SURFACE HARDNESS OF DIFFERENT SHADES AND TYPES OF RESIN COMPOSITE CURED WITH A HIGH POWER LED LIGHT CURING UNIT

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Keywords

Surface hardness

Microhybrid

Nanocomposite

High power LED

Light curing

Shade

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ABSTRACT

Light-emitting diode (LED) curing lights were introduced to the dental market promising a higher curing efficiency than halogen-based lights. The earlier generation curing lights, however, proved not to be as effective as halogen lights. As a result 3M ESPE introduced a new high-powered LED curing light, the Elipar FreeLight 2, that delivers a greater irradiance, and therefore greater energy density than its precursor. Due to these changes, the light's manufacturer claims that the FreeLight 2 can cure resin composites at half of their recommended curing time.

Aim: The aim of this study was to compare the effectiveness of cure when a FreeLight 2 was used to cure composite samples at 100% and at 50% of the recommended curing time.

Materials & Methods: Effectiveness of cure was determined by measuring the top and bottom surface hardness (VHN) of 2-mm composite specimens. One microhybrid composite (Z250, shades A1, A3.5 and D3) and two nanocomposites (Z350, shades A1, A3.5 and C2; Filtek Supreme XT, shades yellow, clear and grey) were used to prepare 10 samples per experimental condition to a total of 180 samples (3 types of composite x 3 shades each x 2 curing modes x 10). The samples were made up in 15 mm diameter PVC plastic discs, 2mm thick with a 3-mm hole drilled into them. Each sample was prepared in the same manner by the same operator and cured maintaining a distance of 2mm between the specimen and light tip. After 24 hours' storage Vickers micro-hardness measurements were obtained on both sides of the samples, with a load of 50 grams for 10 seconds. Three indentations were performed on each surface of each sample and the Vickers hardness values were obtained.

Data analysis: The MIXED procedure with a GROUP statement with the REPEATED option to allow modeling of the heterogeneous variances was used to analyze the data. Pairs were compared to determine which factor combinations differed from others. A level of significance of 0.01 was used.

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Results: Curing at 50% of the curing time produced significantly lower bottom hardness values and hardness ratios for all the materials tested. The hardness values of Filtek Supreme XT (translucent shades) were the least affected by curing time and by shade.

Conclusion: Curing with a HP LED unit at half the recommended exposure time does not produce as effective polymerization as when cured for the full recommended time. The translucency or opacity of composite materials is an important factor in obtaining adequate cure.

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DECLARATION

I hereby declare that *Surface Hardness of Different Shades and Types of Resin Composite Cured with a High Power LED Light Curing Unit* is my own work, that it has not been submitted before for any degree or examination at any university, and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

TARIQ A. LODHI

Signed:_____

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____ day of _____ 2006

The work reported in this mini thesis was carried out in the Department of Restorative Dentistry, Faculty of Dentistry, University of the Western Cape, Tygerberg, South Africa.

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DEDICATION

This is dedicated to my mother Mariam and father Abbas Lodhi, who have had the patience and courage to allow me, their only son, to leave home to study abroad for eight years.

No words can describe my gratitude to them and no deed I do can ever repay them for their numerous sacrifices for me.

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INTRODUCTION

Light-emitting diode (LED) curing lights were introduced to the dental market claiming several advances over halogen lights including low power consumption, very low heat production during function and little or no degradation of light output over time. Moreover, as most of the light energy radiated by LED curing lights fall within the absorption spectrum of the photoinitiator camphorquinone, these lights also promised to have a higher curing efficacy than halogen-based lights (Clinical Research Associates 2001:1).

Research, however, reported that the earlier generation LED curing units may not be as effective as halogen curing lights when curing composites (Dunn and Bush, 2002:337). One reason for this was that, due to their narrow emission spectra, earlier LED curing lights could not polymerize composite resins that used photoinitiators or co-initiators other than camphorquinone (Uhl, Mills and Jandt, 2003:1787; Uhl, Sigusch and Jandt 2004:1795). A second reason was that the light output of the first generation LED curing units was not high enough (Dunn and Bush, 2002:337). As a result, some companies have recently started to replace their earlier LED curing units with high-power LED curing lights (Clinical Research Associates 2004:2; 2006:1).

One such light that was recently released in South Africa is the Elipar FreeLight2 (3M ESPE, St Paul, MN, USA) that delivers a greater irradiance, with a resultant greater energy density than its precursor. Additionally, the spectral output of the FreeLight2 was shifted to the lower wavelengths with a mean peak output of 455 nm compared to the first generation FreeLight which had a mean peak output of 467 nm (Price, Felix and Andreou, 2005:2633). Due to these changes, the light's manufacturer claims that the FreeLight2 can cure resin composites at half of their recommended curing time (Elipar Technical Product Profile, 2003:11).

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The purpose of this study was to test this claim for three shades each of three contemporary resin composites manufactured by 3M ESPE (Z350, Z250, Filtek Supreme XT) using a surface hardness test.

The first part of the literature review includes information on composite resins, specifically on their composition and properties that may influence an optimal curing hardness. The three contemporary composite restorative materials used in this study are also discussed in detail.

The second part of the literature review discusses the commonly used halogen curing lights, earlier LED lights as well as the high power LED curing units and the scientific findings regarding their advantages and shortcomings.

The third part of the review summarizes research findings on the influence of filler load, particle size and different shades of composite resins on curing.

The final part reviews the methods used to evaluate effective cure of composite resins, with an emphasis on hardness and microhardness tests.

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LITERATURE REVIEW

COMPOSITE RESINS

In addition to their use in anterior teeth, aesthetic composite resin restorative materials are increasingly being used to restore shape and function in posterior teeth. Posterior composite resin restorations, however, are submitted to very large masticatory forces. Therefore the mechanical properties of a composite resin material become even more important in determining long term clinical performance under occlusal forces.

The most important factors that influence the mechanical properties are the composition of the composite resin itself and its degree of cure (Rueggeberg and Craig, 1988:932). While the composition of light cure composites, including the quantity and size of the fillers, the amount and type of photoinitiators, and resin matrix are determined by the manufacturer, the degree of final cure depends on the quality of the curing light and the duration of cure (Rueggeberg, Caughmann and Curtis, 1993:91).

A composite material may be defined as a compound of two or more distinctly different materials, with properties that are superior or intermediate to those of the individual constituents (Anusavice, 1996:274).

Basically, a dental composite is composed of four major components: organic polymer matrix, inorganic filler particles, coupling agent, and the initiator-accelerator system (Powers, 2002:233). Several other components are also added to enhance the composite material, for example pigments are added to achieve an acceptable shade and/or opacity.

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Inorganic Filler Particles

Inert fillers are added to the resins to improve mechanical properties such as compressive and flexural strength and hardness. Improved physical properties include a reduction of polymerization shrinkage and an increase in the modulus of elasticity (Anusavice, 1996:273). The physical and mechanical properties of composite resins are also influenced by the characteristics of the fillers itself, for example their size, distribution and content per volume of the filler particles (Oberholzer, Grobler, Pameijer and Hudson, 2003:211).

The filler particles used in dental composites vary widely in their chemical composition, morphology and dimensions. Most filler particles are silicon dioxide based and are either a) crystalline silica (quartz), b) silica with metals (silicate glass), or c) amorphous silica (colloidal silica) (Anusavice, 1996:276). Boron silicates and lithium aluminum silicates are often used. In many composites the quartz is partially replaced by heavy metal particles such as barium, strontium, zinc, aluminum or zirconium to impart radiopacity (Garcia, Lozano, Vila *et al*, 2006:E217).

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Silica particles of colloidal size (±0.04μm/40nm) are obtained from a pyrolytic or precipitation process of burning $SiCl_4$ in an oxygen and hydrogen gas atmosphere to form SiO_2 macromolecules of colloidal size. Hence, they are known as pyrogenic ('born in fire') silica particles (Anusavice, 2002:276). Colloidal silica particles are also known as microfillers. A disadvantage of microfillers is that they aggregate to form fibrous, chain-like secondary structures which limits filler loading resulting in lower mechanical properties (Mitra, Wu and Holmes, 2003:1389). To improve the filler load, commercial microfills often contain a mixture of silica microfillers and prepolymerised resin particles produced from fumed silica.

The larger filler particles are produced by milling or grinding dense, large particles (mined quartz, melt glasses, ceramics) to produce smaller particle sizes varying from 0.1μm to 100μm. Milling procedures, however, cannot reduce filler particle size below 100nm (Mitra *et al*, 2003:1383).

The latest development in filler technology is nanoparticles and nanoclusters produced by 3M ESPE for their nanocomposites, Filtek Supreme XT and Filtek Z350. Nanoparticles and nanoclusters are being manufactured using synthetic chemical processes to produce building blocks on a molecular scale. Progressively larger structures are assembled and transformed into suitable nanosized fillers (Mitra *et al*, 2003:1383). Aqueous colloidal silica sols are being used to synthesize dry powders of nanosized silica particles 20nm and 75nm in diameter. These particles are treated to prevent aggregation. Two types of nanoclusters with a cluster size range of 0.6 – 1.4 microns have also been developed. One type consists of loosely-bounded agglomerated silica particles and is being used in the translucent shades. The other type consists of agglomerated zirconia/silica particles that are radiopaque and is being used in the enamel, body and dentin shades (Mitra *et al*, 2003:1383; Filtek Technical Product Profile, 2005:5).

A useful way to classify dental composites is according to their filler content, mean particle size and particle type as summarized in Table 1. The classification was adapted from the classification of Willems and his colleagues (1993:650) that was not only based on filler information, but also on other properties like the Young's modulus and surface roughness (hence the inclusion of the categories of compactly-filled and midway-filled microhybrids). The classification includes some of the materials that were used in the studies reviewed in this thesis (see Tables 2 & 3 later in the discussion).

As fillers may affect degree of cure depending on the type and the size of the particles, as well as the concentration of the filler particles, further review of these factors will be provided later in the discussion.

Resin Monomers

The most commonly used dimethacrylates in dental composites are the high-molecular-weight monomers Bisphenol A glycidyl methacrylate (Bis-GMA), urethane dimethacrylate (UDMA), and tri-ethylene glycol dimethacrylate (TEGDMA). The high-molecular-weight monomers, particularly Bis-GMA are extremely viscous.

Table 1. Classification of contemporary composites according to particle size, type and filler load* (adapted from Willems *et al*, 1993:560)

MICROFILLED (Heterogenous)
(35-63 % by weight)

Trade name	Filler content	Particle size	Particle Type
Examples: Filtek A110 (3M ESPE)	56 % by weight 40 % by volume	0.01-0.09 PPF (Silica) = 0.104µm	- Colloidal silica - Pre-Polymerised Silica Filler (PPF)

HYBRIDS (Small-particle hybrids, strengthened with microfillers)	±80 % by weight ±60% by volume	0.5-2µm 0.04µm	- Glass or quartz fillers fillers - Silica microfillers

COMPACT-FILLED SMALL-PARTICLE OR MICRO-HYBRIDS
(>60 volume% ; >80% weight %)

Trade name	Filler content	Particle size	Particle Type
Z100 (3M ESPE)	84.5 % by weight 69 % by volume	0.04 – 4.0 µm	- Zirconia/Silica fillers
Z250 (3M ESPE)	60% by volume	0.01 – 3.5µm	- Zirconia/Silica fillers

MIDWAY-FILLED SMALL-PARTICLE OR MICRO HYBRIDS
(< 60 volume % ; <80% weight %)

Prisma TPH (Dentsply)	74 % by weight 58 % by volume	Mean particle size (MPS) = 1µm	- Ba silicate
Herculite XRV	78 % by weight	MPS = 0.6µm	- Ba silicate

NANO-PARTICLE HYBRID

Esthet X (Dentsply)	77% by weight 66% by volume	0.02 – 2.5 µm MPS = 0.06 – 0.8 µm	- Barium alumino fluoroboro silicate

NANOFILLED COMPOSITE

Trade name	Filler content	Particle size
Filtek Supreme (3M ESPE)	72.5% by weight	Translucent shades: - Nanofillers of silica = 75 nm - Nanoclusters: silica fillers of 75nm (0.6 – 1.4µm range)
	78.5 % by weight	Other shades: - Nanofillers of silica = 20nm - Nanoclusters of zirconia/silica fillers of 5-20nm (0.6 – 1.4 µm range)

*Filler information of the composites obtained from the product brochures or product profiles of the composites' manufacturers or from the studies referred to in Tables 2 & 3.

Diluents (for example TEGDMA) are therefore added to attain high filler levels, but to retain usable handling consistencies. UDMA is similar in molecular weight to Bis-GMA but is considered more flexible. (Anusavice 1996:274).

Most companies add a Bis-GMA/TEGDMA or Bis-GMA/UDMA/TEGDMA combination to their composites (Garcia *et al*, 2006:E216). Some companies use other varieties of monomers to improve the properties of their composite materials. The 3M ESPE company for example, has replaced the majority of the TEGDMA in Z250 with UDMA and Bisphenol A polyethylene glycol diether dimethacrylate (Bis-EMA). As both of these resins have a higher molecular weight and therefore have fewer double bonds per unit of weight it provided for a composite that shrinks less and that is not as stiff as Z100 (Z250 Technical Product Profile, 1998:8). A similar mixture of Bis-GMA/Bis-EMA/UDMA with small amounts of TEGDMA is also used in their new nanocomposites, Filtek Supreme XT and Z350 (Filtek Technical Product Profile, 2005:5).

Methacrylate monomers react via an addition polymerization reaction to form a highly cross-linked structure when light of appropriate wavelength and intensity is applied. Therefore the resin matrix has an important influence on the chemical and physical properties of composite resins as it also contains the initiator system(s) for polymerization.

Photoinitiator

In a light cured resin composite, a diketone type of photo initiator system is included in the resin, which when activated by light of a specific wavelength causes polymerization and hence curing/hardening of the resin. This is achieved through the release of radicals, which start converting the oligomers into a cross linked polymer (Neumann, Miranda, Schmitt *et al*, 2005: 525). After this reaction has taken place the resin composite should be cured to such a degree that it will display the typical physical and chemical properties that are expected of a restorative material of this type.

Camphorquinone

The most commonly used visible light photoinitiator is camphorquinone (CQ). CQ absorbs light in the of 400-500nm range, with a peak absorption at 468nm (Uhl *et al,* 2004: 84; Neumann *et al,* 2005: 526). This range falls in the blue emissions of the visible light spectrum.

The amount of CQ that is added by the manufacturer varies from 0.2% to 1.0% (Powers, 2002:236). An organic tertiary amine that can act as an electron – or proton donor is also added to the resin as an accelerator (Powers, 2002:236).

When CQ is sufficiently excited it reacts with the amine to begin a chain reaction for the formation of free radicals, which, in turn, initiate polymerization of the resin monomers at a molecular scale (Rueggeberg *et al,* 1993:91; Obici, Sinhoreti, Correr-Sobrinho *et al,* 2005:393; Neumann *et al,* 2005:526). As a result the dental composite hardens after a sufficient exposure time that ranges between 20 seconds and 60 seconds (Mills, Jandt and Ashworth, 1999:388).

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The two factors that involve CQ directly and influence the degree of cure of the resin composite are light intensity and exposure duration. While the intensity of the curing light influences the rate at which CQ is raised to the excited state, the exposure duration influences the rate at which the excited CQ molecules collide and react with the reducing agent (amine) to form free radicals (Rueggeberg *et al,* 1993:91). This therefore means that the degree of conversion is dependent on the total light incident on the composite resin, including the intensity of the light and exposure duration (Obici *et al,* 2005:393). Furthermore, Uhl and his colleagues (2003:1793) reported that time of cure influences depth of cure the most. The influence of the composite itself was rated second most important while the least important factor was the light curing unit.

Other Photoinitiators

Despite its wide use, CQ has one important disadvantage: it is a solid unbleachable yellow-shaded compound which leads to yellowing of composite resins when used in large amounts, especially in restorations of very light bleached shades (Neumann *et al,* 2005:526). Therefore manufacturers have begun to include other photoinitiators, sometimes called co-initiators, into the organic matrix, either to act on its own or synergistically with CQ to improve polymerization and to lessen the photoyellowing effects (Neuman *et al,* 2005: 525; Uhl *et al,* 2003:1788). Compounds derived from acylphosphine oxides and alpha diketones are examples of these types of photoinitiators (Neumann *et al,* 2005: 526).

It is important that the absorption requirements of the photoinitiators should correlate with the spectral emission profile of the dental curing light being used. Whereas halogen curing lights emit a broad band emission of the light spectrum (400-500 nm) which should cure most of these photoinitiators efficiently, the same may not be the case in LED lights which only have a narrow band of light emission falling within the blue light wavelength range.

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In the study by Neumann and his colleagues (2005:525) photoinitiators such as phenylpropanedione, monoacylphosphine oxide and bisacylphosphine oxide were tested in addition to CQ. Unlike CQ, the other photoinitiators showed absorption maxima in the ultra violet light region (360-400 nm), though they did extend slightly into the visible light region. This would mean that the generation of free radicals in these coinitiators would have to be with a curing light unit extending its light emission to this region.

In an earlier study, Uhl and his co-workers (2003:1787,1794) found that the earlier LED curing units used in their study could not excite the co-initiators in the composites tested to the extent that a halogen curing light could. Similarly, Neumann and his colleagues (2005:531) also found that most of the photoinitiators and co-initiators used in their study were better excited by QTH curing lights. However, the high power LED they used provided a more efficient cure for one of the co-initiators, Irgacure. These researchers therefore suggested that manufacturers of composite resins should provide the absorption

profile of the photoinitiators used in their products, as well as include the spectral band of light emitted by their curing lights in product labels.

These findings emphasize the fact that the photoinitiator system in dental resin composite materials is an important consideration, as it would determine the final properties of the restoration, especially when curing sources with too narrow emission spectra are being used.

Coupling Agent

The role of the coupling agent is to form a bond between the inorganic filler particles and the organic resin matrix phase of the composite. Bonding is accomplished by treating the surface of the fillers with a coupling agent before mixing it with the unreacted oligomer.

The most common coupling agents are organic silicon compounds called silanes. The silane accomplishes coupling as follows: the methoxy groups on the silane hydrolyse to hydroxy groups and react with the adsorbed moisture (-OH groups) on the filler, to form a film on the surface of the filler. During the setting reaction of the organic resin matrix the carbon double bonds of the silane react with the resin and hence form a bond between the filler and resin (Powers, 2002:235).

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The coupling agents play an important role in the mechanical and chemical properties of a resin composite, especially its durability. A discussion of these issues, however, will go behind the scope of the current review and will therefore not be attempted.

Optical Modifiers

Shading of composite materials is achieved by the addition of minute amounts of inorganic metal oxide pigments (Powers, 2002:236). Shades can range from very white bleaching shades to yellow to gray. Translucency or opacity is provided to simulate enamel or dentin, for example, when an opacifier is added light will not pass through the restoration but be

reflected back and the restoration will look whiter. Titanium dioxide and aluminum oxide are examples of effective opacifiers (Anusavice, 1996:280).

Optical modifiers affect the light transmission ability of a composite. For this reason a review of the influence of the shade/opacity of a composite will be provided later in the discussion.

LIGHT CURING UNITS

There are many types of light curing devices available today including Quartz Tungsten Halogen (QTH) light curing units, Plasma-arc lights and lights utilizing light emitting diodes.

These types of curing units not only differ in the way they produce light, but also in their light intensity, their spectral emission, and in the exposure time required to achieve a certain degree of cure (Caughmann and Rueggeberg, 2002:636).

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Quartz Tungsten Halogen Light Curing Units

QTH light curing units generate white light, which is produced by an electric current flowing through a thin tungsten filament when heated to high temperatures (Benjamin, 2003:334; Obici *et al*, 2005:393). Because the filament acts as a resistor, the passage of current generates heat. When the filament is heated to between 2000 and 3000 °C, a significant portion of the radiation is emitted in the visible light spectrum (shorter wavelengths). Selective filters screen the other wavelengths below 400 and above 500 nm so that only blue light is emitted (Benjamin, 2003:334). Thus most of the halogen lights' emission does not fulfill any function, and furthermore may cause an unwanted increase in tooth temperature and exposed structures (Benjamin, 2003:333; Dunn and Bush, 2002:336; Wiggins, Hartung, Althoff *et al*, 2004:1473).

Due to the high temperature generated, a cooling fan is incorporated into these units with slots in the casing for airflow. This makes the unit noisy as well as difficult to disinfect

(Benjamin, 2003:334; Wiggins *et al,* 2004:1473). The generation of high amounts of heat also led to the gradual degradation of the components of the halogen bulbs. This in turn may cause the output of the lights to fall below the adequate curing intensity levels of 300-400 mW/cm^2 which can lead to incomplete polymerization of restorative materials. The degradation of the components of the QTH curing units like the bulb and filters means that the lifetime of the light bulb is diminished to around 100 hours of optimum performance (Yap and Soh, 2005:758; Dunn and Bush, 2002:335).

