COLOUR CHANGES IN NANO-FILLED AND MICRO-HYBRID COMPOSITE RESINS ON EXPOSURE TO SPICES

A report submitted to the University of Adelaide in partial fulfilment of the requirements for the degree of

DOCTOR OF CLINICAL DENTISTRY

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DDS (UKMALAYSIA)

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Colour changes in composite resins after immersion in beverages such as coffee, tea, alcohol beverage and carbonated drinks have been reported. Although much work has been done to determine the staining susceptibility of composite resins to various liquid beverages, effects of spices on colour stability of composite resins have not been fully researched.

Objectives: The aim of this study is to evaluate the colour stability of nano-filled (Filtek Supreme™) and micro-hybrid (Gradia Direct™) composite resins finished with either Sof-Lex™ discs or mylar strips upon exposure to turmeric, paprika and tamarind.

Materials and methods: Twenty cylindrical specimens were fabricated from two commercially available composite resins; Filtek Supreme XT™ (3M ESPE, St Paul, MN) and Gradia Direct X™ (GC AMERICA). The top surfaces of the specimen were polished with Sof–Lex™ aluminium oxide discs (3M/ESPE, St Paul, MN USA) while the bottom surfaces were mylar strips finished. All samples were subjected to 500 thermocycling rounds between 5 and 55 ºC with 20 seconds dwell time prior to immersion in staining solution. Twenty specimens from each type of composite were then randomly divided into 4 groups (n=5) and immersed in each staining solutions (0.1% turmeric, paprika and tamarind) and distilled water (control) at 37 ºC. Colour measurement at baseline, after thermocycling, 24 hours (1 day), 72 hours (3 days) and 168 hours (7 days) of immersion in staining solutions were recorded with a reflection spectrophotometer under the D65 (daylight) illuminant using CIE L* a* b* parameters. Repeated measures analysis of variance (ANOVA) and Bonferroni post hoc tests were used to determine the significance and possible interactions of each factor.
Results: Among all the staining solutions tested, the highest colour deviation was obtained in the turmeric group, with mean colour change ($\Delta E$) ranging between 17.92 and 55.25. Paprika recorded mean colour change ($\Delta E$) ranging between 1.28 and 3.72, while tamarind produced mean colour change ($\Delta E$) ranging between 1.12 and 5.42. The effect of finishing method on colour stability of composite resins appeared to be dependent on the type of composite resin. Filtek Supreme™ with mylar strips finished generally resulted in significantly more colour changes compared with specimens polished Sof-Lex™ discs, while Gradia Direct™ finished with mylar strips were found to be more resistant to colour changes. Colour change ($\Delta E$) values were significantly influenced by the staining solutions, types of materials and finishing methods.

Conclusion: Within the limitations of this study, all spices used (turmeric, paprika and tamarind) have a potential to stain composite resins; with turmeric causing the most severe discolouration regardless of the type of composite resin or finishing technique employed. The result of this study also suggests that different materials respond differently to staining by spices when either finished with mylar strips or polished with Sof-Lex™ discs. Also, contemporary composite resins available in the market e.g. nano-composite and micro-filled hybrid composite are still susceptible to discolouration by exogenous factors despite advancement in the development of resin based restorative material.
I, Hsu Zenn Yew certify that this work contains no material which has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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Declared by: Dr Hsu Zenn Yew
Witnessed by:_____________________
Date: 
Date:
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CHAPTER 1
INTRODUCTION

One of the quintessential challenges in restorative and aesthetic dentistry is to produce a natural looking restoration that blends harmoniously with the oral environment. Apart from the important parameters of shape and morphology, the colour of a restoration is often regarded as being another essential building block necessary for constructing a ‘biomimetic’ restoration [1-3]. Successful colour matching in a restoration is one of the critical clinical requirements to increase the acceptance of restorations [4]. For a lasting impression of the esthetic outcome, “colour stability” or the ability of the material to retain the matched shade over a long period of time is also crucial. “Colour selection” is nevertheless often considered one of the most fascinating and frustrating areas in dentistry [2, 5-7]. For many years, colour researchers lamented that lack of colour knowledge among clinicians had contributed to this problem [6, 7]. Therefore, an understanding of colour science and its parameters are important tools for optimising the esthetic outcome of restorations. Colour is most commonly generated by the addition of chemical colourants or manipulation of the physico-chemical content of the restorative material. To fully comprehend the influence of material composition on colour perception, the observer needs to have knowledge of the physical aspect of colours. Furthermore, the science of colour physics enables a quantification and comparison of colour differences, which is an essential component in determining the colour stability of material. The first chapter of this research report will discuss the above issues; looking at colour from a physical perspective and highlighting its importance with respect to colour measurement in dentistry.

Considering the importance of aesthetics in restorative dentistry, it is important to know the inherent properties responsible for the long term success of a restoration in terms of colour stability.
This study investigated the colour stability of composite resins when exposed to a range of spices. Composite resins are tooth coloured restorative materials, composed of a mixture of filler and resin polymer [8]. Since their inception over half a century ago [9], composite resins have gained considerable popularity in the mainstream operative dentistry as a direct restorative material for both anterior and posterior teeth. The reasons behind this trend are the inherent property of composite resins to emulate the natural colour of teeth [8] and the increasing demand amongst patients for aesthetics, the perception of mercury toxicity in amalgam restorations and the availability of good adhesive system [10]. Over the last decade, there has been a strong research focus on the improvement of the clinical performance of the material. Through modifications of the filler content, composite resins have evolved into a range of material with various filler sizes. In general, a smaller filler size with a higher filler loading volume contributes to better polishability and the ability to retain a smooth polish surface [11], thus giving a more aesthetically pleasing results. The wake of nanotechnology has seen the incorporation of nano-sized fillers into composite resins. Nano-filled composite resins with filler size of 5 – 100 nanometers, (smaller than its predecessors’ filler size), have been reported to have superior clinical performance and aesthetic qualities [12].

Despite its popularity in satisfying aesthetic demands, previous studies have revealed that composite resins are susceptible to discolouration [13-15]. This may result in patient dissatisfaction [16] and replacement of restorations [17-20]. The discolouration of composite resins may be attributed to intrinsic or extrinsic factors [21-23]. Intrinsic discolouration involves physico-chemical alteration within the material. Alternatively, extrinsic staining involves surface discolouration by extrinsic substances. Research has found that beverages including coffee [24-30], tea [21, 24-27, 30-33], alcohol beverages [26-28, 30, 34, 35], carbonated drinks [24, 26, 28, 33, 34, 36] and fruit juices [24, 33, 34, 36] caused significant colour changes in composite resins, with red wine causing the most severe staining, followed by tea and coffee [26, 27].
Colourants or dyes are usually added to enhance the appearance of food and may have the potential to stain composite resins [11, 37]. Research by Dietschi et al [11] has shown that composite resins are also susceptible to staining by artificial food dyes (erythrosine and sunset yellow). Throughout Asia, spices are used to flavour and colour local dishes. Turmeric, paprika and tamarind are the most common spices used alone or in combination with other mixed spices in Asian cuisine [38].

Although much work has been done to ascertain the staining susceptibility of composite resins to various liquid beverages, the effect of spices on the colour stability of composite resins have not been fully researched. Due to the extensive use of spices in Asian cooking, as well as in many other parts of the world, it would be useful and timely to determine the staining potential of these spices on the colour stability of composite resins. Currently there is a paucity of data pertaining to the discoloration susceptibility of some of the more contemporary composite resins available in the market. The determination of colour stability properties of composite resins is crucial as this information can provide guidance for clinicians on appropriate selection of material for clinical restorative usage. This study may contribute to the development of more stain resistant composite resins.
The aim of this study is to evaluate the colour stability of nano-filled (Filtek Supreme™) and micro-hybrid (Gradia Direct™) composite resins finished with either Sof-Lex™ discs or mylar strips upon exposure to turmeric, paprika and tamarind. The null hypotheses at the present study are:

1. There are no significant colour changes in each composite resins tested on exposure to turmeric, paprika and tamarind spice solutions.
2. There is no colour difference in each composite resins tested in the respective spice solution at baseline, 24 hours (1 day), 72 hours (3 days) and 168 hours (7 days).
3. There is no significant colour difference between the two composite resins tested (Filtek Supreme™ and Gradia Direct™).
4. There is no significant colour difference between Sof-Lex™ discs polished and mylar strips finished composite resins.
CHAPTER 2

LITERATURE REVIEW: THE SCIENCE OF COLOUR

2.1 Principles of Colour.

The “COMMISSION INTERNATIONALE DE L'ECLAIRAGE” [39] (CIE or The International Commission on Illumination) defines (perceived) colour as:

“Attribute of a visual perception consisting of any combination of chromatic and achromatic content. This attribute can be described by chromatic colour names such as yellow, orange, brown, red…etc, or by achromatic colour names such as white, gray, black, etc, and qualified by bright, dim, light, dark, etc., or by combinations of such names.”

A Google search for “colour definition” yields about 162 million results. The Oxford English Dictionary defines colour as: ‘the property possessed by an object of producing different sensations on the eye as a result of the way it reflects or emits light’ [40]. Given the above definition, colour can be considered a multi dimensional phenomenon that is dependent on interactions of three factors, namely, (1) the nature of the light source, (2) the physical properties of the object and (3) the detector [41, 42]. For colour to exist, all three parameters must be present and any change in the condition of any of the three will lead to a change in the perception of colour.
2.1.1 Nature of Light Source

Our modern understanding of light and colour begins with Isaac Newton, when in 1666, he discovered white light can be refracted through a prism into a spectrum of different colours (Figure 2.1) [41-43]. Although at that point in time, Newton did not fully understand the reason why colour was generated, his simple experiment demonstrated that colour comes from light.

![Figure 2.1: Spectrum of colours (adapted from www.physics.arizona.edu[44]).](image1)

NOTE:
This figure is included on page 6 of the print copy of the thesis held in the University of Adelaide Library.

Light is a form of electromagnetic energy consisting of a spectrum of wavelengths including ultraviolet, infrared, and visible light. The eye is only able to discriminate wavelength in the visible part of the spectrum. As illustrated in Figure 2.2, the visible light spectrum is the narrow band of electromagnetic wavelength (within an approximate range of 380 or 400 nm to 760 or 780 nm) that we

![Figure 2.2: The electromagnetic spectrum (adapted from www.physics.arizona.edu[44]).](image2)

NOTE:
This figure is included on page 6 of the print copy of the thesis held in the University of Adelaide Library.
see as colours. Each colour in the spectrum corresponds to a different wavelength as represented in Table 2.1 [41, 42, 45, 46].

Table 2.1: Wavelengths of colours.

<table>
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<th>Colours</th>
<th>Wavelength (nm)</th>
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<tbody>
<tr>
<td>Red</td>
<td>650-800</td>
</tr>
<tr>
<td>Orange</td>
<td>590-649</td>
</tr>
<tr>
<td>Yellow</td>
<td>550-589</td>
</tr>
<tr>
<td>Green</td>
<td>490-539</td>
</tr>
<tr>
<td>Blue</td>
<td>460-489</td>
</tr>
<tr>
<td>Indigo</td>
<td>440-459</td>
</tr>
<tr>
<td>Violet</td>
<td>390-439</td>
</tr>
</tbody>
</table>

As light is a stimulus for colour, without which colour cannot be seen, most colour scientists believe that “colour is not a characteristic of objects but, rather, of light which enters our eyes from them” [47]. However, light comes from a variety of sources. Light that is composed of all spectral wavelengths in equal quantities is rare. If the source does not contain a particular wavelength then obviously the corresponding colour cannot be seen [48]. Therefore, the colour we see depends on the quality and quantity of the light source illuminating the object [49]. This concept mandates consideration of the characteristic of the light source. In research, the term “illuminant” is used to refer to the light source.

The quality of a light source can be characterized numerically by a spectral curve, colour temperature and a colour rendering index [49]. Each light source has its own relative spectral power distribution across the visible spectrum (Figure 2.3). For example, daylight appears blue-green due to its
relatively high spectral power in the blue and green areas of the spectrum. On the other hand, incandescent light looks red as its greatest spectral power distribution is in the red area [49].

Figure 2.3: Spectral relative power curve vs. wavelength (adapted from www.geelighting.com [54]).

Therefore, the colour of the same object viewed under these two light sources, would appear bluish under daylight and reddish under incandescent light. This phenomenon has been described as metamerism. Metamerism is a phenomenon which occurs when these two materials have an identical colour under one illuminant, but different colours under another illuminant [48].

Most light sources emit light that is a mixture of different wavelengths, although some wavelengths are missing from certain kinds of light sources, such as incandescent light (Figure 2.3). Traditionally, natural day light with close to a full spectrum of white light, was considered the “normal” standard in colour rendering [7]. However, it is highly variable depending on the time of the day, season of the year, amount of cloud cover and the degree of atmospheric pollution (Figure 2.4) [2, 5]. Due to these variations, colour corrected lights, which reproduce a similar spectral curve to natural daylight, are recommended as an alternative choice of light source for colour matching [50-52].

Another measurement of light quality is the colour temperature. This numerical characterisation measures the distribution of power, as stated in Kelvin (K), in the spectrum of light (Figure 2.5), and
describes warmth or coolness of the light source. It is derived from equating the light source to the
colour given off by heating the black body radiator. A blackbody is a hollow heated chamber with a small
hole. As the radiator becomes warmer, it begins to glow red, then yellow, white and eventually blue [46,
48]. The ideal colour temperature for colour rendering is 5500 K, the medium temperature that
corresponds to ‘white’ light or natural day light [2, 51, 53].

