

***Physical, Mechanical and Surface  
Properties of Dental Resin-composites***

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## Table of Contents

<b>Table of Contents</b> .....	2
<b>List of Figures</b> .....	9
<b>List of Tables</b> .....	12
<b>List of Abbreviations</b> .....	14
<b>Abstract</b> .....	16
<b>Declaration</b> .....	18
<b>Copyright Statement</b> .....	19
<b>Dedication</b> .....	20
<b>Acknowledgement</b> .....	21
<b>Chapter One</b> .....	22
General Introduction and Literature Review .....	22
1.1 Introduction .....	23
1.2 Composite-Based Resin Materials .....	25
1.2.1 Historical Background of Dental Resin Composites .....	25
1.3 Composition of Dental Resin Composites .....	26
1.3.1 Organic Polymer Resin Matrix .....	26
1.3.1.1 Dimethacrylate.....	26
1.3.1.2 Non-Dimethacrylate.....	29
1.3.2 Polymerization Mechanism.....	29
1.3.3 Initiators and Accelerators .....	31

1.3.3.1	Chemically Activated Resins.....	31
1.3.3.2	Light-Activated Resins .....	31
1.3.4	Inhibitors and Stabilizers.....	33
1.3.5	Pigments.....	33
1.3.6	Viscosity Controllers.....	34
1.3.7	Coupling Agent .....	34
1.3.8	Inorganic Filler.....	36
1.4	Classification of Resin-composites .....	37
1.4.1	Macrofilled (Conventional) Composites.....	37
1.4.2	Microfilled Composites.....	38
1.4.3	Hybrid Composites .....	38
1.4.4	Nanofilled Composites.....	39
1.5	Properties of Resin Composites .....	39
1.5.1	Water Sorption and Solubility.....	39
1.5.2	Hygroscopic expansion .....	40
1.5.3	Fracture toughness .....	40
1.5.4	Surface properties.....	41
1.5.4.1	Colour stability .....	41
1.5.4.2	Gloss .....	41
1.5.4.3	Hardness.....	42
1.6	Summary .....	42

<b>Chapter Two</b> .....	44
General Aims and Objectives .....	44
<b>Chapter Three</b> .....	47
Methodology .....	47
3.1 Introduction .....	48
3.1.1 Accuracy .....	48
3.1.2 Sensitivity.....	48
3.1.3 Linearity .....	48
3.1.4 Resolution .....	49
3.1.5 Threshold .....	49
3.1.6 Repeatability .....	49
3.1.7 Zero stability .....	49
3.1.8 Readability .....	49
3.2 The hygroscopic expansion measurement using a laser scan micrometer .....	50
3.2.1 Calibration.....	52
3.3 Fracture toughness ( $K_{IC}$ ) measurement using a Universal Testing Machine ...	56
3.4 Colour measurement using a Chroma Meter.....	57
3.4.1 Calibration.....	58
3.5 Gloss measurement using a glossmeter.....	58
3.5.1 Calibration.....	59

<b>Chapter Four .....</b>	<b>61</b>
Water Sorption, Solubility and Diffusion coefficient of Dental Resin-composites ....	61
4.1 Abstract .....	62
4.2 Introduction .....	63
4.3 Materials and Methods .....	64
4.3.1 Specimen preparation.....	64
4.3.2 Water Sorption and Solubility.....	67
4.3.3 Reconditioning / Desorption of Specimens.....	67
4.3.4 Diffusion Coefficients .....	68
4.4 Statistical Analysis .....	69
4.5 Results .....	69
4.6 Discussion .....	75
4.7 Conclusions .....	77
<b>Chapter Five .....</b>	<b>78</b>
Hygroscopic Expansion Kinetics of Dental Resin-composites .....	78
5.1 Abstract .....	79
5.2 Introduction .....	80
5.3 Materials and Methods .....	81
5.4 Statistical Analysis .....	84
5.5 Results .....	84
5.6 Discussions .....	87

5.7	Conclusion.....	89
<b>Chapter Six .....</b>		<b>90</b>
Aqueous Storage Modifies Fracture Toughness of Dental-composites .....		90
6.1	Abstract .....	91
6.2	Introduction .....	92
6.3	Materials and Methods .....	93
6.3.1	Scanning Electron Microscopy (SEM) Analysis .....	96
6.4	Statistical Analysis .....	97
6.5	Results .....	97
6.6	Discussion .....	100
6.7	Conclusions .....	103
<b>Chapter Seven.....</b>		<b>104</b>
Effect of Food-simulating Solvents on Surface Micro-hardness of Dental Resin-composites .....		104
7.1	Abstract .....	105
7.2	Introduction .....	106
7.3	Materials and methods.....	107
7.4	Statistical Analysis .....	109
7.5	Results .....	110
7.6	Discussion .....	117
7.7	Conclusions .....	121

**Chapter Eight .....122**

Effect of Food-simulating Solvents on Colour Stability and Gloss Retention of Dental Resin-composites..... 122

8.1 Abstract ..... 123

8.2 Introduction ..... 124

8.3 Materials and Methods ..... 125

8.4 Statistical Analysis ..... 127

8.5 Results ..... 127

8.6 Discussion ..... 140

8.7 Conclusions ..... 145

**Chapter Nine.....146**

Depth of Cure of Bulk Fill Dental-composites..... 146

9.1 Abstract ..... 147

9.2 Introduction ..... 148

9.3 Materials and Methods ..... 149

9.4 Statistical Analysis ..... 152

9.5 Results ..... 152

9.6 Discussion ..... 157

9.7 Conclusions ..... 159

**Chapter Ten .....160**

General discussion, Conclusions and Future Work Recommendations..... 160

10.1 General discussion..... 161

10.2 Conclusions ..... 166

10.3 Recommendation for future work ..... 167

**References ..... 169**

**Word Count: 37,022**



## List of Figures

Figure 1.1: Factors involved in the aetiology of dental caries .....	23
Figure 1.2: Chemical structure of Bis-GMA.....	27
Figure 1.3: Chemical structure of UDMA .....	28
Figure 1.4: Chemical structure of TEGDMA .....	28
Figure 1.5: Molecular structures of Ormocer.....	29
Figure 1.6: The polymerization of dimethacrylate monomers to form the cross-linked polymer network of dental composites .....	30
Figure 1.7: Chemical structures of photo-initiator systems, A) CQ; B) DMAEMA; C) EDMAB; D) CEMA; E) PPD .....	32
Figure 1.8: Chemical structures of inhibitor systems, A) BHT; B) MEHQ .....	33
Figure 1.9: Schematic representation of silane bonding between the fillers and the polymer matrix in dental composites .....	35
Figure 1.10: Chemical structure of MPTMS.....	36
Figure 1.11: Classification of resin composites based on filler size .....	37
Figure 2.1: General outline for studies.....	46
Figure 3.1: Laser scan micrometer (LSM) system.....	50
Figure 3.2: The configuration of the system .....	52
Figure 3.3: Setting the HIGH CAL stepped type gage .....	54
Figure 3.4: Setting LOW CAL with-holder type gages .....	55

Figure 3.5: Universal Testing Machine.....	56
Figure 3.6: KIC specimen mounted on a cast metal jig .....	57
Figure 3.7: Chroma Meter instrument.....	58
Figure 3.8: Glossmeter instrument.....	60
Figure 4.1: The percentage mass change of water sorption and desorption .....	70
Figure 4.2: Water sorption of the examined resin composites after storage in distilled water for 150 days.....	71
Figure 4.3: Solubility of the examined resin composites after storage in distilled water for 150 days.....	72
Figure 4.4: Plot of $M_t/M_\infty$ against the $t_{1/2}$ for A; sorption, B; desorption .....	74
Figure 5.1: Laser scan micrometer.....	83
Figure 5.2: Initial hygroscopic expansion over 7 days .....	85
Figure 5.3: Hygroscopic expansion from 0 to 150 days for four materials, showing high expansion .....	86
Figure 5.4: Hygroscopic expansion from 0 to 150 days for four materials, showing low expansion .....	86
Figure 6.1: A) PTFE mould used for specimen, B) specimen dimensions and geometry .....	96
Figure 6.2: KIC (standard deviation) of composites after 1 and 7 days' storage in water at 37°C.....	98
Figure 6.6.3: Representative micrographs of fracture surfaces of composites examined after 7 days storage at 37°C (A) BL, (B) NCB, (C) Ver, (D) TEC, (E) GSO, (F) Xb, (G) VDF, (H) CXD.....	99

Figure 7.1: Micro-hardness instrument .....	109
Figure 7.2: Vickers micro-hardness (VHN) of the examined resin composites after 30 days' storage in food-simulating solvents at 37°C .....	112
Figure 7.3: Mean values of Vickers hardness (VHN) as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD .....	116
Figure 7.4: Quadratic regression of VHN (all conditions) versus filler loading % (wt), for seven resin composites (BL, NCB, TEC, GSO, XB, VDF, CXD).....	117
Figure 8.1: Mean colour change values ( $\Delta E$ ) of the examined resin composites during 6 months stored in food-simulating solvents at 37°C .....	131
Figure 8.2: Mean gloss values of the examined resin composites during 6 months stored in food-simulating solvents at 37°C .....	132
Figure 8.3: Mean values of colour change ( $\Delta E$ ) as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD .....	136
Figure 8.4: Gloss change as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD .....	140
Figure 9.1: Stainless steel mould with top cover plate .....	152
Figure 9.2: Max.VHN, VHN at 80% of max.VHN and depth at 80% of max.VHN, for bulk fill composites, A) TBF, B) XB, C) VBF, D) FBF, E) SF .....	156
Figure 9.3: Linear regression of max.VHN versus filler loading % (wt), for bulk fill composites.....	157
Figure 10.1: Linear regression of water sorption versus the percentage of volumetric hygroscopic expansion .....	162

## List of Tables

Table 1.1: Properties of an ideal restorative material .....	24
Table 1.2: Number of scientific articles related to resin AND composite .....	25
Table 3.1: Specifications of the LSM unit .....	51
Table 4.1: Materials tested .....	66
Table 4.2: Water sorption ( $W_{so}$ ) and solubility ( $Sol$ ) of resin composites after 150 days' storage in distilled water at 37°C .....	70
Table 4.3: Diffusion coefficient (standard deviation) of water sorption and desorption of composite materials .....	73
Table 5.1: Materials tested .....	82
Table 5.2: Percentages of hygroscopic expansion of the examined resin composites (standard deviation) over 150 days' storage in distilled water at 37°C .....	85
Table 6.1: Materials tested .....	95
Table 6.2: KIC (standard deviation) of composites after 1 and 7 days' storage in water at 37°C .....	98
Table 7.1: Materials tested .....	108
Table 7.2: Vickers Hardness VHN (standard deviation) of resin composites tested after 30 d storage in food simulating solvents at 37°C .....	111
Table 7.3: Solubility parameters of food-simulating solvents .....	118
Table 8.1: Materials tested .....	126
Table 8.2: Colour change $\Delta E$ (standard deviation) of resin composites tested after 6 months stored in food-simulating solvents at 37°C .....	129

Table 8.3: Gloss retention (standard deviation) of resin composites tested after 6 months stored in food-simulating solvents at 37°C .....	130
Table 8.4: Solubility parameters of food-simulating solvents .....	141
Table 9.1: Materials tested .....	151
Table 9.2: Mean (standard deviation) of max.VHN, VHN at 80% of max.VHN and depth at 80% of max.VHN for bulk fill composites examined.....	153

## List of Abbreviations

$\mu\text{g}$	microgram
$\mu\text{m}$	micrometer
$a^*$	the quantity of green-red colour
$b^*$	the quantity of blue-yellow colour
Bis-EMA	2,2-bis[4-(2-methacryloyloxyethoxy)phenyl]propane
BisGMA	bisphenol-A glycidyl methacrylate (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane)
BL	Bright Light <sup>®</sup>
cm	centimetre
CQ	camphoroquinone
CXD	Ceram·X <sup>™</sup> duo
$D$	diffusion coefficient
$d$	day(s)
$d$ (%)	percentage of diameter changed
Exp.VT	Experimental Vertise <sup>™</sup>
FBF	Filtek <sup>™</sup> Bulk Fill
g	gram
GPDM	Glycerol Phosphate Dimethacrylate
GSO	Grandio <sup>®</sup> SO
h	hour(s)
$J$	diffusion flux
$K_{\text{IC}}$	fracture toughness
L	specimen thickness
$L^*$	lightness
m	metre
$m_1$	conditioned mass prior to immersion in water
$m_2$	mass of the specimen at a specific time after immersion in water
$m_3$	equilibrium weight of the specimen after desorption
$M_\infty$	the mass uptake at equilibrium
MMA	methylmethacrylate
MN	MegaNewton

MPa	MegaPascal
$M_t$	the mass uptake at time
NCB	Nanoceram-Bright <sup>®</sup>
nm	nanometre
$\emptyset$	concentration in dimensions
PMMA	poly (methyl methacrylate)
s	second(s)
$S$	slope
SEN	single edge-notched
SF	SonicFill <sup>™</sup>
$Sol$	solubility
t	time
TBF	Tetric EvoCeram <sup>®</sup> Bulk Fill
TEC	Tetric EvoCeram <sup>®</sup>
TEGDMA	triethylene glycol dimethacrylate
UDMA	urethane dimethacrylate
V	volume
$V (\%)$	volumetric hygroscopic expansion
VBF	Venus <sup>®</sup> Bulk Fill
VDF	Venus <sup>®</sup> Diamond Flow
VHN	Vickers hardness number
Vol %	percentage content by volume
$W_i \%$	weight gain percentage
$W_{so}$	water sorption
Wt %	percentage content by weight
XB	X-tra base
$\Delta E$	change in colour
$x$	position [length]
$\pi$	the ratio of the circumference to the diameter of a circle $\approx 3.14$
$\partial$	partial derivative

## Abstract

Since resin composites were first presented to dentistry more than half a century ago, the composition of resin composites has developed significantly. One major change was that the reinforcing filler particles were reduced in size to generate materials of a given filler content that display better physical and mechanical properties. Resin composites may absorb water and chemicals from the surrounding environment but at the same time, composites may release constituents to their surroundings. The physical/mechanical properties of a restorative material provide an indication of how the material will function under stress in the oral environment. The aims of this research were to examine the effects of water at 37°C on the physical and mechanical properties, and the effect of food-simulating solvents of a variety of experimental and contemporary resin composites, on the surface properties. Eight representative resin composites were selected (Exp.VT, BL, NCB, TEC, GSO, XB, VDF and CXD). Due to the recent development of bulk fill materials on the market during the course of this research, the post-cure depth of cure of new bulk fill materials was also investigated. Five representative resin composites were selected: TBF, XB, FBF, VBF and SF.

Water sorption and solubility were investigated at 37°C for 150 days. Sorption and solubility are affected by the degree of hydrophilicity of the resin matrix. The bulk fill materials examined showed the lowest water sorption and solubility. Laser scan micrometer (LSM) was used to investigate hygroscopic expansion. The extent of the hygroscopic expansion positively correlated with the amount of water sorption.

The effect of water on fracture toughness was also examined. A self-adhesive hydrophilic resin matrix decreased in fracture toughness after 7 days of storage at 37°C. By contrast, the least water absorbed bulk fill material increased in fracture toughness over time.

The effect of food-simulating solvents (distilled water, 75% ethanol/water and MEK) on surface micro-hardness, colour stability and gloss retention were investigated. The MEK solvent resulted in the lowest micro-hardness and the greatest colour change ( $\Delta E$ ) for most of the examined composites, while the 75% ethanol/water solution caused the greatest loss in gloss for most of the examined composites. A highly filled nano-composite showed the best result over time, regardless of the condition of storage.



Surface micro-hardness profiles were used as an indirect method to assess the depth of cure of bulk fill resin composites. The examined bulk fill resin composites can be cured to an acceptable depth (4 mm).

## **Declaration**

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Ali Awad Alrahlah

2013

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## Dedication



*“Say: My Lord, increase me in knowledge”*

**IN THE NAME OF ALLAH**

And with His blessing

The All-Knowing, the Most-Wise

I want to dedicate this thesis to my family and friends. I have a special feeling of gratitude to my loving parents, Mr. Awad Alrahlah and Mrs. Felwa Alkahtani, whose care and guidance I always enjoyed. This thesis is also dedicated to my lovely wife Rasha and my daughter Danh and to my brothers and sisters.

Finally I would also like to dedicate this work to all of my friends.

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I would like to show my sincere appreciation to **Ms. Rose-Marie Parr**, for all the help and assistance she has offered to me throughout the years.

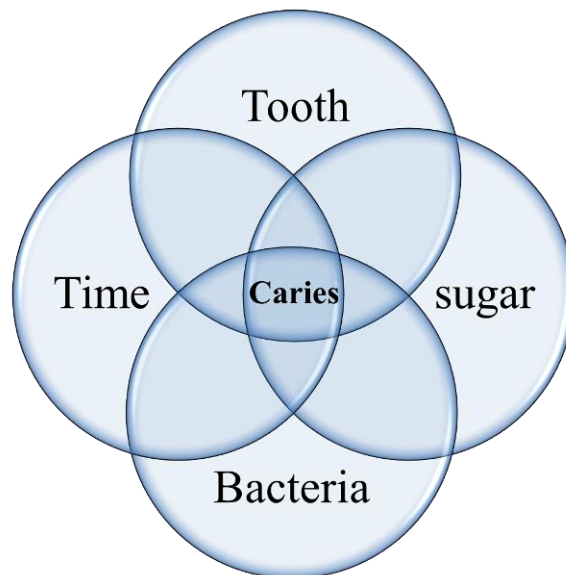
I wish to express my genuine appreciation to **King Saud University, Riyadh, Saudi Arabia** for funding and supporting my study at the University of Manchester.

**Chapter One**  
**General Introduction and Literature Review**

## 1.1 Introduction

Dental caries is the pathological process of localized destruction of tooth tissues by microorganisms [1]. The aetiology of dental caries is multifactorial [2]. For caries to occur there are four basic requirements (Figure 1.1):

- Bacteria in dental plaque on the tooth surface.
- A substrate such as fermentable carbohydrate (dietary sugars).
- A susceptible tooth surface.
- Time.



**Figure 1.1:** Factors involved in the aetiology of dental caries

Repair of destroyed tooth structure is unlikely, although remineralisation of very small carious lesions may occur if dental hygiene is kept at a high level. For smaller lesions, remineralisation can be enhanced by the use of topical fluoride, while for larger lesions, the progression of dental caries can be stopped by treatment, which is aimed at preserving the tooth structure and preventing further destruction of the tooth.

Dental amalgam was introduced more than 150 years ago for tooth filling restoration. It is still one of the most popular restorative materials, despite the introduction of several new filling types. Although dental amalgam is the most popular restorative material for posterior teeth, and has proved outstanding for many years of clinical service [3], there

has been a considerable growth, in recent years, in the restoration of posterior teeth using resin composites. Significant improvements in the adhesion to enamel and dentine as well as the physical properties of resin composites have contributed to the increasing tendency to use resin composite in the posterior teeth [4]. Mercury toxicity has become a convincing justification for replacing amalgam restorations with tooth-coloured materials, although there has been a lack of agreement due to conflicting results in a number of studies [5-9].

Where aesthetics are concerned, resin composite is superior. This is because it can be adjusted to mimic the colour of patients' teeth, and this versatility is one of the key factors in its success. In the last decade, there has been considerable growth in the demand for tooth-coloured restorations [10]. Resin composite has several advantages over silver amalgam, leading in turn to an increase in its popularity. Resin composite is more aesthetically pleasing as it reinforces tooth structure; furthermore, it can conserve more tooth structure in preparation design. Table 1.1 shows the properties of an ideal restorative material.

**Table 1.1:** Properties of an ideal restorative material

<b>Biological</b>	<b>Mechanical</b>	<b>Other</b>
Non-toxic	High strength	Bonds to enamel and Dentine
Non-irritant	Durable/low wear & nonabrasive	Radiopaque
Bio-active (anti-bacterial, promotes formation of reparative dentin)	Dimensionally stable	Aesthetic
	Bio-mimetic (similar mechanical properties to tooth structure)	Good handling Characteristics
	Highly polishable	Non-soluble & non-absorbent



## 1.2 Composite-Based Resin Materials

A composite material is a physical mixture of materials. It is defined as a “three-dimensional combination of at least two chemically different materials with a distinct interface separating the components” [11]. Dental composites are made of three chemically different materials: i) the organic matrix (organic phase), ii) the inorganic matrix (filler or disperse phase), and iii) organosilane (coupling agent) to bond the filler to the organic resin.

Scientific articles related to resin AND composite, appearing from 1960 to 2012, were sought on MEDLINE, ISI Web of Knowledge, Scopus, and Scirus. The searches were limited to articles written in English (Table 1.2). The results showed that the amount of research has increased rapidly across this period of time.

**Table 1.2:** Number of scientific articles related to resin AND composite

Period	MEDLINE	ISI Web of Knowledge	Scopus	Scirus
	Number of articles			
<b>1960-1969</b>	3	5	9	16
<b>1970-1979</b>	368	1,541	1,432	579
<b>1980-1989</b>	1,378	4,751	3,662	2,407
<b>1990-1999</b>	3,576	7,688	5,176	5,540
<b>2000-2012</b>	8,838	17,661	10,070	20,340

### 1.2.1 Historical Background of Dental Resin Composites

Early attempts at aesthetic restoration materials were focused on silicate cements. These cements were a result of reactions between phosphoric acid and acid-soluble glass particles to form a silica gel matrix containing residual glass particles. Solubility problems with these materials gave rise to the development of unfilled acrylic systems.

The 1950s saw the introduction of unfilled acrylic resin based on Methyl Methacrylate. The method of creating fine grains of polymer, which could be softened by a monomer of the same composition, was devised in Germany by Kulzer GmbH. This methodology

allows the production of dental materials in a desired shape. Acrylic-based materials have since retained a prominent position in restorative and prosthetic dentistry [12].

In 1962 Bowen developed the Bis-GMA monomer with a view to improving the physical properties of acrylic resins, as their monomers were limited to the formation of linear chain polymers [13]. Robert Chang in 1969 and Henry Lee in 1970 were the first to implement the use of composite in the paste/liquid form [14]. The late 1970s saw the development of a photo-polymerised resin composite system [15]. Such a polymerisation method provided dentists with the ability to polymerise a composite at a fast rate, upon placing and contouring.

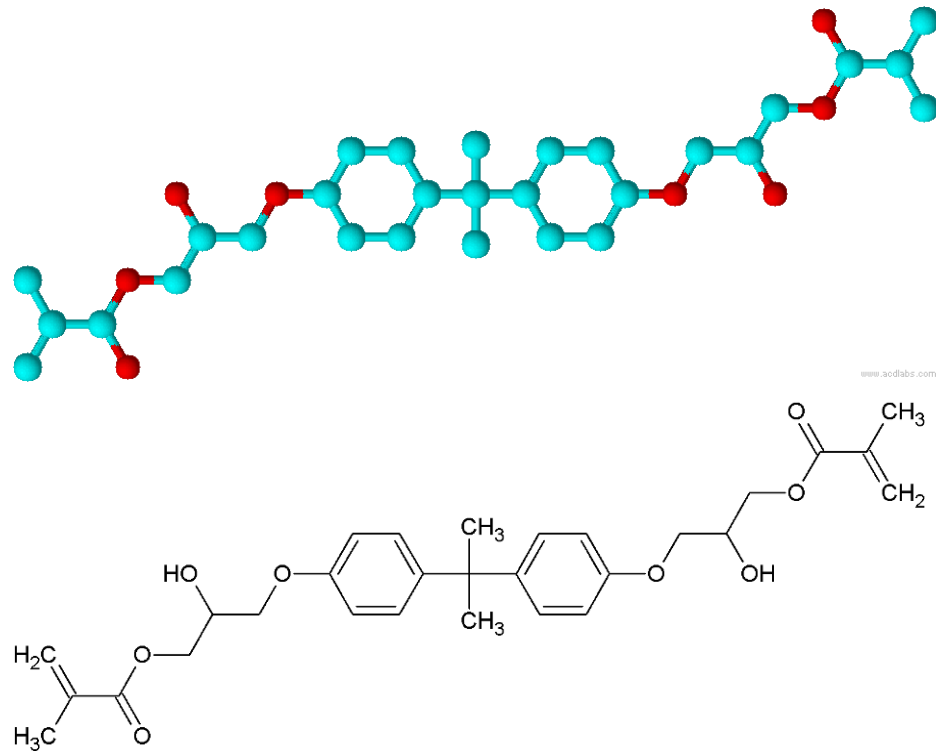
First introduced in the early 1970s, resin composite material development focused primarily on two features: filler content and polymerisation method. A range of fillers, varying in type and size, have been used to present a wide array of resin composites with respect to ease of polishability and strength. Filler particles reduce the volume of polymerizable resin matrix required; this in turn lowers polymerisation shrinkage. As glass and ceramic fillers are used, the overall coefficient of thermal expansion of the resin composite is reduced from that of totally organic composition [16].

### **1.3 Composition of Dental Resin Composites**

#### **1.3.1 Organic Polymer Resin Matrix**

##### **1.3.1.1 Dimethacrylate**

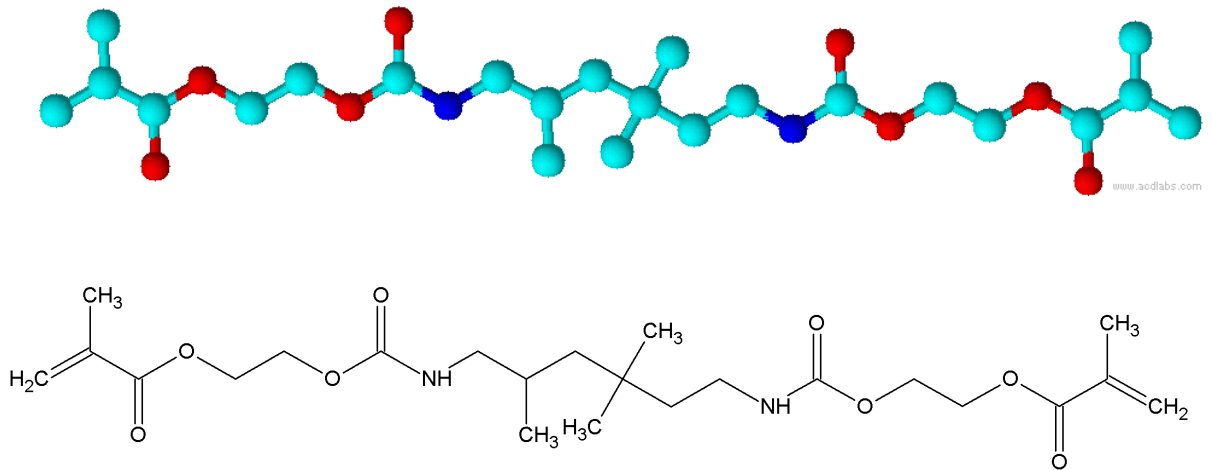
One of the most important events of the 1960s was Dr. Bowen's [17] development of Bis-GMA 2,2-bis[4-[2-hydroxy-3-(methacryloyloxy)propyl]phenyl] monomer (Figure 1.2) from bisphenol A and GMA.



**Figure 1.2:** Chemical structure of Bis-GMA

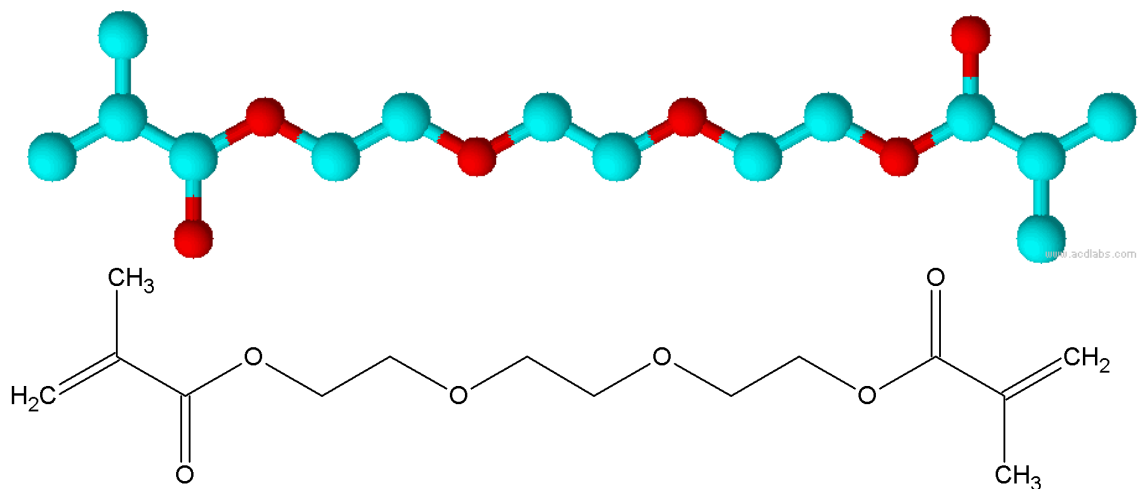
This di-functional monomer has relatively low polymerization shrinkage ( $\approx 6.0\%$ ); free-radical polymerisation, stimulating rapid hardening; low volatility; good mechanical properties when the monomer is cured [18] and production of stronger and stiffer resins [19]. The di-functional monomer is better than methyl methacrylate, due to its large molecular size and chemical structure [19]. As a result of its high strength and hardness, Bis-GMA is more widely used as an organic monomer for dental composite materials [20]. The hydrogen bonding interactions that occur between hydroxyl groups result in the high viscosity of Bis-GMA [21, 22] (1.0-1.2 kPa.s at  $23^\circ\text{C}$ ) [18]. To solve this viscosity issue, manufacturers typically dilute the monomer with a more fluid comonomer: triethylene glycol dimethacrylate (TEGDMA) [16]. In addition to this, the aromatic monomer Bis-GMA is much more rigid than dimethacrylate EGDMA and TEGDMA [19].

Urethane dimethacrylate UDMA (Figure 1.3) 1,6-bis[2-(methacryloyloxy)ethoxycarbonylamino]-2,4,4-trimethylhexane has lower viscosity (approximately 11,000 mPa.s at  $23^\circ\text{C}$ ) and excellent flexibility which leads to better durability [23]. Furthermore, it offers an improvement in mechanical properties compared with Bis-GMA [24-26]. This monomer has been used alone or in combination with other monomers, such as BisGMA and TEGDMA.



**Figure 1.3:** Chemical structure of UDMA

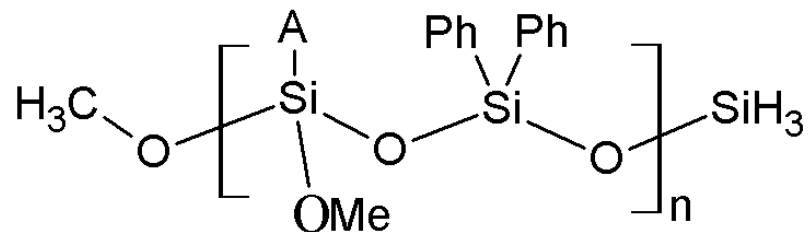
On the other hand, triethylene glycol dimethacrylate TEGDMA (Figure 1.4) has less viscosity than Bis-GMA [21] (10 mPa.s 23°C [19]). Typically, a 1:1 ratio of TEGDMA and Bis-GMA is used. A small flexible molecule is found in this monomer, which not only forms cross links, but is also found to cyclise [27]. TEGDMA results in a clinically objectionable increase in polymerization shrinkage [28, 29]. Thus, monomers such as ethoxylated bisphenol-A dimethacrylate (BisEMA), with low viscosity and high MW, are found in many commercial formulations, either partially or as a replacement of TEGDMA [30].



**Figure 1.4:** Chemical structure of TEGDMA

### 1.3.1.2 Non-Dimethacrylate

Organically Modified Ceramics (Ormocers) are used in high technology industries efficaciously; for instance, optical coatings, electronics, and medical technology [31]. In dental biomaterials, pure Ormocers matrix or a combination of Ormocers organic matrix with dimethacrylate has been used in restorative dentistry to overcome the disadvantages of conventional dimethacrylate matrix; for example, extracted unset monomers to the oral environment [32]. Ormocers are hybrid materials that are prepared by varied processing based on nano-scale technology, which combines organic/inorganic components on a nanoscopic scale through the sol-gel method instead of conventional physical mixing of the different components of a matrix [31]. The characteristic feature of Ormocers is the linkage of the organic groups to the inorganic backbone, formed by hydrolysis and condensation of alkoxides. The organic part is responsible for the cross-linking network, flexibility and optical properties. The inorganic part (glasses, ceramics) provides chemical and thermal stability (Figure 1.5) [31].



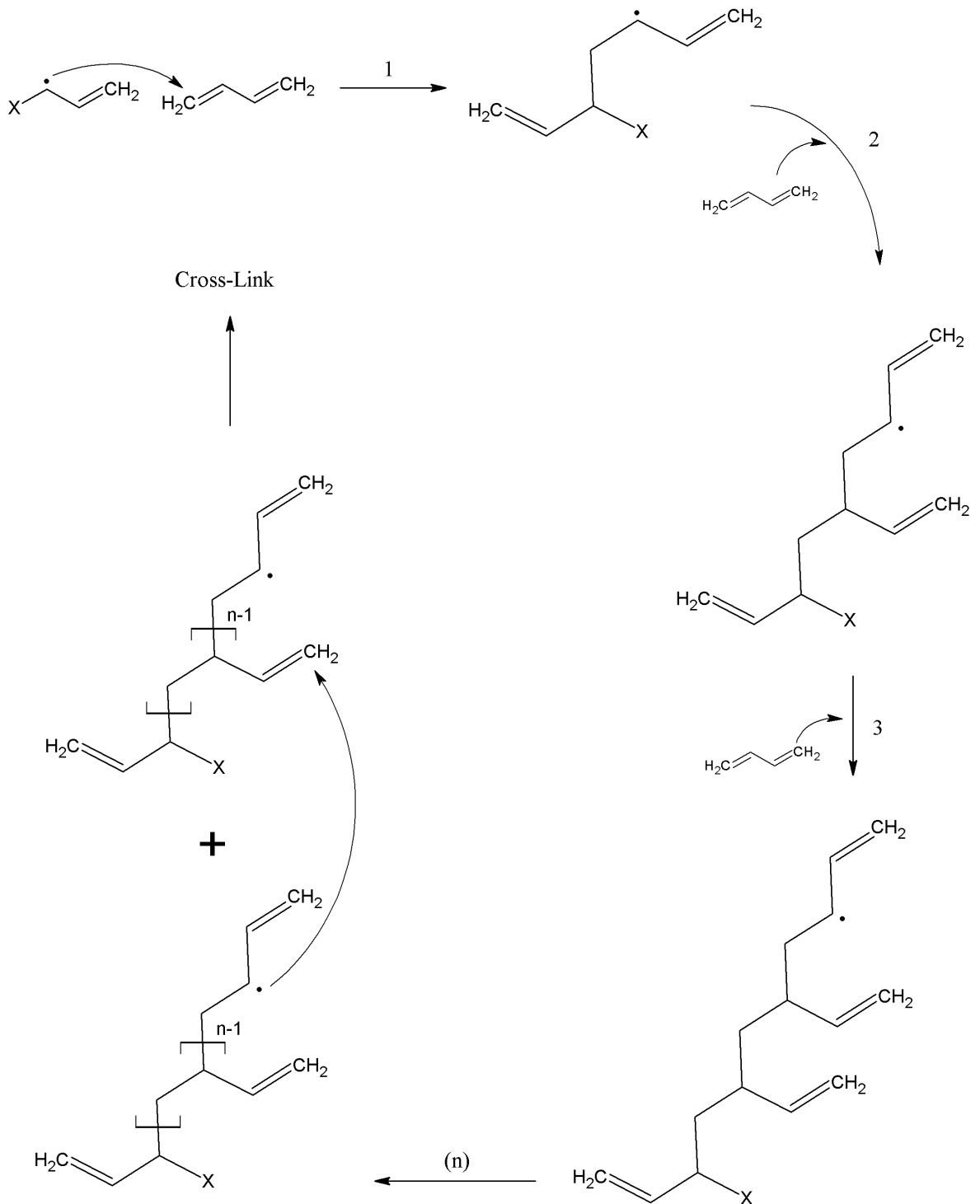
**Figure 1.5:** Molecular structures of Ormocer

### 1.3.2 Polymerization Mechanism

Dental composites are hardened as a result of a chemical reaction between dimethacrylate resin monomers. This creates a rigid and closely cross-linked polymer network surrounding the filler particles (Figure 1.6).

Monomers have incomplete double bond conversion after polymerization when the composite is cured [20, 33]. Furthermore, the mobility of monomers and oligomeric molecules declines when the network is formed. This leads to the trapping of unreacted monomer and pendant methacrylate groups in the materials. Therefore, the materials

have reduced strength as a result of the low level of conversion[34]. The monomer selection affects the reactivity, viscosity, and polymerisation shrinkage, the mechanical properties, water sorption, and hygroscopic expansion [18].



**Figure 1.6:** The polymerization of dimethacrylate monomers to form the cross-linked polymer network of dental composites

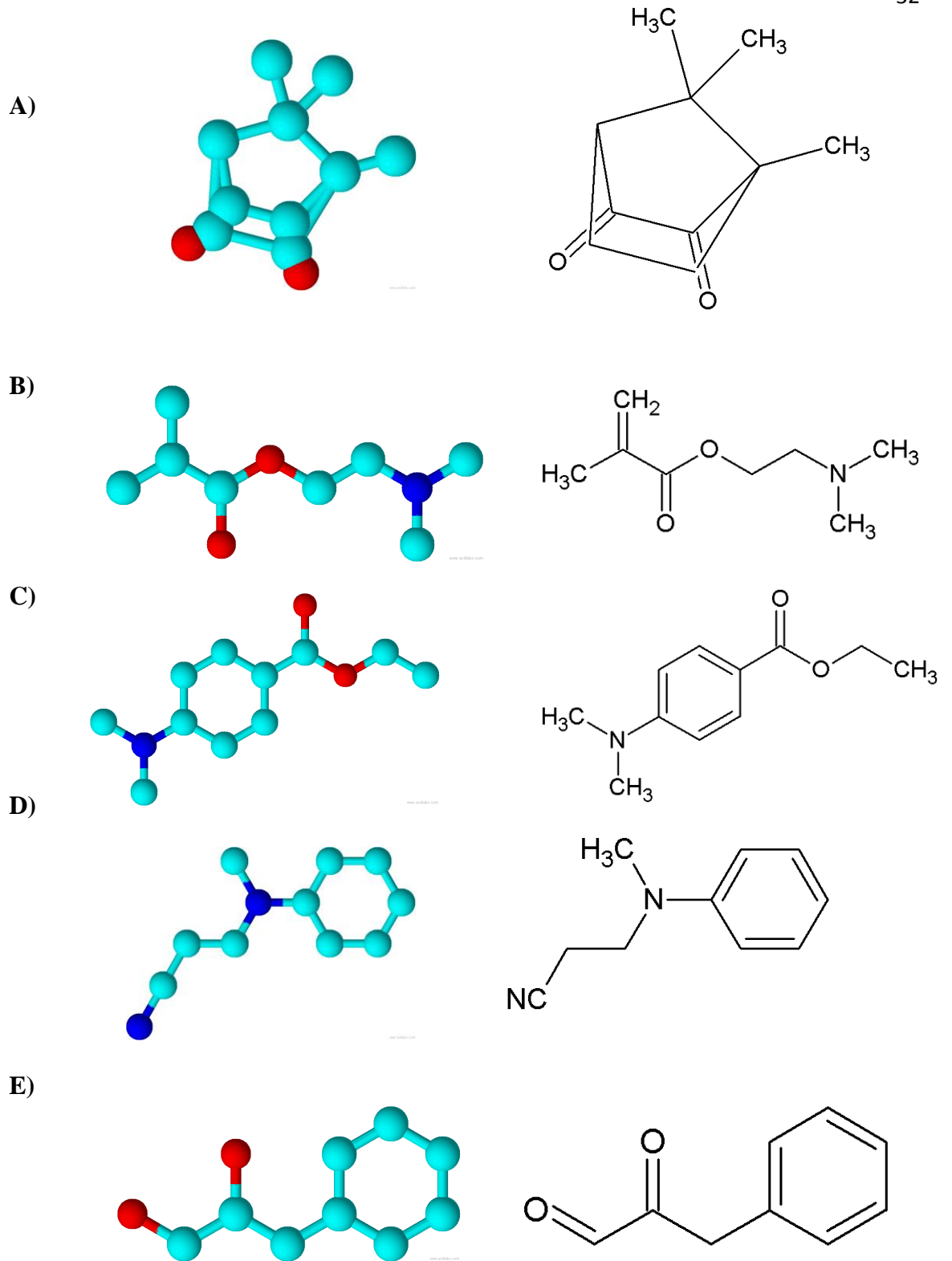
### **1.3.3 Initiators and Accelerators**

#### **1.3.3.1 Chemically Activated Resins**

Reacting benzoyl-peroxide and a tertiary amine initiate the polymerization of chemically activated composite resins. The combination of these two materials (one paste containing a chemical activator and the other containing a chemical initiator) results in the production of a free radical. The initiator, benzoyl peroxide, which is activated by the tertiary aromatic amine N, N-bis (2- hydroxyethyl)-p-toluidine, is the component that most chemically activated composite materials contain. A multistep process leads to the formation of the polymerization-initiating benzoyl radicals [35].

#### **1.3.3.2 Light-Activated Resins**

Light activation is the most common method of curing dental composites. Camphoroquinone (CQ) is the photo-initiator (Figure 1.7) in light-activated dental composites. It is sensitive to blue light in the 470-nm region of the electromagnetic spectrum. CQ reactivity is further improved by the addition of an amine-reducing agent such as dimethylamino ethylmethacrylate (DMAEMA), ethyl-4-dimethylaminobenzoate (EDMAB), or N, N-cyanoethyl-methylaniline (CEMA). CQ and amine concentrations vary in commercial composites from 0.2 to 1.2 wt% [36]. Another photoinitiator, 1-phenyl-1,2-propanedione (PPD), which has an absorption peak near 410 nm [37], has also been suggested as an alternative.

