resins still have shortcomings limiting their application. Inadequate resistance to wear (loss of anatomic form) under masticatory attrition, marginal adaptation,
secondary caries and marginal leakage due to polymerization shrinkage are often cited as being the main problems of composite resins (Full & Hollander, 1993; Ferracane, 1992). Hence, the major and most significant drawback of composite-based resins is that they contract or shrink during the conversion of the monomer to the polymer. The Bis-GMA and UDMA composite resin systems exhibit significant volume shrinkage on curing (Davidson & de Gee, 1984; Eick & Welch, 1986; Roulet, Salchow & Wald, 1991). Commercial composite resins differ greatly in their final polymerization shrinkage because of differences in their monomer composite, various degrees of final polymerization, filler types, and filler concentrations.

### 1.2 Limitations of Light-activated Composite Resins

The development of light-activated composite materials in the 1970s heralded a period of rapid progress in the field of tooth-colored restorations. One of the most obvious changes in dental practice during the 1970’s was the way in which composites became the most popular material for aesthetic anterior restoration (Yearn, 1985). Composite resins undergo a process called polymerization when cured. Polymerization refers to a process whereby a large number of monomers undergo a series of chemical reactions to form macromolecules or polymer.

In the case of light-activated composites, light at an appropriate wavelength is absorbed by an α-diketone, usually camphorquinone (CQ), and in that excited state reacts with an amine reducing agent to produce the free radicals to form a cross linked polymeric matrix (Dart & Nemcek, 1978; Craig, 1981). Each chain addition step in the polymerization process requires a free radical, and
thus it can be seen that the degree of conversion depends not only on the particular chemistry of the formulation, but on the amount of suitable light energy which reaches the catalyst. Thus, light-activated composites cure only where light reaches them and surface layers nearest the light source cure more efficiently than those deeper in the body of the material (Cook, 1980; Baharav & others, 1988).

1.2.1 Depth of Cure

Light-activated composite resins suffer from the fact that they reply upon adequate intensity of light to initiate polymerization. As light pass through the bulk of the composite to initiate curing, it is absorbed and scattered. These factors result in an attenuation of light intensity as it passes through the restoration bulk (Rueggeberg & others, 1993). The result of this attenuation is that cure on the surface is much greater than it is within the depths of the material. At greater depths, part of the light required for further polymerization is absorbed by the already polymerized layers of composite resins (Baharav & others, 1988). Rueggeberg & others (1993) have pointed out that intensity (the rate at which CQ is raised to the excited state) and exposure duration (the rate at which the excited CQ molecule collides and reacts with the reducing agent to form free radicals) are two rate limiting factors influencing composite cure. Intensity of light helps to maintain CQ in the excited (triplet) state for reaction with a reducing agent (an amine) to form free radicals which initiate polymerization. At the surface, a low amount of source intensity and a short exposure time is sufficient to provide a relatively high degree of cure. The duration of exposure will allow the excited CQ molecules to diffuse and react with the amine to help initiate polymerization. When light intensity is not the rate limiting step in polymerization, duration of
exposure becomes of importance. The influence of intensity becomes more important as the thickness of overlying composite increases. Light is absorbed and scattered by the overlying composite that fewer activated CQ molecules are created, resulting in potentially fewer free radicals. This decrease in activated CQ interacts with duration of exposure as the thickness increases. Exposure duration must be increased in order for the lower number of activated CQ molecules to diffuse and successfully collide with the reducing agent to form free radicals. Thus, both source intensity and exposure duration becomes more important as depth of composites increases. The top surface hardness of composite samples nearest the light source are less dependent on curing tip distance (Pires & others, 1993) and light intensity (Hansen & Asmussen, 1993, Rueggeberg & others, 1993) when compared to the bottom surface. Rueggeberg & others (1993) have pointed out that filler type, exposure duration and resin shade predominated as the most influential factors at the surface. At depths of 1 mm, exposure duration, filler type and source intensity predominated but at depths of 2 mm and more, the overwhelming influences on cure were related solely to source intensity and exposure duration.

Depth of cure was found to decrease with increase cavity depths (Yap, 2000). The presence of incomplete curing at the bottom surface of the restoration increases the risk of bulk and marginal fracture. Other possible complications of inadequate restoration polymerization include secondary caries and adverse tissue reactions (Shortall, Wilson & Harrington, 1995). Inadequately polymerized composite will also exhibit poor color stability and greater strain uptake (de Gee, ten Harkel-Hagenaar & Davidson, 1984). Increased rates of water sorption and
solubility have been demonstrated following inadequate polymerization of visible light-activated composite (Pearson & Longman, 1989) and decreased hardness may also contribute to early restoration failure (Fan & others, 1987).

While lighter shades attained greater depth of cure than the darker ones (Swartz, Phillips & Rhodes, 1983; Backer, Dermaut & Bruynooghe, 1985), darker shade composite is capable of attaining an equivalent depth of cure to the lightest shade (Ferracane & others, 1986). Ferracane & others (1986) have pointed out that depth of cure of light activated composite resins may be less dependent upon shade than upon translucency. Ruyter & Øysæd (1982) have also shown that light scattering was the limiting factor for depth of cure in composites and that scattering was maximized when the size of the filler particles was approximately one-half that of the wavelength of the activating light. Other factors which affect the cure depth of light-activated composite resins include light intensity, the type of light source (Tanoue, Matsumura & Atsuta, 1998a), the type of composite resin (Cook, 1983; Ruyter & Øysæd, 1982), temperature of the composite materials (Bennett & others, 1994), thickness of the increment (Kanca, 1986), distance of the light tip from the surface of the materials (Murchison & Moore, 1992), curing time (Rueggeberg & Jordan, 1993) and post-irradiation time (Hansen, 1983; Leung, Fan & Johnston, 1983; Watts, McNaughton & Grant, 1986).

Studies have also shown that the depth of cure of composites was strongly influenced by the exposure time period. Improved depth of cure with increasing exposure time period was observed for most restorative materials (Tanoue, Matsumura & Atsuta, 1998b; 1999; Rueggeberg, Caughman & Curtis, 1994).
Watts, Amer & Combe (1984) and Baharav & others (1988) have shown that greater depth of cure or hardness can be observed with increased exposure time and higher intensity but the extent of cure does not depend linearly on the duration of light exposure. While increasing exposure time resulted in greater hardness, Yap (2000) has shown that effectiveness of polymerization decreased significantly with increased cavity depth regardless of exposure time. It was suggested that increments of composites evaluated should not exceed 2 mm to obtain uniform and maximum cure.

Depth of cure of composites can be evaluated by means of optical microscope where changes in the translucency of light-cured composite resins, which is the demarcation line between the cured and uncured resins, are detected. Scraping technique which involves the scraping away of the soft, unpolymerized resin from the bottom of a polymerized sample and then measuring the depth of the cured material remaining with a micrometer (ISO 4049, 1988) is another indirect method for evaluating depth of cure. However, both methods though easy to perform and correlated well, grossly overestimated adequate cure depth of composites (DeWald & Ferracane, 1987). Indirect method such as Knoop hardness testing where hardness of the top and bottom surface or hardness along the side of a specimen that had been illuminated is widely used to assess depth of cure or the effect of cure of light-activated composites due to simplicity of the test method. Composite resins decreased in hardness as depth increased (Atmadja & Bryant, 1990). In general, higher hardness values are indicative of more extensive polymerization (Asmussen, 1982; Ferracane, 1985) and adequately photo-
activated composite should have a hardness gradient of less than 10-20 % between the top and bottom surfaces (DeWald & Ferracane, 1987; Yearn, 1985).

Good correlation was found between Infrared spectroscopy (IR) and Knoop hardness testing (Ferracane, 1985). IR which is used to determine the degree of conversion (that is, the percentage of carbon double bonds converted to single bonds during the polymerization reaction) of light-activated composites offers a direct technique to evaluate depth of cure. Although Knoop hardness correlated well with degree of conversion, the degree of conversion was more drastically reduced as depth increased. Thus, degree of conversion which involves complex instrumentation is considered the most sensitive testing mode for evaluating depth of cure in light-activated dental composites (DeWald & Ferracane, 1987). Direct measurement of depth of cure can also be achieved by standardized digital penetrometer test method (Harrington & Wilson, 1993). This test method which applied a constant force to achieve consistency of results is a more refine method than that adopted by standard specifications. Dye uptake (de Gee & others, 1984), tactile tests (Fowler, Swartz & Moore, 1994) and nuclear magnetic resonance microimaging (Lloyd, Scrimgeour & Chudek, 1994) are some other methods used for evaluating cure depths.

### 1.2.2 Degree of Conversion

The degree of polymerization in cross-linked polymeric systems has a potentially large role in determining the ultimate physical and mechanical properties of the material. While it is desirable for dental composite resins to achieve 100 % conversion (that is, conversion of all its monomer to polymer during
polymerization reaction) to achieve the ultimate physico-mechanical properties, there is always a significant concentration of unreacted carbon double bonds remaining in the resin when cured. This is due to limitations on the mobility of reactive species imposed by the rapid formation of a cross-linked polymeric network (Ferracane, 1985). High resin viscosity restricted the mobility of reactive species and reduced the frequency and probability of random encounters, which led to a decrease in polymerization propagation (Loshaek & Fox, 1953).

Analysis of degree of conversion can be achieved by Fourier Transform Infrared Spectroscopy (FTIR) (Ferracane & Greener, 1984), Laser Raman Spectroscopy (Louden & Roberts, 1983) and Micro-Raman Spectroscopy (Pianelli & others, 1999). Spectroscopic analysis of the degree of conversion of monomer to polymer in dental resins is a very accurate and reproducible technique although it involves relatively complex and expensive instrumentation (Rueggeberg & Craig, 1988). The degree of conversion was calculated by monitoring the change in absorbance of the aliphatic carbon double bond (C=C) at 1640 cm$^{-1}$ in the cured and uncured states with reference to the absorption of the unchanged aromatic ring (internal standard) at 1610 cm$^{-1}$ (Ferracane, 1985; Rueggeberg & others, 1994). The aromatic absorption functions as an internal standard, eliminating the need for determination of cell-path length or control of the contact area of material when attenuated total reflectance (ATR) is used (Rabek, 1980). Other methods for determining degree of conversion include differential thermal analysis (DTA) (Imazato & others, 2001) and differential scanning calorimetry (DSC) (Urabe, Wakasa & Yamaki, 1991). DSC provides a measure of methacrylate conversion based on the enthalpy of the exothermic polymerization process while DTA which
makes use of a split fiber light source provides a measure of degree of conversion based on the heat of polymerization of composites.

IR techniques such as Potassium Bromide (KBr) pellet transmission method, transmission through thin resin films (Ferracane & Greener, 1984), MIR (multiple internal reflection), NIR (near infrared) (Stansbury & Dickens, 2001), ATR and micro-attenuated total reflection infrared spectroscopy (micro-ATR) (Eliades, Vougiouklakis & Caputo, 1987) are used for analyzing the degree of conversion. Ferracane & Greener (1984) have pointed out that different IR techniques used for the determination of degree of conversion by FTIR gave different results but provide useful and reproducible results for dental resins. The Raman spectroscopy is known to be a useful tool, both for the determination of the molecular composition of materials and for obtaining structural information by molecular vibration analysis (Suzuki, Kato & Wakumoto, 1991). It is a non-destructive technique and allows measurement on the surfaces of the restorations to be performed without any mechanical and chemical pre-treatment which may influence the results (Lundin & Koch, 1992). Degree of polymerization for light-activated ranged from 43.5 to 73.8 % and was highest for the most diluted resins (Ferracane & Greener, 1984; Chung & Greener, 1988; Pianelli & others, 1999).

The degree of conversion of light-activated composites depends on the output intensity of the curing light (Tate, Porter & Dosch, 1999). Sufficient intensity at the correct wavelength and adequate exposure time are critical variables for satisfactory polymerization (Shortall & Harrington, 1996). It is generally accepted that a minimum intensity reading of 300 mW/cm² within the
correct wavelength range (450-500 nm) and exposure duration of 40 seconds are required to ensure effective polymerization of CQ initiated materials to a depth of 2 mm (Tate, Porter & Dosch, 1999; Shortall & Harrington, 1996). Several authors recommended a minimum intensity of 400 mW/cm$^2$ and exposure duration of 60 seconds per increment (Tate & others, 1999; Shortall & Harrington, 1996; Rueggeberg & others, 1994). A minimum intensity of 400 mW/cm$^2$ allows for differences in the type and shade of composite, differences in increment thickness and variations in the distance and intervening substrate (that is, composite resins, porcelain or enamel) between the tip of the light guide and the material being polymerized (Martin, 1998). Though degree of conversion is maximized by the inclusion of a high percentage (40-50 %) of diluents in the resin, the cure is accompanied by significant polymerization shrinkage (1.5-3 vol %) for most commercial materials (de Gee, Feilzer & Davidson, 1993).

1.2.3 Polymerization Shrinkage

The stress associated with the curing contraction is one of the most significant problems for current materials, because it adversely affects the seal at the cavosurface margin and causes occurrence of secondary caries (Qvist, Qvist & Mjör, 1990). While water sorption by polymer network contributes to stress reduction, its effect is minimized as water uptake by composite resins takes place at a much slower rate, requiring hours to reach saturation (Ferracane & Condon, 1990). In addition, water sorption has also been found to weaken the resin matrix and to cause filler/matrix debonding and hydrolytic degradation of the fillers with a subsequent reduction in mechanical properties and wear resistance (Öysæd & Ruyter, 1986; Söderholm & Roberts, 1990; Söderholm, 1981). Water sorption can
be reduced by the use of more hydrophobic monomers, such as BisEMA, which
do not contain unreacted hydroxyl groups on the main polymer chain (Ruyter &
Nilsen, 1993).

While shrinkage stresses can be reduced but not eliminated by increasing
filler loading, the ultimate solution to polymerization shrinkage is to develop
“non-shrinking” resins. Although earlier efforts to synthesize such resins were not
successful, several developments in the last decade are more encouraging.
Stansbury (1992) has synthesized spiro-orthocarbonate monomers (SOCs) which
expand during polymerization through a double-ring opening process. Miyazaki &
others (1994) reported on the development of acrylates and methacrylates
containing spiro ortho esters that were capable of being polymerized by heat,
ionic and free radical initiators. The synthesis of new SOC's polymerized epoxy
via cationic UV photo-initiation has also been reported (Byerley & others, 1992;
Eick & others, 1993). Although these polymers are promising, problems balancing
mechanical properties, water sorption, solubility and expansion still exist.

An optimal degree of conversion and minimal polymerization shrinkage
are generally antagonistic goals. As mentioned earlier, successful photocured
composite resin restorations depend directly on the degree of polymerization and
consequently on the output intensity of curing lights. Sufficient intensity, correct
wavelength (450 to 500 nm) and adequate curing time are critical variables for
maximum polymerization of the composite resin. If any variable is inadequate, the
materials are only partially cured (Yearn, 1985).
The use of high intensity light source has recently been introduced for improving composite properties. However, curing composites with a high intensity light may demonstrate significant disadvantages due to increased shrinkage stress (Unterbrink & Muessner, 1995). High intensity lights provide higher values of degree of conversion and superior mechanical and physical properties but produced higher contraction strain rates during polymerization of composites (Uno & Asmussen, 1991). Properties of composites may also be affected by both photo and heat energy emitted by the light sources during photo exposure which resulted in an increased environmental temperature (Tanoue, Matsumura & Atsuta, 2000). This increase in temperature may be damaging to the pulp (Hussey, Biagioni & Lamey, 1995). The thermal energy contributed by the curing light source and the polymerization exotherm of resin composite together could be dangerous to the dental pulp (Pilo, Oelgiesser & Cardash, 1999). Zach & Cohen (1965) have shown that a 5.5 °C increase in temperature could cause histological changes in the pulp. Curing direct composite restorations with high intensity lights may also lead to reduction in marginal quality (Uno & Asmussen, 1991).

Several studies have shown that marginal integrity can be improved by reducing the light intensity (Unterbrink & Muessner, 1995; Feilzer & others, 1995; Uno & Asmussen, 1991). A reduced light intensity slows down the cure rate of composites which increases the ability for flow and enables partial relaxation of polymerization contraction stress (Feilzer, de Gee & Davidson, 1990). However, curing composites at low light intensity leads to inferior physical properties concerning flexural modulus, flexural strength and microhardness. Hence, the
recent approach to minimizing polymerization shrinkage is through controlled polymerization. The polymerization process appears to be dependent on total light energy rather than light intensity alone (Miyazaki & others, 1996).