The Colour Rendering Index (CRI) is expressed as a rating from 0 to 100 is another
measurement of the quality of light [54]. It is a measure of completeness of the light spectrum. Complete
spectral lighting improves the shade matching procedure. A CRI measure of 100 indicates that the light
source has the entire visible wavelength present. The higher the rate (illustrated by the square loci in
Figure 2.6), the closer the light source in reproducing the colours of various objects in comparison with
an ideal light source. Theoretically, a light source with CR I = 100 is desirable. However, according to
Preston & Bergen [51], CRI greater than 90 will be adequate in shade matching in clinical dental
settings.

NOTE:
This figure is included on page 9 of the print copy of the thesis held in the University of Adelaide Library.

Figure 2.4: Spectral curve of various natural daylights (adapted from www.handprint.com [55]).
Apart from the quality of lights, the amount or quantity of lighting is also crucial. The quantity of light or *luminance*, is commonly measured in lux or foot candles (1 foot candle = 10.8 lux). When illuminance is too dim (amount of light too small), difficulty may arise in assessing fine details and subtle variations in colour. Conversely, a high light intensity may result in glare. Hence, the accuracy of colour rendering is reduced [49]. In dentistry, different levels of light intensity have been suggested for shade or colour determination, ranging from 75 to 250 foot candles [5, 51, 53]. Preston and Bergen [2] have recommended a minimum of 150 foot candles for dental operatory. Another group of researchers [50] have proposed that the intensity of office illumination is not critical in matching tooth shades. They found that dentists can achieve reproducible colour matches at all the foot candle levels, including the two extreme levels of 75 and 300. The authors contend that once a certain light intensity is achieved, colour matching is adequate, and any progression above this intensity does not significantly influence the ability to discriminate colour differences. Instead, greater consideration should be given to the contrast, i.e. the difference between the brightness of an object and its surrounding background (task to ambient light ratio). Excessive contrast causes glare and impedes colour matching. Preston et al [51] recommend that the task-to-ambient-light ratio should not exceed 3:1 to prevent glare.

In summary, one of the major variables affecting colour is the source of light that falls on the object viewed. Understanding the characteristics of the light source and their influence in colour assessment may be beneficial in establishing the proper environment for colour identification procedures. The selection of a light source or illuminant for illumination should take into account the colour temperature, spectral curve and colour rendering index as well as the intensity of the light.
2.1.2 Physical properties of the object

The nature of light and the visible spectrum constitute one part of this three dimensional phenomenon called colour. The next part of the triad involves the interaction of the light with the object. Depending on the characteristics of the object, light may be (1) transmitted, (2) reflected, (3) absorbed, (4) scattered (Figure 2.7) [41,42].

![Diagram of light transmission, reflection, absorption, and scattering](image)

Figure 2.7: Light transmission, reflection, absorption and scattering (adapted from Wyazecski [42]).

Generally, a material transmits light when it allows the light to pass through it. Transparent materials allow all light to pass through (e.g. glass). The colour of a transparent object depends on the colour of light it transmits. If red light passes through a transparent object, the emerging colour is red.
However, light does not pass directly through materials. It changes direction and is scattered as it passes through. This bending of light at the surface of an object is called refraction. The amount of bending not only depends on the angle of incidence, but also on the refractive index (RI) of the material itself. RefRACTive index (RI) is the ratio of the speed of light in a vacuum (i.e. space) to the speed of light in a given material. The RI of a substance is further affected by the wavelength of the light striking it. The red end of the visible spectrum does not refract as much as the violet end. The effect is a visible separation of the wavelengths [41, 46].

Translucent materials partly transmit and partly absorb the light that passes through them (e.g. frosted glass), while in opaque materials none of the light is transmitted [41]. When light strikes an opaque material, it will either be reflected, scattered or a degree of both depending on the surface characteristics of the object.

A smooth or glossy surface is one made up of particles of equal, or nearly equal, refractive index. These surfaces reflect light at an intensity and angle similar or equal to the incident beam - this is called specular reflection or gloss. The more reflective a surface the more wavelength returns to the eye, thus the object may be perceived brighter or more intense in colour [41, 46, 48, 49].

Scattering, or diffusion, is another aspect of reflection. When a substance contains particles of different refractive indices, such as on a rough surface, a light beam striking the surface will be scattered and the individual wavelengths will bend differently, yielding a substantially different spectrum returning to the eye. Therefore, a polished surface can appear bright due to specular reflection but more translucent due to less scattering of the light.

The amount of light scattered depends on the difference in the two refractive indices and also on the size of the particles. Scattering increases in proportion to the particle size. The scattering property of a material can therefore be controlled by selection of particles with appropriate differences in
refractive index and or by control of particle size. A transparent composite material with least scattering can be obtained when the pigment particles are of very small particle size and have a similar refractive index as the surrounding matrix [41].

Finally, some of the light incident upon an opaque or translucent material can be absorbed. Colour is a result of the way in which an object absorbs and reflects light (Figure 2.8). The colour impression that the eyes generate depends on which wavelengths of the visible light spectrum are reflected by an object. For an object to appear red, only the red wavelength is reflected when electromagnetic waves (light) hit the surface of the object, while the remaining visual wavelengths are absorbed. A black object appears black because it absorbs all wavelengths, and reflects nothing. When all wavelengths are reflected equally, the object appears white [41, 46, 48].

NOTE:
This figure is included on page 14 of the print copy of the thesis held in the University of Adelaide Library.

Figure 2.8: Absorption of lights (adapted from www.dba.med.sc.edu [57]).

Similar to spectral power distributions as a property of the light source, the spectral reflectance or transmittance curve is a property of a coloured object. Spectral reflectance (or transmittance) refers to the amount of light at each wavelength reflected from an object as compared to a reflection standard e.g. from a pure white object that reflects 100% at all wavelengths (or the amount transmitted through an object as compared to the amount transmitted through a clear medium such as air.) [41, 46, 48].
The spectral reflectance or transmittance curves (Figure 2.9) contribute toward the definition of colour. The colour of an object is determined by which wavelength in the light spectrum that is reflected or transmitted. So, a red object possesses a higher percentage reflectance at higher wavelengths of the spectrum compared to a white or standard object. This spectral reflectance or transmittance curve is commonly used by colour scientists in the study of colourimetry or colour measurement.

Figure 2.9: Spectral reflectance curve (adapted from www.dba.med.sc.edu [57]).

In summary, when light strikes an object, one or more phenomena can be observed. Colour can be influenced by how an object modifies the light, which in turn depends on the physical properties of the object. Contour and surface texture determine how light is reflected, scattered, transmitted or absorbed, thus affecting the colour perception.
2.1.3 The Detector

Just as there is no colour without light, there is no colour without an observer. To fully appreciate the occurrence of colour, it is necessary to have an understanding of how vision occurs.

Figure 2.10: The structure of the eye (adapted from Schlote(2006) [58]).

The main structures of the eye are the iris, lens, pupil, cornea, retina, vitreous humor, retina and optic nerve (Figure 2.10). However, a discussion of the role of each component and the detailed mechanics of human vision will not be presented here.

Generally, light from the object enters the eye through the cornea and then passes through an aperture called the pupil. The amount of light entering the eye is controlled by the constriction and dilatation of the iris. Light is then focused on the lens. The lens then passes the light through a transparent gel called the vitreous humor and focuses an inverted image of the object being viewed on the retina at the back of the eyeball. The retina is the light-sensitive part of the eye and its surface is composed of photoreceptors or nerve endings. Light reaching these photoreceptors is converted into nerve impulses that are sent through the optic nerve as a stimulus to the occipital lobe of the cerebral cortex where the information is interpreted [2, 58, 59].

NOTE: This figure is included on page 16 of the print copy of the thesis held in the University of Adelaide Library.
Any changes that occur in the pathway of the lights to the brain may result in alteration of colour perception. For example, with advancing age, the lens or the cornea may undergo degeneration and become less efficient in transmitting light. As a consequence, the perception of colour can be altered [2, 58].

There are two types of photoreceptors, rods and cones. The greatest concentration of rods and cones is in an area of the retina called the fovea. The rods contain a pigment called rhodopsin and are light sensitive but not colour sensitive (that is, they are monochromatic), while the cones contain the pigments erythrolabe, chlorolabe, and rhodopsin, which are sensitive to wavelengths in the red, green, and blue parts of the visible spectrum. For this reason, human vision is often referred to as a tri-stimulus response [59]. Furthermore, rods are more acutely sensitive to light, while cones are insensitive to light below a certain level of luminance. Therefore in low light intensity, only black and white colours are evident as only the monochromatic rods receive the light and relay it to the brain.

When the eyes are exposed to a particular colour for a prolonged period, colour adaptation can occur. The red, green and blue cone receptors can to a certain extent adapt independently to the prevailing illumination if one set of cones is more or less strongly stimulated than the others. For example, under incandescent light, blue receptors are less strongly stimulated than green or red receptors, the former increase their relative sensitivity, causing the light to seem less strongly coloured than it otherwise would appear [58, 59].

After prolonged exposure to a particular colour, such as a red stimulus, the red cone receptors sensitive to the stimulus become fatigued. This is due to the depletion of the principal photosensitive pigments in the cone, resulting in the eye progressively become less sensitive to the particular colour and alteration of colour perception. When the stimulus changes, the least depleted cells (the blue and
green receptors) respond more strongly. The object may appear more greenish-bluish, which is the complementary colours to red. This is a negative afterimage [2]. Consideration of the negative afterimage phenomenon is important in the selection of background for colour determination [49]. Owing to the absence of complementary colours, a neutral gray background is advocated for colour determination. Another example in relation to dentistry is the use of a blue–black background to make the eyes more sensitive to yellow-orange colour [53].

Positive afterimage also exists. This is due to continuous stimulation of retinal receptors shortly after the stimulus is removed producing a visual afterimage that retains the same colour relationships as those appearing in the original image. Therefore, after prolonged exposure, the colour of the two objects may appear to be more alike [2, 49].

Similar to spectral power distributions and spectral reflectance curves discussed in the preceding sections, visual sensitivity is also characterized by a graph called a spectral response or sensitivity curve (Figure 2.11). The sensitivity curve reflects the sensitivities of the cones to short (420–440 nm), medium (534–545 nm), and long (564–580 nm) wavelengths that correspond to blue, green and red respectively. The difference in the signals received from the three cone types allows the brain to perceive all possible colours [42].

NOTE:
This figure is included on page 18 of the print copy of the thesis held in the University of Adelaide Library.

Figure 2.1 Spectral sensitivity curve of retina (adapted from Schlote (2006) [58]).
Essentially there are three major elements for the production of colour: a light source, the object that absorbs, transmits, reflects or scatters the light from the source, and the detection by the visual system. These three parameters have been described by an appropriate curve against the wavelength; the light source by spectral power distribution curve; the object by the spectral reflectance and transmittance curve and the detector by the spectral response curve. The stimulus that the brain interprets as a colour is made up of these three spectral curves. In other words, various factors influence the observed colour of a surface, illumination, surface material, texture, surface area and the physiological state of the eye of the observer. Collectively, all these parameters have been employed in many colour measuring devices e.g. spectrophotometer.
2.2 Colour Description

Despite significant improvements in scientific knowledge pertaining to optics, the definition of colour still remains a subject of vigorous debate. Basically, there are two schools of thought: colour has been described either objectively as physical phenomenon or subjectively as a psychological response to a physical stimulus.

The preceding sections described the basic physics of colour. However, colour has also been studied from the perspective of several other disciplines particularly chemistry, physiology, psychology and aesthetics, culminating in a vast number of colour terms used to describe different aspects of the colour sensation. Differing interpretations of colour can be misleading and result in problems in colour communication. Because of the practical need to describe colour accurately and communicate observed colour, various colour order systems have been developed.

2.2.1 Munsell Colour Order System

One of the internationally accepted colour appearance systems is the Munsell Colour Order system [2]. Envisaged by Professor Albert Munsell about a century ago, the colour order system is a three-dimensional model based on the premise that each colour has three qualities or attributes: hue, value and chroma [60]. Munsell defined:

Hue: "the quality by which we distinguish one colour from another." He selected five principle colours: red, yellow, green, blue, and purple; and five intermediate colours: yellow-red, green-yellow, blue-green, purple-blue, and red-purple.

Value: "the quality by which we distinguish a light colour from a dark one." Value is a neutral axis that refers to the grey level of the colour in the Munsell colour tree. (Figure 2.12)
Chroma: “the quality that distinguishes the difference from a pure hue to a gray shade” The chroma axis extends from the value axis at a right angle. However, chroma is not uniform for every hue.

Figure 2.12: Munsell colour tree (adapted from www.britannica.com [61]).

The system uses decimal notation, instead of colour names. For instance, for a fairly saturated red with medium lightness would be 5R 5/10; with 5R meaning the colour is in the middle of the red hue band, 5/ meaning medium lightness and a chroma of 10. It should be noted, too, that Munsell's scale of value is visual or perceptual, and not on a strict set of mathematical values from a light source or illuminant. This method of colour designation has been adopted in dental shade guides and some instrumental colour measurement devices in dentistry.

2.2.2 CIE Colour Ordering System

Another colour ordering system is the CIE XYZ colourimetric system developed by Commission Internationale de l’Eclairage (International Commission on Illumination) in 1931 [62]. Since then, two more colour systems have been developed, the CIE LUV and CIE LAB. Another newly recommended colour system for colour difference is CIEDE2000 [63].
These colour systems are mainly used in science and industry as a standard system enabling the specification of all colours as points in the 3-dimensional colour space (Figure 2.13). The systems are not based on perceptual scale of colour and they do not describe the appearance of colour. Via mathematical calculations of the coordinates in the colour space, these systems may be used to record and specify colour in numbers as well as to quantify and visualize the relationship of colours.

