Temperature-dependent properties of resin-composites before and during the setting process

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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ATR</td>
<td>attenuated total reflectance</td>
</tr>
<tr>
<td>Bis-GMA</td>
<td>bisphenol-A glycidyl methacrylate</td>
</tr>
<tr>
<td></td>
<td>(2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]propane)</td>
</tr>
<tr>
<td>Bis-EMA</td>
<td>2,2-bis[4-(2-methacryloxyethoxy)phenyl]propane</td>
</tr>
<tr>
<td>CEMA</td>
<td>N,N-cyanoethyl-methylaniline</td>
</tr>
<tr>
<td>C factor</td>
<td>configuration factor</td>
</tr>
<tr>
<td>CQ</td>
<td>camphoroquinone</td>
</tr>
<tr>
<td>CTE</td>
<td>coefficient of thermal expansion</td>
</tr>
<tr>
<td>DC</td>
<td>degree of conversion</td>
</tr>
<tr>
<td>DMAEM</td>
<td>dimethylamino ethylmethacrylate</td>
</tr>
<tr>
<td>EDMAB</td>
<td>ethyl-4-dimethylaminobenzoate</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier-transform infrared</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
</tr>
<tr>
<td>GCK</td>
<td>GC Kalore</td>
</tr>
<tr>
<td>GDA</td>
<td>Gradia Direct Anterior</td>
</tr>
<tr>
<td>GDP</td>
<td>Gradia Direct Posterior</td>
</tr>
<tr>
<td>GRO</td>
<td>Grandio</td>
</tr>
<tr>
<td>LCU</td>
<td>light curing unit</td>
</tr>
<tr>
<td>LED</td>
<td>light-emitting diodes</td>
</tr>
<tr>
<td>MMA</td>
<td>methylmethacrylate</td>
</tr>
<tr>
<td>MPS</td>
<td>3-methacryloxypropyl trimethoxysilane</td>
</tr>
<tr>
<td>PEGDMA</td>
<td>Polyethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>PMMA</td>
<td>poly(methyl methacrylate)</td>
</tr>
<tr>
<td>QTH</td>
<td>Quartz tungsten halogen</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>triethylene glycol dimethacrylate</td>
</tr>
<tr>
<td>UDMA</td>
<td>urethane dimethacrylate</td>
</tr>
<tr>
<td></td>
<td>(1,6-bis(methacryloyloxy-2-ethxycarbonylamino)-2,4,4trimethylhexan)</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
</tr>
<tr>
<td>VLC</td>
<td>visible-light cured</td>
</tr>
</tbody>
</table>
A  a pre-exponential factor / area
AC absorbance peak of the cured specimen
AU absorbance peak of the uncured specimen
C temperature coefficient
°C Degrees Centigrade
$C_e$ calibration coefficient for strain measurements
$C_o$ calibration coefficient for stress measurements
cm centimetre
$E_a$ Activation energy
F force
J joule
K Kelvin
kJ kilo joule
$L_0$ original length
$\Delta L$ change in length
MPa megapascal
MPa.s Megapascal.second
mV millivolt
N Newton
nm nanometre
R universal gas constant
r radius
s second(s)
$S_c$ corrected stress
$S_r$ Raw stress
t time
$t_p$ persistence period of peak stress
$\tau$ time constant
T absolute temperature
$\Delta T$ change in temperature
vol% percentage content by volume
V Volt
$V_o$ original volume
ΔV  change in volume
wt%  percentage content by weight
ε    strain
η    viscosity
µm   micrometer
σ    stress
§     section
Abstract

Dental Resin-Composites contain inorganic particles, coated with organic coupling agent, dispersed in an organic resin-matrix. In their precured state they are viscous pastes that change rapidly to a hardened mass after photo-activation. Temperature change is expected to modify several physical properties.

The aims were to determine the extent to which increasing temperature from ambient (23 °C) to body temperature (37 °C) may affect properties before and during the setting process. Six representative resin-composites were selected [GRO, GCK, VDD, FXE, GDP, and GDA].

Temperature-dependence of handling properties (packing stress and viscosity) of pre-cured resin composites was examined using a penetrometer instrument at 23 °C, 30 °C, and 37 °C. Viscosity was reduced significantly by up to 93 % at 37 °C compared to 23 °C.

Temperature-dependence of degree-of-conversion (DC) was measured by FTIR spectroscopy at 23 °C and 37 °C. DC was also time-dependent after photo-activation at both temperatures, with all examined materials having higher DC at 1 h than 0 h.

A modified bonded-disk instrument was used for simultaneous measurement of: shrinkage-strain, exotherm, and Coefficient of Thermal Expansion (CTE) at 23 °C. Shrinkage-strain, exotherm, and CTE were all found to correlate negatively with filler-load. Positive correlation was found also between shrinkage-strain and CTE.

Temperature-dependence of shrinkage-strain kinetics, at 23 °C and 37 °C, was examined with the bonded-disk instrument. Mean 1h shrinkage-strains at 37 °C were numerically and significantly greater (p<0.05) than those at 23 °C for all cases except GDA and GDP. The activation energy ($E_A$) of the shrinkage-strain kinetic process was calculated for each material, and a positive correlation was found between $E_A$ and the percentage of total organic material, calculated from the combustion technique.

The Bioman instrument was used, for the first time, to measure temperature-dependence of shrinkage-stress kinetics at 23 °C and 37 °C. At 23 °C, all materials demonstrated a greater stress at 1h than 2 min after photo-activation. At 37 °C, there were no significant
stress differences between 2 min and 1h. VDD composite showed a reduced stress 1h after photo-activation at 37 °C than at 23 °C. This suggests a pronounced visco-elastic character. Understanding the effects of temperature on dental composites can influence the possible adoption of clinical preheating regimes, prior to light-curing.
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.

Ahmad Abdulkareem Alnazzawi
2012
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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

This work is dedicated to the memory of my late father Abdulkareem Alnazzawi. I am totally indebted to the tremendous inspiration he gave me throughout his life.

I also want to dedicate this thesis to my lovely mother Khadija. I always enjoyed her care and guidance. This thesis is also dedicated to my lovely wife Maha and my daughters Yara, Mayar, and Tala and to my brothers and sisters.

Finally I would also like to dedicate this work to my friends M Hatamleh, H Elbishari, A Alrahlah and A El-Ma`aita.
Acknowledgement

By coming to the end of this scientific journey; first, all praises are due to ALLAH for his merciful guidance throughout my life and during my stay in Manchester.

I would like to express my gratitude and deepest respect to my supervisors Prof David C. Watts and Dr. Nikolaos Silikas for their guidance, encouragement, great care, patience, and continuous support.

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My genuine appreciation to The Taibah University, Madinah, Saudi Arabia for funding and supporting my study at the University of Manchester.
Chapter One

Introduction and General Literature Review
1.1 Introduction to Dental Materials:
Biomaterials are defined by Clemson Advisory Board for Biomaterials as “a systemically and pharmacologically inert substances designed for implantation within or incorporation with living tissue”. In 1973 the Clemson Advisory Board for Biomaterials agreed to this definition after a request from the World Health Organization (UN) [1-3]. Later, Black proposed a revised definition for biomaterial as “a Biomaterial is any pharmacologically inert material, viable or nonviable, natural product or manmade, that is part of or is capable of interacting in a beneficial way with a living organism”. Furthermore, he defined the biomaterial discipline as “The discipline of Biomaterials is the organized study of the materials properties of the tissue and organs of living organisms, the development and characterization of pharmacologically inert materials to measure, restore, and improve function in such organisms and the interactions between viable and nonviable materials” [1].

Indeed, it is difficult to know the exact origin of the term biomaterials and when it became applicable. Ratner tried to clarify this and stated that:

“It is difficult to pinpoint the precise origins of the term biomaterial. However, it is probable that the field we recognized today was solidified through the early Clemson University biomaterials symposia in the late 1960s and early 1970s. The scientific success of these symposia led to the formation of the Society for Biomaterials in 1975. The individual physician-visionaries who implanted miscellaneous materials to find a solution to pressing, often life threatening, medical problems were these Clemson symposia, no longer the dominant force. We had researchers and engineers designing materials to meet specific criteria, and scientists exploring the nature of biocompatibility. Around this term biomaterial a unique scientific discipline evolved. The evolution of this field and the Society for Biomaterials were intimately connected. From biomaterials ideas, many of which originated at the society meetings, other field evolved. Drug delivery, biosensors, and bio separations owe much to biomaterials. Now we have academic departments of biomaterials, many biomaterials programs, and research institutes devoted to education and exploration in biomaterials science and engineering. Paralleling to the research and educational efforts, hundreds of companies that incorporate biomaterials into devices have developed” [4].

The use of such materials to restore lost or defective portions of the body can be traced back to ancient times. Synthetic parts such as teeth, eyes and the nose were presented on Egyptian mummies. Wax, glue, and tissue are widely utilized by the Chinese and on the
Indian subcontinent in the reconstruction of lost or defective portions of the body [5, 6]. Nowadays, biomaterials in different forms and structures are broadly utilized to replace and/or to restore the shape and function of tissues or organs and, therefore, improve the patients’ life quality.

The science of dental materials involves the development, use, characterization, and assessment of the materials used to restore the oral and peri-oral tissues. However, these materials are expected to show characteristics similar to or better than lost human tissues. For instance, filling materials used to restore teeth should possess properties similar to that of dentine and enamel [7]. Good aesthetic is a prerequisite in the restoration of anterior teeth, whereas adequate mechanical properties are needed in posterior restorations.

1.1.1 History of Aesthetic Dental Restorative Materials:

Silicate cement was the first material developed for use as a direct aesthetic restorative material. Introduced in 1871, it was made up from alumino-silicate glass powder and a phosphoric acid liquid. Many disadvantages accompanied the use of silicate cement such as pulpal inflammation, dissolution in oral fluids, discoloration, loss of translucency, and lack of adequate mechanical properties [8]. Irrespective of these drawbacks, silicate cements remained the favored aesthetic material until 1950s [9].