As a result QTH lights need to be maintained diligently to ascertain optimum work performance, including checking and replacement of the bulb, filter and fan motor as necessary (Price *et al,* 2005:2639). It is, amongst others, these disadvantages of the QTH lights that were used to make the light-emitting diode curing lights as appealing as possible to dental clinicians when they were introduced in the late 1990's (Clinical Research Associates 2002:1).

Light Emitting Diode Curing Units

Low power blue LED's based on silicon carbide technology have been around for many years. Their power output, however, was too weak to be considered for the curing of resin based composite materials. The development of blue LED's based on gallium nitride technology in 1995, which provided for a 400 fold increase in power, prepared the way for the development of dental LED curing lights (Mills *et al,* 1999:388,390).

Unlike halogen based light curing units, LED curing units are solid state semiconductor devices that convert electrical energy directly to light (Dunn and Bush, 2002:335; Wiggins *et al,* 2004:1471; Yap and Soh, 2005:759). LED's comprise of semiconductors of two types, referred to as the n-doped and the p-doped. The n-doped contains an excess of movable electrons and thus consists at a higher energy level than the 'p-doped' which contains a deficiency of electrons. When these two types of semiconductors are connected and electricity is applied, the electrons are forced to flow across the band gap between the two semiconductors from the high energy level to the low energy level. As the electrons cross the band gap, energy related in magnitude to the size of the band gap is released in the

form of light. The difference in energy levels between the two conductors also influences the colour of the light. Conductors with fairly similar levels of energy create the low-energy photons of red light, while conductors with larger energy differences can create blue light (Casiday and Frey, 2002:10; Beaty, 1997:1).

The colour of an LED light is thus determined by the chemical composition of the semiconductor combination as well as the band gap between the semiconductors. The chemical composition of the semiconductor combination commonly used in LED LCU's is gallium nitride, which forms the basis for the blue emissions (Dunn and Bush, 2002:335; Wiggins *et al*, 2004:1471; Jandt, Mills, Blackwell and Ashworth, 2000:41).

The advantages over the halogen based curing lights claimed by the first LED curing units that came into the market were numerous. Perhaps the most important advantage was the fact that the LED curing units produced light with a narrow spectral distribution falling within a specific wavelength with a 400-500nm range, with a peak wavelength at 460nm as this conveniently fell within the absorption range of camphorquinone (Wiggins *et al*, 2004:1473; Jandt *et al*, 2000:41). This meant that no filters were needed hence the risk of degradation of the filter that can cause decreased efficiency (as in QTH halogen) lights was removed. As the lights had a higher irradiation in the region of the peak absorption of CQ, it was expected that these lights would be more effective than QTH lights to provide a greater depth of cure (Mills *et al*, 1999:391).

The narrow spectral emission of the LED curing units also meant that little unwanted heat was produced. The LED curing units thus claimed not to degrade as quickly over time with the LED bulbs providing up to 10000 hours as compared to the halogen bulbs that provide only about 100 hours of optimal service (Yap and Soh 2005:759). Furthermore, fans were not needed to cool the light units (Clinical Research Associates 2001:1). Thus, LED curing units can be disinfected easily since they do not contain open vents for cooling. The power consumption of LED curing units is also minimal, meaning that LED curing units can be powered sufficiently with a rechargeable battery. All of these advantages lead to a less cumbersome, cordless lightweight design (Clinical Research Associates 2001:1; 2002:2).

However, despite all these appealing features and expected improvements in curing ability, the earlier LED curing lights demonstrated slow or incomplete cure (Clinical Research Associates, 2001:1), as reviewed in the next session.

Earlier LED curing units

The drawbacks of the first and even some of the second generation LED curing lights were highlighted in many studies, of which just a few will be reviewed (Table 2).

When the lights had a fairly similar, but relatively low irradiance of not much more than 100 – 300mW/cm^2, significantly greater depths of cure or monomer conversion were obtained by the early prototype LED lights than by the QTH lights they were compared to (Mills *et al,* 1999:388; Fujibayashi *et al,* 1998, quoted in Jandt *et al,* 2000:42).

It is, however, important to note that the irradiance or intensity of the commercial LED lights used in some of the other earlier studies was often much less than the irradiance of the QTH lights they were compared with in research (see Table 2 for a summary of the testing conditions of the studies reviewed). This can partly be explained by the fact that the irradiance values measured by curing radiometers involve more than just the narrow camphorquinone spectrum. Therefore halogen-based lights will typically demonstrate higher power densities than LED units (Dunn and Bush, 2002:339).

Dunn and Bush (2002) tested the hardness obtained by curing 2mm increments of microfilled and hybrid resin composites with two QTH halogen light curing units and two commercially available LED curing lights. These authors demonstrated that the hardness values obtained for the QTH halogen light curing units were significantly higher as compared to the LED curing lights, regardless of the type of composite. They therefore concluded that the light output of the LED curing lights was still inadequate in comparison to the QTH lights used and suggested that the number of LED's should be increased to increase the power output of the LED curing light. The LED curing lights used in this study contained seven LED's. A study by Jandt and his colleagues (2000:41) tested an LED light curing unit containing 27 blue LED's but the improved irradiance was not enough to result in depth of cure values that were higher than the values obtained with the QTH light tested.

Table 2. Summary of research studies reviewed involving the earlier LED lights

Authors	Curing lights tested	Curing modus	Composite tested	Shade	Co-initiator present?	Recommended cure time (seconds)	Type of test
Mills *et al* (1999:390)	QTH Coltolux 4 (Coltene) LED Prototype LED	Adjusted to 100 mW/cm^2 290 mW/cm^2 (cured for rec. time)	Microfill Silux Plus (3M ESPE) Post Hybrid P50 (3M) Microfine Hybrid Z100 (3M ESPE)	U U A3.5	No No No	40 60 40	- Depth of cure
Jandt *et al* (2002:41)	QTH Spectrum (Dentsply) LED Prototype LED	755 mW/cm^2 350 mW/cm^2 (cured for rec. time)	Microfine Hybrid Spectrum TPH (Dentsply)	A2, A4	No	40	- Depth of cure - Compressive strength
Dunn and Bush (2002:337)	QTH Optilux 400 (Demetron) Optilux 501 (Demetron) LED Lumacure (Lumalite Inc) Versalux (Centrix)	900 mW/cm^2 1030 mW/cm^2 150 mW/cm^2 150 mW/cm^2 (cured for rec. time)	Microfill Renamel (Cosmedent) Microfine Hybrid Z250 (3M ESPE)	A1 A1		40 40	- Knoop hardness test
Uhl *et al* (2003:1788)	QTH Trilight (3M) LED LED 63 (Prototype) FreeLight (3M ESPE)	660 (1524**) mW/cm^2 638 (1074**) mW/cm^2 270 (624**) mW/cm^2 (5, 10, 20, 40 seconds)	Microfine Hybrid Z100 (3M ESPE) Spectrum TPH (Dentsply) Hybrid Solitaire 2 (Kulzer) Definite (Degussa)	A4 A3.5 A4 A4	No No Yes Yes	40 40 40 40	Knoop hardness test Depth of cure
Uhl *et al* (2004:81)	QTH Polofil (Voco) LED Prototype LED	860 mW/cm^2 901 mW/cm^2 (cured for rec. time)	Hybrid Z100 (3M ESPE) Revolcin Flow (Merz) Ormocer Admira (Voco)	A2, A4 A2, A3.5 A2, A3.5	No Yes No	40 40 40-60	Knoop hardness test Depth of cure
Price *et al* (2003:666i)	QTH Optilux 40 (Demetron) 2nd Generation LED Ultralume 2 (Ultradent) (used 3 of each)	700 mW/cm^2 700 mW/cm^2 (cured for rec. time)	Microhybrid Vit-I- escence (Ultradent) Esthet-X (Dentsply) Hybrid Herculite XRV (Kerr) Filtek Flow (3M ESPE) Revolution (Kerr) PermaFlo (Ultradent) Prodigy Condensable (Kerr) Microfill Heliomolar (Vivadent)	TM, A2 A2, CE A2 dentin A2 A2 A2 A1 A1		20 20 40 20 20 20 40 40	Variable distance of cure (2-9mm) Knoop hardness test
Yap *et al* (2004:411)	QTH Max (Dentsply) Astralis 10 (Ivoclar-Vivadent) Elipar Trilight (3M ESPE) LED GC e-light (GC) Elipar FreeLight (3M ESPE)	400 mW/cm^2 X 40 sec 1200 mW/cm^2 X 10 sec 800 mW/cm^2 X 40 sec 350mW/cm2 X 40 & 600 mW/cm^2 X 20 sec 400 mW/cm^2 X 40 sec	Microhybrid Z100 (3M ESPE)			40	Crosslink density Knoop hardness using a digital microhardness tester

**over the inner 4mm diameter of the light guide – the only part that was used to cure the composite samples

A study by Uhl and his colleagues (2003:1787,1795) investigated the depth of cure and the hardness obtained when resin composites were polymerized with a QTH halogen light, a prototype LED light and a commercially available LED light curing unit. The depth of cure obtained with the QTH halogen light was greater than that obtained with both the LED light curing units for all materials tested, and for the different curing times tested. The results were partly influenced by the fact that some of the resin composites tested contained co-initiators as the LED curing units, due to their narrow spectrum of light emission, could not excite the co-initiators optimally. The authors therefore warned readers that LED curing units should be used very carefully when curing composites containing initiators which need to absorb light at shorter wavelengths.

In a further study, Uhl *et al* (2004:80) used a commercial halogen light and a custom-made LED unit, both of which provided a fairly similar, but higher irradiation (see Table 3) than the lights tested in their previous study, to cure three commercial composite restorative materials. They obtained a statistically significantly greater depth of cure with the custom-made LED unit than with the halogen light for all composites tested. In addition, both lights could bring two of the composites to a similar hardness of cure. The third composite containing a co-initiator, however, was significantly less hard when cured with the LED curing unit. As in their previous study, the authors (2004:86) again suggested that a Knoop hardness test, rather than a depth of cure test, should be used to discriminate between LED and halogen curing units if composites containing co-initiators are being tested.

When Price and his co-workers (2003:666) evaluated the ability of a second generation LED curing unit to cure 10 contemporary composites to a sufficient top-bottom hardness ratio, they found that when the LED lights was used for 20 seconds, only five of the composites were cured as hard as those cured with the QTH lights at a 40 sec curing time. When the curing time with the LED curing units was lengthened to 40 seconds, only six composites were cured as hard as those cured by QTH light. They thus concluded that this second generation LED unit could not polymerize all of the composites as well as the QTH light and that this may be ascribed to a mismatch between the spectral output of the LED curing units and the spectral sensitivity of some of the composites.

Finally Yap and his co-workers (2004:414) concluded that composites cured with earlier LED units were less cross-linked than those cured with conventional QTH lights. Composites with lower cross-link densities may be more prone to hydrolysis and water sorption, which, in turn, may lead to less than optimal material properties and reduced clinical durability (Yap *et al*, 2004:413)

Hence, on the one hand some of these studies proved that the initial LED curing lights as well as some of the later improved LED's, provided insufficiently cured composites which can lead to a greater potential for inferior mechanical properties, for example decreased bond strength, breakdown at the margins, reduced resistance against wear and greater cytotoxicity effects (Uhl *et al*, 2004:80; Price *et al*, 2003:666a; Yap *et al*, 2004:413). On the other hand, the improvements in LED technology have led to an improved intensity output (Table 2), which in some of the studies reviewed above resulted in better depth of cure than obtained with the QTH-lights. These results, however, still depended on the choice of composite, more specifically those light cured resins containing photoinitiators other than camphorquinone as they did not cure adequately, regardless of the intensity of the curing light (Uhl *et al*, 2004:80; Price *et al*, 2003:666f).

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The introduction of high powered LEDs has claimed to overcome these problems and to reduce the curing time (Clinical Research Associates 2006:2).

High Power LED Curing Units

The development of HP LED curing units stems from recent advances in LED technology including the use of a larger semiconductor crystal which enable these high powered LED's capable of delivering a power density of about 1000 mW/cm^2 (CRA Newsletter 2006:1; Rueggeberg, Blalock and Callan, 2005:586; Wiggins *et al*, 2004:1473). The inclusion of a conical reflector consisting of a highly reflective mirror film may also be used at the base of the light guide to increase efficiency in the light delivery (Wiggins *et al*, 2004:1473).

Since the light spectrum produced with all LED's falls within the blue light wavelength range, more efficient curing could be expected with the increased power output, resulting in a reduced curing time as well. A few research studies reported on the performance of one

such HP LED, the Elipar FreeLight 2 manufactured by 3M ESPE (St Paul, MN), as summarized in Table 3 and reviewed in the following section.

Wiggins and her colleagues (2004:1471) compared the efficiency of the FreeLight 2 with other types of curing lights by measuring the depth of cure of three types of resin composites. They found that the curing efficiency of the FreeLight 2 was equivalent to the high-energy halogen light at a 10-second exposure time while the conventional LED curing unit and conventional QTH curing light needed 20 sec exposure time to acquire a similar depth of cure.

Using the total energy concept, which states that a certain dose (intensity x time) of light is needed to adequately cure a specific material, Wiggins *et al* (2004:1478) argued that a HP LED having an intensity at 1000mW/cm^2 and cure time of 10 seconds will be even more effective to cure a specific material than the conventional LED curing light with an intensity of 700mW/cm^2 with a cure time of 20 seconds or the high-energy halogen light at 1500mW/cm^2 with a cure time of 10 seconds. Based on this assumption and on their findings, Wiggins and her colleagues (2004:1471) thus concluded that the FreeLight 2 may be an effective, time-saving alternative for clinicians to use to cure light curing resin-based composites.

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Price and his colleagues (2005:2631) compared a HP FreeLight 2 light with a QTH halogen light by comparing the Knoop hardness of different types of composites at different depths of cure. When the HP LED was used at the manufacturers recommended curing times, it produced significantly harder composites to a depth of 3mm than the QTH halogen lights. When the HP LED was used at 50% of the curing time, the hardness was not significantly different from the hardness obtained with a QTH halogen used at 100% of the recommended curing time. The authors (2005:2635) thus concluded that the FreeLight 2 would be a suitable replacement for an aging QTH curing light. It is important to note that the irradiance of halogen lights when used at a 2mm distance as in this study varied from 400 to 873 mW/cm^2. Although clinically relevant, as suggested by the authors (2005:2639), this could have provided softer, more inferior composite samples against which the FreeLight 2 was evaluated.

Yap and Soh (2005:762) investigated the curing efficiency of the FreeLight 2 and compared it to a conventional LED and a QTH halogen curing light. They tested this by measuring the top and bottom surface hardness of 2mm resin composites using a digital microhardness tester. They found that the curing efficiency of the FreeLight 2 was generally comparable to the conventional LED and QTH halogen lamps, even with a 50% reduction in curing time.

Shortall (2005:906) tested the claim that the Freelight 2 is capable of curing in half the time of its predecessor using a depth of cure test. They found that the light was able to achieve equivalent depths of cure as its predecessor in half the curing time. In a recent study Felix and his co-workers (2006:147) reported that a HP LED showed comparable hardness levels to a QTH light at high power setting when the curing distance was kept at 2mm. At 9mm curing distance, the HP LED was ranked better or equivalent to the QTH light to a depth of 1.5mm. Beyond that, composites cured with the HP LED were significantly softer.

It is clear from the review above that all of the studies evaluating the HP LED FreeLight 2 found it to be a suitable light to use for curing, even at half of the recommended exposure time. It is however also important to note that these studies either evaluated a very narrow range of resin composite types (Table 3) or a narrow range of composite shades or opacities. For example, while Shortall (2005:906) used all the shades of the microhybrid Z250, Yap and Soh (2005:758) only used the A2 shade of Z100. Both Wiggins and colleagues (2004:1473) and Price and colleagues (2005:2633) compared a selection of types and opacities of composites. However, Wiggins and colleagues only used one shade in their study (A3), while Price and colleagues mostly used A3. In the study of Price and his colleagues (2005:2637) different types of resin composites and shades or opacities of resin composites responded differently to each curing light/ time combination. It may be that 50% of the recommended curing time may not be enough if darker, lighter or more opaque shades than those tested in these studies are being cured.

The following section of this paper reviews some additional composite factors that may influence the degree of cure.

Table 3. Summary of research studies reviewed involving the HP LED lights

Authors	Curing lights tested	Curing modus	Composite tested	Shade	Co-initiator present?	Recommended cure time (seconds)	Type of test
Wiggins *et al* (2004:1473)	Conventional QTH		Microhybrid				Depth of cure
	Elipar TriLight (3M)	700 mW/cm^2 X 20 sec	Z250 (3M ESPE)	A3 E		20	
	High-energy QTH		Microfill				
	Optilux 501 (Kerr)	1500 mW/cm^2 X 10 sec	Filtek 110 (3M ESPE)	A3		20	
	Earlier LED		Nanocomposite				
	Elipar FreeLight (3M)	400 mW/cm^2 X 20 sec	Filtek Supreme (3M-ESPE)	A3 B		20	
	HP LED						
	Elipar FreeLight 2 (3M)	1000 mW/cm^2 X 10 sec					
Price *et al* (2005:2633)	QTH		Microhybrid				Knoop hardness at various depths of cure ranging from 0.5 to 3.5mm from the top surface of composite.
	TriLight (3M ESPE)		Z250 (3M ESPE)	A2, B0.5		20, 30	
	Standard setting	666-873 mW/cm^2	TetricCeram	A2, Bleach XL		40, 40	
	Medium setting	400-523 mW/cm^2	Nanohybrid				
		(cured for rec. time)	Esthet-X (Dentsply)	A2B, A2O		20, 20	
	HP LED		Microfill				
	FreeLight 2 (3M ESPE)	914-1119 mW/cm^2	Heliomolar (Vivadent)	A2, 110T		40, 20	
		(rec cure time and 50% of	Nanocomposite				
	(used 3 of each)	cure time)	Filtek Supreme (3M ESPE)	A2D, A2B		40, 40	
Yap and Soh (2005:759)	QTH		Microhybrid	A2			Knoop hardness of 2mm samples
	Max (Dentsply)	400 mW/cm^2 X 40 sec	Z100 (3M ESPE)				
	Astralis 10 (Ivoclar-Vivadent)	1200 mW/cm^2 X 10 sec					
	Elipar Trilight(3M ESPE)	800 mW/cm^2 X 40 sec					
	LED						
	Elipar FreeLight (3M)	400 mW/cm^2 X 40 sec					
	HP Led						
	FreeLight 2 (3M ESPE)	1000 mW/cm^2 X 20 sec					
Shortall (2005:907)	QTH		Microhybrid				Depth of cure (Knoop hardness using a digital penetrometer)
	XL300 (3M ESPE)	716 mW/cm^2 x 40sec	Z250 (3M ESPE)	All Shades			
	Earlier LED						
	FreeLight (3M ESPE)	346 mW/cm^2 X 40 sec					
	HP LED						
	FreeLight 2 (3M ESPE)	1037 mW/cm^2 X 20 & 40 sec					
Felix *et al*, (2006:147)	QTH		Microhybrid				Depth of cure (Knoop hardness)
	TriLight (3M ESPE)	Varied acc to cure distance	Z250 (3M ESPE)	A2, B0.5			Influence of curing distance
	Standard setting	50% of rec curing time	TetricCeram	A2, Bleach XL			
	Medium setting	100% of rec curing time	Nanohybrid				
			Esthet-X (Dentsply)	A2B, A2O			
	HP LED		Microfill				
	FreeLight 2 (3M ESPE)	50% of rec curing time	Heliomolar (Vivadent)	A2, 110T			
			Nanocomposite				
	(used 3 of each)		Filtek Supreme (3M ESPE)	A2D, A2B			

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INFLUENCE OF COMPOSITE TYPE ON DEGREE OF CURE

The optimum light curing of a resin based composite is not only controlled by factors like: a) Wavelength of the curing light used for polymerization; b) Intensity of the curing light; c) Irradiation type; d) Distance of curing tip from the composite; but also by factors like the d) material's filler composition and resin chemistry; and e) its shade and translucency (Rueggeberg *et al*, 1993:91; DeWald and Ferracane, 1987:727).