Most colour differences reported in the dental literature are based on the CIE LAB system. This system has been well reviewed for applications in dentistry by Westland et al [64]. CIELAB indicates these values with three axes: L*, a*, and b*. Similar to the Munsell value axis, the central vertical axis of the system represents lightness (signified as L*) whose values run from 0 (black) to 100 (white). The colour axes are based on the fact that a colour can't be both red and green, or both blue and yellow, because these colours oppose each other. On the a-a' axis, positive values indicate amounts of red while negative values indicate amounts of green. On the b-b' axis, yellow is positive and blue is negative. For both axes, zero is neutral gray [62, 65].

Figure 2.13: CIE colour spaces-CIE XYZ (left) and CIE LAB (right) (adapted from www.britannica.com [61]).

Often, CIELAB colour spaces are used for measurement of colour difference. By comparing data before and after the process, the colour difference can be calculated in a simple way as the Euclidean distance between two coordinates (before and after) in the colour space. Therefore, it can be
expressed by a single number independently of the location of the two coordinates. Differences of two stimuli \((L^{*1}, a^{*1}, b^{*1})\) and \((L^{*2}, a^{*2}, b^{*2})\) can be calculated using the following formula [64]:

\[
\Delta E = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2}
\]

At this point the question might be raised as to the relevance of this colour science to dentistry. The amount of \(\Delta E\) is useful in determining how much colour difference constitutes an acceptable shade mismatch that is perceptible to observers. The threshold of perceptibility and acceptability, however, remains controversial.

Douglas et al [66] found that the predicted colour difference at which 50% of the dentist observers could perceive a colour difference (50/50 perceptibility) was \(\Delta E\) 2.6 units. In terms of acceptability, a colour mismatch of more than \(\Delta E\) 5.5 was considered unacceptable. Seghi et al [67], on the other hand, stated that \(\Delta E\) less than 1 was imperceptible and if the value is greater than 2, colour difference was discernible by most observers. Other authors reported the range of clinically acceptable threshold was from \(\Delta E\) 2 to 4.4 [68-71]. Most considered \(\Delta E\) 3.3 as clinically unacceptable [70, 71]. Based on these studies, colour difference of \(\Delta E\) more than 1 is considered perceivable and clinically unacceptable if greater than 3.3.
2.2.3 Colour Measurements

Colour measurement can be broadly classified into two categories – visual and instrumental colour assessment.

2.2.3.1 Visual Colour Measurement

Subjective colour identification usually involves a visual colour assessment. It is commonly performed by visual comparison with reference colour samples whose specification is known. In dentistry, shade guides are routinely used as the standard colour samples against which a tooth or restoration is compared. Some of the popular shade guides are: Vitapan Classical, Chromascop and Vita System 3D Master. In addition, custom made and specific chroma and value guides are also available.

One major criticism of these shade guides is the lack of a logical and ordered distribution in the natural tooth colour space [72]. Hall [73] pointed out that since a tooth contains more than 100,000 colours compared to the limited number of tabs in the shade guide, the probability of obtaining colour match is approximately 1 in 100,000, assuming that the tooth and shade tabs contain only one colour. This probability is reduced since both tooth and shade tabs consist of more than one colour. Moreover, in a porcelain shade guide, if enamel, dentine, opaque and gingival shades are considered the chance of getting an accurate match is almost nil. To have any realistic chance of obtaining a colour match, the number of tabs in the shade guides would have to be increased to thousands which is not practical. Based on the superimposition of the colour spaces recorded for shade guides and the recorded tooth colour in Munsell, Hall also found that shade tabs were not uniformly positioned to reflect all three colour dimensions.
The most widely used shade guide used for composite materials is made of ceramic. Such shade tabs have been shown to be incompatible with composite resins material [74]. A recent study by Browning et al [75] found that when various shade tabs of Vitapan Classical shade guides were compared with correspondent tabs made of direct restorative composites, no material/shade combination resulted in an acceptable colour difference. They concluded that there was poor match between composite resins and the shade guide.

Visual measurements are generally considered to be easier to perform than instrumental ones. From the preceding sections, we know that there are various physical, physiological and psychological factors affecting the visual perception of colour. Moreover, the level of experience of the clinician performing the shade selection is also crucial. Capa et al [76] evaluated the influence of dentists' and non-dentists' experience, age, sex, eye colour and use of eyeglasses or contact lenses on tooth shade-matching ability. They concluded that only professional experience was associated positively with the outcome, while the other factors did not have any effect on shade-matching results.

As a result, colour perceived may be subjective and vary from one observer to another or even within the observer. To overcome these limitations of visual assessment, many instruments have been developed in the hope of providing a more objective measurement.

2.2.3.2 Instrumental Colour Measurement

An alternative to visual colour evaluation is instrumental colour measurement. There are two main categories of instruments used for colour assessment, spectrophotometers and colourimeters. These methods of measurement and their application in dentistry have been comprehensively reviewed recently by several authors [3, 78, 79].
A spectrophotometer breaks down radiation into its component wavelengths and provides wavelength by wavelength spectral analysis of the reflecting or transmitting properties of the object, while a colourimeter quantifies colour by measuring three primary colour components of light, which corresponding to physiological trichromatic nature of the normal eye.

Compared to a spectrophotometer, a colourimeter is relatively simple and less costly but only provides data in terms of colour coordinates. The spectrophotometer is more elaborate, expensive and bulky. Table 2.2 shows some of the commercially available colour measurement instruments used in dentistry [41, 78, 79].

These two devices are essentially comprised of a standard light source (illuminant), the subject, detector (replacing human eyes) and interpreter. The light created by the light source passes through the subject where some light is usually absorbed, is received by the sensor, and is interpreted into an output such as a CIE chromacity graph. There are multiple illuminants possible, including the CIE Illuminant A, B, C, D, E and F representing various types of light sources. The general recommendation of illuminant for colour matching is D65 [41, 78, 79]. Most instruments are keyed to dental shade guides systems and can be converted into the shade tab. This enables users to cross reference the shade guide tabs in the database and the image captured.

This eliminates human interpretation, thus data can be obtained objectively, overcoming some of the problems associated with visual subjective assessment, including physical elements such as light and reflection, or the physiological and psychological factors of the observer. Another distinct advantage of instrumental colour measurement is the repeatability of the measurement. Intra- and inter- operator consistency using these devices has been demonstrated [80-84], and considered superior to visual assessment [85, 86].
Mathematically, the data can be translated into notations of colour order systems e.g. Munsell or the CIE colour system. Via mathematical calculation, colour can be identified by numbers and colour differences can be determined [78, 87]. Therefore, one of the major advantages of instrumental colour measurement is the quantification of colour changes. Through calculation of colour differences, changes in colour can be precisely and objectively recorded and analysed. These measurements also allow one to quantify and analyse which parameters of colour (hue, chroma and value) have changed and to what extent.

By comparing a test instrument to a reference “correct” instrument, the accuracy of the colour measurement devices has been determined. Varying results have been shown [88, 89] especially in clinical settings, with accuracy levels ranging from 68-91% being reported [90]. Some studies have found the percentage of accurate matching comparable between the two methods [77, 91], while one study found otherwise [92]. Recent studies have shown the accuracy or performance of the some of devices seem to vary according to the dental shade guide systems [88, 89], but the general trend was that instrumental colour evaluation produced less colour mismatch or difference with the standard (better accuracy) compared with the visual colour assessment [93-95].

In dentistry, the instrumental colour measurement also encompasses imaging systems. With an appropriate calibration protocol (eg; object-camera distance, digital camera settings, and suitable illumination conditions), the digital imaging method has been suggested as an alternative colour measurement tool with reasonable accuracy and reliability [96-101]. Schropp et al [102] evaluated the efficacy of digital photographs and computer graphic software for colour matching compared to conventional visual matching, and concluded that the former method is more reliable. In terms of reproducibility, a clinical study conducted by Sagel et al [103] found that the clinical measurement of mean tooth colour from digital images was highly reproducible if proper calibration protocols were used.
From the previous information, it becomes apparent that colour selection of restorative material usually involves the measurement of colour either subjectively (through the human eye) or objectively (with an instrument). Visual methods of specifying colours are subjective, inconsistent and may differ intra or inter-observer. Instrumental colour analysis, on the other hand, allows a more objective, quantitative, accurate and reproducible colour evaluation. Owing to these benefits, instrumental evaluation is the most common colour measurement method employed in all previous studies concerning the colour stability of composite resins. For the purpose of this study, instrumental colour measurement with a reflectance spectrophotometer (Medical High Technology SpectroShade™ Micro, Optic Research, Switzerland; Version 2.41) was used to measure colour changes.
Table 2.2: Some of the instrumental colour measurement devices.

<table>
<thead>
<tr>
<th>Devices</th>
<th>Type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shade-Eye-NCC™</td>
<td>Colourimeter</td>
<td>Shofu Dental Inc., San Marcos, USA</td>
</tr>
<tr>
<td>ShadeVision/ShadeRite™</td>
<td>Imaging</td>
<td>Dental Visiona X-Rite Inc., Grandville, USA</td>
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<tr>
<td></td>
<td>Colourimeter</td>
<td>USA</td>
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<tr>
<td>ShadeScan™</td>
<td>Colourimeter</td>
<td>Cynovad, Montréal, Canada</td>
</tr>
<tr>
<td>Easyshade Compact™</td>
<td>Spectrophotometer</td>
<td>Vident, Brea, CA</td>
</tr>
<tr>
<td>Shade- X-Rite™</td>
<td>Spectrophotometer</td>
<td>Grandville, MI</td>
</tr>
<tr>
<td>SpectroShade Micro MHT™</td>
<td>Imaging</td>
<td>Niederhasli, Switzerland</td>
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<tr>
<td></td>
<td>Spectrophotometer</td>
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<tr>
<td>CrystalEye™</td>
<td>Imaging</td>
<td>Olympus America, Center Valley</td>
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<tr>
<td></td>
<td>Spectrophotometer</td>
<td></td>
</tr>
<tr>
<td>ClearMatch™</td>
<td>Digital image analysis</td>
<td>Clarity Dental, Salt Lake City, UT</td>
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</tbody>
</table>
3.1 Historical Perspective

According to McLean, German chemists during World War II developed a self cured methacrylate resin. The material was the first plastic material introduced to replace the only dental aesthetic material previously available; silicate cements. Despite their initial success, chemically cured acrylic resins were plagued with poor colour stability and associated with inferior mechanical properties in concert with a high polymerisation shrinkage of 7% that predisposed them to microleakage [104].

In an attempt to minimize the drawbacks of acrylic resin, particularly the high polymerisation shrinkage, many researchers added filler particles to the acrylic resin. One of these researchers, Dr Rafael Bowen, explored the possibility of using epoxy resins (di-glycidyl ether of bisphenol-A) mixed with silica particles. However, the polymerisation of the material was inhibited in the presence of moisture [105]. To overcome this problem, Bowen added methyl methacrylate groups to the end groups of the epoxy resin resulting in the discovery of the famous Bis-GMA (bisphenol-A-glycidyl methacrylate) in 1959 [9]. This pivotal discovery of the Bowen resin instigated the eventual introduction of composite resins into the field of restorative dentistry. Together with acid etching of dental enamel, proposed by Buonocore in 1955 [106], the introduction of composite resins have revolutionized dentistry or more specifically aesthetic restorative dentistry.
3.2 Composition

In polymer technology, the term composite is defined as a multiphase substance formed from a combination of materials that differ in composition or form, that remain bonded together and retain their identities and properties [107]. The interfaces between components are maintained and act synergistically to provide an improved physical mixture that is not obtainable in any of the original components acting alone [108]. In restorative dentistry, dental composite resins consist of three main components: (1) organic resin (matrix phase), (2) inorganic filler particles (dispersed phase), and (3) the coupling agent that chemically bonds the inorganic filler to the resin matrix (surface interfacial phase) [109].

3.2.1 The Resin Matrix

The organic phase of composite resins is generally composed of a polymeric matrix built up by a chain of repetitive mono-, di- or tri-functional monomers [8, 109]. Various types of monomers systems have been used in composite resins. To this day, almost 80-90% of commercial composite resins contain a monomers system based on the Bis-GMA resin pioneered by Bowen [110]. Bis-GMA has a high molecular weight monomers system and an associated high viscosity that makes it more difficult to add filler to the monomers. In order to lower the viscosity and to accommodate better filler load, manufacturers add low molecular weight (low viscosity) monomers e.g. tri-ethyleneglycol dimethacrylate (TEGDMA) and ethyleneglycol methacrylate (EGDMA).

The bulky aromatic groups in the central part of Bis-GMA form a larger barrier for the monomers chains to rotate and align for cross linking during the polymerisation process resulting in a lower degree of conversion. The addition of long chain, flexible dimethacrylates of TEGDMA has been shown to increase the degree of conversion of composite resins. As a consequence, the degree of conversion in Bis-GMA and TEGDMA copolymers has been found to decrease with an increasing content of Bis-GMA.
The presence of residual unreacted monomers increases the susceptibility of the organic resin matrix to degradative reactions that in turn result in discolouration of the material [8]. However, TEDGMA have been shown to be hydrophilic and absorb water that could lead to penetration of staining agents [112, 113].