Controlled polymerization can be achieved by application of short pulses of energy (pulse activation) or pre-polymerization at low-intensity light followed by a final cure at high intensity (soft-start polymerization). Studies have shown that smaller marginal gap, increased marginal integrity and lower shrinkage can be achieved by these polymerization techniques without affecting the degree of conversion in composite (Sakaguchi & Berge, 1998; Mehl, Hickel & Kunzelmann, 1997; Kanca & Suh, 1999). The reduction in polymerization shrinkage and its accompanying stress by these polymerization techniques was attributed to the capacity for flow in light-activated composites. Flow was defined as the amount by which the shrinkage stresses exceed the elastic limit (Davidson & de Gee, 1984). Flow is thought to be the ability of molecules within the forming polymer to slip into new positions before being restricted by cross-linking. This allows deformation to occur and decreases the amount of tensile force exerted by the hardening resin. It was suggested that flow tended not to occur in the light-activated material because of its characteristically more rapid polymerization and the more rapid achievement of cross-linking and of the elastic limit. Thus the rate of polymerization has a significant effect of the strain development (Kanca & Suh, 1999). However, several other studies have also shown that polymerization shrinkage was not significantly affected by the application of the different polymerization technique when compared to standard
Polymerization of the resin matrix produces a gelation in which the restorative material is transformed from a viscous-plastic into a rigid-elastic phase. The gel point is defined as the moment at which the material can no longer provide viscous flow to keep up with the curing contraction. Therefore, the results of shrinkage determinations are dependent on the flow ability of the material in the experiment set-up. Shrinkage determination where the displacement transducer requires activation by way of force, can only monitor the “post-gel” part of the curing contraction, when the material is sufficiently strong to exert forces (Davidson & Feilzer, 1997). Following gel formation, the polymerization process is accompanied by a rapid increase in elastic modulus which induces stress within the polymer and distributes it to the boundary layers. This post-gel shrinkage influences the strength of the bond between composite resins and tooth structure which may lead to bond failure arising from defects in the composite-tooth bond. Microleakage, postoperative sensitivity and recurrent caries may also arise due to post-gel stresses (Eick & Welch, 1986).

The total amount of volumetric curing contraction which includes both the pre-gel and post-gel shrinkage of composites can be determined by mercury dilatometer (Penn, 1986; Iga & others, 1991) and water dilatometer (Rees & Jacobsen, 1989; Lai & Johnson, 1993). The total polymerization shrinkage determined by both dilatometry is laborious and time-consuming and is also subjected to data scattering when used for low viscosity resins. Other methods for
determination of total polymerization shrinkage include deflecting-disk technique (Cash & Watts, 1991), density change determination (Hay & Shortall, 1988) which requires the density measurements of the materials and the maintenance of temperature with extreme care so that the volume of the liquid media remains constant; and linometer (de Gee, Feilzer & Davidson, 1993). The linometer is a simple and fast device for the measurement of linear polymerization shrinkage of composites and is insensitive to temperature fluctuations and is operational at any temperature.

When flow ceases after gelation and can no longer compensate for shrinkage stresses, post-gel polymerization shrinkage develops. The measurement of post-gel shrinkage of composite restoratives can be determined by the use of electrical resistance strain gauges. The small size of the gauge allows it to measure localized shrinkages as the gauge can be precisely located. This becomes very useful in the restored tooth where stress transfer to the hard tissue due to the bonded composite can be measured in simulated clinical conditions in the laboratory. Thus, stain gauge method is a suitable method for real-time measurement of the curing process and provides a means for studying the kinetics of polymerization (Sakaguchi & others, 1991). Other recent methods for the determination of polymerization shrinkage include optical measurement of linear shrinkage that does not interfere with physical deformation (Aw & Nicholls, 1997); gas pycnometer for the determination of total polymerization shrinkage, particularly for the measurement of shrinkage of composites which are sensitive to water absorption (Cook, Forrest & Goodwin, 1999); and laser interferometric method for monitoring linear shrinkage (Fogleman, Kelly & Grubbs, 2002).
The long term success of clinical composite restorations depends, apart from optimal materials and a suitable dentine bonding system, upon complete and appropriate polymerization. As research continues on new monomers and modifiers that will offset polymerization shrinkage during and after curing, one solution to polymerization shrinkage has been light curing systems and curing techniques.

1.3 Light Curing Systems

The use of visible light to cure dental materials has expanded over recent years to incorporate a vast array of products, including luting cements, temporary restorative materials, periodontal pack materials, reline and impression materials, in addition to composite resins, glass ionomers and bonding agents. Successful use of these products depends directly on correct functioning of the visible light curing unit (Martin, 1998). Three essential components required for adequate polymerization include sufficient radiant intensity, correct wavelength of the visible light and ample curing time (Takamizu & others, 1988; Rueggeberg, 1993). Diminished light output can result in restorations which are incompletely polymerized. Possible consequences include a reduction in the mechanical properties resulting in marginal breakdown, increased wear, decreased strength, color stability and increased water sorption (Leung, Fan & Johnston, 1983; Pearson & Longman, 1989; Ferracane & others, 1997). These problems can subsequently be responsible for secondary caries, pulpal irritation and decreased longevity of the restoration.
1.3.1 Halogen Lamps

Curing of dental composites with blue light was introduced in the 1970s with the introduction of light-activated composites (Bassiouny & Grant, 1978). The source of blue light is normally a halogen bulb combined with a filter, so that blue light in the 410 nm to 500 nm region of the visible spectrum is produced. Light in this range of wavelengths is most effectively absorbed by the camphorquinone (CQ) photoinitiator that is present in the resin component of light activated dental composites (Cook, 1982). The absorption spectrum of CQ lies in the 450 nm to 500 nm wavelength range, with peak absorption at 470 nm (Lee & others, 1993; Denehy & others, 1993). The light causes excitation of the CQ, which in combination with an amine produces free radicals. This results in polymerization of resin monomers at the molecular scale. Macroscopically, the dental composite hardens, typically after light exposure times ranging from 20s to 60s.

For many years, halogen lamps have been more widely employed than any other device as a practical alternative method to cure resins. Presently, halogen lamps being a low cost technology are still the most frequently used light sources for polymerization of dental materials. Their light is produced by an electric current flowing through an extremely thin tungsten filament. This filament functions as a resistor and is so strongly heated by the current that it emits electromagnetic radiation in the form of visible light. Operating with a white halogen bulb filtered by a dielectric pass-band filter to remove the undesirable wavelengths, conventional composite-curing lamps operate in the deep blue region of the spectrum. However, this type of equipment still emits a considerable number of other wavelengths. The spectral impurities of the conventional curing
lights deliver several wavelengths that are highly absorbed by dental materials, inducing heating of the tooth and resin during the curing process (Miyazaki & others, 1998; Martin, 1998).

Other inherent drawbacks in the use of conventional curing lights include limited effective lifetime of about 40-100 hours for halogen bulbs; bulb, reflector and filter degrade over time due to high operating temperatures and large quantity of heat produced during the curing cycles (Jandt & others, 2000). One major drawback of halogen curing lights is the need for intensive fan cooling. As the cooling air current enter and exit through slots in the casing, disinfection of the handpiece is incomplete and bacterial aerosol present in the patient’s mouth may be dispersed. The fore-mentioned resulted in a reduction of the light curing unit’s curing effectiveness over time (Barghi, Berry & Hatton, 1994). The clinical implication is that with an ageing light curing unit (LCU), light activated dental materials will be less well cured with poorer physical properties and an increased risk of premature failure of restorations-assuming no compensation for decreased LCU irradiance (Jandt & others, 2000).

Several studies have also shown that many halogen LCUs used by dental practitioners do not reach the minimum power output specified by the manufacturers (Barghi & others, 1994; Martin, 1998; Miyazaki & others, 1998) due to lack of maintenance such as failure to replace the filter and/or the halogen bulb from time to time and LCU’s irradiance is not checked regularly. The measured irradiance of LCUs also depends on the radiometers used and it appears
that there is little consistency of irradiance measured with radiometers used in

**1.3.2 Plasma-Arc Lights**

In the past few years, alternative methods of light curing such as plasma-arc lights (PAC) have been developed. PAC functions differently from halogen light sources. Instead of a filament, these lights contain two tungsten electrodes separated by a small gap, between which a high voltage is generated. The resulting spark ionizes the gaseous environment (Xenon) and creates a conductive gas known as plasma. These lights produce large amounts of electromagnetic energy, and the units must contain extensive filtering to remove harmful or unusable wavelengths. The most effective filter in this type of unit is the liquid-filled light guide that transmits light from the base unit to the curing tip. This cord is more durable than conventional glass-fibered cords that may break if the cord is twisted or bent sharply. PAC units typically produce power densities greater than 2000 mW/cm$^2$, and have been shown to polymerize composite in the shortest time (Rueggeberg, Ergle & Mettenberg, 2000).

Manufacturers of these expensive fast curing devices claim that PAC are capable of polymerizing composites with mechanical properties of the cured materials being comparable to those cured with conventional halogen lamps. However, scientific studies have demonstrated that these shorter curing times have a negative impact on the mechanical properties of the polymerized materials. Potential negative clinical aspects of the use of this type light are the intrapulpal temperature rises of the restored teeth (Caughman, Rueggeberg & Moss, 2002)
and increases in polymerization shrinkage forces exerted on the restoration/tooth complex (Bouschlicher & Heiner, 2001).

Extended tooth exposure to PAC lights can produce a significant increase in pulpal temperature. A 10 seconds PAC exposure is the maximum time necessary to adequately polymerize a 2 mm increment of composite, and the pulpal temperature rise associated with this polymerization process is comparable to that observed with a halogen LCU 40 seconds exposure (Caughman & others 2002). When curing bonding resin with a PAC light in an unfilled preparation, the maximum exposure time should be reduced to three seconds because of the lack of dentin insulation to the pulp and the fact that this thin layer does not require an extended exposure.

Since PAC light polymerizes composite much faster than other types of curing lights, it seems logical that this activation method would produce increased shrinkage forces. As a result, some manufacturers have produced PAC lights with ramped curing modes. However, it was suggested that the initial ramped output power density must be less than 100 mW/cm² to be effective, and the initial output delivered by PAC lights at their lowest possible emission value is much higher than this (Caughman & Rueggeberg, 2002).

### 1.3.3 Lasers

Recently, curing device such as lasers (Cobb, Vargas & Rundle, 1996) has been used in clinical practice to polymerize dental composites with the advantage of a reduced curing time. The used of continuous wave argon lasers for curing of
microfilled composites also exhibited a greater degree of polymerization (Hinoura, Miyazaki & Onose, 1993). However, only a low power argon laser should be used to avoid temperature rise and high contraction values (Meniga & others, 1992). Nicholls (2000) has pointed out that lasers do not fully polymerize some composites due to (1) the light energy being emitted does not have the correct wavelength to polymerize the composite, or (2) the light energy being emitted has a very low intensity for the required wavelength. The range of wavelengths emitted by the laser is small compared to the standard blue light. Laser curing unit also has a more complex construction and is more costly compared with halogen sources. In addition, lasers require stringent additional safety precautions.

1.3.4 Light Emitting Diodes

The most recent breakthrough in dental light curing systems is the development of blue light emitting diodes (LEDs) for the curing of dental composites (Whitters, Girkin & Carey, 1999). To overcome the several drawbacks of halogen LCUs, blue LED LCUs have been developed as an alternative light curing device for the polymerization of light-activated dental composite resins. These newly developed light sources make use of blue gallium nitride (GaN) LEDs as the source of visible blue flux.

Solid state LEDs, which are a combination of two different semiconductors (n and p doped semiconductors), emit blue light by quantum-mechanical effects. The p-type region is doped with impurities having more holes and the n-type region is doped with impurities having more electrons. Junctions of
Doped semiconductors (p-n junctions) are used for the generation of light (Nakamura, Mukai & Senoh, 1994). Under proper forward biased conditions, electrons from the conduction band of the n-type region are injected across the potential barrier into the conduction band of p-type region. A potential barrier refers to a forbidden zone, bandgap, where no energy level can exist. Holes from the valence band of the p-type region are injected across the bandgap into the valence band of the n-type region (Figure 1.1). The electrons and holes recombine at the LED’s p-n junction leading, in the case of GaN LEDs, to the emission of blue light (Figure 1.2). A small polymer lens in front of the p-n junction partially collimates the light. The spectral output of GaN blue LEDs falls conveniently within the absorption spectrum of the CQ photoinitiator (450-500 nm) present in light activated dental materials, so that no filters are required in LED LCUs (Jandt & others, 2000).

Figure 1.1 The p-n junction.
LEDs have an expected lifetime of several thousand hours without significant degradation of light flux over time. They are resistant to shock and vibration and their relatively low power consumption make them suitable for portable use. The narrower spectral output of these blue LED of 440 – 490 nm falls within the CQ absorption spectrum and therefore produces an almost ideal bandwidth of the light that is required (Mills, Jandt & Ashworth, 1999). Furthermore, LED LCUs which produces lesser heat than halogen LCUs eliminates the need for cooling fan and lesser potential for gingival and pulpal irritation (Leonard & others, 2002).

With its inherent advantages, such as a constant power output over the lifetime of the diodes, LED LCUs have great potential to achieve a clinically consistent quality of composite cure. Recent studies have shown that LED LCUs have the ability to polymerize a range of composites to depths of cure (Mills &
others, 2002), compressive strengths (Jandt & others, 2000; Mills & others, 2002),
flexural strengths and modulus (Stahl & others, 2000) that are not statistically
significantly different from the values obtained with a halogen LCU. Mills &
others (1999) have shown that an LED LCU with an irradiance of 64 % of a
halogen LCU achieved a significantly greater depth of cure. Greater depth of cure
was also observed with a prototype LED which had 78 % of the irradiance of the
halogen LCU (Mills, Uhl & Jandt, 2002). Composites polymerized with a halogen
LCU with an irradiance of 755 mW/cm$^2$ and a LED LCU with an irradiance of
350 mW/cm$^2$ were found to have compressive strengths equivalent to those cured
with a conventional halogen LCU (Jandt & others, 2000). The depth of cure of
composites polymerized with the LED LCU was found to be 20 % lower than
those cured with the conventional halogen LCU and may be due to the great
differences in irradiance produced. However, both LCUs exceeded by far the
minimum of composite depth of cure according to ISO 4049.

In a study by Kurachi & others (2001), composites cured by LED-based
devices shown an inferior hardness values when compared with the halogen lamp
at the typical curing time of 40 seconds. Dunn & Bush (2002) have also
demonstrated that the top and bottom surface hardness were significantly lower
for composites cured with LED LCUs. Thus, it was suggested that the LED LCU
required considerably longer exposure times to adequately polymerize resin
composites (Leonard & others, 2002). While the fore-mentioned studies have
shown that composites cured with LED LCUs exhibited inferior hardness,
Hofmann, Hugo & Klaiber (2002) have demonstrated that LED LCUs have the
ability to polymerize a range of composites to hardness values not significantly
different from the halogen LCUs. Shrinkage strain after 60 minutes was also found to be significantly lower with LED LCUs when compared to the halogen LCU.

Lower degree of conversion and temperature rise were also observed with composites cured by LED LCUs (Knežević & others, 2001; Tarle & others, 2002). The differences in the degree of conversion values between halogen curing units and blue LEDs is not so significant because of great differences in the curing intensity. The low temperature increase in blue LED is due to the slow polymerization reaction as a result of low curing energy of the blue LEDs. When equal light energy was irradiated, the degree of conversion by LED was not significantly different from halogen lamp (Yoon & others, 2002).

Studies (Mills & others, 1999; Jandt & others, 2000; Stahl & others, 2000; Hofmann & others, 2002) have shown that blue LED LCUs have the potential to polymerize dental composites without having the drawbacks of halogen LCUs. The numbers of studies on the efficiency of LED lights are, however, still limited and differences in findings have yet to be explained.
CHAPTER 2

2. Research Programme

2.1 Objectives

From the review in chapter 1, it is apparent that polymerization shrinkage, depth of cure, effectiveness of cure and degree of conversion of composites still remain a clinical concern in dentistry. The advantages and disadvantages governing the use of various techniques to minimize shrinkage have also been reviewed in chapter 1. While composite resins continue to advance, one way to control or minimize polymerization shrinkage has been the light curing units. Section 1.3 reviewed on the different type of light curing systems applied in dentistry. While LED has shown great potential in polymerizing composites without the inherent drawbacks of halogen lights, the numbers of studies on the efficiency of LED lights are still limited. Hence, the objectives of this research were:

1) To quantify the thermal emission of LED and halogen lights.

2) To compare the effectiveness of composite cure between LED and halogen lights at varying cavity depths.

3) To investigate the depth of composite cure of LED and halogen lights.

4) To determine and compare the post-gel shrinkage of LED and halogen lights.

5) To determine the degree of conversion of LED and halogen lights.

6) For curing lights that offer multiple modes of curing, differences in thermal emission, depth and effectiveness of cure, shrinkage and degree of conversion between soft start / pulse / turbo activation were also compared to standard continuous cure.
2.2 Materials

2.2.1 Light-activated Composite Resins

A minifilled composite resins, Z100 (3M-ESPE, St Paul, Mn 55144, Lot no: 20010517) (Figure 2.1) of shade A2, was used in this study. The various compositions in Z100 are shown in Table 2.1.

**Figure 2.1** Minifilled composite resins, Z100.

<table>
<thead>
<tr>
<th>Table 2.1</th>
<th>Components present in Z100.</th>
</tr>
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</table>

**Composition of Z100**

Composite resins: Bis-GMA / TEGDMA  
**Coupling Agent:** Silane

**Fillers:** Zirconia Silicate  
**Activator-Initiator:** Camphoroquinone

**Filler size (μm):** 0.5 – 0.7 (mean)  
**Inhibitors:** Butylated hydroxytoluene

**Filler content (% by vol.):** 66%
2.2.2 Light Curing Units Employed In This Study

Five LCUs and ten light curing regimens were investigated in this study. Details of the various lights and curing regimens are listed in Table 2.2. Two LED lights (Elipar FreeLight [FL]; GC e-Light [EL]), a high intensity halogen LCU (Elipar TriLight [TL]), a very high intensity halogen light with short exposure duration (Astralis 10 [AS]) and a conventional halogen LCU (Max [MX] (control)) were chosen for this study to represent a wide range of products. The curing lights are described below.