When curing composite resin, adequate light penetration is essential. However, as the light passes through the bulk of the composite during curing, scattering or absorption occurs. These factors results in an attenuation of the light intensity which leads to a reduction of the penetration of the light photons to the deeper parts of the material (DeWald and Ferracane, 1987:729). As a result fewer CQ molecules are being activated in these parts, resulting in potentially fewer free radicals. Therefore curing time 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 (Rueggeberg *et al,* 1993:94). At the top surface, however, since there is no overlying composite, there is no light attenuation. Therefore, even if quite large decreases in intensity have taken place, sufficient energy will still be provided to adequately cure the resin composite at the surface.

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FILLER LOAD, PARTICLE SIZE, PARTICLE SIZE DISTRIBUTION

Light scattering is related to filler load, particle size and particle size distribution. Different types of composite, for example microfill and hybrid composite, will reduce light transmission at different rates (Leonard, Charlton, Roberts *et al*, 2001:176).

Light scattering within the composite is increased as the particle size of the fillers in the composite approaches the wavelength of the curing light and is maximized when the effective particle size is one half the wavelength of the curing light or approximately 0.25 μm (Ruyter and Oysaed, 1982:179). As the SiO_2 particles in microfilled composites are approximately 0.04μm, it has been suggested that the agglomeration of the submicron filler particles can produce a particle size equivalent to the wavelength of the curing light and

that this may be the reason why the microfill resin in their study showed a reduced depth of cure (DeWald and Ferracane, 1987:729). In comparison to this the composite resins with a larger particle size (8-10 μm), as well as higher filler percentage (62% volume), have shown to have a greater depth of cure.

Leonard and his colleagues (2001:176) found that a microfilled composite required nearly twice as much irradiance (542mWcm^2 v. 260mW/cm^2) as that of a hybrid composite to obtain an adequate hardness of cure at 2mm depth during an exposure time of 40 seconds. The reason for this has been attributed to the smaller filler particle size which decreased the effectiveness of light curing.

When Dunn and Bush (2002:335) compared the hardness of a microfilled composite to a hybrid composite, the hybrid produced much higher hardness values than the microfilled composite, regardless of the type of curing light used, at the top and especially at the bottom of the curing sample. Similarly, very poor hardness results were obtained at the bottom surfaces of the microfill resin samples in comparison to microhybrid samples, regardless of the light source (Peris, Mitsui, Amaral and Ambrosana, 2005:653). Like Dunn and Bush, the researchers of this study also ascribed this poor results to the possible light scatter brought about by the small particle sizes of the composite group.

In a recent study by Wiggins and colleagues (2004:1475), three different types of resin based composite materials were cured with a high powered LED. These materials included a microfill, a nanocomposite and a hybrid composite. They did not found any significant difference in the depth of cure of these three types of composites. A reason for this may be the fact that the researchers determined depth of cure by scraping away the soft resin prior to measuring the thickness of the remaining composite as this may have overestimated the actual depth of cure (Price *et al,* 2005:2633). A more sensitive method to determine depth of cure would be the use of hardness tests.

Only three composites were able to maintain a Knoop hardness that was more than 80% of their maximum hardness when Price and his colleagues (2005:2634) tested the depth of cure of a variety of composites. All of these were hybrid composites. The composites that

did not maintain this hardness for the full curing depth were two nanofilled composites, two nano-hybrids, two micro-filled composites and one hybrid with a very opaque shade. It is, however, important to note that this finding could have been due to filler size, shade or to the presence of co-initiator as the study was not designed to test specifically for these effects.

SHADE/OPACITY

Light transmission through darker and lighter shades is diminished because of their opacity. While the darker shades absorb the light, the white pigments in the light opaque shades diffuse the light, which limits light penetration through the composite (Sakaguchi, Douglas and Peters, 1992:183; Aguiar, Lazzari and Lima, 2005:302).

In a study by Aguiar and his co-workers (2005: 302) it was seen that a darker shade of resin composite (C2) had the lowest hardness values compared to the universal (A3.5) and lighter (A1) shade. The lighter A1 showed highest hardness means and was statistically different from the C2 shade on the bottom surface. Myers and his colleagues (1994:149) showed that the measured light intensity at 1mm depth of an A4-shaded hybrid sample was half of that measured when A-1 shade was used. At 2mm depth, the light intensity through the darker shade was only 30% of the light intensity that passed through the more translucent shade. Therefore, working in increments of 1mm was suggested.

When Tanoue and his colleagues (2001:618) determined the depth of cure of different shades of a photo-activated prosthetic composite material, the light shades showed greater depths of cure than the dark shades. A longer exposure period for polymerization was thus suggested for the darker shades. In contrast, in the study by Price and colleagues (2005:2631) the data showed that a darker shade (B0.5) of a microhybrid resin composite (Z250) showed greater hardness values as compared to the lighter shade (A2). The authors, however, did not remark about this contradictory finding.

The role that shade and filler type play is however not as straightforward as it may have seemed until now. Rueggeberg and his colleagues (1993:91) evaluated all the variables

that may be influential in maximizing cure of composites. According to them, at the top surface, in the order of the most influential factors, is filler type, exposure duration and resin shade. At 1mm depth, it is exposure duration, filler type and source intensity. At depths of 2mm and more, influences on cure relate solely to source intensity and exposure duration. This means that shade is only an attributing factor at the surface of the restoration, and a small factor at that, especially when shades are being chosen to reflect the clinical situation (thus no extremes). More extreme shades, however, will influence the final cure more significantly. Concerning filler type, it was found to have a significant influence on resin cure. This influence, however, decreased a lot once a depth of 2mm is reached.

Another consideration is the fact that degree of translucency/ opacity also influence light transmission. It is therefore not just a case of dark and light shades: some shades may be light and more translucent, other may be light, but more opaque. The latter will reduce light transmission more effectively, therefore having a greater influence on depth/degree of cure (Shorthall, 2005).

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MICROHARDNESS TESTS

Hardness is commonly correlated to physical properties of composite resins like mechanical strength, rigidity and resistance to intra-oral softening (Uhl *et al*, 2003:1793). The hardness of composites is influenced by several factors, for example organic matrix composition, type and amount of filler particles and degree of conversion (Correr, 2005:222).

Several direct and indirect methods can be used to evaluate the degree of polymerization of resin composites. As the direct methods are complex and expensive, the indirect methods such as visual, scrape and hardness testing are more popular (Bouschlicher, Rueggeberg and Wilson, 2004:703; Poskus, Placido and Cardoso 2004:727; Yap and Soh, 2005:758). DeWald and Ferracane (1987:727,729) compared four of these methods and found that the visual and scraping methods correlated well, but severely overestimated depth of cure as compared with hardness tests or a degree of conversion analysis. Furthermore, this study,

as well as other studies, have found that hardness values show a positive correlation with degree of conversion (Rueggeberg and Craig, 1988;932; Bouschlicher *et al*, 2004:698).

Hardness is defined as the resistance to permanent indentation or penetration. Hardness testing has been widely used in the study of optimum cure of composite resins and includes Knoop and Vickers hardness testing. The Knoop and Vickers tests are classified as microhardness tests in comparison with the Brinell, Rockwell macrohardness tests (Anusavice, 1996:69). The hardness tests involve the use of a static diamond tip under a specific load, over a tested material and over a specific period of time, which forms an indent after removal of the load. This indent is microscopic and in a Vickers hardness test, the shape resembles a pyramid-square shaped impression (Poskus *et al,* 2004:730). The Vickers hardness number (VHN) is calculated by dividing the load by the surface of the indentation. The lengths of the diagonals of the indentation are measured and means values are obtained and the VHN is read from a table. The limitation of this test is that it is not suitable for the measuring of materials that are resilient, as they tend to recover rendering the indentation inaccurate (Anusavice, 1996:69; Poskus *et al*, 2004:730).

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The Knoop hardness test is the most commonly used method for the evaluation of resin composites because it minimizes the effect of elastic recovery. When the Knoop and Vickers hardness methods were compared in a study on placement techniques of composites, it was reported that both the Knoop and Vickers hardness measurements showed statistically similar results and good correlation, although Vickers values were higher: VHN = 14.7 + 0.954 x Knoop hardness number (KHN). These authors' conclusion was that both tests can be used for the indirect evaluation of degree of polymerization of composites (Poskus *et al,* 2004:727, 731).

Advantages of the surface hardness tests is that surface hardness is a good predictor for resin conversion as it is especially sensitive to small changes in polymer cross-linking in areas of high conversion (Dietschi, Marrett and Krejci, 2003:499). Surface hardness tests furthermore allows for measurements at specific locations within the sample while its simplicity allows evaluation of large number of specimens. Their one disadvantage is that they cannot be used for direct comparisons among materials. They are, however, a very useful tool for relative measurements within the same material (Dietschi *et al,* 2003:499).

Generally studies use bottom:top hardness ratios (B/T ratios) to obtain a percentage depth of cure, and if that value exceeded 80%, specimens are considered to be adequately polymerized (Leonard *et al*, 2001:176; Yap and Soh, 2005:758). Furthermore, a B/T ratio of 80% corresponds to 90% of the maximum conversion possible at the top surface of a composite (Bouschlicher *et al*, 2004:703). The percentage depth of cure calculated as such, however, can easily be misinterpreted as a specimen could have been cured poorly throughout, and still provided a ratio that exceeds 80% (Dunn and Bush, 2002:340; Price *et al*, 2003:666e).

Price and his colleagues (2003:666f) thus calculated this ratio by using the mean KHN obtained at the bottom of the samples cured with the weaker light system with the mean KHN obtained at the top of the samples cured with the light that provided the highest hardest values. Bouschlicher and his co-workers (2004:703) suggest that this problem can be overcome by normalizing the maximum hardness at the sample's top surface. This can be achieved by allowing top surface conversion to go on beyond the exposure time recommended by the manufacturer. If this was done, B/T hardness ratios can be used to compare the relative extent of cure of different composites with different curing strategies.

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The Vickers hardness method is therefore an appropriate indirect test to use to evaluate the degree of cure of composites. While a B/T ratio of 80% or the so-called percentage depth of cure can be helpful to point out adequately cured composite samples, care should be taken not to misinterpret the results and not to make comparisons among groups, but only within groups.

AIMS AND OBJECTIVES

The aim of this study was to determine whether there was a significant difference in surface microhardness when different types and shades of resin composite materials were cured with a HP LED curing unit operated at 50% and at 100% of the recommended exposure time.

The objectives of this study were:

1. to determine the surface microhardness of the top and bottom surfaces of three shades each of a microhybrid and two nanofilled composites;
2. to determine the bottom to top hardness ratio (%) of each resin composite material;
3. to compare the top and bottom surface hardness values of the different types and shades of composite materials;
4. to compare the bottom to top hardness ratio (%) obtained at the two different exposure times.

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The null hypothesis for this study was that a high-power LED curing unit operated for half the recommended curing time would yield comparable microhardness values for different types and shades of resin composite materials than when operated for the full recommended exposure time.

MATERIALS

COMPOSITE RESINS

Two main types of light cured composites restorative materials were included in this study (Table 4), namely a microhybrid composite and two nanocomposites (Filtek Technical Product Profile 2005:5, Z350 Technical Product Profile 2005:5, Z250 Technical Product Profile, 1998:29). The difference between the two is mainly the fillers, which are different in size affecting their filler load.

Table 4. Composition of Filtek Z250, Filtek Z350 and Filtek Supreme XT.

	Filtek Z250	Filtek Z350	Filtek Supreme XT
Manufacturer	3M ESPE	3M ESPE	3M ESPE
LOT	6XW, 6HK, 6UN	6BG, 5BC, 5AB	4AN, 5BG, 6AJ
TYPE	Microhybrid	Nanocomposite	Nanocomposite
Shade	A1, A3.5, D3	A1, A3.5, C2	Clear, Yellow, Gray
Filler load	60% by volume	78.5% by weight	72.5% by weight
Filler particle size	0.01-3.5μm (average = 0.6μm)	Effective particle size = 5-20nm Cluster particle size = 0.6-1.4μm	Particle size = 20- 75 nm Cluster size = 0.6-1.4μm
Recommended curing time	All = 20 sec for 2.5mm layer	All = 20 secs for 2mm layer	All = 20 secs
Filler type	Zirconia/silica	Zirconia/silica nanocluster and silica particles	Pre-polymerized filler and pyrogenic silica

1. Microhybrid

Filtek Z250

- Contains filler sizes ranging from 0.19 to 3.3 micrometers (μm), with a filler volume of 60 percent.
- Light (A1), universal (A3.5) and darker (D2) shades that are commonly being used in practice have been chosen for the study. Another reason for the choice is that the same shades are available for Z350 for comparative purposes.

2. Nanocomposites

Filtek Z350

- Contains a unique combination of individual 20 nm silica nanoparticles and loosely bound agglomerated zirconia/silica nanoclusters consisting of agglomerates of primary zirconia/ silica particles sized 5-20 nm with a total filler load of 78.5% by weight.
- Light (A1), universal (A3.5) and darker (C2) shades that are commonly being used in practice have been chosen for the study.
- Note that these shades are similar to those labeled A1B, A3.5B and C2B in Filtek Supreme XT (personal communication, R Coventry, 3M ESPE Professional Advisor, 2006), in other words as body opacity shades (Fig. 1).
- The more opaque shade is, amongst others, a result of the use of zirconium/silica nanoclusters in stead of silica nanoclusters as in the more translucent Filtek Supreme XT shades (Filtek Technical Product Profile 2005:11).

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Filtek Supreme XT (FS XT)

- Also contains a combination of individual 75 nm silica nanofillers and loosely bound agglomerated silica nanoclusters, consisting of primary silica nanoparticles sized 5-20 nm with a total filler load of 78.5% by weight.
- Only translucent shades have been used in this study, namely the grey, yellow and violet shades. The translucent shades are the least opaque of all the shades of FS XT (Fig.1).

Fig. 1. Diagram illustrating the degree of opacity in the different types of shades of Z350 (body shades) and Filtek Supreme (dentin, body, enamel, translucent shades) (Filtek Technical Product Profile 2005:6).

HIGH POWER LIGHT EMITTING DIODE CURING LIGHT

A HP LED was used to photocure the resin composites in this study. These curing lights have a light intensity of approximately 1000mW/cm^2 and emit light in the wavelength range of 430-480nm (Elipar Technical Product Profile, 2003:30).

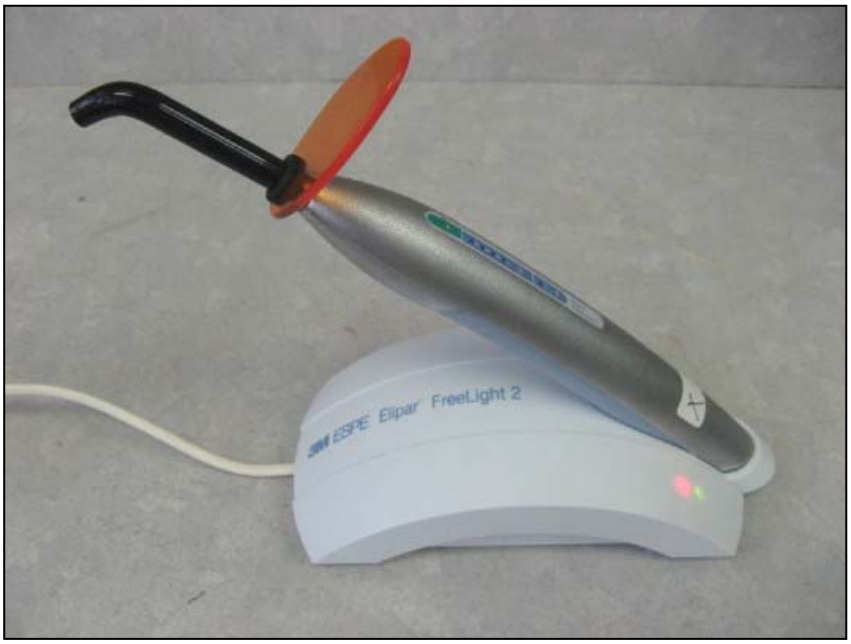
Elipar FreeLight 2

- This high power light emitting diode curing light has been claimed by the manufacturer to adequately polymerize resin composites with a 50 % reduction in curing time.
- Two different units were used in this study in order to represent more accurately this brand of the curing light.
- Both the curing lights were set on the Standard mode of curing.

Brand name **: Elipar FreeLight 2**

Manufacturer **: 3M ESPE, St Paul, MN, USA**

Serial numbers **: 939820005741 and 939820005740**



METHODOLOGY

The methodology of the study included the following steps:

A. Calibration of microscope.

B. Set-up of the HP LED curing lights

C. Specimen discs.

D. Curing of the specimens.

E. Vickers Indentation of specimens.

F. Measurement of the Vickers indents.

G. Data analysis

A. CALIBRATION OF MICROSCOPE

The Vickers microhardness tester (Fig. 2) was assembled and connected (Model M12a, Vickers Ltd, York-England. Transmitter number M07356, Indenter objective number BB4276) and the reading objective of 40 X magnification was put into view. A metal stage micrometer was placed on the stage of the microscope and the draw tube of the microscope adjusted until 0.1mm on the stage (1 block) was equal to seven and a half divisions of the fixed scale of the filar eye piece. The microscope was hence calibrated at a magnification of 75 X.

Fig. 2. Vickers microhardness tester

A test measurement using a preformed indent on the metal stage was carried out. This was done by focusing the microscope as well as the moving the stage of the microscope forwards, backwards and sideways. The indent was adjusted next to lie between a vertical line of the fixed scale and the other vertical line of adjustable scale of the filar eyepiece.

The span of the indent was consequently measured by counting the number of vertical lines of the fixed scale to denote the first digit (a hundredth). The other 2 digits would be noted as it appeared on the adjusting knob of the filar eyepiece.

B. SET-UP OF THE HP LED CURING LIGHTS

Both the HP LED curing lights were put on charge to charge the batteries by placing them on the charging base. After charging was complete, both the curing units were tested for intensity. This was carried out using a built in tester incorporated in the charging base. Both lights indicated the 80% level considered to be adequate for curing by the manufacturers (Elipar Technical Product Profile, 2003:22). The intensity was checked randomly throughout the study.

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The curing units were mounted on a stand, so that 1) the curing tip was kept at a standard distance of 2 mm away from specimen discs when curing, and 2) the curing tip would be directly above the 3 mm diameter hole where the materials to be tested would be packed.

The decision to use a 2 mm curing distance was based on the method followed by Price and his colleagues (2005:2633). These researchers measured the distance from the light guide to the surfaces of composite restorations in sectioned molars containing Class I restorations and found 2.0 ± 0.1 mm to be a clinically relevant radiation distance.

C. SPECIMEN DISCS

A total of 180 specimen discs were fabricated. Ten samples were made of each type of composite, each shade of composite and each curing period as set out in Table 5. Half of these samples were cured with one of the curing lights and the other half with the other.

The material used for fabricating the specimen discs was opaque PVC rods of 15mm diameter. These rods were sliced in thickness of 2mm each using precision instruments. Holes were made at the centre of each disc measuring 3mm in diameter. The thickness of all specimen discs was measured using calipers (Fig. 3) and those discs not measuring 2mm were discarded and not used in the study. The upper surface of each disc was marked to denote a letter used to represent a resin composite. Roman numerals were used to denote the curing time while the colour used for this denoted which one of the LED unit was used.

To avoid investigator bias to a degree (the syringes had distinct colors for the different types of material) the labels of the syringes were covered with white masking tape and denoted with a number by an independent person (Fig. 4).

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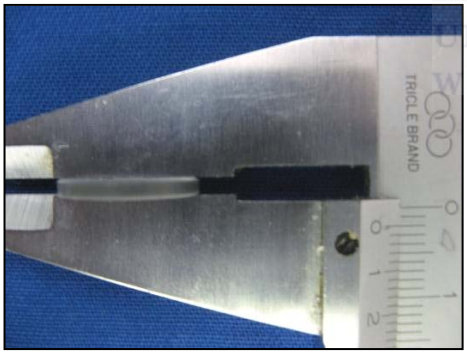

Fig. 3. Measuring of discs

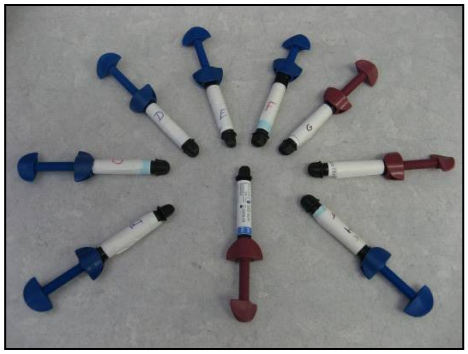

Fig. 4. Masked composite syringes

Table 5. Summary of experimental groups, sample sizes and curing times

Type of composite	Shades	Curing times	Number of samples
Filtek Z250	**A1**	20 seconds 10 seconds	10 10
	A3.5	20 seconds 10 seconds	10 10
	D3	20 seconds 10 seconds	10 10
Filtek Z350	**A1**	20 seconds 10 seconds	10 10
	A3.5	20 seconds 10 seconds	10 10
	C2	20 seconds 10 seconds	10 10
Filtek Supreme XT	**Clear**	20 seconds 10 seconds	10 10
	Yellow	20 seconds 10 seconds	10 10
	Grey	20 seconds 10 seconds	10 10

D. CURING OF THE SPECIMENS

A transparent glass slide was placed on a dark non reflective surface and a specimen disc placed above it. Some of the resin composite to be cured was extruded and carried to the specimen disc using a plastic instrument and the hole at the centre of the disc was overfilled. A transparent Mylar strip was placed over the filling at the centre of the disc and a second glass slide placed over it. Finger pressure was applied for 30 seconds over the second slide to remove the excess material, the second glass slide was removed, leaving the Mylar strip in place.