Another monomers frequently used as the matrix for resin composites is urethane dimethacrylate (UDMA). Introduced by Knight et al in 1973, this monomers has been used alone or in combination with other monomers systems such as Bis-GMA. Results of in-vitro studies indicate that the monomers exhibited not only improved mechanical properties, but also less hydrophilicity hence, less water absorption, than did polymers of Bis-GMA or of TEGDMA [8, 111]. According to Sideriduo et al [113], gradual replacement of TEGDMA with UDMA or/and Bis-EMA in co-polymerisation with Bis-GMA resulted in more flexible resins with lower water absorption, depending on the TEGDMA content. These favourable properties, according to some authors, are associated with better colour stability of the material [114].

Bis-GMA has been controversially implicated in the leaching of estrogenic bisphenol-A monomers into the environment [115, 116]. However, this remains a subject of debate in the dental literature [117]. Due to ongoing discussion on the (possible) side effects of Bis-GMA, it became the philosophy of some manufacturers (e.g. GC America) to avoid the incorporation of this monomers system in their direct restorative products.

Apart from a monomers system, there are other important resin matrix components including an initiator (e.g. camphoroquinone and amine for light cured composite resins and amine-peroxide system in self-cured composite resins), co-initiators, polymerisation inhibitors (to extend working time and storage stability) and various pigments. Earlier studies have shown that the presence of amine contributed to the discolouration of the composite. This is thought to be related to the tendency of
isomeric dimethacrylates to form yellow-tinted charge-transfer complexes with the tertiary aromatic amines [109, 126].

3.2.2 The Inorganic Filler Particles

The disperse phase of composite resins is made up of inorganic fillers. Some common filler particles include ground quartz, alumina silicate, pyrolytic silica, lithium aluminum silicates, or borosilicate glass. In many composites, quartz is partially replaced by heavy metal oxides of barium, strontium, zinc, aluminium or zirconium to impart radio-opacity to the material [109]. The addition of inorganic fillers was pioneered at the time when various attempts were being made to improve the physical and mechanical properties of acrylic resin. Alterations in the filler particle size, distribution, and quantity were noted to dramatically affect mechanical properties including compression strength and/or hardness, flexural strength, the elastic modulus, dimensional stability, coefficient of thermal expansion, water absorption, and wear resistance [8, 10, 109, 118, 127-131]. A plethora of investigations have been published on these properties.

The more significant advances in composite resins are largely attributable to the remarkable improvements and modifications in the inorganic component of the material. Manufacturers have employed various techniques to increase filler loading, such as milling or grinding, air abrasion, precipitation, ultrasonic interaction, erosion or through condensation to produce filler particles of various sizes [130].

The first classification system of composite resins was introduced by Lutz and Phillips [132]. This was based on the average size of the filler particles, manufacturing techniques, and the chemical composition of the filler particles. The authors divided composite resins into macro-filler composites (particles from 0.1 to 100 μm), micro-filler composites (0.04 μm particles) and hybrid composites (fillers
of different sizes). Several other classification systems based on filler content have since been suggested by numerous authors [133].

Traditional composite resins are described as containing macro-filler particles which are mechanically ground or crushed from larger pieces of purely inorganic materials (such as quartz), into particles or splinters of irregular shape, with sizes ranging from 0.1 to 100µm. Due to the large size and extreme hardness of the filler particles, the resin matrix tends to wear faster than the fillers. Clinically, this can give rise to a rough surface after polishing, wear from prolonged function, and increased susceptibility to discolourations [8, 132].

Micro-filled composites, as their name implies, are composites that are filled with very small pyrogenic or colloidal silica particles with size averages in the order of 0.04 µm [132]. The small filler particles in the micro-filled composite resins render the material highly polishable. However, the high surface area-to-volume ratio of the colloidal silica particles creates problems in attaining the higher level of loading found in composites containing homogenous filler particles. Consequently the materials have poor mechanical properties and are less than ideal for use in heavy stress bearing situations. To increase the filler loading, most manufacturers add pre-polymerised resin particles. The pre-polymerised filler particles are produced by adding colloidal silica to the resin matrix, which is then polymerized and subsequently ground into particles averaging approximately 25 µm. These smaller particles of highly filled resin are then added to a resin matrix creating a heterogenous micro-filled material [8, 109].

A composite resin classified as a hybrid contains colloidal silica particles of different sizes [132], typically 1-µm to 5-µm with a filler loading that approximates nearly 75% by weight. Hybrid composites were created to overcome the inherent weakness of micro-filled composites (lack of mechanical strength) and macro-filled composites (excessive wear and lack of esthetics). Although demonstrating good handling characteristics and initial high polishability, polish retention is rather poor due to the presence of substantially larger filler particles similar to the macro-fillers.
The presence of larger filler particles also results in a significant refractive index mismatch with the resin matrix. In preceding sections (Section 2.1.2) it has been shown that when a substance contains particles of a different refractive index, a light beam striking the substance will be scattered and individual wavelengths will bend differently, yielding a substantially different spectrum returning to the eye and produce an opaque material. Therefore, manufacturers developed micro-hybrids with reduced particle sizes of 0.04-µm to 1-µm. Gradia Direct™ from GC America is an example of composite resins containing this type of system. The manufacturer claims that micro-hybrid resin composite with pre-polymerised resin fillers have ‘much appreciated’ advantages in terms of aesthetic, polishability and wear resistance [134].

The emergence of nanotechnology has seen the incorporation of nano-sized fillers into composite resins. Unlike conventional particles that are milled or ground down from larger-sized particles into smaller particles (from one to several microns), nano-particles, are built up on the molecular level. There are two types of nano-composites; nano-filled and nano-hybrids. Nano-filled composite resins e.g. Filtek™ Supreme Plus (3M ESPE) are composed of nanomeric particles dispersed as single units within the resin matrix and/or in combination with agglomerated clusters of the nano-particles [12]. According to the manufacturer, the nano-cluster filler particles consist of loosely bound aggregates of engineered nano-filler particles. As the particles in the nano-cluster are not tightly sintered, their wear rate and pattern during abrasion are more similar to the nano-filled matrix. The manufacturer states that the nano-particles in the nano-cluster wear by breaking of the individual particles rather than plucking of the whole cluster, resulting in better polish retention [135].

A nano-hybrid composite (Premise™ Kerr/Sybron) combines both nanometer-sized particles with more conventional filler technology [129]. Another type of nano-composite, Ceram-X™ (Dentsply) is considerably different. It is an ormocer-based nano-composite. Rather than existing as an individual particle or an agglomerated cluster, the nano-particle becomes part of the resin matrix [129].
Nano-fillers have a significant effect on the optical properties of composite resins [12]. As the size of the particles is far below the wavelength of visible light, they are unmeasurable by the refractive index. Therefore, there is an almost negligible scattering of light, and most of the longer wavelengths of the light transmit directly through the material resulting in a high translucency [12].

Based on their filler content, composite resins can be further classified into flowable composite, packable / condensable composite and fiber reinforced composites, however, this will not be presented here. There appears to be a strong research focus on filler technology, especially in the development of bioactive or “smart” composite with caries prevention capacity eg calcium and phosphate or fluoride ion-releasing [129, 136].

3.2.3 The Interfacial Phase

The third basic component of composite resins, the interfacial phase or the coupling agent, connects the resin matrix and the inorganic filler. Commonly, vinyl, epoxy and methyl silanes are used. The compound molecules have a silane group at one end and a methacrylate group at the other end, and can bond with both the filler and the resin matrix respectively. The interface between the filler and resin matrix involves three types of molecular interaction – covalent bonds, hydrogen bonds and hydrophobic interactions. The covalent bonds are derived from double carbon bonds (C=C) between the residual double carbon group in the pre-polymerised fillers and the methacrylate matrix monomers, while the hydrogen bonds are derived from polar constituents such as the – OH, – NH, and – C=O groups. The hydrophobic interactions involve molecular bonds between organic groups such as alkyl groups [134]. The quality of the bond is crucial as it influences the abrasion resistance, polishability and surface hardness of the restorative material [125].
3.3 Finishing and Polishing Systems

Following placement of composite resins, it has been established that finishing and polishing are essential in determining the success of a restoration [137]. For this reason, manufacturers have introduced a wide variety of burs, diamonds, abrasives, strips and pastes for finishing and polishing composite resins [137]. Polishing techniques range from multiple steps with sequential use of less abrasive materials to those with one-step polishing technique [138-140].

The effect of polishing on the colour stability of composite resins may be related to the surface topography of the material after the polishing procedure [141]. Generally, the rougher the surface, the more susceptible the material is to extrinsic staining [142]. Surface morphology following polishing is closely related to the filler size, shape, and loading in the resin composite. The larger the filler particles, the rougher the surface will be after polishing [143, 144]. Factors related to the abrasive system such as flexibility of the material in which the abrasive is impregnated, hardness of the abrasive, and geometry, speed and form of application of the instruments used are also crucial [145].

Many studies have been conducted to establish a finishing and polishing procedure that will produce a smooth-surfaced restoration. Studies have shown the smoothest composite surface is obtained under polyester matrix film [28, 138-140, 146-148]. Park et al [149] have shown that in micro-hybrid composite resins, there is no difference in surface discolouration between mylar strips finished and the polished surface. They have postulated that this is due to the relatively smaller filler particles, a shorter inter-filler distance in the micro-hybrid composites and the lower resin component present on the surface of the mylar strips finished micro-hybrid composites. However, several other investigations have shown that removal of the polymer-rich, outermost resin layer is essential in achieving a stain-resistant, more esthetically stable surface [71, 138, 150-152].
Aluminum oxide-based abrasives devices such as Sof-Lex™ discs have also proven their efficiency in finishing and polishing composite restorations [143, 151, 153-158]. It has been shown that when used in sequentially decreasing abrasiveness, they promote uniform wear as both fillers and matrix are reduced evenly. Some studies [159, 160] support the idea that multiple-step polishing techniques provide a lower degree of discolouration for both composite resins, while others [138, 139, 161] promote the use of one-step polishing method. Recently, Berger et al [162] recommended the use of finishing systems supplied by the composite’s manufacturer as they observed a lower surface roughness and staining in composite resins polished with finishing systems from the same company. However, there is no consensus in the literature about the effectiveness of different finishing and polishing procedures in relation to the staining susceptibility of composite resins.
3.4 Colour Stability of Composite resins

Composite resins have been shown to be prone to discolouration on exposure to an oral environment over a period of time. Horsted – Bindslev and Mjor [163] believe the discolouration of the composite resins may be caused by intrinsic and extrinsic factors. Intrinsic factors involve alterations or changes in the chemical structure of the composite resins under physical and chemical conditions, while extrinsic factors are mainly due to surface staining from absorption or adsorption of exogenous substances [21, 22].

3.4.1. Intrinsic Staining

As described earlier, the chemical structure of composite resins can be represented in four parts: an organic resin matrix, inorganic filler particles, a silane coupling agent that bonds both organic and inorganic phase and the initiator–accelerator system [8]. An alteration or changes to any of these components within the material may result in a permanent discolouration at the subsurface and internal layers of composite resins.

The susceptibility of composite resins to intrinsic staining varies according to the chemical composition of resin matrix, types and amount of filler and initiator and accelerator system [164-167]. Different monomers type in the organic resin matrix may affect the colour stability of composite resins [168]. Studies have found that this may be directly related to monomers hydrophobicity [11, 169] and water absorption properties [70, 114, 171]. Water absorption produces deleterious effects including hygroscopic swelling, plasticization, softening, oxidation and hydrolysis of the resin matrix that leads to penetration of staining pigments [172, 173].

It has been shown that urethane dimethacrylate (UDMA) exhibits less staining compared to Bisphenol A-glycidyl methacrylate (Bis-GMA), which is the common resin monomers used [70].
Conversely, composite resins with hydrophilic monomers e.g. triethylene glycol dimethacrylate (TEDGMA) exhibit higher water absorption [174], and therefore permits penetration of any hydrophilic colourant into the resin matrix. This is further substantiated in investigations by Douglas and Craig [114], who have concluded that composite resins with lower water sorption rates arising from the use of hydrophobic (less affinity to water) resin monomers are less prone to discoloration.

The colour properties of composite resins are influenced by their filler content [11, 175, 176]. Arikawa et al [177] have demonstrated that the light transmittance/diffusion characteristics of composite resins and colour are significantly affected by the size and shape of filler particles as well as filler load. This is in agreement with results from another study by Lim et al [178], in which the effect of filler on colour parameters (lightness, hue and chroma) was evaluated. It was found that the amount of filler significantly influenced the lightness of composite resins.

The staining potential of composite resins is related to its surface structure. The rougher the surface, the more susceptible the material is to extrinsic staining [142]. The surface characteristic of composite resins depends on types of fillers used [178-180] and finishing or polishing technique. Fillers appear to affect how well a composite finishes [168]. In general, smaller filler particles allow better polishability, thus producing a smoother surface [11]. Recently, composite resins with nano-sized particles have been developed with this thought in mind. It has been demonstrated that nano-filled or nano-hybrid composite resins with average filler particle size of 5-100 nanometers [12] have less discolouration [36] compared to the traditional micro-filled composite resins with quartz particles of various size ranging from 0.01 – 0.1µm. However, studies by Ertas et al and Guler et al [26, 182] have shown contradicting results. Nano-composite resins did not exhibit greater stain resistance to the colourant tested. This study will therefore investigate the colour stability of nano-filled composite resins.

Besides fillers, the initiator or accelerator in composite resins can also produce colour changes in composite resins [183-186]. Studies found that initiators such as tertiary amine (N,Ndimethyl-p-
toluidine) in chemically cured resin or the photoinitator (camphoroquinone) in light polymerized based cement may oxidize into a yellowish-brownish coloured compound thus leading to the discolouration of the composite resins [185, 187-190]. In addition, hydroquinone used as the inhibitor for spontaneous polymerisation of composite resins, was also found to cause discolouration [190].