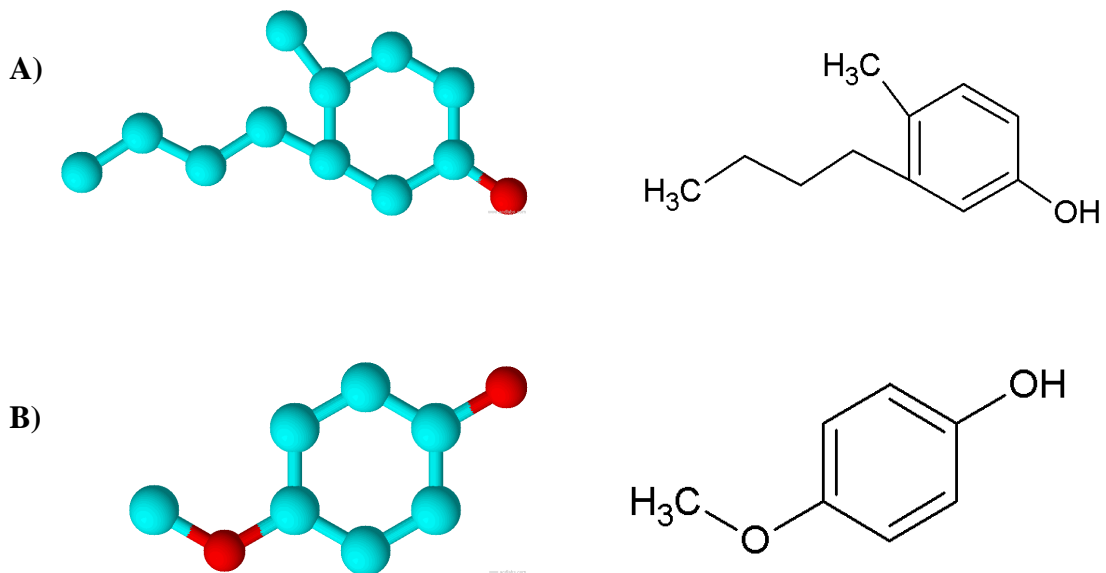


**Figure 1.7:** Chemical structures of photo-initiator systems, A) CQ; B) DMAEMA; C) EDMAB; D) CEMA; E) PPD



### 1.3.4 Inhibitors and Stabilizers

Inhibitor systems such as phenols, e.g. 2, 6-di-tert-butyl-methylphenol (BHT) and hydroquinone monomethylether (MEHQ) (Figure 1.8) are used for their chemical stability in order to optimise the product's storage life before curing. UV photostabilizers provide colour stability and minimize the effects of UV light on the amine compounds in the initiator system, which can otherwise cause discolouration over a medium to long time period. Examples of such photostabilizers include 2-hydroxybenzophenones and 3-(2-hydroxyphenyl)-benzotriazols, in amounts of 0.10 to 0.50% wt [38].



**Figure 2.8:** Chemical structures of inhibitor systems, A) BHT; B) MEHQ

### 1.3.5 Pigments

The main advantage of dental resin composites is their ability to approximate the natural colour of teeth. A variety of shades and translucencies of dental restorative materials were introduced in the 1950s. This allowed an improvement in the aesthetic performance of restorations [39]. Visual colouration of dental composites (shading) is achieved by adding different pigments, which often consist of different metal oxides

that are added in minute amounts. Metal oxides pigments, such as ferric oxide ( $\text{Fe}_2\text{O}_3$ , red) or ferric hydroxide ( $\text{Fe}(\text{OH})_3$ , yellow), are the most commonly used pigments[38].

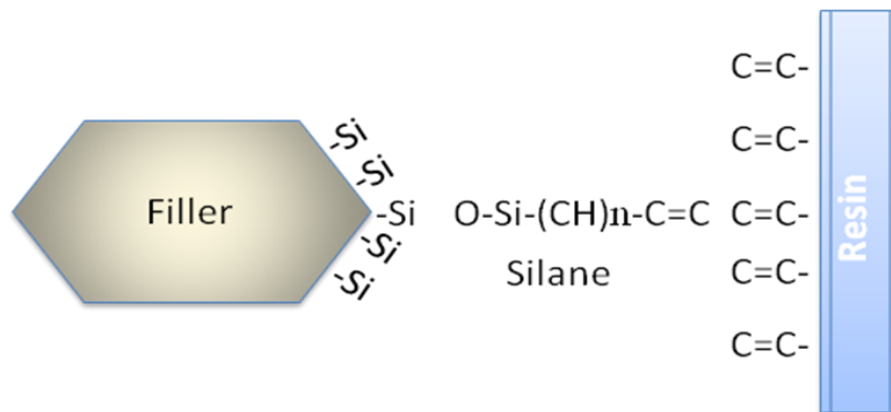
### 1.3.6 Viscosity Controllers

Viscosity is a measure of the resistance of a fluid. This resistance may be a result of shear stress or extensional stress. The flow of uncured resin composites is dependent on the intrinsic rheology of the matrix monomers [40]. The Bis-GMA monomer has a high viscosity at room temperature as a result of its rigid molecular structure and hydrogen bonds. This in turn results in the need to dilute Bis-GMA with a low viscosity monomer to form an organic matrix. Studies have shown that the viscosity of a resin composite decreases with an increase in the amount of low molecular weight diluting monomer (TEGDMA) [41-43]. TEGDMA is the lowest viscous resin, as compared with the other two most commonly used monomers: 2-hydroxyethyl methacrylate (HEMA) and 3-hydroxypropyl methacrylate (HPMA). This may be due to the fact that TEGDMA is a larger molecule [40].

The rheological properties of resin composites can be controlled with the use of inorganic fillers. Larger filler particles have a lower viscosity than smaller filler size particles since a smaller filler size requires a higher number of filler particles to preserve the filler volume. Consequently, the total active area increases, resulting in an increase in interactions between filler particles and the resin matrix, and between the filler particles themselves [41].

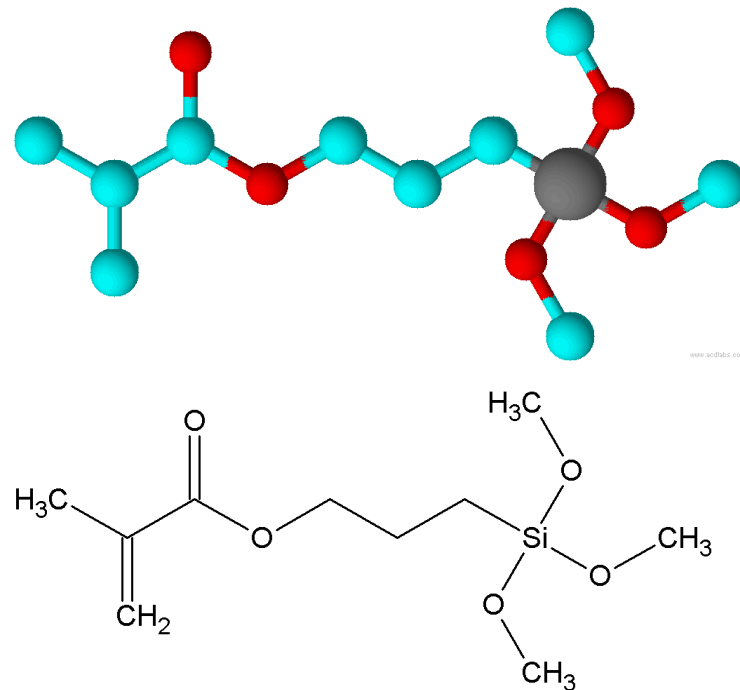
### 1.3.7 Coupling Agent

Silane coupling agents are used to promote adhesion between different materials, not only in dentistry [44], but also in many technical applications[45]. The coupling agent used for dental resin composites typically consists of a molecule that has silanol ( $\text{Si-OH}$ ) groups on one side and methacrylate groups (containing  $\text{C}=\text{C}$ ) on the other. These molecules have the ability to bond covalently, with both the silicon-oxygen groups in the silica-based fillers and the methacrylate groups of the resin matrix (Figure1.9).



**Figure 1.9:** Schematic representation of silane bonding between the fillers and the polymer matrix in dental composites

In methacrylic resin based dental composites, the bond between the polymer matrix and the filler particles is usually accomplished by the use of the silane coupling agent, 3-methacryloxypropyl trimethoxysilane (MPTMS) (Figure 1.10). It is a bifunctional molecule capable of reacting through its alkoxy silane groups with the filler, with itself, and with the resin, by virtue of its methacrylate functional group [46]. In order to improve the quality and durability of the matrix/filler interface, more hydrophobic and flexible silane coupling agents other than MPTMS have been used [47]. A significant advantage of silane coupling agents is that the hydrolysis (and reformation) of the chemical bond between silane coupling agents and filler materials is a reversible process. This is beneficial as it may reduce internal stresses in the material[48].



**Figure 1.10:** Chemical structure of MPTMS

### 1.3.8 Inorganic Filler

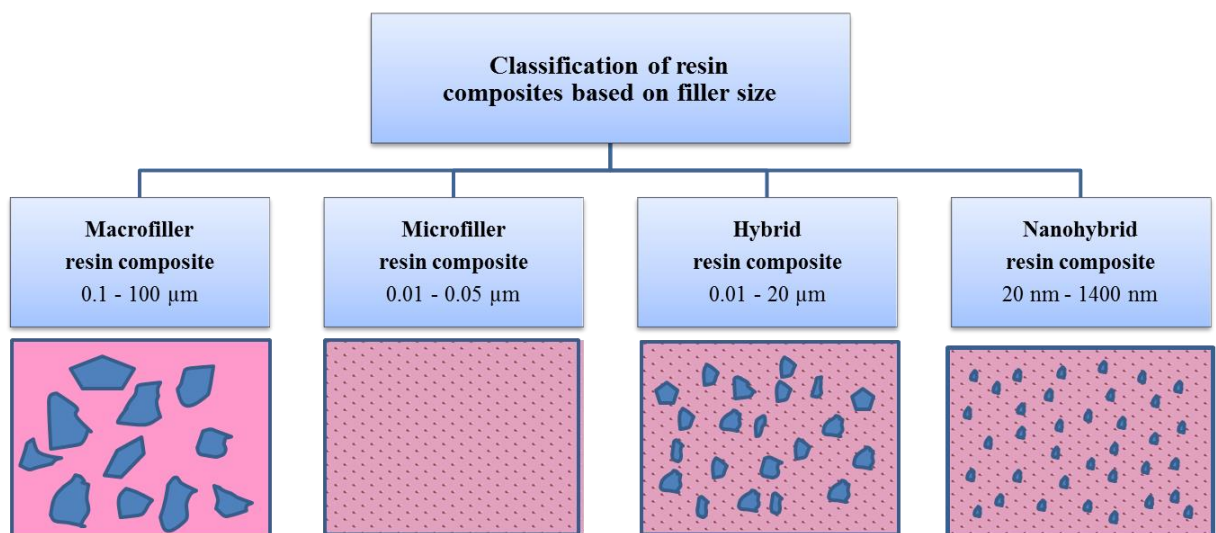
Many properties of material for composite restoration are improved by increasing the amount of fillers [19]. Fillers are used in dental composites to provide strengthening [49, 50], increased stiffness [51, 52], reduced dimensional change when heated and cooled [53, 54], reduced setting contraction [55], increased radiopacity [56], enhanced aesthetics, and improved handling [21]. There is a direct relation between the physical/mechanical properties of the resin composite and the amount of filler added.

There is a wide range of fillers available. Glass particles are the most common, due to their improved optical properties. Previously, quartz was favoured and very commonly used. This was because of its better mechanical properties, availability and stability in contrast to other fillers [57]. However, due to the hardness of quartz particles, enamel attrition was increased [58]. This feature has led to the decline of quartz and increase in popularity of glass. Other commonly used fillers include borosilicate glass, lithium, barium aluminium silicate, and strontium or zinc glass.

Silica particles are commonly used because of their enhanced polishability. A range of silica-based glass fillers is available, including amorphous or colloidal silica, fused silica and sol-gel zirconia silica. Currently, nano-fillers sized particles are used because of their mechanical and aesthetic properties [21].

#### 1.4 Classification of Resin-composites

Filler types may be divided into groups in accordance with the sizes of the filler particles. Traditionally, composites were classified as either hybrid, conventional or macrofilled composites, and this method of classification is still valid. Filler particles are classified based on size, as follows [59-61] (Figure1.11).



**Figure 1.11:** Classification of resin composites based on filler size

##### 1.4.1 Macrofilled (Conventional) Composites

Macrofilled composites were first introduced in the late 1950s [62]. They were the result of grinding larger particles, consisting of radiopaque glass, quartz or ceramics, into smaller particles by mechanical means [38]. Fillers of this nature contained glass or quartz filler particles, with sizes ranging from 0.1 $\mu\text{m}$  to 100  $\mu\text{m}$ , added to the resin matrix up to 70-80% wt. This resulted in better properties as compared to unfilled resin

polymers. As a result of the colour match between the resin and the quartz particles, these composites had good optical properties. High filler loadings cause filler particles to come into contact with one another and consequently contribute substantially to the reinforcing mechanism, as a result of the interaction of the particles with one another. Macrofilled composites do remain stronger than microfilled composites. They are most commonly used for stress-bearing restorations [63].

However, there were also many disadvantages, including poor wear resistance due to crack propagation at the matrix/filler interface and loss of the filler particles [64], which in turn leads to poor polishability [65]; as well as early discolouration and staining due to surface roughness.

#### **1.4.2 Microfilled Composites**

Microfilled resin composites were a development of the late 1970s. The filler size averages about 0.02  $\mu\text{m}$  within a range of 0.01- 0.05 $\mu\text{m}$  of amorphous silica particles in an organic matrix, to obtain filler content of 35% wt. The filler loading may be increased by pre-polymerizing the resin containing the colloidal silica, grinding it into particles and incorporating it as filler. This would allow an increase of 50-60% wt [21, 66].

Microfilled resin composites give the final finish a high degree of smoothness, while the surface becomes even smoother with time, which is highly advantageous. They are most favoured where a moderate strength is required in conjunction with an aesthetic and smooth finish restoration [67].

#### **1.4.3 Hybrid Composites**

Hybrid composites combine the features, and particularly the advantages of both microfilled and macrofilled composites. Hybrid composites cover a broad range of particle sizes. This wide range of particle sizes may cause high filler loading with resultant high strength. Typically, hybrid composites contain a filler with an average particle size of 15- 20  $\mu\text{m}$  and 0.01- 0.05 $\mu\text{m}$  [63].

#### **1.4.4 Nanofilled Composites**

Nanotechnology has led to the development of a new resin composite. This is characterised by the inclusion of nanoparticles, 20 or 75 nm in size, and nanoaggregates of approximately 0.6-1.4  $\mu\text{m}$ , which are made up of zirconium/silica or nanosilica particles. In order to ensure that the aggregates bind to the resin, they are treated with silane. The distribution of the filler, aggregates and nanoparticles gives a high load, up to 75% wt [68].

Nanocomposites are available as nanohybrid types. An increased filler load is achieved by the reduced dimensions of the particles, along with their wide size distribution. This consequently reduces the polymerization shrinkage and increases the mechanical properties, such as tensile strength, compressive strength and fracture resistance. These characteristics are higher than those of universal composites and significantly superior to those of microfilled composites [18, 67, 69].

### **1.5 Properties of Resin Composites**

#### **1.5.1 Water Sorption and Solubility**

The properties of composite resin fillings are affected by water sorption. Water behaves as a plasticizer and stress corrosion agent, weakening the particle matrix interface. Deterioration of the physical and mechanical properties can occur as a result of water ingress into dental resin composites in the oral cavity. This is primarily a result of the hydrolytic breakdown of the bond between silane and filler particles, the matrix/filler interface or the fillers [70].

Debonding, as a result of the occurrence of localised swelling at the matrix/filler interface, may lead to hydrolytic breakdown. This breakdown on the surface of resin composites is further facilitated by temperature fluctuations and solvent effects. There is a direct correlation between temperature and water sorption, as the higher the temperature, the faster the water sorption [71]. Other negative impacts of water sorption have been found. These include tensile strength [72], modulus of elasticity, flexural strength [73] and wear resistance [74].

A study of the physical properties of resin composites prepared from Bis-GMA, TEGDMA, UDMA and Bis-EMA show that TEGDMA appears to make the densest polymer network. Furthermore, it is the most flexible, absorbs the maximum amount of water and produces the minimum amount of unreacted monomer. On the other hand, UDMA and Bis-EMA generate more rigid networks than TEGDMA, absorb less water and release higher unreacted monomer. Bis-GMA resin can form the most rigid network, which absorbs a lesser amount of water than the resin made by TEGDMA. However, Bis-GMA is still higher than the resins made by UDMA and Bis-EMA [75].

### 1.5.2 Hygroscopic expansion

Hygroscopic expansion of the resin composite may compensate the polymerisation shrinkage and, therefore, lead to enhanced marginal sealing [76, 77]. Subsequently, in polymerization, the inner movement of water molecules causes saturation of ions within the matrix and outer movement of unset monomers and ions extracted from activators and fillers. Extracted components contribute to more shrinkage and loss of weight, whereas hygroscopic expansion leads to a swelling and weight gain [78, 79].

### 1.5.3 Fracture toughness

The bulk fracture of resin composite restorations is considered a main cause of clinical failure [80]. Fracture toughness ( $K_{IC}$ ) is a mechanical property for determining the brittleness of materials, for instance dental composites [81]. For fracture resistance,  $K_{IC}$  is a more representative measure *in vivo* [82].  $K_{IC}$  determines the stress intensity at the tip of a crack or flaw [83]. Propagation of the fracture through the resin composites due to flaw initiation may occur through the resin matrix or matrix/filler interface commonly, but is unlikely to occur through the filler, owing to its high strength and modulus [81]. Many factors may affect  $K_{IC}$ ; for instance, chemical composition, fillers (loading and size), bond of matrix/filler interface, or degree of conversion of the resin matrix [83]. A greater value of  $K_{IC}$  reflects a material unlikely to chip or fracture easily [84].  $K_{IC}$  values of hybrid and nano-filled resin composites are significantly greater than those of micro-filled resin composites [85]. The effect of water storage on  $K_{IC}$  has been studied in relation to a range of materials and specimen geometries [86, 87]. The long-term storage of resin composites in aqueous media may cause undesirable effects, such



as degradation of the bonds between the matrix/filler interface [88, 89], leakage or evacuation of filler elements [70, 90], and softening of the resin matrix [91, 92]. Subsequently, these effects may lead to changes in  $K_{IC}$  values.

## **1.5.4 Surface properties**

### **1.5.4.1 Colour stability**

The colour shade mismatch of resin composites is a main reason for replacing restorations [93], since the change of colour of resin composite restoration is regarded as a major aesthetic failure [94]. The colour change in resin composites develops as a result of intrinsic and extrinsic factors. Intrinsic factors include chemical changes in the material's composition. The chemical colour change is ascribed to the amine accelerator oxidation, exposure to different energy sources, and storage in water over time. Extrinsic factors include bond staining or diffusion of stains resulting from food and drink such as beverages and stained drinks [94-96]. After ageing, differences in scattering and absorption of light may develop for materials associated with colour changes [97]. Due to an inadequate resin polymerisation, the resin composites easily absorb stains and the colour may change [95, 98]. Hydrophilic resin composites tend to absorb more water than hydrophobic. Hence, hydrophilic stains are readily soluble in aqueous solutions and penetrate easily into materials [99]. Hydrophobic resin composites thus exhibit superior colour stability and resistance to colour change [93, 94].

### **1.5.4.2 Gloss**

Gloss is defined as the capability of the material to reflect direct light [100]. When all the light is reflected opposite or close to the direction of the incident light, the material surface exhibits high gloss [101]. Because of mechanical wear and chemical degradation, surface roughness may affect the gloss surface of resin composites, as such a surface would scatter light [96]. Gloss is affected by the morphology and size of fillers besides the resin matrix [102]. The surface roughness resulting from wear and chemical degradation may affect gloss and increase discolouration [98]. Also, light scattering due to the rough surface of the filler with a larger surface area may produce a change in

colour and gloss [103]. Clinically, materials that show a high gloss surface exhibit a better aesthetic appearance.

#### **1.5.4.3 Hardness**

Hardness refers to the material's resistance to indentation [104]. Most researchers have chosen the Vickers and Knoop hardness tests for investigating the hardness of resin composites or denture teeth [105]. Hardness is one of the most important properties, being associated with compressive strength, wear resistance and the degree of conversion [106, 107]. Hardness depends on applied load and time during the test [105]. The surface hardness of resin composites can be influenced by water sorption and hydrolytic degradation [108]. A low hardness value of a resin composite indicates poor chemical/physical bonding between the matrix and filler interface [107].

### **1.6 Summary**

Dental amalgam was introduced more than 150 years ago as a tooth filling restoration. It is still one of the most popular restorative materials, despite the introduction of several new filling types. Although dental amalgam is the most popular restorative material for posterior teeth, and has proven outstanding for many years of clinical service, there has been a considerable growth, in recent years, in the restoration of posterior teeth using composite resins. Significant improvements in the adhesion to enamel and dentine as well as the physical properties of resin composites have contributed to the increasing tendency to use resin composite in the posterior teeth. Moreover, mercury toxicity has become a convincing justification for replacing amalgam restorations with tooth-coloured materials.

Resin composite has become the material of choice for restoring anterior and posterior teeth. There are several advantages of using resin composite over silver amalgam, which have led in turn to an increase in its popularity. Resin composite is more aesthetically pleasing as it reinforces tooth structure, and furthermore can conserve more tooth structure in preparation design.

Recently, a manufacturer has developed new materials that reduce the technique-sensitivity of composite application, and also help to decrease the amount of time the

patient spends in the dental chair, by reducing the number of layering increments. Experimental self-adhesive resin and bulk fill materials have introduced to achieve this purpose. Due to some modification of these materials having taken place, it is essential to predict their performance in comparison with contemporary resin composites.

The water sorption behaviour of resin composites is very important and can affect the long-term service of restorations. Water sorption by a resin composite may cause expansion that affects the dimensions of the composite filling, leading to inferior mechanical properties. Furthermore, exposure of food-simulating solvents to resin composites may affect surface and optical properties. Additionally, assessment of depth of cure of bulk fill composites is important to confirm the optimal curing depth of the materials.

In the following chapters, the effects of water and solvent on selected physical, mechanical and surface properties of experimental and contemporary resin composites, as well as depth of cure of new bulk fill composites, will be reported and discussed followed by a final conclusion and recommendation for further studies.

## **Chapter Two**

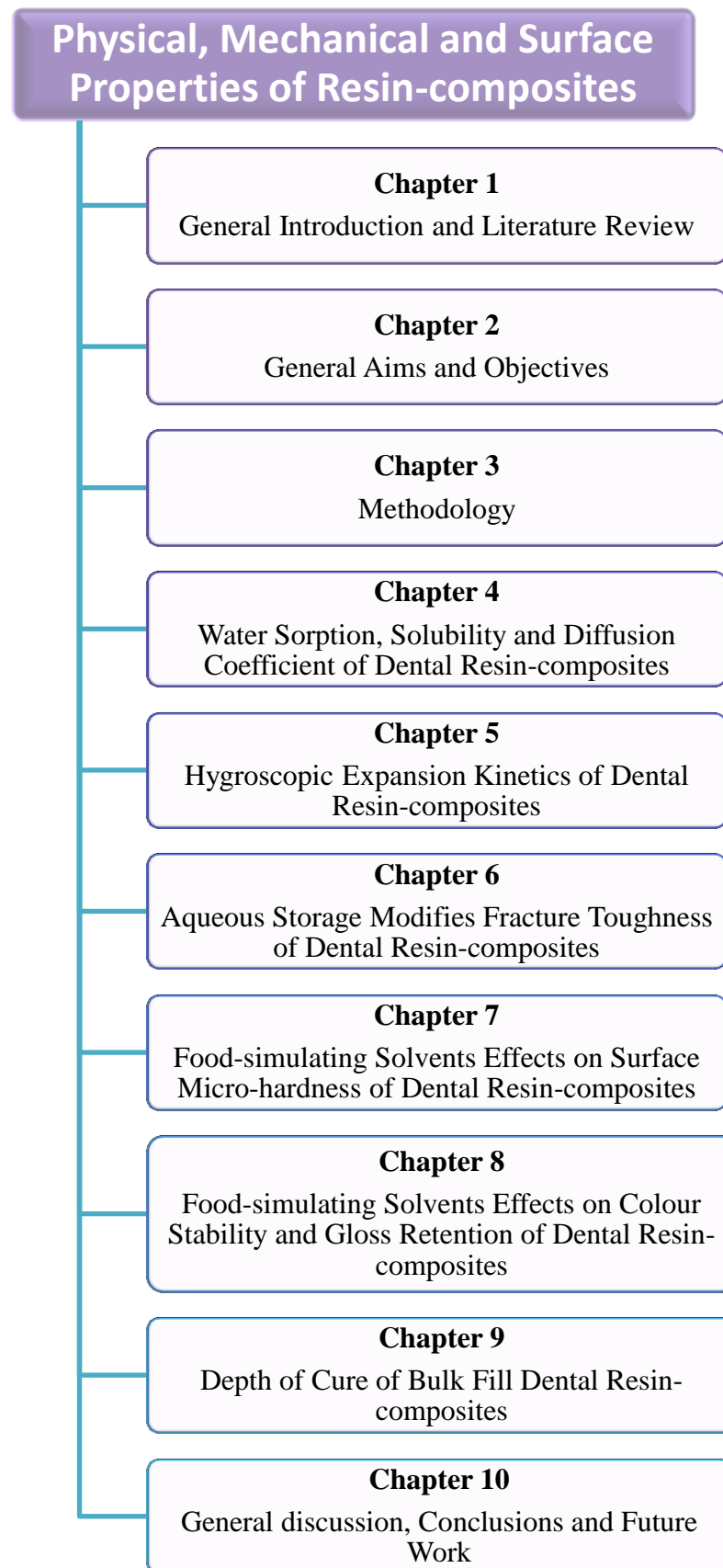
### **General Aims and Objectives**

The aims of this research were to study the effect of water (at 37°C) on a range of resin composites and their physical and mechanical properties. As well as the effect of food-simulating solvent on surface properties. In addition, the depth of cure of the new bulk fill materials was investigated.

The specific objectives were to investigate experimental and contemporary resin composites in order to:

- Study water sorption, solubility and diffusion coefficient, the specimens ageing in water for 150 days at 37°C.
- Investigate the effect of water storage on the hygroscopic expansion kinetics, the specimens ageing in water for 150 days at 37°C.
- Investigate the effect of water storage on fracture toughness, the specimens ageing in water for 1 day and 7 days at 37°C.
- Investigate the effect of food-simulating solvents on surface micro-hardness, ageing in food-simulating solvent for 1 day and 1 month at 37°C.
- Investigate the effect of food-simulating solvents on colour stability and gloss retention, ageing in food-simulating solvent for 1 day, 1 month and 6 months at 37°C.
- Examine depth of cure of bulk fill resin composite, dry ageing 24 hours post-curing at 37°C.

The outline of the studies is shown diagrammatically in Figure 2.1:



**Figure 2.1:** General outline for studies

# **Chapter Three**

## **Methodology**

### **3.1 Introduction**

Both established and new techniques were applied to meet the objectives of the current research. Standard techniques were used to investigate properties such as micro-hardness, colour stability, gloss and fracture toughness of resin composite. In this chapter, some techniques conducted in the present research will be explained further, including:

- Hygroscopic expansion measurement using a non-contact laser scan micrometer (LSM) system.
- Fracture toughness ( $K_{IC}$ ) measurement using a Universal Testing Machine.
- Colour measurement using a chroma meter.
- Gloss measurement using a glossmeter.

The instruments used in the present study have been designed to embody and comply with the basic rules of "engineering measurements". These rules include [109]:

#### **3.1.1 Accuracy**

This is the closeness with which the measuring instrument can determine the true value of the property under specified conditions of use.

#### **3.1.2 Sensitivity**

This is the linear or non-linear relationship between a change in the output reading for a given change of input. Sensitivity is often known as a scale factor or instrument magnification, and an instrument with a large sensitivity will specify a large movement of the indicator for a small input change.

#### **3.1.3 Linearity**

Most instruments are specified as functioning over a particular range and the instruments can be assumed to be linear when additional changes in the input and output



are constant over the specified range. The amount of non-linearity accepted is normally quoted as a percentage of the operating range.

#### **3.1.4 Resolution**

This is defined as the smallest input increment change that provides some small but definite numerical change in the output.

#### **3.1.5 Threshold**

If the instrument input is very slowly increased from zero, there will be a minimum value needed to give a measurable output change. This minimum value defines the threshold of the instrument.

#### **3.1.6 Repeatability**

This is the capability of an instrument to give the same indications, or responses, for recurrent applications of the same value of the measure and under specified conditions of use.

#### **3.1.7 Zero stability**

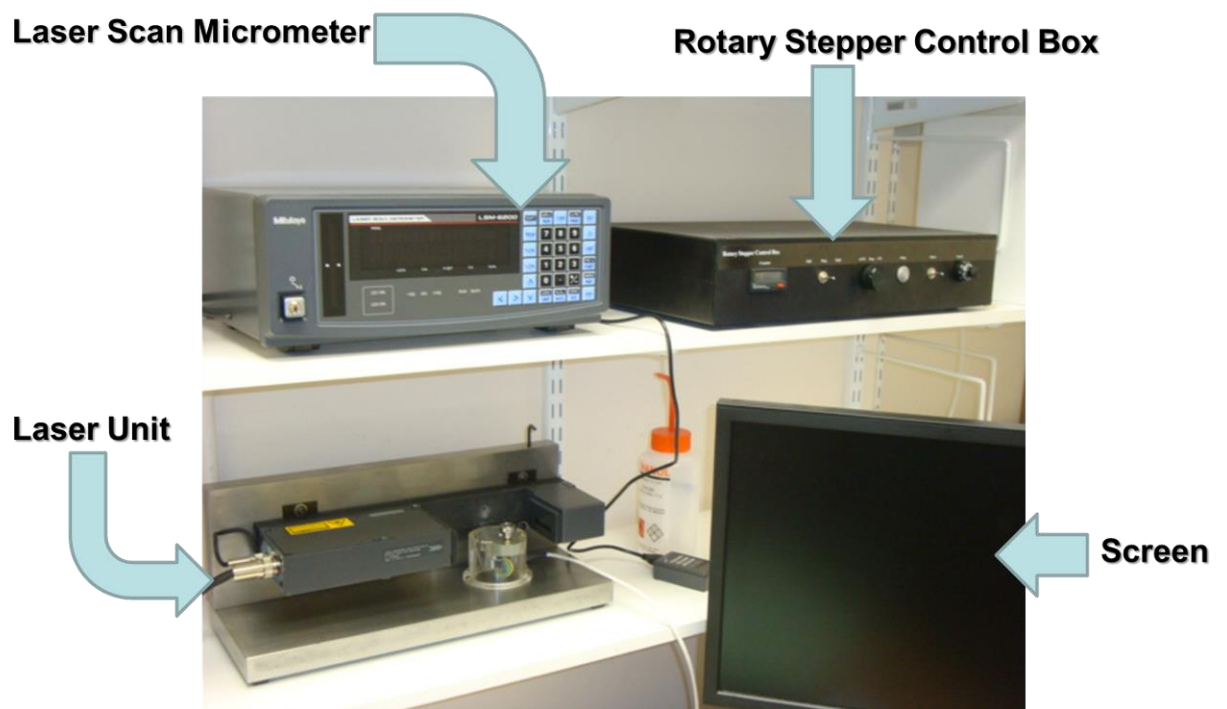
This is the measure of the capability of the instrument to return to zero reading after the measurement and variables, such as temperature, pressure and vibration have been removed.

#### **3.1.8 Readability**

This is defined as the ease with which readings may be taken with an instrument. Problems with readability may often occur owing to parallax mistakes when an observer is watching the position of a pointer on a calibrated scale.

### 3.2 The hygroscopic expansion measurement using a laser scan micrometer

The instrument consists of a laser scan micrometer (LSM) system (Measuring Unit LSM-503s and Display Unit LSM-6200, Mitutoyo Corporation, Japan), mounted on a heavy stainless steel base, 25 mm thick, with rubber feet. A disk specimen holder was rotated in a horizontal plane around a vertical axis by an electronic stepper-control unit. The LSM was interfaced, via the Display Unit, to a PC, with a USB input, for further recording and data processing (Figure 3.1). The technical specifications of the laser micrometer are listed in Table 3.1.

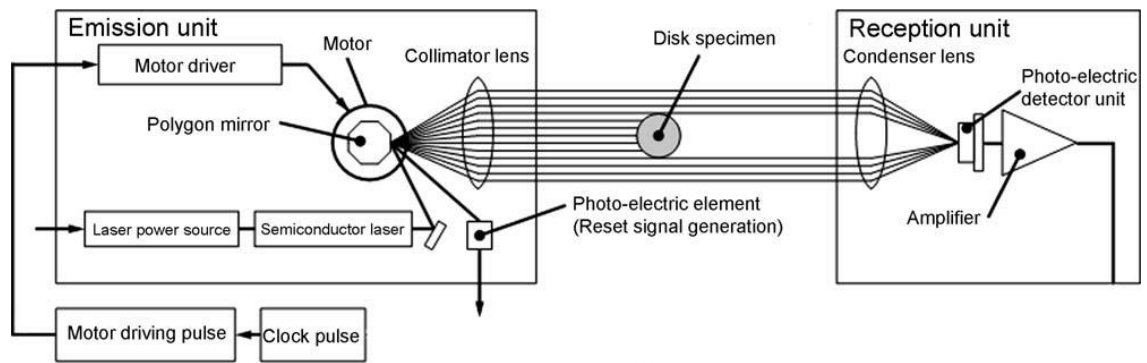


**Figure 3.1:** Laser scan micrometer (LSM) system

**Table 3.1:** Specifications of the LSM unit

<b>Model</b>	Mitutoyo, LSM-503S
<b>Laser type</b>	Visible semiconductor laser
<b>Laser wavelength</b>	650 nm
<b>Scanning range</b>	Up to 30 mm
<b>Measuring range</b>	0.3 to 30 mm
<b>Resolution</b>	200 nm
<b>Repeatability</b>	$\pm 0.1 \mu\text{m}$
<b>Speed of rotation</b>	28 steps/s
<b>Scanning rate</b>	3200 scans/s
<b>Laser scanning speed</b>	226m/s

The measuring LSM system (Figure 3.2) has obtained the specimen dimensional data rapidly and accurately using a highly directional parallel-scanning laser beam. The laser beam, generated by a laser oscillator, was directed at a polygonal mirror rotating at high speed and synchronized by clock pulses. Then the reflected laser beam passed through a collimator lens and maintained its constant direction through the beam window towards the disk specimen. The measurement light rays travelled as "parallel beams" towards a photo-electric detector unit, but were partially obstructed by the disk specimen. The extent of the beam-obstruction was directly proportional to the disk diameter. The resulting electrical output signal changed according to the duration over which the beam was obstructed. This was processed by the Display Unit CPU and the dimensions of the disk were displayed digitally. The laser beam system was able to measure each disk specimen diameter to a resolution of 200 nm.



**Figure 3.2:** The configuration of the system

The stepper-control unit has maintained the stepwise rotation of the disk specimen (mounted on its holder) with a total of 800 steps per rotation. The speed of rotation was 28 steps per second. The laser scanning speed of the laser beam was 3200 scans/second and so 91,428 diametral measurements were taken per revolution; these were averaged, in sets of 1024, to give 89 recorded reading/revolution. In each sorption time-period, specimens were measured over five complete rotations. Therefore, the diametral values presented for each specimen at each time point were obtained as overall averages of 445 data values, which were transferred to an Excel file. The grand mean for the 5 specimens per group was then obtained for each sorption time-period.

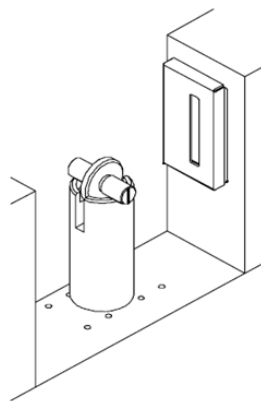
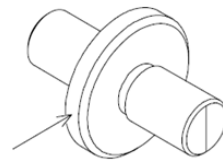
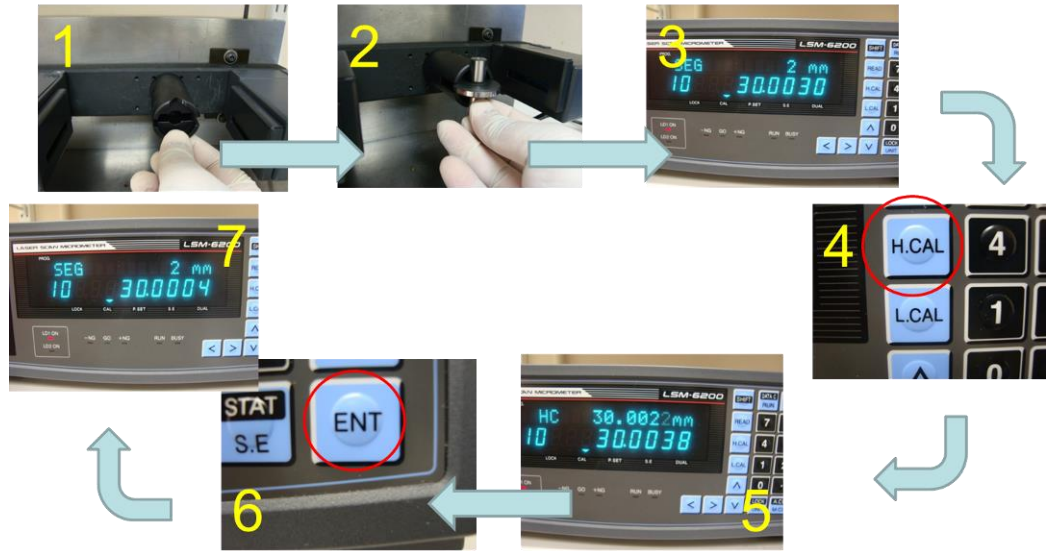
### 3.2.1 Calibration

The LSM system can be calibrated quite easily and with high accuracy. The system was calibrated before each measurement, using two reference gages according to the manufacturer's instructions. For entering the calibration mode, a gage stand and 2 supported calibration gages were used. At the beginning, the power was turned on and the system took at least 30 minutes to thermally stabilize. Prior to use the gages, the gage and gage stand were wiped with a cloth soaked in alcohol to remove any dust. Also, the plastic cylinder mount was unscrewed to provide a space for the stand and gages.

For setting the HIGH CAL stepped type gage (Figure 3.3), the HIGH CAL gage was mounted on the stand. The centre point of the gage, which is indicated by an arrow ( $\rightarrow$ ), was the calibration point. The mark (|) on the end face of the gage comes to vertical. In

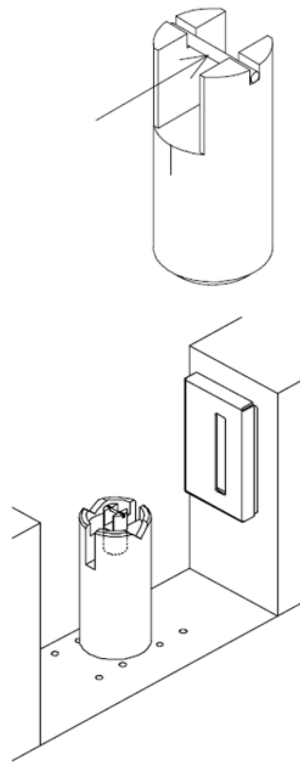
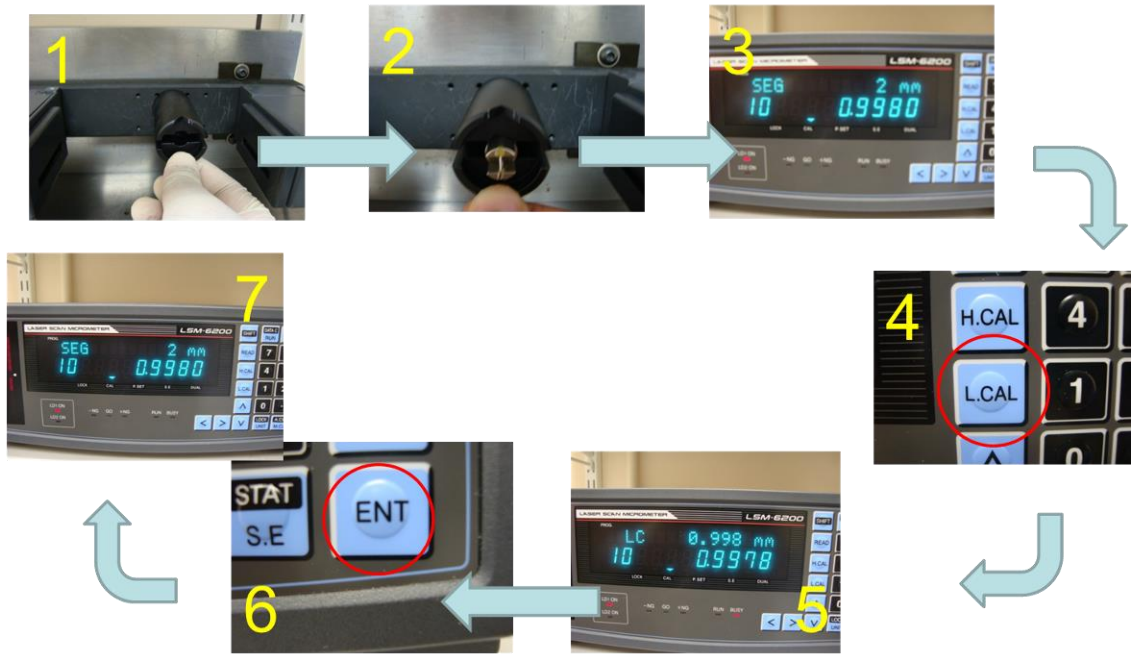
the ready state, the H.CAL key was pressed. The previous set HIGH CAL value was displayed, and the HIGH CAL setup mode was entered.