Elipar FreeLight

Elipar FreeLight (Figure 2.2) is an advanced LED light that requires less than 10% of the electrical power consumed by conventional halogen lights. It consists of 19 LEDs aligned on three consecutive planes (Figure 2.3) and emits light mainly in the wavelength range of 440 to 490 nm (that is the wavelength range for CQ containing products).

FL has two exposure modes namely the standard and exponential modes. The standard mode provides full light intensity for the entire exposure period of 10, 20, 30 or 40 seconds. The exponential mode provides light increasing to full intensity over the course of 12 seconds for a period of 40 seconds. The gentle initiation of polymerization is designed to reduce shrinkage stress. The two curing modes investigated in this study were standard for 40 seconds and exponential.
Figure 2.2 Elipar FreeLight.

Figure 2.3 (a) Array of 19 LEDs in FL (b) Schematic illustrations of 19 LEDs aligned on three consecutive planes.

(a)
**GC e-Light**

The GC e-Light (Figure 2.4) produces visible blue light in the wavelength range between 440 and 490 nm for photopolymerization of dental materials. EL consists of 64 LEDs (Figure 2.5) and a whole range of curing regimens. Range of curing regimens includes fast curing (4 curing programmes), pulse curing (3 programmes) and traditional curing (4 different programmes). Four light curing regimens were selected in this study. They are pulse curing (pulse 10 x 2), standard, turbo and soft-start curing A. The pulse curing regimen produces full power in a pulsation mode, that is, an emission of successive flashes in different intervals with a relaxation period of 250 milli-seconds in between the light exposures. The intensity and exposure duration for each curing regimens investigated in this research study are detailed in Table 2.2.
Figure 2.4 GC e-Light.

Figure 2.5 64 LEDs in GC e-Light.
**Max**

Max LCU (Figure 2.6) is the control light unit in this research. Max LCU is a conventional halogen light curing unit which provides only one standard exposure mode at full light intensity of 400 mW/cm² for the entire exposure period of 40 seconds.

**Figure 2.6** The conventional halogen LCU, Max.

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**Astralis 10**

Astralis 10 (Figure 2.7) is a fast curing, high performance halogen curing light that is capable of delivering a very high light intensity of 1200 mW/cm² in 10 seconds (high power programme). This curing unit is characterized by its very high light intensity, which is achieved with the specially developed 100 watt lamp.
AS covers the entire range of blue light from 400 to 510 nm and can be used to cure the most popular materials.

AS halogen LCU features four polymerization programmes. They are the high power, adhesive programme, pulse programme and ECS-programme. Only the high power programme was investigated in this study. The high power programme polymerized composites in 10 seconds with a very high intensity of 1200 mW/cm². The high intensity and short exposure duration is designed to help clinicians maximized and reduced curing time.

**Figure 2.7** Astralis 10, the very high intensity halogen LCU.
**Elipar TriLight**

Elipar TriLight (Figure 2.8) is a high intensity halogen curing light with an exponential “soft-start” polymerization feature to improve marginal adaptation and physical properties. The soft-start polymerization mode ensures that the curing reaction is produced in a more uniform reaction rate. TL consists of three operating modes (exponential, standard and medium) with exposure duration of 10, 20, 40, 60 and 80 seconds. Both the exponential and standard modes with exposure duration of 40 seconds were investigated in this study. The exponential mode (Figure 2.9) feature an output intensity that increases automatically from 100 mW/cm\(^2\) to 800 mW/cm\(^2\) for the duration of the curing time selected. The standard mode (Figure 2.10) features a consistent high level output intensity of 800 mW/cm\(^2\).

**Figure 2.8** The high intensity halogen curing light, Elipar TriLight.
**Figure 2.9** Exponential Mode.

**Figure 2.10** Standard Mode.
Table 2.2 Details of the light curing units (LCU) and the various curing modes evaluated.

<table>
<thead>
<tr>
<th>LCU</th>
<th>Curing Modes</th>
<th>Curing Profiles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elipar FreeLight (LED)</td>
<td>Standard (FL1)</td>
<td>400 mW/cm² (40 seconds)</td>
</tr>
<tr>
<td>3M-ESPE, Seefeld, Germany</td>
<td>Exponential (FL2)</td>
<td>0-400 mW/cm² → 400 mW/cm² (12 seconds) → 400 mW/cm² (28 seconds)</td>
</tr>
<tr>
<td>GC e-Light (LED)</td>
<td>Pulse Curing (EL1)</td>
<td>750 mW/cm² (10 pulses x 2 seconds)</td>
</tr>
<tr>
<td>GC Europe, Leuven, Belgium</td>
<td>Standard (EL2)</td>
<td>350 mW/cm² (40 seconds)</td>
</tr>
<tr>
<td></td>
<td>Turbo (EL3)</td>
<td>600 mW/cm² (20 seconds)</td>
</tr>
<tr>
<td></td>
<td>Soft-start curing A (EL4)</td>
<td>0-600 mW/cm² (20 seconds) → 600 mW/cm² (20 seconds)</td>
</tr>
<tr>
<td>Max (Halogen)</td>
<td>Standard (MX)</td>
<td>400 mW/cm² (40 seconds)</td>
</tr>
<tr>
<td>Dentsply-Caulk, Milford, DE</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Elipar TriLight (Halogen)</td>
<td>Standard (TL1)</td>
<td>800 mW/cm² (40 seconds)</td>
</tr>
<tr>
<td>3M-ESPE, Seefeld, Germany</td>
<td>Exponential (TL2)</td>
<td>100-800 mW/cm² → 800 mW/cm² (15 seconds) → 800 mW/cm² (25 seconds)</td>
</tr>
<tr>
<td>Astralis 10 (Halogen)</td>
<td>High Power (AS1)</td>
<td>1200 mW/cm² (10 seconds)</td>
</tr>
<tr>
<td>Ivoclar-Vivadent, Schaan, Liechtenstein</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Curing profiles are based on manufacturers’ information.
The results obtained in this study will provide clinicians with useful information on the different type of dental curing lights. It will also help clinicians maximize chair time productivity, by placing restorations of better mechanical stability in less time under clinical conditions, as well as allowing them to optimize the use of light curing units. This research study also provides an insight on the scientific background of light curing units and also the opportunities that different light sources, especially LED LCUs, open up for the future developments. The detailed experimental techniques carried out in this research study can be found in the subsequent chapters.
3. Thermal Emission

3.1 Introduction

The potential damaging effects of temperature increase on the pulp tissue during restorative treatment has been a matter of concern to dentistry for many years. Light curing units (LCUs) can cause a temperature increase that could damage the pulp (Hussey, Biagioni & Lamey, 1995; Hannig & Bott, 1999). Thermal transfer to pulp is affected by material shade, thickness, composition, porosity, curing time and residual dentin thickness (McCabe, 1985; Goodis & others, 1989; Shortall & Harrington, 1998). It also varies with the type of curing unit, quality of light filter, output intensity and irradiation time (Goodis & others, 1997; Shortall & Harrington, 1998; Hannig & Bott, 1999). Temperature rise during the curing of restorative materials is, however, contributed mainly by the light source (Lloyd, Joshi & McGlynn, 1986).

LED (Light-Emitting Diodes) LCUs which have the inherent advantages as described in section 1.3.4 were recently introduced to the dental professional to overcome the several drawbacks of halogen lights. While some research has been conducted on the use of LED lights on composite hardness, modulus, depth of cure, compressive and flexural strengths ((Mills, Jandt & Ashworth, 1999; Stahl & others, 2000; Jandt & others, 2000; Kurachi & others, 2001), the thermal emission of LED lights has not been investigated.
This chapter quantified the thermal emission of two LED and three halogen lights. Temperatures changes associated with various curing modes of each LCU were also compared where applicable.

### 3.2 Methods and Materials

The light curing units selected for this study included two LED lights (Elipar Freelight [3M-ESPE]; GC e-light [GC]) and three halogen lights (Max [Dentsply-Caulk]; Elipar Trilight [3M-ESPE]; Astralis 10 [Ivoclar-Vivadent]) as described in chapter 2. Details of the various LCUs and the different curing modes evaluated are shown in Table 2.2. Thermal emission of the various LCUs was measured by a K-type thermocouple and a digital thermometer (305, Peacock Precision Instruments, Singapore). The thermocouple was secured onto a groove in an acrylic base-plate so that the surface of the thermocouple was flushed against the top surface of the base-plate (Figure 3.1). Two clear acrylic plates of 3 mm and 6 mm in thickness with a 7 mm diameter hole served as spacers to control the thermocouple-light guide exit window distance. The experimental set-up allowed the thermocouple to be positioned at the centre of the 7 mm hole (Figure 3.2). The light guide exit windows of the various LCUs were placed over the 7 mm hole of the upper acrylic plates and activated. Temperature rise during irradiation can, therefore, be measured at distances of 3 mm and 6 mm away from the thermocouple.
**Figure 3.1** Diagrammatic representation of the experimental set-up.

**Figure 3.2** Thermocouple positioned at the centre of the 7 mm hole.
A pilot study was first conducted to determine the effects of environmental temperature on temperature rise during light irradiation using the Max polymerization unit (the control unit in this research). The experiment was conducted in a controlled and enclosed environment (Concept 300 Workstation; Ruskin Technology Limited, Yorkshire, UK) at preset temperatures of 25 ºC and 37 ºC (Figure 3.3). Temperature rise associated with the Max polymerization unit at both preset environmental temperatures were measured at distances of 3 mm and 6 mm. Five readings were taken at five-minute intervals for each preset temperature and distance. Results were analyzed with paired samples t-test at significance level 0.05. At 3 mm, temperature rise was 15.2 ± 0.1 and 15.3 ± 0.2 ºC for environmental temperatures of 37 ºC and 25 ºC respectively. At 6 mm, temperature rise was 10.8 ± 0.2 and 10.8 ± 0.3 ºC for environmental temperatures of 37 ºC and 25ºC respectively. As no significant difference in temperature rise was observed between the two environmental temperatures at both distances, the main experiment was conducted under ambient room temperature.

The ambient room temperature was recorded and maximum temperature rise during light activation was obtained for the different LCUs and curing modes. Seven readings were obtained for each light-curing mode combination. To minimize the effects of heating, a 5 minutes hiatus was implemented between each curing cycle. The temperature rise profiles of the various lights and their different curing modes were also determined by obtaining 10 temperature readings at equal time intervals over the light curing period. Data was subjected to one-way ANOVA/Scheffe’s post-hoc test and Independent Samples t-test at significance level 0.05. The mean maximum temperature rise of the different LCUs/curing
modes was compared to the conventional halogen LCU (Max). In addition, differences between curing modes for the same light and different LED/halogen lights were also compared. Temperature changes at 3 mm and 6 mm were also contrasted.

**Figure 3.3** The experimental set-up in a controlled and enclosed environment at preset temperatures of 25 °C and 37 °C.

### 3.3 Results

Table 3.1 shows the mean maximum temperature rise observed with the various LCUs/curing modes. Results of statistical analysis are shown in Tables 3.2 and 3.3. The temperature rise profiles of the various LCUs/curing modes are reflected in Figures 3.4 to 3.8.
Table 3.1 Mean maximum temperature rise observed with the various LCUs/curing modes.

<table>
<thead>
<tr>
<th>Light-curing units</th>
<th>Light-curing modes</th>
<th>At 3 mm [°C]</th>
<th>At 6 mm [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>12.9 (0.17)</td>
<td>6.6 (0.18)</td>
</tr>
<tr>
<td></td>
<td>FL2</td>
<td>10.9 (0.31)</td>
<td>7.2 (0.24)</td>
</tr>
<tr>
<td>GC e-Light</td>
<td>EL1</td>
<td>8.1 (0.16)</td>
<td>4.9 (0.20)</td>
</tr>
<tr>
<td></td>
<td>EL2</td>
<td>5.5 (0.10)</td>
<td>3.4 (0.23)</td>
</tr>
<tr>
<td></td>
<td>EL3</td>
<td>7.5 (0.20)</td>
<td>4.1 (0.24)</td>
</tr>
<tr>
<td></td>
<td>EL4</td>
<td>8.4 (0.16)</td>
<td>4.5 (0.13)</td>
</tr>
<tr>
<td>Max</td>
<td>MX</td>
<td>17.4 (0.70)</td>
<td>12.7 (0.28)</td>
</tr>
<tr>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>26.7 (0.39)</td>
<td>19.8 (0.32)</td>
</tr>
<tr>
<td></td>
<td>TL2</td>
<td>22.6 (0.16)</td>
<td>18.3 (0.41)</td>
</tr>
<tr>
<td>Astralis 10</td>
<td>AS1</td>
<td>36.0 (0.88)</td>
<td>20.2 (0.20)</td>
</tr>
</tbody>
</table>

Standard deviations in parentheses.

Table 3.2 Comparison of mean maximum temperature rise of the various LCUs/curing modes to the conventional halogen LCU (Max polymerization unit).

<table>
<thead>
<tr>
<th>Light guide exit window distance</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mm</td>
<td>AS1, TL1, TL2 &gt; MX &gt; EL1, EL2, EL3, EL4, FL1, FL2</td>
</tr>
<tr>
<td>6 mm</td>
<td>AS1, TL1, TL2 &gt; MX &gt; EL1, EL2, EL3, EL4, FL1, FL2</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test (p < 0.05). > indicates statistical significance.
Table 3.3 Comparison of mean maximum temperature rise of the various curing modes for the same LCU.

<table>
<thead>
<tr>
<th>Light guide exit window distance</th>
<th>Light Curing Unit</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 mm</td>
<td>Elipar Freelight</td>
<td>FL1 &gt; FL2</td>
</tr>
<tr>
<td></td>
<td>GC e-light</td>
<td>EL1, EL4 &gt; EL3 &gt; EL2</td>
</tr>
<tr>
<td></td>
<td>Elipar Trilight</td>
<td>TL1 &gt; TL2</td>
</tr>
<tr>
<td>6 mm</td>
<td>Elipar Freelight</td>
<td>FL2 &gt; FL1</td>
</tr>
<tr>
<td></td>
<td>GC e-light</td>
<td>EL1 &gt; EL4 &gt; EL3 &gt; EL2</td>
</tr>
<tr>
<td></td>
<td>Elipar Trilight</td>
<td>TL1 &gt; TL2</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test or Independent Samples t-test (p < 0.05). > indicates statistical significance.

The temperature rise observed at 3 mm was significantly higher than at 6 mm. At 3 mm the temperature rise observed with LED lights ranged from 5.5 to 12.9 °C, while the halogen lights showed a range of 17.4 to 36.0 °C. At 6 mm, temperature rise ranged from 3.4 to 7.2 °C and 12.7 to 20.2 °C for LED and halogen lights, respectively. Thermal emission of LED lights was significantly lower than halogen lights at both distances (Table 3.2). Significant differences in temperature rise between different curing modes of the same curing light are reflected in Table 3.3. For FreeLight and e-Light, minor variations in significant differences between curing modes were observed between 3 and 6 mm. Among the halogen lights, curing with AS1 mode resulted in the most heat generation. Maximum or peak temperatures were consistently observed towards the end of curing cycles and duration lasted not more than 15 seconds (Figure 3.4 to 3.8).
Figure 3.4 Temperature rise profile of Elipar FreeLight.

Figure 3.5 Temperature rise profile of GC e-light.
Figure 3.6 Temperature rise profile of Max.

Figure 3.7 Temperature rise profile of Elipar Trilight.
3.4 Discussion

Light guide exit window distances of 3 mm and 6 mm were used to mimic distances encountered when curing deep Class I and Class II cavities. The experimental set-up also allowed for the simulation of a confined cavity as in the case of a Class II cavity with matrix and rubber dam placement. In addition, the 3 mm distance approximates the proximity of the light guide exit window to the top layer of restorative materials during clinical restorative procedures. Since the acrylic spacers used have a low thermal conductivity, the maximum temperature rise observed represents the worst case scenario. Restorative materials and teeth were excluded from the experiment design to minimize the number of variables involved. By doing so, the data obtained can also be applied to light (heat)
enhanced bleaching procedures and thermal expansion of composites during curing.

In this study, temperature rise decreased significantly with increased light guide exit window distance. Results concur with those of Shortall and Harrington (1998), who investigated temperature rise due to radiation energy at various cavity depths. Although the light output of LCUs (350 and 710 mW/cm²) used by the latter group were similar to that of Max and Trilight (400 and 800 mW/cm², respectively) in this study, maximum temperature rise observed at 6 mm distance was considerably lower (2.0 °C and 3.7 °C, compared to 12.7 °C and 19.8 °C). This may be partially attributed to the use of black nylon spacers, which may absorb part of the heat emitted, instead of clear acrylic ones.

The thermal emission of LED lights was significantly lower than halogen lights at both distances. Rather than a hot filament (as in halogen bulbs), LEDs use junctions of doped semiconductors (p-n junctions) for the generation of light (Nakamura, Mukai & Senoh, 1994). Under proper forward biased conditions, electrons and holes recombine at the LED’s p-n junctions leading to the emission of blue light in the case of gallium nitride LEDs. As the spectral output of gallium nitride blue LEDs falls within the absorption spectrum of the camphoroquinone photoinitiators, no light filters are required. The latter (light filters), however, serves as partial thermal buffers in curing lights (Shortall & Harrington, 1998). From Table 3.1, it is apparent that LED LCUs still emit heat and the thermal emission from different LED lights varies significantly. The temperature rise observed with FreeLight was significantly higher than e-Light despite a lesser
number of LEDs used (Freelight 19 LEDs; e-Light 64 LEDs). The maximum temperature observed with Freelight is expected to be even higher if not for the aluminium casing cum handle used. This serves to conduct heat and cool the unit. Reasons for the higher thermal emission of FreeLight are not known. Possible hypotheses include LED size and inter-LED spacing.