Results from laboratory studies reveal that the degree of polymerisation also plays a role in the colour stability of composite resins [183-186]. Suboptimal polymerisation leaves unreacted initiators or accelerators in the composite resins that in turn result in a yellowing of the composite resins [190, 193]. Furthermore, incomplete conversion of monomers as a result of insufficient polymerisation is related to increased water absorption of the composite resins which subsequently could potentiate the risk of discolouration [194].

Several studies have investigated various physico-chemical conditions in the oral environment that may alter or change the chemical structure within composite resins. The effect of daylight [195] or ultraviolet irradiation [196, 197], thermal changes and water [195, 198-200] on colour properties of composite resins have been widely documented. Rosentritt [201] evaluated the colour of composite resins after 24 hours of photo-aging found that the composite resins become yellower, greener and darker after exposure. Similar findings were also observed by other researchers [202-207].

Apart from photo-aging, colour change in composite resins as a result of water aging has been described. Brauer [208] has reported that there was significant colour change in composite resins when stored in 60°C water. This result is consistent with a report by Vichi et al (2004) [200]. However, in the oral environment, a slow intermittent temperature fluctuation is more likely. When composite resins was subjected to intermittent exposures of high and low temperatures in a humid or moist environment (thermocycling) to simulate the oral condition, the material become darker and decreased in translucency after thermocycling [205, 209-216].
The colour change of composite resins upon exposure to various aging conditions is time and dose dependent, and may be attributed to changes in the surface microstructure and chemical composition within the matrix of the composite resins [217]. Changes have been observed not only within the matrix but also at the interface between organic matrix and filler particles. On this note, Schulze et al [167] found that there is a decrease in barium and silicone on the surface of the composite leading to surface degeneration along with rearrangement of the polymer molecule(s). Similarly, Lin et al [218] postulate that a weakening of the chemical bonds in the organic polymer create pores within the resin matrix as well as exposure of filler particles, thereby contributing to the colour changes in composite resins. Surface deterioration induced by the physico-chemical changes creates microcracks within the material that facilitate the penetration of stains.

In this study, the selected composite resins will be subjected to accelerated aging through thermocycling prior to immersion in staining solution.

### 3.4.2. Extrinsic Staining

Extrinsic discolouration of composite resins may occur as a result of staining by the pigments from exogenous contaminants. Unlike intrinsic staining, extrinsic discolouration involves surface or subsurface adsorption or absorption of chromogenic substances and can be removed mechanically or chemically [26]. Colour alteration of composite resins after immersion in various liquid beverages has been a subject of great interest in many studies. Coffee [24-30, 36, 37, 219-222], tea [21, 24-27, 30-33, 221-223], alcoholic beverages [26-28, 30, 34, 35, 37, 207, 219, 222], carbonated drinks [24, 26, 28, 33, 34, 36, 207, 220-224] and fruit juices [24, 33, 34, 36, 222, 225] are the common staining agents investigated.

Staining by red wine may be attributed to the presence of alcohol and low pH. This is supported in conclusions of a study by Villalta et al [35], where presence of alcohol and low pH (as in red wine)
resulted in surface degradation of the composite resins, therefore contributing to the intrinsic colour changes. In another study [227], SEM analysis of a composite resin after pH cycling revealed that there was disintegration of the polymer matrix and degradation of silane bonding between filler and organic matrix, leading to protrusion of filler particles as well as voids from particle loss. Consequently, surface roughness was noted. As indicated earlier, rough surfaces increase the retention of chromogenic agents or colour pigments.

Similarly, alcohol affects the colour of composite resins through softening of the surface material [228], facilitating the absorption of external pigments [229]. A recent study by Aguir et al [230] showed that alcohol caused only superficial staining. It was believed that because of the presence of water in the subsurface of the composite resins, alcohol was ineffective in removing the polymer in the subsurface. Furthermore, the surface dissolution by alcohol might be more selective in the linear polymer than the cross linked structure. In addition, Satou et al [171] believe that the discolouration of composite resins are the result of binding between hydrophilic un-reacted component in the initiators in the composite resins and the hydrophilic pigments in the red wine.

There has been a lot of speculation about the discolouration of composite resins by coffee and tea. According to Um and Ruyter [21], discolouration caused by coffee and tea is due to yellow colourants in the beverages. The investigators believe that yellow colourants in tea have higher polarity compared with coffee. Therefore, tea caused adsorption of colourant on surface of composite resins and can be mechanically removed. While coffee stains composite resins by adsorption and absorption of colourant into the organic matrix of material as a result of the compatibility of yellow colourant in coffee with the organic matrix of composite resins. Another group of researchers [25] found that the penetration of the stain is noted to be superficial, approximately 3- 5 µm, and mechanical cleaning could reduce the staining. The greatest degree of discolouration by coffee is observed during first week of immersion. Addition of sugar in coffee accentuates the staining by coffee [231, 232]. This is thought to be caused by the sticky effect produced by sugar. [231].
Colour alteration in composite resins when subjected to various organic and chemical substances has been reported. Staining by alcohol based mouthwashes [30, 233], fluoride varnishes [234] and bleaching agents [235-238] has been described. Khokhar et al [70] and Omata et al [27] found that the addition of chlorhexidine and saliva increased the staining effect of coffee and tea. Leard et al [32] explains that this phenomenon may be attributed to the binding of the cationic (positive charged) in the anti-septic mouthwash surface anionic (negative charged) surfaces of chromogenic agents in beverages.

Salivary esterase was found by Lee et al [239] to cause increased in surface roughness and perceivable colour change in composite resins. The following year, the same group of researchers [240] published their work on the effect of the combined treatment of organic and chemical solutions on the colour of composite resins. They discovered that the discolouration of composite resins by methylene blue dye after immersion in a combined organic solution (mucin and serum) and chlorhexidine or carbamide peroxide was due to absorption of the stains by a deteriorated resin.

Colourants or dyes are usually added to enhance the appearance of food and may have potential to stain composite resins [241]. Research by Dietschi et al [11] showed that composite resins are also susceptible to staining by artificial food dyes (erythrosine and sunset yellow). This is supported in recent findings by Rutkunas et al [37]. The researchers noted that the concentration of food colourant used by the manufacturers ranged from 0.02% up to 3%. They used food colourant sunset yellow and quinoline yellow dyes at a concentration of 0.1%.

In Asia, spices are used to flavor and colour local dishes. Turmeric, paprika and tamarind are the common spices used to enhance the colour of Asian cuisine [242, 243]. The effect of these spices on the colour stability of composite resins, however, has not been fully researched. Only one study by Stober et al [30] reported that 0.1% turmeric solution caused severe discolouration, with total amount of
colour difference (represented as Delta E) more than 10. In a more recent study by Imamura et al [244],
curry is noted to stain composite resins. However, neither author describes the staining mechanism of
the spices. Due to the extensive use of spices in Asian countries, the aim of this study is to determine
the effects of spices on the colour stability of composite resins.
CHAPTER 4

LITERATURE REVIEW: BASIC COMPOSITION OF SPICES

The American Food and Drug Administration, in the code of Federal Regulations on food labeling: Spices, Flavourings, Colourings and Chemical Preservatives, states that:

“Spices are aromatic vegetable substances, in the whole, broken, or ground form, whose significant function in food is seasoning rather than nutrition. They are true to name and from them no portion of any volatile oil or other flavouring principle has been removed.” [245].

Spices include turmeric, paprika and tamarind.

4.1 Turmeric

Turmeric is a spice derived from the rhizome curcuma longa, belonging to the Zingiberaceae (ginger) family. Turmeric is a perennial herb with thick, fleshy orange-brown or pale yellow rhizomes (Figure 4.1)[242].

Curcumin is the major constituent of turmeric that imparts the yellow gold colour of the spice [246, 247]. Chemically, curcumin, desmethoxycurcumine and bis-desmethoxycurcumine, are polyphenolic [248] compounds of diferulomethane that contain flavonoids and free anthraquinone [249]. The spectrum of standard curcumin reveals three peaks having maximum values of 413, 412, and 404 nm, representing curcumin, demethoxycurcumin, and bis-demethoxycurcumin, respectively [250]. The absorption peak in the visible region (420 nm) explains the yellow colour appearance of the substance.
For centuries, turmeric has been used for both its colour and flavour. In the food industry, turmeric is used in mustard paste, curry powder, canned beverages, baked products and dairy products. It is used mainly as a natural colourant replacing synthetic colourants such as tartrazine [243].

Known as the Indian Gold, turmeric has been extensively researched and has been shown to have great promise as a therapeutic agent due to its anti-oxidant, anti-inflammatory, anti-viral, anti-bacterial, anti-fungal, and potential anti-cancer actions. These properties are attributed to the presence of curcumin, an active component in turmeric [246, 251-253].

NOTE:
This figure is included on page 47 of the print copy of the thesis held in the University of Adelaide Library.

Figure 4.1: Turmeric (adapted from www.purplesage.org.uk [279]).
4.2 Paprika

Paprika, a fruit of the genus *Capsicum annum* is a member of the Solanaceae family that includes tomato, potato, tobacco and petunia. Spices belonging to the Genus Capsicum are numerous, including all major peppers (Figure 4.2) [246].

Paprika oleoresin is an extract of capsicum that has been used as a natural dye, colourant and flavour. There has been extensive research into isolation and characterization of the colour of paprika. Chromatography evaluation has revealed that the bright red colour of paprika originates from the carotenoid and capsaicinoids pigments contained in the paprika. In spectrophotometry, these pigments show maximum absorption at about 462 nm and 470 nm. Capsaicin is the major flavouring compound, whereas capsanthin and capsorubin are major colouring compounds [255].

Paprika is widely used as a seasoning ingredient to flavour meat as well as colouring agent in both household and commercial use such as cheese, chilli sauce, salad dressing and curries. It gives a bright red colour, and an exquisite pungency, taste and aroma to the food. In addition, it is used dried or fresh in various pharmacological preparations. It has a long history as a source of biologically active compounds, such as flavonoids, phenols, carotenoids and capsaicinoids [242].

NOTE:
This figure is included on page 48 of the print copy of the thesis held in the University of Adelaide Library.

Figure 4.2: Paprika (adapted from www.homecooking.com [280]).
4.3 Tamarind

Tamarind comes from the fruit of *Tamarind indica*, belonging to the Leguminosae family. *Tamarindus indica* is a multipurpose tropical fruit tree. Almost all parts of the tree find some use or other in the food, chemical, pharmaceutical and textile industries. The properties of this species have been extensively studied, particularly with reference to the fruit pulp (Figure 4.3)[256].

The fruit of the tamarind has blackish brown pods with seeds containing naturally occurring plant acids such as tartaric acid, carboxylic acids, palmitic acid as well as sugar that contribute to the outstanding sweet acidic taste. The fruit contains a variety of pigments e.g. the red colour is due to the water-soluble red-rose anthocyanin pigment. Flavonoid is the major brown/black colour pigment [257].

The tamarind fruit pulp has been an important culinary ingredient for souring curries, sauces, chutneys and beverages for a long time. Tamarind fruit is also reported to be used for the preparation of wine like beverages. In South East Asia, fibres are removed from the fruit pulp, which is mixed with sugar, wrapped in paper and sold as toffees [242].

Tamarind is also extensively used in traditional medicine for treating several common ailments as an anti-fungal and anti-bacterial. The pharmacological potentials of tamarind are associated with the presence of flavonoid or poly-phenol components, for example gallic acid [246].

NOTE:
This figure is included on page 49 of the print copy of the thesis held in the University of Adelaide Library.

Figure 4.3: Tamarind (adapted from www.manjulaskitchen.com [281]).
CHAPTER 5
MATERIALS & METHODS

5.1 Test material preparations

Two commercially available composite resins shown in Table 5.1 were used in this study.

Table 5.1: Composite resins used in this study.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Type of composite</th>
<th>Material composition</th>
<th>Shade</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek Supreme XT™</td>
<td>Nano-composite</td>
<td>Filler: 78.5% by weight (63.3% by volume); non-aggregated 20 nm silica filler, 4 to 11 nm zirconia filler, and cluster filler (comprised of 20 nm silica and 4 to 11 nm zirconia particles)</td>
<td>A2</td>
</tr>
<tr>
<td>Gradia Direct X™</td>
<td>Micro-filled</td>
<td>Fillers: 73% by weight (64% by volume) silica and pre-polymerised fillers (average particle size 0.85 microns)</td>
<td>A2</td>
</tr>
<tr>
<td></td>
<td>hybrid</td>
<td>Resin: UDMA and Bis-GMA.</td>
<td></td>
</tr>
</tbody>
</table>
Based on the results obtained in the pilot study and power calculations, a sample size of 5 for each group was determined. Twenty cylindrical specimens were fabricated from each type of composite resin investigated utilising a stainless steel matrix with a central round hole of 8mm in diameter, 3 mm in depth (Figure 5.1).

![Figure 5.1: Composite resins in stainless steel matrix.](image)

Each matrix was placed between two glass slabs which were lined with mylar strips. Each composite resin was placed in two increments of 1.5 mm each into the mould. The specimens were then covered with mylar strips and a glass slide placed over the material to extrude the excess material.

The composite resins were light polymerized with a LED curing light (Satelec™ Mini LED/ with output power of 1250 mW/cm²) according to the manufacturer’s instructions. The following chart (Table 5.2) shows irradiation time and depth of cure for each composite resins as recommended by the manufacturer. After polymerisation, all specimens were removed from the mould and all surfaces were further light cured for another 20 seconds.
Table 5.2: Irradiation time and depth of cure.