The specimen disc, with the filling material at the centre and covered with a Mylar strip was cured using one of the FreeLight 2 curing lights, maintaining a distance of 2mm between the sample and the outlet of the curing tip. Radiation was applied at a standard, nonexponential curing mode for the duration of either 20 seconds or 10 seconds as set out in Table 5. After a group of specimens was cured, they were placed in a dry specimen bottle and kept in an incubator (Memmet, W.Germany) at a dry and constant 37 °C, for 24 hours.

E. VICKERS INDENTATION OF SPECIMENS

After 24 hours, each sample was placed on the stage of the microscope and a lower magnification of 10X was used to adjust and bring into focus the centre of the resin composite material in the disc to identify a smooth surface, devoid of voids or other irregularities (Figs. 5, 6).

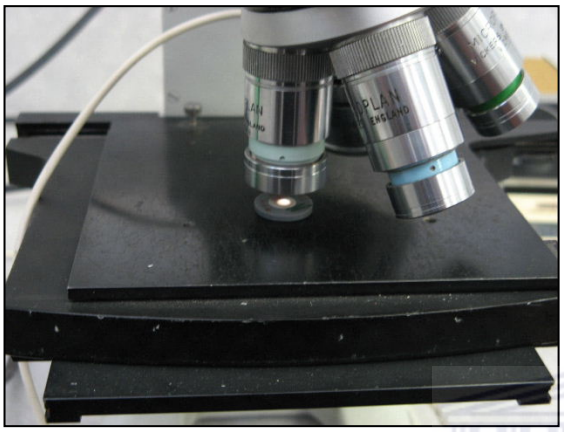

Fig. 5. Microscope on low magnification to bring surface of sample into focus.

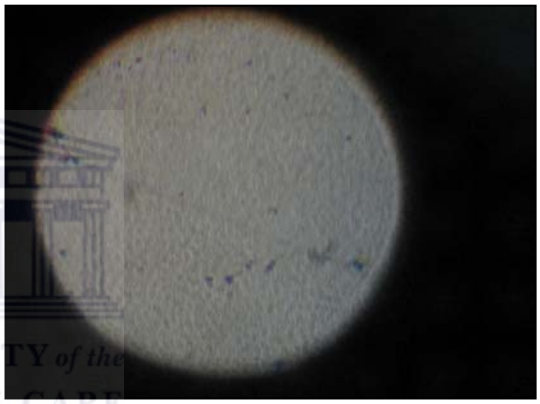

Fig. 6. Identification of a smooth surface devoid of voids and other irregularities.

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The Vickers hardness tester was adjusted to a load of 50 g and the Vickers objective which is connected to the microscope via an umbilicus, was turned into place, above the specimen disc (Fig. 7).

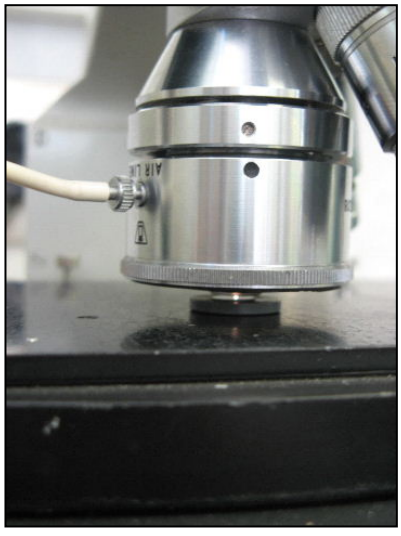

Fig. 7. Vickers hardness indenter while indent is being placed.

The lever on the main Vickers hardness tester was pushed down for 10 seconds and the duration timed accurately using a stop watch. The activation of the lever caused an indenter on the objective to push into the resin composite material to create the diamond shaped indent. After the 10 seconds, the lever was pushed back up releasing the indenter from the material.

F. MEASUREMENT OF THE VICKERS INDENTS

A higher magnification objective of 40X was next put into view, since the calibration of the microscope was done at this magnification (Fig. 8) and the indent was brought into focus with the adjusting knobs. One edge of the indent was adjusted to lie against a vertical line on the fixed scale (Fig. 9).

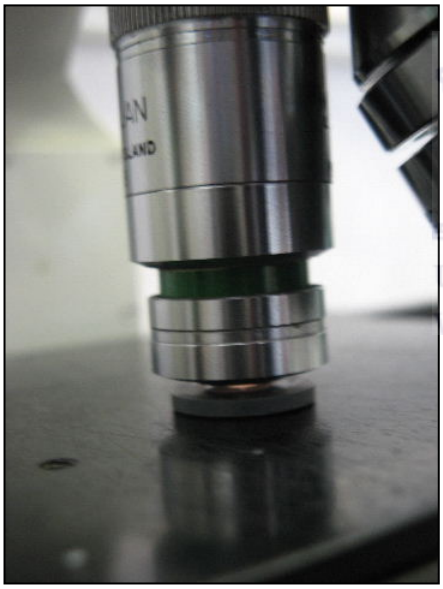

Fig. 8. Higher magnification objective.

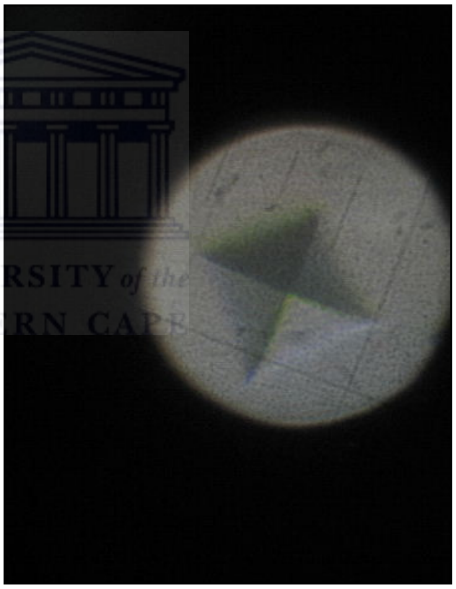

Fig. 9. Focusing onto the indent.

The filar eyepiece knob was adjusted to bring the movable vertical line to lie against the opposite edge of the indent, as well as lie parallel to the vertical line on the fixed scale. The number of vertical lines in between the fixed scale and movable filar lines were counted to denote the filar micrometer divisions. Each line would denote a hundredth of that number, for example two lines would mean 200. The scale on the filar eyepiece knob was then checked, which would denote the second and third digit of the reading (Figs. 10 - 12). For example 38 would mean the reading of the indent is 238.

Fig. 10. Filar adjustment knob.

Fig. 11. Filar eyepiece with the filar adjustment knob.

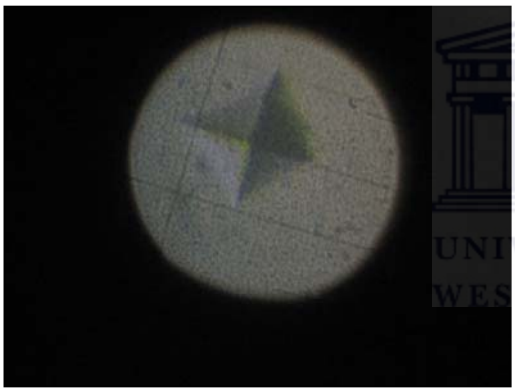

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Fig. 12. Example of correctly aligned indent.

This number was then used to read the Vickers hardness number (VHN) from the Vickers hardness table for a 50 gram load. For example the value for 238 is equivalent to a VHN of 92.

A total of 3 indents were made on each side of each specimen disc, totaling 6 indents per disc/sample. Each indent were measured, the Vickers hardness number obtained and tabulated using an Excel spreadsheet. The rough data for all experimental groups are attached (Appendix A).

G. DATA ANALYSIS

After it was ascertained using an analysis of variance that there were no significant difference between the data deriving from the two curing lights all the data of the two lights were pooled. The means with the standard deviation (± SD) of the hardness values produced by the two HP LEDs are depicted in Table 6.

Table 6. Mean top and bottom hardness values (VHN) for the two HP LEDs

	Top surface means (±SD)	Bottom surface means (±SD)
Light 1	99.67 (9.2)	66.84 (17.8)
Light 2	98.90 (7.1)	63.83 (17.7)

The top and bottom hardness values of the materials were compared according to the experimental conditions including composite type (3 levels), shade (3 levels), and curing time (2 levels). The information about upper and lower was further evaluated by the T/B Ratio (100*Lower/Upper).

Since the aim of the study was to compare the effect of all of these factors, an analysis which looked at the factors together rather than one at a time was adopted. Therefore, this was done by using a 3-way (or 3-factor) analysis of variance. The usual approach to this analysis is based on the assumption that the variances of the responses at all levels of the factor combinations are the same. However inspection of plots of the data indicated that this may not be the case. Consequently an analysis that allows for heterogeneous variances was also done. Analysis was done using the SAS (SAS Institute Inc., Cary, NC, USA) software. The MIXED procedure was used with a GROUP statement with the REPEATED option to allow modeling of the heterogeneous variances. The analysis of variance model included interaction terms. Pairwise comparisons were made to determine which factor combinations differed from others. In view of the large number of comparisons being done, a more stringent level of significance of 0.01 was used.

The summary statistics as well as some plots showing mean values for the various factor combinations are attached (Appendix B).

Following Price and his colleagues' example (2005:2635) a line representing 80% of the mean maximum hardness of each composite was drawn on Fig. 13 so that the hardness values could be compared to the 80% level of acceptable hardness. Price et al supported the use of 80% by referring to several studies that suggested that a resin composite sample is adequately cured when there is no more than a 20% difference between the maximum hardness at the top of the sample and the hardness at the bottom of the sample. Specimens are considered to be adequately cured when the B/T ratio exceeds 80% (Leonardt *et al*, 2001:176; Yap and Soh, 2005:758). Furthermore, a B/T ratio of 80% corresponds to 90% of the maximum conversion possible at the top surface of a composite (Bouschlicher *et al*, 2004:703). A line representing 80% of the B/T ratio mean of each type of composite was drawn on Fig. 18 so that the B/T ratio values for the different curing times could be compared to the 80% acceptable level.

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RESULTS

The microhardness mean values (± SD) for all the experimental conditions are presented in Table 7 and Figs. 13 and 14. Figure 13 is included purely for descriptive and explanatory purpose and plotted data should be seen as discrete values. The top and bottom hardness values for each type of composite are depicted in Fig. 15 (Z250), Fig. 16 (Z350) and Fig. 17 (FS XT) and further summarized for Z350 and Z250 in Tables 8 and 9.

For all experimental conditions, the top surface showed much higher hardness values than the bottom surface (Table 7 and Fig. 13). From Figs. 13 and 14 it is clear that Z250 shows slightly higher top hardness values than Z350 and FS XT, while the latter two show more or less similar top hardness values. Concerning curing time, the 20 second hardness values are slightly higher than the 10 second hardness values. All the top hardness values are above the 80% line.

The bottom hardness values, however, show larger differences amongst the various experimental conditions. FS XT shows the highest hardness values. In Figure 13 this is clearly illustrated where the 20 second hardness means values of FS XT are situated just above the 80% line and the 10 second hardness means very close to it. The 20 second bottom hardness values for Z250 are a bit lower than those of FS XT with the values of Z350 quite lower. The 10 second bottom hardness values for both Z250 and Z350 follows the same trend as the 20 second values, but at a much lower hardness level.

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Table 7. Vickers hardness means (± SD) and B/T hardness ratio means (± SD) for the three types of composites at 20 seconds and 10 seconds curing time.

		20 seconds			10 seconds		
Type	**Shade**	**Top**	**Bottom**	**B/T Ratio (%)**	**Top**	**Bottom**	**B/TRatio (%)**
Z250	**A1**	107.7(3.7)	80.2(5.7)	74.6(7.0)	103.3(2.5)	56.2(7.9)	54.3(6.8)
	A3.5	106.7(3.9)	74.4(6.6)	69.8(6.3)	104.6(3.7)	53.1(7.2)	50.8(6.9)
	D3	114.3(9.2)	85.2(5.0)	74.7(3.5)	109.8(5.1)	63.2(4.0)	57.7(4.1)
Z350	**A1**	100.7(3.9)	66.1(7.3)	65.5(5.9)	94.7(2.3)	38.6(5.0)	40.7(4.7)
	A3.5	97.6(5.0)	57.6(2.9)	59.1(3.2)	92.9(6.1)	34.6(2.0)	37.4(3.4)
	C2	99.8(5.0)	56.1(8.5)	56.1(6.6)	89.4(4.3)	32.3(0.6)	36.2(1.6)
FS XT	**Clear**	95.1(2.0)	83.0(5.7)	87.3(5.4)	93.1(3.6)	75.0(3.4)	80.7(3.7)
	Yellow	96.9(6.6)	81.5(5.9)	84.2(3.6)	91.0(4.5)	76.1(3.6)	83.7(3.9)
	Grey	96.8(5.6)	83.7(8.6)	86.3(6.0)	93.0(3.5)	79.2(4.3)	85.2(3.6)

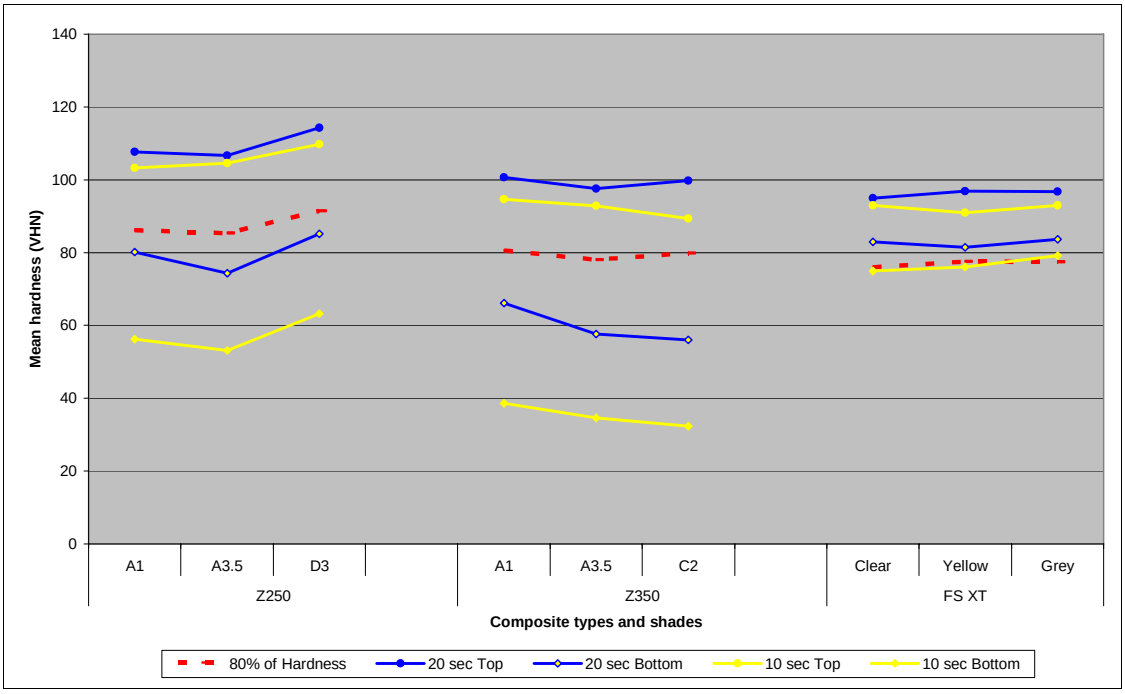

Fig. 13. Top and bottom hardness values of the different shades of Z250, Z350 and FS XT irradiated at either 20 seconds or 10 seconds with the FreeLight 2. The 80% line represents 80% of the maximum hardness developed for each experimental group.

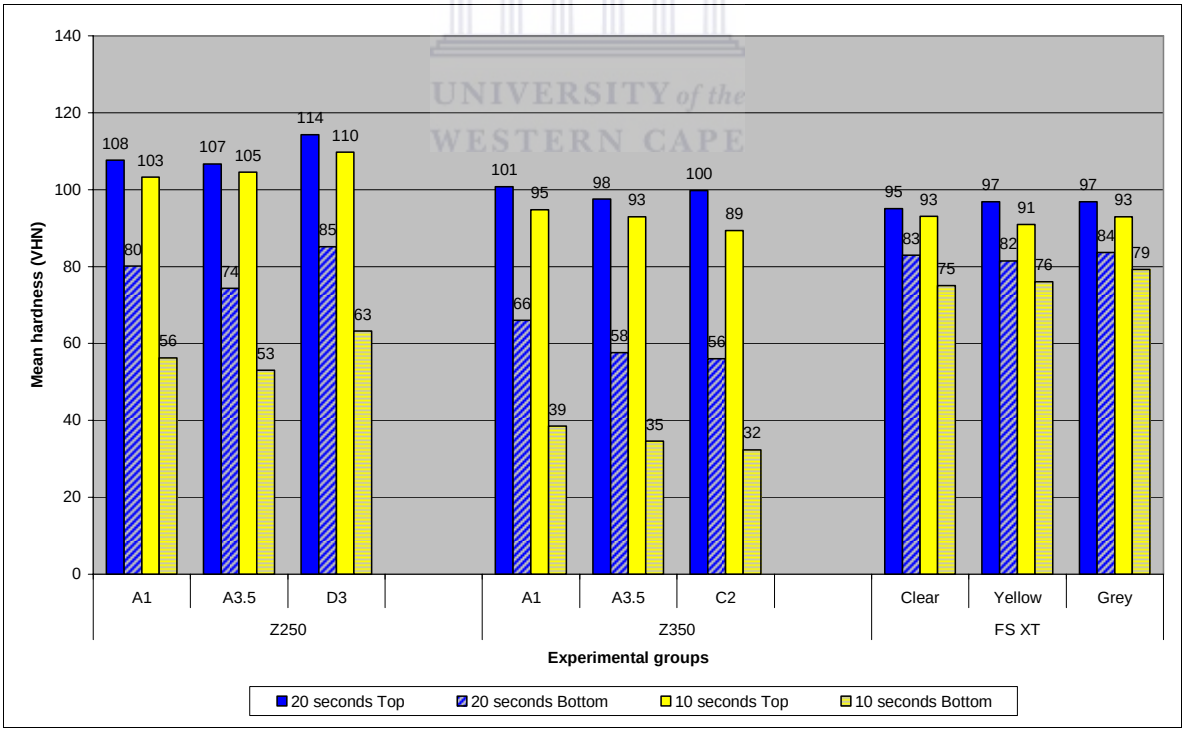

Fig. 14. Bar graph of the top and bottom hardness (VHN) of the different shades of Z250, Z350 and FS XT irradiated at either 20 or 10 seconds with the FreeLight 2.