For setting LOW CAL with-holder type gages (Figure 3.4), the LOW CAL gage on the stand was mounted. The centre point of the gage, which is indicated by an arrow ( $\rightarrow$ ), was the calibration point. The laser beam was aligned with the vertical line (|) marked on the side of the gage. In the ready state, the L.CAL key was pressed. The previously set LOW CAL value was displayed, and the LOW CAL setup mode was entered. The gage stand and was removed and plastic cylinder was remounted into its place. Thus, the LSM was calibrated and ready to use.



Stepped type

**Figure 3.3:** Setting the HIGH CAL stepped type gage



With-holder type

**Figure 3.4:** Setting LOW CAL with-holder type gages

### 3.3 Fracture toughness ( $K_{IC}$ ) measurement using a Universal Testing Machine

$K_{IC}$  measurements of dental materials are often used to investigate the properties of new or experimental materials. In this study a Universal Testing Machine (Zwick/Roell-2020) was used to conduct this experiment (Figure 3.5).

Both the British Standard (BS) and the American Society for Testing and Materials (ASTM) specify the requirements for any test. For measuring  $K_{IC}$ , for instance, the size and shape of the specimen should be determined to ensure the plane strain condition at the crack tip. Any size and shape can be used, as long as they are consistent with mode I crack displacement and the stress intensity calibration is known. The method used in this study was to bend single edge-notched (SEN) specimens. The specimens were loaded until they fractured and then the fracture loads were used to compute  $K_{IC}$ . The cast metal jig, which was attached to the Universal Testing Machine, was used to conduct this experiment (Figure 3.6).



**Figure 3.5:** Universal Testing Machine





**Figure 3.6:** KIC specimen mounted on a cast metal jig

#### **3.4 Colour measurement using a Chroma Meter**

The Chroma Meter CR-221 (Figure 3.7) is a compact tristimulus colour analyser for measuring the reflected colours of surfaces. It has a 3mm diameter measuring area, and uses a 45° illumination angle and a 0° viewing angle for measuring precise areas of printed matter and other glossy surfaces. CIE illuminant D<sub>65</sub> lighting conditions were used for the measurements. Absolute measurements were taken in L\*a\*b\* Commission Internationale de l'Eclairage Standard (CIE 1976). The colour difference was measured as  $\Delta E$ .



**Figure 3.7:** Chroma Meter instrument

### 3.4.1 Calibration

The Chroma Meter has 20 different calibration channels numbered from 00 to 19. Channel 00 should be calibrated to a standard white plate (Calibration Plate CR-A45 for CR-221); channels 01 to 19 may be calibrated to any user-selected surface. By providing 20 memory channels for storing calibration data, the Chroma Meter allows the appropriate calibration channel to be chosen based on the sample surface and measurement conditions. For best results, calibration and measurements should be performed under the same conditions.

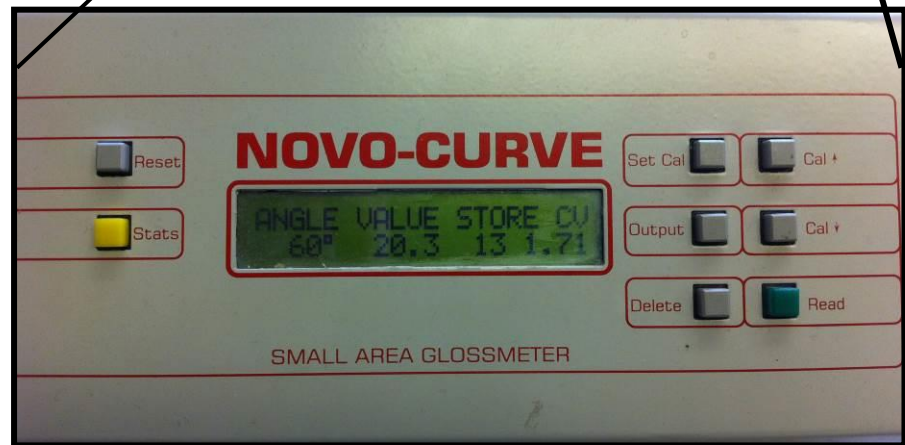
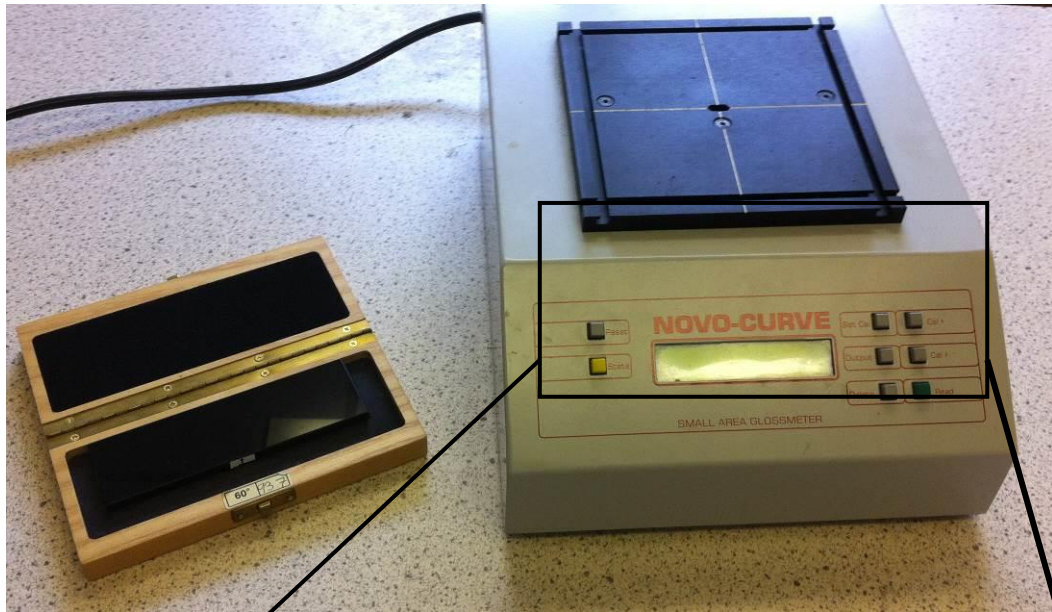
### 3.5 Gloss measurement using a glossmeter

The gloss is measured by directing a light beam at an angle of  $60^\circ$  to the test surface and monitoring the light reflected at the same angle. In this study a glossmeter was used to conduct this experiment (Figure 3.8).

### 3.5.1 Calibration

Instrument calibration should be checked regularly and if required the instrument should be adjusted. When positioning the tile on the instrument, care should be taken to align the arrows with the white grid lines on the plate; then the reading can be taken. The value displayed was compared with the value assigned to the tile (93.7%) for the matching measurement angle. If the values vary by more than  $\pm 0.5$  (GU or %) it will be necessary to adjust the calibration. This should be done with the instrument in place on the tile. Holding the CAL  $\uparrow$  button will incrementally increase the value, while the CAL  $\downarrow$  button will decrease it. Releasing the button will set the calibration at the displayed value.

Once the calibration has been adjusted to the appropriate level it can be checked by pressing the READ button. The calibration value is stored in memory when the unit switches off, so there is no need to recalibrate the instrument each time it is switched on.



**Figure 3.8:** Glossmeter instrument

## **Chapter Four**

### **Water Sorption, Solubility and Diffusion coefficient of Dental Resin-composites**

A. Alrahlah, N. Silikas, D.C. Watts

## 4.1 Abstract

**Objective:** To investigate the long-term water sorption and desorption processes of resin composites at 37°C.

**Materials and Methods:** Eight resin composites were examined: 1 micro-hybrid (Bright Light<sup>®</sup>), 5 nano-hybrids (Experimental Vertise<sup>™</sup>; Nanoceram-Bright<sup>®</sup>; Tetric EvoCeram<sup>®</sup>; Grandio<sup>®</sup> SO; Ceram·X<sup>™</sup> duo) and 2 flowables (X-tra base; Venus<sup>®</sup> Diamond Flow). Five disks (15 x 2 mm) of each material were prepared. The specimens were first desiccated to obtain a constant mass. They were then stored in distilled water at 37±1°C and weighed for 150 days at fixed time intervals, then reconditioned dry to study desorption for another 75 days at 37±1°C. Data were analysed by repeated measures ANOVA, one-way ANOVA and Tukey's *post hoc* test ( $\alpha = 0.05$ ).

**Results:** The water sorption after 150 days storage ranged from 7.34 to 39.99 µg/mm<sup>3</sup>. The solubility ranged from 0.31 to 10.26 µg/mm<sup>3</sup>. Experimental Vertise had the highest sorption and solubility ( $p < 0.001$ ), while X-tra base showed the lowest sorption ( $p < 0.001$ ). X-tra base, GrandioSO and Ceram·X duo showed low solubility. The diffusion coefficients ranged from  $1.66 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$  (GrandioSO in sorption) to  $4.27 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$  (Venus Diamond Flow in desorption).

**Conclusion:** The high water sorption and solubility of the experimental self-adhesive composite (Experimental Vertise) is significant amongst resin composites which may also influence clinical performance. The bulk fill composite (Xtra base) had the lowest water sorption amongst the resin composites studied.

**Key words:** resin composites, water sorption, solubility, diffusion coefficient, micro-hybrid, nano-hybrids

## 4.2 Introduction

The superior advantage of resin composites over other direct restorative materials is their excellent aesthetics. The resin composite materials widely used today are based on dimethacrylate resins. However, compared to earlier resin composites, the modification of filler morphology and reduction in the filler size has enhanced the mechanical properties and aesthetics. The latest modification results in an increase in surface area and enhanced filler loading [18].

Water sorption of resin composites may have significant effects on their physical and mechanical properties such as strength, hardness, elastic modulus and dimensional stability [110, 111]. Furthermore, other properties including wear resistance, biocompatibility, hygroscopic expansion and colour stability may also be affected [112]. In aqueous environments, resin composites can absorb water and may release unreacted monomers. These may encourage the growth of bacteria or stimulate allergic reactions [113]. Moreover, silane hydrolysis and microcrack formation resulting from water sorption can decrease the longevity of resin composites [70]. Notably, the late stage of water sorption may break down the bonding between the matrix and filler [114] and as a result compromise the mechanical properties [115].

Since water diffuses through the matrix, matrix/filler interfaces, pores and flaws, it gradually degrades the filler particles [116]. There are many factors that have an effect on water sorption and the diffusion coefficient. These factors are: the copolymer structure and the nature of the solvent, filler type, polymeric matrix/filler interface, degree of polymerization, cross-linking, temperature, catalyst and initiator systems concentration, presence of entrapped air voids within the matrix and the water sorption cycle [110, 112, 114].

However, while the oral environment is normally wet there are clinical circumstances, such as dry mouth syndrome, where this is not the case. But in laboratory experiments, idealised conditions are frequently used such as successive sorption and desorption cycles. In the sorption part of such a cycle, specimens are immersed in water or similar aqueous or solvent media. In the specimen-desorption part of the cycle, previously aqueous-equilibrated specimens are placed in a desiccator environment which promotes gradual evaporation of solvent (water) from the specimen. Exposure to water, or other solvent, can leach out residual monomers and oligomers, filler particles and ions from

its surfaces thereby reducing specimen mass and causing shrinkage, unless – as is often the case - the solvent/water uptake causes a net mass increase and/or dimensional expansion. At the completion of a long-term desorption process, the resin composite may have either the same or less mass than at the beginning of the cycle [117, 118].

The aim of this study was to determine the water sorption and water solubility of a set of resin composites over an extended time-period of water uptake. The cycle was to be completed by a further extended process of desorption. The null hypotheses were that: there is no difference in either water sorption or solubility between the materials after 150 days aqueous exposure.

### **4.3 Materials and Methods**

#### **4.3.1 Specimen preparation**

Eight representative resin composites were investigated (Table 4.1) over an extended time period of 150 days, rather than the short period of 7 days required in ISO basic performance measurements. Five disk-shaped specimens (n=5) were prepared for each material, using brass moulds. The materials were manipulated and polymerized according to ISO 4049: 1999 [119] and their manufacturers' instructions. Each mould (15 x 2 mm) was sandwiched between two pieces of transparent Mylar™ strip with two glass slides on either side and then pressed together. Five overlapping sections on each side of the specimen were irradiated in turn using a halogen curing unit with a tip diameter of 10 mm, approximately 1 mm away from both sides of the specimens (Optilux® 501, SDS, Kerr, Danbury, CT, USA) under the standard curing mode (output wavelength range: 400-505 nm; output irradiance: 580–700mW/cm<sup>2</sup>, applied for 40 s). A calibrated radiometer was used to verify the irradiance at each use of the light cure unit. Each specimen was carefully removed from its mould and any edge 'flash' was removed with a 1000 grit silicon carbide abrasive paper. After that, the specimens were transferred to a desiccator containing silica gel at 37 ± 1 °C. After 24 h, the desiccator was removed from the incubator and stored at 23 ± 1 °C for 1 h. Specimens were then weighed on a precision calibrated balance to an accuracy of ± 0.01 mg (Ohaus Analytical Plus, Ohaus Corporation, USA). This cycle was repeated until a constant



mass  $m_1$  was obtained, that is, until the mass loss of each specimen was not more than 0.2 mg in a 24 h period.

**Table 4.1:** Materials tested

Code	Product	Manufacturer	Matrix	Filler type	Filler %W/W	Lot Number
BL	Bright Light®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Ba glass, mixed oxide 0.04-0.25 µm	81	610230
NCB	Nanoceram-Bright®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Barium glass, mixed oxide 0.05-0.7 µm	80	630212
Exp.VT	Expermintal Vertise™	Kerr Corp, Orange, USA	GPDM and methacrylate co-monomers	Prepolymerized filler, Ba glass; nanoscale SiO <sub>2</sub> & YbF <sub>3</sub>	-	3379131
TEC	Tetric EvoCeram®	Ivoclar Vivadent AG, Schaan, Liechtenstein	Bis-GMA, UDMA	Ba glass, silicate, SiO <sub>2</sub> , mixed oxide 40nm-3000nm	76	L56579
GSO	Grandio SO	Voco GmbH Cuxhaven, Germany	Bis-GMA, Bis-EMA, TEGDMA	Ba glass 1µm SiO <sub>2</sub> 20-40 nm	89	1048014
XB	X-tra base	Voco GmbH Cuxhaven, Germany	Aliphatic di-methacrylate, Bis-EMA	Ba glass, YbF <sub>3</sub> , fumed silica	75	V45252
VDF	Venus® Diamond Flow	Heraeus Kulzer GmbH Hanau, Germany	UDMA, EBADMA	Ba-Al-F silicate glass, YbF <sub>3</sub> and SiO <sub>2</sub>	65	010100
CXD	Ceram-X™ duo	Dentsply GmbH Konstanz, Germany	Methacrylate modified polysiloxane, Dimethacrylate	Barium-aluminium-borosilicate glass, SiO <sub>2</sub>	76	0811000572

### 4.3.2 Water Sorption and Solubility

Sorption measurements were performed according to a modification of the method in the International Standard ISO 4049 [119]. Each of the five specimens was separately immersed in 10 ml of distilled water in small glass bottles, fitted with polyethylene caps, and maintained at 37°C for periods of time: 1 and 3 hours, and 1, 2, 3, 4, 5, 6, 7, 14, 21, 28, 60, 90, 120 and 150 days. At each time interval, each specimen was removed from its bottle, using stainless steel tweezers, and was carefully dried on filter paper and weighed 1 min after removal from the water. It was then returned to aqueous storage, maintaining the total volume of water as 10 ml. The masses recorded are denoted  $m_2(t)$ .

### 4.3.3 Reconditioning / Desorption of Specimens

Following the sorption cycle, the specimens were dried in a desiccator containing silica gel and weighed at regular intervals of 1, 2, 3, 4, 5, 6, 7, 14, 21, 28, 50, 60, 75 days, until the mass loss of each specimen was not more than 0.2 mg in any 24 h period, to obtain a constant final mass  $m_3$ .

Specimen percentage weight increase  $W_i$  (%) and water sorption  $W_{so}$ , were calculated as follows:

$$W_i(\%) = 100 \left[ \frac{m_2(t) - m_1}{m_1} \right] \quad \text{Eq.1}$$

$$W_{so} = \left[ \frac{m_2(t) - m_3}{V} \right] \quad \text{Eq.2}$$

The solubility ( $Sol$ ) values were obtained, in micrograms per cubic millimetre, using the following equation:

$$Sol = \left[ \frac{m_1 - m_2}{V} \right] \quad \text{Eq.3}$$

Here  $m_1$  is the conditioned mass prior to immersion in water,  $m_3$  is the equilibrium mass of the specimen after desorption in micrograms, as previously described, and  $V$  is the volume of the specimen, in cubic millimetres.

#### 4.3.4 Diffusion Coefficients

Fick's first law of diffusion relates the diffusive flux to the concentration field, by postulating that the flux goes from regions of high concentration to regions of low concentration, with a magnitude proportional to the concentration gradient (spatial derivative). In one (spatial) dimension the diffusion flux is represented by Eq.4:

$$J = -D \frac{\partial c}{\partial x} \quad \text{Eq.4}$$

where  $J$  is the diffusion flux,  $D$  is the diffusion coefficient,  $c$  is the concentration of diffusing substance and  $x$  is the position (length) [117].

Thus,  $-\frac{\partial c}{\partial x}$  is the concentration gradient, which is the driving force for one-dimensional diffusion in ideal solutions or mixtures.

At the molecular level,  $D$  is proportional to the squared velocity of the diffusing particles, which depends on the temperature, the viscosity of the fluid and the size of the particles, according to the Stokes-Einstein relation.

Fick's second law predicts how diffusion causes the concentration field to change with time (t).

It can be derived from Fick's first law and the mass balance, as in Eq.5:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Eq.5}$$

The method of calculating the diffusion coefficient was taken from an established diffusion theory, which was developed previously for estimating the water uptake behaviour of dental composites. According to Fick's law, Eq.6 predicts that for a disk-shaped specimen, in the early stages of water sorption (when  $M_t/M_\infty \leq 0.6$ ):

$$\frac{M_t}{M_\infty} = 2 \left[ \frac{D}{\pi L^2} \right]^{1/2} \quad \text{Eq.6}$$

where  $M_t$  is the mass uptake (g) at time  $t$  (s),  $M_\infty$  is the mass uptake (g) at equilibrium, and  $L$  is the specimen thickness (m).  $D$  is the diffusion coefficient ( $\text{cm}^2 \text{ s}^{-1}$ ) and is calculated from the linear (early) gradient of the plot  $M_t/M_\infty$  against  $t^{1/2}$ .

Thus, if the sorption (or desorption) is diffusion-controlled, then a plot of  $Mt/M_\infty$  versus  $t^{1/2}$

should give a straight line of slope:

$$S = 2 \left[ \frac{D}{\pi \cdot L^2} \right]^{1/2} \quad \text{Eq.7}$$

from which  $D$ , if  $S$  is in  $\text{min}^{1/2}$ , can be calculated:

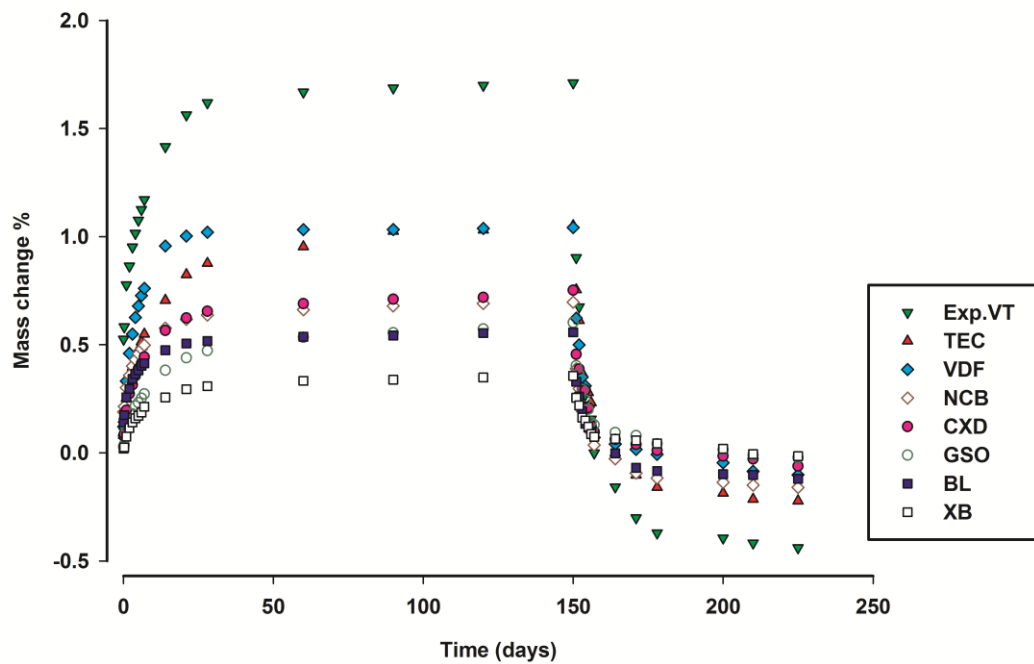
$$D(\text{cm}^2 \cdot \text{s}^{-1}) = \left[ \frac{S^2(\text{min}^{1/2})}{240} \right] \cdot \pi \cdot L^2 \quad \text{Eq.8}$$

#### 4.4 Statistical Analysis

Data were analysed using SPSS (Version 20.0, IBM, New York, USA). The means and standard deviations of water sorption and solubility were calculated. Repeated measures ANOVA was applied for water sorption during 150 days ( $\alpha = 0.05$ ). A one-way ANOVA was achieved for water sorption and solubility at 150 days, followed by the Tukey's *post hoc* tests (at  $\alpha = 0.05$ ).

#### 4.5 Results

All resin composites showed a percentage mass change during the water sorption/desorption cycle (Figure 4.1). All materials showed increases in mass of different magnitudes by their water uptake until they reached equilibrium after 150 days. After they were transferred to a dessicator environment, they rapidly decreased in their mass due to desorption until they reached constant mass within 75 days. All materials had a lower reconditioned mass ( $m_3$ ) than their initial mass ( $m_1$ ).



**Figure 4.1:** The percentage mass change of water sorption and desorption

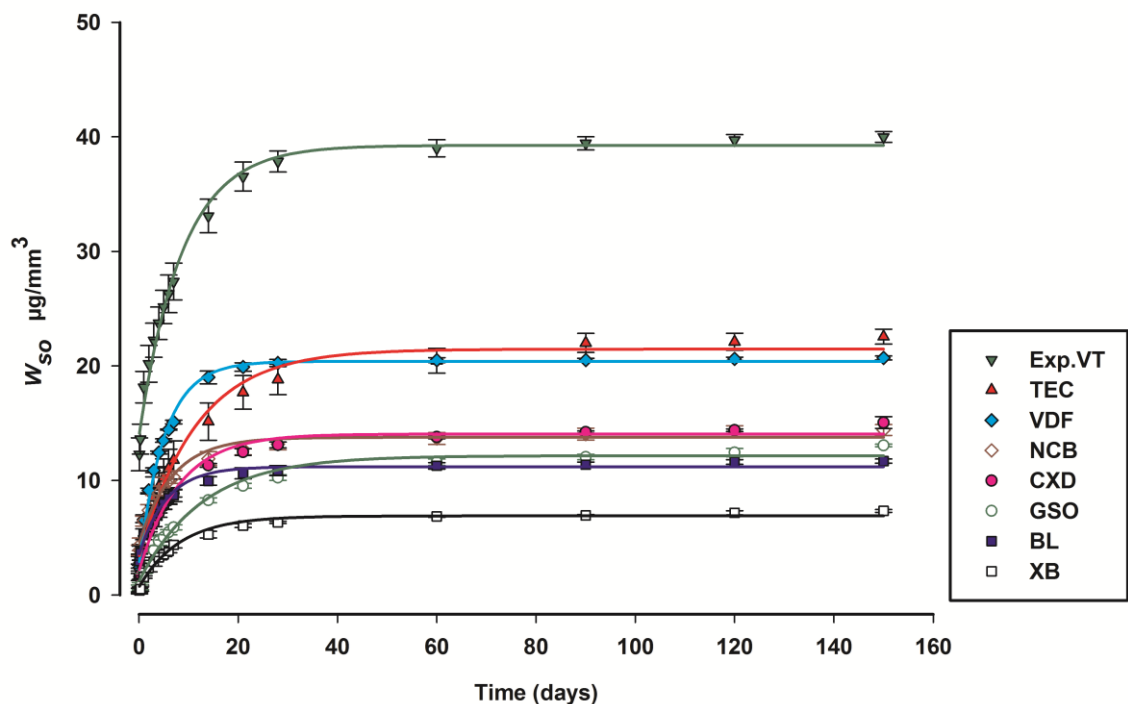
**Table 4.2:** Water sorption ( $W_{so}$ ) and solubility ( $Sol$ ) of resin composites after 150 days' storage in distilled water at 37°C

Materials	$W_{so}$ ( $\mu\text{g}/\text{mm}^3$ )	$Sol$ ( $\mu\text{g}/\text{mm}^3$ )
	Mean (Std)	Mean (Std)
BL	<b>11.69</b> (0.19) <sup>a</sup>	<b>2.52</b> (0.55) <sup>a,b</sup>
NCB	<b>14.41</b> (0.48) <sup>b</sup>	<b>3.32</b> (0.47) <sup>b</sup>
Exp.VT	<b>39.99</b> (0.47) <sup>c</sup>	<b>10.26</b> (1.39) <sup>c</sup>
TEC	<b>22.55</b> (0.65) <sup>d</sup>	<b>4.21</b> (0.56) <sup>d</sup>
GSO	<b>13.06</b> (0.11) <sup>e</sup>	<b>0.48</b> (0.28) <sup>e</sup>
XB	<b>07.34</b> (0.13) <sup>f</sup>	<b>0.31</b> (0.16) <sup>e</sup>
VDF	<b>20.69</b> (0.17) <sup>g</sup>	<b>2.02</b> (0.49) <sup>a,b</sup>
CXD	<b>15.05</b> (0.52) <sup>b</sup>	<b>1.23</b> (0.25) <sup>e,a</sup>
The same superscript small letters indicate a homogeneous subset (columns) ( $p < 0.05$ )		

Water sorptions and solubilities at 37°C are shown in Table 4.2. All materials showed rapid water sorption during the first 30 days. After this time, further changes were gradual until equilibrium was reached (Figure 4.2).

During 150 days water immersion, repeated measures ANOVA showed significant differences in water sorption of all resin composites. As shown in Table 4.2, water sorptions at 150 days ranged from 7.34 to 39.99  $\mu\text{g}/\text{mm}^3$ . Exp.VT had the highest sorption ( $p < 0.001$ ), followed by TEC and VDF, while the lowest was XB ( $p < 0.001$ ). There was no significant difference between NCB and CXD ( $p \geq 0.05$ ). NCB was significant greater than BL ( $p < 0.001$ ).

The permitted sorption limit in ISO Standard 4049 is 40  $\mu\text{g}/\text{mm}^3$  after 7 days storage. All the resin-composites complied with this standard, even Exp.VT - which was essentially equivalent to the limit value. However, in our prolonged experiments, the aqueous challenge was more severe than in the ISO procedure, so the greater sorption for Exp.VT should not be a cause for concern.

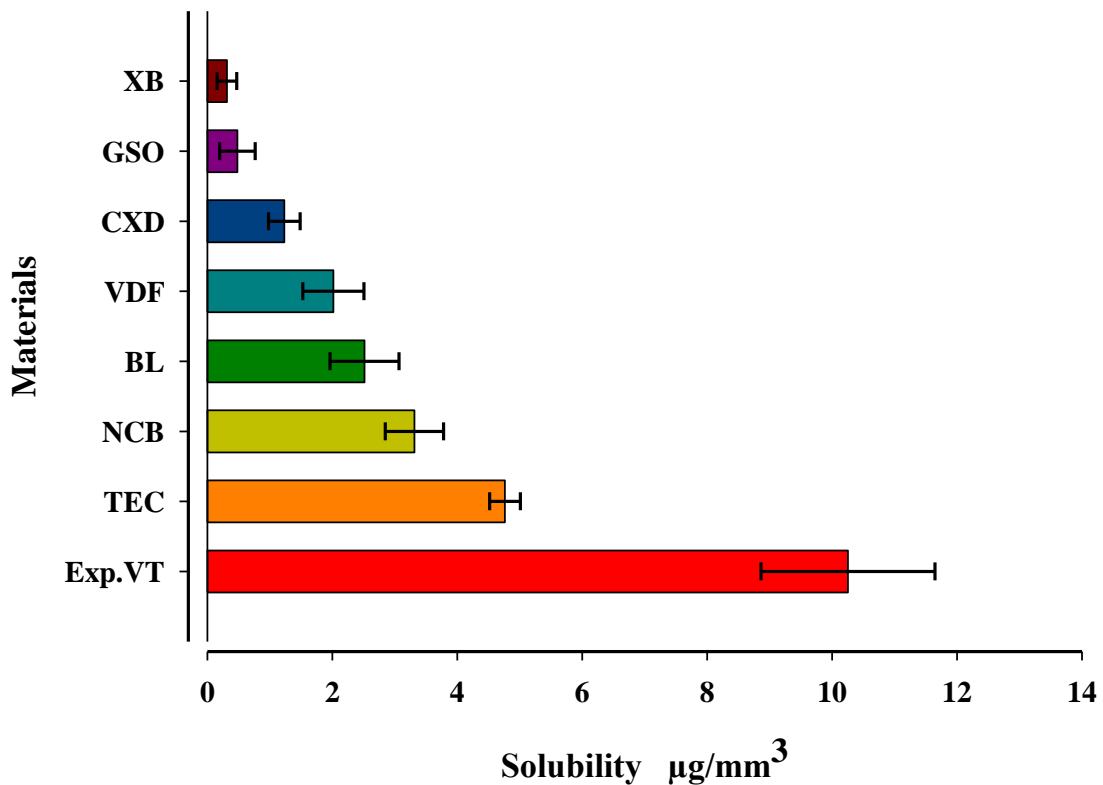


**Figure 4.2:** Water sorption of the examined resin composites after storage in distilled water for 150 days

The solubility of the composites ranged from 0.31 to 10.26 ( $\mu\text{g}/\text{mm}^3$ ) (Figure 4.3). Exp.VT also was the most soluble, being almost double the solubility of the other composites ( $p < 0.001$ ). XB, GSO and CXD had the lowest solubilities ( $p \geq 0.05$ ).

The diffusion coefficients ( $D$ ) were calculated from the linear portion of the plots of  $Mt/M_\infty$  against  $t^{1/2}$  (Figure 4.4), in accordance with equations 7 and 8, as given in Table 4.3. All these composites exhibited higher diffusion coefficients for desorption than for sorption.

$D$  ranged from  $1.66$  to  $4.27 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ . VDF had the highest diffusion coefficients in both sorption and desorption ( $3.59/4.27 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ). GSO had the lowest diffusion coefficients ( $1.66/2.16 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ ).

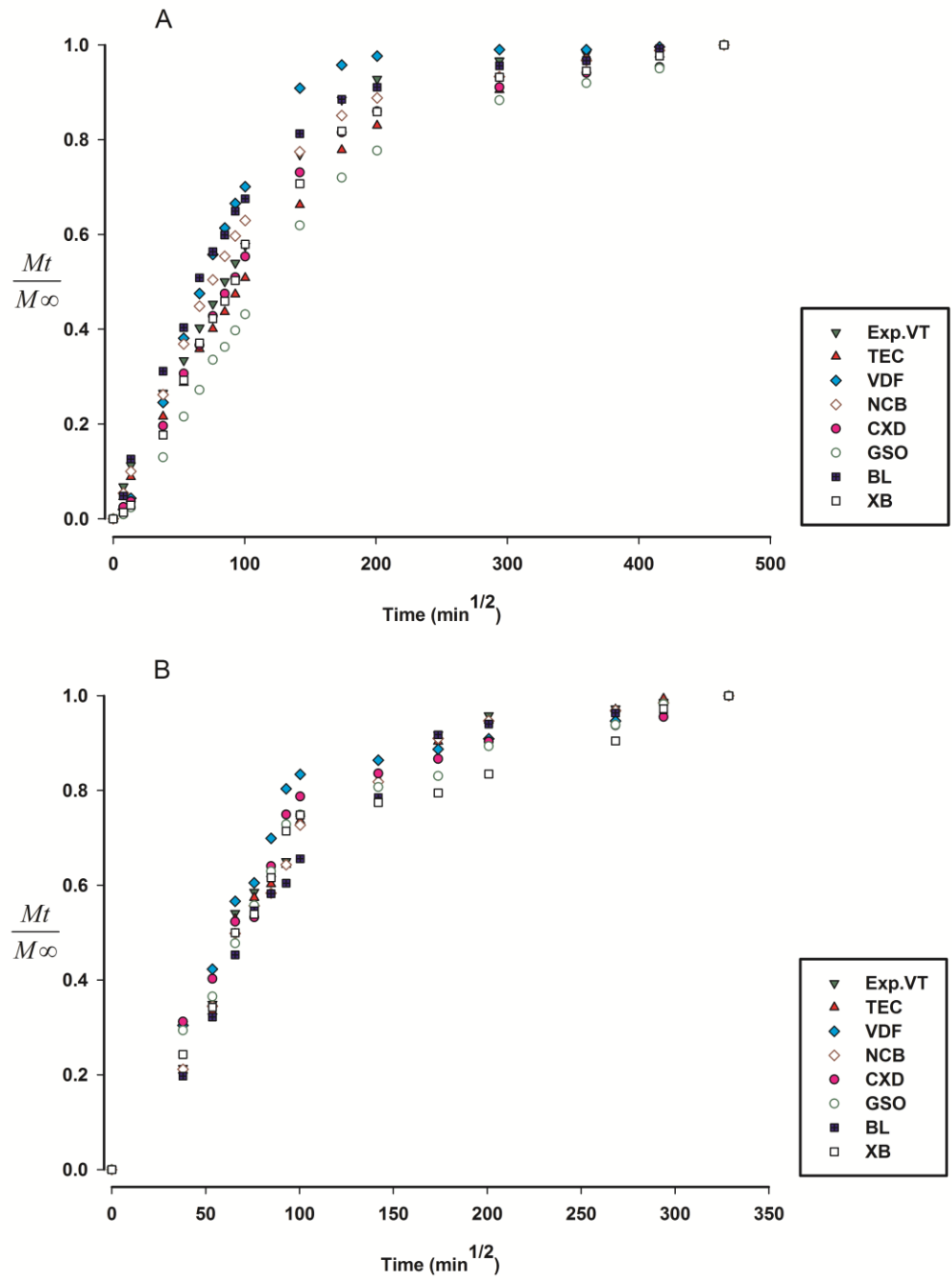


**Figure 4.3:** Solubility of the examined resin composites after storage in distilled water for 150 days



**Table 4.3:** Diffusion coefficient (standard deviation) of water sorption and desorption of composite materials

<b>Materials</b>	<b>Diffusion coefficient (<math>10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}</math>)</b>	
	<b>Sorption</b>	<b>Desorption</b>
<b>BL</b>	2.59 (0.22)	2.67 (0.29)
<b>NCB</b>	2.46 (0.11)	2.61 (0.12)
<b>Exp.VT</b>	2.08 (0.17)	3.96 (0.03)
<b>TEC</b>	1.69 (0.08)	3.72 (0.17)
<b>GSO</b>	1.66 (0.10)	2.16 (0.29)
<b>XB</b>	2.23 (0.03)	2.41 (0.13)
<b>VDF</b>	3.59 (0.06)	4.27 (0.08)
<b>CXD</b>	2.72 (0.08)	3.86 (0.13)



**Figure 4.4:** Plot of  $M_t/M_\infty$  against the  $t^{1/2}$  for A; sorption, B; desorption

## 4.6 Discussion

In considering the subject of water uptake by resin-composites, consideration can be given to those intrinsic and extrinsic factors that *promote* it as well as the varied *consequences* of water uptake. The water sorption of resin composites must depend on the *structural* factors of: resin matrix monomers, filler composition and matrix/filler interface, together with bulk and/or surface variables such as roughness [73]. The choice of monomers used in resin composites, particularly their hydrophilicity, strongly affects their reactivity, viscosity and polymerization shrinkage, but also their mechanical properties, water sorption and swelling [18]. There are also *extrinsic* factors in water uptake: storage time period [120], temperature [121, 122], and applied stress [75]. In terms of *consequences*, water sorption can: (i) deteriorate the resin matrix, (ii) lead to debonding between filler and matrix, and (iii) cause hydrolytic degradation of fillers, with consequent decrease in mechanical properties and wear resistance [73].

It is difficult – but not impossible - to correlate findings from different studies owing to different units expressed, different storage times [120] and different specimen dimensions used [123]. Furthermore, water sorption is a slow process and may not reach equilibrium even after 30 days [124]. Therefore, the time-period for uptake in this study was set as 150 days to give sufficient time to reach equilibrium.

Statistically significant differences were found (Table 4.2) between materials for both water sorption and solubility after 150 days. Thus, the null hypotheses were rejected.

Water sorption by resin composites is a diffusion-controlled process [125]. Figure 3 shows the sorption and desorption diffusion process, where  $Mt/M_\infty$  is plotted against  $t^{1/2}$ . It can be seen in Figure 4.3 that the relationship between  $Mt/M_\infty$  and  $t^{1/2}$  is linear in the initial stages of sorption/desorption cycles. Diffusion coefficients of sorption and desorption ranged from  $1.66$  to  $4.27 \times 10^{-8} \text{ cm}^2 \cdot \text{s}^{-1}$ . The diffusion coefficients during desorption were greater than that during sorption, for all materials, with the ratio  $D_d/D_s$  ranging from 1.06 to 2.21. The lower values of  $D_s$  must have a molecular explanation [126]. Since the desorption process starts from an expanded polymer matrix it will be easier and faster for water molecules to diffuse and then evaporate from that matrix. By contrast, in the earlier sorption process, when water is diffusing into a dry matrix, the process will be relatively slow. It is known that highly cross-linked polymers have reduced network free volume [125]. Thus GSO, which had the lowest diffusion

coefficient, may be highly cross-linked, but this composite was also the most highly filled (w/w). Increased filler loading may reduce sorption, simply by increased substitution for the resin phase [114]. Several other factors can affect the diffusion coefficient: resin type, filler size, the glass reactivity, the degree of silanization and the presence of porosity [126, 127].

In the present study, filler loading (w/w) seems to have no significant systematically decreasing effect on the magnitude of water sorption;  $r = -0.436$ . However, there was a slightly stronger negative correlation of both  $D_s$  ( $r = -0.742$ ) and  $D_d$  ( $r = -0.787$ ) with filler loading. The filler phase could contribute to water sorption owing to its surface coating of silanol (Si–O–H) groups, which will tend to adsorb water [114].

Exp.VT had the highest water sorption and solubility. Its matrix contains GPDM (glycerol phosphate dimethacrylate), a hydrophilic monomer, containing acidic phosphate groups that may promote a significant increase in water sorption [117]. Exp.VT also had the highest solubility, which may be due to a possible lower degree of conversion, although this was not measured.

Composites based on matrices that are more hydrophobic than Bis-GMA, such as Bis-EMA (a non-hydroxylated homologue of Bis-GMA), generally have reduced water sorption. Bis-EMA has ether groups (-O-) creating weaker hydrogen groups with water than the hydroxyl group in Bis-GMA. GSO and XB showed low water sorption and solubility and incorporate some Bis-EMA.

Water sorptions of TEC and VDF were similar and of an intermediate level, both containing UDMA which absorbs proportionately more water than comparable Bis-GMA composites [75, 120].

CDX and NCB sorptions were not statistically different. Also, CDX had low solubility. Modifications in the Ormocer containing matrix may have produced a more water resistant material [128].

The water sorption and solubility of resin composites is important clinically. Excessive water sorption and solubility of resin composites, in addition to insufficient polymerisation, may cause monomer leaching. This may cause reduced biological compatibility as well as inferior mechanical/physical properties [120]. Therefore, degradation may occur that may subsequently result in the failure of the restoration.

The most prevalent matrices in these resin composites are susceptible to water absorption via the two hydroxyl groups of Bis-GMA and/or the urethane groups. Moreover, TEGDMA contains three ethylene oxide linkages which can accept hydrogen bonds but cannot donate them [129].

Water sorption is affected by a poor filler/matrix interface bond [130] and resin composites are likely to accommodate more water at the filler/matrix interface [131]. When matrix and filler are well coupled, water sorption is reduced significantly [116].

#### **4.7 Conclusions**

The water sorption and desorption followed a diffusion law pattern with the diffusion coefficient for desorption being in several cases twice the value for sorption. The sorption process was normally complete after 1 month, for specimens of the size and shape considered. The equilibrium water sorption varied by a factor of five within the set. A self-adhering composite had the greatest water uptake.

## **Chapter Five**

# **Hygroscopic Expansion Kinetics of Dental Resin-composites**

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Published in Dental Materials

## 5.1 Abstract

**Objective:** to evaluate the extent and rate of hygroscopic expansion of resin composites at 37°C.

**Methods:** Eight resin composites were examined: 1 micro-hybrid (Bright Light<sup>®</sup>), 5 nano-hybrids (Experimental Vertise<sup>™</sup>; Nanoceram-Bright<sup>®</sup>; Tetric EvoCeram<sup>®</sup>; Grandio<sup>®</sup> SO; Ceram-X<sup>™</sup> duo) and 2 flowables (X-tra base; Venus<sup>®</sup> Diamond Flow). Five disks (15 x 2 mm) of each material were prepared. The mean change in specimen diameter was recorded by a custom-built non-contact laser micrometer. Specimens were initially measured dry and then at fixed time intervals, over 150 days, after storage in distilled water at 37±1°C. Data were re-expressed in volumetric terms and analysed by repeated measures ANOVA, one-way ANOVA and Tukey's *post hoc* test ( $\alpha = 0.05$ ).