In 1945 self-curing unfilled acrylic resin which was made from methyl methacrylate were introduced as a substitute for silicate cement [9]. However, this resin was suffered from poor colour stability. Further research pointed that this colour alteration came from the use of amines as a co-initiators. A better colour stability was achieved by utilization of sulfinic acid reaction as a substitution to amines co-initiators. Although these acrylic resins partially overcame some disadvantages of silicate, they suffered major problems such as high polymerization shrinkage, high coefficient of thermal expansion compared to tooth tissues, high wear rate, low modulus of elasticity and poor adhesion to the tooth tissues. These shortcomings hindered their clinical use [8, 10].

In the 1960s, Bowen was the first who introduced the filled bis-phenol glycidyl methacrylate (Bis-GMA) resin. It was a combination of hard, inorganic filler particles bonded to Bis-GMA resin [11]. After Bis-GMA was introduced into dentistry, which
satisfied most of requirements of the resin matrix for filling materials, resin composites replaced acrylic resins as restorative materials. Furthermore, the mechanical and physical properties of resin composites were superior to those of acrylic resins. As a result of the addition of filler phase these materials possessed higher mechanical properties than unfilled resin [9]. This resin composite material was in the powder-liquid form.

Since the 1960s, resin composites have undergone several improvements in composition and structure. First of all, the two paste-paste chemical cured resin composites were introduced in dental practice in 1970 by Henry Lee [10]. Further advancements in resin composites led to the development of ultraviolet light cured, then visible-light cured (VLC) resin composites [12]. VLC unit was introduced: February 24, 1976 and the first VLC resin composite filling was placed in the Turner School of Dentistry in Manchester [13]. One of the advantages of resin composites is that their refractive index can match the look of the natural tooth. So they are commonly used for the restoration of posterior teeth as well as anterior teeth. Moreover, the amount of tooth structure that is removed during cavity preparation to accomplish adequate strength is less than amalgam.

In the late 1960s, by bringing together the silicate and polyacrylate systems, Wilson and Kent developed the first glass-ionomer cement [14]. Glass-ionomer cement possesses many advantages and disadvantages. These advantages include easy mixing, good resistance to acid dissolution, high strength and stiffness, leachable fluoride, potentially adhesive characteristics, and translucency. In contrast, disadvantages of glass-ionomer cement include an initial slow setting and moisture sensitivity, variable adhesive characteristics, radiolucency, and possible pulpal sensitivity [9].

A further evolution was the combination of resin composite and glass-ionomer cement to produce two new types of materials; resin-modified glass-ionomer cements and polyacid-modified composite resins (compomers). Resin-modified glass-ionomer cements were formed by adding methacrylates to the glass-ionomer formula. They were introduced to the market in 1992. Compomers were introduced in 1993, which were formed by the addition of acidic monomers to the original dimethacrylate resin matrix. Both of these materials were developed to improve the clinical handling and physical properties of conventional glass ionomer cements [15, 16].
1.1.2 Requirements of Tooth-Coloured Restorative Materials:

The design features for materials to restore tooth structure are complex and extensive. In general, a tooth coloured restoration needs to have similar properties to the enamel and dentine tissues and also to be capable of bonding to them.

Dentists are always aiming for the perfect dental restorative materials. Ideally, these materials should have the capacity to be tooth-coloured, strong, adhere to tooth structure, long lasting, and easily to apply within the cavity preparation [10]. The requirements of an ideal tooth-coloured restorative material are summarized in table 1.1.

Table 1.1: Requirements for an ideal tooth-coloured restorative material

<table>
<thead>
<tr>
<th>Aesthetic</th>
<th>Mechanical</th>
<th>Dimensional stability</th>
<th>Biological</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Match tooth colour</td>
<td>High strength</td>
<td>No shrinkage</td>
<td>Biocompatible</td>
<td>Adhere to enamel and dentin</td>
</tr>
<tr>
<td>Maintain desired colour</td>
<td>Resemble tooth structure in stiffness</td>
<td>No swelling</td>
<td>Not irritant to oral/dental tissues</td>
<td>Easily applied</td>
</tr>
<tr>
<td>Highly polishable</td>
<td>Resist wear and non-abrasive</td>
<td>Resemble tooth structure in reaction to temperature changes</td>
<td>Inhibit caries</td>
<td>Easily repaired</td>
</tr>
<tr>
<td>Maintain smooth and polished surface</td>
<td></td>
<td>No creep</td>
<td></td>
<td>Radiopaque</td>
</tr>
</tbody>
</table>

Unfortunately, there is no available restorative material that can possess all of these requirements. However, a proper understanding of the chemical and physical properties of these materials, will aid the clinician to get the outmost of their beneficial characteristics [17].

1.2 Resin composites:

Generally, composite materials are engineered materials prepared from more than one constituent materials with diverse chemical or physical properties that remain discrete and distinct within the final structure [18-20]. The matrix and reinforcement are the
major constituent materials in composites. Commonly, the polymers function as matrix materials, which enclose and bond the reinforcement filler materials [12]. Resin composites were initially developed for Class III and Class V where aesthetics are crucial, and for class I, as moderate occlusal stresses occur. In the 1990s, further advancements in resin composites and their application techniques extended their application to Class II and Class IV [11]. In regard to resin composites, they are composed of:

- An organic polymer resin matrix (continuous phase):
  - Monomer system
  - Initiators and accelerators
  - Inhibitors and stabilizers
  - Viscosity controllers
- Inorganic filler particles (the dispersed phase).
- Coupling agents (the interfacial phase).

The presence of each of these components is crucial to the success of the final restoration [12, 18, 19].

1.2.1 Organic Resin Matrix:

1.2.1.1 Monomer system:

The resin matrix is the chemically active portion of the resin composite. It is originally one or more monomer/oligomers converted into a hard cross-linked polymer by mean of polymerization reaction either chemical or photochemical initiated [21]. The most commonly used monomer in resin composites is an aromatic dimethacrylate, such as Bis-GMA (Figure 1.1) [11, 18]. Due to its large molecular weight (512 g/mole), this monomer has a lower volatility, higher compressive strength and hardness, less water sorption and polymerization shrinkage, and production of stiffer and stronger resin [11]. However, the stiff central backbone structure and the pendant hydroxyl (-OH) groups make this monomer quite viscous. In order to decrease the viscosity and improve the workability of Bis-GMA, low molecular weight monomers like triethylene glycol dimethacrylate (TEGDMA) or methyl methacrylate (MMA) are used to lower the viscosity (Figure 1.2 and 1.3, respectively) [9]. Furthermore, as the viscosity of the monomers mixture decreased, the more filler particles may be incorporated into the mixture [18].
Owing to its excellent viscosity and copolymerization properties, TEGDMA is a favored diluent monomer for Bis-GMA or the less viscous urethane dimethacrylate (UDMA) (Figure 1.4). 75 % Bis-GMA and 25 % TEGDMA would be a typical formulation. Monofunctional monomers such as ethylene- and hexamethylene-glycoldimethacrylate and benzyl methacrylate added to augment polymer chain elongation and degree of cure are examples of other diluents [19]. The addition of TEGDMA or other low-molecular-weight dimethacrylates allow extensive cross-linking to occur between polymer chains. This will increase the resistance to solvent degradation. However, resins that contain a high percentage of low molecular weight dimethacrylates exhibit a higher polymerization shrinkage [18, 22].

Figure 1.1: Bis-phenol glycidyl methacrylate (Bis-GMA) monomer.
Many other products use aliphatic dimethacrylates, such as UDMA where a urethane group is added into the dimethacrylate monomer molecule. This monomer system has been used in some materials, in which all or part of the Bis-GMA is substituted by UDMA to obtain lower viscosity; higher degree of conversion; lower water sorption and greater toughness [10]. The water sorption and viscosity can be reduced by the synthesis and use of a Bis-GMA analogue, which does not comprise pendant hydroxyl groups on their main polymer chain [12, 23, 24]. The hydrophobic non-hydroxylated homologues of Bis-GMA such as 2,2-bis[4-(2-methacryloyloxyethoxy)phenyl]propane (Bis-EMA) is an example of Bis-GMA analogues and its utilization resulted in reduced water sorption and, therefore, improved maintenance of mechanical properties [18].
Figure 1.4: Urethane dimethacrylate (UDMA) monomer

Most current resin composites use methacrylate-based chemistry and free radical polymerization reaction. Indeed, any of these materials has definite shortcomings [10]. Firstly, setting reaction is associated with volumetric shrinkage which result from decreased molecule-to-molecule distance between monomers in unpolymerized resin (Van der Waals distance) and those after polymerization (covalent bond) [10, 25]. The larger the monomer unit, the fewer the number of covalent bonds are needed to build the final polymer network. As a result, higher polymerization shrinkage is associated with utilization of low molecular weight monomers. Contemporary resin composites including flowable types exhibit a volumetric polymerization shrinkage ranging from less than 1 to 6 % [26, 27].

Secondly, polymerization reactions of all methacrylate based resin composites are exothermic. This result from excess energy arose when carbon-carbon double bond opens during polymerization reaction. The resultant heat may affect the pulp tissue especially when there is a minute thickness of dentin remains to provide adequate insulation. Furthermore, extra heat is added from exposure to the light source energy [28-33]. Some previous studies reported temperature rises of more than 20 °C during photo-activation of resin composites [34, 35]. Theoretically, transmission of heat through dentin can damage pulpal tissues. However, in the clinical situation the actual temperature increase transferred to the pulp would be much lower due to low thermal conductivity of dentin.

Thirdly, free radical-based polymerization reactions, which are the case in all methacrylate, are inhibited by the existence of oxygen. This inhibition is caused by the greater affinity for the free radicals to combine with oxygen molecules, to make
unreactive radicals, than with a methacrylate carbon-carbon double bond. Therefore, this process may retard or end up with termination of polymerization reaction with unpolymerized monomer remains [36].