Among the halogen lights, curing modes utilizing high light outputs generally resulted in significantly greater thermal emission. The lowest temperature rise was observed with the Max polymerization unit that had the lowest light output among the three halogen lights evaluated. The clinical experience with conventional halogen LCUs (< 500 mW/cm²) indicates that the pulp appears able to recover from transient heating from light-curing. Zach and Cohen (1965) reported that 15% of the teeth in rhesus monkeys developed necrosis when the healthy pulps were exposed to a temperature increase of only 5.5°C. These findings and those of Pohto and Scheinin (1958) suggest that the critical temperature for irreversible damage to the pulp begins at 42 to 42.5°C. Hannig and Bott (1999) measured the pulp chamber temperature increase induced during composite resin polymerization with various LCUs using a tooth model (Class II cavity with a 1 mm dentin layer between pulp chamber and proximal cavity wall), K-type thermocouple positioned at the pulp-dentin junction and 2 mm composite layers. They found that LCUs with outputs greater than 670 mW/cm² generated temperature increases of more than 5.5°C when used for 40 seconds. Taking this into consideration, the maximum temperature rise detected in TriLight (800 mW/cm² for 40 seconds) should be viewed as critical, especially where residual dentin thickness is limited. In spite of the very high value observed
with Astralis High Power mode (AS1 – designed for curing composite restorations), the very short-term temperature peak may not be relevant to pulpal damage (Figure 3.8).

For an individual tooth, it is nearly impossible for a clinician to predict the temperature rise that may occur when curing a restoration. In general, the thicker the dentin and the shorter the curing time, the smaller the temperature increase (Loney & Price, 2001). Clinicians should be aware of the potential thermal hazard associated with using high intensity lights when curing composites in deep cavities. Minimum irradiation times should also be used when curing bonding agents with these lights in view of the absence of a composite thermal buffer. A simple and effective way to protect the pulp is to apply a cement base or lining material to the cavity floor (Hansen & Asmussen, 1993). As the heat emitted by LED lights are significantly lower than halogens, they exhibited a potential advantage over halogen lights in the curing of composites. The data obtained in this chapter will be useful for understanding composite post-cure and thermal expansion during polymerization in the later chapters.

3.5 Conclusions

For this section, the following conclusions can be made:

1. LED lights emit significantly less heat than halogen lights.

2. The heat emitted by individual curing lights depends on the curing mode used.

3. The heat emitted by different LED/halogen lights varies significantly.
CHAPTER 4

4. Effectiveness of Composite Cure

4.1 Introduction

The use of visible-light-activated dental composites for the restoration of teeth has increased substantially over the past decade (Kurachi & others, 2001). Depth and effectiveness of composite cure are two important properties. One limitation of light activated composite materials is that a hard top surface is not an indication of adequate polymerization throughout the depth of restoration (Pilo & Cardash, 1992; Hansen & Asmussen, 1993). Poorly polymerized resin can lead to undesirable effects such as gap formation, marginal leakage, recurrent caries, adverse pulpal effects and ultimate failure of restoration (Ferracane, 1993). Effective composite cure is important not only to ensure optimum physico-mechanical properties (Asmussen, 1982) but also to ensure that clinical problems do not arise due to the cytotoxicity of inadequately polymerized material (Caughman & others, 1991). Greater depth of cure eliminates the need to refill a cavity preparation with several layers of resin. The depth of cure of visible-light activated composites is affected by factors such as the material’s filler composition, resin chemistry, shade and translucency, catalyst concentration, the intensity and spectral distribution of the light source and duration of irradiation (Shortall, Wilson & Harrington, 1995).

The use of blue LED LCUs to polymerize light-activated dental materials was first proposed by Mills, Jandt & Ashworth (1999). While LED LCUs have shown great potential in achieving an effectiveness of cure equivalent to halogen
curing lights (Hofmann, Hugo & Klaiber, 2002), others have found that the effectiveness of cure by LED LCUs resulted in significantly inferior top/bottom hardness values when compared to halogen lights (Kurachi & others, 2001; Dunn & Bush, 2002). Thus, it was suggested that the LED LCU required considerably longer exposure times to adequately polymerize resin composites (Leonard & others, 2002).

Despite the marked increase in availability of LED dental curing lights, research comparing composite cure associated with halogen and LED curing lights are generally limited. Thus, the objective of this study was to compare the effectiveness of composite cure between LED and halogens at various cavity depths. For curing lights with a variety of cure modes, effectiveness of cure between modes was also compared.

4.2 Methods and Materials

A minifilled composite resin (Z100; 3M-ESPE, St. Paul MN 55144) of A2 shade and five LCUs were selected for this study. They included two blue LED (Elipar FreeLight, [3M-ESPE, Seefeld, Germany]; GC e-Light, [GC Europe, Leuven, Belgium, Europe]), a high intensity halogen (Elipar TriLight, [3M-ESPE, Seefeld, Germany]), a very high intensity halogen (Astralis 10, [Ivoclar Vivadent, Schaan, Liechtenstein]) and a conventional halogen (Max, [Dentsply-Caulk, Milford DE 19963]) lights. The ten light curing regimens evaluated are detailed in Table 2.2. Intensity of all the curing lights was checked with a radiometer (Cure Rite, EFOS INC, Ontario, Canada) prior to use to ensure consistency in intensity output from the light source. Standard deviations ranging from 2.17 to 5.34 mW/cm² were
obtained for the various lights. The emission spectrum of each light unit in standard mode was analyzed by a photometer (662, Schmidt Scientific, Metrohm, Switzerland) equipped with a light guide measuring cell with attached reflector (Figure 4.1). Direct measurements (n = 3) were obtained for each wavelength over a range of 430-500 nm.

**Figure 4.1** Photometer equipped with a light guide measuring cell.

The hardness testing methodology used to assess effectiveness of cure was based upon that used by Yap (2000). The resin composite was placed in black delrin molds with square cavities 2, 3 and 4 mm deep and 4 mm wide/long and confined between two opposing acetate strips (Hawe-Neos Dental, Bioggio, Switzerland). A white delrin backing was used beneath the molds. A glass slide (1 mm thick) was then placed on the molds and excess material was extruded by pressure application. The composite was then irradiated from the top through the glass slide and acetate strip using the different light-curing modes. Immediately after light polymerization, the acetate strips were removed, and the specimens in their molds were positioned centrally beneath the indenter of a digital
microhardness tester (FM7, Future-Tech Corp, Tokyo, Japan) (Figure 4.2) to assess the Knoop’s Hardness Number (KHN) of the top and bottom surfaces. A 500 g load was then applied through the indenter with a dwell time of 15 seconds. The KHN corresponding to each indentation was computed by measuring the dimensions of the indentations and using the formula KHN = 1.451 x (F/d^2) where F is the test load in Newtons and d is the longer diagonal length of an indentation in millimetres. Five specimens were made for each light-curing mode. Three readings were taken for each specimen and these were averaged to form a single value for that specimen. The mean KHN and hardness ratio (which indicates the effectiveness of cure) of the 5 specimens were then calculated and tabulated using the following formula: Hardness ratio = KHN of bottom surface / KHN of top surface. The interaction between light-curing modes and cavity depths was examined using two-way analyses of variance (ANOVA). Hardness data were subjected to one-way ANOVA / Scheffe’s post-hoc test and Independent Samples t-test at a significance level of 0.05.

Figure 4.2 (a) Specimens in their molds positioned centrally beneath the indenter.
4.3 Results

The mean KHN and hardness ratio associated with the different light curing regimens for the different LCUs and cavity depths are shown in Table 4.1 and Figures 4.3 to 4.5. Results of the statistical analysis for the different depths are shown in Table 4.2. Table 4.3 shows the comparison of the mean KHN of the various light curing regimens for the same LCU at the different depths while Table 4.4 shows the comparison of the various depths for the different light curing regimens. Emission spectra of each LCU are shown in Figures 4.6 to 4.10.
Table 4.1 Mean KHN and hardness ratio observed for the different LCUs and their respective curing modes at a depth of 2, 3 and 4 mm.

<table>
<thead>
<tr>
<th>Depth</th>
<th>LCU</th>
<th>Light-Curing Modes</th>
<th>Top KHN</th>
<th>Bottom KHN</th>
<th>Hardness Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mm</td>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>68.54 (1.46)</td>
<td>66.46 (1.18)</td>
<td>0.97 (0.02)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FL2</td>
<td>68.20 (1.80)</td>
<td>64.66 (1.18)</td>
<td>0.95 (0.02)</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>69.90 (1.34)</td>
<td>68.70 (1.34)</td>
<td>0.98 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TL2</td>
<td>73.14 (0.97)</td>
<td>70.50 (0.87)</td>
<td>0.96 (0.01)</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>MX</td>
<td>65.44 (0.17)</td>
<td>65.30 (0.17)</td>
<td>1.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>Astralis 10</td>
<td>AS1</td>
<td>62.64 (1.87)</td>
<td>62.26 (1.93)</td>
<td>0.99 (0.00)</td>
</tr>
<tr>
<td>3 mm</td>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>65.48 (0.19)</td>
<td>58.92 (0.95)</td>
<td>0.90 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FL2</td>
<td>64.90 (0.57)</td>
<td>52.52 (1.05)</td>
<td>0.81 (0.02)</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>73.42 (0.52)</td>
<td>65.58 (0.69)</td>
<td>0.89 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TL2</td>
<td>70.98 (0.44)</td>
<td>61.96 (0.52)</td>
<td>0.87 (0.01)</td>
</tr>
<tr>
<td></td>
<td>Max</td>
<td>MX</td>
<td>61.80 (1.10)</td>
<td>52.24 (0.48)</td>
<td>0.85 (0.01)</td>
</tr>
<tr>
<td></td>
<td>Astralis 10</td>
<td>AS1</td>
<td>60.28 (0.41)</td>
<td>51.80 (0.76)</td>
<td>0.86 (0.01)</td>
</tr>
<tr>
<td>4 mm</td>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>64.84 (0.78)</td>
<td>41.96 (0.95)</td>
<td>0.65 (0.01)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>FL2</td>
<td>63.98 (0.31)</td>
<td>36.48 (1.42)</td>
<td>0.57 (0.02)</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>67.78 (1.95)</td>
<td>49.84 (0.59)</td>
<td>0.74 (0.02)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TL2</td>
<td>71.12 (1.49)</td>
<td>44.40 (1.42)</td>
<td>0.62 (0.01)</td>
</tr>
<tr>
<td></td>
<td>Astralis 10</td>
<td>AS1</td>
<td>59.58 (3.60)</td>
<td>30.26 (2.00)</td>
<td>0.51 (0.02)</td>
</tr>
</tbody>
</table>
Figure 4.3 Mean KHN of the top surface at the different cavity depths for the different light curing regimens.
Figure 4.4 Mean KHN of the bottom surface at the different cavity depths for the different light curing regimens.
Figure 4.5 Mean hardness ratio at the different cavity depths for the different light curing regimens.
Table 4.2 Results of mean KHN and hardness ratio of various LCU and modes to conventional halogen LCU for the different depth.

<table>
<thead>
<tr>
<th>Depth</th>
<th>Variable</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 mm</td>
<td>KHN Top</td>
<td>EL1, EL3, EL4 &lt; MX &lt; TL1, TL2</td>
</tr>
<tr>
<td></td>
<td>KHN Bottom</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; TL2</td>
</tr>
<tr>
<td></td>
<td>Hardness Ratio</td>
<td>EL1, EL2, EL3, EL4, FL2 &lt; MX</td>
</tr>
<tr>
<td>3 mm</td>
<td>KHN Top</td>
<td>EL3 &lt; MX &lt; FL1, FL2, TL1, TL2</td>
</tr>
<tr>
<td></td>
<td>KHN Bottom</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; FL1, TL1, TL2</td>
</tr>
<tr>
<td></td>
<td>Hardness Ratio</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; FL1, TL1</td>
</tr>
<tr>
<td>4 mm</td>
<td>KHN Top</td>
<td>MX &lt; FL1, TL1, TL2</td>
</tr>
<tr>
<td></td>
<td>KHN Bottom</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; FL1, TL1, TL2</td>
</tr>
<tr>
<td></td>
<td>Hardness Ratio</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; FL1, TL1, TL2</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test (p < 0.05). < indicates statistical significance.
Table 4.3 Comparison of mean KHN of the various curing modes for the same light.

<table>
<thead>
<tr>
<th>Variable</th>
<th>LCU</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2 mm</td>
</tr>
<tr>
<td><strong>KHN Top</strong></td>
<td>Elipar</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>FreeLight</td>
<td>EL2 &gt; EL4 &gt; EL1 &gt; EL3</td>
</tr>
<tr>
<td>GC e-Light</td>
<td></td>
<td>TL2 &gt; TL1</td>
</tr>
<tr>
<td><strong>KHN Bottom</strong></td>
<td>Elipar</td>
<td>FL1 &gt; FL2</td>
</tr>
<tr>
<td></td>
<td>FreeLight</td>
<td>EL1, EL2, EL4 &gt; EL3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TL2 &gt; TL1</td>
</tr>
<tr>
<td><strong>Hardness ratio</strong></td>
<td>Elipar</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>FreeLight</td>
<td>EL1 &gt; EL2, EL3</td>
</tr>
<tr>
<td>GC e-Light</td>
<td></td>
<td>TL1 &gt; TL2</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test or Independent Samples t-test (p < 0.05). > indicates statistical significance while NS denotes no statistical significance.
### Table 4.4 Comparison of composite resin hardness at different depths for the different light curing modes.

<table>
<thead>
<tr>
<th>LCU</th>
<th>Modes</th>
<th>Top Surface</th>
<th>Bottom Surface</th>
<th>Hardness Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elipar FreeLight</strong></td>
<td>FL1</td>
<td>2 &gt; 3, 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td></td>
<td>FL2</td>
<td>2 &gt; 3, 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td><strong>GC e-Light</strong></td>
<td>EL1</td>
<td>3 &gt; 2, 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td></td>
<td>EL2</td>
<td>2 &gt; 4 &gt; 3</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td></td>
<td>EL3</td>
<td>3, 4 &gt; 2</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td></td>
<td>EL4</td>
<td>4 &gt; 3</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td><strong>Max</strong></td>
<td>MX</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td><strong>Elipar TriLight</strong></td>
<td>TL1</td>
<td>3 &gt; 2, 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td></td>
<td>TL2</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
<tr>
<td><strong>Astralis 10</strong></td>
<td>AS1</td>
<td>NS</td>
<td>2 &gt; 3 &gt; 4</td>
<td>2 &gt; 3 &gt; 4</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test or Independent Samples t-test (p < 0.05). > indicates statistical significance while NS denotes no statistical significance.

Two-way ANOVA revealed significant interaction between light-curing modes and cavity depths. Therefore, the effects of light-curing modes on hardness were depth dependent. At the top surface of 2 mm specimens, KHN after polymerization with MX (control) was significantly higher than EL1, EL3 and EL4 and significantly lower than both modes of TL. At the top surface of 3 mm specimens, KHN after polymerization with MX was significantly higher than EL3 and significantly lower than both modes of FL and TL. At the top surface of 4 mm specimens, KHN after polymerization with MX was significantly lower than FL1, TL1 and TL2 (Table 4.2).
At the bottom surface of the 2 mm specimens, KHN after polymerization with MX was significantly higher than all modes of EL and significantly lower than TL2. At the bottom surfaces of 3 and 4 mm thick specimens, KHN after polymerization with MX was significantly higher than all modes of EL and significantly lower than FL1, TL1 and TL2.

The bottom-to-top surface hardness ratio of 2 mm specimens was significantly greater than that for the 3 and 4 mm depths for all curing modes. The hardness ratios of the 3 mm specimens were, in turn, significantly higher than those of the 4 mm specimens (Table 4.4). There is, therefore, a significant decrease in the effectiveness of polymerization with increased cavity depths. The hardness ratios associated with EL1 to EL4 and FL2 were significantly lower than MX for the 2 mm thick specimens. For the 3 mm thick specimens, hardness ratio after polymerization with MX was significantly higher than all modes of EL and significantly lower than FL1 and TL1. For the 4 mm deep specimens, the hardness ratio after polymerization with MX was found to be significantly higher than EL1, EL2, EL3 and EL4 and significantly lower than FL1, TL1 and TL2.

Significant differences in top KHN, bottom KHN and hardness ratio among different curing modes of the same curing light are reflected in Table 4.3. For Elipar Trilight and GC e-light, minor variations in significant differences among curing modes were observed between 2, 3 and 4 mm. No significant difference in top KHN was observed between the two curing modes for FreeLight.
The emission spectra of LED LCUs are shown in Figures 4.6 and 4.7. Elipar FreeLight emitted light mainly in the wavelength range of 440 to 490 nm, while GC e-Light produced light between 440 to 500 nm. Emission spectrum of FreeLight for effective CQ absorption was found to be narrower than GC e-Light (Figures 4.6 to 4.7). Halogen LCUs (Figures 4.8 to 4.10) were found to have wider spectra compared to LED with the exception of Elipar TriLight.