<table>
<thead>
<tr>
<th>Brand Name</th>
<th>Irradiation time (seconds)</th>
<th>Depth of cure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filtek Supreme XT™</td>
<td>20</td>
<td>2.0 mm</td>
</tr>
<tr>
<td>Gradia Direct™</td>
<td>24</td>
<td>2.5mm</td>
</tr>
</tbody>
</table>

Subsequently, all specimens were polished with Sof-Lex™ aluminium oxide discs (3M/ESPE, St Paul, MN USA) mounted on a electric handpiece in progressively finer grits; at 10,000 rpm for 15 seconds with coarse and medium discs and followed by fine and superfine discs at 30,000 rpm for 15 seconds. Surfaces were rinsed and dried between disc sequences. This procedure was performed only on top surfaces while bottom surfaces were mylar strips finished.

After polishing, all specimens were stored in distilled water at 37°C for 24 hours. All specimen preparation and finishing procedures were carried out by the same operator, to reduce variability.

5.2 Thermocycling process

In order to simulate oral conditions, all samples were subjected to 500 thermocycle rounds between 5 and 55 °C with 20 seconds dwell time [282] prior to immersion in staining solution.
Figure 5.2: Chart representing sample preparation.
5.3 Staining process

Three staining solutions as described in Table 5.3 were used. Distilled water was used as the control group. In concurrence with Stober et al [30], 0.1% turmeric, paprika and tamarind solutions were prepared by diluting 1g of spice in 1000ml of boiled distilled water.

Table 3.3: Type of staining solutions used in this study.

<table>
<thead>
<tr>
<th>Type of staining solution</th>
<th>Brand name</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>Faculty of Health Sciences, University of Adelaide, Australia</td>
<td></td>
</tr>
<tr>
<td>0.1% Turmeric</td>
<td>MasterFoods™</td>
<td>Mars Food Australia</td>
</tr>
<tr>
<td>0.1% Paprika</td>
<td>MasterFoods™</td>
<td>Mars Food Australia</td>
</tr>
<tr>
<td>0.1% Tamarind</td>
<td>Maharajah's Choice™</td>
<td>Ostindo International Ltd</td>
</tr>
</tbody>
</table>

Twenty specimens from each type of composite were then randomly divided into 4 groups (n=5). Each specimen was arranged vertically in a customized holder (Figure 5.3) to ensure both finished surfaces exposed to the staining solutions and immersed in a container containing 50 ml of each staining solution and distilled water (control) at 37 ºC.

All specimens were kept in an incubator and vibrator (Figure 5.4) to prevent precipitation of the spice particles in the solution for 24 hours. Fresh solutions were prepared every day. Prior to colour measurements, all specimens were rinsed with distilled water at 37 ºC.
Figure 5.3: Vertically placed specimens in customized holder.

Figure 5.4: Staining solutions in incubator and vibrator.
5.4 Colour Assessment

The colour of composite resins can be determined by varying methods, including visual assessment and instrumental measurement by a colourimeter or spectrophotometer. In this study, a reflectance spectrophotometer (Medical High Technology SpectroShade™ Micro, Optic Research, Switzerland; Version 2.41) was used to measure colour changes. This system uses two D65 (daylight) light sources illuminated at 45° and reflected to the detector screen at 0°. CIE L*a* b* parameters and equations were used.

5.4.1 Spectrophotometer set-up

A customized positioning jig made from self cure acrylic (Figure 5.5) was fabricated to obtain consistent and standardised orientation of specimen for colour measurement. All specimens were placed within the circle on the neutral grey background. The indices on the jig (as indicated by the arrows) allow consistent repositioning of the sensor headpiece of the spectrophotometer over the jig. The black jig also eliminates the influence of external light during colour evaluation.

![Figure 5.5: Positioning jig.](image)

Prior to any measurement, the spectrophotometer was calibrated to white and green ceramic tiles supplied by the manufacturer. Measurements were performed according to ISO 7491 guidelines [278] using a neutral gray background.
5.4.2 Colour Measurement

Colour measurement at baseline, after thermocycling, 24 hours (1 day), 72 hours (3 days) and 168 (7 days) [283] of immersion in staining solutions were recorded with a reflection spectrophotometer under the D65 (daylight) illuminant over a white background using CIE L* a* b* parameters. L* represents value (ranges from (100) white to (0) black), a* refers to chromacity in red and blue axis (+a red/ -a green) and b* refers to chromacity in yellow and blue axis (+b yellow/ -b blue).

The following CIE formula will be used to determine the total colour difference after immersion in staining solution.

\[ \Delta E = \left[ (\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right]^{1/2} \]

A total colour change (\( \Delta E \)) more than 1 is visually perceptible, and (\( \Delta E \)) more than 3.3 is considered clinically unacceptable [68-71].

5.5 Statistical Analysis

SPSS Version 17.0 was used for statistical analysis. Descriptive analysis that includes mean and standard deviation was determined for each of the test groups. To test the significance and possible interactions of each factor, repeated measures analysis of variance (ANOVA), with one within-unit factor (three measurement times) and three between-unit factors (two materials, finishing methods and four staining solutions) were used. Bonferroni post hoc tests were applied to each factor where significant differences between-unit factors were found. The level of significance for all statistical testing was pre-determined at a p-value of 0.05 or less.
CHAPTER 6

RESULTS

The variables used in this study were:

(1) Staining solutions (turmeric, paprika, tamarind and distilled water),
(2) Immersion time (24 hours (1 day), 72 hours (3 days), 168 hours (7 days)),
(3) Materials (Filtek Supreme™ and Gradia Direct™),
(4) Finishing methods (Sof-Lex™ discs and mylar strips),

The mean and standard deviations for colour changes (ΔE) by the type of composite are presented in Table 6.1. The results indicated that there was colour difference in both types of composite resins after thermocycling before immersion in the staining solution. Calculated mean colour difference (ΔE) values were between 1.53 and 2.94. The average magnitude of the colour difference (ΔE), however, was below the clinically unacceptable value (3.33).

6.1 Effect of Spices on Colour Stability of Composite resins.

Among all the staining solutions tested, the highest colour deviation was obtained in the turmeric group, with mean ΔE ranges between 17.92 and 55.25 (Table 6.1). The colour differences exhibited were significantly higher than the other staining solutions. As clearly depicted in Figure 6.1, this finding was confirmed by the post-hoc test. Regardless of the method of finishing, both composite resins presented clinically perceptible colour changes after 24 hours immersion in the solution and ΔE values increased with the staining time. After remarkable colour changes in the
first 24 hours, there was steady increase in the ΔE values throughout the investigation period in Filtek Supreme™, while in Gradia Direct™, gradual changes in the ΔE values were observed between 24 and 72 hours before the values increased considerably thereafter (Figure 6.2).

Paprika, on the hand, showed clinically noticeable colour changes (ΔE > 3.3) only after 72 hours immersion (Table 6.1). This was detected in Gradia Direct™ finished by either Sof-Lex™ discs or mylar strips, whereas no clinically discernible colour differences were noted in the Filtek Supreme™ throughout the period of the study. Both of the composites tested showed intense colour changes after the first 24 hours. For Gradia Direct™, there was a steady increase followed by a leveling out after 72 hours. Colour changes after 72 hours were clinically unacceptable. Filtek Supreme™ polished with Sof-Lex™ discs showed a slow increase in colour difference from 24 hours to 72 hours with steady increase noted thereafter, while an equable increase was shown by Filtek Supreme™ with mylar strips finished throughout the period of investigation (Figure 6.2).

Colour changes in the composite resins after immersion in tamarind solution ranged between 1.12 and 5.42 (Table 6.1). The colour differences (ΔE) greater than 3.33; (above clinical perceptible limit) were recorded only after 168 hours immersion with mylar strips finished Filtek Supreme™ and Gradia Direct™ finished with both methods. Gradia Direct™ displayed a different trend of colour changes to Filtek Supreme™. For Gradia Direct™, a sharp increase occurred at 24 hours followed by a gradual rise until 72 hours before an exponential increase in colour change was noted. Filtek Supreme™ also showed similar trend in the first 24 hours, followed by steady increase thereafter. None of the composite resins tested had ΔE higher than this limit (ΔE> 3.33) after storage in distilled water, yet most colour changes occurred in the first 24 hours of immersion (Figure 6.2). No significant colour changes were observed between paprika, tamarind and control solutions.
<table>
<thead>
<tr>
<th>Composite</th>
<th>Finishing method</th>
<th>Staining solution</th>
<th>24hrs</th>
<th>72hrs</th>
<th>168hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>∆L</td>
<td>∆a</td>
<td>∆b</td>
<td>∆E(SD)</td>
</tr>
<tr>
<td>Filtek Supreme™</td>
<td>Sof-Lex™</td>
<td>Turmeric</td>
<td>-3.50</td>
<td>1.33</td>
<td>15.05</td>
</tr>
<tr>
<td></td>
<td>Paprika</td>
<td>-0.25</td>
<td>0.06</td>
<td>1.13</td>
<td>1.28(0.40)</td>
</tr>
<tr>
<td></td>
<td>Disc</td>
<td>Tamarind</td>
<td>-0.67</td>
<td>0.64</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-1.24</td>
<td>-0.38</td>
<td>-0.83</td>
<td>1.85(0.55)</td>
</tr>
<tr>
<td>Filtek Supreme™</td>
<td>Mylar strips</td>
<td>Turmeric</td>
<td>-4.75</td>
<td>0.51</td>
<td>35.8</td>
</tr>
<tr>
<td></td>
<td>Paprika</td>
<td>-0.34</td>
<td>0.06</td>
<td>1.04</td>
<td>1.12(0.64)</td>
</tr>
<tr>
<td></td>
<td>Tamarind</td>
<td>-0.52</td>
<td>0.78</td>
<td>0.99</td>
<td>1.54(0.59)</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-0.08</td>
<td>-0.42</td>
<td>-1.85</td>
<td>1.95(0.35)</td>
</tr>
<tr>
<td>Gradia Direct™</td>
<td>Sof-Lex™</td>
<td>Turmeric</td>
<td>-5.70</td>
<td>1.98</td>
<td>37.96</td>
</tr>
<tr>
<td></td>
<td>Paprika</td>
<td>-0.79</td>
<td>0.16</td>
<td>1.91</td>
<td>2.13(0.56)</td>
</tr>
<tr>
<td></td>
<td>Disc</td>
<td>Tamarind</td>
<td>-0.87</td>
<td>0.45</td>
<td>1.81</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-1.24</td>
<td>-0.38</td>
<td>-0.83</td>
<td>1.85(0.87)</td>
</tr>
<tr>
<td>Gradia Direct™</td>
<td>Mylar strips</td>
<td>Turmeric</td>
<td>-5.03</td>
<td>1.39</td>
<td>29.56</td>
</tr>
<tr>
<td></td>
<td>Paprika</td>
<td>-0.89</td>
<td>0.60</td>
<td>1.64</td>
<td>2.06(0.31)</td>
</tr>
<tr>
<td></td>
<td>Tamarind</td>
<td>-1.10</td>
<td>0.70</td>
<td>2.04</td>
<td>2.71(2.16)</td>
</tr>
<tr>
<td></td>
<td>Control</td>
<td>-0.85</td>
<td>-0.31</td>
<td>-0.88</td>
<td>1.45(0.73)</td>
</tr>
</tbody>
</table>
Figure 6.1: Mean colour changes (ΔE) of specimens immersed in turmeric, paprika, tamarind and control solutions by type of composite and finishing methods.

- 24 Hours
- 72 Hours
- 168 Hours

- Turmeric
- Paprika
- Tamarind
- Control

- Sof-Lex™ Disc
- Mylar
- Filtek Supreme™
- Gradia Direct™
Figure 6.2: Mean colour changes $\Delta E$ of specimens immersed in turmeric (A), paprika (B), tamarind (C) and control (D) solution (expanded scale).

- **Turmeric**
  - Filtek Supreme™ Soflex
  - Filtek Supreme™ Mylar
  - Gradia Direct™ Soflex
  - Gradia Direct™ Mylar

- **Tamarind**
  - Filtek Supreme™ Sof-Lex™
  - Filtek Supreme™ Mylar
  - Gradia Direct™ Sof-Lex™
  - Gradia Direct™ Mylar

$\Delta E$ values over hours: 0 to 192.
6.2 Effect of Immersion Time on Colour Stability of Composite resins.

After immersion in the staining solutions, it was observed that the colour differences (ΔE) increased in all composite resins over the experimental period, regardless of staining solution. The most intense colour change occurred in the first 24 hours and the ΔE values were noted to increase with time. According to repeated measures variance test (Table 6.2), the colour changes (ΔE) values as the function of immersion time were significantly influenced by the types of materials and staining solutions.

Table 6.2: Repeated Measure Analysis ANOVA (Within Subject Analysis).

<table>
<thead>
<tr>
<th>Source</th>
<th>Type III Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hours</td>
<td>1248.527</td>
<td>1</td>
<td>1248.527</td>
<td>769.166</td>
<td>.000</td>
</tr>
<tr>
<td>Hours * Material</td>
<td>36.395</td>
<td>1</td>
<td>36.395</td>
<td>22.422</td>
<td>.000</td>
</tr>
<tr>
<td>Hours * Finishing</td>
<td>2.114</td>
<td>1</td>
<td>2.114</td>
<td>1.302</td>
<td>.258</td>
</tr>
<tr>
<td>Hours * Staining</td>
<td>1835.244</td>
<td>3</td>
<td>611.748</td>
<td>376.873</td>
<td>.000</td>
</tr>
<tr>
<td>Hours * Material * Finishing</td>
<td>.221</td>
<td>1</td>
<td>.221</td>
<td>.136</td>
<td>.713</td>
</tr>
<tr>
<td>Hours * Material * Staining</td>
<td>71.503</td>
<td>3</td>
<td>23.834</td>
<td>14.683</td>
<td>.000</td>
</tr>
<tr>
<td>Hours * Finishing * Staining</td>
<td>11.694</td>
<td>3</td>
<td>3.898</td>
<td>2.401</td>
<td>.076</td>
</tr>
<tr>
<td>Hours * Material * Finishing * Staining</td>
<td>5.632</td>
<td>3</td>
<td>1.877</td>
<td>1.157</td>
<td>.333</td>
</tr>
</tbody>
</table>

As described in the previous section, a diverse trend in the ΔE values was observed in different materials immersed in different staining solutions. The details of performance of each staining solution and materials tested can be seen more clearly in the expanded scale graph (Figure 6.2).
6.3 Effects of Finishing Methods and Type of Composite resins on Colour Stability of Composite resins.