Finally, biocompatibility concerns have been raised due to patient consumption of the unpolymerized monomer that may leach from resin composites restoration. Furthermore, formation of formaldehyde has been linked to unreacted monomer.

A number of alternative monomer systems have been developed to overcome these drawbacks of methacrylate resin composites. Non- or minimally-shrinking resin composites are one of these alternatives, and many researches were conducted on them. Silorane resin composite is an example of low shrinkage resin composites. This monomer undergoes a cationic ring opening reaction during polymerization providing low setting shrinkage [10]. The major difference between polymerization of silorane and methacrylate based composite is that, silorane are polymerized by opening of oxirane ring via cationic intermediates, whereas Di-methacrylate are polymerized by free radical intermediates [10, 37].

Silorane monomer system is developed from reaction of oxirane and siloxane molecules (Figure 1.5). Oxirane molecule is the responsible part of the monomer for the cationic ring opening reaction during polymerization, whereas siloxane molecule gives the hydrophobic characteristics to the silorane. As a result, silorane-based resin composites possess several advantages compared to methacrylate-based resin composites. For instance, lower polymerization shrinkage, higher hydrophobicity, insensitivity to oxygen, and greater biocompatibility [27, 36, 38-41].

Weinmann et al. compared polymerization shrinkage of Silorane and methacrylate-based resin composites by using the bonded-disk and Archimedes methods. They found that Silorane exhibited the lowest polymerization shrinkage among all examined resin composites (0.94 % for bonded-disk method and 0.99 % Archimedes method) [27]. Also, Ilie et al. [39] compared shrinkage stress of resin composite based on silorane to a regular resin composite based on methacrylate. They concluded that silorane-based resin composite showed lower shrinkage stress values.
In addition to the monomer, other additives are blended within the matrix resin including an activator-initiator system; inhibitors; ultraviolet light absorbers, pigments, and opacifiers [12].

**1.2.1.2 Inhibitors and Stabilizers:**

Inhibitors are working by minimizing or stopping spontaneous polymerization of monomers. As a result of addition of inhibitors to resin composites, their shelf life can be increased. Butylated hydroxytoluene is a typical inhibitor and it work by binding to any formed free radical. By this binding it could prevent any chain propagation. On the other hand, stabilizers are added to resin composites to absorb ultraviolet light to prevent darkening with age. Benzophenones is an example for stabilizer [12].

**1.2.1.3 Initiators and Accelerators:**

Composites are either visible light-cured (photo-activated) or chemically activated (self-cured), with the former being more common [9].

In photo-activated resin composites, materials are supplied in a single paste. Polymerization reaction is initiated by exposing the material to blue light with a wavelength of about 470 nm. The light is absorbed by a photo-activator like camphoroquinone (CQ), the reaction is accelerated by the presence of an organic amine containing a carbon double bond (co-initiator), such as dimethylamino
The concentration of CQ and that of the co-initiator have an important effect on polymerization. Application of more than the optimum concentration of CQ may compromise the aesthetics and biocompatibility of the resin composite. In contrast, a less than acceptable concentration of CQ may result in insufficient polymerization, poor biocompatibility, poor colour stability, reduced mechanical and physical properties, reduced wear resistance, and possibly early failure of the restoration. Therefore, it is crucial to apply the lowest (optimal) concentration of CQ required for maximum polymerization and augment biocompatibility without deteriorating the mechanical and physical properties of resin composite. However, CQ concentration added by the manufacturer in amounts varying from 0.2 to 1.0% [42, 43].

Currently, some manufacturers use photoinitiators other than CQ. These alternatives were applied to minimize tinting where translucency is important such as in heavily filled resin composites. These compounds are mainly sensitive to ultraviolet radiation with a small portion that are sensitive to the visible spectrum [10].

In chemically-cured resin composites, materials are supplied in two pastes. One paste containing an organic amine (catalyst) while, the other containing organic peroxide (universal paste). Upon mixing of the two pastes together a chemical reaction occur and result in production of free radicals, which in turn attack the carbon double bonds starting polymerization. Some resin composites are dual cured, such as provisional and core resin composites. These products encompass initiators and accelerators which allow photo-activation followed by chemical-curing [11].

1.2.1.4 Viscosity Controllers:

Viscosity of liquid is defined as a measure of liquid’s resistance to forces that cause it to flow. The flow of unset resin composite is highly influenced by the rheology of the resin matrix monomer [44]. To overcome the high viscosity of Bis-GMA, low viscosity monomers such as methyl methacrylate (MMA) or triethyleneglycol dimethacrylate (TEGDMA) are blended with the resin matrix to improve its handling properties [22].
1.2.1.5 Other additives:

There are other components that are added to resin composite for specific purposes. For instance, inorganic oxides are added in small proportions to give a range of shades that matches the different tooth shades. Another example is UV absorbers which are added to minimize colour changes of resin composites [45].

1.2.2 Inorganic Fillers (dispersed phase):

Addition of inorganic filler particles to the resins has many advantages include higher strength, lower coefficient of thermal expansion, increased stiffness, reduced polymerization shrinkage, control rheological properties, improve thermal properties, radiopacity, enhanced aesthetics and improved handling [9, 19, 46, 47]. There is a limit on the amount of maximum possible filler particles that can be loaded into a resin composite. Usually, by employing a larger volume fraction of fillers, dental composites become stiffer and stronger [19, 48]. However, adding too much filler can result in a resin composite with higher viscosity, lower polymerization degree and low toughness. Thus, there is a compromise between the filler loading and desired properties of the resin composites [49].

Optical characteristics of the resin composite are an important issue to consider during fillers selection. Fillers should have a refractive index within the range of that for monomer resins. Refractive index for monomer resins is approximately 1.55, whereas glasses can have refractive indices within the range of 1.4 to 1.9. Mismatching of the refractive index between fillers and monomer resins resulting in visually opaque resin composite and causing aesthetic and curing problems [19].

The most commonly used filler particles is quartz; fused silica (colloidal silica) and other types of glass such as barium glasses or strontium glasses (provide radiopacity to the composite). They are mainly manufactured by grinding or milling glasses or quartz (ceramic) into particles of different sizes, approximately from 0.1 μm to 100 μm [12, 23]. The main advantage of quartz is that, it is chemically inert and has exceptional optical characteristics to match with resin. On the other hand, quartz has its own shortcomings. It is abrasive to the enamel and other restorations, difficult to polish, and not radiopaque [23].
Colloidal or pyrolytic silica is small sized particles (about 0.04 µm), sometimes called as micro fine particles. Because of its small size these particles have high surface area, viscosity of the composite is high at lower levels of filler loading than with larger particles [50]. Filler loading of only about 40 wt% is possible before the material becomes too stiff and difficult to manipulate. To overcome this problem, manufacturers prepare prepolymerized blocks of resin containing a high filler loading of silica. The block is ground to give particles of resin (containing silica) up to 100 µm in diameter. These particles are blended with monomer and other resin composite additives to form pastes [50]. Many types of microfilled composites are commercially available, although almost all still have less filler than do composites with a larger particle.

The best combination of aesthetics and durability in resin composites is achieved with the hybrid composite. Hybrid composites contain a mixture of different filler sizes, ranging from small to microfine particles, typically from 0.04 µm to 1.5 µm [51]. Typical filler loading is in 70 to 80wt% [23]. However, hybrid composites are still inferior in polishability compared to microfilled composites.

In recent years, nano composites were introduced to the market. Nano-sized filler particles (below the wavelength of visible light), either agglomerated as nanoclusters (0.6-1.4 µm) or as individual nanomers (20-75 nm) are used in these resin composites [37]. These types of fillers are unable to scatter or absorb visible light and, therefore, provide a means for integrating radiopacity without affecting the aesthetic. In addition, the extremely small sizes of the particles may occupy the spaces between larger particles and, in theory, permit filler loading levels for up to 90-95 wt% [37, 51].

1.2.3 Coupling agent (interfacial phase):

Successful resin composites should have a good bonding between the two phases (inorganic filler particles and the organic matrix). This bonding is achieved by coating the surface of the filler with a coupling agent, an organosilane (silane). The silane contains functional groups, which react with the inorganic filler, as well as unsaturated organic groups that react with the oligomer during polymerization [11]. The quality of the interfacial phase can directly affect some of the characteristics of the resin composite. These include mechanical properties, polymerization stress, and durability of resin composites in the vigorous oral environment [52].
The most commercially available resin composites comprise fillers based on silica and, therefore, utilize silane coupling agent with functional methacrylate groups. 3-methacryloxypropyl trimethoxysilane (MPS) is the most commonly used organosilane in resin composites (Figure 1.6). This bifunctional molecule is capable of forming covalent bonds via its alkoxy groups with the surface of silica fillers through silicon-oxygen groups and with the methacrylate groups in the resin matrix by its methacrylate functional group [19, 21, 53, 54].

![Chemical structure of 3-methacryloxypropyl trimethoxysilane (MPS)](image)

**Figure 1.6:** 3-methacryloxypropyl trimethoxysilane (MPS)

Physical, chemical and mechanical properties of resin composites are affected by those of the interfacial phase. However, interfacial properties are affected by many factors, either related to the chemical and physical nature of the coupling agent or to its application process. Functionality, hydrophobicity, molecular size, reactivity, and chemical structure are among the factors related to the nature of coupling agent. On the other hand, application process factors may include degree of filler particles coverage and orientation of the coupling agent layer [21].
An appropriately applied coupling agent can improve physical and mechanical properties of the resin composites. Furthermore, proper application of the coupling agent can provide hydrolytic stability to the resin composites by preventing water penetration along the resin-filler interface [12]. Owing to its higher ionic character, the covalent bond between the inorganic fillers and coupling agent is more prone to hydrolysis. On the other hand, the covalent bond between the resin matrix and coupling agent is more stable and, therefore, less susceptible to hydrolysis. The use of coupling agent with more hydrophobicity than MPS was suggested [21].