**Figure 4.6** Emission Spectra of Elipar FreeLight.
Figure 4.7 Emission Spectra of GC e-Light.
**Figure 4.8** Emission Spectra of Max.
Figure 4.9 Emission Spectra of Elipar TriLight.
4.4 Discussion

The effectiveness of composite cure may be assessed directly or indirectly. Indirect methods have included scraping (Cook, 1980), visual (Murray, Yates & Newman, 1981) and surface hardness (Asmussen, 1982). Incremental surface hardness has been used in many studies because surface hardness has been shown to be an indicator of the degree of polymerization (Asmussen, 1982). Direct methods that assess the degree of conversion, such as infrared spectroscopy and laser Raman spectroscopy, are complex, expensive and time-consuming (Rueggeberg & Craig, 1988; Pianelli & others, 1999). DeWald and Ferracane (1987) compared four commonly used methods for evaluating depth of cure in
light-activated composites. They found that visual and scraping methods correlated well, but severely overestimated depth of cure as compared with hardness testing or degree of conversion. Degree of conversion appeared to be the most sensitive test for depth of cure. A good correlation between the results of hardness and infrared spectroscopy experiments using Knoop hardness testing was also reported. Hardness testing appears to be the most popular method for investigating factors that influence effectiveness of cure because of the relative simplicity of the method (Yap, 2000).

The actual intensity of light for curing is dependent on the intensity produced by the curing unit, the distance of the light curing tip from the surface of the material, and internal light scattering within the composite (Bayne, Heymann & Swift, 1994). Hence, to assess the effectiveness of cure by the different curing light units, the composite material investigated and the distance of light-cure tip from composite (1 mm via usage of glass slide) were standardized in this study. A2 shade was selected to minimize the effects of colorants on light polymerization (Bayne & others, 1994). As a minimum intensity of 400 mW/cm² has been suggested for routine polymerization (Rueggeberg, Caughman & Curtis, 1994; Tate, Porter & Dosch, 1999), this light intensity (Max polymerization unit), together with the manufacturer’s recommended cure time of 40 seconds was used as control in this study.

Optimization of the physical properties of light-activated dental materials is achieved by the ability of LCUs to deliver enough light at appropriate wavelength of the respective photoinitiator systems in resin-based composites.
Unlike halogen LCUs, the LEDs emission spectrum is narrow and is located close to the absorption maximum of CQ. LEDs produce light by electroluminescence while halogen lamps produce light by incandescence, whereby a filament is heated and causes the excitation of atoms over a wide range of energy levels producing a very broad spectrum. A filter is therefore required to restrict the emitted light to the blue region of the spectrum required for curing. In general, LED emitted light over a narrower wavelength as compared to halogen with the exception of TL in this research. At the various cavity depths, the cure associated with EL was lower than FL. This may be due to the wider wavelengths as compared to FL and the peak emission wavelength being located away from the absorption maximum of CQ (Figure 4.7). The emission spectrum of an LED depends upon the level of doping within its active region. A heavily doped region emits light over a wider spectral range while a lightly dope region produces light with a narrower spectral range. Fujibayashi & others (1998) have shown that a 61 LEDs source using a 470 nm peak wavelength produced a depth of cure significantly greater than a halogen and a 450 nm LEDs source. This correlated well with the results obtained in this study where superior depth of cure was observed with TL and FL with peak wavelength located near 470 nm when compared to the rest of the light sources with peak wavelength located away from 470 nm. Elipar FreeLight contains 19 LEDs that are aligned on three consecutive planes while GC e-Light contains 64 LEDs lights.

The top surface was not as susceptible to the effects of light intensities as compared to the bottom surface. This finding agrees with Hansen & Asmussen (1993) where inferior curing units were able to polymerize the surface just as
effectively as good light sources. Hence, effectiveness of cure cannot be assessed by top surface hardness alone. Rueggeberg & others (1994) have concluded that at the top surface, only irradiation time is a significant factor contributing to monomer conversion. This phenomenon accounted for the significant difference in top KHN of EL1 and EL3 modes (which utilize a total irradiation time of 20s) when compared to the control. At the top surfaces, slight variations in KHN were observed for the different cavity depths. One possible hypothesis for this includes the use of a white backing where reflection could cause an increase in the total light received and hence an increase in the top KHN in the more shallow samples.

As light passes through the bulk of the restorative material, its intensity is greatly decreased due to light absorption and scattering by composite resins, thus decreasing the potential for cure (Ruyter & Øysæd, 1982). Therefore, intensity of the light source becomes the more critical factor in determining the effectiveness of polymerization at the bottom surfaces. At depths greater than 2 mm, the polymerization of composite is very susceptible to changes in light energy density (Rueggeberg & others, 1994). For the different depths investigated, all four curing modes of GC e-Light exhibited significantly lower bottom KHN than the control. One possible hypothesis for this phenomenon includes difference in the determination of light intensity and the spectral distribution of the light source. Harder bottom KHN was found with TL2 curing regimen at a depth of 2 mm. At a depth of 3 and 4 mm, harder bottom KHN was found with both TL1 and TL2. This phenomenon can be explained by the use of higher light intensity. FL1 exhibits significant harder bottom than the control at a depth of 3 and 4 mm. This
was attributed to the higher irradiance obtained in the region of the peak absorption for CQ.

An ideal bottom-to-top hardness ratio of 1:1 should be achieved for a completely effective polymerization as the degree of polymerization should be the same throughout its depth. Light scattering and attenuation may have accounted for the minor differences in hardness between the top and bottom surfaces of the light-activated composites evaluated in this study. It has been suggested that hardness gradient should not exceed 10-20% (i.e., hardness ratio should be greater than 0.8) for adequately photo-activated composite resins (Pilo & Cardash, 1992; Yearn, 1985). Results of hardness ratio were found to correlate well with results of KHN bottom. Hardness ratio of all light curing regimens at depth of 2 mm was found to be above 0.8. The hardness ratios of EL1, EL2, EL3 and EL4 at 3 mm depth and all light curing regimens at depth of 4 mm were lower than 0.8. Based on the recommended hardness ratio of 0.8, clinical usage of all modes of EL for curing 3 mm composite increments is not advised. All composites should not be cured in 4 mm increments regardless of the curing lights used.

When the different modes of the same LCU were compared, significant differences in top and bottom KHN of the composite were observed using soft-start and pulse activation regimens of GC e-Light at cavity depth of 2, 3 and 4 mm. Pulse activation and soft-start polymerization resulted in significantly lower bottom KHN than continuous cure despite similar or higher light energy densities (intensity x time) for both GC e-Light and Elipar FreeLight. Polymerization with
pulse activation and soft-start techniques may therefore interfere with light transmission during the final cure (Yap, Soh & Siow, 2002).

### 4.5 Conclusions

For this section, the following conclusions can be made:

1. The depth of cure associated with LED curing lights is light-unit and mode dependent.
2. Increased cavity depth resulted in a significant decrease in the effectiveness of cure for all light curing regimens.
3. Increments of the composite evaluated should be no greater than 2 mm to obtain effective cure for GC e-Light.
4. Increments of the composite evaluated should be no greater than 3 mm to obtain effective cure for Max, Astralis 10, Elipar FreeLight and Elipar TriLight.
5. Composites should not be cured in 4 mm increments regardless of curing lights used.
CHAPTER 5

5. Depth of Composite Cure

5.1 Introduction

In addition to the effectiveness of composite cure, the depth of cure is another important property of curing lights. This chapter will focus on the depth of cure of LED and halogen curing lights.

Depth of cure can be defined as the extent of quality resin cure deep down from the surface of composite restoratives. The extent of resin cure is affected by filler size, light source intensity, duration of exposure and resin shade (Rueggeberg & others, 1993). While studies have shown that darker shades exhibit lower depth of cure when compared to the lighter shade (Newman, Murray & Yates, 1983; Swartz, Phillips, Rodes, 1983), Ferracane (1986) has demonstrated that depth of cure of light-activated composite resins of the darkest shade was equivalent to that of the lightest shade and hence suggested that depth of cure may be less dependent upon shade than upon translucency. Intensity of the light source and attenuating power of the material are two important factors that influence the depth of cure. Attenuation of light in the material is controlled by both absorption and scattering of the light by filler particles. Hence, light transmissions of resin composite as well as light source system are two important factors for achieving greater cure depth (McCabe & Carrick, 1989). The presence of inadequate polymerization throughout the depth of restoration can lead to undesirable effects such as gap formation, marginal leakage, recurrent caries, adverse pulpal effects and ultimate failure of restoration (Ferracane, 1993).
LED LCUs were developed in recent years to overcome the several inherent drawbacks of halogen LCUs as mentioned in 1.3.1. While studies have found that an LED source with the same or lower irradiance as a halogen source is capable of producing significantly greater depths of cure than halogen source (Fujibayashi & others, 1998; Mills, Jandt & Ashworth, 1999; Mills, Uhl & Jandt, 2002), others have found lower depths of cure values or values that are not statistically significantly different from halogen LCU (Mills & others, 2002; Jandt & others, 2002). High intensity LCUs have also been introduced to decrease cure time and increase depth of cure (Tanoue, Matsumura & Atsuta, 1999).

While technology research on LED LCUs continues to advance, the number of studies conducted on the depth of cure by LED LCUs are still limited. The depth of cure by various curing regimens of LED LCUs has also not been investigated. Thus, the objective of this study was to determine the depth of cure associated with different modes of LED, high intensity and very high intensity halogen lights. The depths of cure with these lights were compared to a conventional halogen light.

5.2 Methods and Materials

A minifilled composite resin (Z100; 3M-ESPE, St. Paul MN 55144) of A2 shade and five LCUs / ten light curing regimens as reported in chapter 2 were selected for this study. The depth of cure was determined by three methods: scraping, penetration and micro-indentation.
Scraping method: The test methodology was carried out by means of a scraping technique based on ISO 4049 (2000) (International Organization for Standardization for polymer based filling materials). The composite was placed in black teflon molds with square cavities 6.7 mm deep and 4 mm wide/long and confined between two opposing acetate strips (Hawe-Neos Dental, Bioggio, Switzerland). A white delrin base was used beneath the molds. A glass slide (1 mm thick) was then placed on the molds and excess material was extruded by pressure application. The composite was then irradiated from the top through the glass slide and acetate strip using the different light-curing modes. Immediately after light polymerization, the acetate strips were removed followed by the specimens in their molds. Uncured materials were then removed with a plastic spatula. Height of the cured material was measured with a digimatic caliper (Mitutoyo Corporation, Japan). Depth of cure was tabulated as the total remaining length after uncured material is removed (ISO 4049, 1988) \([S1]\) and 50 percent of the remaining length (ISO 4049, 2000) \([S2]\). Five specimens were prepared for each light-curing mode.

Penetration method: The depth of cure testing methodology used was based upon that used by Harrington & Wilson (1993). An Instron microtester (Model 5848, Instron Corporation, CA, USA) (Figure 5.1) was used as a penetrometer. Specimens preparation was identical to the scraping method. The specimens in their molds were inverted after irradiation with the uncured surface facing the penetration needle after light curing (Figure 5.2). A force of 12.5 N was exerted through 0.5 mm diameter needle at a rate of 1 mm/ min in the middle of
the uncured composite. Depth of cure of the specimens was computed using the formula: depth of cure = depth of mold (6.7 mm) – depth of penetration.

**Figure 5.1** Instron microtester.
Micro-indentation method: The composite was placed in black teflon molds with square cavities 6.7 mm deep and 4 mm wide/long as illustrated in Figure 5.3a. Specimens preparation was identical to the scraping method described above. Immediately after light polymerization, all acetate strips were removed and the specimens in their molds were positioned centrally beneath the indenter of a digital microhardness tester (FM7, Future-Tech Corp, Tokyo, Japan) to assess the Knoop’s Hardness Number (KHN) of the top surface. A 500g load was applied through the indenter with a dwell time of 15 seconds. The KHN corresponding to each indentation was computed by measuring the dimensions of the indentations and using the formula $KHN = 14.2 \times \left(\frac{F}{d^2}\right)$ where $F$ is the test load in kgf and $d$ is the longer diagonal length of an indentation in millimetres. KHN values of side surface were measured at 1 mm intervals from the top.
surface, using the same testing parameters (Figure 5.3b). Five specimens were made for each light-curing mode. Depth of cure was set at 80 percent of the top surface hardness.

**Figure 5.3** Schematic illustration of (a) the preparation of specimens for Knoop hardness indentations and (b) increasing Knoop hardness indentations with depth in a cross-sectional plane of a composite mold.

(a)

(b)
The interaction between light-curing modes and testing methods was examined using two-way analyses of variance (ANOVA). All data obtained were subjected to one-way ANOVA / Scheffe’s post-hoc test at a significance level of 0.05. Data from the three testing methods were also subjected to Pearson’s Correlation at significance level of 0.01.

5.3 Results

The mean depth of cure as determined by the three testing methods is shown in Table 5.1. Table 5.2 shows the mean KHN obtained at increasing depths using the micro-indentation method. Table 5.3 shows the significant differences in mean depth of cure between the various LCUs modes and the control light source (MX). Correlations between the different methods are shown in Table 5.4. Figure 5.4 summarizes and compares the depth of cure of different light curing regimens as evaluated by the different methods.

Two-way ANOVA revealed significant interaction between light-curing modes and methods. Therefore, the effect of light-curing modes on depth of cure was test method dependent. For S1 and S2 techniques, all four curing modes (EL1-EL4) of GC e-Light had significantly lower depth of cure than the control (MX) while both curing modes (TL1, TL2) of Elipar TriLight had greater depth of cure than MX. For the penetration technique, depth of cure of MX was significantly greater than all four modes of GC e-Light (EL1-EL4) and AS1, but lower than TL1. For micro-indentation technique, depth of cure of MX was found to be significantly greater than EL1 and EL3, and lower than TL1.
A significantly strong (correlation coefficient, $r = 0.93$) and positive relationship between penetration and scraping (S1 and S2) tests was observed. No significant correlation was observed between micro-indentation and penetration methods and between micro-indentation and scraping (S1 and S2) methods.

Table 5.1 Mean depth of cure observed for the different LCUs and their respective curing modes evaluated with the different techniques.

<table>
<thead>
<tr>
<th>LCU</th>
<th>Curing Modes</th>
<th>Curing depth / mm</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>6.15 (0.02)</td>
<td>3.07 (0.01)</td>
<td>6.01 (0.07)</td>
<td>2.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>FL2</td>
<td>5.84 (0.11)</td>
<td>2.92 (0.06)</td>
<td>5.96 (0.07)</td>
<td>2.00 (0.00)</td>
</tr>
<tr>
<td>GC e-Light</td>
<td>EL1</td>
<td>4.85 (0.20)</td>
<td>2.43 (0.10)</td>
<td>4.89 (0.08)</td>
<td>1.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>EL2</td>
<td>5.31 (0.11)</td>
<td>2.66 (0.05)</td>
<td>4.95 (0.20)</td>
<td>1.20 (0.45)</td>
</tr>
<tr>
<td></td>
<td>EL3</td>
<td>4.67 (0.12)</td>
<td>2.34 (0.06)</td>
<td>4.75 (0.11)</td>
<td>1.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>EL4</td>
<td>4.97 (0.04)</td>
<td>2.49 (0.02)</td>
<td>5.06 (0.08)</td>
<td>2.00 (0.00)</td>
</tr>
<tr>
<td>Max</td>
<td>MX</td>
<td>5.86 (0.19)</td>
<td>2.93 (0.10)</td>
<td>6.04 (0.11)</td>
<td>1.80 (0.45)</td>
</tr>
<tr>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>6.41 (0.15)</td>
<td>3.21 (0.08)</td>
<td>6.48 (0.11)</td>
<td>3.00 (0.00)</td>
</tr>
<tr>
<td></td>
<td>TL2</td>
<td>6.26 (0.10)</td>
<td>3.13 (0.05)</td>
<td>6.31 (0.06)</td>
<td>2.40 (0.55)</td>
</tr>
<tr>
<td>Astralis 10</td>
<td>AS1</td>
<td>5.94 (0.10)</td>
<td>2.97 (0.05)</td>
<td>5.62 (0.24)</td>
<td>2.00 (0.00)</td>
</tr>
</tbody>
</table>

Standard deviations in parentheses.
Figure 5.4 Depth of cure of the different light curing regimens evaluated by the different techniques.
Table 5.2 Results of mean KHN obtained at different intervals for depth of cure evaluated by micro-indentation technique.

<table>
<thead>
<tr>
<th>LCU</th>
<th>Curing Modes</th>
<th>Top KHN</th>
<th>Distance from top surface / mm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Elipar FreeLight</td>
<td>FL1</td>
<td>77.5 (0.6)</td>
<td>77.4 (1.6)</td>
</tr>
<tr>
<td></td>
<td>FL2</td>
<td>71.4 (1.1)</td>
<td>77.9 (2.3)</td>
</tr>
<tr>
<td>GC e-Light</td>
<td>EL1</td>
<td>74.2 (1.9)</td>
<td>67.5 (2.8)</td>
</tr>
<tr>
<td></td>
<td>EL2</td>
<td>75.1 (1.3)</td>
<td>72.5 (2.2)</td>
</tr>
<tr>
<td></td>
<td>EL3</td>
<td>73.4 (1.0)</td>
<td>74.9 (2.2)</td>
</tr>
<tr>
<td></td>
<td>EL4</td>
<td>76.8 (0.2)</td>
<td>77.7 (4.8)</td>
</tr>
<tr>
<td>Max</td>
<td>MX</td>
<td>70.2 (2.5)</td>
<td>74.3 (6.1)</td>
</tr>
<tr>
<td>Elipar TriLight</td>
<td>TL1</td>
<td>76.8 (1.6)</td>
<td>81.2 (2.1)</td>
</tr>
<tr>
<td></td>
<td>TL2</td>
<td>74.8 (0.6)</td>
<td>77.4 (1.0)</td>
</tr>
<tr>
<td>Astralis 10</td>
<td>AS1</td>
<td>75.4 (0.5)</td>
<td>73.7 (0.7)</td>
</tr>
</tbody>
</table>

Standard deviations in parentheses.