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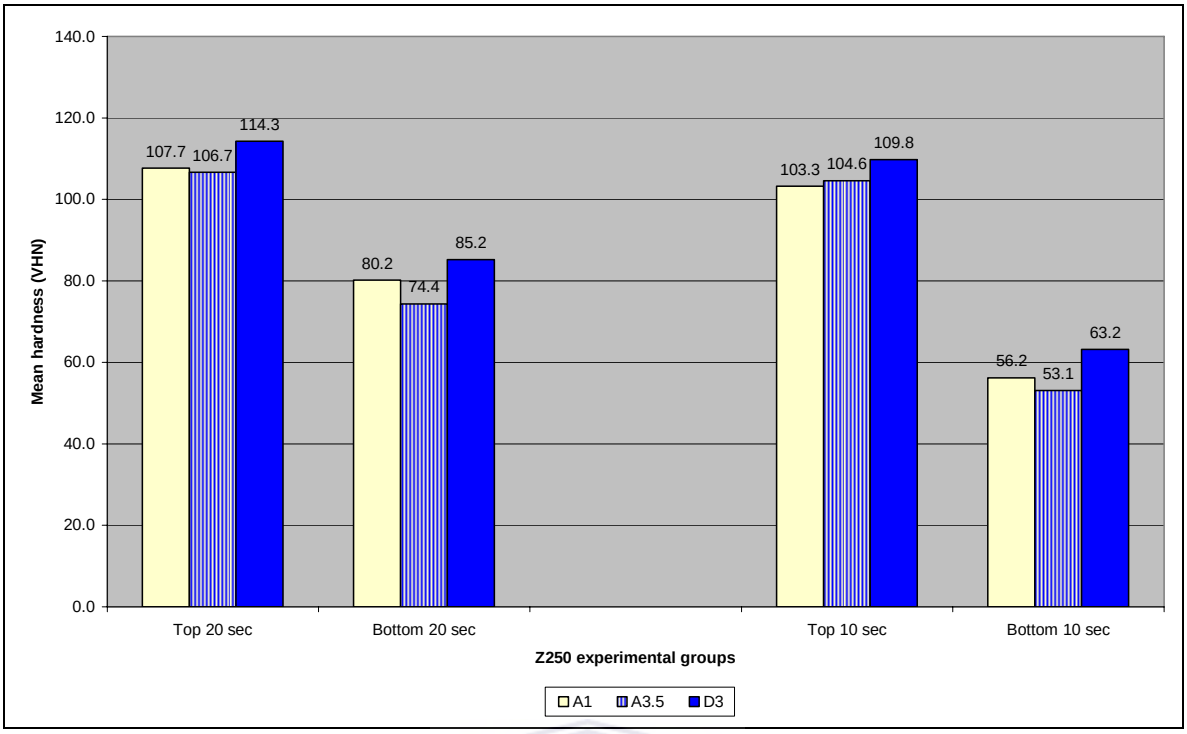

Fig. 15. Top and bottom hardness (VHN) of Z250 irradiated for 20 and 10 seconds with the FreeLight 2.

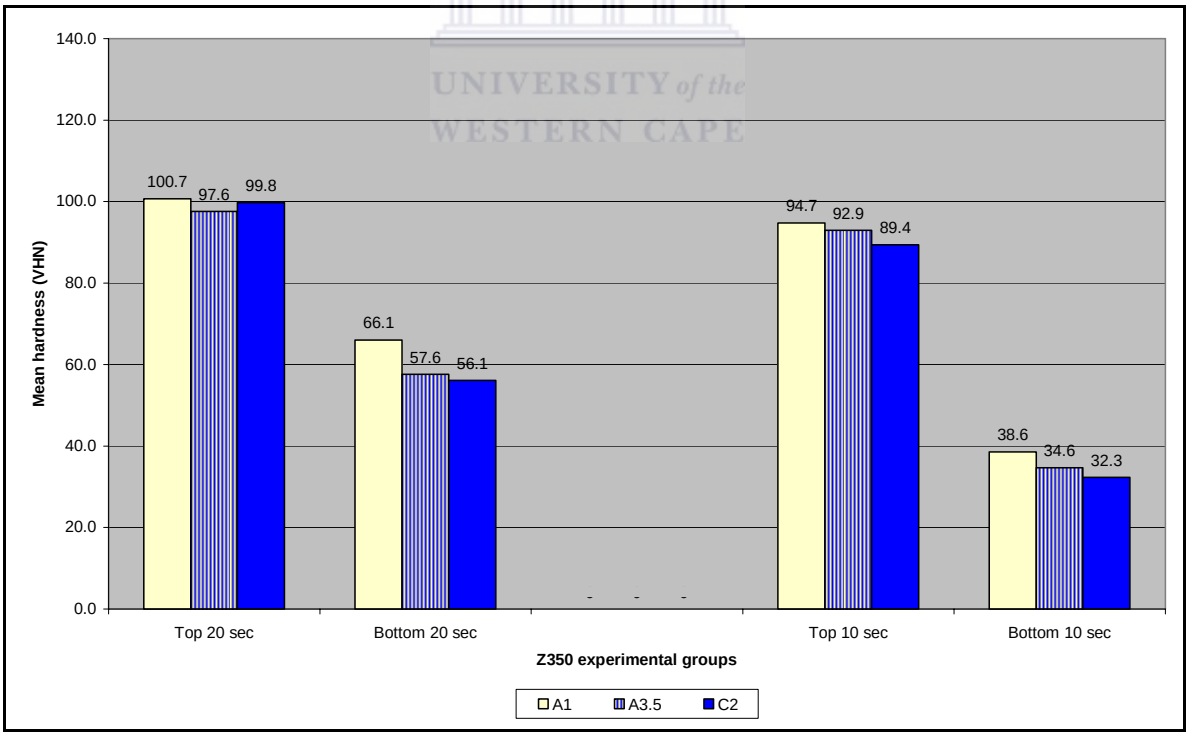

Fig. 16. Top and bottom hardness (VHN) of Z350 irradiated for 20 and 10 seconds with the FreeLight 2.

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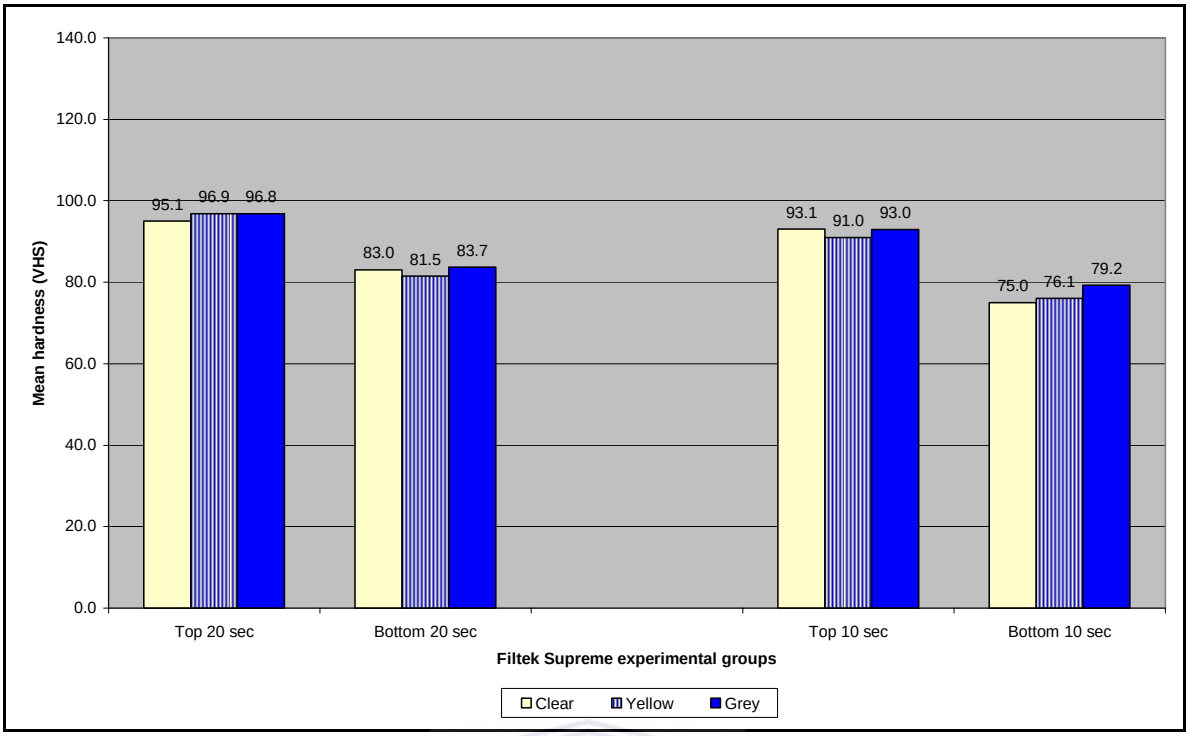

Fig. 17. Top and bottom hardness (VHN) of FS XT irradiated for 20 and 10 seconds with the FreeLight 2.

Table 8. Vickers hardness values for Z250 and Z350 cured for 20 seconds.

TYPE	Microhybrid			Nanocomposite		
TRADE NAME	Z250 (3M ESPE)			Z350 (3M ESPE)		
SHADE	A1	A3.5	D3	A1	A3.5	C2
TOP	107.7	106.7	114.3	100.7	97.6	99.8
BOTTOM	80.2	74.4	85.2	66.1	57.6	56

Table 9. Vickers hardness values for Z250 and Z350 cured for 10 seconds.

TYPE	Microhybrid			Nanocomposite		
TRADE NAME	Z250 (3M ESPE)			Z350 (3M ESPE)		
SHADE	A1	A3.5	D3	A1	A3.5	C2
TOP	103.3	104.6	109.8	94.7	92.9	89.4
BOTTOM	56.2	53.1	63.2	38.6	34.6	32.3

TOP HARDNESS

Type of composites (Fig. 14)

Even though small, all of the top hardness values for Z250 (Fig. 14) were significantly higher than the values for Z350 and for FS XT. Concerning Z350, most of the top hardness values were slightly higher than those of FS XT. However, only one of these differences, although small, was significant, namely between Z350 shade A1 and FS XT Clear.

Shade of composites (Table 10 – lowercase letters relating to the columns)

In the 20 second group no differences in top hardness were noted amongst the different shades of composites within each type of composite. In the 10 second group the same hold true only for FS XT. The darker shade of Z250 (D3), however, was cured significantly harder than its light shade (A1) in the 10 second group, while for Z350 the lighter shade (A1) was cured significantly harder than the darker shade (C2).

Curing time (Table 10 – uppercase letters relating to the rows)

When comparing top hardness values for the 20 second group with the 10 second group, significant differences were noted for Z250 shade A1, Z350 shade A1 and Z350 shade C2.

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Table 10. Microhardness means (± SD) for the top surface of three types of composites for 20- and 10 seconds curing time.

		20 seconds		10 seconds	
Type	**Shade**	**Top**		**Top**	
Z250	**A1**	107.7(3.7)	A,a	103.3(2.5)	B,a
	A3.5	106.7(3.9)	A,a	104.6(3.7)	A,a,b
	D3	114.3(9.2)	A,a	109.8(5.1)	A,b
Z350	**A1**	100.7(3.9)	A,a	94.7(2.3)	B,a
	A3.5	97.6(5.0)	A,a	92.9(6.1)	A,a,b
	C2	99.8(5.0)	A,a	89.4(4.3)	B,b
FS XT	**Clear**	95.1(2.0)	A,a	93.1(3.6)	A,a
	Yellow	96.9(6.6)	A,a	91.0(4.5)	A,a
	Grey	96.8(5.6)	A,a	93.0(3.5)	A,a

Different lower case letters within any column indicate statistically significant differences for the comparison of the different shades within each type of composite. Uppercase letters within any row indicate statistically significant differences among the two exposure time-periods for each shade of composite ($p < 0.01$).

BOTTOM HARDNESS

Type of composites (Fig. 14)

In both the 20 and 10 second curing groups FS XT showed the highest bottom hardness values. In the 20 second group the bottom hardness values of FS XT was slightly higher, but not different from Z250. In the 10 sec group, however, it was significantly different. The bottom values of Z350, however, were significantly lower than Z250 and FS XT in both the 20 and 10 second groups.

Shade of composites (Table 11 – lowercase letters relating to the columns)

For FS XT the shade did not appear to affect the bottom hardness in both the 20 and the 10 second curing group. The darkest shade (C2) in Z350 had the lowest hardness (C2 [dark] < A3.5 [universal] < A1 [light]). The shade A1 was significantly harder than A3.5 and C2 in the 20 second group. However, in the 10 second group both A1 and A3.5 were significantly harder than C2. In Z250, in the 20 and the 10 second group, the darkest shade had the highest hardness (D3 [dark] > A1 [light] > A3.5 [universal]), while in both groups D3 was significantly harder than A3.5.

Curing time (Table 11 – uppercase letters relating to the rows)

Twenty seconds curing time leads to significantly higher values than 10 seconds of curing, irrespective of the type of composite or the shade of composite. The only exceptions being the yellow and gray shades of FS XT where the differences were not significant.

Table 11. Microhardness means (± SD) for the bottom surface of three types of composites for 20- and 10 seconds curing time.

Type	Shade	20 seconds Bottom		10 seconds Bottom	
Z250	**A1**	80.2(5.7)	A,a,b	56.2(7.9)	B,a,b
	A3.5	74.4(6.6)	A,b	53.1(7.2)	B,b
	D3	85.2(5.0)	A,a	63.2(4.0)	B,a
Z350	**A1**	66.1(7.3)	A,a	38.6(5.0)	B,a
	A3.5	57.6(2.9)	A,b	34.6(2.0)	B,a
	C2	56.1(8.5)	A,b	32.3(0.6)	B,b
FS XT	**Clear**	83.0(5.7)	A,a	75.0(3.4)	B,a
	Yellow	81.5(5.9)	A,a	76.1(3.6)	A,a
	Grey	83.7(8.6)	A,a	79.2(4.3)	A,a

Different lower case letters within any column indicate statistically significant differences for the comparison of the different shades within each type of composite. Uppercase letters within any row indicate statistically significant differences among the two exposure time-periods for each shade of composite ($p < 0.01$).

HARDNESS RATIOS (%)

The B/T hardness ratios (%) are presented in Table 13 and Fig. 18. Figure 18 is included purely for descriptive and explanatory purpose and plotted data should be seen as discrete values. All the hardness ratios associated with Z250, Z350 and FS XT Clear were found to be significantly lower for the 10-second curing group than for the 20 sec curing group. The hardness ratios for the FS XT yellow shade and grey shade were nearly similar. FS XT was also the only resin composite which had B/T hardness ratios above 80% for both the 10 and 20 second curing time.

Table 12. Bottom to top hardness ratio means (%) (± SD) of the different shades of Z250, Z350 and FS XT irradiated for 20 seconds and 10 seconds with the FreeLight 2.

	Z250			Z350			FS XT		
Cure time	A1	A3.5	D3	A1	A3.5	D3	Clear	Yellow	Gray
20 sec	74.6(7.0)	69.8(6.3)	74.7(3.5)	65.5(5.9)	59.1(3.2)	56.1(6.6)	87.3(5.4)	84.2(3.6)	86.3(6.0)
10 sec	54.3(6.8)	50.8(6.9)	57.7(4.1)	40.7(4.7)	37.4(3.4)	36.2(1.6)	80.7(3.7)	83.7(3.9)	85.2(3.6)

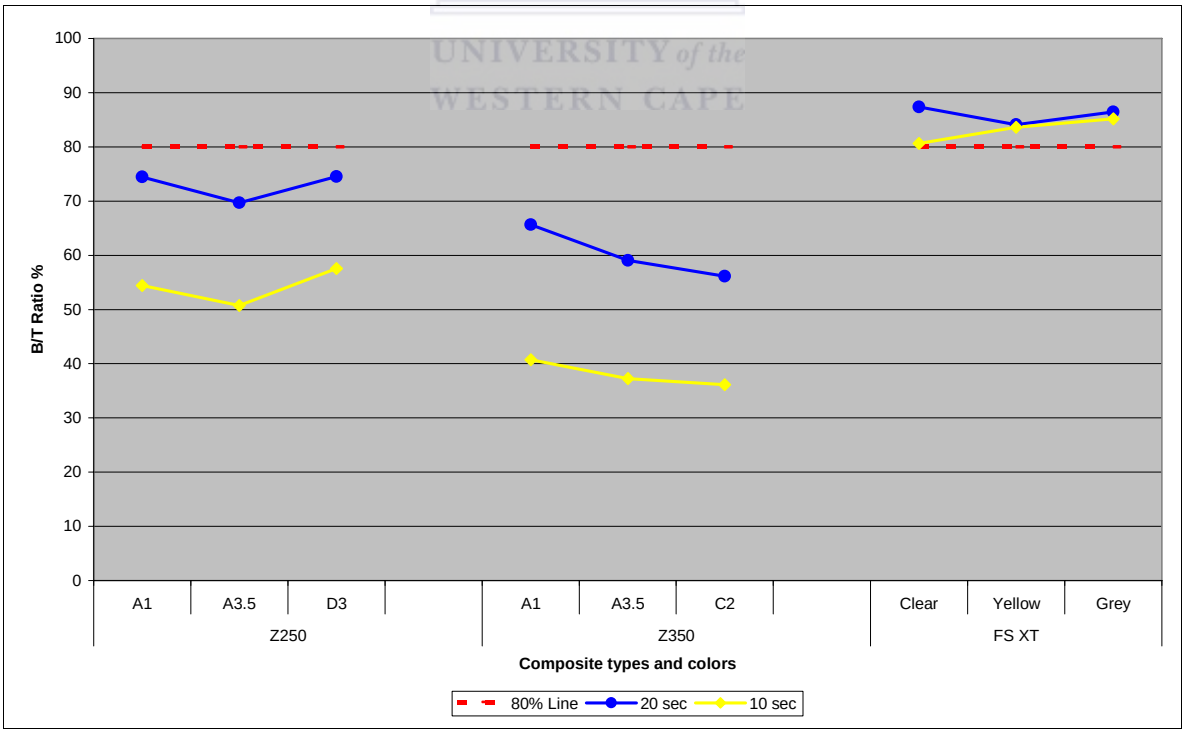

Fig. 18. Bottom to top hardness ratio means (%) of the different shades of Z250, Z350 and FS XT irradiated for 20 seconds and 10 seconds with the FreeLight 2.

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DISCUSSION

This study tested the claim that the Elipar FreeLight 2 can cure composite material as effectively at 50% as at 100% of the manufacturer's recommended curing time. Additional aims of the study were to evaluate the influence of composite shade and type of composite on the microhardness of the top and bottom of composite surfaces.

Adequate polymerization is a crucial factor in obtaining optimal physical performance of composite materials and is related to better clinical performance. There are, however, many variables that affect degree of cure; for example, filler type and size, light source intensity, duration of exposure and resin shade (Rueggeberg *et al*, 1993:91-95). Of these factors, filler type and size, shade, and duration of exposure have been tested in this study.

The physical and mechanical properties of a composite material are determined by the size, distribution and content per volume of the filler particles in the matrix. Therefore the hardness of a composite will be dependent on these variables; for example, hardness can be increased by using smaller particles and a higher filler content (Oberholzer et al, 2003:214).

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At the top surface, Z250 showed small, but significantly higher top hardness values than Z350. Z350, on the other hand, had slightly harder top hardness values than FS XT (Figure 13 & 14). Such a small variation in top hardness was expected as all of these composites contain a very high filler load. All the composites are also produced by the same manufacturer and have the same proprietary resin matrix.

The slight variation in hardness between the three composites can probably be explained by the small differences in filler load. The filler load of Z250 is 60% by volume, which is about 80% by weight, while the filler load of Z350 is 78.5% by weight and of FS XT is 72.5% by weight. The fact that Z350 is closer in hardness to FS XT, although its filler load is closer to that of Z250, may be due to the similar filler particle size distribution to that of FS XT (Table 4). Z350 and FS XT are nanocomposites while Z250 is a microhybrid. Price and colleagues (2005:2636) also report a higher top hardness for Z250 than for FS XT.

Concerning the influence of shade on top hardness, no differences in top hardness values were noted amongst the different shades when cured for 20 seconds (Table 10, Fig. 15-17). When cured for 10 seconds, small differences in surface hardness values were noted. The darker shade D3 of Z250 was cured significantly harder than its light shade A1, while for Z350 the lighter shade A1 was cured significantly harder than the darker shade C2. All the translucent shades of Filtek Supreme, however, were cured to the same hardness. The order of the most influential factors in maximizing cure at the surface of a restoration is filler type, exposure duration and resin shade (Rueggeberg *et al*, 1993:91). This means that shade is only a small contributing factor at the surface of the restoration, and even more so with less extreme shades. Filler type and exposure time are not factors in the analysis above: the different shades being compared fall within the same type of composite and the same exposure group. Therefore, this finding agrees with Rueggeberg and his colleagues that the influence of shade on top surface hardness is very small.. The Z250 findings are similar to those of Aguiar and his colleagues (2005:302) who also did not find a difference in Knoop hardness values for the upper surface when they cured different shades (A1, A3.5, C2) of Z250 for 20 seconds.

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Concerning the influence of exposure time (Table 10, Fig. 13), all composites had lower top hardness values when cured for 10 seconds, though only a few of these differences were significant. However, these differences are quite small, and clinically probably not relevant, as all of these hardness values are situated above the line that indicates 80% of the maximum top hardness for that specific composite after a 20 second cure. A relatively high degree of cure can be obtained on the surface of restorations, even when a low intensity curing light is used for a short exposure time (Rueggeberg et al, 1993:94). Hence, the influence of exposure duration cannot be assessed by top surface hardness.