1.3 Classification of resin composites:

There are many ways that have been proposed in the classification of resin composites (Figure 1.7). Firstly, according to the size of filler particles, resin composites can be classified into macrofilled, microfilled, hybrid and nanofilled. Secondly, it could be grouped into chemically activated or light activated depending on the mode of activation. Lastly, based on its clinical application, resin composites could be anterior, posterior or anterior/posterior composites [17, 55, 56].
1.3.1 **According to filler size:**

1.3.1.1 **Macrofilled resin composites (conventional):**

Macrofilled resin composites were marketed in 1970s. The first macrofilled resin composite contained relatively large quartz or glass filler particles of size ranged from 15 to 100 µm. Current macrofilled resin composites contain filler particles with an average size of 20-40 µm and filler loading of approximately 75% wt [23].

In comparison to unfilled resin, macrofilled resin composites possess a significant improvement in physical properties. For instance, compressive strength, elastic modulus, tensile strength and hardness were increased while polymerization shrinkage...
and coefficient of thermal expansion were decreased [48]. However, macrofilled resin composite has a major disadvantage which is the difficulty in getting a polished surface. This is because of the presence of the large filler particles, and any loss of these particles at the surface will lead to surface roughness [23].

1.3.1.2 Microfilled resin composites:

Microfilled resin composites were developed in the late 1970s, to overcome the poor polishability of the macrofilled resin composites [57]. Microfillers are small spherical colloidal silica particles with diameter around 0.04 μm, produced by a chemical process that includes heating in a flame [23]. As mentioned earlier, due to their small size and high surface area, viscosity of the composite is high at lower levels of filler loading than with larger particles [50]. Filler loading of only about 40 wt% is possible before the material becomes too stiff and difficult to manipulate. To overcome this problem, manufacturers prepare prepolymerized blocks of resin containing a high filler loading of silica. The block is ground to give particles of resin (containing silica) up to 100 μm in diameter. These particles are blended with monomer and other resin composite additives to form pastes [50]. Many types of microfilled resin composites are commercially available, although almost all still have less filler than do composites with a larger particle.

The introduction of microfillers into resin composites has overcome the disadvantage of surface finishing of macrofilled resin composites. Microfilled resin composites can be polished to a very smooth and shiny surface. However, microfilled resin composites exhibit several disadvantages such as greater water absorption, a higher coefficient of thermal expansion, decreased elastic modulus and a higher polymerization shrinkage than heavily filled resin composites [45, 58].

1.3.1.3 Hybrid resin composites:

As the name implies, fillers in this type of resin composites are a mixture of both micro-fillers and macro-fillers and also combine the characteristics of being both microfilled and macrofilled. Hybrid resin composites contain colloidal silica (0.04 μm) and ground glass particles (0.6-1.0 μm) [19]. The hybrid composites differ from blended composites because they do not contain prepolymerized resin particles [17].
A filler content of 83% or higher can be achieved with this type of resin composites, by using filler loadings 75% of fillers size (1-50 μm) and 8% of submicron fillers with size (0.04 μm) [50]. The particulate reinforcement due to increased filler loading of hybrid resin composites improves the stress transferred between individual fillers within the matrix. This is due to reduced interparticle distance, which leads to the transferring of stress from one filler to another, and in turn, less stress would be delivered to the resin matrix [17].

1.3.1.4 Nano resin composites:

With the introduction of nanotechnology which allows the uses of nano scale in the range 0.1-100 nm, a large number of researches are being conducted to improve resin composites properties through incorporation of nanofillers [37]. Nano-sized filler particles (below the wavelength of visible light), either agglomerated as nanoclusters (0.6-1.4 μm) or as individual nanomers (20-75 nm) are used in these resin composites [37]. These types of fillers are unable to scatter or absorb visible light and, therefore, provide a means for integrating radiopacity without affecting the aesthetic. Hence, combining nanomers and nanoclusters permits increased filler loading and decreased viscosity and, therefore, improved mechanical and handling properties. Additionally, these resin composites demonstrated reduced volumetric polymerization shrinkage and shrinkage stress [37].

As the filler loading increases due to the combination of nanomers and nanoclusters, the interparticle distance decreases. Therefore, nano resin composites show reduced load bearing stress on the resin, improved fracture resistance, higher hardness, higher wear resistance, and better and longer retention of surface polish [37].

1.3.2 According to modes of activation:

Resin composites can be classified according to the method of activation into:

(1) Chemically activated composites.
(2) Photo-activated composites.
(3) Heat-cured composites.
(4) Dual-cured composites.
1.4 Polymerization Mechanism:

Resin composite polymerization is a free radical polymerization reaction. In this type of polymerization reaction, no by-products are obtained [45]. The free radicals are formed by reactive agents named initiators. In general, these are molecules have one relatively weak bond which undergo decomposition to form two reactive molecules each of them has an unpaired electron [50]. Decomposition of this bond can be accomplished by two methods:

*One of them involves the use of heating or reaction with a chemical activator. An example of widely used initiator in dental polymers that decompose by this method is benzoyl peroxide. However, the use of a chemical activator enables polymerization to occur at a room temperature. Aromatic tertiary amines such as \(N, N'\text{ dimethyl-}p\text{-toluidine, are example of activators used with peroxide initiators.}

**The other method involves the use of radiation to decompose a suitable radiation-sensitive initiator. For instance, exposure of benzoin methyl ether to ultraviolet radiation will lead to its decomposition to form free radicals. Furthermore, certain ketones in the presence of a tertiary amine are able of producing free radicals when exposed to radiation in the visible spectrum range.

However, polymerization reaction takes place in four stages namely: activation, initiation, propagation and termination.

1.4.1 Activation:

Activation takes place due to the presence of an activator, such as heat, ultra-violet light, visible light, or other chemicals, such as tertiary amines. In chemically activated systems, free radicals are generally created from the reaction of an organic peroxide initiator and an amine accelerator. On the other hand, the photo-activated system contains a camphorquinone which absorbs the light in the range 440-480 nm and divides producing two molecules with one unshared electron each [42, 45].

1.4.2 Initiation:

In this stage, the free radicals produced due to activation will attack the double bonds of available monomer molecules. As a result, activated monomer molecules will be
produced, by changing of the unshared electron to the end of the monomer molecules [45, 50].

1.4.3 Propagation:

After initiation, the newly formed free radical reacts with further monomer molecules. This reaction results in the formation of new free radical which in turn reacts with another monomer molecules and the propagation process continues [8].

1.4.4 Termination:

It could be possible for the propagation to continue until it has exhausted all the monomer molecules supply [12, 45]. Unfortunately, propagation may terminate earlier as a result of other reactions and produce dead polymer chains. For instances termination when two growing chains are combined to form one dead chain. Other examples of termination, when growing chains react with initiator molecules, dead polymer, impurity or solvent [8, 45].

1.5 Handling properties of resin composites:

In its precured state, resin composites are paste type viscoelastic materials and are positioned intermediately between viscous and elastic materials. Handling properties of resin composites are a key factor to consider during their selection. Flow, stickiness to hand instruments and tooth, pack-ability, and slumping resistance are associated with ease of placement and shaping, chair time, and success of the restoration [59-62]. Most of these properties are directly related to the viscosity of resin composites [60, 62-65]. Different actions are applied on resin composites during clinical application and manipulation. These may include; apply and press, by a plugger, to pack the resin composite in the cavity, and sculpt, by a carver, to shape the occlusal anatomy. Resin composites are viscoelastic material and, therefore, display complex rheological characteristics such as shear thinning (as the shear rate increases the viscosity decreases), thixotropy (take time to return to its original viscosity after cessation of the shear force), and yield stress (need sufficient applied stress to flow) [66, 67]. Also, viscoelastic materials are characterized by a phenomenon called stress relaxation, where after removal of the load, the shear stress decays gradually to zero [67].
1.5.1 Factors affecting resin composites viscosity:

Resin composites are composed of inorganic fillers coated with coupling agent dispersed in an organic resin matrix [37]. Therefore, resin components and filler particles, and their interactions can play a marked role on resin composites viscosity [59, 60, 68].

1.5.1.1 Monomer matrix:

As mentioned earlier (§ 1.2.1.1) Bis-GMA monomer is widely used because of its lower volatility, higher compressive strength and hardness, less water sorption and polymerization shrinkage, and production of stiffer and stronger resin [11]. The stiff central backbone structure and the pendant hydroxyl (-OH) groups make this monomer quite viscous at room temperature and, therefore, a low molecular weight monomer is added to decrease the viscosity of organic matrix and allow more filler loading [18]. Although, increasing the proportion of the low molecular weight monomer leading to a decrease in viscosity of resin composites [61, 69], this leading to increase in their polymerization shrinkage [61].

1.5.1.2 Filler content:

As mentioned before (§ 1.2.2) filler particles have an important role in determining the viscosity of resin composites. Fillers shape and size, interlocking between fillers, and interactions between fillers and resin matrix are among determinants of the viscosity of resin composites [60]. Also, increasing filler loading lead to an increase in the viscosity of resin composites [59, 60]. Lee et al [60] studied experimental composites composed of an identical resin matrix of Bis-GMA and TEGDMA and contained different types and fractions of fillers. They reported that, for similar filler volumes, the viscosity increased as the filler size decreased. This is due to a higher number of smaller fillers that are needed to fill the same volume. Therefore, the total surface area of fillers increased, which resulted in higher interactions between the fillers and resin matrix, and the fillers itself.