Table 5.3 Statistical analysis of depth of cure of various LCUs and modes to conventional halogen LCU for the different techniques.

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scarping 1 (ISO 1988)</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; TL1, TL2</td>
</tr>
<tr>
<td>Scarping 2 (ISO 2000)</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; TL1, TL2</td>
</tr>
<tr>
<td>Penetration</td>
<td>EL1, EL2, EL3, EL4, AS1 &lt; MX &lt; TL1</td>
</tr>
<tr>
<td>Micro-indentation</td>
<td>EL1, EL3 &lt; MX &lt; TL1</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test (p < 0.05). < indicates statistical significance.
Table 5.4 Correlations between the different techniques used for the determination of depth of cure.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Penetration</td>
<td>-</td>
<td>NC</td>
<td>0.931 (S)</td>
<td>0.931 (S)</td>
</tr>
<tr>
<td>Micro-indentation</td>
<td>NC</td>
<td>-</td>
<td>NC</td>
<td>NC</td>
</tr>
<tr>
<td>Scraping 1 (ISO 1988)</td>
<td>0.931 (S)</td>
<td>NC</td>
<td>-</td>
<td>1.00 (S)</td>
</tr>
<tr>
<td>Scraping 2 (ISO 2000)</td>
<td>0.931 (S)</td>
<td>NC</td>
<td>1.00 (S)</td>
<td>-</td>
</tr>
</tbody>
</table>

S indicates statistical significance while NC denotes no significant correlation.

5.4 Discussion

Shade of A2 was selected for this study to minimize the effects of colorants on light polymerization (Bayne, Heymann & Swift, 1994). As a minimum intensity of 400 mW/cm² has been suggested for routine polymerization (Rueggeberg, Caughman & Curtis, 1994; Tate, Porter & Dosch, 1999), this light intensity (Max polymerization unit), together with the manufacturer’s recommended cure time of 40 seconds was used as control in this study.

The depth of cure of composite was found to decrease with increasing depth as observed in the results obtained for micro-indentation method (Table 5.2). Resins nearer to the light source underwent more complete polymerization. For most curing modes, higher KHN values were observed at 1 mm below the surface as compared to the top. This may be due to the oxygen inhibition and finding corroborate with that of Unterbrink & Muessner (1995). The depth of cure of EL, which consists of 64 LEDs, was found to be significantly lower than conventional halogen light (MX) while TL, the high intensity light, was found to be significantly higher than MX for all test methods used in this study. FL, which consists of 19 LEDs, and AS1 had depths of cure comparable to MX. Possible
hypothesis for this phenomenon may be due to the differences in light energy density (intensity x time). The light energy density of the standard mode of EL, FL, MX, TL and AS1 was computed according to the manufacturer profiles and was found to be 14000, 16000, 16000, 32000 and 12000 mJ/cm$^2$ respectively. The inferior depth of cure observed in EL may be due to lower light energy density, wider emission spectrum and lower thermal emission produced when compared to the halogen lights. It was speculated that heat produced by curing lights, may be useful for the polymerization process. The very high intensity LCU (AS1), which has an energy density lower than EL, had a depth of cure comparable to the control. This may be due to the high thermal energy produced by the curing unit. The thermal emission by the different LCUs had been evaluated and reported in chapter 3 and the hypothesis that heat produced by the different LCUs plays a part in the polymerization process warrants further investigation.

The different light curing regimens met the ISO depth of cure requirement of 1.5 mm except for most modes of GC e-Light as evaluated by the micro-indentation technique. Differences in results were observed between the three different methods evaluated in this study (Figure 5.4). Despite the slight variation in results observed for penetration and scraping methods, good correlation between the two techniques was observed. The ISO scraping technique used to determine depth of cure was easy to perform and required minimal instrumentation. However, this test provides no indication of quality of cure at any point, including the lower layers adjacent to the soft resin which has been removed (Yearn, 1985). In the scraping technique, the degree of force applied is not reproducible and is usually based on the subjective judgment of the operator.
While the ISO defines depth of cure as 50 percent of the length of composite specimens after removal of the uncured material, some studies (Swartz & others, 1983; DeWald & Ferracane, 1987; Baharav & others, 1988; Hansen & Asmussen, 1993) have defined depth of cure as the total remaining length after uncured material is removed. Results obtained in this study have demonstrated that S1 severely overestimated depth of cure while S2 was found to be more reasonable in determining depth of cure with values closer to the micro-indentation technique. Depth of cure for most modes or LCUs except some modes of EL was found to be 2 mm while a value of 3 mm was achievable by that of TL1 as determined by the micro-indentation technique and supported by S2 method.

The penetration method that was employed in this study proved to be simple, reproducible and more refined than the simple scraping test adopted for the standard specifications. Measurements were made near the center of the mold of composite material and well away from the mold walls. Both the penetration and the scraping methods measure the height of cured specimens, the main difference is that the penetration technique applies a constant force allowing consistency of results. Both methods were found to correlate well and this excellent relationship accounted for the almost similar results obtained in this study. However, both techniques overestimated depth of cure when compared to hardness testing. Results obtained were found to correlate well with DeWald & Ferracane (1987), Yearn (1985) and McCabe & Carrick (1989).

The micro-indentation technique indicates that cure within the body of the composite falls from that at the surface, it does not predict quantitatively the actual levels of conversion which have been achieved. Good correlation was,
however, observed between degree of conversion and that of hardness testing at the top surfaces (Hansen & Asmussen, 1993). A laboratory technique using micro-indentation has been shown to provide a convenient means of assessing cure throughout the depth of a composite sample, which relates to the clinical situation. Using this method, it is possible to demonstrate the physical and chemical formulation factors; the nature of the light source; and the control exercised by the clinicians, are all important in determining the quality of cure achieved and hence long term performance of the restoration (Yearn, 1985).

Studies (Fujibayashi & others, 1998; Mills & others, 1999; Mills & others, 2002; Mills & others, 2002) have shown that an LED LCU with a lower or similar irradiance than the halogen LCU is capable of achieving a greater depth of cure. These observations were attributed to the LED LCUs emission spectra which coincide with the absorption spectrum of the CQ photoinitiator present in the composite. Although LED LCUs have been shown to be able to achieve greater or similar depth of cure of composites, not all LED LCUs have the same performance as shown by the results in this study. Depth of cure with most modes of EL was found to be lower than the control while all modes of FL were found to be comparable to the control. Hence, more studies on blue LED technology are warranted.

5.5 Conclusions

From the results obtained in this section, the following conclusions can be made:

1. Depth of cure associated with LED and halogen curing lights was found to be light-unit and mode dependent.
2. Both penetration and scraping techniques were found to correlate well but overestimated depth of composites cure.

3. Depth of cure of all modes of GC e-Light was generally significantly lower than the conventional halogen light.

4. Depth of cure of Astralis 10 was found to be comparable to conventional halogen light when evaluated by S1, S2 and micro-indentation techniques.

5. Depth of cure of Elipar FreeLight was found to be comparable to conventional halogen light.

6. Depth of cure of Elipar TriLight was found to be higher than the conventional halogen light.
CHAPTER 6

6. Post-gel Polymerization Shrinkage

6.1 Introduction

Light-activated composites have revolutionized modern restorative dentistry in the mid 1960s and have since undergone developmental improvements in performance characteristics such as esthetics, wear rate and handling (Tolidis, Nobecourt & Randall, 1998). Despite improvements in components and characteristics of composite materials, polymerization shrinkage still remains a clinically significant problem (Carvalho & others, 1996; Davidson & Feilzer, 1997; Yap & others, 2000; Sakaguchi & others, 1991). Dental composites exhibit the inherent problem of 2-4 % volumetric shrinkage during polymerization process (Feilzer, de Gee & Davidson, 1988). The total shrinkage can be divided into pre-gel and post-gel phases. During the pre-gel polymerization, the composite is able to flow and stresses within the structure are relieved (Davison & de Gee, 1984). After gelation, flow ceases and cannot compensate for shrinkage stresses. Post-gel polymerization thus results in significant stresses in the surrounding tooth structure and composite tooth bond (Feilzer, de Gee & Davidson, 1987). These stresses may produce defects in the composite-tooth bond, leading to bond failure, microleakage, post-operative sensitivity and recurrent caries. Such shrinkage stresses could also cause deformation of the surrounding tooth structure if the composite-tooth bond is good (Sheth, Fuller & Jensen, 1988), predisposing the tooth to fracture.
The effect of post-gel shrinkage and contraction stress can be minimized by clinical techniques such as incremental layering of composite during placement (Kemp-Scholte & Davidson, 1990) and application of low elastic modulus liner between the tooth and contracting composite restorative (Choi, Condon & Ferracane, 2000). A recent method to minimize polymerization shrinkage without affecting degree of conversion of light-activated composites is to allow flow during setting by means of controlled polymerization. This can be achieved by application of short pulses of energy (pulse activation) or pre-polymerization at low-intensity light followed by a final cure at high intensity (soft-start techniques). While some studies have shown that these polymerization modes resulted in lower shrinkage, smaller marginal gap, increased marginal integrity and improved material properties (Kanca & Suh, 1999; Uno & Asmussen, 1991; Mehl, Hickel & Kunzelmann, 1997), others have found no significant difference in shrinkage when compared to continuous cure modes (Koran & Kürschner, 1998; Price, Rizkalla & Hall, 2000; Silikas, Eliades & Watts, 2000; Yap, Ng & Siow, 2001; Yap, Soh & Siow, 2002).

Several studies have shown that blue LED LCUs have the potential to polymerize dental composites without having the drawbacks of halogen LCUs (Mills & others, 1999; Jandt & others, 2000; Stahl & others, 2000). Hofmann, Hugo & Klaiber (2002) found that LED LCUs resulted in a lower polymerization shrinkage strain after 60 minutes when compared to a halogen LCU. In addition, the hardness values obtained with the LED LCUs were not significantly different from the halogen LCUs.
While blue LED LCUs have the potential to reduce polymerization shrinkage, the number of studies on post-gel shrinkage of LED and their various cure modes are still limited. Hence, the objective of this study was to determine and compare the post-gel shrinkage of various curing regimens of two LED lights (FL, EL), a high intensity (TL) and a very high intensity (AS) halogen lights to a conventional (MX [control]) halogen light. For curing lights that offer multiple modes of curing, differences in polymerization shrinkage between soft start / pulse / turbo activation was compared to standard continuous cure.

### 6.2 Methods and Materials

A minifilled composite resin (Z100; 3M-ESPE, St. Paul MN 55144) of A2 shade and five LCUs were selected for this study. Details of the five LCUs and the ten light curing regimens evaluated are listed in Table 2.2. A conventional continuous cure halogen LCU (Max) served as the control light source. Intensity of all the curing lights was checked with a radiometer (Cure Rite, EFOS INC, Ontario, Canada) prior to use to ensure consistency in intensity output from the light source. Standard deviations ranging from 2.17 to 5.34 mW/cm² were obtained for the various lights.

The experimental set-up for measuring post-gel polymerization shrinkage was based upon that used by Yap and co-workers (Yap & others, 2000; 2001; 2002). A diagrammatic representation of the test configuration for measuring polymerization shrinkage is shown in Figure 6.1.
A glass slide served as the base of the set-up and a stiff black delrin frame (inner length 7.0 mm, width 4.0 mm, and height 2.0 mm) was used to circumscribe the composite sample with the exception of a window for the strain gauge leads. Foil electrical resistance strain gauges (Foil Strain Gauge, RS Components Ltd, Singapore) were attached onto the flat surfaces on the glass slides. The gauges were 2 mm in length and had an electrical resistance $120\ \Omega$ and gauge factor 2.00. With the strain gauges in place, the composite resins were placed into the cavity of the delrin frame. Care was taken to ensure complete filling of the frame and excess composite material was extruded using pressure applied through a second glass slide and removed. The surface tack of the composite was adequate to ensure adhesion between the strain gauge and the composite materials (Figure 6.2).
leads from the strain gauge were connected to a strain-monitoring device (Strain Gauge Recorder, Cole Parmer Instruments, IL 60061) initially balanced at zero (Figure 6.3). The strain-monitoring device consisted of a chart recorder which functions by rationing sense voltage to signal voltage and converting it to analog output. Dimensional changes are thus effectively transferred to the gauges and measured in terms of resistance.

Figure 6.2 Adhesion between the strain gauge and the composite materials.
The composite specimens were then light polymerized with the tip guide of the light unit placed on the glass slide above the restorative composite. A total of five specimens were made for each light curing regimen. Dimensional change during and post light polymerization was monitored in air at room temperature (25 ± 1°C). A total of 10 polymerization shrinkage measurements at equal time intervals during light polymerization were taken while post light polymerization shrinkage measurements were taken at 0 (immediately after light polymerization), 1, 10, 30 and 60 minutes after removal of the curing light. Percentage linear shrinkage was derived from the following equation:

\[
\text{Percentage linear shrinkage} = \frac{\Delta L}{L} \times 100 = \frac{\Delta R}{R} \times K \times 100
\]

where \(\Delta L\) = Change in length, \(L\) = Original length, \(\Delta R\) = Change of resistance, \(R\) = Original resistance (i.e. 120 Ω) and \(K\) = Gauge factor (i.e. 2). Data was
subjected to one-way ANOVA and Scheffe’s post-hoc tests and Independent Samples t-test at significance level 0.05.

6.3 Results

The mean linear percent shrinkage of the various light curing units and their curing regimens evaluated during light polymerization are shown in Figures 6.4 to 6.8. The mean linear percent polymerization shrinkage at the various post light polymerization time intervals is shown in Table 6.1 and Figure 6.9. Results of statistical analysis are shown in Table 6.2 and 6.3.

Post-gel polymerization shrinkage ranking of the various light curing regimens at 0 and 60 minutes were as follows: 0 minute (immediate post curing) – TL1 > AS1 = FL1 > MX > FL2 > TL2 > EL2 > EL4 > EL1 > EL3; and at 60 minutes post light polymerization - AS1 > TL1 > FL1 > MX > TL2 = FL2 > EL1 = EL4 > EL2 = EL3. At 0 and 1 minute after light polymerization, post-gel shrinkage of EL1 to EL4 were significantly lower than the control (MX). Post-gel shrinkage of AS1 at 1 minute after light polymerization was significantly higher than MX. No significant difference in post-gel shrinkage was observed between control and all light curing regimens at 10, 30 and 60 minutes after light polymerization. At all time intervals, post-gel polymerization shrinkage of soft-start light curing modes of FreeLight and TriLight (FL2 and TL2) was found to be significantly lower than their respective continuous light curing mode (FL1 and TL1).
Table 6.1 Mean linear percent polymerization shrinkage at the various post light polymerization time intervals.

<table>
<thead>
<tr>
<th>Light curing modes</th>
<th>0 minute</th>
<th>1 minute</th>
<th>10 minutes</th>
<th>30 minutes</th>
<th>60 minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL1</td>
<td>0.36 (0.02)</td>
<td>0.42 (0.02)</td>
<td>0.46 (0.02)</td>
<td>0.48 (0.02)</td>
<td>0.50 (0.03)</td>
</tr>
<tr>
<td>FL2</td>
<td>0.28 (0.02)</td>
<td>0.34 (0.03)</td>
<td>0.37 (0.04)</td>
<td>0.39 (0.04)</td>
<td>0.41 (0.04)</td>
</tr>
<tr>
<td>EL1</td>
<td>0.17 (0.01)</td>
<td>0.28 (0.03)</td>
<td>0.34 (0.02)</td>
<td>0.37 (0.02)</td>
<td>0.39 (0.02)</td>
</tr>
<tr>
<td>EL2</td>
<td>0.21 (0.03)</td>
<td>0.28 (0.03)</td>
<td>0.33 (0.04)</td>
<td>0.35 (0.04)</td>
<td>0.37 (0.05)</td>
</tr>
<tr>
<td>EL3</td>
<td>0.16 (0.02)</td>
<td>0.24 (0.03)</td>
<td>0.31 (0.04)</td>
<td>0.34 (0.05)</td>
<td>0.37 (0.06)</td>
</tr>
<tr>
<td>EL4</td>
<td>0.20 (0.03)</td>
<td>0.26 (0.03)</td>
<td>0.32 (0.04)</td>
<td>0.35 (0.04)</td>
<td>0.39 (0.03)</td>
</tr>
<tr>
<td>MX</td>
<td>0.32 (0.04)</td>
<td>0.38 (0.04)</td>
<td>0.41 (0.05)</td>
<td>0.43 (0.04)</td>
<td>0.45 (0.05)</td>
</tr>
<tr>
<td>TL1</td>
<td>0.38 (0.04)</td>
<td>0.45 (0.05)</td>
<td>0.49 (0.06)</td>
<td>0.51 (0.06)</td>
<td>0.52 (0.07)</td>
</tr>
<tr>
<td>TL2</td>
<td>0.27 (0.03)</td>
<td>0.34 (0.04)</td>
<td>0.38 (0.04)</td>
<td>0.40 (0.05)</td>
<td>0.41 (0.05)</td>
</tr>
<tr>
<td>AS1</td>
<td>0.36 (0.04)</td>
<td>0.49 (0.04)</td>
<td>0.52 (0.05)</td>
<td>0.54 (0.04)</td>
<td>0.56 (0.04)</td>
</tr>
</tbody>
</table>

Standard deviations in parentheses.