As light passes through the bulk of restorative material, its intensity is decreased due to light absorption and scattering by the composite resin. This may lead to a lower depth of cure value (Tsai, Meyers and Walsh, 2004:364) or lower hardness values at the bottom of a specimen (Aguiar 2005:305). In the present study the bottom surface showed much lower hardness values than the top surface for all of the experimental conditions (Table 7, Figs.

13, 14). FS XT showed the highest bottom hardness values in both the 20- and 10 second curing groups (Table 12, Fig. 13). The bottom hardness values of Z250 were slightly lower, but not significantly different from FS XT in the 20-second group. Z350, however, had significantly lower hardness values than both Z250 and FS XT in the 20- and 10 second curing group.

There are various factors that could have led to these differences in bottom hardness values. The light reduction that takes place as light passes through composite resin is quite complex. Light scattering is related to filler load, particle size and particle size distribution (Leonard *et al*, 2001:176). Different types of composite, for example microfill and hybrid composite, will reduce light transmission at different rates (Leonard *et al*, 2001:176). Lower hardness values in deeper layers of microfill composites in comparison to hybrid composites have been reported (Poskus *et al*, 2004:730). The reason provided for this is that the microparticles increase light dispersion, leading to a lower degree of polymerization in the deepest layers.

In this study Z250 contains a blend of microfillers and very small particles, while Z350 and FS XT are filled with nano-sized fillers and nanoclusters. If filler size was a factor, more similar bottom hardness values would have been expected of the nanocomposites, Z350 and Z250. This, however, was not the case. Transmission of light also depends on the opacity or translucency of a resin composite (Poskus *et al*, 2004:726). Bouschlicher *et al* (2004:703) reported a similar degree of conversion for a microfill than for a hybrid composite. They suggested that this unexpected result was probably due to the microfill composite's higher translucency. The shades used for the FS XT samples had a very high translucency in comparison to the shades used for Z350, which were quite opaque. The filler load of Z350 is also slightly higher than that of FS XT. Filler load can also influence light transmission. Light transmission decreases as filler load increases (Bouslicher *et al*, 2004:702). The reason why the bottom hardness levels of Z250 were significantly harder than those of Z350 may also be due to a lower opacity and the larger particle size of the fillers of Z250.

Depth of polymerization is more dependent on the opacity or translucency of a resin composite than on the shade itself (Poskus et al, 2004:726). This is confirmed by this study where very small, non-significant differences in bottom hardness values were noted for the translucent FS XT shades (clear, yellow, gray)(Fig. 17). In contrast to this, a significantly lower bottom hardness value was noted for the dark, more opaque C2 shade of Z350 in comparison to its universal and lighter shades (Fig. 16).

Darker shades would normally be associated with a lower degree of cure or hardness value since the pigments in darker shades absorb more light, as confirmed by the following studies. Aguiar and his colleagues (2005:302) found the lighter shade to have a higher hardness value than the darker shade. The shades of Z250 that they tested were C2 (darker) and A1 (lighter). Shortall (2005:909) reported lower depths of cure for the darker shades of Z250, for example C2 and D3, than for the lighter shade A1.

In this study, however, the darkest shade of the three Z250 shades tested (D3), showed the highest bottom hardness value (Table 11, Fig. 15). Interestingly, this value was not significantly different from the value obtained for the lightest shade (A1). When Tsai and his colleagues (2004:364) evaluated depth of cure with a few Z250 shades, they also found that the darker shade (C4) had a greater depth of cure than the lighter shade (B1). After direct examination of the C4 shade they suggested that its greater translucency, as well as the underlying optical properties of its fillers and tints, may have contributed to this difference. According to Shortall (2005:910), however, both C4 and D3 are more opaque than A1. The finding by Tsai and his colleagues, as well as the result in the present study therefore remains unexplained.

Duration of cure had a significant effect on the bottom hardness values (Table 11, Figs. 13, 14). The bottom hardness values for the 10 second exposure group were significantly lower than the 20 second group for all the shades of Z250 and Z350. For all three shades of FS XT the differences in hardness values were much less and probably not of clinical significance. When Rueggeberg and his colleagues investigated the factors that influences depth of cure they found that when curing 2 mm or greater thicknesses of composites, light intensity and exposure duration become by far the most important influence above either

shade or filler types (Rueggeberg *et al*, 1993:95). Although these authors considered the influence of shade in their study, they used very moderate shades and did not consider the role of opacity as a factor. A shorter exposure time did not influence the hardness of the translucent shades of FS XT much. However, it did influence the hardness of Z350, which is also a nanocomposite, significantly. The reason for this may be that Z350 has a higher filler load, a greater opacity and a different filler composition.

Previous studies have used Knoop or Vickers bottom:top hardness ratios to obtain a percentage depth of cure and, if that value exceeded 80%, specimens were considered to be adequately polymerized (Aguiar *et al*, 2005:305; Dunn and Bush, 2002:340; Oberholzer *et al*, 2003:214; Yap & Soh, 2005:762). Using this criterion, with the exception of FS XT, the HP LED failed to adequately cure the different shades of Z250 and Z350 for the 20 second and 10 second exposure duration. All the hardness ratios associated with Z250, Z350 and FS XT Clear were found to be significantly lower for the 10 second curing group than for the 20 second curing group (Table 12). FS XT was the only resin composite which had a hardness ratio-% above 80 for both the 10- and 20 second curing time (Fig. 18). Both Z250 and Z350 failed to produce such high values.

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Previous studies that investigated the curing efficiency of the FreeLight 2 were satisfied with its performance at half the recommended curing time. It is important to note, however, that some of these studies (Table 3) compared the HP LED light to standard QTH lights, earlier LEDs or high-power QTH-lights, using the composites' recommended exposure or half of that (Price et al, 2005:2633; Wiggins et al, 2004:1473). Yap and Soh (2005:759) used it for a 20 second exposure. Although Shortall (2005:907) reported that the HP LED they tested met the manufacturer's claim for halving the curing time, they did not half the curing time for their study. They used a 40 second and a 20 second exposure to cure Z250 samples.

Wiggins et al (2004:1473) used the total energy concept, which states that a certain dose (intensity x time) of light is needed to adequately cure a specific material, to argue that a HP LED will be more effective than a conventional LED curing light to cure a specific material. Of note is that Wiggins and her colleagues used a depth of cure test where the

soft composite is scraped away prior to depth of cure measurements. The unreliability of scraping tests were noted in previous studies, for example DeWald and Ferracane (1987:727,729) reported that the scraping method correlated well, but severely overestimated depth of cure compared to hardness tests or a degree of conversion analysis.

The kinetics of polymerization has been found to be highly complex and a simple linear relationship between power density and exposure duration does not exist (Peutzfeldt and Asmussen, 2005:661). In their study, Peutzfeldt and Asmussen saw that the influence of the combination of power density and exposure duration occasionally resulted in degrees of cure and/or mechanical properties that were significantly inferior to those obtained at a lower energy density. Therefore, according to them, this implies that for a given energy density, long exposures at low power density lead to a higher degree of cure than short durations at high power density. These researchers thus suggest that while the high-power curing units of today may save the clinician and the patient some time, they may also be expected to result in less than optimally cured resin composite restorations. The low B/T hardness ratios reported in the present study confirm this suggestion.

The main concern is that the HP LED tested in this study could only cure one type of composite to an acceptable hardness at 100% as well as at 50% of the recommended curing time. All the composites tested were manufactured by the manufacturer of the curing light. It is thus logical to expect that the light should be able to cure the products. This, however, was not the case in the present study. Although the FreeLight 2 managed to cure FS XP to an acceptable hardness, the same was not true for Z350 and Z250. These composites were not cured to an acceptable hardness after a 10 second or 20 second exposure duration.

If clinicians were to use this HP LED at 50% of the recommended exposure time, they should be aware that composite increments will not be cured to an acceptable hardness at the bottom of the increment. Furthermore, even at full exposure time, the findings from this study suggest that only the most translucent nanocomposites will cure to an acceptable hardness. Otherwise, composites should be placed and cured in thinner increments.

This study did not test the whole range of available shades of the composites tested. It is recommended to extend the current work to include all of the shades, especially the more extreme shades of Z250 and of Filtek Supreme (dentin and body shades).

LIMITATIONS OF THE STUDY

The effectiveness of polymerization was assessed using the Vickers microhardness test, the reasons being that hardness tests are cheap and relative simple to perform. They are also popular, therefore making comparisons to other researchers' work possible. More importantly, hardness tests are an accurate indirect method of evaluating the degree of polymerization of different types of composites (Poskus et al., 2005:730) as they show a positive correlation to degree of conversion (Bouschlicher et al., 2004:703). The only disadvantage of conventional microhardness tests is that a direct visual measurement of the indentation length is performed after removal of the load as error may occur due to elastic recuperation. Such error may lead to an overestimate of hardness when the Vickers (or Knoop) microhardness tests are used (Poskus et al., 2004:730). If this held true for the present study, it may mean that the actual surface hardnesses of the specimens were even lower than the hardness values reported.

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Light intensity decrease with increasing distance from the curing tip, which will result in a softer bottom hardness of a 2-mm specimen (Aguiar *et al*, 2005:302; Felix *et al*, 2006:147). Therefore the distance of the light-cure tip from the composite surface was standardized at 2mm. Although some researchers use a 1mm distance (Yap *et al*, 2004:412; Oberholzer *et al*, 2005:3983), a 2mm distance was regarded as clinically a more relevant distance (Price *et al*, 2005:2633; Felix *et al*, 2006:147). Using a 2mm distance in stead of a 1mm distance could have provided lower hardness values than those reported in the studies that used a smaller distance, explaining the low hardnesses achieved. The spin-off, however, is that the results obtained mimic the clinical setup where cusps prevent close positioning of the light tip when a posterior occlusal restoration is cured.

CONCLUSIONS

This *in vitro* study compared the effectiveness of cure by a HP LED operated at 100 % of the manufacturer's recommended exposure time to the effectiveness of cure when operated at 50% of the exposure. As the results showed statistically significant differences between the two exposure durations, the null hypothesis was rejected.

On the basis of the surface microhardness measured at the top and the bottom of 2 mm thick specimens of three shades each of a microhybrid and two nanohybrid composites irradiated at 100% and 50% of the recommended exposure time, the following conclusions were reached:

- The 10 second exposure resulted in significantly lower bottom hardness values for all evaluated materials when compared to the 20 second exposure.
- The 10 second exposure resulted in significantly lower hardness ratios for all evaluated materials when compared to the 20 second exposure.
- For all three shades of FS XT, the differences referred to above were quite small and probably not of clinical significance.
- An acceptable hardness ratio-% of above 80 was reached for only one of the three composites tested, FS XT (shades Clear, Yellow and Gray) at 20 seconds and at 10 seconds exposure.
- The translucency or opacity of resin composite materials, rather than shade or type of composite, is an important factor to be considered for obtaining adequate polymerization.

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1	2	10	97.5	95.5	96.5	96.5	78	77	76	77.0
1	3	20	107	111	105	107.7	82	85.5	82	83.2
1	3	10	92.5	91.5	90.5	91.5	74.5	74.5	74.5	74.5
1	4	20	96	99.5	100	98.5	91.5	92.5	90.5	91.5
1	4	10	98.5	93.5	95.5	95.8	75	74.5	76.5	75.3
1	6	20	95.5	97.5	101	98.0	60	62	61.5	61.2
1	6	10	85.5	88.5	90.5	88.2	32	32	32	32.0
2	2	20	97.5	94.5	97.5	96.5	81	85.5	84	83.5
2	2	10	98.5	96.5	93.5	96.2	75	78	75	76.0
2	3	20	104	96.5	98.5	99.7	82	83.5	81	82.2
2	3	10	96	99.5	95.5	97.0	74.5	77	78	76.5
2	4	20	108	100	101	103.0	93.5	87.5	89.5	90.2
2	4	10	98.5	92.5	90.5	93.8	82.5	82	79.5	81.3
2	6	20	92	94.5	102	96.2	60	59	59	59.3
2	6	10	108	102	107	105.7	34.5	36.9	35.7	35.7
1	2	20	92	98.5	95.5	95.3	85.5	83.5	83.5	84.2
1	2	10	98.5	95.5	92.5	95.5	77	81.5	78	78.8
1	3	20	103	108	102	104.3	88.5	92	91.5	90.7
1	3	10	94.5	90.5	92.5	92.5	79	76.5	78	77.8
1	4	20	103	108	107	106.0	94.5	91.5	93.5	93.2
1	4	10	92.5	95.5	98.5	95.5	82	85	88.5	85.2
1	6	20	108	106	110	108.0	64.5	61.5	63	63.0
1	6	10	91.5	96.5	92.5	93.5	34.6	36.1	36.5	35.7
1	1	20	104	107	108	106.3	91.5	71	90.5	84.3
1	1	10	107	103	104	104.7	65	67.5	63.5	65.3
1	1	20	133	126	124	127.7	88.5	86	87.5	87.3
1	1	10	107	114	111	110.7	61.5	62.5	61	61.7
1	1	20	137	129	128	131.3	93.5	92	96.5	94.0
1	1	10	115	115	123	117.7	64	64.5	62	63.5
1	1	20	111	123	114	116.0	90.5	91.5	92.5	91.5
1	1	10	119	117	115	117.0	65.5	62	63.5	63.7
1	1	20	113	118	116	115.7	87	89	86	87.3
1	1	10	110	114	107	110.3	68	68.5	69	68.5
2	2	20	96	93.5	96.5	95.3	88.5	85.5	85.5	86.5
2	2	10	99.5	96.5	95.5	97.2	77	78	76	77.0
2	3	20	99.5	104	101	101.5	87.5	86	89	87.5
2	3	10	95.5	96.5	95.5	95.8	78	79.5	76	77.8
2	4	20	97.5	100	104	100.5	92	89.5	89	90.2
2	4	10	96.5	101	98.5	98.7	79	81	87	82.3
2	6	20	113	104	99.5	105.5	53.3	56	54.3	54.5
2	6	10	88.5	95.5	96	93.3	32	32	32	32.0
2	1	20	107	111	116	111.3	87.5	85.5	85	86.0
2	1	10	106	103	104	104.3	74	64	61	66.3
2	1	20	115	107	116	112.7	81.5	82	81	81.5
2	1	10	123	108	105	112.0	62.5	61	55.5	59.7
2	1	20	108	123	108	113.0	79	82	83.5	81.5
2	1	10	116	99.5	104	106.5	63.5	55	53.9	57.5
2	1	20	96	107	103	102.0	77	80	78	78.3
2	1	10	113	108	113	111.3	68	70	66	68.0
2	1	20	103	110	108	107.0	80	79	81.5	80.2
2	1	10	100	107	103	103.3	55.5	59	59	57.8

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APPENDIX B

Combo=Composite 1-2-3, Color=Lt,Univ,Dk, Time=10,20 16:49 Thursday, October 19, 2006 5

The MEANS Procedure

composite	color	Time	N Obs	Variable	N	Mean	Median	Std Dev	Minimum	Maximum
Z250	Light	10	10	lower	10	56.210	58.500	7.910	41.200	65.800
				Upper	10	103.260	103.500	2.465	97.833	105.667
				ratio	10	54.339	56.273	6.845	42.112	62.271
		20	10	lower	10	80.170	79.600	5.728	72.400	89.700
				Upper	10	107.650	107.000	3.730	103.200	116.667
				ratio	10	74.619	75.747	6.689	62.057	84.357
	Universal	10	10	lower	10	53.060	52.200	7.240	41.500	64.300
				Upper	10	104.553	104.167	3.662	100.167	113.000
				ratio	10	50.760	49.797	6.867	39.776	64.108
		20	10	lower	10	74.380	75.750	6.569	60.400	83.000
				Upper	10	106.667	108.000	3.888	97.000	110.333
				ratio	10	69.783	70.169	6.336	57.143	79.691
	Dark	10	10	lower	10	63.200	63.600	3.967	57.500	68.500
				Upper	10	109.783	110.500	5.065	103.333	117.667
				ratio	10	57.649	55.844	4.100	53.304	63.546
		20	10	lower	10	85.190	85.150	5.026	78.300	94.000
				Upper	10	114.300	112.833	9.158	102.000	131.333
				ratio	10	74.701	75.214	3.524	68.381	79.279
Z350	Light	10	10	lower	10	38.570	37.850	4.975	32.000	49.500
				Upper	10	94.723	94.333	2.260	92.000	100.200
				ratio	10	40.678	40.735	4.670	33.862	49.401
		20	10	lower	10	66.070	64.950	7.313	57.200	78.700
				Upper	10	100.727	101.333	3.935	93.667	107.000
				ratio	10	65.529	65.828	5.901	55.000	73.551
	Universal	10	10	lower	10	34.630	34.900	1.996	32.000	37.200
				Upper	10	92.917	92.017	6.105	86.300	105.667
				ratio	10	37.417	36.477	3.362	33.785	42.857
		20	10	lower	10	57.630	56.750	2.874	54.400	63.000
				Upper	10	97.587	95.600	5.030	93.200	108.000
				ratio	10	59.141	59.261	3.235	51.659	62.449
	Dark	10	10	lower	10	32.290	32.000	0.615	32.000	33.600
				Upper	10	89.383	89.667	4.328	82.500	96.167
				ratio	10	36.189	35.890	1.591	33.276	38.788
		20	10	lower	10	56.080	53.550	8.453	47.400	77.200
				Upper	10	99.790	97.583	5.020	95.200	108.700
				ratio	10	56.077	55.687	6.569	49.375	71.021
Filtek	Light	10	10	lower	10	75.030	76.100	3.411	69.800	79.500
				Upper	10	93.063	93.650	3.618	86.700	97.167
				ratio	10	80.678	80.150	3.733	74.840	89.527
		20	10	lower	10	83.000	83.850	5.672	68.200	87.700
				Upper	10	95.063	95.267	1.968	90.800	98.300
				ratio	10	87.289	88.235	5.380	72.941	92.105
	Universal	10	10	lower	10	76.090	76.750	3.582	71.300	82.800
				Upper	10	90.963	91.500	4.450	81.200	97.000
				ratio	10	83.740	82.764	3.913	78.866	90.148
		20	10	lower	10	81.500	82.100	5.879	68.500	90.700
				Upper	10	96.877	96.600	6.566	87.200	107.667
				ratio	10	84.168	85.771	3.608	77.276	87.374
	Dark	10	10	lower	10	79.220	79.300	4.329	72.700	85.200
				Upper	10	92.983	93.350	3.492	87.200	98.667
				ratio	10	85.208	84.702	3.635	78.574	90.054
		20	10	lower	10	83.670	85.250	8.594	65.800	93.200
				Upper	10	96.820	96.900	5.577	87.700	106.000
				ratio	10	86.309	87.837	5.960	71.756	92.893

The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
composite	2	162	132.12	<.0001
color	2	162	2.63	0.0750
composite*color	4	162	5.00	0.0008
Time	1	162	47.09	<.0001
composite*Time	2	162	2.38	0.0957
color*Time	2	162	0.83	0.4381
composite*color*Time	4	162	1.14	0.3390

Tests of Effect Slices

Effect	composite	color	Num DF	Den DF	F Value	Pr > F
composite*color*Time	Filtek		5	162	2.66	0.0246
composite*color*Time	Z250		5	162	5.89	<.0001
composite*color*Time	Z350		5	162	9.91	<.0001
composite*color*Time		Dark	5	162	29.29	<.0001
composite*color*Time		Light	5	162	35.84	<.0001
composite*color*Time		Universal	5	162	20.82	<.0001

Time differences

Obs	Effect	Composite	Color	Time	_Composite	_Color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
109	composite*color*Time	Z250	Light	10	Z250	Light	20	-4.3900	1.4137	162	-3.11	0.0022	0.05	-7.1816	-1.5984
139	composite*color*Time	Z350	Dark	10	Z350	Dark	20	-10.4067	2.0962	162	-4.96	<.0001	0.05	-14.5460	-6.2673
148	composite*color*Time	Z350	Light	10	Z350	Light	20	-6.0033	1.4348	162	-4.18	<.0001	0.05	-8.8367	-3.1699

Color differences

Obs	Effect	Composite	Color	Time	_Composite	_Color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
89	composite*color*Time	Z250	Dark	10	Z250	Light	10	6.5233	1.7813	162	3.66	0.0003	0.05	3.0058	10.0408
91	composite*color*Time	Z250	Dark	10	Z250	Universal	10	5.2300	1.9766	162	2.65	0.0089	0.05	1.3268	9.1332
140	composite*color*Time	Z350	Dark	10	Z350	Light	10	-5.3400	1.5441	162	-3.46	0.0007	0.05	-8.3891	-2.2909