1.5.1.3 Temperature:

Previous studies demonstrated an inverse relation between resin composites temperature and viscosity (Figure 1.8); i. e. the viscosity of resin composites decreased as the
temperature increased [44, 60]. The temperature dependence of viscosity is given by the Arrhenius equation:

\[ \eta = Ae^{\frac{E_a}{RT}} \]  

----- (Equation 1.1)

Therefore, where \( \eta \) is the viscosity and \( A \) the pre-exponential factor with \( E_a \) the activation energy and \( T \) temperature in kelvin and \( R \) the gas constant (8.31451 kJ mol\(^{-1}\)); this relation could explain the decrease in viscosity in accordance to the increase in temperature.

![Figure 1.8: Temperature-dependence of the viscosity.](image)

1.6 Degree of conversion:

Set resin composites composed of a complex cross-linked organic matrix reinforced by inclusion of inorganic fillers sometimes blended with organic filler [70]. The degree of conversion is the percentage of carbon-carbon double bonds converted to single bonds as a result of the polymerization process [12]. Resin composites are characterized by a partial conversion of carbon-carbon double bonds, which leaves a considerable amount of unreacted methacrylate groups [46, 71, 72]. This happens as a result of the rapid development of the polymeric network after photo-activation, which leads to mobility restrictions of reactive species [71, 73]. Inadequate levels of the degree of conversion may lead to lower mechanical properties, lower wear resistance and colour instability of resin composites. Additionally, residual monomers and initiators may leach from resin
composites, resulting in loss of biocompatibility [74]. On the other hand, maximizing degree of conversion to improve those properties may lead to increased polymerization shrinkage and establish brittle resin composites [75].

1.6.1 Factors affecting degree of conversion:

The degree of conversion of resin composites is affected by many factors, including the concentration of polymerization promoters and inhibitors [76, 77], monomers chemistry and diluent concentration [77, 78], fillers content [79, 80], temperature [72], and energy density delivered by the LCU [81, 82]. As mentioned above, the viscosity of resin composites is decreased with increased temperature. This will lead to increase in the mobility of free radicals and, therefore, resulting in more polymerization and degree of conversion. Additionally, the collision between the unreacted groups and free radicals is increased due to photo-activation at elevated temperature. Trapped radicals become more free due to increased mobility and increased additional free volume caused by temperature rise, which result in further conversion [72]. Emami and Söderholm [82] reported that degree of conversion is related to the energy density (J/cm²) irrespective of the differences in light irradiance (mW/cm²). They recommended energy density of 21-24 J/cm² for proper polymerization of 2 cm thick resin composite specimens. Furthermore, a positive correlation were found between energy density and degree of conversion, i.e. as the energy density increased the degree of conversion of resin composites increased [81, 83].

1.6.2 Methods for measuring the degree of conversion:

The degree of conversion of resin composites can be measured by various methods. These methods include halogenation of residual carbon double bonds, differential scanning calorimetry, differential thermal analysis (DTA), infrared spectroscopy, and Fourier-transform infrared (FTIR) [71, 74]. Among these techniques, FTIR spectroscopy has been widely used as a reliable, relatively easy, and non-destructive technique to determine the degree of conversion of resin composites. It is based on the absorption of infrared radiation owing to the molecular vibrations of the polymer’s functional groups.

Surface microhardness is sometimes used as indirect method to estimate the degree of conversion. Previous studies [73, 84, 85] reported positive linear correlation between
degree of conversion and Knoop microhardness. In a recent study, Price et al. [73] investigated the effect of specimen temperature on the degree of conversion and Knoop microhardness of resin composite. They concluded that the degree of conversion is positively correlated with the Knoop microhardness. Moreover, specimens demonstrated a higher degree of conversion and Knoop microhardness, and with a greater and quicker maximum rate of polymerization at elevated temperature.

1.7 Polymerization shrinkage:

1.7.1 Polymerization shrinkage strain:

As mentioned earlier, resin composites are a heterogeneous material with three main constituents, the resin matrix (continuous phase), the filler particles (dispersed phase), and coupling agent [37, 86, 87]. During setting, they undergo a polymerization reaction which is a chemical process involve the linking of smaller monomer molecules to form a cross-linked network. As a result of polymerization, resin composite shrinks because of the conversion of inter-molecular distances, which are a Van der Waals bond (0.3-0.4 nm) into covalent bond (0.15 nm) [10, 18, 25]. Typically, the smaller the monomer unit, the higher the number of covalent bonds is needed to form the final polymer. As a result, higher polymerization shrinkage is associated with utilization of low molecular weight monomers. However, polymerization shrinkage is affected by many factors, including the functionality of monomer, average molecular weight, degree of conversion, filler loading, and temperature [18, 86, 88-93]. The polymerization shrinkage strain ($\varepsilon$) is defined as the change in length ($\Delta L$) or volume ($\Delta V$) to the original length ($L_0$) or volume ($V_0$), respectively i. e.:

$$\Delta L = L - L_0$$

----- (Equation 1.2)

Or

$$\Delta V = V - V_0$$

----- (Equation 1.3)

Therefore, the strain ($\varepsilon$) is:
\[ \varepsilon\% = 100 \frac{\Delta L}{L_0} \approx 100 \frac{\Delta V}{V_0} \]  
\[ \text{------ (Equation 1.4)} \]

Polymerization shrinkage is considered as the most significant problems of resin composites [19]. As in the clinical situation, resin composite is cured while is bonded to rigid tooth structures. Therefore, shrinkage must be compensated by some kind of volume generation. This can originate from strain on the material, destruction of the restoration-tooth bond, increase in porosity or internal loss of coherence [94]. Disruption of the restoration-tooth bond may lead to microleakage, passage of fluids, bacteria, molecules, ions or air along the restoration-tooth interface. On the other hand, polymerization shrinkage may lead to cuspal movements due to stress generation on the surrounding tooth tissues and this may endanger the longevity of the restoration [86].

Polymerization shrinkage depends on the resin organic matrix and on the number of carbon-carbon double bonds convert to carbon-carbon single bond within it [90]. The polymerization reaction produces a gelation in which the material transforms from a viscous-plastic phase into a rigid-elastic one. This gelation process is characterized by the presence of gel point, which is described as the point at which the material can no longer able to provide viscous flow to keep up with polymerization shrinkage [94]. Therefore, polymerization reaction can be divided into two stages; pre-gel and post-gel stages [95]. During pre-gel stage of polymerization, the resin composite can flow easily and any resultant stress due to shrinkage could be relieved by this flow compensation. Unfortunately, after gel point the material becomes stiff and not able to compensate any stress by means of flow and stress starts to build up within the resin composite restoration. However, magnitude, direction and time-dependence are considered as fundamental aspects of the polymerization shrinkage strain [96].

The magnitude and direction of polymerization shrinkage strain (or vector character of strain) are affected by material factors and the geometry of the host environment i.e. the restored cavity shape and size. Furthermore, the polymerization kinetics and network formation influenced the final shrinkage strain and its rate. Typically, immediately after photo-activation, a quite fast polymerization reaction starts (autoacceleration) and shrinkage strain happens. This is followed by a period of slow down of polymerization
reaction (autodeceleration), due to increase in the cross-linking of the polymeric network which restrict rapid micro-Brownian motion of monomer and chain-segments, and, therefore, the material is changed into a rigid-glassy solid [96]. As a result of continued reaction and crosslinking, mobility is reduced further, and the system becomes more viscous until the reaction stops due to polymer vitrification [97].

1.7.1.1 Methods for measuring the shrinkage strain:

Various techniques have been used for determining polymerization shrinkage. Methods of measurement include volume dilatometry [98-100], the use of a microscope to measure linear shrinkage [94, 101], using water or mercury; applications of Archimedes principle [102], the use of bonded strain-gages [103], the ‘bonded-disk’ method [104], the linometer and a modified linometer used for continuous recording of volumetric polymerization shrinkage principle of linear measurement on a non-bonded disk or layer of material [105, 106], Laser beam scanning [107], and the laser interferometric method used to measure linear polymerization shrinkage [108]. However, Watts and Cash [104] developed the ‘bonded-disk’ method of measurement of shrinkage strain kinetics that has also been applied by a number of other laboratories. The careful design and development of the bonded-disk geometry had ensured [109]:

1. A defined C factor that if needed could be adjusted over a limited range.
2. The direction of shrinkage is determined by the configuration of the specimen, instead by the light irradiation direction.
3. Maximum shrinkage strain happens in axial direction and, therefore, it corresponds closely to the volumetric shrinkage strain.
4. Specimen disk diameter matching those of LCUs light guide.
5. Low specimen thickness (1 mm), which make sure of equal conversion at upper and lower surfaces.
6. It is feasible to control and adjust the temperature of specimen and light intensity.

1.7.2 Polymerization shrinkage stress:

As mentioned earlier, polymerization shrinkage and subsequent shrinkage stress that occur during polymerization are still significant disadvantages of resin composites
This stress may lead to post-operative pain, bond disruption between tooth and restoration, marginal discolouration, recurrent caries, cusp deflection and enamel micro-cracks [111, 112]. Shrinkage stress results when the dimensional changes due to polymerization are obstructed by bonding to cavity walls and the material is rigid enough to flow. Therefore, stress starts to build-up at a very short time after commencement of photo-activation [111]. Stress (σ) is described as the force (F) per unit area (A), as follow:

\[
\sigma = \frac{F}{A}
\]  

Shrinkage stress is dependent on the interactions between material properties, geometry, and boundary conditions of the restorations. The configuration factor (C factor), which is the ratio of the bonded surfaces to the unbounded surface, is found to be linearly related to shrinkage stress, i.e. as the C factor decreases the shrinkage stress decreases [113]. Material factors that play a role in stress development include the degree of conversion, polymerization rate, shrinkage strain, elastic modulus, pre-gel flow, and post-gel shrinkage [87, 111, 114-117]. Curing condition such as light cure irradiance is another important factor that shows an ability to affect resultant stress. Soft-start photo-activation, in which a lower irradiance is applied at the start of photo-activation, may result in better marginal gaps [118]. This is due to the slowly advancing reaction which gives the material an ability to flow during polymerization and, therefore, slow development of modulus, reduction of post-gel shrinkage, and dissipation of stress [119, 120].