**Results:** The volumetric hygroscopic expansion ranged from 0.58% to 2.26% and can be considered in three bands. First, Experimental Vertise had the highest expansion ( $p < 0.001$ ). Venus Diamond Flow, Tetric EvoCeram and Ceram-X duo were the second band. The third band, with still lower expansion, consisted of Bright light, Grandio So, Nanoceram-Bright and *X-tra base*, with no significant difference between them.

**Conclusion:** For the size (2 mm thickness) and shape of specimen measured, equilibrium was attained in all cases by 60 days. Within this set of resin-composites the equilibrium expansion varied by almost 400 % of the lowest material.

**Key words:** resin composites, hygroscopic expansion, laser scan micrometer, nano-hybrid, micro-hybrid, bulk fill, self-adhering

## 5.2 Introduction

There is increasing concern amongst clinicians about dimensional changes of dental resin composites during and after curing [132]. Recently, several in vitro laboratory studies have investigated long-term dimensional instability and suggested that this might lead to clinical problems such as: post-operative pain, secondary caries, marginal staining, breakdown of the restorations, gap formation, micro-leakage and enamel crack propagation [132-135]. Dimensional stability of resin composites can be caused by polymerization shrinkage, thermal contraction/expansion and interactions with an aqueous environment [136].

An appropriate cavity design, filling technique and bonding agent may reduce gap formation caused by polymerisation shrinkage [137]. Also, water sorption by a resin composite may cause expansion of the composite filling and reduce any gap formed due to polymerisation shrinkage [118, 138, 139]. Hygroscopic expansion could also relax any internal stresses of the resin matrix and compensate for resin composite shrinkage [76, 140, 141]. However, shrinkage occurs within minutes but water sorption takes from days to months. So to get full compensation, the absorption may need to occur for an extended period of several weeks [142]. Consequently, the positive effect of water sorption on marginal gap compensation still requires further direct evidence [140].

There are two contrasting processes during water sorption by composite restoratives in the oral aqueous environment. Firstly, water can leach out unreacted monomers, if they are present, which can lead to loss in mass, shrinkage and changes in mechanical properties [136, 143]. Secondly, water diffusing into the material leads to mass increase and usually can cause a progressive bulk expansion until equilibrium [118, 124, 144, 145].

The aim of this study was to evaluate the extent and rate (kinetics) of hygroscopic expansion of resin composites stored in distilled water at 37<sup>0</sup>C. The null hypotheses were that there would be no difference in either (i) the final magnitude or (ii) the rates of hygroscopic expansion between the examined materials.



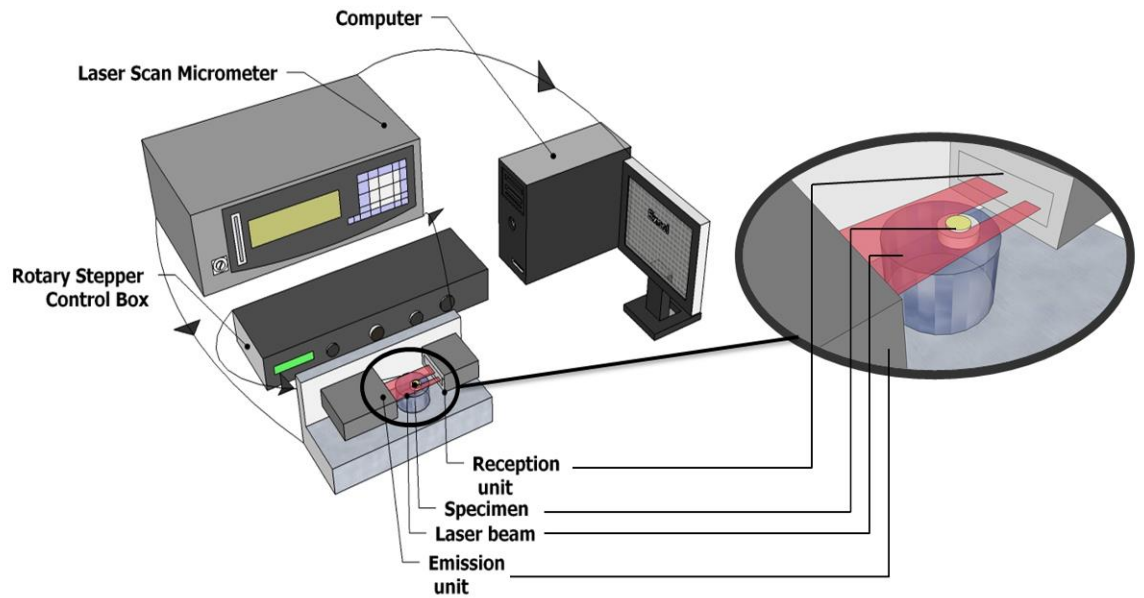
### 5.3 Materials and Methods

Eight representative resin composite materials were investigated (Table 5.1). Five disk-shaped specimens (n=5) were prepared of each material according to ISO 4049: 1999 [119] and their manufacturers' instructions. Care was taken to minimize entrapped air while the uncured material was placed into brass ring moulds (15 x 2 mm) in a laboratory environment at 23 ( $\pm 1$ ) °C. The mould was sandwiched between two transparent Mylar<sup>TM</sup> strips with two glass slides on either side and then pressed together. Five overlapping sections on each side of the specimen were irradiated in turn using a halogen curing unit with a tip diameter of 10 mm approximately 1 mm away from the specimens for both sides (Optilux<sup>®</sup> 501, SDS, Kerr, Danbury, CT, USA) under the standard curing mode (output wavelength range: 400–505 nm; output irradiance: 580–700mW/cm<sup>2</sup>, applied for 40 s). A calibrated radiometer was used to verify the irradiance for each use of the light cure unit. Each specimen was carefully removed from its mould and any edge 'flash' was removed with a 1000 grit silicon carbide abrasive paper. Then the specimens were stored separately in glass vials in a lightproof desiccator with silica gel at 37  $\pm$  1 °C, until the mass change of each specimen was less than 0.2 mg in a 24 h period, which indicated sufficient completion of dehydration. Each specimen was weighed using a calibrated electronic analytical balance with a precision of 0.01mg (Ohaus Analytical Plus, Ohaus Corporation, USA).

The mean change in diameter of the specimens was recorded by a custom-built non-contact laser micrometer to a resolution of 200 nm. The device consisted of a laser-scan micrometer (LSM) system (Measuring Unit LSM-503s and a Display Unit LSM-6200, Mitutoyo Corporation, Japan), mounted on a heavy stainless steel base. A disk specimen holder was rotated in a horizontal plane around a vertical axis by an electronic stepper-control unit. The LSM was connected via the Display Unit to a computer with USB input for further recording and data processing (Figure 1). The LSM system working mechanism was previously described [146].

**Table 5.1:** Materials tested

Code	Product	Manufacturer	Matrix	Filler type	Filler %W/W	Lot Number
BL	Bright Light®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Ba glass, mixed oxide 0.04-0.25 µm	81	610230
NCB	Nanoceram-Bright®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Barium glass, mixed oxide 0.05-0.7 µm	80	630212
Exp.VT	Expermental Vertise™	Kerr Corp, Orange, USA	GPDM and methacrylate co-monomers	Prepolymerized filler, Ba glass; nanoscale SiO <sub>2</sub> & YbF <sub>3</sub>	-	3379131
TEC	Tetric EvoCeram®	Ivoclar Vivadent AG, Schaan, Liechtenstein	Bis-GMA, UDMA	Ba glass, silicate, SiO <sub>2</sub> , mixed oxide 40nm-3000nm	76	L56579
GSO	Grandio SO	Voco GmbH Cuxhaven, Germany	Bis-GMA, Bis-EMA, TEGDMA	Ba glass 1µm SiO <sub>2</sub> 20-40 nm	89	1048014
XB	X-tra base	Voco GmbH Cuxhaven, Germany	Aliphatic di-methacrylate, Bis-EMA	Ba glass, YbF <sub>3</sub> , fumed silica	75	V45252
VDF	Venus® Diamond Flow	Heraeus Kulzer GmbH Hanau, Germany	UDMA, EBADMA	Ba-Al-F silicate glass, YbF <sub>3</sub> and SiO <sub>2</sub>	65	010100
CXD	Ceram-X™ duo	Dentsply GmbH Konstanz, Germany	Methacrylate modified polysiloxane, Dimethacrylate	Barium-aluminium-borosilicate glass, SiO <sub>2</sub>	76	0811000572



**Figure 5.1:** Laser scan micrometer

The initial mean diameter  $d_1$  of each specimen was measured. Then the specimens were immersed in 10 ml of distilled water at  $37\pm 1^\circ\text{C}$  for periods of time. Measurements of the diameter were taken after 1 and 3 h, and 1, 2, 3, 4, 5, 6, 7, 14, 21, 28, 60, 90, 120 and 150 d, to allow sufficient time for equilibrium to be achieved. The mean diameter  $d_2$  was measured at each time  $t$  and  $d_\infty$  at 150 days. For each measurement, each specimen was carefully taken out of storage medium, dried on filter paper until there was no visible moisture and then mounted onto the specimen holder. The multiple diametral measurements were obtained, after which the specimen was returned to water storage. After 150 d of water immersion each specimen diameter had reached a constant value. The percentage diameter change  $\Delta d$  (%) was calculated by:

$$\Delta d(\%) = 100 \times \left[ \frac{d_1(t) - d_2}{d_1} \right] \quad \text{Eq.1}$$

The percentage volumetric hygroscopic expansion  $V$  (%) can be calculated using the following equation, which assumes isotropic expansion behaviour [146]:

$$V(\%) = 100 \times \left[ \left( 1 + \frac{\Delta d(\%)}{100} \right)^3 - 1 \right] \quad \text{Eq.2}$$

#### 5.4 Statistical Analysis

Data were analysed using SPSS (Version 20.0, IBM, New York, USA). The mean percentage volumetric changes of hygroscopic expansion and standard deviations were calculated. Repeated measures ANOVA was applied for the percentage hygroscopic expansions during 150 days ( $\alpha = 0.05$ ). The final hygroscopic expansions at 150 days, for each material, were compared by one-way ANOVA, followed by Tukey's *post hoc* test at ( $\alpha = 0.05$ ).

#### 5.5 Results

During 150 d water immersion, repeated measures ANOVA showed significant differences in hygroscopic expansion of all resin composites ( $p \leq 0.015$ ). Means and standard deviations of the volumetric hygroscopic expansions, for all the resin composites, after 150 days at 37°C are shown in Table 5.2. Figures 5.2-4 show the percentage hygroscopic expansions of the materials. In Figure 2, the initial hygroscopic expansions over the first 7 days are plotted, which ranged from 0.24 to 1.05. The final hygroscopic expansions at 150 days ranged from 0.58 to 2.26, and can be considered in three bands, based on homogenous subsets (Table 5.2).

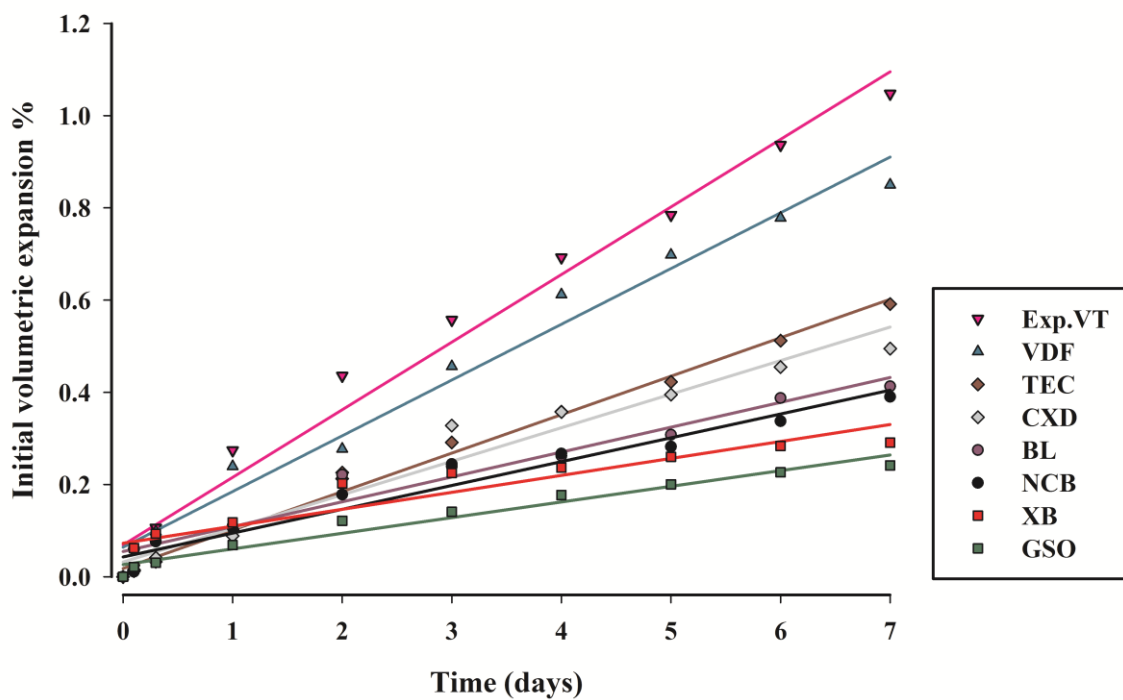
First, Exp.VT had the highest expansion ( $p < 0.001$ ). VDF, TEC and CXD were the second band. The third band, with still lower expansion, consisted of BL, GSO, NCB and XB, with no significant difference between them.

Each material reached an equilibrium hygroscopic expansion within 60 days. Thereafter, between 60 and 150 days, any apparent changes were not statistically significant.

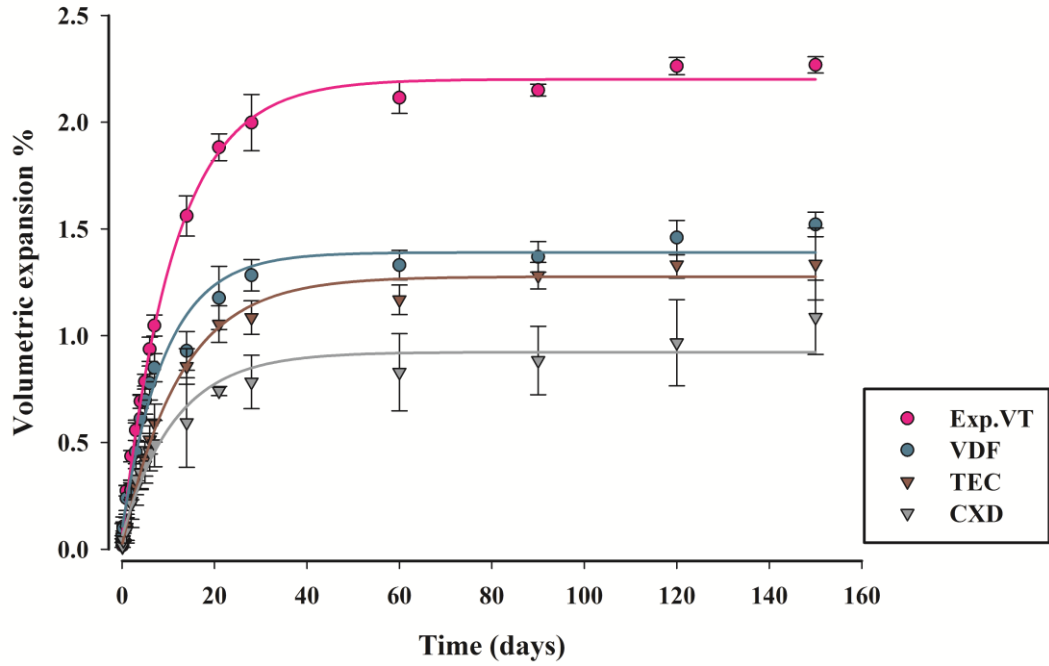
**Table 5.2:** Percentages of hygroscopic expansion of the examined resin composites (standard deviation) over 150 days' storage in distilled water at 37°C

Materials	Linear expansion %	Volumetric expansion %
BL	0.19 (0.01) <sup>a</sup>	0.58 (0.04) <sup>a</sup>
NCB	0.23 (0.02) <sup>a</sup>	0.70 (0.05) <sup>a</sup>
Exp.VT	0.75 (0.01) <sup>b</sup>	2.26 (0.04) <sup>b</sup>
TEC	0.44 (0.06) <sup>c,d</sup>	1.34 (0.17) <sup>c,d</sup>
GSO	0.23 (0.04) <sup>a</sup>	0.69 (0.13) <sup>a</sup>
XB	0.22 (0.07) <sup>a</sup>	0.67 (0.19) <sup>a</sup>
VDF	0.50 (0.02) <sup>d</sup>	1.52 (0.06) <sup>d</sup>
CXD	0.36 (0.06) <sup>c</sup>	1.08 (0.17) <sup>c</sup>

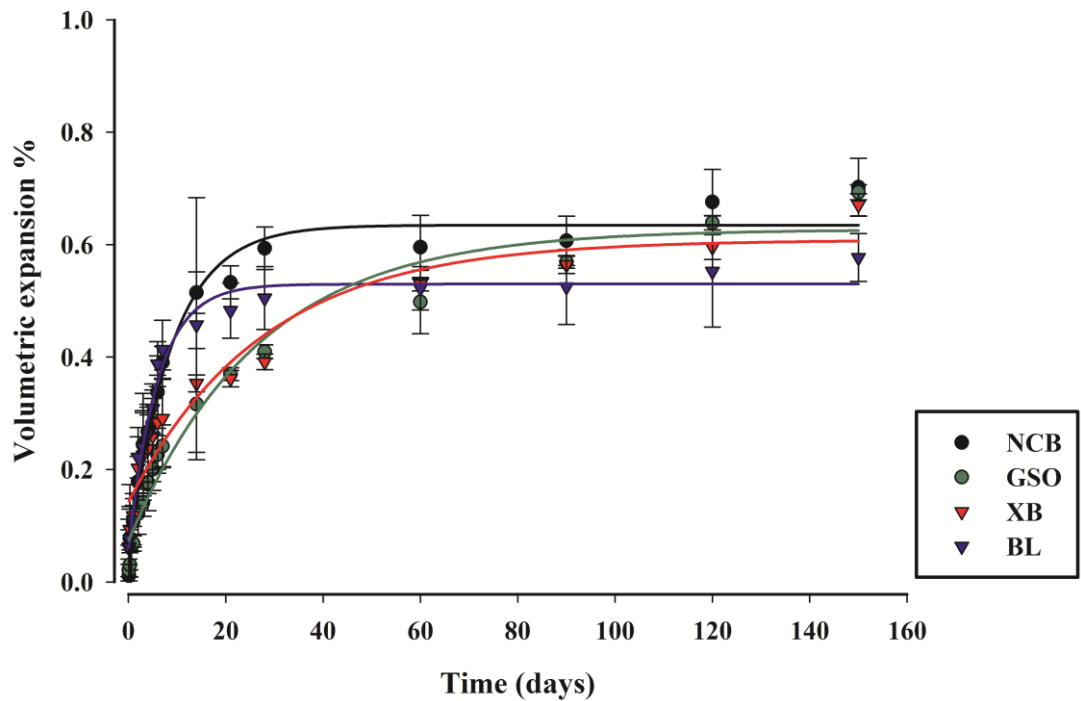
The same superscript small letters indicate a homogeneous subset (columns) ( $p < 0.05$ ).



**Figure 5.2:** Initial hygroscopic expansion over 7 days



**Figure 5.3:** Hygroscopic expansion from 0 to 150 days for four materials, showing high expansion



**Figure 5.4:** Hygroscopic expansion from 0 to 150 days for four materials, showing low expansion

## 5.6 Discussions

In preparing specimens for this study, they were thoroughly light cured on the upper and lower disk surfaces, so that their polymerisation would have been optimal.

Several methods have been applied to measure hygroscopic dimensional changes, which include: Archimedes' principle [132, 136, 140, 147], optical scanning [148], scanning with a contact profilometer [145], electronic micrometer [149] microscope [137] and precision laser micrometer [127, 150]. The impact of the storage medium on the accuracy of the Archimedes' method has been recognised, as aqueous contact with the specimen is intrinsic to the method [150, 151]. It is important that there be no chemical reaction with the specimen, apart from the sorption process, as the solution density may be affected by solubility and temperature. A custom-built laser micrometer was used in the current study, as this non-contact system is accurate and reproducible for measuring very small dimensional changes [150, 151].

Hygroscopic expansion occurs when water diffuses into the polymer network and separates the chains, especially when the water molecules are able to attach themselves to the polymer hydrophilic groups [132, 140]. However, absorbed water can sometimes be accommodated in micro-voids and free volume existing between chains in the resin network without causing a change in volume [118, 152]. It has been shown that an expansion of the matrix to accommodate the absorbed water takes place because water diffuses mostly into the resin phase [153]. The association between change in dimensions and water sorption in resin composites was established by Hirasawa et al. [149]. There are several factors that may affect hygroscopic expansion: the monomer type (chemistry and structure), the degree of cross-linking, porosity of the polymer network, the interaction between polymer and water, the bond strength, the filler and the resin/filler interface [18, 145, 154].

The equilibrium or final hygroscopic expansions varied significantly within the total set of materials and could be grouped into three bands. Therefore, the null hypothesis with regard to expansion magnitude was rejected. It was apparent from Figure 2 that the rates of expansion also differed significantly (Table 5.2), so the second null hypothesis was also rejected. For the size (2 mm thickness) and shape of specimen measured,

equilibrium was attained in all cases by 60 days, which might therefore also happen with clinical restorations using a comparable, or lower, volume of material.

Exp.VT showed the highest hygroscopic expansion after 150 days of water storage. This may be because its matrix contains GPDM (glycerol phosphate dimethacrylate), a self-adhesive monomer. Previous reports [155, 156] have demonstrated that the hydrophilicity of self-adhesive monomers makes the resin matrix softer due to water sorption. Furthermore, the hydrophilic acidic phosphate group and the short spacer group in GPDM may increase water sorption significantly [117]. Thus, extensive water sorption induces more hygroscopic expansion and may be the cause of cuspal flexure or microcracks of restored teeth [157].

VDF showed a relatively high expansion, perhaps due to lower filler loading and thus the presence of more resin. TEC and CXD contain more filler than VDF and their water sorption was lower [139, 149].

BL had lower expansion along with NCB, XB and GSO. Reduced hygroscopic expansion can occur when the resin is hydrophobic [145]. GSO and XB contain Bis-EMA, which is more hydrophobic than Bis-GMA [1]. Differences in the extent of polymerisation may also have an effect, but we have no evidence that this is the case here.

Viscoelastic stress relaxation of resin composites may be enhanced due to water uptake and internal plasticization of matrix polymer networks [126]. Thus, hygroscopic expansion of resin composites may, after sufficient time, partially or totally compensate for polymerisation shrinkage and its clinical effects [137, 148]. This possibility will depend on the size, shape and location of a restoration. Although the mass and volume of our specimens was greater than most restorations, the disk specimen thickness was only 2 mm, which is the critical dimension for water uptake. Hence the size-dependent expansion rates could be comparable to clinical situations.



## **5.7 Conclusion**

For the resin-composites studied, the equilibrium expansion varied by almost 400 % of the lowest material. For the size (2 mm thickness) and shape of specimen measured, which is roughly comparable to clinically used amounts, equilibrium was attained in all cases by 60 days.

## **Chapter Six**

### **Aqueous Storage Modifies Fracture Toughness of Dental-composites**

A. Alrahlah, N. Silikas, L.A. Turner, D.C. Watts

## 6.1 Abstract

**Objectives:** To study the effects of water storage on fracture toughness ( $K_{IC}$ ) of contemporary resin composites.

**Methods:** Eight resin composite materials were examined: one micro-hybrid, five nano-hybrids, two flowable, and one nano-ceramic (Bright Light<sup>®</sup>, Experimental Vertise<sup>™</sup>, Nanoceram-Bright<sup>®</sup>, Tetric EvoCeram<sup>®</sup>, Grandio<sup>®</sup>SO, X-tra base, Venus<sup>®</sup> Diamond Flow and Ceram·X<sup>™</sup> duo, respectively). Six Single edged-notched (SEN) specimens of each material type were prepared in a PTFE-lined brass mould. The beam dimensions were (3mm x 6mm x 34mm), with a sharp 3mm-long notch made perpendicular to half the beam height. Specimens of each composite material were assigned to two groups (n=3) according to the period of water storage: 1 and 7 days at 37°C. The  $K_{IC}$  ( $MNm^{-1.5}$ ) for each specimen was tested using three-point bending with a Zwick Universal Testing Machine at  $23 \pm 1^\circ C$ . The fracture surfaces of these composites were examined using scanning electron microscopy (SEM) to determine the relationships between the  $K_{IC}$  and microstructures. Data was analysed through the adoption of a two-way ANOVA and one-way ANOVA using Tukey *post hoc* tests ( $\alpha = 0.05$ ). The independent *t*-test was used to detect differences ( $\alpha = 0.05$ ) in  $K_{IC}$  between groups for each material.

**Results:** There was a statistically significant interaction between resin composites and storage times ( $p = 0.027$ ). The  $K_{IC}$  values ranged from 1.48 to 2.72  $MNm^{-1.5}$ . At both time points, Venus Diamond Flow showed the highest  $K_{IC}$  while Ceram·X duo showed the lowest values. There were significant increases in  $K_{IC}$  of X-tra base over time ( $p = 0.036$ ). Conversely, Experimental Vertise showed a significant decrease ( $p = 0.029$ ) in  $K_{IC}$  over time.

**Conclusion:** The water storage of resin composites can modify  $K_{IC}$ . X-tra base showed increases of  $K_{IC}$  after 7 days' storage, whereas Experimental Vertise decreased.

**Key words:** resin composites, fracture toughness, single edge-notched, water storage

## 6.2 Introduction

The fracture of restorations, which determines the success and longevity of restorative materials, is a major concern for clinicians. Exposure to moist oral environments, attrition of materials, and masticatory forces contribute to the bulk fracture and wear of dental composites [158]. Thus, the fracturing of restorations is considered to be one of the major clinical failures of direct resin composites [67, 159]. Other clinical failures of dental resin composites include fracture of the tooth, discolouration, post-operative sensitivity, marginal staining, poor anatomic form, recurrent caries, wear and marginal fracture [160]. Once stress/strain of the crack tip reaches a critical value, fracture of the materials will occur [52]. Fracture toughness ( $K_{IC}$ ) is an intrinsic parameter of resistance of the material to crack propagation caused by flaws or cracks, which defines the amount of energy required to initiate and propagate the crack through the material [161]. Measures of fracture toughness are an appropriate predictor of the clinical performance of resin composites [162], as compared with compressive or tensile strength measurements [163], whereby values may be affected by different storage conditions [164]. Resin composites with lower fracture toughness are more susceptible to catastrophic failure during function than those with higher fracture toughness.

Dental restoration failure may occur owing to reduced load-bearing capacity caused by the degradation of the material in the oral environment [165]. The oral cavity contains saliva that influences the mechanical properties of materials due to altered properties of dental composite in water [166]. The effect of water storage on fracture toughness has been studied in relation to a range of materials and specimen geometries [86, 87]. Some factors can affect  $K_{IC}$  results, such as specimen geometry, fabrication of the specimen, and the sharpness of the notch [83, 167]. The single edge-notched (SEN) method has been used widely with the objective of evaluating the  $K_{IC}$  of dental composites [82, 167].

Because of the impact associated with exposing restorative materials to the oral environment, it is essential to establish the behaviour of resin composites in hydrated conditions. A number of studies have found significant differences in the mechanical properties of resin composites when stored in water [92, 126, 168]. Resin composites absorb water from the oral environment due to the polar nature of the resin matrix. Water absorbed through such composites may react with the filler/matrix interface or

the inorganic filler [18], or otherwise affect the matrix structure [87, 169], which may subsequently result in changes in  $K_{IC}$  values. The long-term storage of resin composites in aqueous media may cause undesirable effects, such as the degradation of the silane-coupling agent that bonds the resin matrix to filler particles [88, 89], leakage or evacuation of filler elements [70, 90], and the softening of the resin matrix [91, 92].

This study focuses on assessing the effect of water storage on  $K_{IC}$  of experimental and contemporary dental composites. Therefore, the objective of this study was to evaluate the effects of water storage on the  $K_{IC}$  of a set of resin composites over time on  $K_{IC}$ . The null hypothesis was that there would be no difference in  $K_{IC}$  between materials at 1 and 7 days of water storage at 37°C.

### 6.3 Materials and Methods

Eight resin composite materials (Table 6.1) were evaluated. For each material, six single edge-notched (SEN) specimens were prepared in a polytetrafluoroethylene (PTFE)-lined brass mould, conforming to British Standard 907:1983. The beam dimensions were (3mm x 6mm x 34mm) with a sharp 3mm-long notch perpendicular to half the beam height (Figure 6.1). Specimens of each composite material were assigned into two groups ( $n = 3$ ) according to the period of water storage: 1 and 7 days. Each specimen was photo-polymerised for 40 s, using a visible light curing unit with tip diameter 10 mm (Optilux 501, Kerr Corporation, USA) under the standard curing mode (output wavelength range: 400–505 nm; output irradiance: 580–700mW/cm<sup>2</sup>). A calibrated radiometer was used to verify the irradiance at each use of the light curing unit. Multiple overlapping areas of irradiation were used along the length of each specimen. A glass slab was placed over the mould so as to ensure that the material was flush with the top surface of the mould. After initial curing from the top, the mould was disassembled partially. Each side was further cured to ensure optimal curing depth.

Each specimen was finished with 320 grit metallographic papers, and subsequently placed in a small bottle of distilled water, and stored in an incubator at 37°C for the allotted time (1 and 7 days). The fracture toughness value,  $K_{IC}$  (MNm<sup>-1.5</sup>) for each specimen was determined through the use of a three-point bending with a Universal Testing Machine (Zwick/Roell-2020, 2.5 kN load cell) at 23 ± 1°C. A central load was

applied to each beam specimen in a 3-point bending mode at a crosshead speed of 0.1 mm/s until the point of specimen fracture was reached [162, 164].

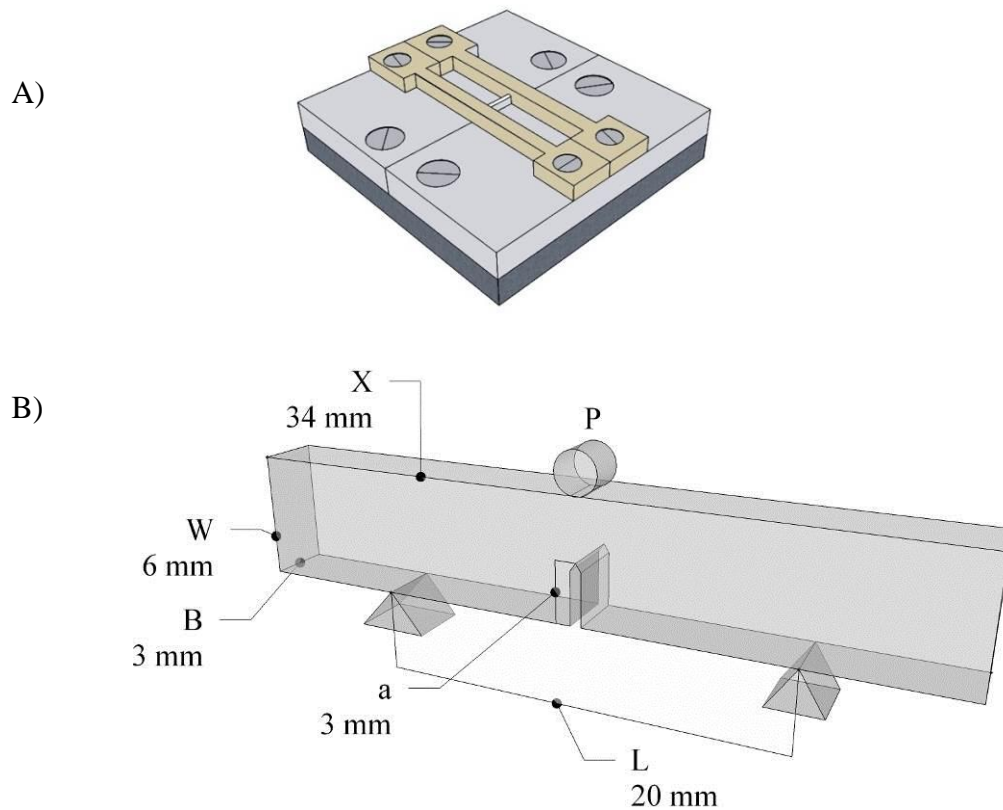
The fracture toughness was calculated using the following equation [170]:

$$K_{IC} = \left[ \frac{3PL}{BW^{1.5}} \right] Y$$

where:  $P$  = load at fracture ;  $L$ = distance between the supports;  $W$ = width of the specimen;  $B$ = thickness of the specimen;  $Y$ = calibration functions for given geometry  
 $Y = [1.93(a/w)^{1/2} - 3.07(a/w)^{3/2} + 14.53(a/w)^{5/2} - 25.11(a/w)^{7/2} + 25.80(a/w)^{9/2}]$

**Table 6.1:** Materials tested

Code	Product	Manufacturer	Matrix	Filler type	Filler %W/W	Lot Number
BL	Bright Light®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Ba glass, mixed oxide 0.04-0.25 µm	81	610230
NCB	Nanoceram-Bright®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Barium glass, mixed oxide 0.05-0.7 µm	80	630212
Exp.VT	Expermintal Vertise™	Kerr Corp, Orange, USA	GPDM and methacrylate co-monomers	Prepolymerized filler, Ba glass; nanoscale SiO <sub>2</sub> & YbF <sub>3</sub>	-	3379131
TEC	Tetric EvoCeram®	Ivoclar Vivadent AG, Schaan, Liechtenstein	Bis-GMA, UDMA	Ba glass, silicate, SiO <sub>2</sub> , mixed oxide 40nm-3000nm	76	L56579
GSO	Grandio SO	Voco GmbH Cuxhaven, Germany	Bis-GMA, Bis-EMA, TEGDMA	Ba glass 1µm SiO <sub>2</sub> 20-40 nm	89	1048014
XB	X-tra base	Voco GmbH Cuxhaven, Germany	Aliphatic di-methacrylate, Bis-EMA	Ba glass, YbF <sub>3</sub> , fumed silica	75	V45252
VDF	Venus® Diamond Flow	Heraeus Kulzer GmbH Hanau, Germany	UDMA, EBADMA	Ba-Al-F silicate glass, YbF <sub>3</sub> and SiO <sub>2</sub>	65	010100
CXD	Ceram-X™ duo	Dentsply GmbH Konstanz, Germany	Methacrylate modified polysiloxane, Dimethacrylate	Barium-aluminium-borosilicate glass, SiO <sub>2</sub>	76	0811000572



**Figure 6.1:** A) PTFE mould used for specimen, B) specimen dimensions and geometry

### 6.3.1 Scanning Electron Microscopy (SEM) Analysis

After seven days of storage in water at 37°C, the SEM analysis of fracture surface was carried out. Each sample was fixed with resin on SEM aluminium stubs. All specimens were vacuum sputter-coated with gold (Edwards S1580) for a period of two minutes. The microstructure of these specimen fracture surfaces was observed by SEM (Zeiss Evo 60 EPSEM, Carl Zeiss AG, Switzerland) with the use of an 8 kV accelerating voltage.



## 6.4 Statistical Analysis

Univariate two-way ANOVA, one-way ANOVA and Tukey *post-hoc* tests (Version 20.0, IBM, New York, USA) ( $\alpha=0.05$ ) were used to analyse significant differences in  $K_{IC}$  (dependent variable) between different materials and ageing groups (independent variables). The independent *t*-test was used to detect differences ( $\alpha = 0.05$ ) in  $K_{IC}$  between groups for each material. All data were subjected to Levene's test of homogeneity of variance ( $\alpha= 0.05$ ) following the assumption of equal variances.

## 6.5 Results

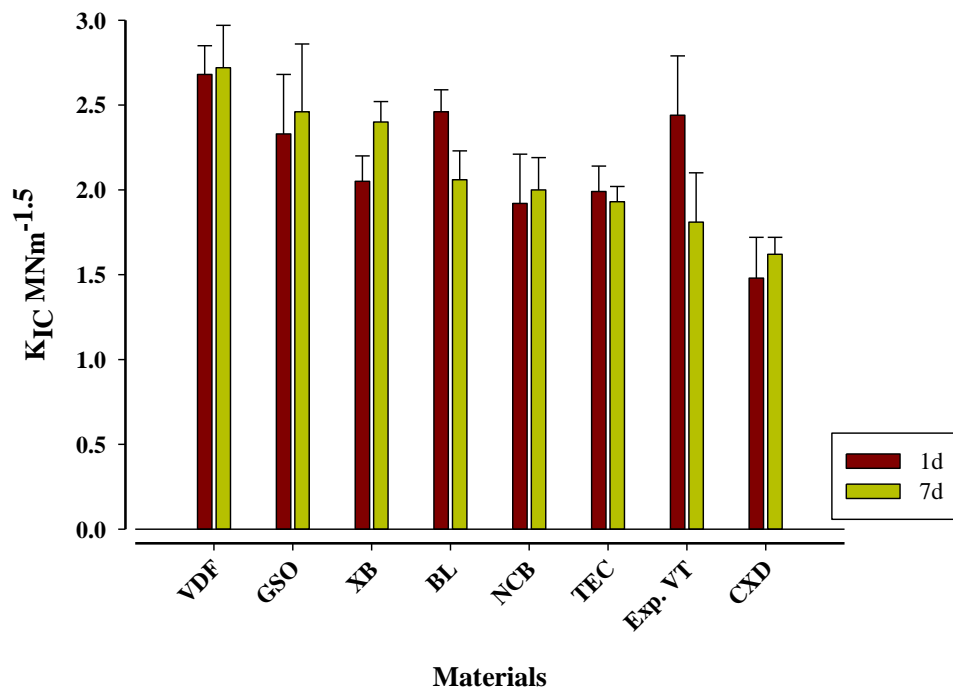
The  $K_{IC}$  values for the composites examined during this study are presented in Table 6.2 and shown graphically in Figure 6.2, which gives the mean and standard deviation values for each resin composite. The  $K_{IC}$  values ranged from 1.48 - 2.72  $\text{MNm}^{-1.5}$ . There were statistically significant interactions between resin composites and storage times ( $p = 0.027$ ). VDF showed the highest  $K_{IC}$  values, while CXD showed the lowest values (after both 1 and 7 days' storage) ( $p < 0.05$ ).  $K_{IC}$  increased significantly with increased storage time for XB ( $p = 0.036$ ). On the other hand, Exp.VT showed a significant decrease ( $p = 0.029$ ) in  $K_{IC}$  with an increased storage time.

Representative SEM micrographs of the resin composites examined after 7 days' storage are shown in Figure 6.3, with standardised magnifications of approximately 7750 X. The SEM images showed that, for all samples, crack propagation was mostly through the matrix and the matrix/filler interface (no fractured filler was observed). Furthermore, observations of the fracture surfaces showed the presence of internal voids for all composites examined, and the presence of filler particles of various spherical-irregular-shapes and sizes. Compared to other samples, GSO showed filler agglomeration, and had a rough fracture surface (Figure 6.3E). Pre-polymerised filler particles were observed in the Exp.VT sample. Moreover, CXD showed a more porous fracture surface (Figure 6.3H).