Table 6.2 Results of statistical analysis.

<table>
<thead>
<tr>
<th>Time</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 minute</td>
<td>EL1, EL2, EL3, EL4 &lt; MX</td>
</tr>
<tr>
<td>1 minute</td>
<td>EL1, EL2, EL3, EL4 &lt; MX &lt; AS1</td>
</tr>
<tr>
<td>10 minutes</td>
<td>NS</td>
</tr>
<tr>
<td>30 minutes</td>
<td>NS</td>
</tr>
<tr>
<td>60 minutes</td>
<td>NS</td>
</tr>
</tbody>
</table>

< denotes statistically significant differences. Results of one-way ANOVA/Scheffe’s post-hoc test (p < 0.05). NS denotes no statistical significance.
Table 6.3 Comparison of polymerization shrinkage between curing modes for LCU that offer different polymerization regimens.

<table>
<thead>
<tr>
<th>Time</th>
<th>LCU</th>
<th>Differences</th>
</tr>
</thead>
</table>
| 0 minute| **Elipar FreeLight** FL2 < FL1  
                   **GC e-Light** EL3 < EL2  
                   **Elipar TriLight** TL2 < TL1 |
| 1 minute| **Elipar FreeLight** FL2 < FL1  
                   **GC e-Light** NS  
                   **Elipar TriLight** TL2 < TL1 |
| 10 minutes| **Elipar FreeLight** FL2 < FL1  
                   **GC e-Light** NS  
                   **Elipar TriLight** TL2 < TL1 |
| 30 minutes| **Elipar FreeLight** FL2 < FL1  
                   **GC e-Light** NS  
                   **Elipar TriLight** TL2 < TL1 |
| 60 minutes| **Elipar FreeLight** FL2 < FL1  
                   **GC e-Light** NS  
                   **Elipar TriLight** TL2 < TL1 |

Results of One-way ANOVA/Scheffe’s post-hoc test or Independent Samples t-test (p < 0.05). < indicates statistical significance while NS denotes no statistical significance.
Figure 6.4 Mean shrinkage during light polymerization for Elipar FreeLight.
Figure 6.5 Mean shrinkage during light polymerization for GC e-Light.
Figure 6.6 Mean shrinkage during light polymerization for Max.
Figure 6.7 Mean shrinkage during light polymerization for Elipar TriLight.
Figure 6.8 Mean shrinkage during light polymerization for Astralis 10.
Figure 6.9 Mean shrinkage post light polymerization.
6.4 Discussion

The shrinkage behavior of light-activated composite depends on the irradiation temperature (Hofmann & others, 2002), host temperature and environment, the irradiation regime and intrinsic factors such as monomer system, concentration of the catalyst, amount of filler, filler type, size and coating (Pananakis & Watts, 2000). Polymerization shrinkage of composite occurs by bond formation between monomers during polymerization. The distance between monomers due to van der waals’ forces are transformed into the distance of covalent bonds of the polymer that is formed. Magnitude of shrinkage is determined by the number of covalent bonds formed and the size of monomers (Ferracane, 1995).

Various techniques have been developed to measure the polymerization shrinkage of composites. These include water and mercury dilatometers (Penn, 1986; Feilzer & others, 1988; de Gree, Davidson & Smith, 1997), cuspal deflection (Suliman, Boyer & Lakes, 1994), measuring specific gravity (Puckett & Smith, 1992) and optical measurement of linear shrinkage (Aw & Nicholls, 1997). The experimental set-up for measuring post-gel polymerization shrinkage in this study was based upon that used by Yap and co-workers (Yap & others, 2000; 2001; 2002) where measurement of linear shrinkage was evaluated by the use of electrical strain gauges. Strain gauges are extremely sensitive to linear dimensional changes. When the gauge is bonded to a substrate, the linear dimensional changes in the substrate are efficiently transferred to the gauge and readily measured. This linear dimensional change is only transferred when the substrate has a measurable modulus (post-gel) to induce stress on the gauge and may therefore be applicable to the measurement of post-gel shrinkage (Sakaguchi
& others, 1991). Linear shrinkage measurements are comparable to shrinkage measurements obtained using a mercury dilatometer (de Gee, Feilzer & Davidson, 1993).

Z100 was selected for this study as it exhibited the greatest contraction stress amongst various composites (Versluis, Sakaguchi & Douglas, 1993). Factors influencing the transmission of light include the thickness of the restorative material, the presence and size of filler particles, and the distance of the light tip to the restoration surface (Tate, Porter & Dosch, 1999). As these factors were all standardized in the present study, any reduction in polymerization shrinkage may be attributed to the light-curing regimen. 2 mm thick composite specimens were used to ensure uniform and maximum polymerization (Yap, 2000). A2 shade was selected to minimize the effects of colorants on light polymerization (Bayne, Heymann & Swift, 1994). As a minimum intensity of 400 mW/cm² has been suggested for routine polymerization (Rueggeberg, Caughman & Curtis, 1994; Tate & others, 1999), this light intensity (Max polymerization unit), together with the manufacturer’s recommended cure time of 40 seconds was used as control in this study.

It was observed in this study that the rate of shrinkage for all light-curing techniques was the greatest during light polymerization reaction and continued after removal of curing light (Figures 6.4 to 6.9). The shrinkage observed after removal of the light source may be attributed to thermal contraction due to loss of radiant heat and the progressive cross-linking reaction in the resin phase of the materials that occurred after light activation (Sakaguchi & others, 1991; Yap &
others, 2000). The high shrinkage rate observed during the first one minute after cure may be clinically significant. The integrity of the tooth composite interface is rapidly challenged during the early phases of polymerization, when the bond between enamel or dentin and the composite is still maturing (Yap & others, 2000).

AS1 had significantly higher post-gel shrinkage when compared to the control at one minute after light polymerization. This may be attributed to the high intensity employed, which resulted in a high temperature rise during polymerization. In an earlier study in chapter 3, AS1 was found to have the highest irradiation temperature among the light curing modes investigated. The temperature rise during polymerization and heating from radiation of LED LCUs was significantly lower than that of halogen LCUs. Results corroborated that of Hofmann & others (2002) where the temperature rise observed with halogen light irradiation was higher than with LED. It was also speculated that the high radiation heat produced by AS1 results in an additional acceleration of the polymerization reaction and consequently produces a faster increase of contraction strain. Polymerization with high intensity light sources has been related to increased depth of cure and improved mechanical properties. However, high intensity light sources have also been related to high polymerization shrinkage stresses (Uno & Asmussen, 1991; Feilzer & others, 1995).

All curing modes of EL were found to be significantly lower at 0 and 1 minute after polymerization when compared to the control. This may be due to lower rates of polymerization and lower emission temperature arising from the
low irradiance and light energy density employed for the various curing modes. An earlier study in chapter 4 conducted on EL showed that the effectiveness of cure for all curing modes of EL was inferior when compared to the Max curing units.

No significant difference between MX and various cure modes were observed at 10, 30 and 60 minutes post light polymerization. The polymerization velocity of composites affects the magnitude of internal stresses (Cehreli & Canay, 2002) and the irradiation energy affects the speed of conversion (Davidson-Kaban & others, 1997). Lower irradiation energy slows down the rate of conversion. Asmussen and Peutzfeldt (2001) have pointed out that a slow start polymerization may be associated with few centers of polymer growth while a high-intensity in the initial phase of the irradiation period will initiate a multitude of growth centers. However, ultimate conversion of the various light curing regimens was achieved despite the varying irradiation energy and rate of conversion. When total irradiation dose was sufficient to completely polymerize the specimens, total shrinkage was essentially independent of the various light-curing intensities used during the curing process (Koran & Kürschner, 1998). This was corroborated by the findings of the present study where that no significant difference in post-gel shrinkage was observed between control and all light curing regimens at 10, 30 and 60 minutes after light polymerization.

When different modes of EL were compared, polymerization shrinkage of EL2 was found to be higher than that of EL3 immediately after light polymerization. Rate of polymerization with EL2 may be faster than EL3 due to
the higher light energy density employed by EL2. No significant difference was observed between pulse activation (EL1) and continuous (EL2) mode. At all time intervals, post-gel shrinkage associated with continuous cure was found to be significantly higher than the soft-start curing mode for FL and TL. Soft-start polymerization, which employs different intensity distribution during polymerization, allows higher material flow which reduces contraction stresses in the cavity during polymerization and preserves marginal integrity (Price & others, 2000). Soft-start curing regimens may also reduce the likelihood of pulp damage caused by excessive heat generated by the light-curing units. In an earlier study in chapter 3, the thermal emission produced by soft-start curing modes was found to be significantly lower than continuous curing modes. With an adequate total irradiation dose, the properties of resin composite cured with soft-start polymerization were as good as or better than those obtained using conventional continuous curing method.

### 6.5 Conclusions

For this section, the following conclusions can be made:

1. Post-gel shrinkage immediately after light polymerization ranged from 0.16 % to 0.36 % for LED LCUs.
2. Post-gel shrinkage immediately after light polymerization ranged from 0.27 % to 0.38 % for halogen LCUs.
3. The polymerization shrinkage of all curing modes of EL was found to be significantly lower than the control at 0 and 1 minute after light polymerization.
4. Polymerization shrinkage of AS1 was found to be significantly greater than the control at 1 minute after light polymerization.

5. At 10, 30 and 60 minutes after light polymerization, no significant difference in post-gel shrinkage was observed between control and all light curing regimens.
7. Analysis of the Degree of Conversion using Micro-Raman Spectroscopy

7.1 Introduction

The degree of polymerization in cross-linked polymeric matrix systems plays a potentially significant role in determining the ultimate physical and mechanical properties of the material (Ferracane & Greener, 1984). Inadequate polymerization results in inferior physico-mechanical properties such as poor resistance to wear, poor color stability, secondary caries and adverse tissue reactions, increased rates of water sorption, solubility and early restoration failure (Vargas, Cobb & Schmit, 1998; Venhoven, de Gee & Davidson, 1993; Shortall, Wilson & Harrington, 1995; Pearson & Longman, 1989; Fan & others, 1987). While, it is desirable for dental composite resins to achieve high levels of conversion, there is always a significant concentration of unreacted carbon double bonds remaining in the resin when cured. This is due to limitations on the mobility of reactive species imposed by the rapid formation of a cross-linked polymeric network (Ferracane, 1985). In addition, high levels of conversion also resulted in higher contraction strain rates during polymerization (Sakaguchi & Berge, 1998). This usually results in gaps around the cavity margins, resulting in microleakage, pulpal irritation, thermal sensitivity, recurrent caries and internal stresses (Uno & Asmussen, 1991; Feilzer, de Gee & Davidson, 1990).
Several analytical methods as mentioned in section 1.2.2 exist for the measurement of conversion in dental polymers. Differential scanning calorimetry provides a measure of methacrylate conversion based on the enthalpy of the exothermic polymerization process (Miyazaki & Horibe, 1988; Urabe, Wakasa & Yamaki, 1991). The extent of polymerization shrinkage has also been used as a means to calculate conversion (Venhoven & others, 1993; Rueggeberg & Tamareselvy, 1995). However, the majority of analyses done to assign conversion in dental resins and composites have been based on the use of infrared spectroscopy, which provides a direct measure of unreacted methacrylate groups.

Fourier transform infrared spectroscopy (FTIR) has been proven to be a powerful and reliable technique used widely for detecting the C=C stretching vibrations directly before and after curing of materials (Imazato & others, 1995; Sakaguchi & Berge, 1998; Ruyter & Øysæd, 1982; Eliades, Vougiouklakis and Caputo, 1987). As the polymerized specimens need to be pulverized, the procedure is time consuming when measuring the degree of conversion of bulk composites. In addition, the results obtained reflect the polymerization of a small portion of the specimen, and may be inaccurate when the curing of the specimen is disproportionate. Studies (Lundin & Koch, 1992; Pianelli & others, 1999; Leloup & others, 2002) have shown that Raman spectroscopy which involves scattering rather than absorption when compared to FTIR may be an alternative spectroscopic method for direct measurement of methacrylate conversion. Degree of conversion by Raman technique is non-destructive and allows measurement on the surfaces of the restorations to be performed in vivo and in vitro without any mechanical or chemical pretreatment which may influence the results. In this method, the measurement of cure are made on a relative basis by comparison of
the vibration band of the residual unpolymerized methacrylate C=C band at 1640 cm\(^{-1}\) with the aromatic stretching band at 1610 cm\(^{-1}\). Thus, Raman spectroscopy may be a more convenient and accurate technique than FTIR for the determination of degree of conversion.

The aspect of polymerization under greatest control by the clinician is the application of the curing light (Sakaguchi & Berge, 1998). To overcome the several drawbacks of halogen lights, blue LED (light-emitting diodes) LCUs have been developed for polymerization of light-activated dental materials (Mills, Jandt & Ashworth, 1999). The various advantages of LEDs and the inherent drawbacks of halogen lights have already been discussed in section 1.3. When equal light energy was irradiated, the degree of conversion by LED was not significantly different from halogen lamp (Yoon & others, 2002). However, studies (Knežević & others, 2001; Tarle & others, 2002) have also shown that composites cured by LED LCUs resulted in a lower degree of conversion when compared to the halogen LCUs.

The number of studies on the degree of conversion of LED lights is still limited and differences in findings have yet to be explained. Hence the objective of this study was to determine the degree of conversion of composites cured with the various LED and halogen lights by the non-destructive micro-Raman spectroscopy. The degree of conversion by the various pre-programmed light curing modes was also investigated and compared to the standard continuous modes.
7.2 Methods and Materials

A mini-filled composite resin (Z100; 3M-ESPE, St. Paul MN 55144) of A2 shade and five LCUs (LED – Elipar Freelight [FL] and GC e-light [EL]; high intensity halogen light – Elipar Trilight [TL]; very high intensity halogen light – Astralis 10 [AS]; conventional halogen light - Max [MX]) were selected for this study. Pulse (EL1), continuous (FL1, EL2, TL1), turbo (EL3, AS1) and soft-start (FL2, EL4, TL2) curing modes of the various lights were examined. A conventional continuous cure halogen LCU (Max) served as the control light source in this study. Details of the five LCUs and the ten light curing regimens evaluated are listed in Table 2.2. Intensity of all the curing lights was checked with a radiometer (Cure Rite, EFOS INC, Ontario, Canada) prior to use to ensure consistency in intensity output from the light source. Standard deviations ranging from 2.17 to 5.34 mW/cm² were obtained for the various lights.

The composite material was placed in customized acrylic molds with square cavities of 2 mm deep and 3 mm wide/long confined between two opposing acetate strips (Hawe-Neos Dental, Bioggio, Switzerland). A glass slide was placed over the acetate strip and pressure was applied to extrude excess material. The composite specimens were then polymerized using the various curing lights and modes. Immediately after light polymerization, the acetate strips were discarded and the specimens were stored in a light proof container at room temperature of (25 ± 0.2) °C for 1 hour. Five specimens were prepared for each light curing mode.
Micro-Raman spectra of both unpolymerized and polymerized resins (top and bottom surfaces) were measured at room temperature in the backscattering geometry using Spex 1702/04 single-grating Raman spectrometer with an Olympus microscope attachment and equipped with a liquid-nitrogen-cooled CCD detector (Figure 7.1). The instrumental resolution was ~ 0.7 cm⁻¹. The 632.8 nm lines of a He-Ne laser was used as the excitation source and the scattered laser light was rejected using a pair of super-notch filters which allowed the Raman signal to reach the spectrograph (Figure 7.2). Typical Raman spectra were recorded with 10 mW laser power using a 100x microscope objective with NA 0.95. The Raman spectra were recorded in the region of 1580-1740 cm⁻¹, with the following conditions: confocal hole: 200; irradiation time: 60 seconds; number of accumulations: 5. A standard baseline technique was used to calculate the degree of conversion. Degree of conversion was calculated using the following formula:

\[
\text{Degree of conversion (\%)} = \left[ 1 - \frac{R_{\text{polymerized}}}{R_{\text{unpolymerized}}} \right] \times 100\% 
\]

where \( R \) = band height of \( \text{C=C} \) at 1640 cm⁻¹ /band height of aromatic group at 1610 cm⁻¹.

The mean conversion ratio for the five specimens was calculated using the following formula: conversion ratio = degree of conversion of bottom surface / degree of conversion of top surface. All data obtained was subjected to one-way ANOVA/Scheffe’s post-hoc tests and Independent Samples t-test at significance level 0.05.
Figure 7.1 Micro-Raman spectroscopy.

Figure 7.2 He-Ne laser (632.8 nm) used as the excitation source.
7.3 Results

Typical Raman spectra recorded for both the polymerized and unpolymerized specimens is shown in Figure 7.3. The mean degree of conversion and conversion ratio of the various light curing modes are shown in Table 7.1 and Figures 7.4 and 7.5. Results of statistical analysis are shown in Tables 7.2 and 7.3.

No significant difference in degree of conversion was observed when comparing the different light curing modes with control (MX) and within the same lights. The degree of conversion of LED and halogen lights for the top surface ranged from 55.98 ± 2.50 to 58.10 ± 0.66 % and 56.21 ± 1.08 to 59.78 ± 1.27 % respectively. For the bottom surface, degree of conversion of LED and halogen lights ranged from 51.90 ± 3.36 to 57.20 ± 1.18 % and 54.89 ± 1.36 to 57.28 ± 1.56 % respectively. The degree of conversion at both the top and bottom surfaces of the specimens polymerized with soft-start curing regimens by LED LCUs was observed to be higher than the standard cure modes, that is FL2 > FL1 and EL4 > EL2.
Table 7.1 Mean degree of conversion of the various light curing modes.