Composite differences

Obs	Effect	Composite	Color	Time	_Composite	_Color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
6	composite*color*Time	Filtek	Dark	10	Z250	Dark	10	-16.8000	1.9455	162	-8.64	<.0001	0.05	-20.6417	-12.9583
23	composite*color*Time	Filtek	Dark	20	Z250	Dark	20	-17.4800	3.3907	162	-5.16	<.0001	0.05	-24.1758	-10.7842
39	composite*color*Time	Filtek	Light	10	Z250	Light	10	-10.1967	1.3843	162	-7.37	<.0001	0.05	-12.9303	-7.4630
54	composite*color*Time	Filtek	Light	20	Z250	Light	20	-12.5867	1.3336	162	-9.44	<.0001	0.05	-15.2201	-9.9532
60	composite*color*Time	Filtek	Light	20	Z350	Light	20	-5.6633	1.3912	162	-4.07	<.0001	0.05	-8.4106	-2.9161
68	composite*color*Time	Filtek	Universal	10	Z250	Universal	10	-13.5900	1.8226	162	-7.46	<.0001	0.05	-17.1891	-9.9909
81	composite*color*Time	Filtek	Universal	20	Z250	Universal	20	-9.7900	2.4129	162	-4.06	<.0001	0.05	-14.5549	-5.0251
93	composite*color*Time	Z250	Dark	10	Z350	Dark	10	20.4000	2.1069	162	9.68	<.0001	0.05	16.2395	24.5605
104	composite*color*Time	Z250	Dark	20	Z350	Dark	20	14.5100	3.3025	162	4.39	<.0001	0.05	7.9884	21.0316
114	composite*color*Time	Z250	Light	10	Z350	Light	10	8.5367	1.0574	162	8.07	<.0001	0.05	6.4486	10.6247
123	composite*color*Time	Z250	Light	20	Z350	Light	20	6.9233	1.7144	162	4.04	<.0001	0.05	3.5379	10.3088
131	composite*color*Time	Z250	Universal	10	Z350	Universal	10	11.6367	2.2513	162	5.17	<.0001	0.05	7.1911	16.0822
138	composite*color*Time	Z250	Universal	20	Z350	Universal	20	9.0800	2.0103	162	4.52	<.0001	0.05	5.1102	13.0498

UNIVERSITY of the WESTERN CAPE

The UNIVARIATE Procedure
Variable: Resid (Residual)

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.975502	Pr < W	0.0029
Kolmogorov-Smirnov	D	0.084759	Pr > D	<0.0100
Cramer-von Mises	W-Sq	0.261213	Pr > W-Sq	<0.0050
Anderson-Darling	A-Sq	1.416875	Pr > A-Sq	<0.0050

```
   Stem Leaf                                         #  Boxplot
     16 0                                            1     0
     14
     12 84                                           2     0
     10 48                                           2     0
      8 4902                                         4     |
      6 01123822599                                 11     |
      4 156957                                       6     |
      2 01233334445788812344677                     23  +-----+
      0 0011112333344444455555667891344445556778    40  |  +  |
     -0 99877666644333320999986666666543222110      38  *-----*
     -2 88733332097666444211                        20  +-----+
     -4 8754211109864443333                         19     |
     -6 43196541                                     8     |
     -8 87710                                        5     |
    -10
    -12 3                                            1     0
        ----+----+----+----+----+----+----+----+
```

```
                        Normal Probability Plot
    17+                                                           *
      |
      |                                                       *  *
    11+                                                    *  * +++
      |                                                 ***+++
      |                                            *****+
     5+                                        ++**+
      |                                    +*****
      |                               *******
    -1+                          ******
      |                      *****
      |                 ******
    -7+            ******
      | *  **+*+
      |+++
   -13+*
       +----+----+----+----+----+----+----+----+----+----+
            -2        -1         0        +1        +2
```

%%%

Analysis for lower measure of hardness 17:07 Friday, October 20, 2006 8

The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
composite	2	162	558.57	<.0001
color	2	162	9.54	0.0001
composite*color	4	162	10.47	<.0001
Time	1	162	437.63	<.0001
composite*Time	2	162	51.52	<.0001
color*Time	2	162	1.47	0.2320
composite*color*Time	4	162	0.08	0.9880

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Tests of Effect Slices

Effect	composite	color	Num DF	Den DF	F Value	Pr > F
composite*color*Time	Filtek		5	162	5.38	0.0001
composite*color*Time	Z250		5	162	48.35	<.0001
composite*color*Time	Z350		5	162	188.72	<.0001
composite*color*Time		Dark	5	162	580.59	<.0001
composite*color*Time		Light	5	162	110.46	<.0001
composite*color*Time		Universal	5	162	296.92	<.0001

Analysis for lower measure of hardness 17:07 Friday, October 20, 2006 9
Time differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
34	composite*color*Time	Filtek	Light	10	Filtek	Light	20	-7.9700	2.0931	162	-3.81	0.0002	0.05	-12.1032	-3.8368
88	composite*color*Time	Z250	Dark	10	Z250	Dark	20	-21.9900	2.0249	162	-10.86	<.0001	0.05	-25.9887	-17.9913
109	composite*color*Time	Z250	Light	10	Z250	Light	20	-23.9600	3.0883	162	-7.76	<.0001	0.05	-30.0586	-17.8614
126	composite*color*Time	Z250	Universal	10	Z250	Universal	20	-21.3200	3.0914	162	-6.90	<.0001	0.05	-27.4247	-15.2153
139	composite*color*Time	Z350	Dark	10	Z350	Dark	20	-23.4820	2.6872	162	-8.74	<.0001	0.05	-28.7885	-18.1755
148	composite*color*Time	Z350	Light	10	Z350	Light	20	-27.3760	2.7671	162	-9.89	<.0001	0.05	-32.8403	-21.9117
153	composite*color*Time	Z350	Universal	10	Z350	Universal	20	-23.0334	1.1437	162	-20.14	<.0001	0.05	-25.2920	-20.7749

Analysis for lower measure of hardness   17:07 Friday, October 20, 2006 10
Color differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
91	composite*color*Time	Z250	Dark	10	Z250	Universal	10	10.1400	2.6105	162	3.88	0.0001	0.05	4.9849	15.2951
102	composite*color*Time	Z250	Dark	20	Z250	Universal	20	10.8100	2.6158	162	4.13	<.0001	0.05	5.6446	15.9754
140	composite*color*Time	Z350	Dark	10	Z350	Light	10	-6.0960	1.5442	162	-3.95	0.0001	0.05	-9.1454	-3.0466
142	composite*color*Time	Z350	Dark	10	Z350	Universal	10	-1.9986	0.7469	162	-2.68	0.0082	0.05	-3.4734	-0.5237
145	composite*color*Time	Z350	Dark	20	Z350	Light	20	-9.9900	3.5346	162	-2.83	0.0053	0.05	-16.9699	-3.0101
152	composite*color*Time	Z350	Light	20	Z350	Universal	20	8.4400	2.4848	162	3.40	0.0009	0.05	3.5333	13.3467

Analysis for lower measure of hardness   17:07 Friday, October 20, 2006 11
Composite differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
6	composite*color*Time	Filtek	Dark	10	Z250	Dark	10	16.0200	1.8567	162	8.63	<.0001	0.05	12.3535	19.6865
12	composite*color*Time	Filtek	Dark	10	Z350	Dark	10	46.6220	1.3962	162	33.39	<.0001	0.05	43.8648	49.3791
29	composite*color*Time	Filtek	Dark	20	Z350	Dark	20	27.5900	3.8120	162	7.24	<.0001	0.05	20.0624	35.1176
39	composite*color*Time	Filtek	Light	10	Z250	Light	10	18.8200	2.7240	162	6.91	<.0001	0.05	13.4409	24.1991
45	composite*color*Time	Filtek	Light	10	Z350	Light	10	36.3360	1.8635	162	19.50	<.0001	0.05	32.6560	40.0159
60	composite*color*Time	Filtek	Light	20	Z350	Light	20	16.9300	2.9266	162	5.78	<.0001	0.05	11.1508	22.7092
68	composite*color*Time	Filtek	Universal	10	Z250	Universal	10	23.0300	2.5542	162	9.02	<.0001	0.05	17.9862	28.0738
74	composite*color*Time	Filtek	Universal	10	Z350	Universal	10	41.4934	1.3285	162	31.23	<.0001	0.05	38.8700	44.1168
87	composite*color*Time	Filtek	Universal	20	Z350	Universal	20	23.8700	2.0694	162	11.53	<.0001	0.05	19.7835	27.9565
93	composite*color*Time	Z250	Dark	10	Z350	Dark	10	30.6020	1.2843	162	23.83	<.0001	0.05	28.0658	33.1381
104	composite*color*Time	Z250	Dark	20	Z350	Dark	20	29.1100	3.1100	162	9.36	<.0001	0.05	22.9686	35.2514
114	composite*color*Time	Z250	Light	10	Z350	Light	10	17.5160	2.9267	162	5.98	<.0001	0.05	11.7367	23.2953
123	composite*color*Time	Z250	Light	20	Z350	Light	20	14.1000	2.9376	162	4.80	<.0001	0.05	8.2990	19.9010
131	composite*color*Time	Z250	Universal	10	Z350	Universal	10	18.4634	2.3923	162	7.72	<.0001	0.05	13.7392	23.1876
138	composite*color*Time	Z250	Universal	20	Z350	Universal	20	16.7500	2.2675	162	7.39	<.0001	0.05	12.2723	21.2277

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Mean lower by composite and time   17:07 Friday, October 20, 2006 12

The UNIVARIATE Procedure
Variable: Resid (Residual)

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.979841	Pr < W	0.0104
Kolmogorov-Smirnov	D	0.060342	Pr > D	0.1071
Cramer-von Mises	W-Sq	0.129391	Pr > W-Sq	0.0457
Anderson-Darling	A-Sq	0.813032	Pr > A-Sq	0.0367

```
   Stem Leaf                                     #  Boxplot                    Normal Probability Plot
     20 1                                        1     0         21+                                                  *
     18                                                            |
     16                                                            |
     14                                                            |
     12 6                                        1     0           |                                               +*+
     10 82                                       2     |           |                                           ++**
      8 125682556                                9     |           |                                       *****
      6 00123355778                             11     |           |                                   ****
      4 11455789349                             11     |           |                                +***
      2 0011112455667889001145668               25  +-----+        |                            +*****
      0 133334455557789900011112222556667777    36  *--+--*        |                       ******
     -0 9998865552111998655332211               25  |     |        |                   *****
     -2 99977775432219877522200                 23  +-----+        |                ****+
     -4 7655420988855442                        16     |           |            ****+
     -6 98841955544                             11     |           |        *****
     -8 971                                      3     |           |      **++
    -10 6                                        1     |           |  +++*
    -12 0                                        1     0           |+++ * *
    -14 080                                      3     0           | *  *
    -16 9                                        1     0        -17+*
        ----+----+----+----+----+----+----+-                        +----+----+----+----+----+----+----+----+----+----+
                                                                         -2        -1         0        +1        +2
```

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The Mixed Procedure

Type 3 Tests of Fixed Effects

Effect	Num DF	Den DF	F Value	Pr > F
composite	2	162	932.32	<.0001
color	2	162	5.31	0.0058
composite*color	4	162	6.66	<.0001
Time	1	162	379.30	<.0001
composite*Time	2	162	76.80	<.0001
color*Time	2	162	3.10	0.0477
composite*color*Time	4	162	0.34	0.8528

Tests of Effect Slices

Effect	composite	color	Num DF	Den DF	F Value	Pr > F
composite*color*Time	Filtek		5	162	2.86	0.0167
composite*color*Time	Z250		5	162	40.12	<.0001
composite*color*Time	Z350		5	162	127.65	<.0001
composite*color*Time		Dark	5	162	517.43	<.0001
composite*color*Time		Light	5	162	127.40	<.0001
composite*color*Time		Universal	5	162	252.01	<.0001

Time differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
34	composite*color*Time	Filtek	Light	10	Filtek	Light	20	-6.6112	2.0708	162	-3.19	0.0017	0.05	-10.7003	-2.5220
88	composite*color*Time	Z250	Dark	10	Z250	Dark	20	-17.0523	1.7097	162	-9.97	<.0001	0.05	-20.4284	-13.6762
109	composite*color*Time	Z250	Light	10	Z250	Light	20	-20.2798	3.0265	162	-6.70	<.0001	0.05	-26.2562	-14.3034
126	composite*color*Time	Z250	Universal	10	Z250	Universal	20	-19.0224	2.9547	162	-6.44	<.0001	0.05	-24.8570	-13.1877
139	composite*color*Time	Z350	Dark	10	Z350	Dark	20	-19.8880	2.1375	162	-9.30	<.0001	0.05	-24.1089	-15.6671
148	composite*color*Time	Z350	Light	10	Z350	Light	20	-24.8514	2.3798	162	-10.44	<.0001	0.05	-29.5509	-20.1520
153	composite*color*Time	Z350	Universal	10	Z350	Universal	20	-21.7247	1.4752	162	-14.73	<.0001	0.05	-24.6379	-18.8115

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Color differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
2	composite*color*Time	Filtek	Dark	10	Filtek	Light	10	4.5301	1.6475	162	2.75	0.0066	0.05	1.2768	7.7835
91	composite*color*Time	Z250	Dark	10	Z250	Universal	10	6.8889	2.5292	162	2.72	0.0072	0.05	1.8944	11.8833
140	composite*color*Time	Z350	Dark	10	Z350	Light	10	-4.4886	1.5603	162	-2.88	0.0046	0.05	-7.5697	-1.4076
145	composite*color*Time	Z350	Dark	20	Z350	Light	20	-9.4521	2.7925	162	-3.38	0.0009	0.05	-14.9664	-3.9377
152	composite*color*Time	Z350	Light	20	Z350	Universal	20	6.3880	2.1281	162	3.00	0.0031	0.05	2.1857	10.5903

Composite differences

Obs	Effect	composite	color	Time	_composite	_color	_Time	Estimate	StdErr	DF	tValue	Probt	Alpha	Lower	Upper
6	composite*color*Time	Filtek	Dark	10	Z250	Dark	10	27.5589	1.7327	162	15.91	<.0001	0.05	24.1374	30.9805
12	composite*color*Time	Filtek	Dark	10	Z350	Dark	10	49.0187	1.2547	162	39.07	<.0001	0.05	46.5410	51.4964
23	composite*color*Time	Filtek	Dark	20	Z250	Dark	20	11.6074	2.1896	162	5.30	<.0001	0.05	7.2836	15.9313
29	composite*color*Time	Filtek	Dark	20	Z350	Dark	20	30.2315	2.8050	162	10.78	<.0001	0.05	24.6924	35.7706
39	composite*color*Time	Filtek	Light	10	Z250	Light	10	26.3387	2.4654	162	10.68	<.0001	0.05	21.4702	31.2073
45	composite*color*Time	Filtek	Light	10	Z350	Light	10	39.9999	1.8906	162	21.16	<.0001	0.05	36.2666	43.7333
54	composite*color*Time	Filtek	Light	20	Z250	Light	20	12.6701	2.7146	162	4.67	<.0001	0.05	7.3095	18.0306
60	composite*color*Time	Filtek	Light	20	Z350	Light	20	21.7597	2.5253	162	8.62	<.0001	0.05	16.7729	26.7465

68	composite*color*Time	Filtek	Universal	10	Z250	Universal	10	32.9801	2.4993	162	13.20	<.0001	0.05	28.0447	37.9155
74	composite*color*Time	Filtek	Universal	10	Z350	Universal	10	46.3237	1.6312	162	28.40	<.0001	0.05	43.1025	49.5449
81	composite*color*Time	Filtek	Universal	20	Z250	Universal	20	14.3851	2.3057	162	6.24	<.0001	0.05	9.8320	18.9382
87	composite*color*Time	Filtek	Universal	20	Z350	Universal	20	25.0263	1.5324	162	16.33	<.0001	0.05	22.0003	28.0523
93	composite*color*Time	Z250	Dark	10	Z350	Dark	10	21.4598	1.3908	162	15.43	<.0001	0.05	18.7133	24.2063
104	composite*color*Time	Z250	Dark	20	Z350	Dark	20	18.6241	2.3574	162	7.90	<.0001	0.05	13.9689	23.2793
114	composite*color*Time	Z250	Light	10	Z350	Light	10	13.6612	2.6204	162	5.21	<.0001	0.05	8.4867	18.8357
123	composite*color*Time	Z250	Light	20	Z350	Light	20	9.0896	2.8207	162	3.22	0.0015	0.05	3.5195	14.6597
131	composite*color*Time	Z250	Universal	10	Z350	Universal	10	13.3436	2.4178	162	5.52	<.0001	0.05	8.5691	18.1181
138	composite*color*Time	Z250	Universal	20	Z350	Universal	20	10.6412	2.2496	162	4.73	<.0001	0.05	6.1990	15.0835

The UNIVARIATE Procedure
Variable: Resid (Residual)

Tests for Normality

Test	--Statistic---		-----p Value------	
Shapiro-Wilk	W	0.98099	Pr < W	0.0148
Kolmogorov-Smirnov	D	0.053258	Pr > D	>0.1500
Cramer-von Mises	W-Sq	0.122284	Pr > W-Sq	0.0577
Anderson-Darling	A-Sq	0.880827	Pr > A-Sq	0.0239

```
   Stem Leaf                                 #  Boxplot                 Normal Probability Plot
     14 9                                    1     0        15+                                                  *
     12 3                                    1     0          |                                                 *
     10                                                       |                                              +++++
      8 078179                               6     |         9+                                          ***+**
      6 444699                               6     |          |                                      +****
      4 0244677888800449                    16     |          |                                  +*****
      2 0001133455555678802234445578999     31  +-----+      3+                              *******
      0 0223345688888899000233444566677888  34  *--+--*       |                         ******
     -0 988887766432110098888776633200      30  |     |       |                     *****
     -2 87765333222110976655443333          26  +-----+     -3+                ******
     -4 86541983322                         11     |          |             ****+
     -6 85419876633                         11     |          |         *****
     -8                                            |        -9+     ++++
    -10 05                                   2     0          |+++++ **
    -12 662                                  3     0          |   ** *
    -14 63                                   2     0       -15+**
        ----+----+----+----+----+----+----                    +----+----+----+----+----+----+----+----+----+----+
                                                                   -2        -1         0        +1        +2
```

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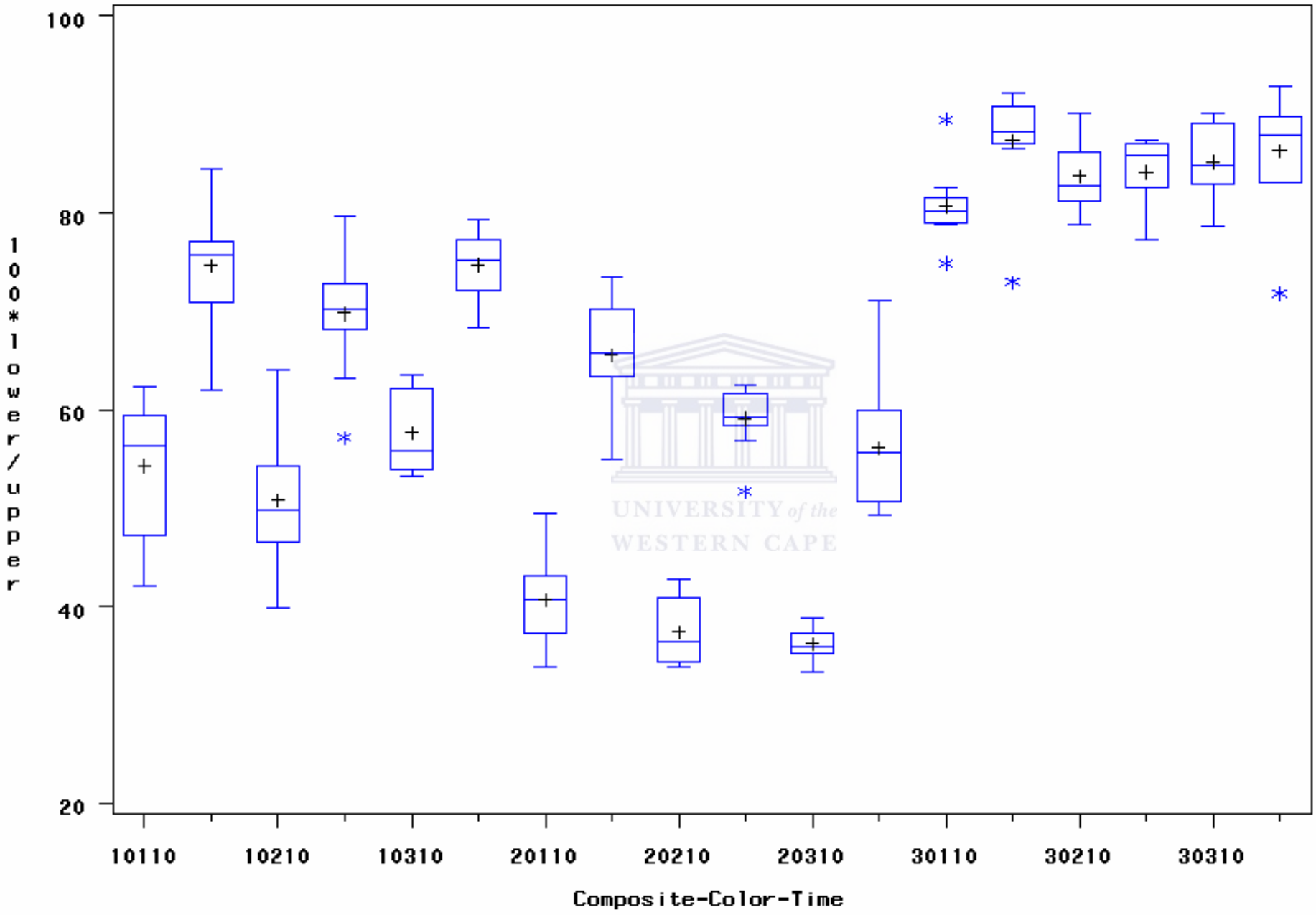