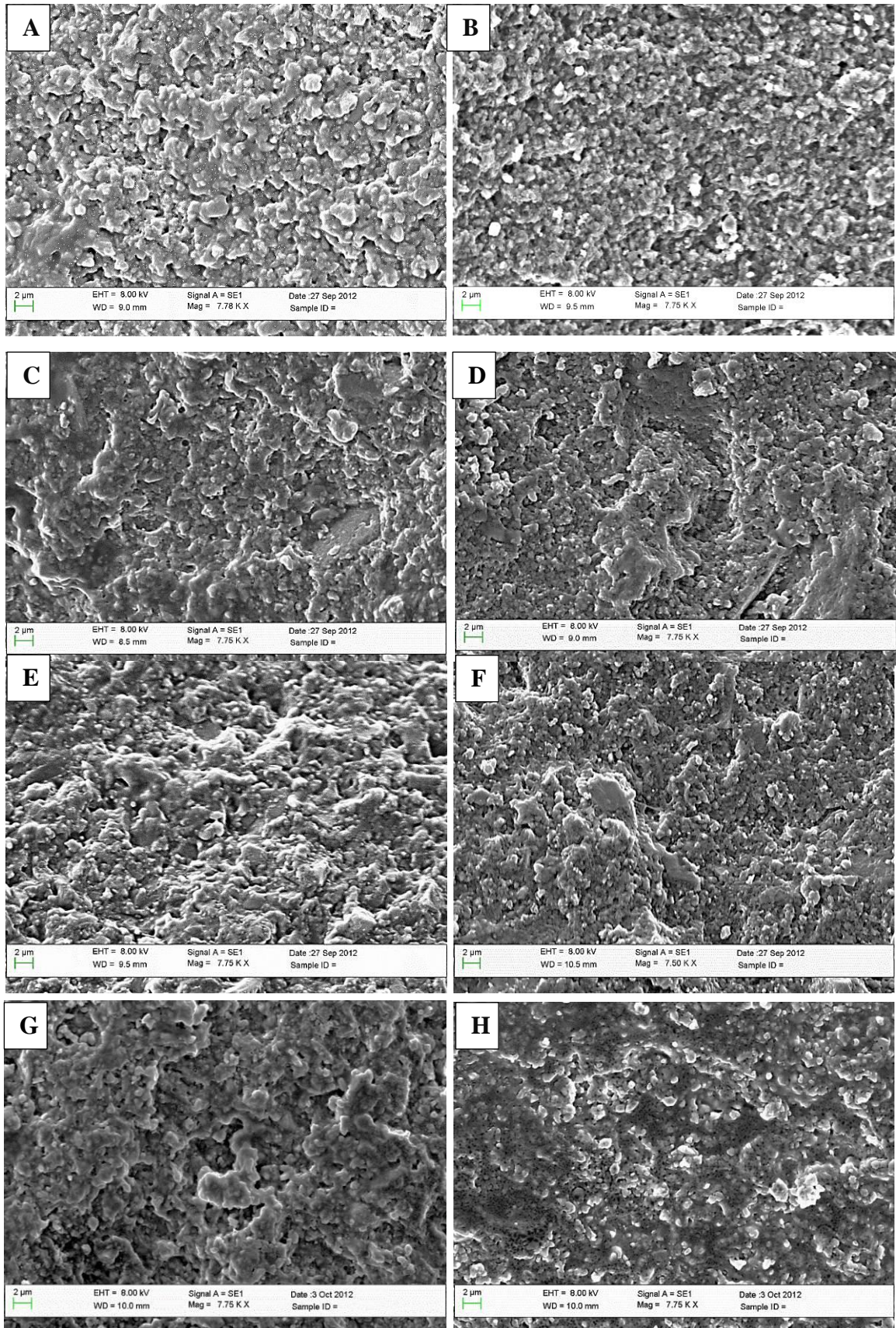
**Table 6.2:** KIC (standard deviation) of composites after 1 and 7 days' storage in water at 37°C

Materials	Storage time (d)	
	1	7
BL	2.46 (0.13) <sup>a, b</sup>	2.06 (0.17) <sup>a, b</sup>
NCB	1.92 (0.29) <sup>a, c</sup>	2.00 (0.19) <sup>a, c</sup>
Exp.VT	2.44 (0.35) <sup>a</sup>	1.81 (0.29) <sup>a*</sup>
TEC	1.99 (0.15) <sup>a, c</sup>	1.93 (0.09) <sup>a, c</sup>
GSO	2.33 (0.35) <sup>a, b</sup>	2.46 (0.40) <sup>a, b</sup>
XB	2.05 (0.15) <sup>a</sup>	2.40 (0.12) <sup>a*</sup>
VDF	2.68 (0.17) <sup>b</sup>	2.72 (0.25) <sup>b</sup>
CXD	1.48 (0.24) <sup>c</sup>	1.62 (0.10) <sup>c</sup>

The same superscript small letters indicate a homogeneous subset (columns) ( $p < 0.05$ )  
 \* indicated significant differences between storage time (rows) ( $p < 0.05$ )



**Figure 6.2:** KIC (standard deviation) of composites after 1 and 7 days' storage in water at 37°C



**Figure 6.6.3:** Representative micrographs of fracture surfaces of composites examined after 7 days storage at 37°C (A) BL, (B) NCB, (C) Ver, (D) TEC, (E) GSO, (F) Xb, (G) VDF, (H) CXD

## 6.6 Discussion

The present study observed variation in the effect of water storage on the  $K_{IC}$  of resin composites. Previous studies reported a reduction in  $K_{IC}$  of resin composites stored in water for different periods of time [169, 171, 172]. Some studies have shown no change, or an increase, in  $K_{IC}$  after ageing in water [173-175]; this conflict in results may be due to filler particle sizes, filler/matrix interfaces, degrees of cure of the matrix, storage times, and/or hydration media [83]. This study confirms that  $K_{IC}$  value can be increased, decreased or undergo no change after water storage.  $K_{IC}$  values of an experimental and a variety of contemporary resin composites ranged from 1.48 to 2.72  $MNm^{-1.5}$ . There were statistically significant differences in  $K_{IC}$  between materials; however, the objective of this study was centred on evaluating the effect of water storage on  $K_{IC}$  of these resin composites over time. This study found statistically significant differences in  $K_{IC}$  from 1 to 7 days storage at 37°C for eight composites tested ( $p = 0.027$ ). Therefore, the null hypothesis was rejected.

$K_{IC}$  is considered a better fracture mechanical parameter, sensitive to the flaw characteristics of resin composite, compared with other strength parameters [162]. There are several specimen geometries that can be used to determine  $K_{IC}$  described previously in the literature [161]. These include: mini-short rod [176], compact tension [177], double torsion [178], single edge-notched (SEN) [82] and diametral tensile test (Brazilian disk) [85]. In this study, the SEN specimen geometry was employed owing to ease of use [179] and lack of need for pre-crack fatigue.  $K_{IC}$  is dependent on the load needed for crack growth to occur [180].

The testing geometry and other material variables such as matrix type, filler loading, and filler surface treatment can affect  $K_{IC}$  [85, 181]. Although previous studies established a positive association between filler loading and  $K_{IC}$ , Kim *et al.* report that the  $K_{IC}$  of resin composites increased with filler loading until 55% volume was reached, after which  $K_{IC}$  decreased with filler loading [182, 183]. In the present study, the volume fraction of filler for all materials is not reported; thus, its effect cannot be determined. For mechanical properties of resin composites, the size, shape and distribution of filler particles may be more important than the total quantity of the fillers [184].

Adding filler to matrix results in greater strengthening, and further provides additional toughening mechanisms. This strength of matrix is achieved by distributing stress to the strong specific fillers. Accordingly, fillers are more fracture-resistant owing to their improved capability to absorb energy [185]. Furthermore, due to the high strength of the fillers, the propagation of the crack might occur through matrix and matrix/filler interface [81]; however, catastrophic failure may occur under an applied load as the consequences of failure to resist crack propagation [164].

SEM micrographs of the fractured surface of the resin composites (Figure 6.3) reveal that there was good adhesion between the matrix resin and the fillers of Exp.VT, TEC, GSO, XB, and VDF. In contrast, BL and NCB show some interfacial de-bonding, while CXD showed more voids on the fracture surface (Figure 6.3H).

In this study, VDF (flowable composites) had the highest numerical  $K_{IC}$  value (2.72  $MNm^{-1.5}$ ) after seven days' storage in water. Moreover, significantly greater values were shown when compared to all other materials examined ( $p < 0.04$ ) except GSO and BL. This high  $K_{IC}$  value of the VDF composite may be related to the blunted crack tip through plastic deformation due to higher amounts of the plastic matrix [164]. VDF contains EBADMA (ethoxylated bisphenol A dimethacrylate); it is known to have lower viscosity than Bis-GMA due to the absence of hydroxyl groups, which prevents hydrogen bond-formation between monomers [186]. Another study [33] acknowledges that there was a steady increase in reactivity, with increasing amounts of the base resin when the non-hydrogen bonding EBADMA resin was used. Such properties lead to higher conversion and reaction rates.

In terms of the high  $K_{IC}$  observed for GSO (highly filled nano-hybrid composite), there are several potential explanations for the increase in  $K_{IC}$ ; this may be due to a decrease in the number of flaws, decrease in the inherent flaw size and/or an increase in the amount of polymer converted [187]. It has been shown that content, size and distribution of the filler particles may affect the physical/mechanical properties of resin composites; also the filler volume fraction of resin composites correlate with the material fracture toughness [188]. Another possible explanation is that the crack growth could be deflected by filler, which would minimise the crack tip stress intensity factor and thus improve fracture resistance. Moreover, nano-fillers can increase  $K_{IC}$  through enhancing the bonding between the filler/matrix interface via an increased surface area

volume ratio, and a high filler strength [189]. Therefore, enhancing the strength and fracture resistance of the matrix should improve the fracture toughness of the resin composite. SEM showed GSO filler agglomeration as a result of being highly filled, and also a rougher fracture surface (Figure 6.3E). Rougher fracture surfaces may indicate that the absorption of more energy is required, resulting in high fracture-resistance [190].

BL (micro-hybrid resin composite) was found to show no significant differences in  $K_{IC}$ , except with NCB ( $p < 0.001$ ). This present finding is consistent with previous studies that have established no difference in  $K_{IC}$  between micro-hybrid and nano-hybrid composites due to the optimal ratio between the filler size and volume fraction of the filler in these materials [179, 191].

The current study also identified no statistical differences in  $K_{IC}$  between 1 and 7 days' storage ( $p > 0.05$ ) with the exceptions of Exp.VT and XB ( $p < 0.04$ ). Notably, Exp.VT (self-adhering resin composite) had a significantly decreased  $K_{IC}$  value over time ( $p = 0.029$ ). This reduction may be related to water sorption by the resin. Exp.VT contains GPDM (Glycerophosphate-dimethacrylate) resin, which tends to absorb more water because of its hydrophilic nature [117]; thus, the softening of the resin matrix through swelling the network and decreasing the frictional forces between polymer cross-links, as well as more degradation between the matrix/filler interface, may occur and may be the cause of the effect observed in regard to mechanical properties [117]. In addition, Exp.VT contains pre-polymerised filler particles (as shown in SEM, Figure 6.3C), which shows significantly lower flexural strength and flexural modulus than resin composites with round or irregular filler [181].

XB (Bulk fill resin composite) shows significantly increasing  $K_{IC}$  values over time ( $p = 0.036$ ). These findings suggest that extra energy is needed in order to propagate a crack after water storage. It is difficult to explain this result, although it may be related to the degree of silanization of filler to the matrix after polymerisation. Significantly, It has been shown that silanization and the filler fraction can affect the mechanical properties of ageing resin composites [192]. Alternatively, there may be a relation to the monomeric composition of the resin (which is hydrophobic). Moreover, increasing  $K_{IC}$  values can be explained by all or one of the following phenomena owing to water sorption possibly encouraging the plasticisation of the resin matrix, leading to: 1) the

relief of internal stresses that occurred during polymerisation shrinkage, 2) a reduction in the stress concentration with blunting of the crack tip, and 3) the residual compressive stress generated at the crack tip [193].

CXD (nano-ceramic composite) showed the lowest numerical  $K_{IC}$  value amongst the materials examined, which was statistically significantly different ( $p \leq 0.004$ ) when compared with other materials, with the exception of NCB and TEC. A possible explanation might be that CXD had a number of porosities on its surface (confirmed using SEM, Figure 6.3H). These voids may have extended into the internal structure, which may have induced reductions in mechanical properties [194].

Research suggests several plausible mechanisms for the influence of filler-loading on fracture toughness [49, 52, 181, 182]; however, filler-loading, in itself, might not have a decisive effect on  $K_{IC}$ . Furthermore, it has been suggested that highly cross-linked material has higher fracture toughness and thus greater wear-resistance [195].

## 6.7 Conclusions

- Flowable VDF, highly-filled nano-hybrid GSO and micro-hybrid BL composites showed the highest  $K_{IC}$  values while CXD (nano-ceramic composite) showed the lowest values, independent of storage time in water.
- The  $K_{IC}$  of XB (bulk fill resin composite) significantly increased, whereas Exp.VT (self-adhering resin composite) significantly decreased after 7 days' storage in water.

## **Chapter Seven**

### **Effect of Food-simulating Solvents on Surface Micro-hardness of Dental Resin-composites**

A. Alrahlah, N. Silikas, D.C. Watts



## 7.1 Abstract

**Objective:** To study the effect of exposure to food-simulating solvents on Vickers micro-hardness (VHN) of resin composites.

**Methods:** Eight resin composite materials were examined: 1 micro-hybrid (Bright Light<sup>®</sup>), 5 nano-hybrids (Experimental Vertise<sup>™</sup>; Nanoceram-Bright<sup>®</sup>; Tetric EvoCeram<sup>®</sup>; Grandio<sup>®</sup> SO; Ceram-X<sup>™</sup> duo) and 2 flowables (X-tra base; Venus<sup>®</sup> Diamond Flow). Disk specimens (6 x 2 mm) were prepared (n=9) for each material via manipulation and photo-polymerisation, according to the manufacturers' instructions. Specimens of each composite material were assigned as three groups (n=3), into solvents of increasing solubility parameter: distilled water, 75% ethanol/water, and MEK (methyl ethyl ketone). Materials were measured post-irradiation at 1 h, then after storage at  $37 \pm 1$  °C for 1 day and 30 days. Vickers hardness was measured under a load of 300 g for 15 s at  $23 \pm 1$ °C. Data were analysed by three-way ANOVA, one-way ANOVA and Tukey *post hoc* tests ( $\alpha = 0.05$ ).

**Results:** There was a statistically significant interaction between resin composites, conditions and storage times ( $p < 0.001$ ). VHN ranged from 26.82 to 112.76 at baseline and 11.73 to 110.10 after solvent-ageing. GrandioSO had the highest VHN before and after ageing, followed by Experimental Vertise and Nanoceram-Bright. Venus Diamond Flow had the lowest VHN ( $p < 0.001$ ). VHN significantly decreased after conditioning in ethanol/water and MEK for all investigated materials ( $p \leq 0.006$ ).

**Conclusion:** MEK caused the greatest softening (reduction in VHN) for most of the composites examined. A highly filled nano-hybrid composite GrandioSO had the highest VHN over time, regardless of the storage conditions.

**Key words:** resin composites, Vickers micro-hardness, nano-hybrid, micro-hybrid, food-simulating solvent, MEK, ethanol/water

## 7.2 Introduction

The continuous process of intra-oral degradation is a result of chemical, aqueous, thermal and mechanical influences [196]. A number of surface properties, for instance, micro-hardness and wear resistance, are affected by degradation. Over time, intra-oral degradation may cause reduction in the fracture strength of biomaterials leading to inferior durability of restorations [197]. If composite oral biomaterials absorb water between the filler/matrix interface, hydrolytic degradation can occur that may lead to displacement of inorganic particles [198].

The surface hardness of resin composites may be significantly affected by water sorption, temperature, and exposure time to aqueous media [198, 199]. In addition, the oral environment intermittently includes chemicals derived from food and drink. These may also degrade resin composites [200, 201]. On the other hand, continuous exposure may occur from chemical elements absorbed by the adherent remains of food particles or calculus, or may be produced by bacterial decomposition at the restoration margins [201, 202].

Surface hardness is the resistance of a material to indentation. It is used as a predictor of the wear resistance of the material [104]. However, chemical softening of resin composites may cause decreases in physical/mechanical properties. These properties of resin composites are significantly affected by their chemical composition and media exposure. Ageing dental materials in solvents with the aim of simulating the oral environment has shown acceleration in the degradation process [203]. Moreover, there is concern that the influence of the solvents' sorption and degradation may result in a reduction in performance and longevity of composite restorations [204].

When testing the durability of food containers, the US Food and Drug Administration (FDA, 1976), used organic solvents with solubility parameters from  $1.5$  to  $4.8 \times 10^{-4}$  ( $\text{J}/\text{m}^3$ )<sup>0.5</sup> to simulate foods [192]. It was found that when the value of the solubility parameter of a solvent is equivalent to that of the matrix of the composites, a maximum softening effect may occur. The conditioning of materials with the food-simulating solvents led to the softening of composites, and consequently to a decrease in surface hardness [205].

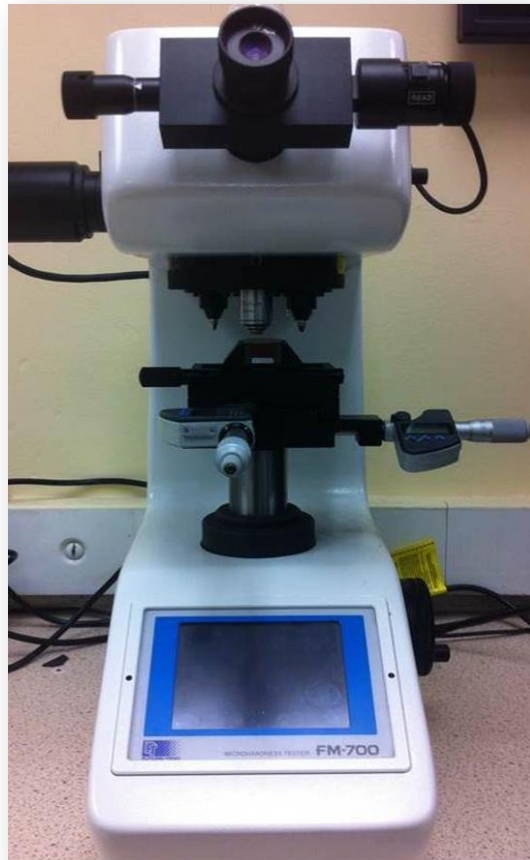
The objective of this study was to investigate the effect of food-simulating solvents over time on the micro-hardness of eight resin composite materials. The null hypotheses were that: i) there would be no difference in VHN between materials examined over time, ii) there would be no differences in their VHN values after storage in solvents, and iii) there would be no correlation between VHN and filler loading.

### **7.3 Materials and methods**

Eight resin composites (Table 7.1) were studied in this research. Nine disk-shaped specimens (6 x 2 mm) were prepared (n=9) for each material via manipulation and photo-polymerisation according to manufacturers' instructions. Specimens were polymerised using a halogen curing unit with a tip diameter of 10 mm (Optilux<sup>®</sup> 501, SDS, Kerr, Danbury, CT, USA) under the standard curing mode (output wavelength range: 400–505 nm; output irradiance: 580–700mW/cm<sup>2</sup>). A calibrated radiometer was used to verify the irradiance at each use of the light cure unit. The specimens were then removed from the mould and lightly finished manually from both sides after the preparation. This finishing procedure was carried out with a series of polishing disks (OptiDisc; Kerr Hawe SA, Bioggio, Switzerland), with a hand piece at 15,000 rpm for 15s for each disk (medium, fine, and superfine). This allowed the removal of a weak resin-rich layer, giving a smooth-flat testing surface. Specimens of each composite material were assigned as three groups (n=3), into solvents of increasing solubility parameter: distilled water, 75% ethanol/water and MEK (methyl ethyl ketone). Materials were measured post-irradiation with a Vickers Micro-hardness Tester (FM-700, Kawasaki, Kanagawa, Japan) (Figure 7.1) at 1 hour, then after storage at 37 ± 1 °C for 1 and 30 days. Vickers hardness was measured under a load of 300 g for 15 s at 23 ± 1°C. Three equally spaced indentations were randomly made of each specimen. They were 1 mm apart from adjacent indentations or the margin of the specimens.

**Table 7.1:** Materials tested

Code	Product	Manufacturer	Matrix	Filler type	Filler %W/W	Lot Number
BL	Bright Light®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Ba glass, mixed oxide 0.04-0.25 µm	81	610230
NCB	Nanoceram-Bright®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Barium glass, mixed oxide 0.05-0.7 µm	80	630212
Exp.VT	Expermintal Vertise™	Kerr Corp, Orange, USA	GPDM and methacrylate co-monomers	Prepolymerized filler, Ba glass; nanoscale SiO <sub>2</sub> & YbF <sub>3</sub>	-	3379131
TEC	Tetric EvoCeram®	Ivoclar Vivadent AG, Schaan, Liechtenstein	Bis-GMA, UDMA	Ba glass, silicate, SiO <sub>2</sub> , mixed oxide 40nm-3000nm	76	L56579
GSO	Grandio SO	Voco GmbH Cuxhaven, Germany	Bis-GMA, Bis-EMA, TEGDMA	Ba glass 1µm SiO <sub>2</sub> 20-40 nm	89	1048014
XB	X-tra base	Voco GmbH Cuxhaven, Germany	Aliphatic di-methacrylate, Bis-EMA	Ba glass, YbF <sub>3</sub> , fumed silica	75	V45252
VDF	Venus® Diamond Flow	Heraeus Kulzer GmbH Hanau, Germany	UDMA, EBADMA	Ba-Al-F silicate glass, YbF <sub>3</sub> and SiO <sub>2</sub>	65	010100
CXD	Ceram-X™ duo	Dentsply GmbH Konstanz, Germany	Methacrylate modified polysiloxane, Dimethacrylate	Barium-aluminium-borosilicate glass, SiO <sub>2</sub>	76	0811000572



**Figure 7.1:** Micro-hardness instrument

#### **7.4 Statistical Analysis**

Data were analysed by a three-way ANOVA, one-way ANOVA, and Tukey *post hoc* tests (Version 20.0, IBM, New York, USA)  $\alpha=0.05$  to determine significant differences in VHN (dependent variable) according to different materials, solvents and times (independent variables). All data were subjected to Levene's test of homogeneity of variance ( $\alpha= 0.05$ ), following the assumption of equal variance. Quadratic regression analysis was performed to investigate the relationships between VHN and filler loading.

## 7.5 Results

The VHN values for the composites examined are presented in Table 7.2 and shown graphically in Figure 7.2. There was a statistically significant interaction between resin composites, conditions and storage times ( $p < 0.001$ ). VHN ranged from 26.82 to 112.76 at the baseline and from 11.73 to 110.10 after solvent-ageing. GSO had the highest VHN before and after storage ( $p < 0.001$ ), followed by the Exp.VT (self-adhering composite) and NCB, while VDF Flow had the lowest VHN ( $p < 0.001$ ).

In water storage, the surface hardness values showed no change ( $p > 0.05$ ), with the exception of Exp.VT, XB and CXD. Exp.VT showed a decrease in VHN after 30 days of storage ( $p = 0.043$ ) whereas XB and CXD showed increases ( $p \leq 0.03$ ).

In 75% ethanol/water storage a significant reduction in VHN from the baseline ( $p < 0.001$ ) was seen, with no significant differences between materials after storage. In MEK storage, a significant reduction in VHN was seen from the baseline ( $p < 0.001$ ), with a significant reduction after 30 days of storage for NCB, Exp.VT and CXD.

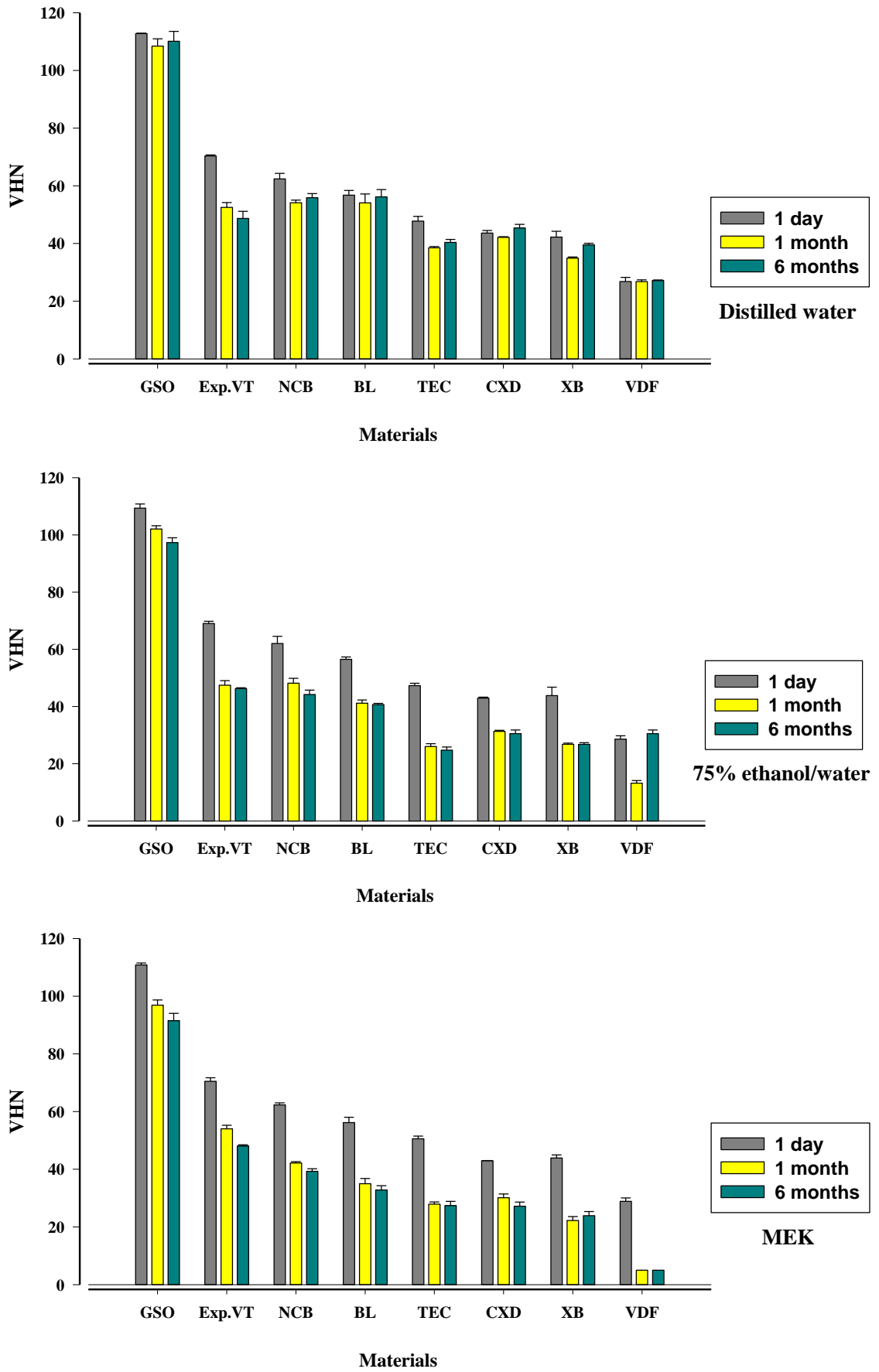
In comparing 75% ethanol/water and MEK solvents, the MEK solvent showed more degradation for BL, NCB, GSO, XB, VDF and CXD ( $p \leq 0.09$ ). Exp.VT showed more resistance to degradation in MEK after 1 day than it did in water/ethanol. In addition, TEC showed no differences after storage in ethanol/water or MEK ( $p > 0.05$ ). In general, VHN significantly decreased after conditioning in both ethanol/water, and MEK, for all the investigated materials ( $p < 0.001$ ). Quadratic regression has confirmed a positive correlation between VHN and filler loading for the baseline and after storage in water, 75% ethanol/water and MEK (Figure 7.3).

HVN showed a negative quadratic regression function with log time for most materials (figure 7.3).

**Table 7.2:** Vickers Hardness VHN (standard deviation) of resin composites tested after 30 d storage in food simulating solvents at 37°C

Materials	Distilled water			75% ethanol/water			MEK		
	Dry	1 d	30 d	Dry	1 d	30 d	Dry	1 d	30 d
<b>BL</b>	56.76 (1.64) <sup>a,A</sup>	54.09 (3.08) <sup>a,A</sup>	56.17 (2.54) <sup>a,A</sup>	56.50 (0.82) <sup>a,A</sup>	41.18 (1.10) <sup>a,B</sup>	40.69 (0.42) <sup>a,B</sup>	56.17 (1.84) <sup>a,A</sup>	34.99 (1.79) <sup>a,C</sup>	32.79 (1.52) <sup>a,C</sup>
<b>NCB</b>	62.40 (1.89) <sup>b,A</sup>	54.11 (0.92) <sup>a,B</sup>	53.49 (1.70) <sup>b,a,B</sup>	62.06 (2.49) <sup>b,A</sup>	48.19 (1.70) <sup>b,C</sup>	44.21 (1.55) <sup>b,C,D</sup>	62.34 (0.66) <sup>b,A</sup>	42.17 (0.47) <sup>b,D</sup>	39.29 (0.90) <sup>b,E</sup>
<b>Exp.VT</b>	70.34 (0.37) <sup>c,b,A</sup>	52.51 (1.69) <sup>a,B</sup>	48.68 (2.47) <sup>c,b,C</sup>	69.06 (0.76) <sup>c,A</sup>	47.46 (1.60) <sup>b,C</sup>	46.31 (0.27) <sup>b,C</sup>	70.50 (1.23) <sup>c,A</sup>	54.03 (1.22) <sup>c,B</sup>	48.07 (0.41) <sup>c,C</sup>
<b>TEC</b>	47.76 (1.64) <sup>d,A</sup>	38.49 (0.44) <sup>b,d,f,B</sup>	40.39 (1.03) <sup>d,B</sup>	47.33 (0.82) <sup>d,A</sup>	26.04 (0.99) <sup>c,C</sup>	24.77 (1.09) <sup>c,C</sup>	50.56 (0.93) <sup>d,a,A</sup>	27.89 (0.78) <sup>d,C</sup>	27.38 (1.48) <sup>d,C</sup>
<b>GSO</b>	112.76 (0.15) <sup>e,A</sup>	108.42 (2.55) <sup>c,A</sup>	110.10 (3.44) <sup>e,A</sup>	109.34 (1.50) <sup>e,A</sup>	102.09 (1.12) <sup>d,B</sup>	97.31 (1.68) <sup>d,B</sup>	110.83 (0.67) <sup>e,A</sup>	96.88 (1.81) <sup>e,B,C</sup>	91.50 (2.55) <sup>e,C</sup>
<b>XB</b>	42.23 (2.03) <sup>f,A</sup>	34.91 (0.41) <sup>d,B</sup>	39.52 (0.56) <sup>f,d,A</sup>	43.82 (2.97) <sup>d,A</sup>	26.81 (0.40) <sup>c,C</sup>	26.78 (0.59) <sup>c,D,C</sup>	43.89 (1.06) <sup>f,A</sup>	22.24 (1.35) <sup>f,D</sup>	23.91 (1.44) <sup>d,C,D</sup>
<b>VDF</b>	26.82 (1.43) <sup>g,A</sup>	26.79 (0.62) <sup>e,A</sup>	27.14 (0.22) <sup>g,A</sup>	28.63 (1.17) <sup>f,A</sup>	13.21 (0.93) <sup>e,B</sup>	11.73 (0.24) <sup>e,B</sup>	28.87 (1.20) <sup>g,A</sup>	*Not measured <sup>g,C</sup>	*Not measured <sup>g,C</sup>
<b>CXD</b>	43.64 (0.89) <sup>f,A,B</sup>	42.13 (0.22) <sup>f,B</sup>	45.38 (1.27) <sup>h,c,d,A</sup>	42.93 (0.34) <sup>d,A,B</sup>	31.31 (0.39) <sup>f,C</sup>	30.54 (1.26) <sup>f,C</sup>	42.93 (0.10) <sup>f,A,B</sup>	30.13 (1.28) <sup>d,C</sup>	27.20 (1.44) <sup>d,D</sup>

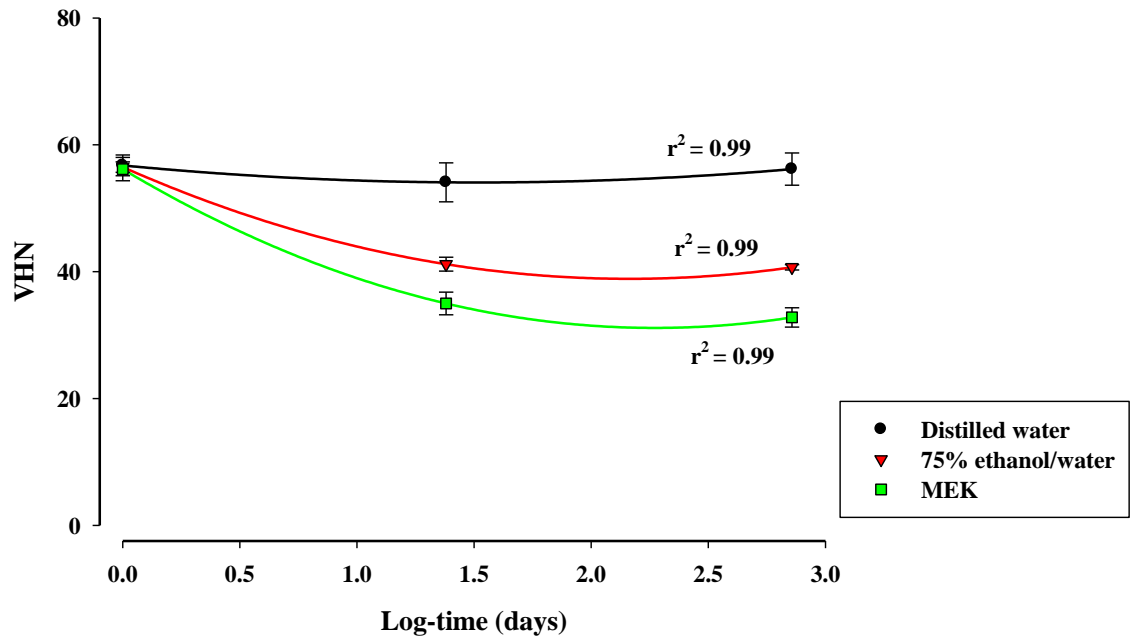
The same superscript small letters indicate a homogeneous subset (columns) ( $p < 0.05$ )  
The same superscript capital letters indicate a homogeneous subset (rows) ( $p < 0.05$ )  
\*VHV < 10



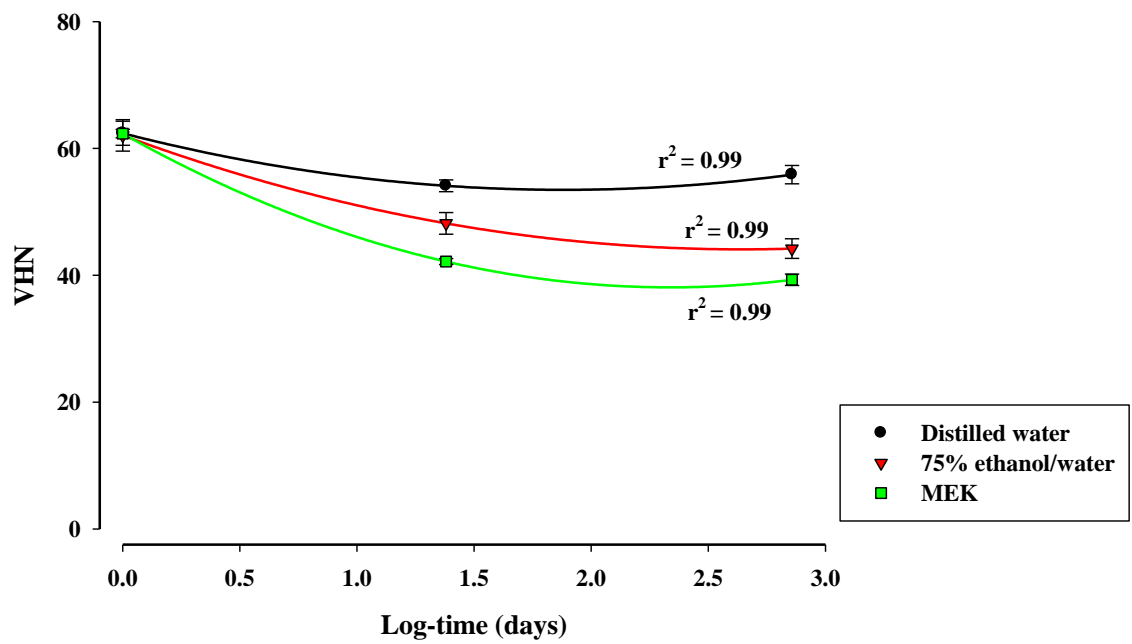
**Figure 7.2:** Vickers micro-hardness (VHN) of the examined resin composites after 30 days' storage in food-simulating solvents at 37°C