Data analysis in Table 6.3 showed that the colour change (ΔE) values were significantly influenced by the types of materials, finishing methods and staining solutions. Significant main effects and interactions were observed for all parameters.

Table 6.3: Repeated Measure Analysis ANOVA (Between Subject Analysis)

<table>
<thead>
<tr>
<th>Source</th>
<th>Type III Sum of Squares</th>
<th>df</th>
<th>Mean Square</th>
<th>F</th>
<th>Sig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>94.665</td>
<td>1</td>
<td>94.665</td>
<td>17.198</td>
<td>.000</td>
</tr>
<tr>
<td>Finishing</td>
<td>167.184</td>
<td>1</td>
<td>167.184</td>
<td>30.373</td>
<td>.000</td>
</tr>
<tr>
<td>Staining</td>
<td>56856.869</td>
<td>3</td>
<td>18952.290</td>
<td>3443.174</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Finishing</td>
<td>762.660</td>
<td>1</td>
<td>762.660</td>
<td>138.557</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Staining</td>
<td>120.248</td>
<td>3</td>
<td>40.083</td>
<td>7.282</td>
<td>.000</td>
</tr>
<tr>
<td>Finishing * Staining</td>
<td>329.536</td>
<td>3</td>
<td>109.845</td>
<td>19.956</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Finishing *</td>
<td>1925.589</td>
<td>3</td>
<td>641.863</td>
<td>116.611</td>
<td>.000</td>
</tr>
</tbody>
</table>

Changes in colour were significant among the type of composites. Post hoc testing confirmed that Gradia Direct™ revealed statistically significant higher colour change values than Filtek Supreme™ (p<0.05). With respect to finishing methods, mylar strips finished specimens showed more colour differences than Sof-Lex™ discs polished specimens. (Figure 6.3)
Figure 6.3: Mean colour changes $\Delta E$ of specimens immersed in turmeric (A), paprika (B), tamarind (C) and control solutions (D) by types of composite and finishing methods.
There was a statistically significant difference in the colour changes for each material with respect to finishing methods (p<0.05). Filtek Supreme™ with mylar strips finished produced significantly more colour changes compared with specimens polished with Sof-Lex™ discs. Contradictory results were observed with Gradia Direct™. Gradia Direct™ finished with mylar strips were found to be more resistant to colour changes.

6.4 Changes in ∆L*, ∆a*, ∆b* Values

The direction of colour change was determined from analysing the ∆L*, ∆a* and ∆b* coordinates in the CIELAB colour space. L* represents value (ranges from (100) white to (0) black), a* refers to chromacity in red and blue axis (+a red/-a green) and b* refers to chromacity in yellow and blue axis (+b yellow/-b blue). The mean and standard deviations of colour change (∆E) in terms of ∆L*, ∆a* and ∆b* are illustrated in Table 6.1.

In all composite resins tested, there was a decrease in ∆L*, ∆a* and ∆b* values after thermocycling resulting in darker, more green and blue specimens.

In this study, changes in the ∆E values were almost exclusively the result of a significant shift in the b value (Table 6.4). The changes are obvious in the series of graphs plotted in the same scale. (Figure 6.4, 6.6, 6.8 and 6.10). The b* values increased in all composite resins immersed in the staining solution test group. Positive ∆b value indicates all staining solutions caused yellower and lesser blue appearance in the respective specimens. Conversely, in the control group, b* values dropped. Significant main effects and interactions were observed for material, finishing methods and staining solutions (Table 6.4).

Similar observation was also noted with the a* parameter. The a* values increased in all composite resins. This indicates a chromacity shift to redder and less green in the composite resins.
after immersion but differences between staining solution were not significant. Statistically significant differences in \(a^*\) colour parameters were observed only between materials and finishing methods. (Table 6.4).

Value \((L^*)\) parameters dropped in all specimens including those in the control group. Negative values of \(\Delta L^*\) indicate a darker appearance of all specimens. Statistically significant differences in \(L^*\) colour parameters were observed between each material and finishing methods (Table 6.4).

Table 6.4: Repeated Measure Analysis (ANOVA): \(p\) values for each variable and interaction term for \(\Delta L^*, \Delta a^*, \Delta b^*\).

<table>
<thead>
<tr>
<th>Source</th>
<th>(\text{Sig}(L^*))</th>
<th>(\text{Sig}(a^*))</th>
<th>(\text{Sig}(b^*))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Finishing</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Staining</td>
<td>.539</td>
<td>.462</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Finishing</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Staining</td>
<td>.914</td>
<td>.042</td>
<td>.002</td>
</tr>
<tr>
<td>Finishing * Staining</td>
<td>.347</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Material * Finishing * Staining</td>
<td>.834</td>
<td>.602</td>
<td>.000</td>
</tr>
</tbody>
</table>

Changes in \(\Delta L^*, \Delta a^*, \Delta b^*\) values were also evaluated as a function of time (Table 6.5). For specimens stored in turmeric solution, the \(L^*\) value decreased gradually over 24 hours (1 day), 72 hours (3 days) and 168 hours (7 days) respectively. There was an exponential increase in the \(a^*\) value after 72 hours, while sharp increase in the \(b^*\) value was evident after the first 24 hours for Gradia Direct™ and after 72 hours for Filtek Supreme™, followed by gradual increase thereafter (Figure 6.5).
Paprika also presented gradual decrease in L* value. An inverse relationship was noted in the b* value. A different trend was observed in the a* value. For Filtek Supreme™, a dip in the value was shown at 24 hours before an intense increase thereafter. While for Gradia Direct™, there was gradual rise in the a* value up throughout the period of investigation. (Figure 6.7).

Table 6.5: Repeated Measure Analysis (ANOVA): p values for each variable and interaction term for ∆L*, ∆a* and ∆b* as a function of time.

<table>
<thead>
<tr>
<th>Source</th>
<th>Sig (L*)</th>
<th>Sig.(a*)</th>
<th>Sig.(b*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hour</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Material</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Finishing</td>
<td>.730</td>
<td>.398</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Staining</td>
<td>.000</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Material * Finishing</td>
<td>.517</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Material * Staining</td>
<td>.205</td>
<td>.000</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Finishing * Staining</td>
<td>.314</td>
<td>.022</td>
<td>.000</td>
</tr>
<tr>
<td>Hour * Material * Finishing * Staining</td>
<td>.814</td>
<td>.000</td>
<td>.000</td>
</tr>
</tbody>
</table>

In the tamarind group, a sharp decline was recorded within L* parameters especially after 72 hours in all specimens. The opposite tendency was shown in a*. Exponential increase in the parameter was observed after 72 hours. The colour parameter b* values changed steadily throughout the period of investigation (Figure 6.9).
A different trend of colour changes was observed in the control group. Filtek Supreme™ caused gradual decrease in the L* value, while Gradia Direct™ produced a distinct drop after 24 hours. Both Filtek Supreme™ and Gradia Direct™ created a subtle increase in the b* value throughout the period of the study. For the a* value, dramatic increase was seen in the first 24 hours in Gradia Direct™, while in Filtek Supreme™, a dip in the value was shown at 24 hours before a gradual increase thereafter.
TURMERIC

Figure 6.4: Means of L*, a*, b* coordinates of specimens immersed in turmeric solution for Filtek Supreme™ and Gradia Direct™ finish ed by either Sof-Lex™ discs or mylar strips (For standard deviations, please refer Table 6.1).

Figure 6.5: Means of L*, a*, b* coordinates of specimens immersed in turmeric solution for Filtek Supreme™ and Gradia Direct™ finish ed by either Sof-Lex™ discs or mylar strips in expanded scale (For standard deviations, please refer Table 6.1).
Figure 6.6: Means of L*, a*, b* coordinates of specimens immersed in paprika solution for Filtek Supreme™ and Gradia Direct™ finished by either Sof-Lex™ discs or mylar strips. (For standard deviations, please refer Table 6.1).

Figure 6.7: Means of L*, a*, b* coordinates of specimens immersed in paprika solution for Filtek Supreme™ and Gradia Direct™ finished by either Sof-Lex™ discs or mylar strips in expanded scale. (For standard deviations, please refer Table 6.1).
TAMARIND

Figure 6.8: Means of L*, a*, b* coordinates of specimens immersed in tamarind solution for Filtek Supreme™ and Gradia Direct™ finished by either Sof-Lex™ discs or mylar strips. (For standard deviations, please refer Table 6.1).

Figure 6.9: Means of L*, a*, b* coordinates of specimens immersed in tamarind solution for Filtek Supreme™ and Gradia Direct™ finished by either Sof-Lex™ discs or mylar strips in expanded scale. (For standard deviations, please refer Table 6.1).
Figure 6.10: Means of L*, a*, b* coordinates of specimens immersed in control solution for Filtek Supreme™ and Gradia Direct™ finish prepared by either Sof-Lex™ discs or mylar strips. (For standard deviations, please refer Table 6.1).

Figure 6.11: Means of L*, a*, b* coordinates of specimens immersed in control solution for Filtek Supreme™ and Gradia Direct™ finish prepared by either Sof-Lex™ discs or mylar strips in expanded scale. (For standard deviations, please refer Table 6.1).
In this study, the colour changes in two commercially available composite resins (Filtek Supreme™ and Gradia Direct™) finished with two different methods (Sof-Lex™ discs and mylar strips) were measured and compared with the values obtained after 24 hours (1 day), 72 hours (3 days) and 168 hours (7 days) storage in three different spices solutions (turmeric, paprika and tamarind solutions). After statistical analysis of the results (Table 6.3) the staining agent was the most significant factor affecting colour change ($F$-value=3443), followed by finishing technique ($F$-value=30.37) and type of material ($F$-value=17.90).

### 7.1 Effect of Spices on Colour Stability of Composite resins

The first null hypothesis in this study was that there was no significant colour change in each composite resins tested on exposure to turmeric, paprika and tamarind spices solution. Since there were statistical differences found among the staining solutions in producing the colour alterations in composite resins, the first hypothesis was rejected. Colour changes ($\Delta E$) in composite resin with respect to staining solutions can be summarised as follows:

- **Turmeric:** visually perceptible $\Delta E$ ($\Delta E > 1$) and clinically unacceptable colour deviations ($\Delta E > 3.3$) were recorded after 24 hours immersion.
- **Paprika:** visually noticeable ($\Delta E >1$) values were exhibited in both composite after 24 hours storage. However, clinically unacceptable values ($\Delta E >3.3$) were not demonstrated until 72 hours (3 days) immersion.
• Tamarind: visually perceptible changes were noted after 24 hours immersion. Nonetheless, total colour difference (ΔE) exceeding clinically unacceptable level (>3.3) was recorded only after 168 hours (7 days) immersion.

Turmeric was shown to cause the highest colour changes in both composite resins, regardless of finishing methods with mean ΔE ranges between 17.92 and 55.25 (Table 6). This finding is in agreement with the results reported by Stober et al [30]. They investigated colour stability of highly filled indirect composite resins used as facings in the removable denture. In this study, various beverages including 0.1% turmeric were used as staining solution. Turmeric solution was found to cause severe discolouration with total colour difference (ΔE>10) after 4 weeks of storage.

With paprika solution, mean colour changes (ΔE) values were between 1.12 and 3.72. Tamarind, on the other hand showed mean ΔE ranging between 1.12 and 5.42 (Table 6.1). To the best of our knowledge, no study has specifically examined the colour stability of composite resins upon exposure to paprika and tamarind, making findings in this study preliminary in nature. Further in vitro and in vivo studies are necessary to confirm our results.

The mechanism behind colour alteration of composite resins after immersion in various liquid beverages has been a subject of great interest in many studies. The absorption and adsorption of colourant with different polarities found in beverages such as coffee and tea on the surface of composite resins have been implicated [21]. Discolouration by food dyes (sunset yellow and quinoline yellow) has also been investigated. Canay et al [169] postulate that these food colourants are soluble in water and possess electrostatic charges that may be involved in the surface staining of the composite resins. This result is in contrast to that of Rutkunas et al [37] which found that water soluble dyes with electrostatic forces may not be significant in the discolouration of composite resins due to the hydrophobic nature of the composite resins.
The role of poly-phenols play in the dietary constituents as a causative agent in dental staining has generated great interest in many researchers. Poly-phenols represent a variety of compounds, mostly derivatives and/or isomers of flavonoids and tannins including catechins and anthocyanidin that occur in plants [258, 259]. This chemical compound is commonly found in beverages eg tea, wine, legumes, fruits and cereal [258, 259]. It has also been found that poly-phenols have high affinity with proteins. This is confirmed by a study conducted by Proctor et al [260], who investigated the interactions of dietary poly-phenols with salivary protein. It was found that there was increased binding of poly-phenols with hydroxyapatite in the presence of proline rich proteins.