<table>
<thead>
<tr>
<th>Light curing modes</th>
<th>Top Surface</th>
<th>Bottom Surface</th>
<th>Conversion Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>FL1</td>
<td>55.98 (2.50)</td>
<td>53.49 (3.48)</td>
<td>0.96 (0.40)</td>
</tr>
<tr>
<td>FL2</td>
<td>58.10 (0.66)</td>
<td>57.20 (1.18)</td>
<td>0.98 (0.15)</td>
</tr>
<tr>
<td>EL1</td>
<td>56.88 (1.36)</td>
<td>53.17 (3.00)</td>
<td>0.93 (0.50)</td>
</tr>
<tr>
<td>EL2</td>
<td>56.85 (3.24)</td>
<td>53.94 (3.09)</td>
<td>0.95 (0.87)</td>
</tr>
<tr>
<td>EL3</td>
<td>56.03 (1.46)</td>
<td>51.90 (3.36)</td>
<td>0.93 (0.72)</td>
</tr>
<tr>
<td>EL4</td>
<td>57.80 (1.15)</td>
<td>54.10 (2.71)</td>
<td>0.94 (0.55)</td>
</tr>
<tr>
<td>MX</td>
<td>57.34 (1.00)</td>
<td>54.89 (1.36)</td>
<td>0.96 (0.27)</td>
</tr>
<tr>
<td>TL1</td>
<td>59.00 (2.76)</td>
<td>57.28 (1.56)</td>
<td>0.97 (0.56)</td>
</tr>
<tr>
<td>TL2</td>
<td>59.78 (1.27)</td>
<td>56.55 (1.58)</td>
<td>0.95 (0.02)</td>
</tr>
<tr>
<td>AS1</td>
<td>56.21 (1.08)</td>
<td>56.14 (1.51)</td>
<td>1.00 (0.38)</td>
</tr>
</tbody>
</table>

Standard deviations in parentheses.

Table 7.2 Results of statistical analysis.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top Surface</td>
<td>NS</td>
</tr>
<tr>
<td>Bottom Surface</td>
<td>NS</td>
</tr>
<tr>
<td>Conversion Ratio</td>
<td>NS</td>
</tr>
</tbody>
</table>

Results of one-way ANOVA/Scheffe’s post-hoc test (p < 0.05). NS denotes no statistical significance.
Table 7.3 Comparison of mean degree of conversion between curing modes for LCU that offer different polymerization regimens.

<table>
<thead>
<tr>
<th>Variable</th>
<th>LCU</th>
<th>Differences</th>
</tr>
</thead>
<tbody>
<tr>
<td>KHN Top</td>
<td>Elipar FreeLight</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>GC e-Light</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>NS</td>
</tr>
<tr>
<td>KHN Bottom</td>
<td>Elipar FreeLight</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>GC e-Light</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>NS</td>
</tr>
<tr>
<td>Conversion Ratio</td>
<td>Elipar FreeLight</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>GC e-Light</td>
<td>NS</td>
</tr>
<tr>
<td></td>
<td>Elipar TriLight</td>
<td>NS</td>
</tr>
</tbody>
</table>

Results of One-way ANOVA/Scheffe’s post-hoc test or Independent Samples t-test (p < 0.05). NS denotes no statistical significance.
Figure 7.3 Raman spectra of light-activated composite Z100.
Figure 7.4 Mean degree of conversion of the top and bottom surfaces of 2 mm specimens for the different light curing regimens.
Figure 7.5 Mean conversion ratio of 2 mm specimens for the different light curing regimens.
7.4 Discussion

The cure of dental resins is important from a practical as well as a fundamental viewpoint. Studies (Eliades & others, 1987; Ferracane, 1985; Ferracane & others, 1997; Asmussen & Peutzfeldt, 2002) have shown a direct correlation between the degree of conversion of the resins and bulk properties such as hardness, wear, polymerization shrinkage, tensile and compressive strength. Thus, it will be useful to have a quick and reliable method of determining degree of cure of dental resins.

Raman spectroscopy is an attractive technique for dental materials analysis since samples can be examined irrespective of thickness or form by simply illuminating them with a laser beam. In principle, this allows qualitative and quantitative analysis of chemical and physical structure without sample modification. The ability to handle ‘difficult’ samples is a key advantage over mid-infrared spectroscopy, which requires the preparation of thin films, KBr disks, Nujol mulls, or solutions. This is indeed very important for morphology studies since sample preparation can easily perturb morphology.

Raman spectroscopy, like infrared spectroscopy (IR), is a vibrational technique, and as such is sensitive to the vibrational modes of molecules (Szymanski, 1967). In dental resins, the vibrational bands of interest are typically the C=C double bond, the C=O vibration, the aromatic ring of the monomers and crosslinked networks. For highly symmetrical molecules, the quantum mechanical selection rules determine which modes of vibration will be IR or Raman active. For the unsymmetrical monomers and polymers used in dental resins, most of the vibrations have both infrared and Raman activity. However, there are still two
important differences between the IR and Raman spectroscopy of these systems: (1) IR spectroscopy is an absorption technique, whereas Raman spectroscopy is a scattering method and (2) intensities in IR measurements are determined by changes in the dipole moments of the vibrations, whereas for Raman measurements, the relevant quantity is the change in the polarizability tensor. These differences affect both the method of obtaining data from samples and the parameters which are necessary for calibration curves (Shin & others, 1993). In Raman scattering, the relevant quantity is the Raman scattering cross section of the band of interest which depends on the intensity of the incoming light and on the polarizability tensor of the particular vibration (Hendra, Jones & Warnes, 1991). Thus, it is always useful to have one band whose intensity can act as an internal standard.

When light energy was supplied to activate the composites for polymerization to take place, the C=C vibration decreased with respect to the aromatic group mode after polymerization (Figure 7.3). The aromatic group which remains unchanged before and after curing was identified as the internal reference in this study. The carbonyl (C=O) group, which have a characteristic frequency in the range of 1600 to 1800 cm\(^{-1}\) was ruled out as the internal reference as the exact location of the C=O frequency varies depending on the atoms attached to the carbonyl. Electron donating groups, electron withdrawing groups, resonance effects, and hydrogen bonding all cause the force constant of the C=O bond to vary and therefore the frequency of the carbonyl absorption to change. In a conjugated system, the C=C frequencies may fall near aromatic bands. The carbonyl bands, which absorbs strongly in IR, can also obscure the original
position of C=C vibrations, making it very difficult to interpret. Usually, the C=C stretch band has a much more distinctive Raman band, which is high in intensity, and is not disturbed by the weaker infrared intensity of the C=O stretch band. As conjugated double bonds are more sensitive to Raman spectroscopy than to infrared, any change occurring within the double bond can be predicted more precisely by using this technique (Rehman, Harper & Bonfield, 1996).

Mini-filled composite resins, Z100, of A2 shade were selected for this study to minimize the effects of colorants on light polymerization (Bayne, Heymann & Swift, 1994). Factors influencing the transmission of light include the thickness of the restorative material, the presence and size of filler particles, and the distance of the light tip to the restoration surface (Tate, Porter & Dosch, 1999). As these factors were all standardized in the present study, any differences in degree of conversion may be attributed to the light-curing regimen. 2 mm thick composite specimens were used to ensure uniform and maximum polymerization (Yap, 2000). As a minimum intensity of 400 mW/cm² has been suggested for routine polymerization (Tate & others, 1999; Rueggeberg, Caughman & Curtis, 1994), this light intensity (Max polymerization unit), together with the manufacturer’s recommended cure time of 40 seconds was used as control in this study. Raman spectra were recorded at 1 hour post light irradiation as degree of conversion shows a gradual increase after light exposure and maximum hardness was attained after the first hour polymerization (Pilo & Cardash, 1992). In addition, post-gel shrinkage of composites as observed in chapter 6 and Yap & others (2000) was found to occur most rapidly during the first hour of post light irradiation.
The degree of composite cure is proportional to the amount of light to which they are exposed. The degree of conversion was found to be higher on the top surfaces than the bottom surfaces. However, top surface hardness is not an adequate clinical indicator of an adequately polymerized composite restoration, because even a very poor light source may produce a well-cured surface which conceals inadequately or even unpolymerized resin in the deeper parts of the cavity (Hansen & Asmussen, 1993). At the bottom surfaces, no significant difference in degree of conversion was found between all light curing regimens and control (MX). All light curing regimens were found to achieve degree of conversion greater than 51 % for both surfaces. Results corroborated well with earlier studies where degree of conversion was found to range from 43.5 to 73.8 % (Pianelli & others, 1999; Yoon & others; Chung & Greener, 1988). However, it must be noted that the degree of conversion does not indicate the degree of polymerization of Bis-GMA or TEGDMA itself but indicates the conversion rate of the aliphatic C=C bond in the methyl methacrylate group into a C-C bond. The 51 % of degree of conversion does not mean that that 49 % of monomer remains but indicates that 49 % of C=C bonds remain.

The conversion ratio obtained in this study was found to be greater than 0.90 for all light curing regimens. The difference in conversion ratio can be attributed to light scattering and absorption as light passed through the bulk of the composite (Ruyter & Øysæd, 1982). This scattering of light accounted for the minor differences in degree of conversion between the top and bottom surfaces of the 2 mm composite evaluated in this study.
The use of high intensity light source has recently been introduced for improving composite properties. High intensity lights provide higher values of degree of conversion and superior mechanical and physical properties but produced higher contraction strain rates during polymerization of composites (Uno & Asmussen, 1991). The use of very high light intensities for short durations (turbo cure) has also been developed. These curing regimens were established primarily to reduce clinical time and have been shown not to increase polymerization stresses if the total light energy density (intensity x time) is maintained (Yap, Wong & Siow, 2003). The use of high intensity (TL) and very high intensity (AS) lights in this study did not result in degree of conversion significantly different from the control (MX) for both the top and bottom surfaces of the specimens evaluated. The same results were also observed in chapter 6 where no significant difference in post-gel shrinkage of high and very high intensity halogen lights was observed when compared to control. This illustrated the potential use of high intensity lights or turbo cure mode for dental restorations. However, it must be noted that the application of high intensity lights resulted in an increase in temperature which may be damaging to the pulp as observed in chapter 3.

From the results obtained in this study, the degree of conversion by LED was not significantly different from halogen LCU. However, the degree of conversion at both the top and bottom surfaces of the specimens polymerized with LED soft-start curing regimens (FL2, EL4) was observed to be higher (though not significantly) than the standard cure modes (FL1, EL2) when comparing the different modes of the same light. The soft-start polymerization may improve
marginal adaptation by allowing “viscous” flow of the material during polymerization. Results suggested that superior properties of composite cure may be achieved with the use of LED soft-start curing regimens. Given the inherent advantages of the LED principle and swift progress in semiconductor technology, LED LCUs appear to have greater potential in future clinical applications than halogen LCUs.

7.5 Conclusions

From the results obtained in this section, the following conclusions can be made:

1. Micro-Raman spectroscopy is an easy and performant technique for the measurements of degree of conversion.

2. The degree of conversion was independent of curing lights, light source and light curing regimens.

3. The degree of conversion at both the top and bottom surfaces by LED, high intensity and very high intensity lights was found to be comparable to the conventional halogen light.
8. General Conclusions and Future Perspectives

8.1 General Conclusions

Light-activated composite resins which offer clinicians the freedom in timing the initiation of polymerization, the ease of placing and contouring the restorative materials have been widely employed in clinical dentistry since their introduction in the late 1970s. Despite vast improvements, all composites shrink during curing. Other limitations include the depth of cure and inadequate polymerization. The undesirable clinical effects accompanying these limitations have been reviewed in Chapter 1. While research on the development of new dental composite with zero net polymerization dimensional change continues, the numbers of light curing systems that claim to reduce polymerization shrinkage, improve cure depths and degree of cure have also increased rapidly.

This research study was designed to investigate the curing efficiency of two newly introduced LED curing units, high intensity and very high intensity (established primarily to reduce clinical time) halogen lights. The efficiency was assessed by measuring selected properties of a dental composite. The results obtained for each study were compared with a conventional halogen light. The various techniques for reducing polymerization shrinkage as discussed in section 1.2.3 were also investigated where applicable.

In this study, the thermal emission of LEDs was found to be lower than the halogen lights. The lower thermal emission produced by LED LCUs eliminate the
need for cooling fan and decrease the potential for gingival and pulpal irritation and hence offer an advantage over halogen lights in the curing of composites. The high thermal emission produced by the high and very high intensity halogen lights may be potentially damaging to the pulp tissue during restorative treatment. This high radiation heat may, however, increase the rate of polymerization reaction and hence result in a faster increase of contraction strain as evidenced from results obtained with AS1 in chapter 6.

The depth of cure values obtained in this study was found to be greater than the minimum values required in the ISO standard for all curing lights investigated except for most modes of EL. Thus, depth of cure by LED was found to be light unit and modes dependent. Similar conclusions were also reached when the effectiveness of cure by the different curing lights was investigated. The effectiveness and depth of cure by FL was found to be greater than EL. The depth and effectiveness of cure by EL was found to be lower than the conventional halogen light while FL and AS were found to be comparable to the conventional halogen light. The high intensity halogen light, TL, was found to achieve an effectiveness and depth of cure higher than the conventional halogen light.

Polymerization shrinkage associated with LED and halogen lights was also investigated in this study. The polymerization shrinkage of all light curing units/curing regimens investigated in this study was found to be comparable to the conventional halogen light at 60 minutes post light polymerization. Results were found to relate very well with the results obtained for degree of conversion of the various curing lights investigated with the micro-Raman spectroscopy. In the
latter study, no significant difference in degree of conversion was observed for LED and high intensity halogen lights when they are compared to the conventional halogen light. A high value for final contraction of a composite resin is indicative of a high degree of conversion and thus optimal properties. When total light energy density applied was sufficient to completely polymerize the specimens, total shrinkage and degree of conversion was independent of the various light-curing intensities used during the curing process.

From the results obtained for the different light curing regimens, it was observed that the soft-start curing regimen of FL have the potential to polymerize dental composites without the drawbacks of halogen lights. FL2 was found to achieve a lower thermal emission than the standard curing regimen, FL1. In addition, post-gel polymerization shrinkage for FL2 was found to be significantly lower than FL1 and the degree of conversion by FL2 was also found to be higher (though not significantly higher) than FL1. Thus, marginal adaptation may be improved with the use of soft-start curing regimen of LED.

In conclusion, the curing efficiency of LED was curing light dependent. FL was found to have the potential to polymerize composites without the drawbacks of halogen lights. The properties investigated was found to be comparable than MX. EL was found to be inferior when compared to MX and was thus not recommended for use. The high intensity light, TL was found to achieve better cure depths and effectiveness of cure without increasing in polymerization shrinkage when compared to MX. Hence, the use of high intensity light may be
recommended. Although the use of AS may result in properties comparable to MX, it should be used with caution due to its high thermal emission produced.

8.2 Future Perspectives

While LED does display potential to polymerize composites without the drawbacks of halogen lights in this study, one inherent drawback of LED is that the narrow emission spectrum emitted by LED units may not be compatible with composites and dental adhesives that do not have CQ as the major initiator. It is thus important to investigate the efficiency of blue LED lights in polymerizing composites containing initiators other than CQ. It is also of interest to develop an LED source besides blue LED to polymerize composites that contains initiators other than CQ.

Mills & others (1999) used an LED LCU that consisted of 25 LEDs for their study. Jandt & others (2000) found that an LED LCU that consisted of 27 blue LEDs gave adequate polymerization. Fujibayashi & others (1998) have also found that LCUs, which consisted of 61 blue LEDs, gave an effective curing depth and degree of conversion. Dunn & others (2002) have cited that the poor performance of LED LCU used in their study might result from the use of only seven blue LEDs. The afore-mentioned studies appear to suggest that the effectiveness of cure of LED LCUs may depend on the number of LEDs. This was not corroborated in the current study. In the current study, the author observed that the effectiveness of cure of composites with FreeLight, which consisted of 19 LEDs, was comparable to conventional halogen LCUs. However, the effectiveness of cure of composites with e-Light, which consisted of 64 LEDs,
resulted in a softer bottom as compared to the conventional halogen LCUs. Hence, it is also of interest to design a study that investigates the effect of the number of LEDs and new generation high intensity LEDs on the cure of composites.

Good correlation was found between Infrared spectroscopy (IR) and Knoop hardness testing as illustrated by Ferracane (1985). Although Knoop hardness correlated well with the degree of conversion, the relationship was not determined in this study due to differences in time. The effectiveness of cure by Knoop hardness tester was carried out immediately after polymerization while the degree of conversion was done one hour after light polymerization based on the results obtained for post-gel shrinkage. Hence, it is of interest to determine the relationship, if any, between Knoop hardness and Raman spectroscopy by carrying out further work to monitor the hardness values at one hour after polymerization. Further mechanical properties such as compressive strengths, flexural strengths and modulus may also be carried out to further evaluate the efficiency of curing lights.

While LED lights continue to progress in semiconductor technology and have wider and greater potential in future clinical applications than halogen lights, the ultimate solution to polymerization shrinkage will be the development of a dental composite with zero net polymerization dimensional change.
CHAPTER 9

9. References (Chapter 1 – 8)


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