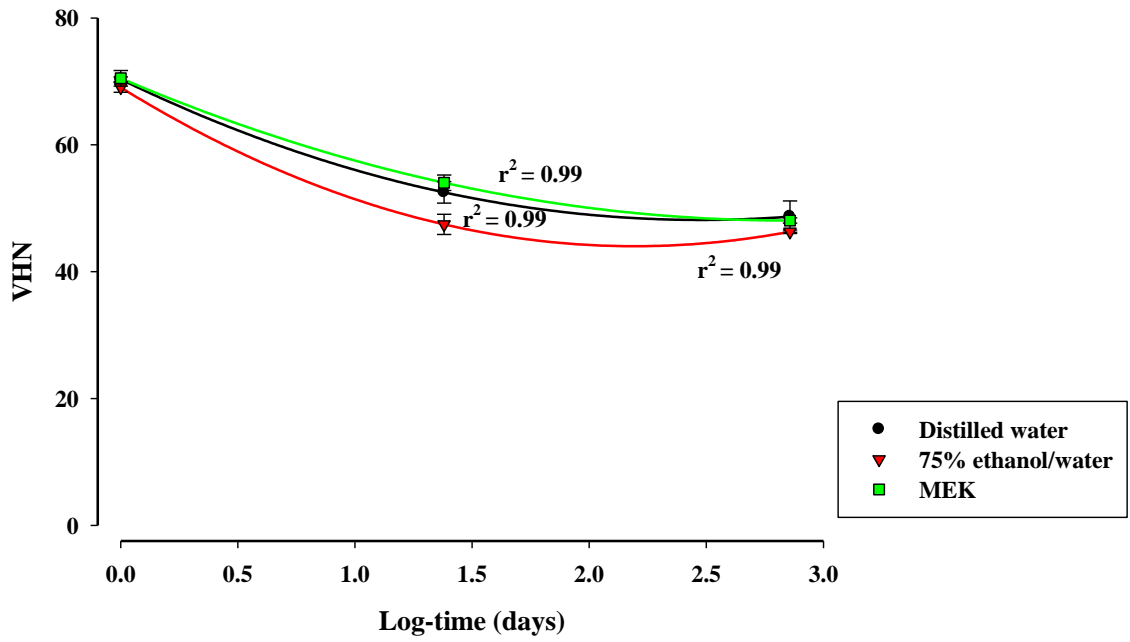
A) BL



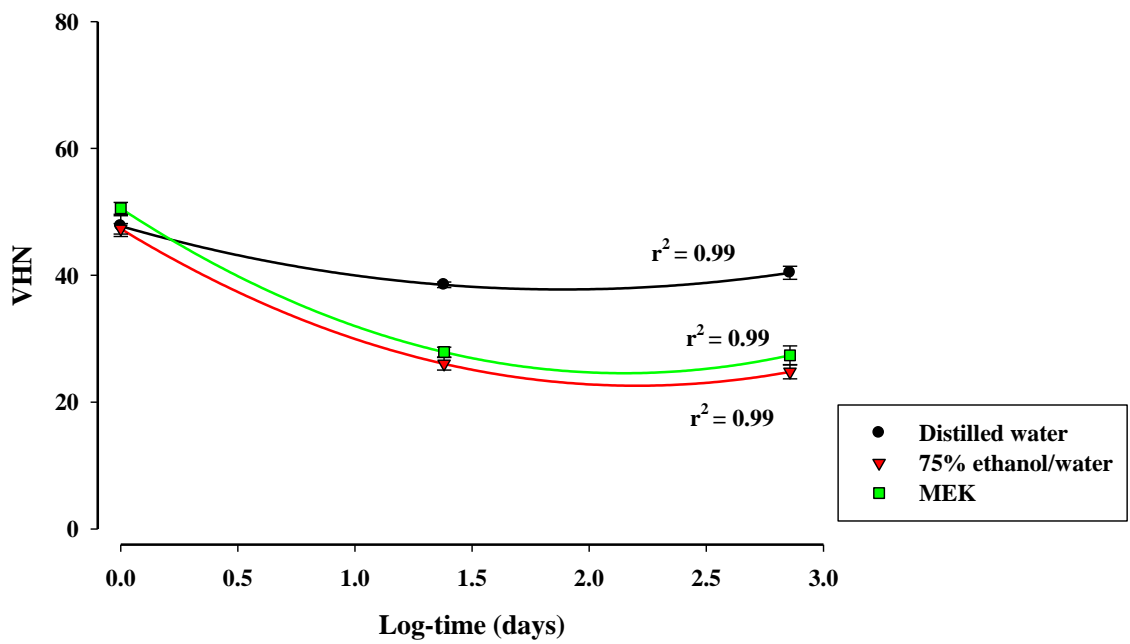
B) NCB



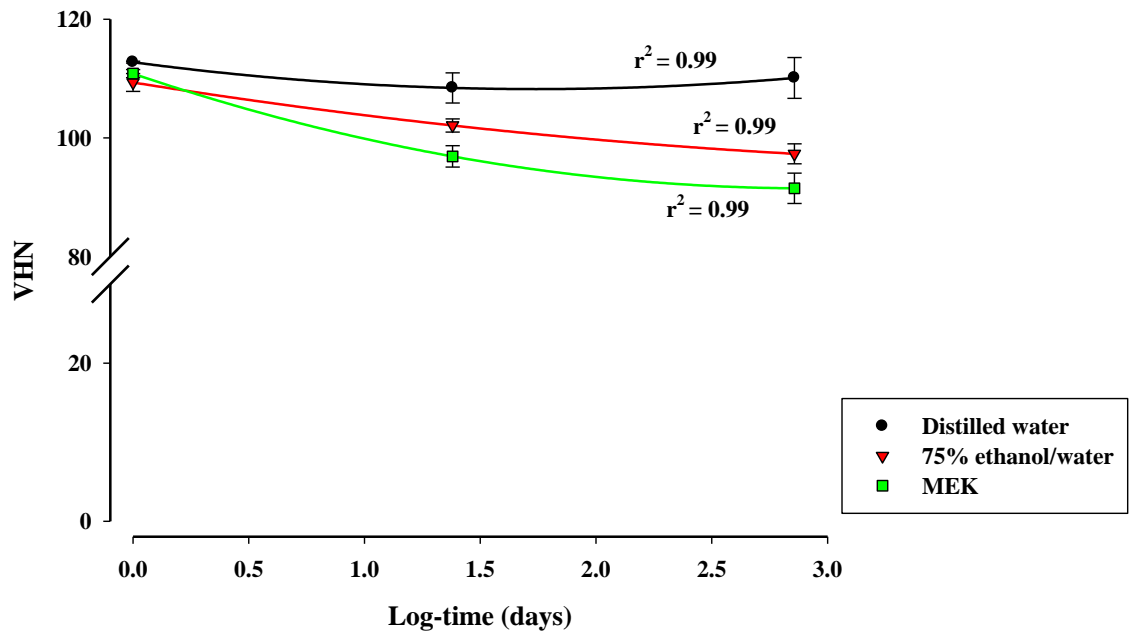
C) Exp.VT



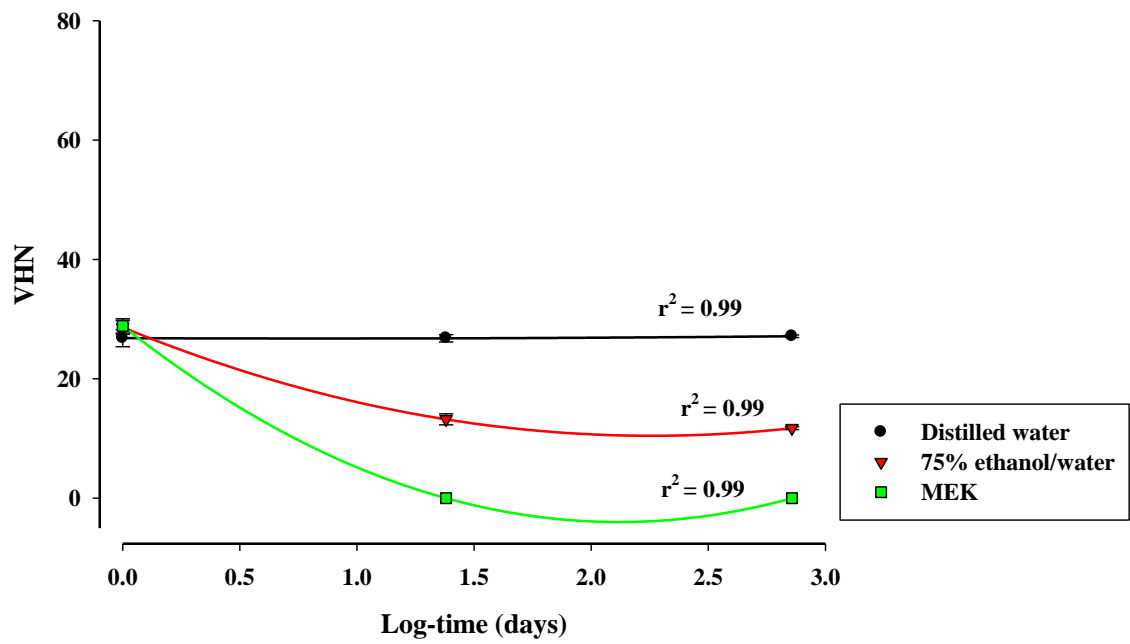
D) TEC



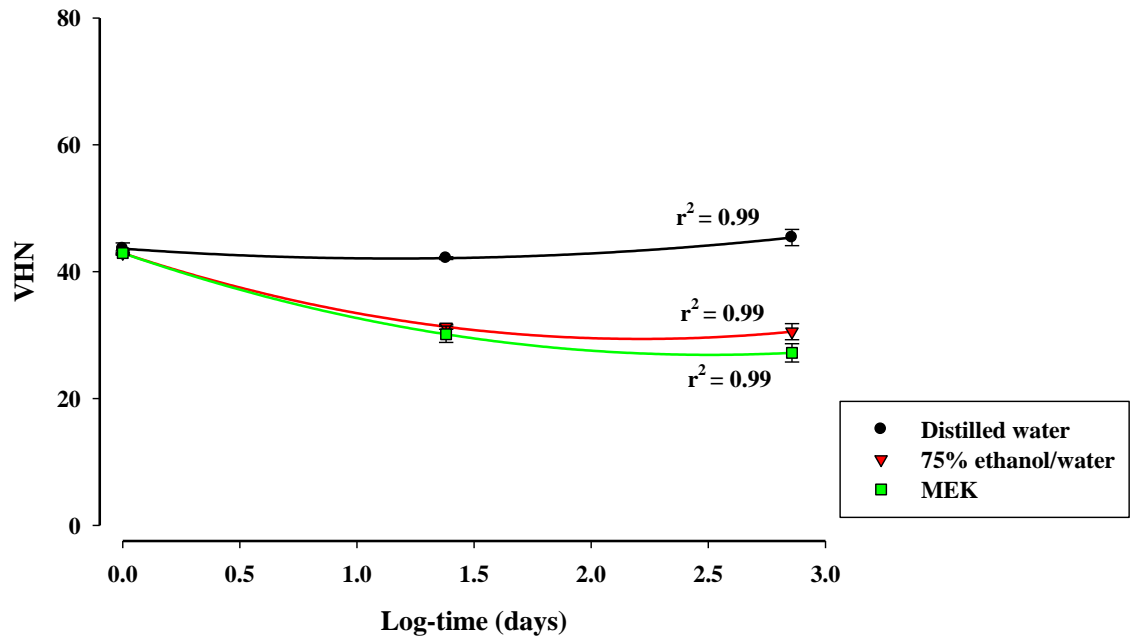
## E) GSO



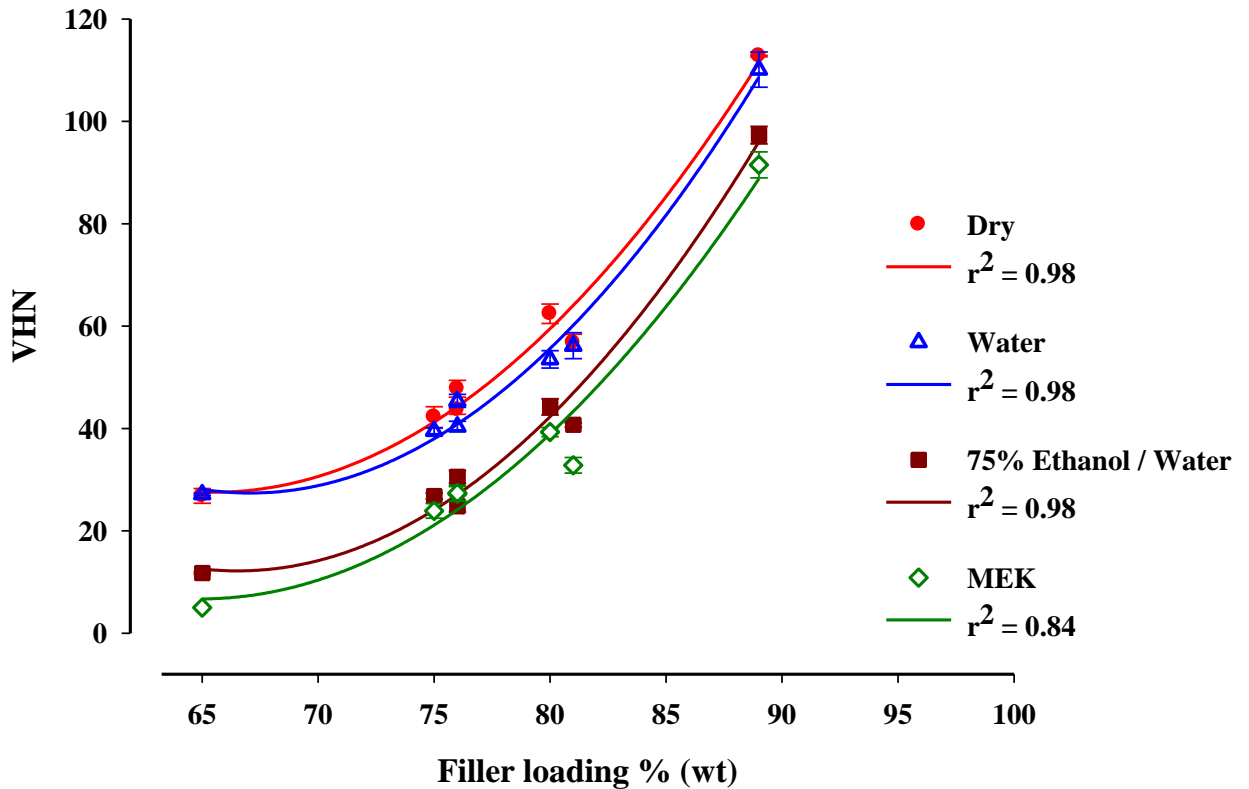
## F) VDF



## G) CXD



**Figure 7.3:** Mean values of Vickers hardness (VHN) as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD



**Figure 7.4:** Quadratic regression of VHN (all conditions) versus filler loading % (wt), for seven resin composites (BL, NCB, TEC, GSO, XB, VDF, CXD)

## 7.6 Discussion

This study reported the effect of food-simulating solvents on Vickers micro-hardness of resin composites (water, 75% ethanol/water, MEK) by increasing the solubility parameter as shown in Table 7.3 [205, 206]. Significant effects on surface hardness were observed according to materials, condition, and storage time ( $p < 0.001$ ). Moreover, quadratic regression analysis showed a significant positive correlation between VHN and filler loading. Thus, the null hypotheses were rejected.

**Table 7.3:** Solubility parameters of food-simulating solvents

<b>Food-simulating solvents</b>	<b>Solubility Parameter <math>\delta \times 10^{-4} \text{ (J/m}^3\text{)}^{0.5}</math></b>	<b>Examples of drinks and foods Simulated</b>
MEK	1.9	Naturally existing in very low concentration in food such as meats, yogurt, vegetables and fruits
75% ethanol/water	3.15	Light Beverages, Alcohol, Candy, Syrups, Wine, Beer
Distilled water	4.79	Water

The top surface of the specimen was selected to measure the surface hardness. It has been suggested that the irradiance was reduced through the bulk of the composite, owing to the light being scattered by filler particles and resin matrix [207]. Thus, the top surface provides an accurate measurement due to the photo-irradiation tip of the light cure unit focusing directly on the examined surface. Furthermore, a finishing polishing system was used for all composite specimens to allow the removal of a weak resin-rich layer to give a smooth, flat testing surface [208].

The hardness is generally associated with resistance to intra-oral softening, rigidity, and mechanical strength of the material. Measuring hardness is an indirect way of assessing the relative degree of polymerisation, for which a higher hardness value indicates that more polymerisation has occurred [209].

Reduction in the mechanical properties due to storage in water has been ascribed to the water sorption by the resin matrix. This sorption causes swelling of the cross-linked polymer network resulting in decreases in the frictional forces between the polymer chains. Thereafter, when the matrix is saturated with water, the material becomes stable [203].

In 75% ethanol/water storage, a significant reduction was seen in VHN from the baseline ( $p \leq 0.006$ ), with no significant differences after storage at 1 and 30 days. This finding is in agreement with that of a previous study which reported a significant reduction in hardness after 1 day's storage in ethanol [210]. The 75% ethanol/water solution causes degradation of the resin and matrix/filler interface. It easily diffuses and swells the resin matrix because of tensile stress near the matrix/filler interface, which increases the diffusion and leaching [88]. Previous research has observed a decrease in surface hardness and wear resistance after storing resin composites in ethanol and ascribed these differences to its chemical softening influences [176].

However, composites based on Bis-GMA are highly prone to softening by chemicals with a solubility parameter ranging from  $1.82 \times 10^{-4}$  to  $2.97 \times 10^{-4}$  ( $\text{J/m}^3$ )<sup>0.5</sup>. The solubility parameter of 75% ethanol was quite similar to that of Bis-GMA resin [211]. It has been shown that resin composites stored in ethanol had a significant decrease in hardness, while those in water showed an increase in hardness after two weeks of storage [212].

MEK naturally exists at quantifiable levels in foods such as meats, yogurt, vegetables and fruits. It has been approved by the FDA as a direct additive to food for use as a flavouring agent for human consumption [213]. Usually a MEK solvent has more softening action and a deterioration effect on resin composites. When resin composites are stored in MEK, more monomer is leached out than in other solvents [214]. Thus, influences may occur on their mechanical properties and long-term stability.

In this study, a positive correlation between VHN and filler loading is confirmed. This positive correlation has been established between filler content and the hardness of resin composite [215]. The main finding of this study was that GSO showed resistance to degradation and had the highest VHN at significant levels of difference with all examined materials, regardless of storage time and conditions ( $p < 0.001$ ). In contrast, VDF had the lowest VHN amongst the materials examined ( $p < 0.001$ ). This might be due to GSO having the highest filler loading, while VDF has the lowest. Therefore, resin composites with higher filler loadings lead to higher levels of hardness and flexural properties [181]. This finding is in agreement with another study showing that GSO has the highest nano-hardness amongst the investigated materials [216].

In addition to that observation, it is seen that the VDF has the lowest filler content. This study thus confirms that filler loading is linked with hardness values [217]. This means that an increase in the filler content causes an increase in the surface hardness of the resin composites [218]. The VDF also showed the worst degradation in organic solvents, particularly the MEK solvent, which cannot be measured by the micro-hardness instrument. A possible explanation is that a smaller amount of cross-linking polymer may cause a greater degree of swelling and subsequently promote a higher amount of softening [210]. Also, VDF contains UDMA (urethane dimethacrylate), which is a monomer that may soften in water or in oral simulating solvents more easily than Bis-GMA based composites. Thus, the instability of UDMA resin may be due to a higher amount of unreacted monomer [196]. It is consistent with other studies, which found that VDF had lower hardness [219, 220].

Exp.VT was lower in VHN after 30 days storage in water ( $p = 0.043$ ), which may be because its matrix has GPDM resin and may absorb more water [117]. Storage in the water has shown that most resin composites may be irreversibly degraded as a result of the filler particle degradation, the matrix weakening, or debonding of the filler/matrix interface [221].

Furthermore, in respect of Exp.VT, this demonstrated more resistance to degradation in MEK after 1 day than in water/ethanol, with no change after 1 day's storage in water ( $p > 0.05$ ). The cross-link polymer inhibits the solvent from achieving sufficient solvent/polymer interaction, and thus may prevent the softening of linear and branched polymers by stopping molecules from leaching out into the solvent [210]. In contrast, NCB and CXD showed more degradation after 30 days' storage in MEK.

The degradation of resin composites seems to be greater in 75% ethanol/water and in MEK as compared with degradation in distilled water. This difference can be ascribed to the superior ability of the organic solvent to leach unreacted monomers after penetrating and swelling the polymer network [79].

The micro-hybrid resin composite BL showed lower VHN than NCB, both of which have the same matrix composition (Bis-GMA, TEGDMA), and approximately the same filler loading percentage. These differences in results may be due to the type of filler,



since it shows that the nano-filled composite has hardness superior to that of the micro-filled composite [222].

On the other hand, XB and CXD showed higher HVN after 30 days of storage in water ( $p \leq 0.03$ ). This increase may be due to continued polymerisation after the initial curing, which leads to increased cross-links, and thus may extend to as long as 30 days [199]. This finding corroborates those of a previous study [223] which suggests that a long period of time is required to reach the maximum degree of polymerisation for resin composites after curing.

Softening solvents play a role in the degradation of composites, and this affects the long-term durability of composites by weakening their resistance to the oral chemical environment.

## **7.7 Conclusions**

- MEK caused the greatest softening (reduction in VHN) of most of the composites tested.
- A highly filled nano-hybrid composite GSO was the least affected over time regardless of the storage conditions.
- Flowable resin-composites VDF was more affected over time than those of the conventional hybrid resin-composites and bulk fill.

## **Chapter Eight**

### **Effect of Food-simulating Solvents on Colour Stability and Gloss Retention of Dental Resin-composites**

A. Alrahlah, N. Silikas, D.C. Watts

## 8.1 Abstract

**Objective:** To study the effect of exposure to food-simulating solvents at 37°C on colour stability and gloss retention of resin composites.

**Methods:** Seven resin composite materials were examined: 1 micro-hybrid (Bright Light<sup>®</sup>), 5 nano-hybrids (Experimental Vertise<sup>™</sup>; Nanoceram-Bright<sup>®</sup>; Tetric EvoCeram<sup>®</sup>; Grandio<sup>®</sup> SO; Ceram·X<sup>™</sup> duo) and 1 flowable (Venus<sup>®</sup> Diamond Flow). Disk specimens (10 x 2 mm) were prepared (n=9) for each material via manipulation and photo-polymerisation, according to manufacturers' instructions. Specimens of each composite material were assigned as three groups (n=3) into solvents of increasing solubility parameter: distilled water, 75% ethanol/water and MEK (methyl ethyl ketone) at 37 ± 1 °C. Colour change ( $\Delta E$ ) and surface gloss were evaluated after 1 day, 1 month and 6 months at 23 ± 1 °C. Data were analysed by three-way ANOVA, one-way ANOVA and Tukey *post hoc* tests ( $\alpha = 0.05$ ).

**Results:** There was a statistically significant interaction between resin composites, conditions and storage times ( $p < 0.001$ ) for both colour and gloss. 75% ethanol/water and MEK showed changes in  $\Delta E$  for all materials ( $p < 0.001$ ). All material in water showed stability in colour over 6 months' time ( $\Delta E \leq 1.32$ ). After 6 months' storage in 75% ethanol/water, GrandioSO and Venus Diamond Flow showed a colour stability of  $\Delta E = 2.76$  and 2.90 respectively, whereas after 6 months storage in MEK, Experimental Vertise and GrandioSO showed a colour stability of  $\Delta E = 2.55$  and 2.04 respectively. In general, the MEK solvent exhibited more effects on colour, except that Ceram·X duo showed no change. All materials stored in water showed reduction in gloss ( $p \leq 0.021$ ), except Nanoceram-Bright and Ceram·X duo. In 75% ethanol/water storage, all materials showed reduction in gloss ( $p \leq 0.034$ ). In MEK, loss in gloss was recorded for all materials ( $p \leq 0.015$ ) except GrandioSO and Venus Diamond Flow. GrandioSO showed the highest gloss values in 75% ethanol/water and MEK. In general, 75% ethanol/water exhibited more effects on gloss, whereas Bright Light and Nanoceram-Bright showed no change.

**Conclusion:** MEK solvent has caused the greatest colour change ( $\Delta E$ ) for most of the composites examined, whereas the 75% ethanol/water solution caused the greatest reduction in gloss. A highly filled nano-hybrid composite GrandioSO had the greatest colour stability and gloss retention over time, regardless of the storage conditions.

**Key words:** resin composites, colour stability, gloss, nano-hybrid, food-simulating solvent, MEK, ethanol/water

## 8.2 Introduction

The high aesthetic demands of the patient require an optimal colour match of resin composite restorations for the duration of their clinical service. The aesthetics of resin composite restorations are affected by several factors such as colour, thickness of restoration, optical properties, cavity substrate [224-226], surface roughness and gloss [227]. One of the issues that may lead to the replacement of dental resin composites is their failure to maintain their optical properties over time [228].

Resin composites may be susceptible to various degrees of discolouration on exposure to the oral aqueous environment [229]. Colour change in resin composites has been ascribed to the structural changes in the material as a result of ageing, a coloured degradation product formation, change in the morphology of the surface, extrinsic staining [230], chemical differences of resin components such as polymeric structure and a photo-initiator system [231].

Gloss represents the capability of the surface of the material to reflect light [232]. As a result of reducing the filler to nano-size, nano-composites can be polished to achieve a higher gloss surface compared to larger filler size resin composites [233, 234]. The gloss of resin composites may be affected by staining agents that change the stability of the colour [232].

Water sorption causes a series of adverse consequences on the resin composite such as reduction of mechanical properties and change of colour stability, though it has the advantage of reducing polymerization shrinkage stress [141]. In addition, it has been shown that water acts as a carrier of staining agents during the water sorption process [217]. Also, beverages can significantly affect the colour stability and gloss retention of dental materials [232].

The oral chemical environment has a noticeable impact on the resin composites degradation [235]. In 1976, the US Food and Drug Administration (FDA) used organic solvents with solubility parameters from 1.5 to  $4.8 \times 10^{-4} \text{ (J/m}^3)^{0.5}$  to simulate foods when testing the durability of food containers [192]. The solubility parameter is defined as a numerical value that describes the degree with which molecules of one material permeate and soften another material, for instance, a polymer [79]. It was found that when the value of the solubility parameter of a solvent is equivalent to that of the matrix

of the composites, a maximum softening effect may occur [205]. Also, it has been shown that when resin composites are stored under certain physical/chemical conditions, the colour of these materials may change [93].

This study focuses on evaluation of colour stability and gloss retention of experimental and contemporary dental composites, when immersed in three different solvents. Therefore, the objective of the study was to investigate the effect of food-simulating solvents over time on colour stability and gloss retention of seven resin composite materials. The null hypotheses were that: i) there would be no difference in colour stability between materials examined over time after storage in solvents, ii) there would be no difference in gloss retention between materials examined over time after storage in solvents, and iii) there would be no differences in colour stability and gloss retention values after storage between solvents.

### **8.3 Materials and Methods**

Seven resin composites (Table 8.1) were examined. Nine disk-shaped specimens (10 x 2 mm) were prepared (n=9) for each material via manipulation and photo-polymerisation, according to manufacturers' instructions. Specimens were polymerised using a halogen curing unit with a tip diameter of 10 mm (Optilux<sup>®</sup> 501, SDS, Kerr, Danbury, CT, USA) under the standard curing mode of an output wavelength range of 400-505 nm and output irradiance of 580-700mW/cm<sup>2</sup>. A calibrated radiometer was used to verify the irradiance at each use of the light cure unit. The light tip was approximately 1 mm away from the specimens for both sides. Finishing and polishing procedures were applied to one side (examined surface) of the specimens. Specimens were polished with a series of polishing disks (OptiDisc; Kerr Hawe SA, Bioggio, Switzerland), with an electric hand piece, at 15,000 rpm for 15s for each disk (medium, fine, and superfine). This allowed removal of a weak resin-rich layer, giving a smooth-flat testing surface. The specimens were placed in an ultrasonic water bath (Transonic T 310, Camlab Limited, Cambridge, England) for 2 min to remove any remaining debris. Specimens of each composite material were assigned to three groups (n=3) of solvents of increasing solubility parameter: distilled water, 75% ethanol/water, and MEK (methyl ethyl ketone).

**Table 8.1:** Materials tested

Code	Product	Manufacturer	Matrix	Filler type	Filler %W/W	Lot Number
BL	Bright Light®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Ba glass, mixed oxide 0.04-0.25 µm	81	610230
NCB	Nanoceram-Bright®	DMP Ltd, Greece	Bis-GMA, TEGDMA	Barium glass, mixed oxide 0.05-0.7 µm	80	630212
Exp.VT	Expermental Vertise™	Kerr Corp, Orange, USA	GPDM and methacrylate co-monomers	Prepolymerized filler, Ba glass; nanoscale SiO <sub>2</sub> & YbF <sub>3</sub>	-	3379131
TEC	Tetric EvoCeram®	Ivoclar Vivadent AG, Schaan, Liechtenstein	Bis-GMA, UDMA	Ba glass, silicate, SiO <sub>2</sub> , mixed oxide 40nm-3000nm	76	L56579
GSO	Grandio SO	Voco GmbH Cuxhaven, Germany	Bis-GMA, Bis-EMA, TEGDMA	Ba glass 1µm SiO <sub>2</sub> 20-40 nm	89	1048014
VDF	Venus® Diamond Flow	Heraeus Kulzer GmbH Hanau, Germany	UDMA, EBADMA	Ba-Al-F silicate glass, YbF <sub>3</sub> and SiO <sub>2</sub>	65	010100
CXD	Ceram-X™ duo	Dentsply GmbH Konstanz, Germany	Methacrylate modified polysiloxane, Dimethacrylate	Barium-aluminium-borosilicate glass, SiO <sub>2</sub>	76	0811000572

These were positioned against a white ceramic plate, which worked as a background and was also used to calibrate the colorimeter before measurements were taken. Three repeated measurements for each specimen were taken to find the colorimetric measurements. The differences from the zero value were computed by means of the colorimetric values  $\Delta L^*$ ,  $\Delta a^*$  and  $\Delta b^*$ . Thus, the total colour difference  $\Delta E$  for each sample was computed using the following equation:

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

Surface gloss was determined by a glossmeter (Novo Curve, Rhopoint, Instrumentation Ltd, East Sussex, England), which was calibrated against a black glass standard provided by the manufacturer. Three measurements were taken at the same place for each specimen on a 60° light incidence.

Both colour measurements and gloss were evaluated after 1 day, 1 month and 6 months. Before each measurement, the specimens were cleaned by an ultrasonic water bath and then dried.

#### 8.4 Statistical Analysis

Data were analysed by the three-way ANOVA, one-way ANOVA, and Tukey *post hoc* tests (Version 20.0, IBM, New York, USA) ( $\alpha=0.05$ ), to determine significant differences in  $\Delta E$  and gloss (dependent variable) according to the use of different solvents and storage times (independent variables). All data were subjected to Levene's test of homogeneity of variance  $\alpha=0.05$ , following the assumption of equal variance. Quadratic regression analysis was performed to investigate relationships for  $\Delta E$  and gloss with a function of log time.

#### 8.5 Results

There was a statistically significant interaction between resin composites, conditions and storage times ( $p < 0.001$ ) for  $\Delta E$  and gloss. Mean values and standard deviations for  $\Delta E$  and gloss for all materials are presented in Tables 8.2 and 8.3 (Figures 8.1 and 8.2) respectively.  $\Delta E$  values ranged from 0.22 to 1.32 for distilled water, from 0.55 to 6.24 for 75% ethanol/water, and from 0.67 to 9.41 for MEK. Gloss values ranged from 43.20

to 83.13 for distilled water, from 41.37 to 80.53 for 75% ethanol/water and from 45.83 to 82.33 for MEK.  $\Delta E$  showed a positive quadratic regression function of log time for all materials (Figure 8.3), while gloss showed a negative quadratic regression function of log time for all materials (Figure 8.4).

$\Delta E$  values showed no change ( $p > 0.05$ ) after 6 months stored in water, with the exception of Exp.VT, GSO and VDF ( $p \leq 0.016$ ). Both the 75% ethanol/water and MEK showed changes in  $\Delta E$  for all materials ( $p < 0.001$ ). MEK showed a higher change in  $\Delta E$  for BL, NCB, TEC and VDF ( $p < 0.001$ ) than 75% ethanol/water, whereas Exp.VT and GSO showed more change in ethanol/water ( $p < 0.001$ ) after 6 months of storage. CXD showed no differences in ethanol/water and MEK after 6 months' storage ( $p > 0.05$ ). CXD showed the highest  $\Delta E$  value in 75% ethanol/water storage, whereas, GSO and VDF showed the lowest. BL showed the highest  $\Delta E$  in MEK, while Exp.VT and GSO showed the lowest.

All materials stored in water showed a reduction in gloss ( $p \leq 0.021$ ), with the exception of NCB and CXD ( $p > 0.05$ ). In the 75% ethanol/water storage, all materials showed reduction in gloss ( $p \leq 0.034$ ). In general, after 6 months, the 75% ethanol/water had more effect on gloss for Exp.VT, TEC, GSO, VDF and CXD ( $p \leq 0.009$ ), whereas, BL and NCB underwent no change.

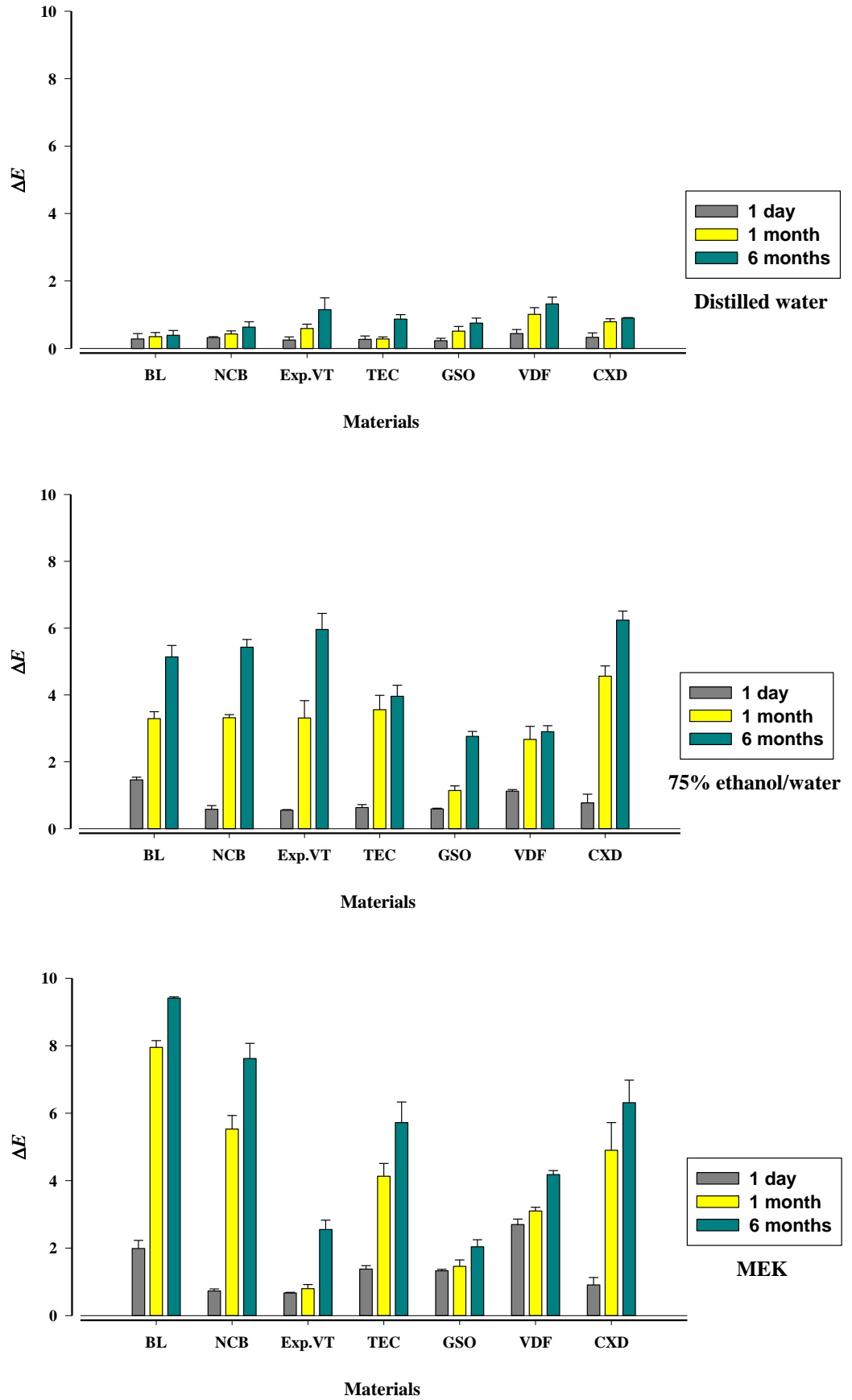


**Table 8.2:** Colour change  $\Delta E$  (standard deviation) of resin composites tested after 6 months stored in food-simulating solvents at 37°C

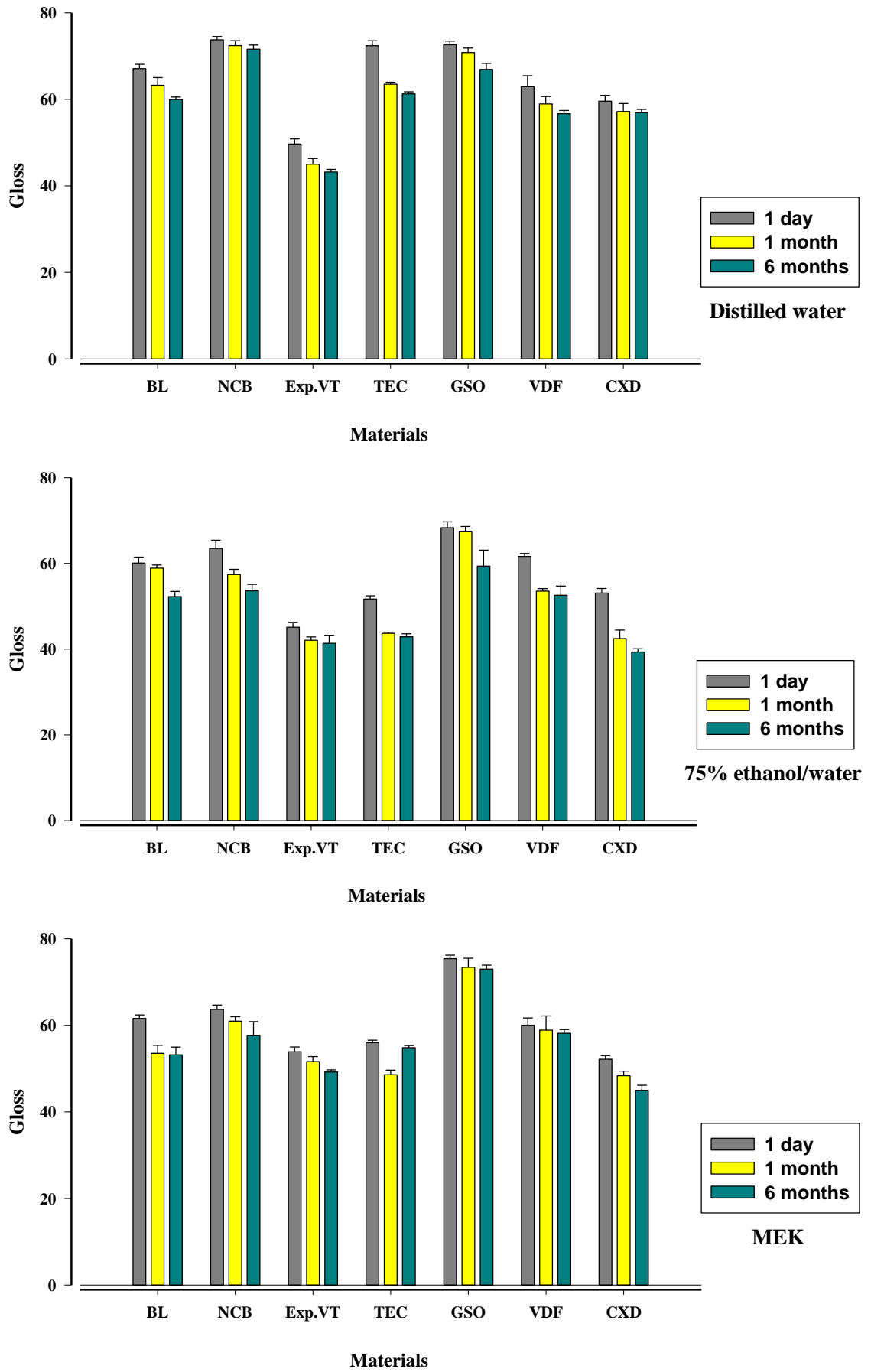
Materials	Distilled water			75 % ethanol/water			MEK		
	1day	1month	6 months	1 day	1 month	6 months	1 day	1 month	6 months
<b>BL</b>	0.28 (0.16) <sup>a, A</sup>	0.35 (0.12) <sup>a, A</sup>	0.39 (0.14) <sup>a, A</sup>	1.46 (0.08) <sup>a, B</sup>	3.29 (0.21) <sup>a, C</sup>	5.14 (0.34) <sup>a, D</sup>	1.99 (0.24) <sup>a, B</sup>	7.95 (0.20) <sup>a, E</sup>	9.41 (0.04) <sup>a, F</sup>
<b>NCB</b>	0.32 (0.03) <sup>a, A</sup>	0.43 (0.09) <sup>a, A</sup>	0.63 (0.16) <sup>a, b, A</sup>	0.58 (0.11) <sup>b, A</sup>	3.32 (0.09) <sup>a, B</sup>	5.43 (0.23) <sup>a, d, C</sup>	0.73 (0.06) <sup>b, A</sup>	5.53 (0.40) <sup>b, C</sup>	7.62 (0.45) <sup>b, D</sup>
<b>Exp. VT</b>	0.25 (0.09) <sup>a, A</sup>	0.59 (0.13) <sup>a, c, A, B</sup>	1.15 (0.35) <sup>b, c, B</sup>	0.55 (0.02) <sup>b, A, B</sup>	3.31 (0.52) <sup>a, C</sup>	5.96 (0.48) <sup>a, d, D</sup>	0.67 (0.02) <sup>b, A</sup>	0.80 (0.12) <sup>c, A</sup>	2.55 (0.28) <sup>c, C</sup>
<b>TEC</b>	0.27 (0.10) <sup>a, A</sup>	0.28 (0.06) <sup>a, A</sup>	0.87 (0.13) <sup>a, b, c, A, C</sup>	0.63 (0.09) <sup>b, A, C</sup>	3.56 (0.43) <sup>a, B</sup>	3.96 (0.33) <sup>b, B</sup>	1.38 (0.10) <sup>c, C</sup>	4.13 (0.38) <sup>d, e, B</sup>	5.72 (0.61) <sup>d, D</sup>
<b>GSO</b>	0.23 (0.07) <sup>a, A</sup>	0.51 (0.14) <sup>a, c, B, A</sup>	0.75 (0.15) <sup>a, b, B</sup>	0.59 (0.02) <sup>b, B, A</sup>	1.14 (0.14) <sup>b, C</sup>	2.76 (0.15) <sup>c, D</sup>	1.33 (0.04) <sup>c, C</sup>	1.46 (0.19) <sup>c, C</sup>	2.04 (0.21) <sup>c, E</sup>
<b>VDF</b>	0.44 (0.12) <sup>a, A</sup>	1.01 (0.20) <sup>b, B</sup>	1.32 (0.20) <sup>c, B</sup>	1.12 (0.05) <sup>c, B</sup>	2.67 (0.39) <sup>a, C</sup>	2.90 (0.18) <sup>b, c, C</sup>	2.70 (0.16) <sup>d, C</sup>	3.10 (0.11) <sup>e, C</sup>	4.18 (0.12) <sup>e, D</sup>
<b>CXD</b>	0.33 (0.13) <sup>a, A</sup>	0.79 (0.09) <sup>c, b, A</sup>	0.90 (0.16) <sup>a, b, c, A</sup>	0.77 (0.26) <sup>b, A</sup>	4.56 (0.31) <sup>c, B</sup>	6.24 (0.27) <sup>d, C</sup>	0.91 (0.22) <sup>b, A</sup>	4.90 (0.82) <sup>b, d, B</sup>	6.31 (0.67) <sup>d, C</sup>
<p>The same superscript small letters indicate a homogeneous subset (columns) (<math>p &lt; 0.05</math>)</p> <p>The same superscript capital letters indicate a homogeneous subset (rows) (<math>p &lt; 0.05</math>)</p>									

**Table 8.3:** Gloss retention (standard deviation) of resin composites tested after 6 months stored in food-simulating solvents at 37°C

Materials	Distilled water			75 % ethanol/water			MEK		
	1day	1month	6months	1day	1month	6months	1day	1month	6months
<b>BL</b>	67.10 (1.00) <sup>a, A</sup>	63.23 (1.79) <sup>a, B</sup>	59.97 (0.55) <sup>a, B, C</sup>	60.07 (1.39) <sup>a, B, C</sup>	58.90 (0.72) <sup>a, C</sup>	52.27 (1.20) <sup>a, D</sup>	61.60 (0.79) <sup>a, b, B, C</sup>	53.54 (1.83) <sup>a, D</sup>	53.20 (1.78) <sup>a, D</sup>
<b>NCB</b>	73.77 (0.76) <sup>b, A</sup>	72.43 (1.14) <sup>b, A</sup>	71.60 (0.95) <sup>b, A</sup>	63.50 (1.91) <sup>a, B</sup>	57.40 (1.22) <sup>a, C, D</sup>	53.60 (1.51) <sup>a, D</sup>	63.67 (1.01) <sup>b, B</sup>	60.97 (1.02) <sup>b, B, C</sup>	57.70 (3.14) <sup>b, C, D</sup>
<b>Exp. VT</b>	49.67 (1.17) <sup>c, A</sup>	45.00 (1.31) <sup>c, B</sup>	43.20 (0.61) <sup>c, B, C</sup>	45.10 (1.14) <sup>b, B</sup>	42.07 (0.78) <sup>b, B, C</sup>	41.37 (1.86) <sup>b, C</sup>	53.90 (1.10) <sup>c, d, D</sup>	51.63 (1.15) <sup>c, a, D, A</sup>	49.23 (0.47) <sup>a, c, A</sup>
<b>TEC</b>	72.40 (1.13) <sup>b, A</sup>	63.50 (0.44) <sup>a, B</sup>	61.27 (0.47) <sup>a, C</sup>	51.70 (0.75) <sup>c, D</sup>	43.07 (0.25) <sup>b, E</sup>	42.87 (0.71) <sup>b, E</sup>	56.00 (0.56) <sup>b, f, F</sup>	48.60 (1.04) <sup>c, a, G</sup>	45.83 (0.50) <sup>c, e, H</sup>
<b>GSO</b>	72.63 (0.83) <sup>b, A, C</sup>	70.80 (1.05) <sup>b, A, B</sup>	66.90 (1.40) <sup>d, B</sup>	68.33 (1.36) <sup>d, B, C</sup>	67.50 (1.13) <sup>c, B</sup>	59.37 (3.72) <sup>c, D</sup>	75.40 (0.80) <sup>d, A</sup>	73.40 (2.09) <sup>d, A</sup>	73.00 (0.90) <sup>d, A, C</sup>
<b>VDF</b>	62.93 (2.52) <sup>d, A</sup>	58.93 (1.72) <sup>d, A, B</sup>	56.67 (0.76) <sup>e, B, D</sup>	61.63 (0.68) <sup>a, A, B</sup>	53.53 (0.60) <sup>d, C, D</sup>	52.57 (2.15) <sup>a, D</sup>	60.03 (1.67) <sup>a, A, B</sup>	58.90 (3.28) <sup>b, A, B</sup>	58.17 (0.85) <sup>b, A, B, C</sup>
<b>CXD</b>	59.57 (1.35) <sup>a, d, A</sup>	57.17 (1.85) <sup>d, A</sup>	56.90 (0.78) <sup>e, A, B</sup>	53.50 (1.05) <sup>c, B, C</sup>	42.47 (1.97) <sup>b, D, E</sup>	39.33 (0.76) <sup>b, E</sup>	52.17 (0.85) <sup>c, C</sup>	48.37 (1.03) <sup>c, B, F</sup>	45.00 (1.15) <sup>e, F, D</sup>
<p>The same superscript small letters indicate a homogeneous subset (columns) (<math>p &lt; 0.05</math>)</p> <p>The same superscript capital letters indicate a homogeneous subset (rows) (<math>p &lt; 0.05</math>)</p>									