1.7.2.1 Methods for measuring the shrinkage stress:

Methods and techniques for measuring the shrinkage stress of resin composites face more problems than those measuring the shrinkage strain. This is partially due to that the specimen holder must become efficiently bonded to the specimen during measurement [121].

The first effort to measure shrinkage stress of resin composites was accomplished by utilizing an Instron universal testing machine (UTM) [122, 123]. The ACTA group
added major developments in the field by eliminating the effect of system compliance with the use of servo-hydraulic UTM [124]. At first, chemically cured resin composites were studied [113] and later VLC resin composites [125]. However, this equipment has limitation such as expense, complex procedure, and size. Other techniques were reported in literatures such as the use of strain gauges, a ring slitting method, photo-elastic, Moire method, Finite Element analysis, and Bioman instrument [111, 121]. The Bioman instrument is based in fixed beam compliance and proved to be convenient, and gave reproducible results [126].

1.7.3 Methods to control the polymerization shrinkage of resin composites:

As mentioned earlier polymerization shrinkage strain and subsequent shrinkage stress are still major drawbacks of resin composites [110]. Therefore, numerous studies were conducted to study polymerization shrinkage phenomenon and its determinants. Several techniques were proposed to tackle polymerization shrinkage and to mitigate the resultant stress, these may include:

1.7.3.1 Redesigning of materials:

In an attempt to primarily decrease the polymerization shrinkage of resin composites, different monomer chemistry and combinations were developed. Silorane and other cyclic monomers that open their rings during polymerization providing lower shrinkage [10]. Silorane resin composites possess several advantages compared to methacrylate resin composites, such as lower polymerization shrinkage, lower shrinkage stress, higher hydrophobicity, insensitivity to oxygen, and better biocompatibility [27, 36, 38-41].

Another technique to reduce shrinkage stresses is by introducing discontinuities within resin matrix to act as stress relieving sites. This may include, addition of glass microsphere, presence of voids, introduction of functionalized flexible monomers, incorporation of non-bonded nanofillers, and loading with non-functional silane treated nanofillers [111, 127]. Previous studies [127, 128] reported that the addition of non-bonded nanofillers may act as stress relieving sites within resin composites, whereas non-functional silane treated nanofillers lead to reduction of 50 % in stress compared to the functional silane treated resin composites.
Another approach to reduce shrinkage stress involves the addition of ultra-high molecular weight polyethylene (UHMWPE) fibres, which has the ability to undergo plastic deformation and, therefore, relaxing any stress build-up [129]. Also, alteration in the photoinitiators and inhibitors was suggested to reduce stress build in resin composites. Shrinkage stress and its rate were reduced as a result of increased the concentration of inhibitor (BHT) [130]. Replacement of part of the photoinitiator (camphorquinone) by phenyl-propanedione resulted in reduction of the stress rate without affecting the ultimate degree of conversion [131].

1.7.3.2 The placement techniques:

As mentioned above the C factor of the restoration has direct influence on the shrinkage stress. Therefore, various placement techniques such as the horizontal and oblique incremental layering techniques (Figure 1.9 and 1.10, respectively) were introduced to fill the cavity in order to ensure adequate depth of cure and to mitigate the developing stress. Park et al. compared the bulk fill technique with the horizontal and oblique techniques [132]. They concluded that the incremental layering techniques (either horizontal or vertical) showed a lower cuspal deflection than the bulk fill technique. This was in agreement with their previous study [133], where they found a positive relation between cuspal deflection and C factor, i.e. cuspal deflection increased as the C factor increased.

![Figure 1.9: Horizontal layering technique.](image)
1.7.3.3 Light-curing procedures:

Different photo-activation techniques and regimes have been encouraged to decrease the polymerization shrinkage stress. As mentioned earlier soft-start regime, in which the photo-activation procedure starts with a period of lower irradiance followed by full light irradiance. Previous study showed better marginal integrity with the use of this regime [118]. This is due to the slowly advancing reaction which gives the material an ability to flow during polymerization and, therefore, slow development of modulus, reduction of post-gel shrinkage, and dissipation of stress [119, 120, 134].

1.8 Thermal expansion:

After placement in the oral cavity, resin composite restorations are subjected to changes in their dimensions due to thermal variations. This dimensional changes can be expressed by resin composites coefficient of thermal expansion (CTE) [135]. The oral environment is subjected to fluctuations in temperature due to intake of hot and cold food. Palmer et al. reported intraoral temperature range from 0 °C to 67 °C [136]. Hence CTEs of enamel and dentin are 17 (10^{-6}/°C) and 11 (10^{-6}/°C), respectively according to a previous study [137]. It is ideal if the CTE of resin composites are in the range of enamel and dentin to help preserve the tooth-restoration bond. Mismatch between the CTE of the resin composite and tooth structure may lead to thermally induced stresses which may affect the marginal integrity of the restoration.

Previous studies showed the CTE of filler particles ranges from 0.5 to 6 (10^{-6}/°C), and that of the resin matrix ranges from 110 to 190 (10^{-6}/°C) [138, 139]. Additionally, it is agreed that the CTE of resin composites is inversely related to the filler loading, i.e. as
the filler loading of resin composites increases the CTE decreases [135, 138, 140-142]. The literature shows that the CTE of resin composites ranged from $20 \times 10^{-6}/\degree C$ to $80 \times 10^{-6}/\degree C$ [143].
Chapter 2

General Aims and Objectives
The aims of this research were to study the effect of temperature change (at 23°C & 37°C) on the resin composite properties before and during the setting process.

The specific objectives were to investigate a series of representative resin composites in order to:

- Investigate the effect of temperature on handling properties of uncured resin composites.
- Investigate the effect of temperature on the degree of conversion.
- Simultaneous determination of shrinkage strain and temperature changes of resin composites.
- Examine the effect of temperature on shrinkage strain kinetics of resin composites.
- Investigate the effect of temperature on shrinkage stress kinetics of resin composites.

The outline of the studies is shown diagrammatically in Figure 2.1:
Figure 2.1: General outline for studies.
Chapter 3

Methodology
3.1 Introduction:
A range of standard and novel techniques were employed to meet the objectives of the current research. Standard techniques applied in the current study were:

(1) FTIR spectroscopy to measure the degree of conversion. (Chapter 5)
(2) Bonded-disk instrument to measure the shrinkage strain kinetics. (Chapter 7)
(3) Bioman instrument to measure the shrinkage stress kinetics. (Chapter 8)

All these methodologies are thoroughly described in their relevant chapters.

The new techniques applied in the current research were:

(a) The use of packing stress instrument to measure the packing stress and viscosity of uncured resin composites. (Chapter 4)
(b) Temperature control of the resin composite specimens during degree of conversion measurements by using the PIKE temperature control module to adjust the temperature of the heated ZnSe crystal performance plate of the FTIR spectrometer. (Chapter 5)
(c) Modifications of the bonded-disk instrument to simultaneously determine the shrinkage strain, exotherm, and CTE. (Chapter 6)
(d) Addition of the heating element to the Bioman instrument to control the temperature of resin composite specimens. (Chapter 8)

The instruments used in the current study have been designed to embody and comply with the basic rules of engineering measurements. These rules include [144]:

3.1.1 Accuracy:
This is the closeness with which the measuring instrument can measure the true value of the property and under stated conditions of use.

3.1.2 Sensitivity:
This is the relationship between a change in the output reading for a given change of input. This relationship may be linear or non-linear. Sensitivity is often known as scale factor or instrument magnification and an instrument with a large sensitivity (scale factor) will indicate a large movement of the indicator for a small input change.
3.1.3 Linearity:

Most instruments are specified to function over a particular range and the instruments can be said to be linear when incremental 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 gives some small but definite numerical change in the output.

3.1.5 Repeatability:

This is the ability of a measuring instrument to give identical indications, or responses, for repeated applications of the same value of the measure and under stated conditions of use.

3.1.6 Zero stability:

This is the measure of ability of the instrument to return to zero reading after the measure and has returned to zero and other variations such as temperature, pressure, vibration, etc. have been removed.

3.2 Packing stress instrument:

The penetrometer principle was applied to design a precision instrument used in the current study (Figure 3.1). This instrument composed of a steel base, to which two vertical steel pillars (A and B) were bolted. A lever with an arm pivoting via a load bearing pin was attached to steel pillar A, which form together with the steel base a horizontal U shape with the lever extending beyond the base. The free end of this lever arm was weighted by a 500 g mass, whereas its other end was attached to steel pillar B via a stop plate to control the magnitude of its vertical movements. A plunger with a diameter of 3.18 mm was pushed via the lever arm into each unset resin composite to a controlled depth of 2.5 mm under a constant load. Resin composite samples were contained in a portable sample well (diameter = 6.35 mm and depth = 4.5 mm, giving a cavity volume = 142.6 mm³), constructed from copper and placed onto a temperature
controlled base. Samples temperature was controlled by heating elements embedded into the temperature controlled base and connected to a general purpose variable power supply. The temperature of the samples was monitored by a calibrated thermocouple tip inserted into a hole drilled into the rim of the temperature controlled base. Sufficient resin composite were placed and levelled to the well’s surface by a glass slab. The plunger’s position was adjusted in which its flat end lightly contacted the surface of resin composite. Then experiment was started by pushing the stop plate and change in load was detected by the load cell, the signal from which was fed to the PC via PMD-1608 unit. A representative time-dependent plotting of packing stress is presented in Figure 3.2. It shows an initial “spike” upon the application of the plunger, and the persistence time of peak stress \( t_p \) was taken as the time after initial spike \( t_1 \) to the time before start of stress relaxation \( t_2 \). The mean packing stress \( \sigma \) was calculated as the average of the stress at \( t_1 \) \( \sigma_i \) and \( t_2 \) \( \sigma_f \). The viscosity \( \eta \) was calculated as the mean packing stress multiplied by the persistence period of peak stress as follows:

\[
\eta = \left( \frac{\sigma_i + \sigma_f}{2} \right) \times t_p
\]

------ (Equation 3.1)

**Figure 3.1:** Schematic diagram showing various parts of the packing stress measurement apparatus.
Figure 3.2: Time-dependent packing stress profile (from $\sigma_i$ to $\sigma_f$) followed by relaxation of stress after the plunger stopped moving.