The literature has shown that various pigment compounds are responsible for the colour of the spices used in this study. For turmeric, curcuma is the principal pigment that imparts a deep orange colour. Three compounds (capsanthin, capsorbin and b-carotene) are responsible for the reddish tinge in paprika, while flavonoid is the major brown/black colour pigment in tamarind. All these compounds have a poly-phenol structure, which is non polar and cannot dissolve in water molecules due to the high polarity of water molecules [258]. They are, therefore, hydrophobic. The degree of polarities of these spices varies between manufacturers and is beyond the scope of this thesis. However, the important aspect with regard to polarities is that whether the polarity of these compounds is compatible with the polymer matrix of composite resins; which is not known. Therefore, further investigation is required to ascertain the compatibility of the colourant in the spices and composite resins as this may determine the mechanism of discolouration of composite resins by the spices studied.

Discolouration of tooth-coloured, resin-based materials may be caused by intrinsic and extrinsic factors [163]. Staining by adsorption or absorption of colourants as a result of contamination from exogenous sources has been described as extrinsic discolouration. Studies have shown that extrinsic discolouration maybe related to surface morphology. In search of the mechanism of discolouration of composite resins, another group of investigators, have evaluated the surface morphology of composite resins after immersion in coffee, tea and wine under scanning electron microscopy [261]. It was found
that surfaces of composite resins immersed in wine displayed changes in the surface texture and presence of surface cracks, which in turn facilitate the adsorption of stains. Surface degradation of composite resins in the presence of low pH has also been shown by Vilalta et al [35]. The pH of tamarind used in this study was 5.6 (based on the manufacturer’s description). Whether low pH in the tamarind solution produces similar surface changes warrants further investigation.

### 7.2 Effect of Immersion Time on Colour Stability of Composite resins.

In concert with observations in previous studies, all composite specimens tested in this investigation exhibited more intense colour changes as the immersion time increased [11, 176]. Most intense colour changes occurred within the first 24 hours of immersion. This may be related to the water absorption behaviour of composite resins. Earlier studies indicated that composite resins displayed the highest water sorption rates in the first 24 hours. This water intake pattern may facilitate the ingress of the pigments in the staining solution leading to discolouration of the material [113, 262-266].

Assuming an average person spends approximately 60 minutes (1 hour) per day eating and drinking [284], the immersion time (24 hours, 72 hours and 168 hours) used in this study simulates the equivalent number of days of the composite resins restorations exposure to dietary staining. The pattern of colour changes in composite resins observed in this study may reflect the potential staining susceptibility of the composite resins after 24, 72 and 168 days of dietary intake containing turmeric, paprika or tamarind spices.
7.3  Effects of Finishing Methods and Type of Composite resin on the Colour Stability of Composite resins.

The other null hypotheses tested in this study were that there was no difference in the colour of composite resins 1) among two different finishing methods and 2) among two different types of composite resins.

In this study, Sof-Lex™ discs and mylar strips were compared. The Sof-Lex™ discs polishing method produced lower colour changes (ΔE) than the mylar strips. However, the effect of finishing method on the colour stability of composite resins appeared to be dependent on the type of composite resins. Filtek Supreme™ with mylar strips finished generally resulted in significantly more colour changes compared with specimens polished with Sof-Lex™ discs. Favourable results in the colour stability of Filtek Supreme™ polished with Sof-Lex™ discs has also been demonstrated by several authors [154, 162, 182]. The effect of mylar strips finish on the staining susceptibility of Filtek Supreme™ has also been evaluated. Ergücu et al [138] has investigated the effect of different finishing methods (PoGo™, OptraPol™ and mylar strips) on the colour stability of nano-composite resins including Filtek Supreme™ upon exposure to a coffee. Compared to PoGo™ and OptraPol™, mylar strips finished nano-composite resins showed the most intense staining. This discolouration may be attributed to the presence of a resin-rich surface produced by mylar strips. Therefore, the authors advocated the removal of this superficial resin layer. This result is also supported by other studies [28, 144, 146, 148, 267].

In contrast, Gradia Direct™ finished with mylar strips were found to be more resistant to colour changes. In light of these findings, the second and third hypotheses of this study were rejected.
The results of this study seem to suggest the existence of different effects of different finishing methods on the composites tested. This effect is thought to be related to differences in surface quality of composite resins obtained after different finishing techniques.

The relationship between surface roughness and stain resistance of composite resins has been established in numerous authors [142, 155, 162, 268-270]. Generally, a rougher surface tends to cause higher discolouration of the composite resins. The surface texture of composite resins may also influence the optical properties of the material by affecting the degree of scattering and reflection of light on the material [271]

Previous studies have shown that a smooth surface was achieved when polymerized against a mylar strips [140, 143, 147, 272-274]. This observation may explain the lower colour changes found in Gradia Direct™ cured against mylar strips.

With regard to Sof-Lex™ discs polishing system, many investigators concluded that the polishing method produce favourable surface roughness for most composite resins tested. Koh and Neiva [275] evaluated the differences in the surface roughness of both Gradia Direct and Filtek Supreme™ using four polishing systems: PoGo™/Enhance™ (DENTSPLY/Caulk), Sof-Lex™ discs (3M ESPE), Astropol™ (Ivoclar Vivadent), and Optidisc™ (KerrHawe). Sof-Lex™ discs were found to provide the smoothest final surface when used with either composite. In other studies, evaluation of surface roughness by profilometry showed the lower Ra value for Filtek Supreme™ polished with Sof-Lex™ discs polishing system compared with other polishing methods [140, 150, 155, 162, 268, 269, 276, 277]. Ra values reported were mostly below 0.2 μm. Further observation by scanning electron microscope revealed a homogenous surface with fewer surface irregularities when combination of Filtek Supreme™ and Sof-Lex™ discs polishing system were used. [150, 162, 268, 276, 277]. The lower discolouration found in the Filtek Supreme™ polished with Sof -Lex™ group could be attributed to the smooth final surface of the restoration as has been shown in the above studies.
Generally, composite resins consist of three main components: (1) inorganic filler particles, (2) resin matrix and (3) coupling agent that chemically bonds the inorganic filler to the resin matrix [109]. Obviously, properties including surface morphology and colour stability of the composite resins are dependent upon these three basic components.

Variables such as size and amount of filler particles may affect the surface morphology of composite resins. Both Filtek Supreme™ and Gradia Direct™ have approximately similar filler loading; 72.5% and 77% by weight respectively (Table 5.1). The only difference between these products is the average particle size. Filtek Supreme™ contains nanomer particles with average particle size of 2-20nm filled in the interstitial spaces between nano-clusters (formed by individual primary nano-particles bonded between them by weak intermolecular forces into spherical agglomerates) [12]. Gradia Direct™, on the other hand, is composed of micro-fined filler particles and pre-polymerised resin filler with average particle size of about 0.85 µm [134].

During finishing and polishing procedures, there is a tendency for filler particles to debond from the matrix creating voids and defects on the surface [125,144,276]. The larger the filler particle, the larger the surface defect created, hence the rougher the surface. The average size of filler particles in Gradia Direct™ is 0.85 µm (850nm) - significantly larger than the average particle size (2-20nm) in nano-filled Filtek Supreme™. Furthermore, being a micro-hybrid material, Gradia Direct™ may contain fractions of substantially large filler particle size although the reported average particle size is 0.85 µm. The presence of pre-polymerised filler particles in Gradia Direct™ may add to the intricacy of the filler content. The pre-polymerised filler particles are typically larger than the filler particle and are being added into the resin matrix to increase the filler loading of the material. The interface between pre-polymerised fillers and the resin matrix is critical as breakdown of the bond at this interface during polishing may lead to the detachment of the larger pre-polymerised filler leaving large craters or defects resulting in rough surfaces.
Nevertheless, one can argue that the average size of nano-clusters in Filtek Supreme™ (0.6-1.0 micron) is similar to that of the average particle size in Gradia Direct™. The manufacturer claims that through modification of the sintering process, the nano-cluster is made up of loosely agglomerated nano-particles. These nano-particles in the agglomerates may break away into the matrix during polishing instead of plucking of the agglomerates that leaves void in the matrix [12].

Therefore, the differences in the effect of Sof-Lex™ discs on Gradia Direct™ and Filtek Supreme™ as seen in this study may be expected. On the other hand, the presence of particles of differences sizes and shapes in micro-hybrid composite resins such as Gradia Direct™ may allow easier packing during placement and extrusion of material under mylar strips, hence achieving a smoother surface compare to the spherical filler particles in Filtek Supreme™ [268] which may contribute to the lower colour changes in the Gradia Direct™ with mylar strips finished group.

Apart from filler content, the resin matrix of composite resins may also influence the colour stability of composite resins. The influence of resin monomers on the colour stability of composite resins are associated with the hydrophobicity [11, 169] and water absorption properties of the resin monomers [70, 114]. A study on water absorption of composite resins showed that the highest water intake of composite resins occurred within the first 24 hours of immersion [170]. The intense colour changes in the composite resins during the first 24 hours, as demonstrated in this study, may be related to this pattern of water sorption.

It has been shown that urethane dimethacrylate (UDMA) exhibits less staining compared with bisphenol A-glycidyl methacrylate (Bis-GMA), which is the common resin monomers used in composite resins [70]. Conversely, composite resins with hydrophilic monomers e.g. Tri-ethylene glycol dimethacrylate TEDGMA [170] exhibits higher water sorption [174], and therefore permits penetration of any hydrophilic colourant into the resin matrix. Filtek Supreme™ contains Bis-GMA, UDMA, TEGDMA,
and Bis-EMA(6) resins [135]. While Gradia Direct™ consists of a mixture of urethane dimethacrylate (UDMA) and dimethacrylate co-monomers [134]. According to the manufacturer [134], due to the ongoing discussions on the (possible) side effects of Bis-GMA it is GC Corporation’s policy not to use Bis-GMA in their commercial products. From the aforementioned discussion, based on the resin monomers system in each material, it could be speculated that Gradia Direct™ may be more resistant to colour changes due to the hydrophobicity of the resin matrix. However, in this study, Filtek Supreme™ displayed less colour change on exposure to spices. This finding seems to suggest that due to the heterogenous nature of composite resins, it is difficult to predict the colour stability of the material based solely on the composition of the material. On the other hand, the non-polar hydrophobic nature of the pigments in the spices as discussed above may contribute to the discolouration of the more hydrophobic Gradia Direct™.
7.4 Limitations of the study

The limitations of this study include the in-vitro use of a spectrophotometer to evaluate colour differences of only two types of composite resins material. The specimens used in this study had flat surfaces. In clinical settings, however, various anatomical features including grooves and pits may be present and this may complicate the polishing procedure. Moreover, the materials in the oral environment are subjected to various exogenous and endogenous conditions that may modify the outcome of the material. Due to the in-vitro nature of the study and the complexity of the intraoral environment, the data ought to be interpreted cautiously when extrapolating to clinical settings. Therefore, long term clinical studies may be beneficial to evaluate the colour stability of the material.

Another limitation of this study is the concentration of the spice solutions used. The concentration of spices used as food colourant is highly variable depending on the type of cuisine and individual preference. Therefore, the 0.1% concentration used in this study is a general estimation. Finally, this study only tested the composites’ resistance to staining for 168 hours (7 days).
This study evaluated the colour stability of two contemporary composite resins, nano-filled Filtek Supreme™ and micro-hybrid Gradia Direct™ finished with either Sof-Lex™ discs or mylar strips on exposure to turmeric, paprika and tamarind. Within the limitations of this study, all spices used (turmeric, paprika and tamarind) have a potential to stain composite resins; with turmeric causing the most severe discolouration regardless of the type of composite resins or finishing techniques employed. These spices are commonly used in cuisine in various parts of the world especially the Asian continent. Therefore, patients with spicy food intake in their dietary habit should be educated on the possible colour changes in the restorative material on exposure to these spices. Further in-vivo and in-vitro analysis may be necessary for better understanding of the mechanism of discolouration of composite resins under the influence of spices, and colour stability of the material exposed to these natural food colourants.

Filtek Supreme™ finished with mylar strips generally resulted in significantly more colour change compared with specimens polished with Sof-Lex™ discs. Gradia Direct™ finished with mylar strips produce lower colour changes than the Sof-Lex™ discs group. In clinical setting, mylar strips are usually used to aid contouring of the restoration. As a general rule the restorations are contoured as closely as possible to the intended morphology and surface finish in order to minimize the need for subsequent finishing and polishing of the restorations. The necessity for polishing following placement of the composite resins varies, depending on the need to remove excess material, to adjust anatomic form and occlusion, and, finally, to obtain a smooth surface.
The result of this study suggests that different materials respond differently to staining by spices when either finished with mylar strips or polished with Sof-Lex™ discs. The clinical implication of these outcomes is that the decision to leave the final restorations as mylar strips finished or to proceed with polishing depends on the type of composite resins selected.

Also, contemporary composite resins available in the market (e.g. nano-composite and micro-filled hybrid composite) are still susceptible to discolouration by exogenous factors despite advancement in the development of resin based restorative material. This suggests that further research and development are needed to improve the colour stability of the material.

Recommendations for future studies include a longer period of immersion. In this study, samples were immersed with the staining solutions the entire time. In order to create a more accurate overall view of the whole staining process, an intermittent staining process to simulate a natural dietary consumption pattern should be performed. Furthermore, clinically, staining solutions would be mixed and diluted with saliva. Therefore, future study could include mixture of the staining solutions with, for example, artificial saliva.

The effect of spices in various concentrations and combinations could be of interest and worthwhile to investigate more thoroughly. In addition, as there are a variety of commercial composite resins available in the market, it would be pertinent to include other types of composite resins in future studies.
CHAPTER 9

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