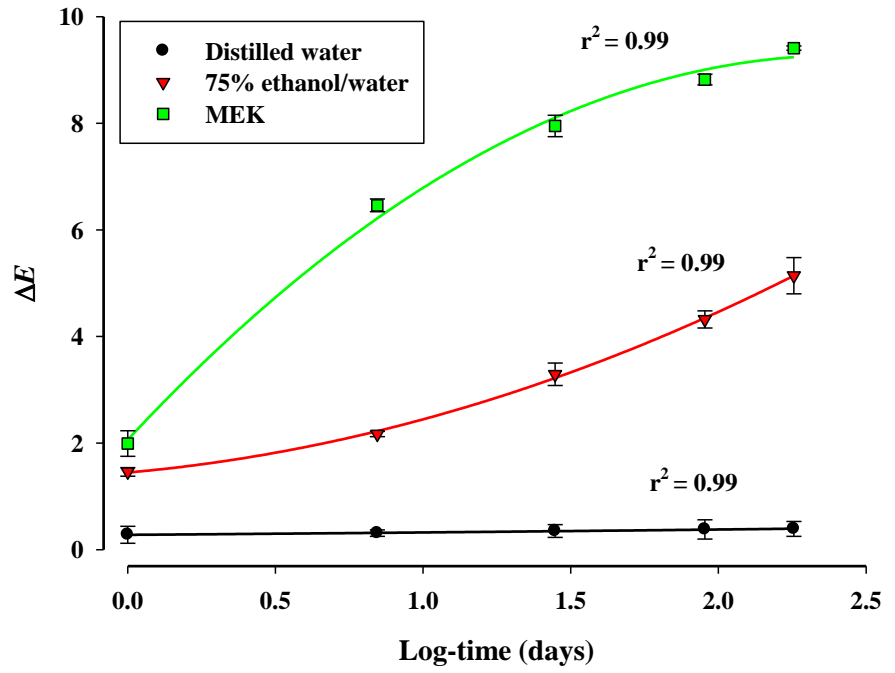


**Figure 8.1:** Mean colour change values ( $\Delta E$ ) of the examined resin composites during 6 months stored in food-simulating solvents at 37°C

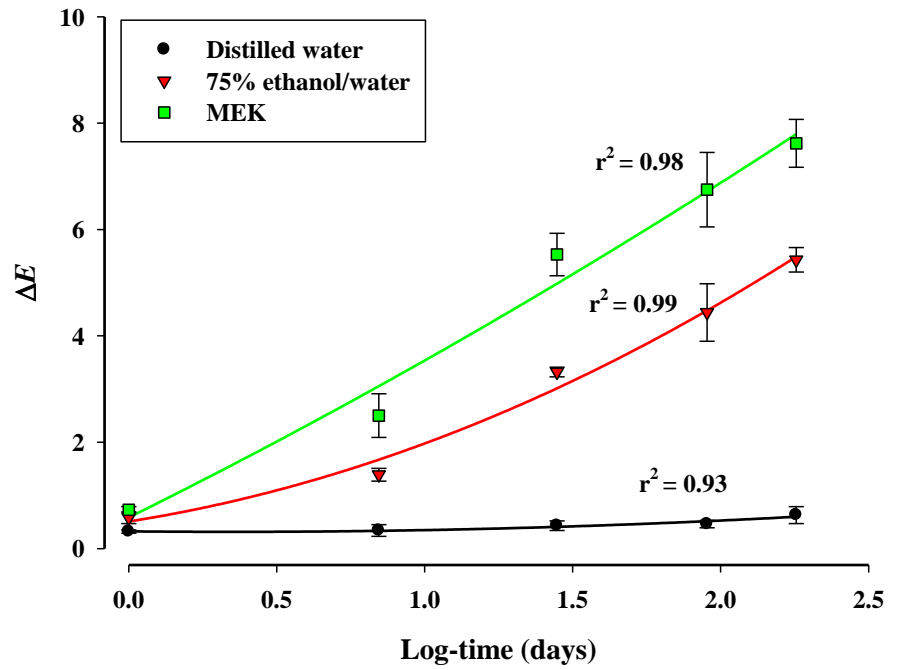


**Figure 8.2:** Mean gloss values of the examined resin composites during 6 months stored in food-simulating solvents at 37°C

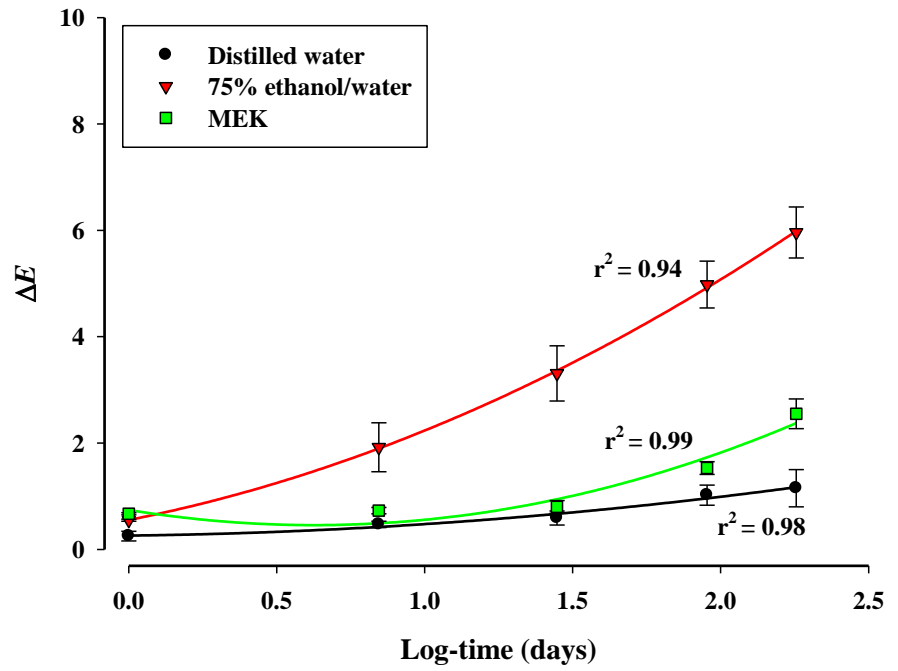
## A) BL



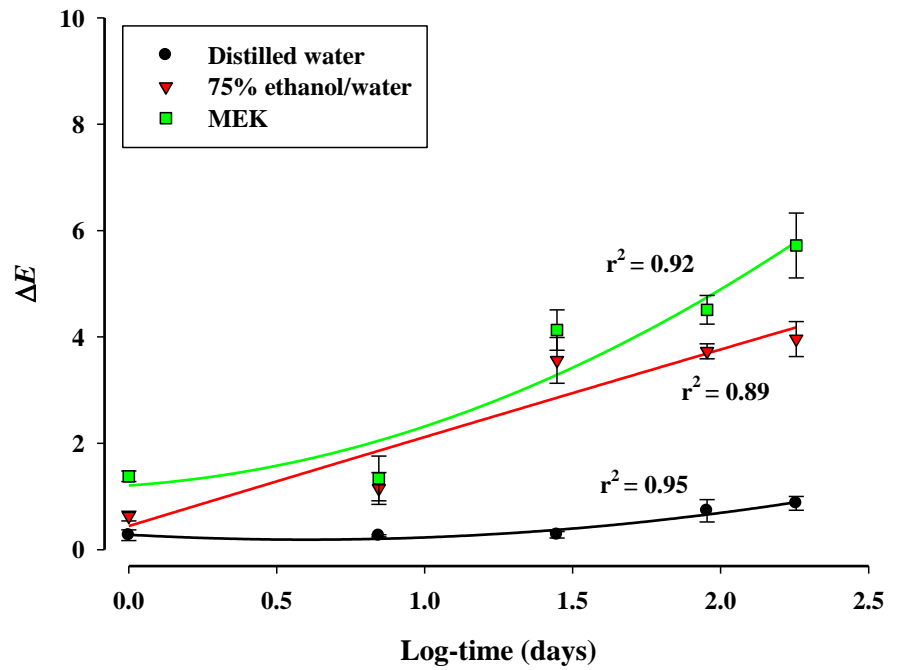
## B) NCB



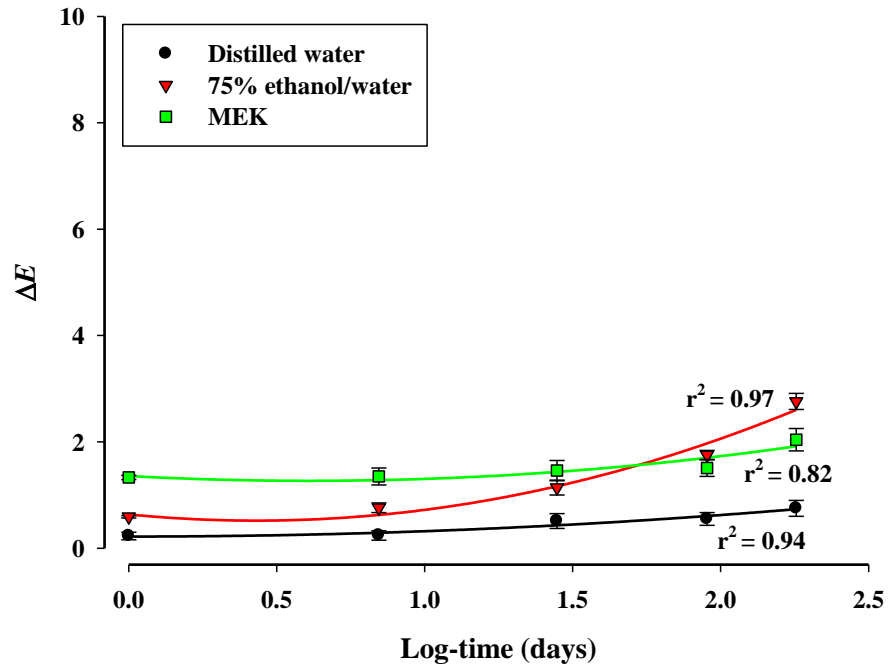
## C) Exp.VT



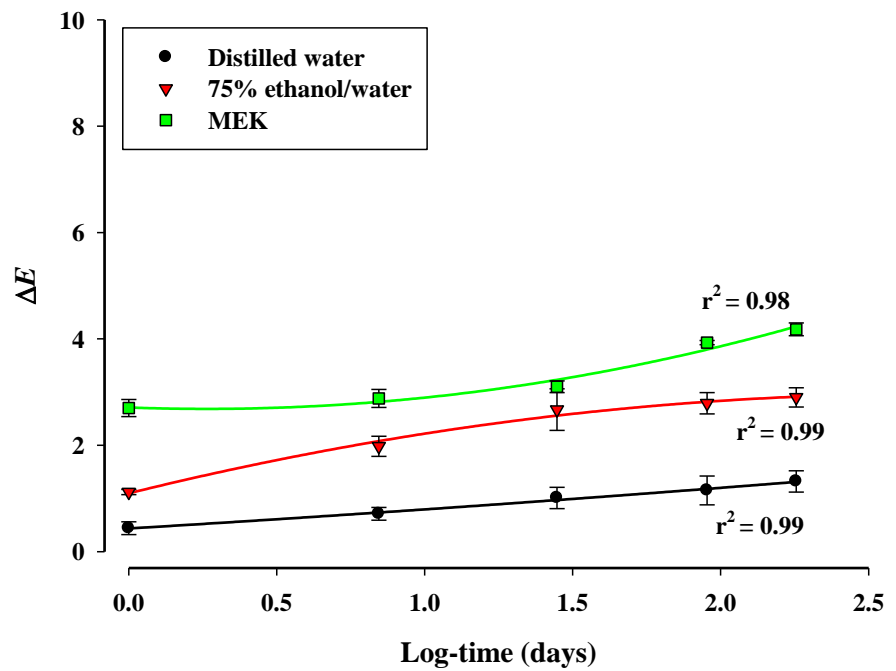
## D) TEC



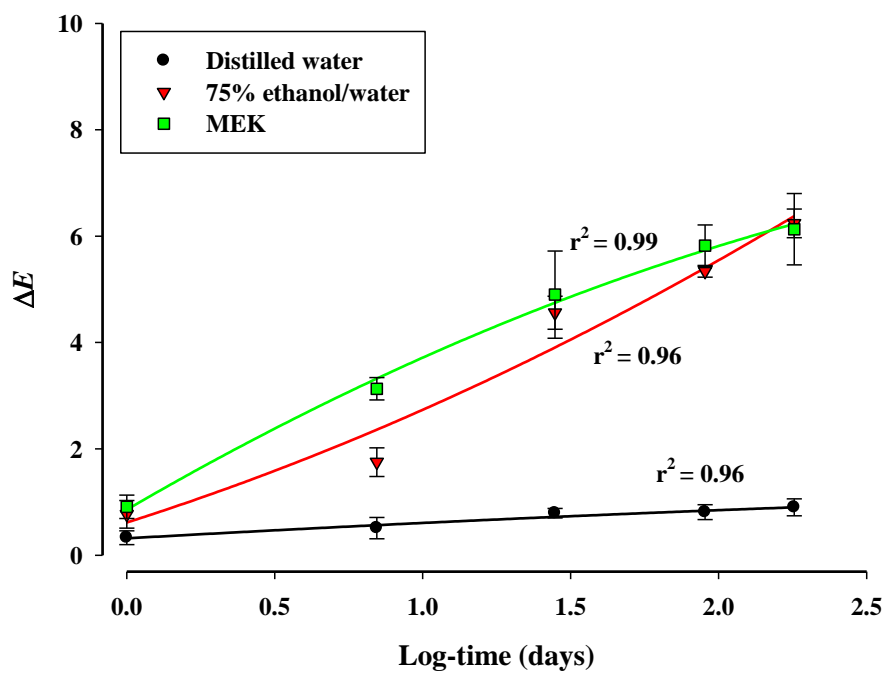
E) GSO



F) VDF



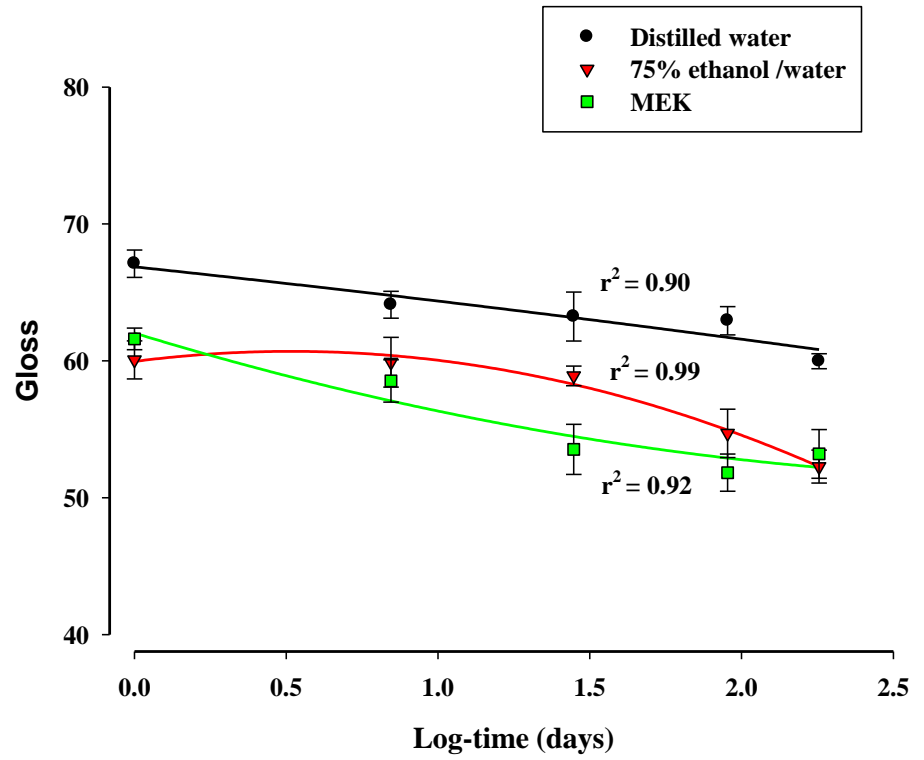
## G) CXD



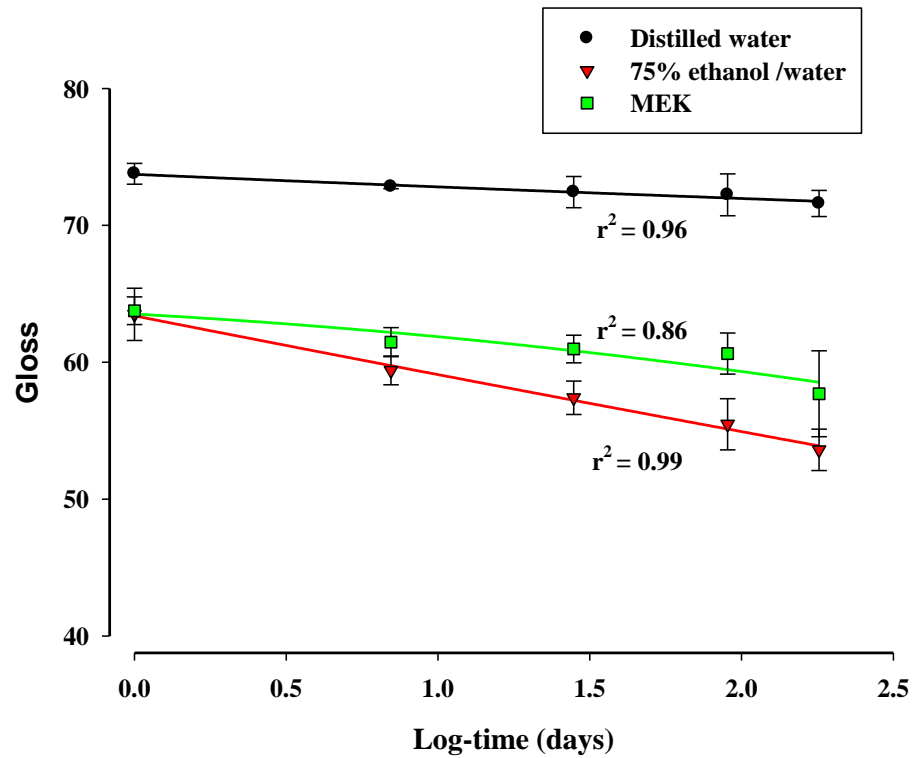
**Figure 8.3:** Mean values of colour change ( $\Delta E$ ) as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD



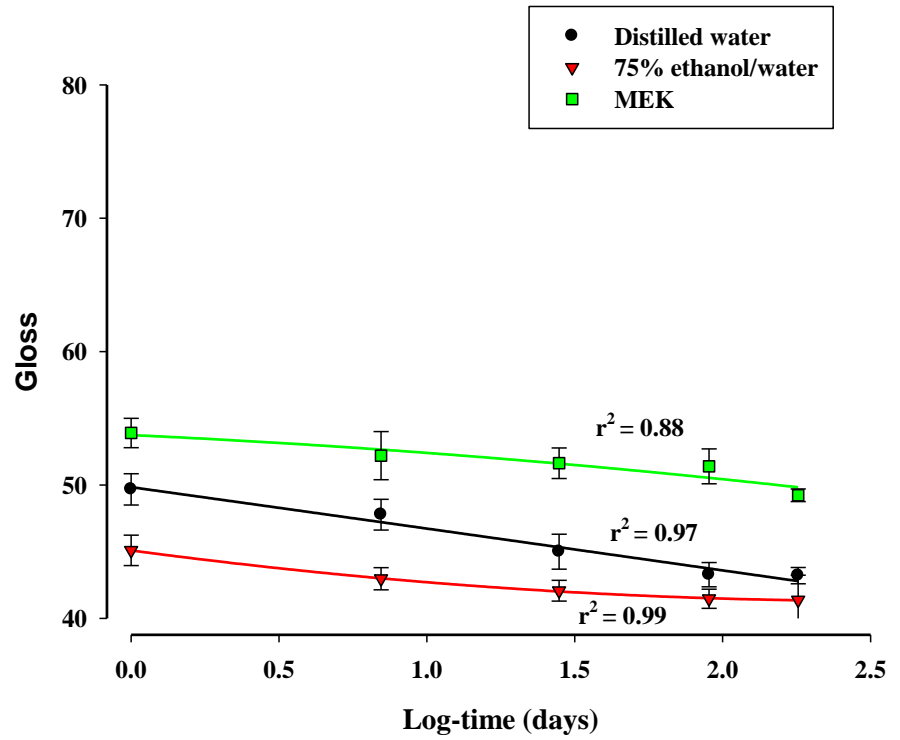
## A) BL



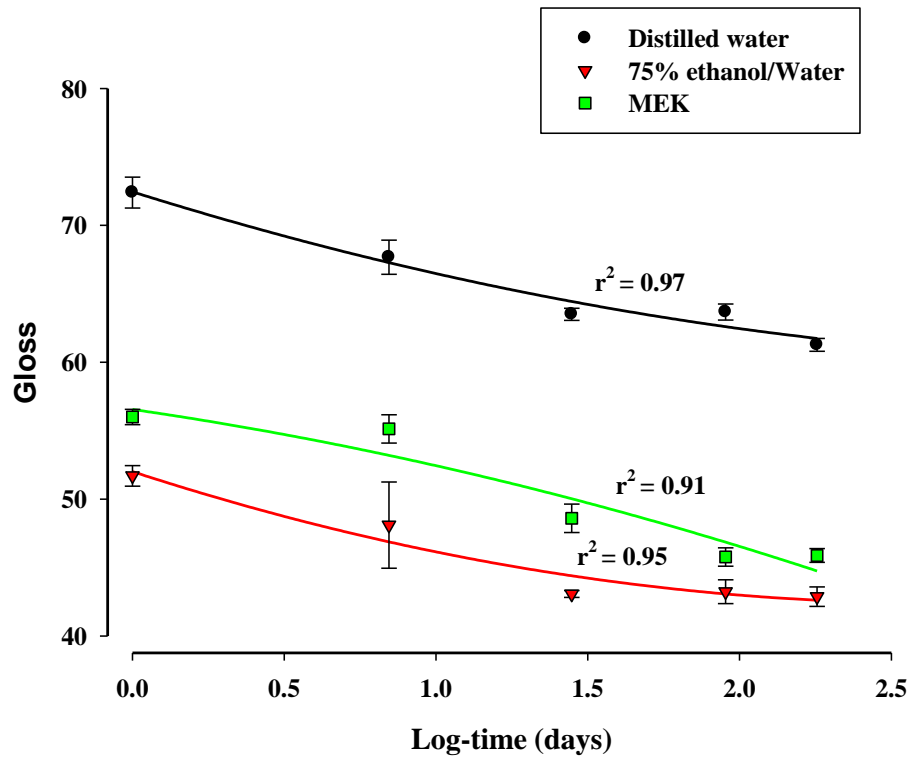
## B) NCB



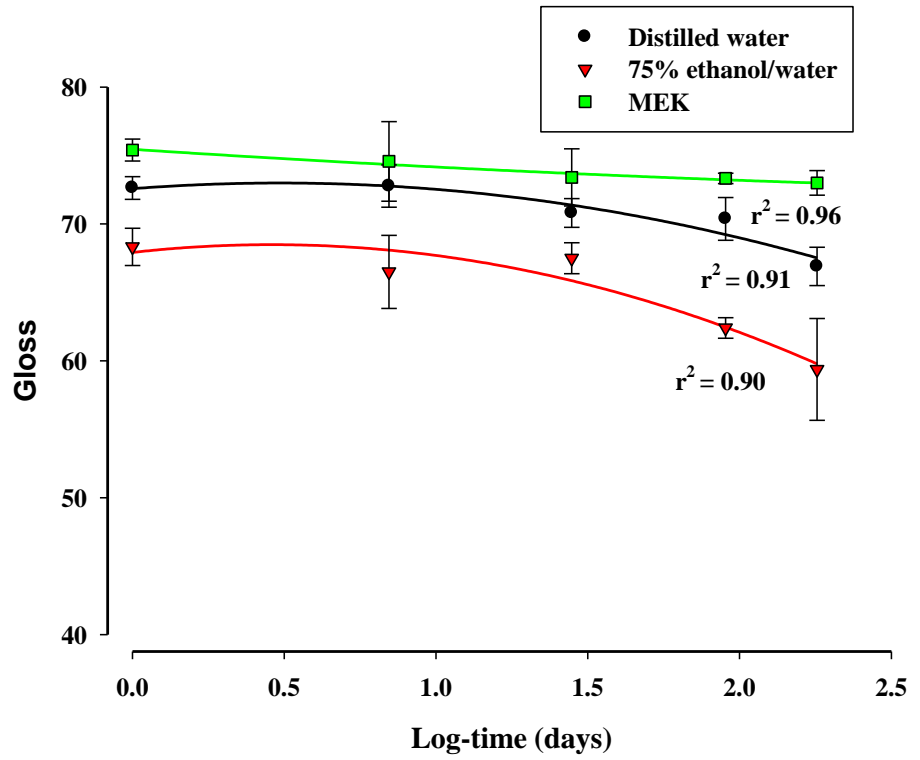
C) Exp.VT



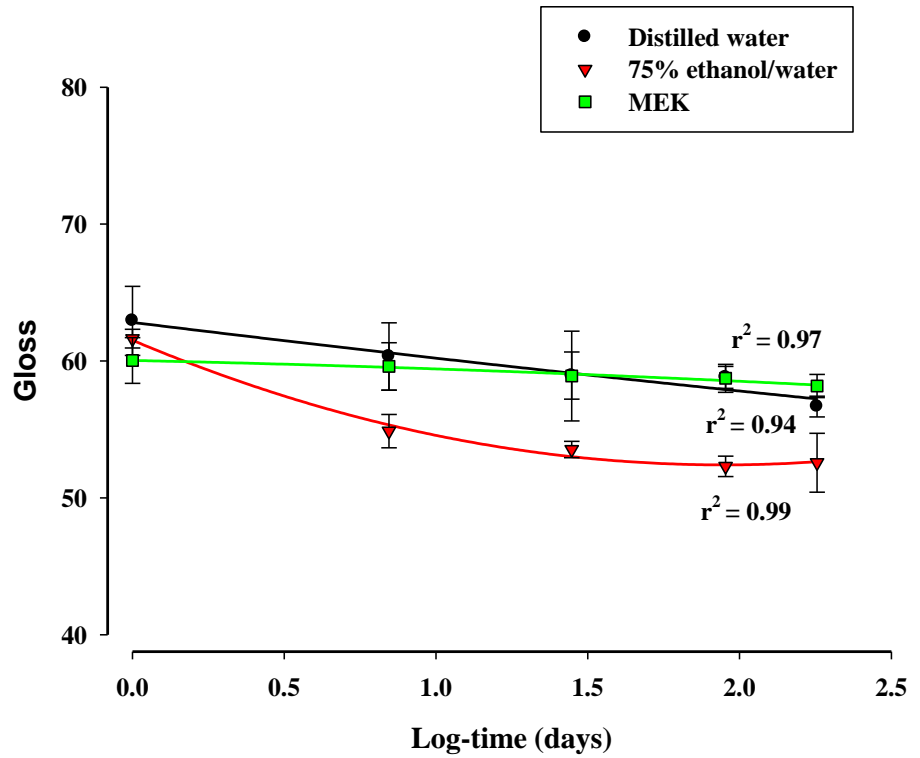
D) TEC



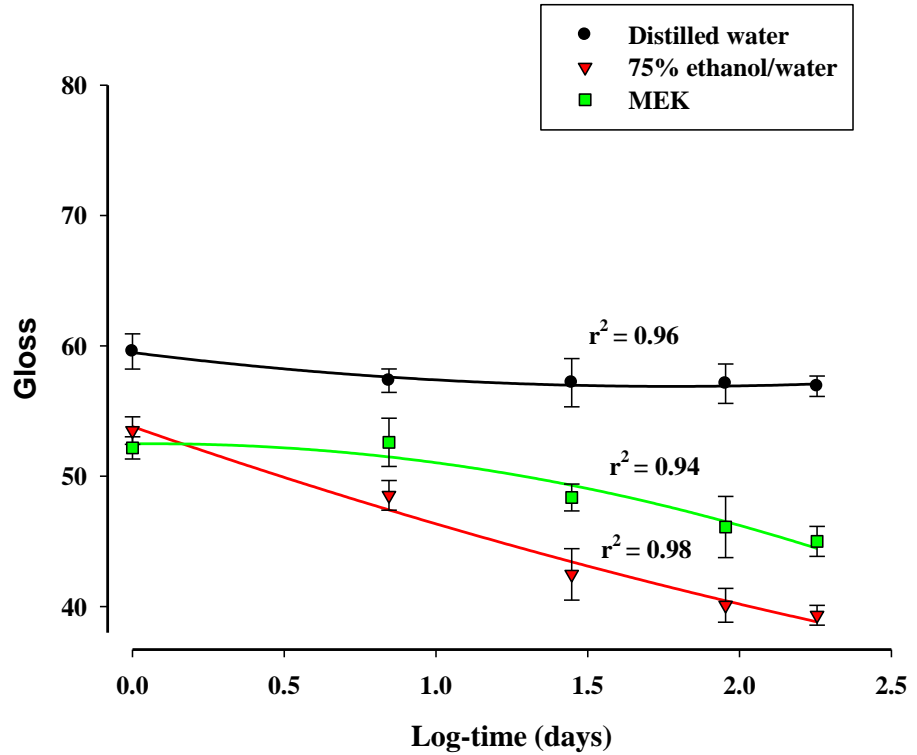
E) GSO



F) VDF



## G) CXD



**Figure 8.4:** Gloss change as a function of log time for A) BL, B) NCB, C) Exp.VT, D) TEC, E) GSO, F) VDF, G) CXD

## 8.6 Discussion

Many factors determine the optical properties of resin composites such as resin matrix type, refractive index, filler (morphology, size and content), pigment and other chemical additives [97, 236, 237]. All materials showed significant changes in both colour and gloss over time ( $p < 0.001$ ) after storage in food-simulating solvents (water, 75% ethanol/water, MEK) through increase in the solubility parameter as shown in Table 8.4 [205, 206]. Furthermore, a quadratic regression function of log time showed a positive trend for  $\Delta E$  and a negative trend for gloss for all materials. Thus, the null hypotheses were rejected.

**Table 8.4:** Solubility parameters of food-simulating solvents

<b>Food-simulating solvents</b>	<b>Solubility Parameter <math>\delta \times 10^{-4} \text{ (J/m}^3\text{)}^{0.5}</math></b>	<b>Examples of drinks and foods Simulated</b>
<b>MEK</b>	1.9	Naturally existing in very low concentration in food such as meats, yogurt, vegetables and fruits
<b>75% ethanol/water</b>	3.15	Light Beverages, Alcohol, Candy, Syrups, Wine, Beer
<b>Distilled water</b>	4.79	Water

There are two possible methods of evaluating colour, qualitative and quantitative. The qualitative one depends on matching the shade guide with specimens. Because of human perception limits, the quantitative method was used in this study to avoid bias [238]. The significance of colour changes was evaluated in relation to human eye perception. The advantages of the system used in this study are that it is similar to human sensitivity to colour, so that the observed colour changes are roughly the same at equal distances [239] and the subjective mistakes in colour evaluation are reduced [95]. Furthermore, the qualitative method of observing the changes in gloss with the naked eye is a subjective source of mistakes [100]. Therefore, the quantitative method was used to evaluate the gloss as well. Finishing and polishing were applied to achieve highly polished surfaces. The ultrasonic water bath method was used to mimic regular oral hygiene and remove the solvent's effect from the surface examined prior to each measurement [94].

According to the established range of colour change perceptibility,  $\Delta E$  values ranging from 0.0 to 1.1 were regarded as not visible and between 1.1 and 3.3 as visually visible but clinically acceptable, while  $\Delta E$  higher than 3.3 were regarded as obviously visible but clinically not acceptable for several studies [96, 238, 240, 241].

Several physical alterations of resin composites have taken place as a result of the polymerisation reaction and following the interaction with the moist oral environment

and chemicals from food and drink. This physical change may cause softening of the resin matrix and decrease of colour change resistance [242].

Some factors can cause variation in colour change values for the same samples, such as a measuring instrument, background colour, illumination and sample size [243]. Other factors include: resin composite, irradiation time, light curing unit, storage conditions and storage period [94, 244]. Some factors may have an effect on the surface gloss: filler particle size, polishing system abrasives, and the duration of polishing procedure [101, 234, 245].

It was stated that the solvents may represent the oral environment in concentration between the more destructive solvents and water [79]. In water storage, a clinically acceptable colour change was detected for all examined resin composites ( $\Delta E \leq 1.32$ ); only slight change in some composites had occurred after 1 month for VDF and Exp.VT, and after 6 months' storage for GSO. This is consistent with previous studies, which reported that the effect of water on colour stability was imperceptible clinically [93, 95].

In the 75% ethanol/water and MEK solvents, time was shown to be an important factor for colour stability of the resin composites examined. Results showed that, as storage time increased, more colour changes occurred. The 75% ethanol/water solution causes degradation of the resin and the matrix/filler interface. It easily diffuses and swells the resin matrix because of tensile stress at the matrix/filler interface, which increases the diffusion and leaching [88]. Composites based on Bis-GMA are highly prone to softening by chemicals with a solubility parameter ranging from  $1.82 \times 10^{-4}$  to  $2.97 \times 10^{-4} (\text{J/m}^3)^{0.5}$ . The solubility parameter of 75% ethanol was quite similar to that of Bis-GMA resin [211].

After 1 month of storage in the 75% ethanol/water solution, all resin composites revealed significant colour changes but were accepted clinically ( $\Delta E < 3.3$ ), with the exception of TEC and CXD, which showed an unacceptable colour change ( $\Delta E > 3.3$ ). After 6 months' storage in 75% ethanol/water, only GSO and VDF showed resistance to colour change ( $\Delta E = 2.76$  and  $2.90$ , respectively).

GSO and VDF showed the best colour stability amongst the examined materials in 75% ethanol/water. For GSO, this is possibly related to the hydrophobic resin and a high

filler loading used [98]. Typically, a highly cross-linked polymer shows greater degradation resistance to solvent [246], suggesting that GSO is extensively cross-linked. VDF matrix contains UDMA and EBADMA. It has been shown that UDMA has greater resistance to colour change than Bis-GMA [96]. Furthermore, it was shown that an increase in reactivity of EBADMA leads to higher conversion and reaction rates [33].

MEK has been approved by the FDA as a direct additive to food for use as a flavouring agent for human consumption. Usually MEK solvent has more softening action and greater deterioration effect on resin composites compared to other solvents. When resin composites are stored in MEK, more monomer is leached out than in other solvents [214]. Thus, influences may occur on long-term stability of restoration.

As a result of the degradation of resin composites, micro-flaws or gaps in the matrix/filler interface allow micro-passageways through which stains can penetrate easily [98]. MEK showed more degradation and colour changes than those materials stored in 75% ethanol/water, except for Exp.VT and GSO, which showed resistance to colour change of  $\Delta E = 2.55$  and 2.04 respectively. The resistance of resin composites to colour change depends on their structures, compositions and manipulations [98, 228]. The explanation for Exp.VT may be related to the filler type and content since the resin used was hydrophilic (GPDM) [117]. This suggests that the filler type and loading appear to play a vital role in resin composite colour stability, as it showed that the filler particle size and distribution are directly associated with optical properties. Also, the smaller filler particles may help to reduce staining and improve the aesthetics of the restoration [247].

CDX showed a significant colour change with no differences between 75% ethanol/water and MEK conditions. The reason may lie in the number of pores that were observed on its surface [194], which may also induce resin composite discolourations [98]. In addition, a resin composite that exhibited rough surfaces showed significant colour changes [232].

Results also showed that BL underwent more colour change than NCB when stored in MEK. The two have the same matrix composition (Bis-GMA, TEGDMA) but different filler sizes. The differences in filler properties may result in different optical properties

and colour change [236]. Also, the filler caused changes in the physical characteristics of light transmittance, which influenced the colour of resin composites [236].

Gloss in water showed less effect compared with 75% ethanol/water and MEK. NCB and CXD showed retained gloss in water over time. It was found that the resin composite stored in water showed minimal gloss changes [232]. In general, CXD showed low values in gloss retention regardless of storage conditions. A previous study has shown that the CXD matrix contains an Ormocer with polysiloxane particles and had lower gloss values than micro-hybrid composites [100]. Moreover, the surface does not seem glossy when resin composites have a rough surface, due to the light being reflected in a random way [232].

In general, after 6 months, a 75% ethanol/water storage had a pronounced effect on gloss for Exp.VT, TEC, GSO, VDF and CXD ( $p \leq 0.009$ ), whereas BL and NCB showed no change. It seems that 75% ethanol/water undergo more chemical degradation over time owing to various factors, which include resin matrix degradation and the debonding resin/filler interface, causing more surface roughness, thus reducing the gloss [100].

In MEK storage, there was reduction in gloss for all materials ( $p \leq 0.015$ ), with the exception of GSO and VDF, where the gloss was retained. GSO (the highest filled nano-hybrid resin composite) showed high gloss results amongst the examined resin composites, regardless of the storage conditions. It was suggested that the nano-filler size is smaller than the wavelength of visible light and so has no effect on the optical properties of the matrix [100].

75% ethanol/water and MEK have a stronger effect than water on the surface of the resin composites examined. The degradation can modify the external part of the filler; therefore, increase in the surface roughness and gloss change of the surface can be result [100]. In addition to surface roughness, gloss may be affected by differences in the refractive indices of the matrix and filler [102].

Although the degradation resistance to food-simulating solvents is important for the long-term clinical performance of resin composite restorations, resin composites with less water sorption, high filler loading, an optimum polymerisation and an acceptable



gloss may bring about a reduced colour change [98]. It is stated that an adequate gloss after polishing helps to decrease the staining of resin composites effectively [98].

### **8.7 Conclusions**

- MEK resulted in the highest colour change, while 75% ethanol/water storage caused the highest reduction in gloss of most of the resin composites examined.
- A highly filled nano-hybrid composite GSO was the least affected, and was characterised as having more colour stability and gloss retention over time, regardless of the storage conditions.

## **Chapter Nine**

### **Depth of Cure of Bulk Fill Dental-composites**

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Published in Dental Materials

## 9.1 Abstract

**Objectives:** To determine the post-cure depth of cure of bulk fill resin composites through using Vickers hardness profiles (VHN).

**Methods:** Five bulk fill composite materials were examined: Tetric EvoCeram<sup>®</sup> Bulk Fill, X-tra base, Venus<sup>®</sup> Bulk Fill, Filtek<sup>™</sup> Bulk Fill, SonicFill<sup>™</sup>. Three specimens of each material type were prepared in stainless steel moulds which contained a slot of dimensions (15 x 4 x 2 mm), and a top plate. The moulds were irradiated from one end. All specimens were stored at 37°C for 24 hours, before measurement. The Vickers hardness was measured as a function of depth of material, at 0.3 mm intervals. Data were analysed by one-way ANOVA using Tukey *post hoc* tests ( $\alpha = 0.05$ ).

**Results:** The maximum VHN ranged from 37.8 to 77.4, whilst the VHN at 80% of max.VHN ranged from 30.4 to 61.9. The depth corresponding to 80% of max. VHN, ranged from 4.14 to 5.03 mm. One-way ANOVA showed statistically significant differences between materials for all parameters tested. SonicFill exhibited the highest VHN ( $p < 0.001$ ) while Venus Bulk Fill the lowest ( $p \leq 0.001$ ). SonicFill and Tetric EvoCeram Bulk Fill had the greatest depth of cure (5.03 and 4.47 mm, respectively) and was significant's different from X-tra base, Venus Bulk Fill and Filtek Bulk Fill ( $p \leq 0.016$ ). Linear regression confirmed a positive regression between max.VHN and filler loading ( $r^2 = 0.94$ ).

**Significance:** Bulk fill resin composites can be cured to an acceptable post-cure depth, according to the manufacturers' claims. SonicFill and Tetric EvoCeram Bulk Fill had the greatest depth of cure among the composites examined.

**Key words:** resin composites, bulk fill, depth of cure, post-cure, micro-hardness

## 9.2 Introduction

One of the problems connected with photo-polymerized resin composites is the depth of cure limitation and the possibility of insufficient monomer conversion at depth [248]. Since photo-polymerised resin composites were introduced, the degree of conversion was acknowledged as vital to the clinical success of these materials [249]. Photo-cured resin composites polymerise only to a certain depth. This depends on the penetration of visible light through the bulk of the material [250]. It has been shown that the insufficient polymerisation may lead to a decrease in the physical/mechanical [34] and biological [251] properties of resin composites.

For sufficient polymerisation, three vital characteristics are essential for the light cure unit: adequate light output, appropriate wavelength range of the light and exposure time [252]. Other factors affect the depth of cure, including resin composite type, shade and translucency, increment thickness, distance from the tip of the light cure unit, post-irradiation period [253] and size and distribution of filler particles [254].

When the cavity is large, incremental layering can be used, with approximately 2 mm thick increments. This technique is used to avoid the depth of cure limitation and to reduce polymerisation shrinkage effects [255]. Insufficient polymerisation may result in the degradation of the resin composite, poor physical properties and adverse biological reactions owing to the leaching of the monomeric components of the unset resin composite [255].

There are various disadvantages associated with incremental techniques, such as incorporating voids or contamination between composite layers, failures in bonding between layers, placement difficulty owing to limited access in small cavities and an extended treatment time for placement of layers and their polymerisation [256].

To overcome these disadvantages “bulk fill” composites have been introduced. They have shown reduced cuspal deflection when compared with a conventional resin composite filled in an oblique incremental layering technique [257]. Also, when marginal integrity was evaluated, bulk fill composites performed well [258].

Several techniques have been employed to determine the depth of cure. The ISO standard for dental composites 4049, advocates scraping of the unset materials,

immediately after irradiation, and measuring the length of the set specimen, which is then divided by two [259]. Other techniques have involved measuring the hardness of the top and bottom specimen surfaces [260], or their the degree of conversion [252]. Optical microscopy has also been used to determine the depth of cure [261], where there is a visual boundary between cured and uncured material.

The surface microhardness of resin composites has been used to evaluate indirectly the extent of polymerisation, and also the efficiency of the light cure unit [199, 262]. As a result of reduced light irradiance passing through resin composites, the degree of conversion decreases with increasing depth [199]. In the present study, a surface microhardness profile was used to assess the depth of cure of different bulk fill resin composites.