3.2.1 Calibration of the load cell:

As the penetrometer plunger pressed the resin composites during investigation, force was transferred to the load cell (3 mm height and 13 mm diameter) in transitory manner. The magnitude of the load is dependent upon resin composite’s stiffness, i.e., as the stiffness of resin composite increases, the load transferred to the load cell increases. The signal from the load cell was fed to a personal computer via a signal conditioning unit (ENTRAN. model PS-30A) and data acquisition software (DASYLab 8 software) as a signal in volts (V). The load cell was calibrated by the application of different masses (0.1kg, 0.2kg, 0.5kg, 1kg, 2kg, and 5kg) placed in or der directly on the load cell. The calibration coefficient $[C_\sigma]$ (the slope of the graph of force in Newton against load signal in volts) was then calculated by linear regression and found to be 0.03 with linear plot ($r = 0.999$) (Figure 3.3).

Packing stress (MPa) and viscosity derived from packing stress (MPa.s) can be calculated as follows:

$$Force(N) = \left[9.8 \times Signal(V)\right] \div C_\sigma \quad \text{------ (Equation 3.2)}$$

$$Area = \pi r^2 \quad \text{------ (Equation 3.3)}$$
Where \( r = 1.59 \text{ mm} \) (diameter of the plunger’s tip = 3.18 mm)

\[
\text{Area} = \pi (1.59)^2 = 7.94 \text{mm}^2
\]

\[
\text{Stress (MPa)} = \frac{\text{Force (N)}}{\text{Area}} \\
\text{Stress (MPa)} = \left[ \frac{9.8 \times \text{Signal (V)}}{C_\sigma} \right] \div \pi r^2
\]

As the calibration of the load cell has been done using force in Newton so:

\[
\text{Stress (MPa)} = \left[ \frac{\text{Signal (V)}}{0.03} \right] \div 7.94
\]

\[
\text{Viscosity (MPa.s)} = \text{Stress (MPa)} \times \text{Time (s)}
\]

--- (Equation 3.4)

--- (Equation 3.5)

**Figure 3.3:** Calibration of the load cell.

### 3.3 Temperature control of the FTIR spectroscopy:

The degree of conversion (DC %) at two temperatures namely 23 °C and 37 °C, was measured using FTIR spectroscopy (Avatar 360, Nicolette Analytical Instrument, Thermo Electron Corp., Cambridge, UK) with an attenuated total reflectance (ATR)
sampling accessory having a heated ZnSe crystal performance plate (PIKE Technologies, Cottonwood Drive, Madison, USA). Specimen’s temperature was controlled by a PIKE temperature control module (PIKE Technologies, Cottonwood Drive, Madison, USA) (Figure 4).

Figure 3.4: FTIR spectrometer with ATR sampling accessory and connected to temperature control module.

The ability of the heated ZnSe crystal performance plate and the temperature control module to control the resin composite specimen’s temperature was checked prior to the collection of the spectra. A resin composite specimen contained the tip of a type-K thermocouple was stabilized on the heated ZnSe crystal performance plate. As the temperature adjusted on the temperature control module, signal from thermocouple was fed to a personal computer via a temperature data logger (Pico TC-08 data logger and PicoLog software; Picotech, Cambridge, UK). Figure 3.5 shows time-dependent graphs when the temperature set at 23 °C and 37 °C. Temperature of the specimen was stabilized at 23 ± 1 °C for 70 min when temperature control module set at 23 °C. On the other hand, when temperature control module was set at 37 °C, the temperature of the specimen was elevated to reach 47 °C within 1.5 min, then cooled down to 37 °C within 8 min. However, specimen’s temperature was stabilized at 37 ± 1 °C for 60 min. Therefore, uncured specimens were left for 10 min before collection of spectra.
3.4 Simultaneous determination the shrinkage strain, exotherm, and CTE:

A modified bonded-disk instrument was used in this study to simultaneously determine the shrinkage strain, exotherm, and CTE (Figure 3.6). Un-set resin composite of standardized weight of 0.12g was manipulated as a ball and placed centrally within a 16 mm internal diameter and 1mm thick brass ring bonded on glass plate of 74 x 25 x 3mm in dimension. A flexible microscope cover-slip of 22 x 22mm in dimension and 0.1mm in thickness (Size 0, Chance-Propper Ltd., Warley, UK) was placed over the specimen and pressed gently by another glass plate until it become flattened and evenly contacting both the specimen and brass ring. A type-K thermocouple was passed beneath the brass ring, in a previously drilled groove extended from the edge of glass plate toward its center, and carefully inserted within resin composite samples. The glass plate, brass ring, specimen, cover-slip and thermocouple assembly was mounted in the bonded-disk instrument. This instrument composed of an aluminum stand to which a Linear Variable Displacement Transducer (LVDT) (RDP Electronics, Wolverhampton, UK) was attached. The LVDT was connected to a signal-controlling unit (E309, RDP Electronics, Wolverhampton, UK) then to a personal computer via data-logging system hardware and software (ADC-20 multi-channel data acquisition unit and PicoLog.
software; Picotech, Cambridge, UK). After mounting of glass plate assembly in the bonded-disk instrument, the LVDT was positioned to lightly touch the center of the cover-slip. As shrinkage took place, this cover-slip was pulled downwards and its movement recorded by the LVDT. Free ends of thermocouple were connected to type-K thermocouple amplifier (TCK-4, Audon Electronics, Nottingham, UK) then to the ADC-20 unit. Therefore, outputs of both the LVDT and thermocouple were simultaneously recorded by the PicoLog software.

Polymerization shrinkage strain and temperature of samples were monitored for 60 min. Samples were irradiated for a second time 60 min after the first irradiation. Expansion strain and temperature of samples were monitored for 3 min. The temperature rise during the first irradiation is caused by the reaction heat (exothermic heat) and by heat due to irradiation itself. However, after 60 min most of the polymerization was already completed and any observed heat would be predominantly from irradiation. Rise in temperature caused by exothermic heat could be calculated by subtracting rise in temperature during the second irradiation from the first one (Figure 3.7). Additionally, a value for the coefficient of thermal expansion (CTE) was calculated from the sample expansion ($\Delta L$) due to irradiation heat related to the rise in sample temperature ($\Delta T$) during the second irradiation as follow:

$$CTE = \frac{\Delta L}{\Delta T \times L_0} \quad \text{(Equation 3.6)}$$

![Figure 3.6: Modified bonded-disk instrument](image)
3.4.1 Calibration of the LVDT:

Prior to testing, the LVDT was calibrated using an apparatus constructed for this purpose (Figure 3.8). The LVDT was tightly clamped onto a horizontal stand upon which it was opposed by the anvil of a modified and calibrated digital micrometer (Mitutoyo, RS Components Ltd., Corby, Northants, UK) with a display accuracy of 1 µm. Incremental displacement in µm and the output of the LVDT in mV were recorded. The calibration coefficient $C_\varepsilon$ (the slope of the graph of displacement µm against Pico units in mV) was then calculated by linear regression and found to be 0.0217 with linear plot ($r = 0.999$) (Figure 3.9).
3.4.2 Calibration of the thermocouple connected to the TCK-4 amplifier:

Manufacturer's data of the relationship between the TCK-4 output (mV) and temperature (°C) were used to determine the conversion-factor from mV to temperature (°C). The conversion-factor (the slope of the graph of temperature against TCK-4 output in mV) was then calculated by linear regression and found to be 0.1 with linear plot \( r = 0.999 \) (Figure 3.10).
3.5 Addition of the heating element to the Bioman instrument:

The Bioman instrument [121, 126] was used in this study to measure shrinkage stress kinetics (Figure 3.11) at 23 °C and 37 °C. This instrument is composed of a cantilever load cell with a compliant end and attached firmly to a 2 cm thick stainless steel baseplate. The compliant end has an integral clamp holding a circular steel rod (10 mm in diameter, 22 mm long) in a vertical and perpendicular orientation to the load cell axis. Resin composite specimens were placed between two surfaces, the lower surface of the rod and a glass plate surface. These two surfaces were lightly sandblasted to promote bonding of the composite specimens. The glass plate (3 mm thick) was held tight by an aluminium clamp and a hollow cylindrical bolt. This hollow cylindrical bolt allows for passage of a straight light curing guide to contact the glass plate. The gap between the rod and glass plate is adjusted with the aid of a feeler gauge to 0.8 mm. Resin composite paste of standardised weight (0.12 - 0.15 g) was introduced into this gap to form specimen disk of 10 mm diameter and 0.8 mm thickness (configuration factor = 6.25). The specimen is then photo-activated from below, through the glass plate across its thickness.

During polymerization, the stress created within resin composite causes displacement of the compliant end of the load cell. The load signal from the cantilever load cell was
detected with a strain gauge. This signal was amplified by a wide-range strain indicator (Model 3800, Vishay, Measurements Group, Raleigh, NC, USA) then connected to a personal computer via data-logging system hardware and software (ADC-20 multi-channel data acquisition unit and PicoLog software; Picotech, Cambridge, UK). The stress value in MPa is then obtained from the recorded load divided by the specimen disk area.

A newly designed heating device which contained a heating element and connected to a power supply (Farnell E20-28, Farnell instruments LTD., Wetherby, Yorkshire, England) was used to provide a heat source for stress measurements at 37°C (Figure 3.12). The heating device was carefully designed to provide heat locally. Therefore, specimen’s temperature may increase without change in the temperature of load cell. The power supply was set at 5.00 Volts to heat up the heating element to 75°C and resin composite sample to 37°C. Resin composite sample’s temperature reached 37°C after 30 minutes then stabilized for the next 60 minutes (Figure 3.13).