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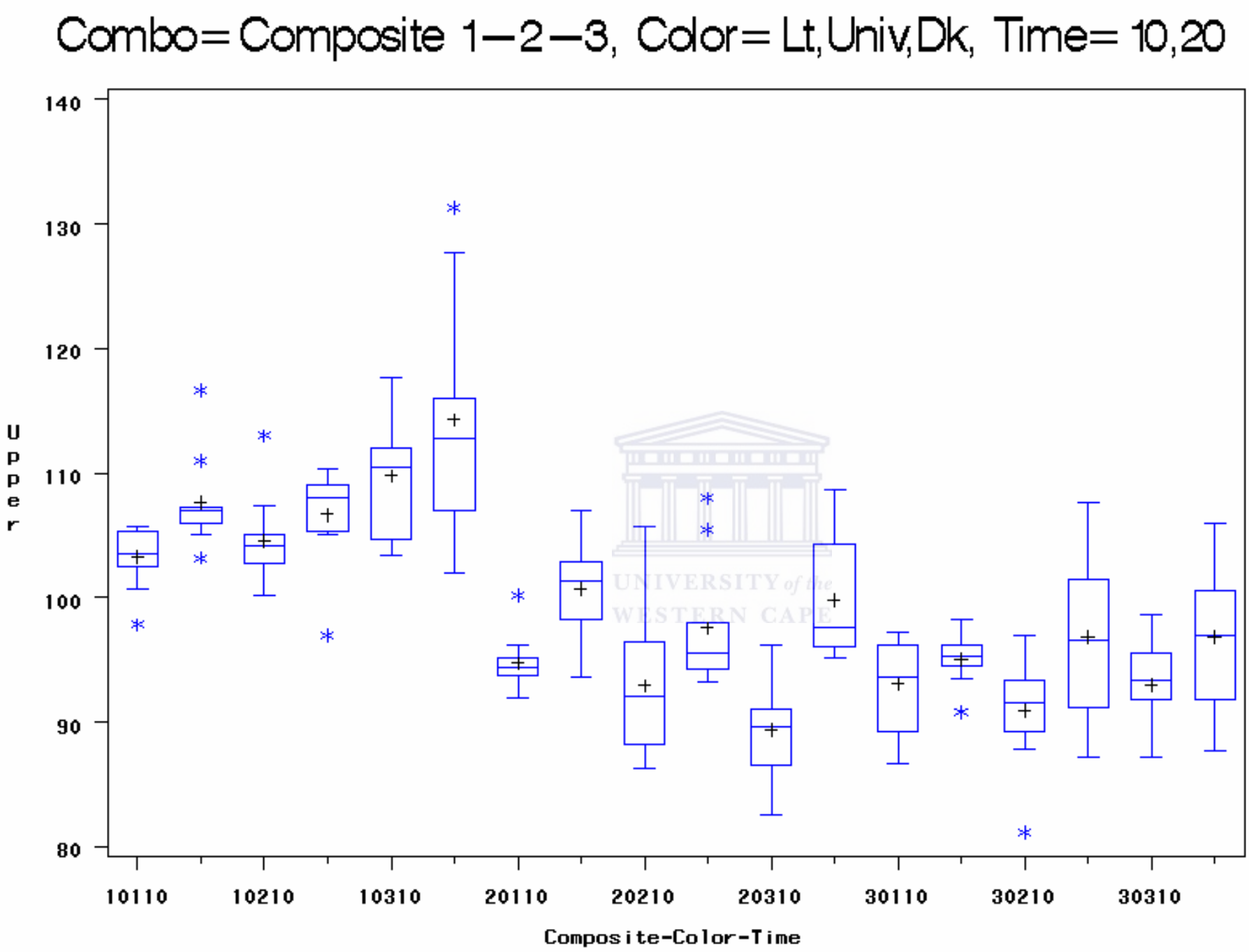

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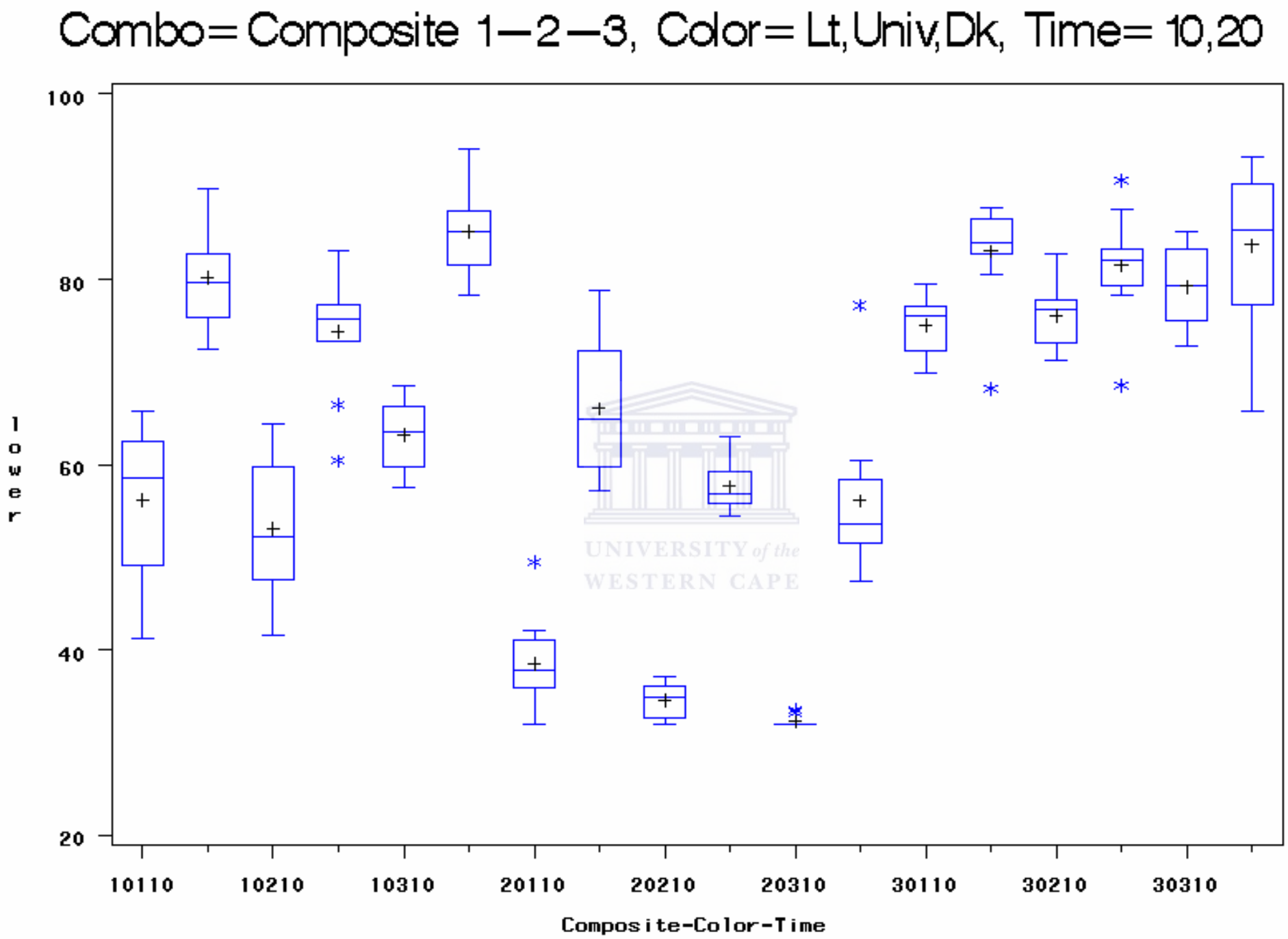

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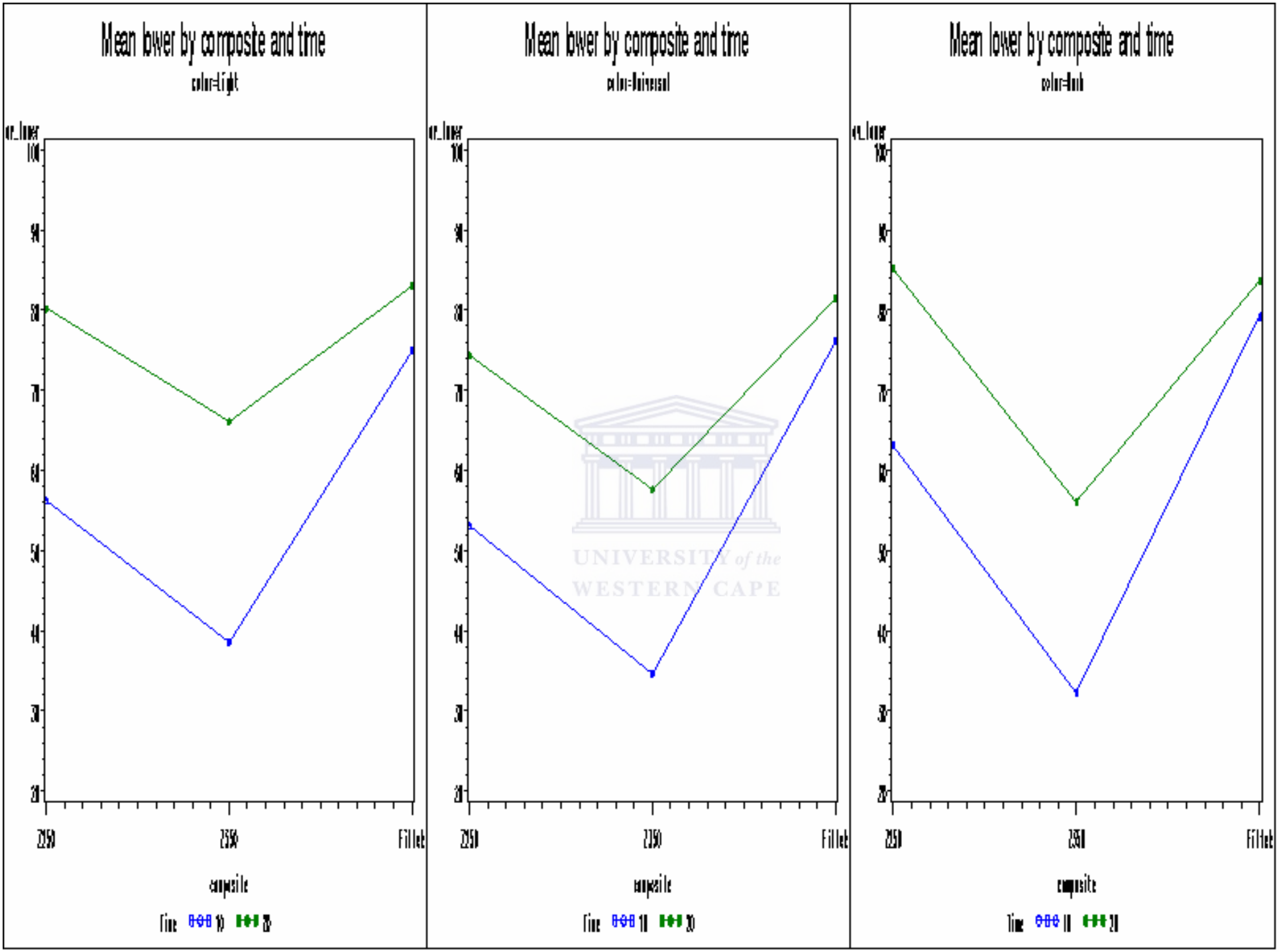

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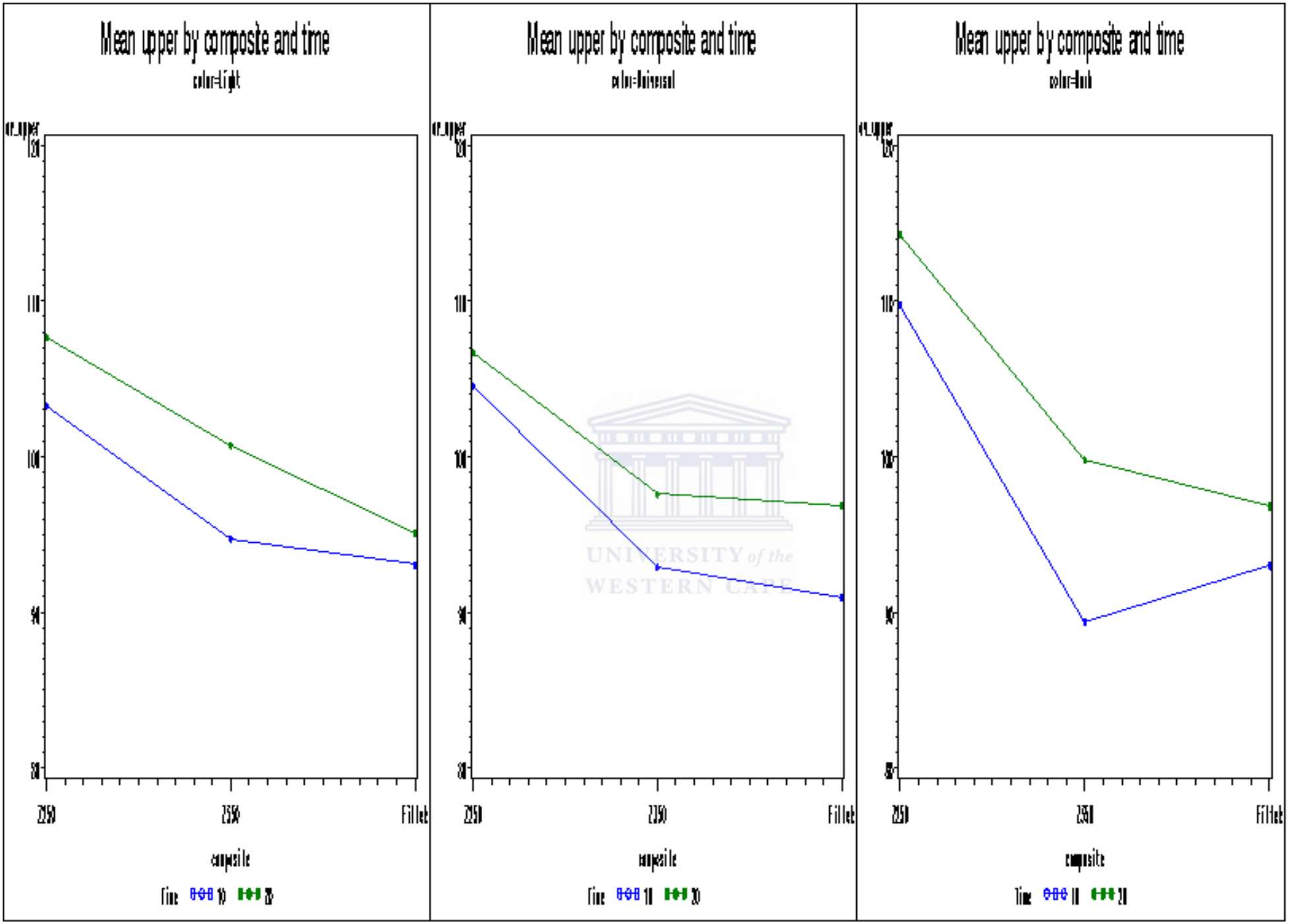

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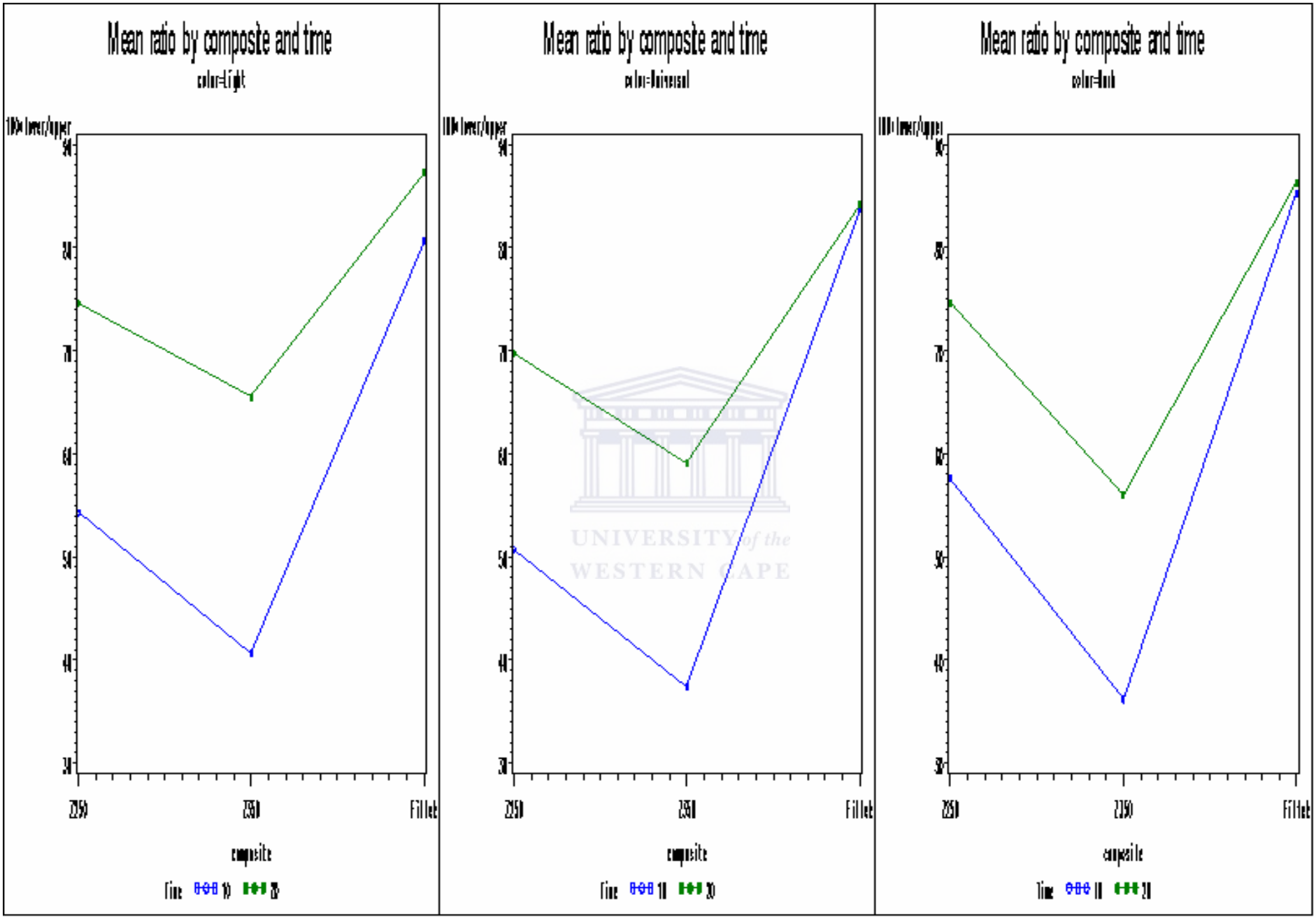

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