The aim of this study was to determine the depths of cure. This was to be achieved by consideration of the following parameters: i) the maximum Vickers microhardness, ii) 80% of the maximum Vickers microhardness and iii) the depth corresponding to 80% of the maximum Vickers hardness. The null hypotheses were that there would be no differences between materials, either in maximum Vickers hardness or in the depth of cure that could be obtained at 80 % of maximum Vickers hardness for bulk fill materials.

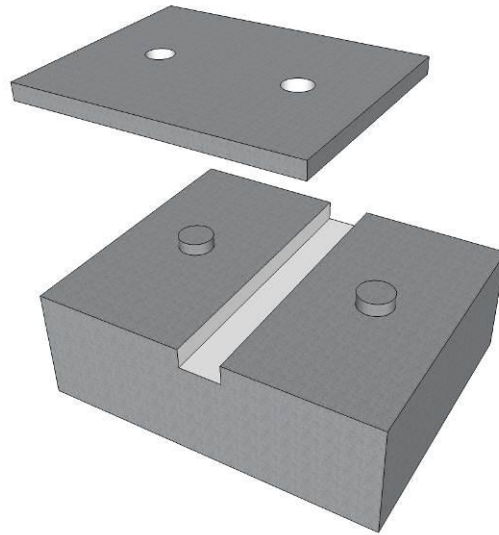
### **9.3 Materials and Methods**

Five bulk fill dental-composites (Table 9.1) were evaluated. The acronym-codes for these materials are included in Table 9.1. Three specimens of each bulk fill resin composite ( $n = 3$ ) were prepared for surface microhardness profile measurements in stainless steel moulds. These contained a slot of dimensions (15 x 4 x 2 mm), and a top plate (Figure 9.1). The mould was overfilled with composite, and a Mylar strip was placed on top of the material with the top plate subsequently pressed into position, followed by the scraping of the excess material from the entrance of the mould. The mould was held together in a clamp. The moulds were irradiated from one end. Each specimen was photo-polymerised for 20 s using a visible light cure unit with a tip diameter 10 mm (Elipar™ S10, 3M ESPE, USA) under the standard curing mode output wavelength range 430-480 nm; output irradiance was 1200 mW/cm<sup>2</sup>). A calibrated radiometer system (MARC, BlueLight Analytics Inc, Halifax, NS, Canada) was used to

verify the irradiance at each use of the light cure unit. All specimens were stored dry at 37°C for 24 h prior to measurement. The top of the mould and the Mylar strip were removed and the Vickers hardness number (VHN) was measured as a function of depth of material at 0.3 mm intervals. All specimens were examined by a microhardness instrument (FM-700, Future Tech Corp., Japan). A fixed load of 300 g was applied for 15 s. Data were calculated as hardness numbers and accordingly plotted as hardness versus depth profiles.

**Table 9.1:** Materials tested

<b>MATERIALS</b>	<b>Code</b>	<b>Type</b>	<b>Shade</b>	<b>Manufacturer increment thickness (mm)</b>	<b>Matrix</b>	<b>Filler % (wt)</b>	<b>Lot number</b>	<b>Manufacturer</b>
<b>Tetric EvoCeram® Bulk Fill</b>	TBF	Bulk Fill	Universal A shade (IVA)	4 mm	Dimethacrylate co- monomers	80	R04686	Ivoclar Vivadent AG, Schaan, Liechtenstein
<b>X-tra base</b>	XB	Bulk Fill	Universal	4 mm	Aliphatic di- methacrylate, Bis- EMA	75	V45252	Voco GmbH Cuxhaven, Germany
<b>Venus® Bulk Fill</b>	VBF	Bulk Fill	Universal	4 mm	UDMA, EBADMA	65	010028	Heraeus Kulzer GmbH Hanau, Germany
<b>Filtek™ Bulk Fill</b>	FBF	Bulk Fill	Universal	4 mm	Bis-GMA, BisEMA, UDMA	64.5	EXD786	3M ESPE GmbH Seefeld, Germany
<b>SonicFill™</b>	SF	Sonic- Activated, Bulk Fill	A3	5 mm	Bis-GMA, TEGDMA, Bis- EMA, SIMA	83.5	4252495	Kerr Corp, Orange, USA



**Figure 9.1:** Stainless steel mould with top cover plate

#### 9.4 Statistical Analysis

Univariate one-way ANOVA, Tukey *post-hoc* tests (Version 20.0, IBM, New York, USA)  $\alpha=0.05$ , were used to analyse the significant differences in the following parameters: (1) Max.VHN, (2) VHN at 80% of Max.VHN and (3) depth at 80% of Max.VHN (dependent variable) between different materials (independent variables). All data were subjected to Levene's test of homogeneity of variance ( $\alpha= 0.05$ ) following the assumption of equal variances.

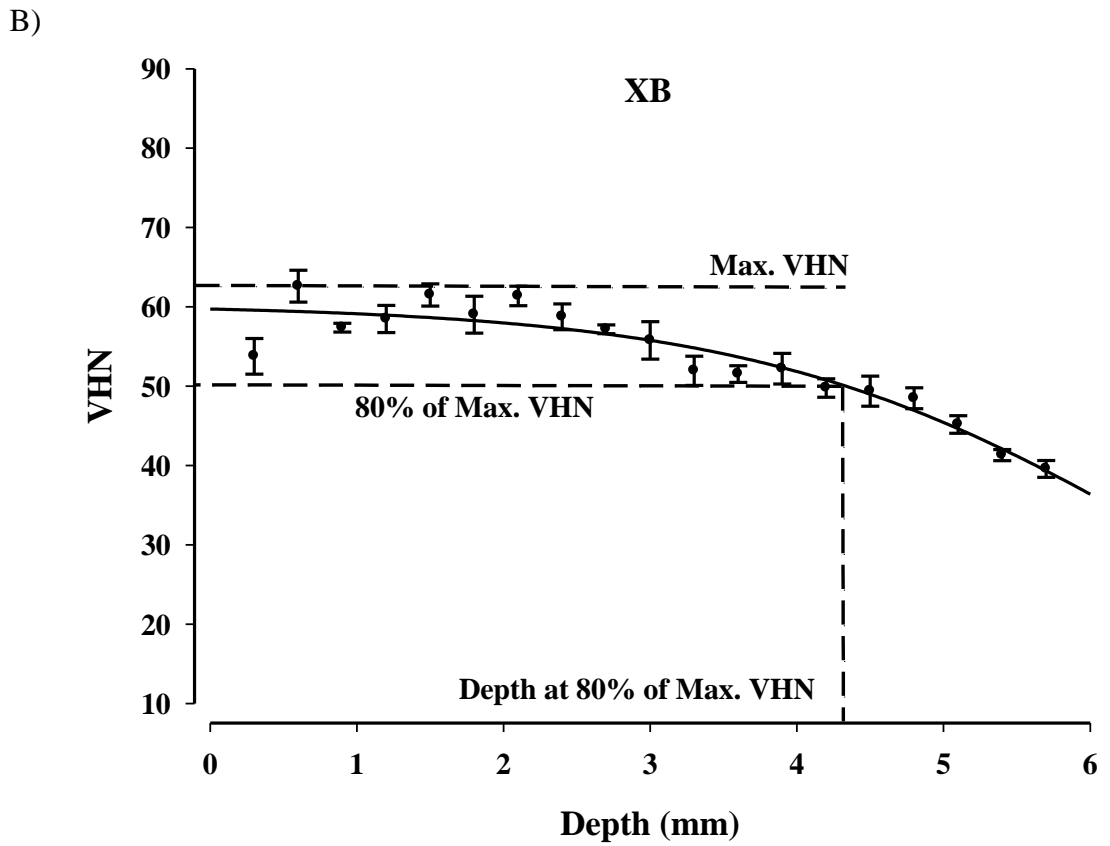
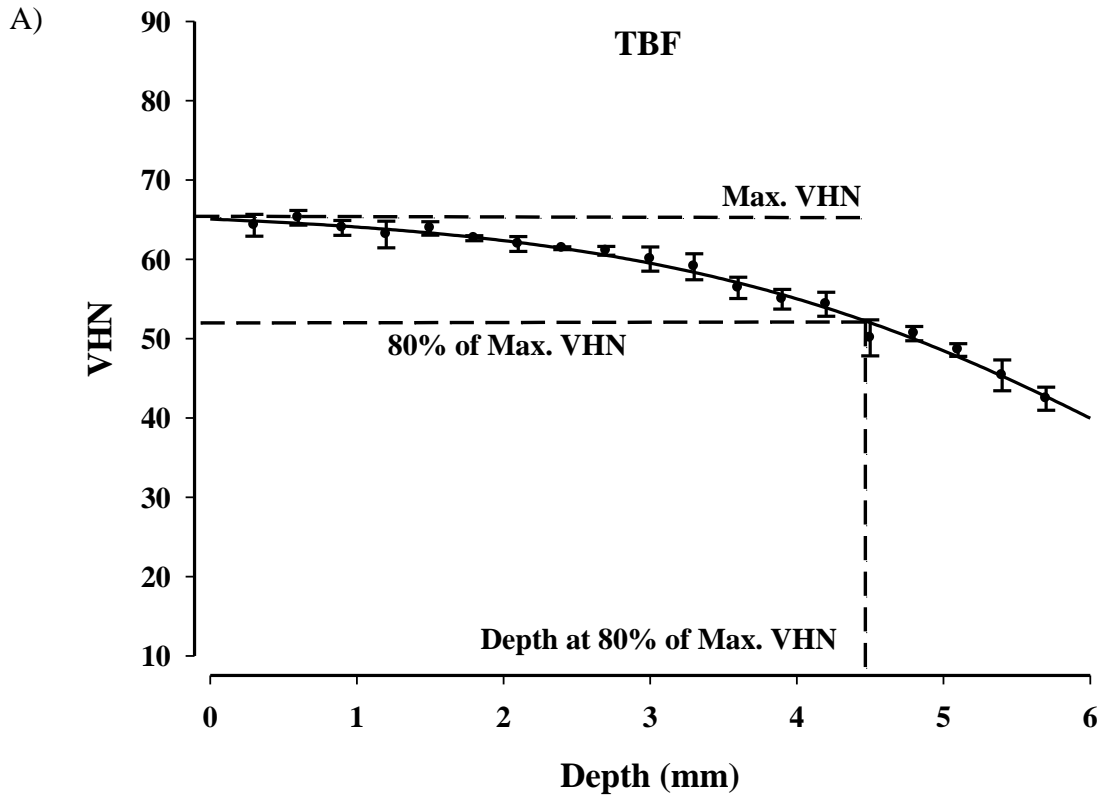
#### 9.5 Results

The Max.VHN, VHN at 80% of Max.VHN and depth at 80% of Max.VHN of each bulk fill resin composite examined are presented in Table 9.2 and further shown graphically in Figure 9.2. The acronym-codes are as given in Table 9.1. The maximum VHN ranged from 37.8 to 77.4, whilst the 80% of max.VHN ranged from 30.4 to 61.9. The depth corresponding to 80% of max.VHN ranged from 4.14 to 5.03 mm. This was taken as the Depth-of-cure (DoC).

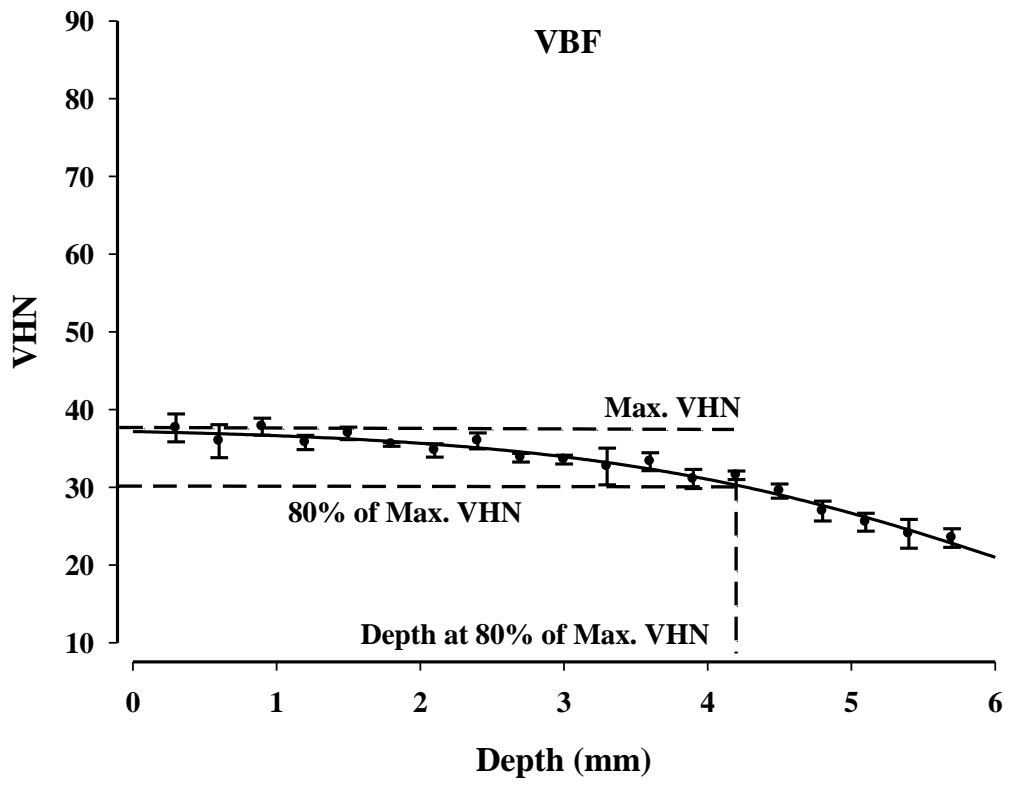


**Table 9.2:** Mean (standard deviation) of max.VHN, VHN at 80% of max.VHN and depth at 80% of max.VHN for bulk fill composites examined

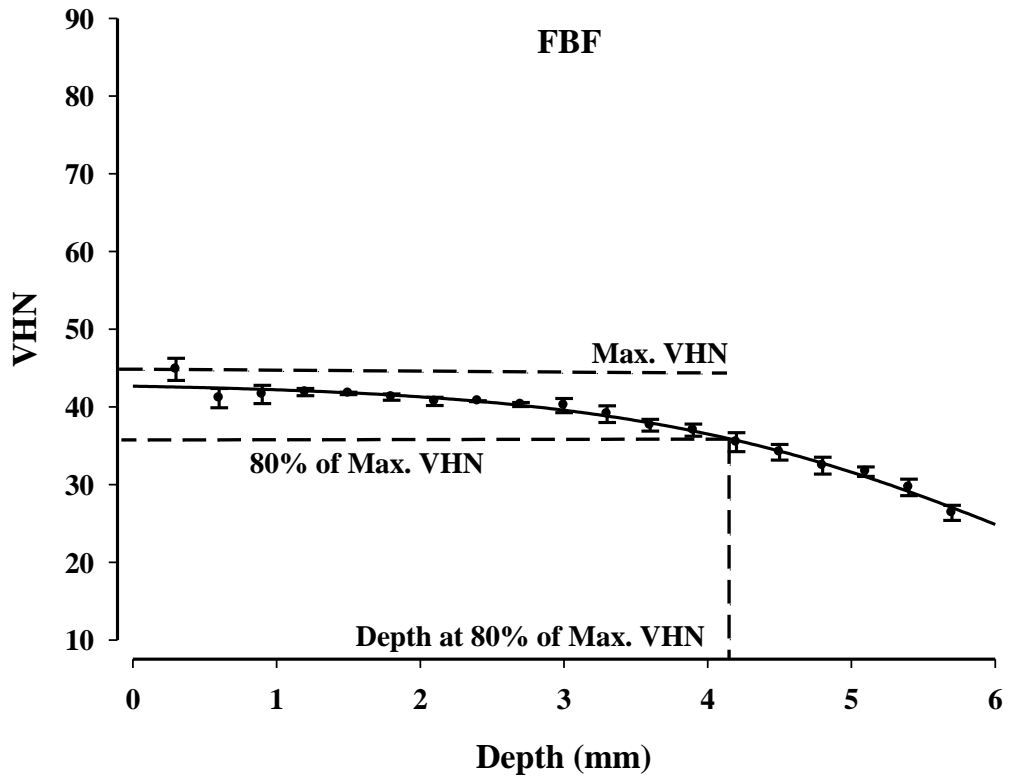
<b>Materials</b>	<b>Max. VHN</b>	<b>VHN at 80% of max.VHN</b>	<b>Depth at 80% of max.VHN (mm)</b>
	<b>Mean (SD)</b>	<b>Mean (SD)</b>	<b>Mean (SD)</b>
<b>TBF</b>	<b>65.23</b> (0.92) <sup>a</sup>	<b>52.19</b> (0.74) <sup>a</sup>	<b>4.47</b> (0.12) <sup>a, b</sup>
<b>XB</b>	<b>62.60</b> (2.01) <sup>a</sup>	<b>50.08</b> (1.61) <sup>a</sup>	<b>4.31</b> (0.27) <sup>a</sup>
<b>VBF</b>	<b>37.80</b> (1.10) <sup>b</sup>	<b>30.41</b> (0.88) <sup>b</sup>	<b>4.19</b> (0.22) <sup>a</sup>
<b>FBF</b>	<b>44.83</b> (1.43) <sup>c</sup>	<b>35.87</b> (1.14) <sup>c</sup>	<b>4.14</b> (0.28) <sup>a</sup>
<b>SF</b>	<b>77.40</b> (1.82) <sup>d</sup>	<b>61.92</b> (1.46) <sup>d</sup>	<b>5.03</b> (0.15) <sup>b</sup>
<b>The same superscript small letters indicate a homogeneous subset (columns) (p &lt; 0.05)</b>			

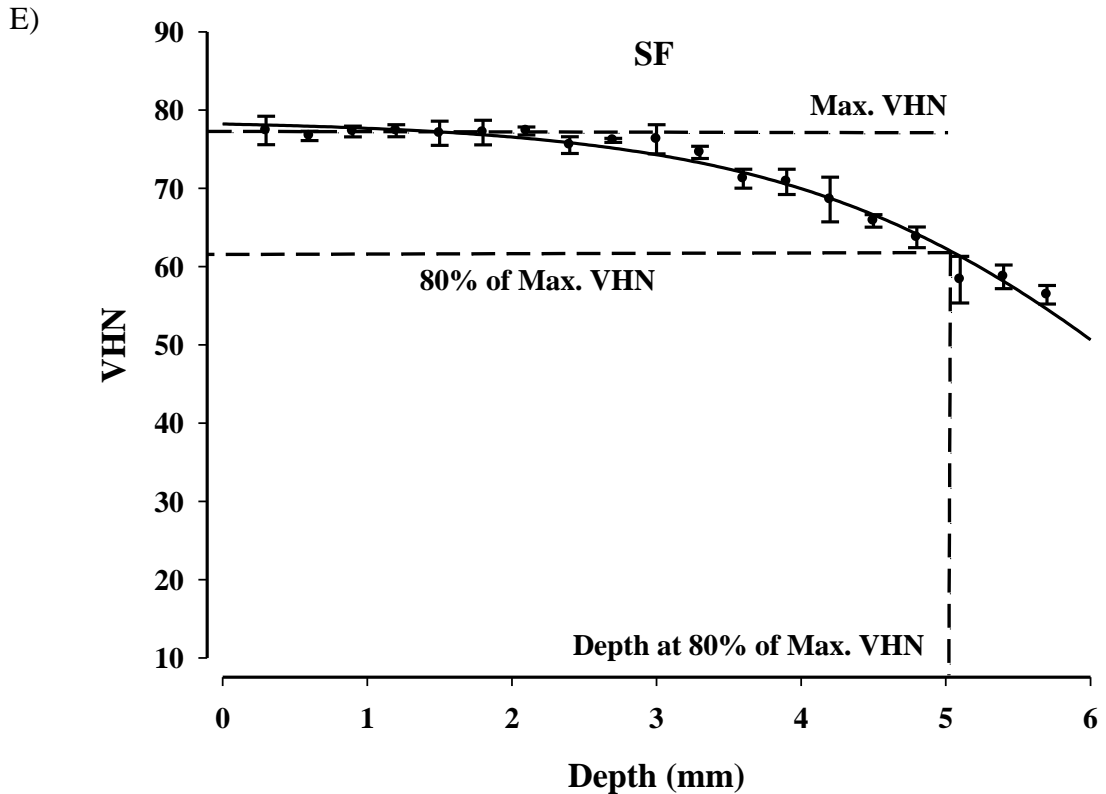


C)



D)



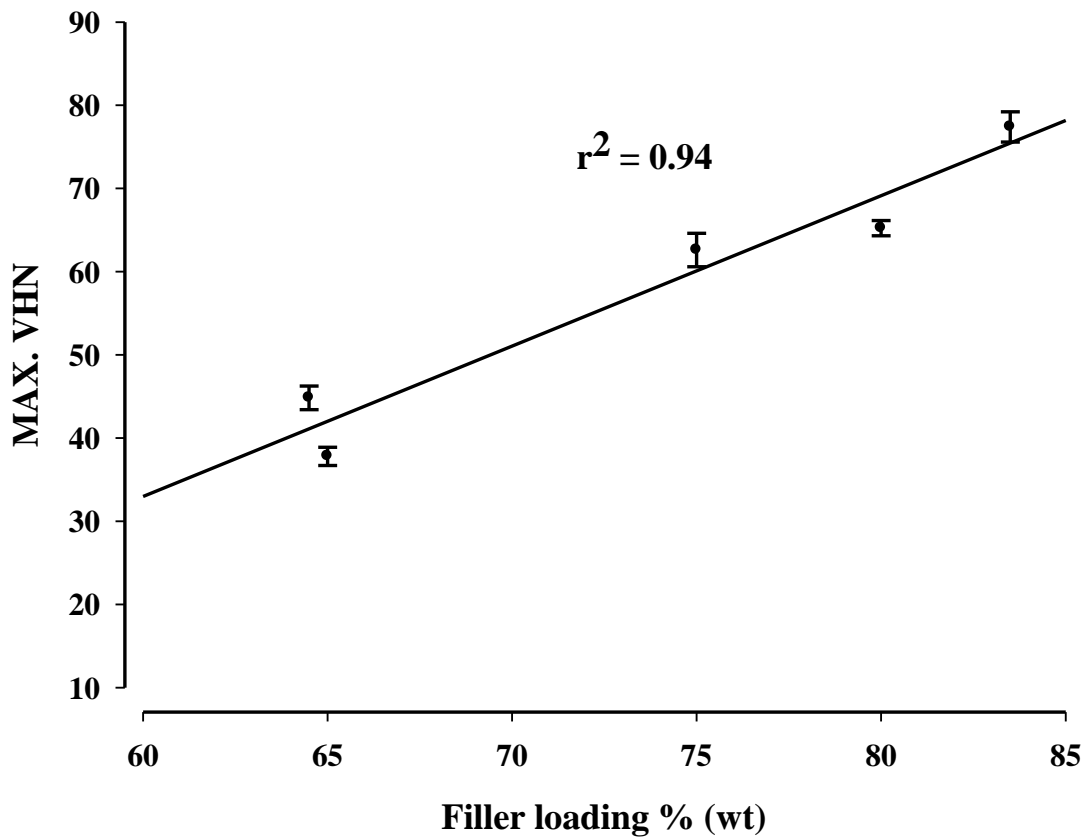


**Figure 9.2:** Max.VHN, VHN at 80% of max.VHN and depth at 80% of max.VHN, for bulk fill composites, A) TBF, B) XB, C) VBF, D) FBF, E) SF

One-way ANOVA showed statistically significant differences between materials for all parameters measured. SF exhibited the highest with significant differences ( $p < 0.001$ ), whilst VBF the lowest ( $p \leq 0.001$ ). TBF and XB showed no significant differences ( $p > 0.05$ ). Furthermore, FBF showed statistically significant differences with VBF ( $p = 0.001$ ).

The depth obtained, for all materials, corresponding to 80% of the max. VHN met each manufacturer's claim. SF and TBF ( $p > 0.05$ ) had the greatest depth of cure (5.03, 4.47 mm respectively). SF showed significant differences with XB, VBF and FBF ( $p \leq 0.016$ ). TBF showed no significant differences in depth of cure with XB, VBF and FBF.

Linear regression confirmed a positive correlation between max.VHN and filler loading ( $r^2 = 0.94$ ) Figure 9.3.



**Figure 9.3:** Linear regression of max.VHN versus filler loading % (wt), for bulk fill composites

## 9.6 Discussion

In this study, the depth of cure of different bulk fill resin composites was measured by the determination of their VHN / depth profiles. There were statistically significant differences in max.VHN and depth of cure, corresponding to 80% of max.VHN, between different bulk fill materials. Thus, the null hypotheses were rejected. The respective manufacturers claim that the depth of cure is 5 mm for SF and 4 mm for the remaining bulk fill composites. The results of the present study confirm the claims of the manufacturers for all these materials.

Optical microscopy and scraping methods may overestimate the depth of cure when compared with hardness and degree of conversion methods [261, 263, 264] as they include some partly-cured material. However, when the network is cross-linked, FTIR is less sensitive than hardness assessment in detecting small changes in the degree of

conversion [265]. The degree of conversion of resin composites is widely evaluated indirectly by surface hardness measurements, whether using Vickers or Knoop indentors, which can give a good determination [266]. Polymerisation of resin composites continues at a slow rate after curing and may reach a termination point at almost 24 h [267], although other studies [199, 263] show some surface hardness increases up to 1 month. Hardness profiles were used to determine the depth of cure in this study after 24 h post-cure. The depth of cure was determined as the depth at which at least 80% of the max.VHN was achieved.

Variations in the depth of cure between bulk fill resin composites may be ascribed initially to light scattering at particle interfaces [268] and light absorbance by photoinitiators and any pigments [269]. Both of these factors reduce the light penetration and thus also the degree of conversion (DC) of matrix monomers, that is determined by the light irradiance at depth. DC is significantly linked with the values of mechanical properties, biocompatibility and colour stability. Therefore, there may be a relation to the clinical success of the restoration [268]. When more extensive polymerisation and cross-linking occurs, greater hardness results [267].

A positive linear regression ( $r^2 = 0.94$ ) was observed between the max.VHN and the filler loading. Increased filler loading reduces the volume of resin matrix for polymerisation and intrinsically increases hardness [270]. Previously we showed that nanohardness values correlate with microhardness for TBF and XB [216]. Also our data on XB is consistent with a recent study [271], which evaluated depth-of-cure by microhardness measurements.

In the present study, we found that SF and TBF had the greatest depth-of-cure amongst the materials, with no significant difference between them ( $p > 0.05$ ). SF has the highest filler content compared with other materials. Sonic energy is applied through a special handpiece to increase the flowability and to further ease the packing of the composite [272]. The good DoC may be due to refractive index matching between the resin and filler, which enhances light transmission. Reduction in refractive index differences between resin and filler improved degree of conversion [273], and increased depth of cure as well as colour shade matching [274].

Camphorquinone (CQ) is a widely used photoinitiator for resin composites, absorbing light from 450–490 nm. Some resin composites contains other photoinitiators besides CQ, that absorb light at about 410 nm [275]. TBF contains a new photo-initiator system (Ivocerin<sup>TM</sup> - a dibenzoyl germanium compound). This absorbs visible light over a wider range of wavelengths from 370 to 460 nm [276]. With suitable formulations, reactivity is enhanced and a greater depths of cure can be achieved.

VBF showed the lowest max.VHN ( $p \leq 0.001$ ) as also observed previously[263]. This is probably due to lower filler loading (65% w/w), which might also reduce flexural modulus [181].

Optical properties of resin composites are vitally important for photo-polymerisation as well as for the subsequent aesthetics [277]. Nanohybrid resin composites have high translucency because the particles are smaller than the wavelength of light and cause minimal or zero scattering of photons, [68, 278].

In general, an adequate polymerisation through the entire recommended depth of the bulk fill composite is important for long-term stability of restorations.

## 9.7 Conclusions

- Bulk fill resin composites can be cured to an acceptable post-cure depth according to the manufacturers' claims.
- SonicFill and Tetric EvoCeram BulkFill had the greatest depth of cure amongst the bulk fill composites examined.

## **Chapter Ten**

### **General discussion, Conclusions and Future Work Recommendations**



## 10.1 General discussion

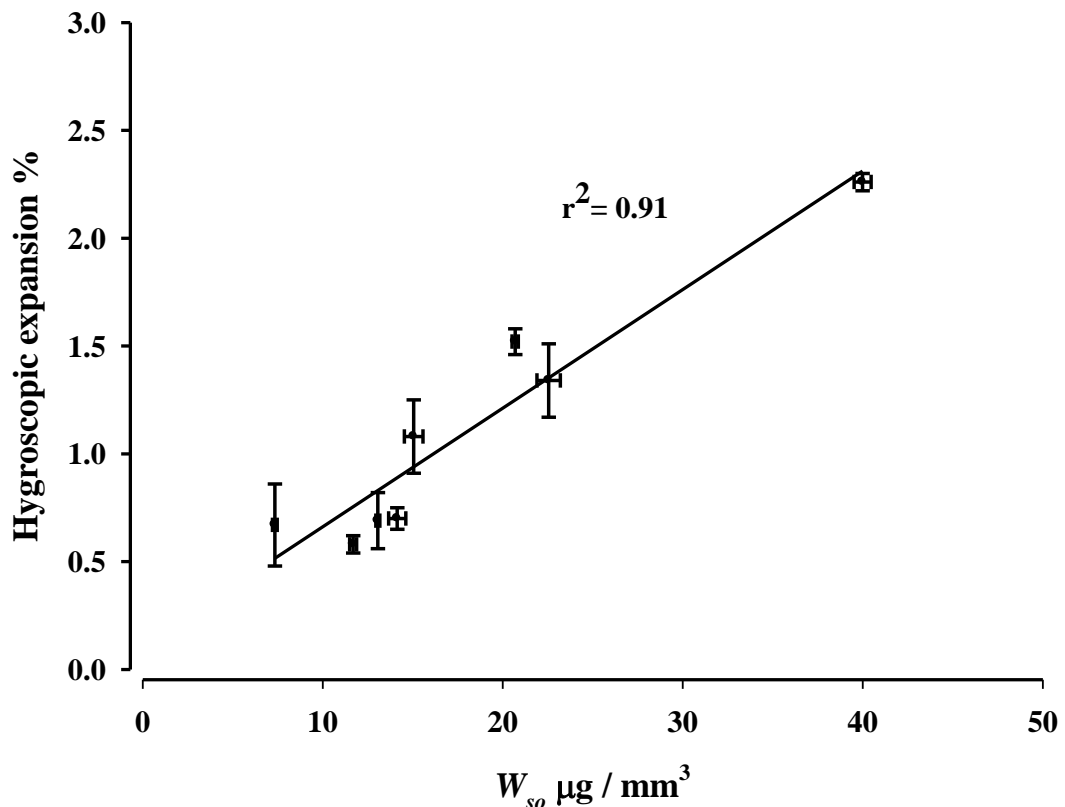
Since resin composites were first presented to dentistry more than half a century ago, the composition has been developed significantly. One of the most vital changes is that the reinforcing filler particles were reduced in size to create materials that show better wear resistance and polish easily [67]. Due to the advantages of resin composites, for instance aesthetics, ease of handling and the ability to adhere to tooth structures, their use is widespread in restorative dentistry [195].

A continuous process of intra-oral degradation results from exposing resin composites to a number of factors, including chemical, thermal and mechanical ones. Surface properties, for instance micro-hardness and wear resistance, are affected primarily. In the long-term, fracture strength is also affected by intra-oral degradation, which results in lower durability of the restoration. In addition, aesthetic properties such as surface texture, gloss and colour of resin composites are affected in consequence of intra-oral softening [197]. Most of the mechanical property investigations of resin composite materials, including international standards, were achieved after storing the specimens for 24h in distilled water [221]. The influence of water on the strength of most resin composites is permanent. Resin composites exposed to water were shown to degrade owing to filler particle degradation, the softening of the matrix, or the debonding of matrix/filler interfaces [221].

The aims of this research were to examine water sorption behaviour as well as hygroscopic expansion kinetics and mechanical properties at 37°C, and also to investigate the effects of food-simulating solvents on surface properties at 37°C. The resin composites used in this research included experimental self-adhesive, micro-hybrid, nano-hybrid, bulk fill and flowable composites. Due to the development of bulk fill materials recently appearing on the market during the course of this research, the post-cure depth of cure of new bulk fill materials was also investigated.

The investigation of these materials using different methodologies focused on whether solvent degradation affects the properties of resin composites. This research aimed to see the effects of different matrix composition and filler loading on physical, mechanical and surface properties of experimental and contemporary resin composites.

The resin composites may absorb water and chemicals from the environment. Subsequently, soluble components may be released. Because of sorption and solubility processes, deleterious effects may affect the structure and function of the materials. These effects include dimensional changes (hygroscopic expansion), physical changes (matrix softening) and chemical changes (hydrolysis) [118]. All materials were stored in distilled water for 150 days until equilibrium was reached for water sorption and hygroscopic expansion experiments, and the results were varied, as shown in Chapters 4 and 5. The relationship between change in dimensions and water sorption in resin composites was established [149]. The relationship between water sorption and the percentage of volumetric hygroscopic expansion in this research suggests a positive linear relationship. This was confirmed by the positive linear correlation  $r^2 = 0.91$  (Figure 10.1).



**Figure 10.1:** Linear regression of water sorption versus the percentage of volumetric hygroscopic expansion

Water sorption by resin composites seems to be a diffusion-controlled process [125]. The results of water sorption of the examined materials were presented in Chapter 4. The bulk fill composite (XB) exhibited the lowest water sorption, followed by the highly filled nano-hybrid composite (GSO), amongst the examined materials. It seems that the amount of water sorption depends on the matrix composition. The choice of monomers used in resin composites strongly affects the reactivity, viscosity and polymerization shrinkage, mechanical properties, water sorption and hygroscopic expansion [18]. It also seems that water sorption is affected by a poor filler/matrix interface bond [130]. Therefore, water sorption by the resin composite may be ascribed to the nature of the filler particle and the coupling agents. Because of the diffusion of water through the resin, resin composites are likely to accommodate more water at the filler/matrix interface [131]. Accordingly, when the matrix and filler are well coupled, the water sorption is reduced significantly [116]. Moreover, the highly cross-linked polymer results in a reduction in the free volume in the network [7]; therefore, reduction of water sorption into the polymer occurs.

The solubility behaviour of resin composites involves the extraction of residual monomers and oligomers, filler particles and ions from its surfaces [118]. The self-adhesive composite (Exp.VT) showed the highest solubility amongst the examined composites. The high solubility may be due to a lower degree of conversion during the polymerisation [114]. The water sorption and solubility of resin composites is important clinically. Excessive water sorption and solubility of resin composites in addition to insufficient polymerisation may cause monomer to be leached out, and this may affect the biological compatibility as well as resulting in inferior mechanical/physical properties of the material [120, 279]. Therefore, degradation may occur that may subsequently result in the failure of the restoration.

The dimensional stability of resin composite materials is affected by polymerization shrinkage, thermal contraction/expansion and interactions with an aqueous environment [136]. Hygroscopic expansion relaxes the internal stresses of the resin matrix, which compensate for the shrinkage of resin composites [76, 140, 141]. The hygroscopic expansion occurs when the water diffuses into the polymer network and separates the chains [132]. The micro-hybrid composite (BL), highly filled nano-hybrid composites (GSO and NCB) and the bulk fill (XB) showed the lowest hygroscopic expansion

amongst the examined materials. It has been shown that an expansion of the matrix occurs to accommodate the absorbed water, because water diffuses mostly into the resin [153].

Dental restoration failure may occur owing to a reduced load-bearing capacity caused by the degradation of the material in the oral environment [165]. The effect of water storage on fracture toughness has been studied in relation to a range of materials and specimen geometries [86, 87]. This study used a single edge notch method, which is one of the two commonly used methods for determining the fracture toughness of restorative materials [161]. The flowable resin composite (VDF) had the highest numerical  $K_{IC}$  value of  $2.72 \text{ MNm}^{-1.5}$  as well as the highly filled nono-hybrid (GSO) and the micro-hybrid (BL) after seven days' storage in water. All materials that showed a high  $K_{IC}$  value had different matrix resin and filler loadings. This may be owing to the dependence of  $K_{IC}$  on the degree of adhesion of resin matrix to filler particles, rather than the filler size [110, 280]. The bulk fill composite (XB) showed an increase in  $K_{IC}$  after 7 days of storage, which reflects the hydrophobicity and continuous polymerisation of the resin matrix. On the other hand, Exp.VT (self-adhesive composite) showed decreases in  $K_{IC}$  due to its hydrophilic matrix and greater degradation.

75% ethanol/water solution and MEK were used besides distilled water for determining surface properties (micro-hardness, colour and gloss). These solvents were selected according to the solubility parameters listed in Table 7.4. Surface hardness is the resistance of a material to indentation. It is used as a predictor of the wear resistance of the material [104]. When resin composites absorb water between the filler/matrix interface, hydrolytic degradation can occur that may lead to the displacement of filler particles [198]. Also, the conditioning of materials with food-simulating solvents led to the softening of composites, and consequently to a decrease in surface hardness [205]. A positive correlation between VHN and filler loading was confirmed (Figure 7.4). This positive correlation between the filler content and the hardness of resin composite has been established previously [215]. The reduction in hardness values for some of the examined resin composites after storage in water indicates the extent of water sorption effect [281]. MEK caused the greatest softening (reduction in VHN) of most of the examined composites. The highly filled nano-hybrid composite (GSO) was the least

affected one over time, regardless of the storage conditions. The flowable resin composite (VDF) was more affected over time than were the conventional hybrid resin-composites and the bulk fill. It was shown that the surface layer was easy to degrade owing to a resin rich surface compared to the bulk material [199].

To achieve a long-term improved colour stability and an adequately smooth surface of restorations after polishing, several modifications have been made in the production of dental resin composites [234]. Results showed that all the examined materials exhibited some colour change ( $\Delta E$ ). The colour of most materials was affected by the MEK solvent, while the gloss of most materials was affected by the 75% ethanol/water solution. A quadratic regression function of log time showed a positive trend for  $\Delta E$  and a negative trend for gloss for all materials (Figures 8.3 and 8.4). According to the established range of colour change perceptibility,  $\Delta E$  values ranging from 0.0 to 1.1 were regarded as not visible, and between 1.1 and 3.3 as visually affected but clinically acceptable, while  $\Delta E$  higher than 3.3 were regarded as obviously visible and clinically not acceptable [96, 238, 240, 241]. For resin composites stored in distilled water,  $\Delta E$  reached its maximum of 1.32 after 6 months of storage. After 6 months of storage in 75% ethanol/water, only GSO and VDF showed resistance to colour change, with  $\Delta E = 2.76$  and 2.90, respectively. In addition, after 6 months of storage in MEK, Exp.VT and GSO showed a resistance to colour change of  $\Delta E = 2.55$  and 2.04 respectively.

Gloss values in water showed a lesser effect compared with the 75% ethanol/water and MEK. In general, after 6 months, 75% ethanol/water storage had an obvious effect on gloss for most of the examined resin composites, except BL and NCB where no change was recorded in 75% ethanol/water and MEK. The highly filled nano-hybrid composite (GSO) was the least affected, and was characterised as having greater colour stability and gloss retention over time, regardless of the storage conditions. It was suggested that the nano-filler size is smaller than the wavelength of visible light and has no effect on the optical properties of the matrix [100].

During the past year, several bulk fill resin composites have been introduced in restorative dentistry. These materials can be placed in layers up to 4 mm. Due to the short period of time in which these materials have been commercially available, there are not adequate data to allow full description of their behaviour. Bulk fill (XB) is one

of the materials previously investigated. It showed good results in terms of physical/mechanical properties.

A simple technique that has most commonly been used for the assessment of depth of cure is micro-hardness [84]. It has been shown that insufficient polymerisation may lead to a decrease in the physical/mechanical and biological properties of resin composites [34, 251]. The examined bulk fill resin composites can be cured to an acceptable depth, according to the manufacturers' claims. SF and TBF showed the greatest depth of cure amongst the examined composites. The refractive index matching between the resin/filler has an influence on the amount of transmission of visible light. A reduction in the refractive index difference between the resin/filler led to enhancing the polymerisation conversion, and thus an increased depth of cure [273, 274].

## 10.2 Conclusions

Within the limitations of this research it was concluded that:

- Non-contact laser scan micrometer (LSM) is a reliable method for detecting the small change in the dimensions of resin composites.
- The water storage of resin composites can modify the fracture toughness of resin composites.
- Bulk fill resin composites can be cured to an acceptable post-cure depth, according to the manufacturers' claims.
- The 75% ethanol/water solution caused the greatest loss in gloss for most of the examined composites.
- For MEK solvent:
  - It has caused the greatest softening (reduction in VHN) for most of the examined resin composites.
  - It has caused the greatest colour change ( $\Delta E$ ) for most of the examined composites.
- For the experimental self-adhesive composite (Exp. VT):

- The excessive water sorption and high solubility is significant amongst the examined composites, which may also influence clinical performance.
- The extensive hygroscopic expansion is a cause for concern, which may affect the mechanical stability.
- It showed decreases of fracture toughness values after 7 days' storage in water.
- For the bulk fill composite (XB):
  - It showed the lowest water sorption value amongst the examined resin composites.
  - It showed increases of fracture toughness values after 7 days' storage in water.
- For highly filled nano-hybrid composite (GSO):
  - It showed the greatest colour stability and gloss retention over time, regardless of the storage conditions.
  - It showed the lowest solubility values amongst the examined resin composite.
  - It showed the highest VHN over time, regardless of the storage conditions.

### **10.3 Recommendation for future work**

In order to complement current studies and future development of knowledge, the following areas of future work are suggested:

- The effect of food-simulating solvents on the behaviour of sorption and solubility for a series of resin composites with different filler loading and matrix composition.
- The effect of food-simulating solvents on the dimensional stability for a series of resin composites with different filler loading and matrix composition.
- Study the bulk fill resin composites in terms of physical/mechanical properties.

- Using different light cure units and curing protocols to determine the depth of cure of bulk fill resin composites.



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