![Bioman instrument diagram](image)

**Figure 3.11:** Bioman instrument.
Figure 3.12: Heating device above the glass plate, shown in the retracted position.

Figure 3.13 Graph of temperatures vs time of heating element and resin composite specimen.

3.5.1 Calibration of the stress beam load cell:

Prior to testing, the Bioman was calibrated by detaching the components opposing the cantilever end with base plate clamped vertically. A series (n = 8) of 5 kg calibration weights were attached to the cantilever end in the axial load direction via a rod-plus-retainer (Figure 3.14). The calibration coefficient \([C_\sigma]\) (the slope of the graph of load (N) against Pico units in mV) was then calculated by linear regression and found to be 0.083 with linear plot (r = 0.999) (Figure 3.15).
Figure 3.14: Load cell calibration arrangement.

Figure 3.15: Calibration of the stress beam load cell.
3.5.2 Calculation of shrinkage stress:

Data collected in mV ($F_{mV}$) were converted to force in Newton ($F_N$) by multiplication by calibration coefficient ($C_\sigma$):

$$F_N = F_{mV} C_\sigma \quad \text{(Equation 3.7)}$$

The raw stress ($S_r$) was calculated by division of the force ($F_N$) by the area of the circular rod ($A$):

$$S_r = \frac{F_N}{A} \quad \text{(Equation 3.8)}$$

Then $S_r$ was multiplied by the correction factor (4) [121] to give the corrected stress ($S_c$). Therefore, the final equation for calculation of $S_c$ is:

$$S_c = 4S_r = 4 \times \frac{F_N}{\pi r^2} \quad \text{(Equation 3.9)}$$
Chapter 4

Temperature-dependent viscosity of resin-composites

A. A. Alnazzawi, N. Silikas, D. C. Watts
4.1 Abstract:

**Objectives:** To examine a set of resin-composites, formulated with a range of monomers matrix composition mostly of dimethacrylate structures, and the effect of changes in temperature on their packing stress and viscosity.

**Methods:** Six representative resin composites were selected [GRO, GCK, VDD, FXE, GDP, and GDA]. A precision instrument, based upon the penetrometer principle, was designed incorporating a flat-ended probe to penetrate composite pastes under a constant applied stress of approximately 1.1 MPa. Composites were contained within a compact cavity, of diameter 6.35 mm, such that penetration was resisted by a wall-effect, comparable to the effect of cavity walls in a dental cavity. With this instrument, it was possible to measure the packing stress (MPa) generated within each composite and the packing period (s). From these two quantities, values for the composite paste viscosity (MPa.s) were calculated. Experiments were conducted at three different temperatures (23 °C, 30 °C, and 37 °C). Six specimens (n=6) were used at each temperature per material.

**Results:** The generated packing stress covered a small range from 2.07 MPa to 1.96 MPa, however the packing (persistence) period varied from about 0.1 to 1.1 s. The viscosity ranged from 2.14 MPa.s to 0.84 MPa.s at 23 °C. Both properties were reduced significantly at 37 °C compared to 23 °C. The temperature coefficient of viscosity ranged from -0.13 to -0.06 [MPa.s/°C]. FXE showed the lowest coefficient and GDA showed the highest coefficient.

**Significance:** Preheating of resin composites reduces the viscosity. A highly filled resin composite, such as GRO, at 37 °C had a viscosity lower than that of the medium filled GDA at room temperature.
4.2 Introduction:

Growing interest in aesthetics has led to the development of tooth-coloured restorative materials. Resin composites are an example of these materials and consists of inorganic fillers coated with coupling agent dispersed in an organic resin matrix [37]. Since their introduction to dentistry, there has been significant progress in compositions and application techniques [145].

Most of the contemporary resin composites are based on dimethacrylate monomers such as 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy) phenyl] propane (Bis-GMA), Urethane dimethacrylate (UDMA) or their variations, typically diluted with a lower molecular weight monomer such as triethylene glycol dimethacrylate (TEGDMA) [74]. Bis-GMA is a highly viscous monomer due to the presence of stiff bisphenol A core, and two pendant hydroxyl groups which are capable to form strong hydrogen bond. Therefore, another monomer (TEGDMA) with much lower viscosity is added as an efficient diluent in resin composites [93, 146]. On the other hand, increasing the filler loading of resin composites decreases its polymerization shrinkage [88, 91, 93, 145] and increases wear resistance and mechanical properties [68, 87]. However, this may lead to an increase in the resin composite’s viscosity and, therefore, the percentage of the diluent monomer has to be raised to counteract the increased viscosity. In summary, it is paramount to achieve a balance between the relative amounts of base monomers and diluents, which leads to trade-offs among resin viscosity, polymer properties, and the degree of conversion [87].

Handling properties of resin composites are a key factor to consider during their selection. Flow, stickiness to hand instruments and tooth, pack-ability, and slumping resistance are associated with ease of placement and shaping, chair time, and success of the restoration [59-62]. Most of these properties are directly related to the viscosity of resin composites [60, 62-65]. In the clinical situation and during placement in cavities, resin composites are subjected to different actions during application and manipulation. These techniques may include; apply and press, by a plugger, to pack the resin composite in the cavity, and sculpt, by a carver, to shape the occlusal anatomy. However, compression and extension strains are the main pattern displayed during packing of resin composites [147].
Preheating of resin composites can increase the flow and the additional free volume significantly, which may lead to an increase in the number of collisions between reacting molecules due to increased molecular mobility [72]. Thus, preheating may improve the degree of conversions, which consequently may lead to improved mechanical properties [148, 149]. Additionally, as a result of increased flow, preheated resin composites may show improvement in adaptability to cavity walls.

Recent efforts in the development of resin composites gave more attentions to the handling properties such as viscosity, pack-ability, and stickiness [60, 62]. For instance, some manufacturers substituted the classical Bis-GMA/TEGDMA formulations with new alternatives. Therefore, several novel monomers have been introduced; among these are DX-511 by Dupont and TCD-DI-HEA. DX-511 monomer found in GCK is a modified UDMA and has a high molecular weight in comparison to Bis-GMA (895 g/mole vs. 512 g/mole) [145]. On the other hand, TCD-DI-HEA found in VDD (Kulzer) is described as a low shrinkage monomer with low viscosity [110, 145].

The aim of the current study was the extent to which increasing specimen temperature of a range of resin composites from ambient (23 °C) to higher temperatures (30 °C and 37 °C) affects the handling properties. The specific objectives were: to measure the packing stress and viscosity of uncured resin composites at three different temperatures (23 °C, 30 °C, and 37 °C).

The null hypotheses were that changes in temperatures have no effect on: (1) the packing stress, and (2) viscosity of uncured resin composites.
4.3 Materials and methods:

Six commercial photo-activated resin composites were selected on the basis of their matrix resin composition and filler loading (Tables 4.1).

<table>
<thead>
<tr>
<th>Code</th>
<th>Resin composites</th>
<th>Filler loading wt.%</th>
<th>Resin matrix</th>
<th>Lot no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>Grandio</td>
<td>87</td>
<td>Bis-GMA, TEGDMA</td>
<td>581793</td>
<td>Voco, Cuxhaven Germany</td>
</tr>
<tr>
<td>GCK</td>
<td>G C Kalore</td>
<td>82</td>
<td>DX-511, UDMA and dimethacrylate comonomers</td>
<td>0906021</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
<td>81.2</td>
<td>TCD-DI-HEA UDMA</td>
<td>010035</td>
<td>Heraeus Kulzer</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
<td>78.5</td>
<td>BIS-GMA, BIS-EMA (6), TEGDMA, PEGDMA and UDMA</td>
<td>N147105</td>
<td>3M ESPE Germany</td>
</tr>
<tr>
<td>GDP</td>
<td>Gradia Direct Posterior</td>
<td>77</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0910191</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>GDA</td>
<td>Gradia Direct Anterior</td>
<td>73</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0909021</td>
<td>GC America Inc.</td>
</tr>
</tbody>
</table>

*Manufacturer data.

The penetrometer principle was applied to design a precision instrument used in the current study (Figure 4.1). This instrument composed of a steel base, to which two vertical steel pillars (A and B) were bolted. A lever with an arm pivoting via a load bearing pin was attached to steel pillar A, which form together with the steel base a horizontal U shape with the lever extending beyond the base. The free end of this lever arm was weighted by a 500 g mass, whereas its other end was attached to steel pillar B via a stop plate to control the magnitude of its vertical movements. A plunger with a diameter of 3.18 mm was pushed via the lever arm into each unset resin composite to a controlled depth of 2.5 mm under a constant load. Resin composite specimens were contained in a portable specimens well (diameter = 6.35 mm and depth = 4.5 mm, giving a cavity volume = 142.6 mm³), constructed from copper and placed onto a temperature controlled base. Specimens temperature was controlled by heating elements embedded into the temperature controlled base and connected to a general purpose variable power supply. The temperature of the specimens was monitored by a calibrated thermocouple tip inserted into a hole drilled into the rim of the temperature controlled
base. Sufficient resin composite were placed and levelled to the well’s surface by a glass slab. The plunger’s position was adjusted in which its flat end lightly contacted the surface of resin composite. Then experiment started by pushing the stop plate and changes in load was detected by the load cell, the signal from which was fed to the PC via PMD-1608 unit. A representative time-dependent plotting of packing stress is presented in Figure 4.2. It shows an initial “spike” upon the application of the plunger, and the persistence time of peak stress ($t_p$) was taken as the time after initial spike ($t_1$) to the time before start of stress relaxation ($t_2$). The mean packing stress ($\sigma$) was calculated as the average of the stress at $t_1$ ($\sigma_i$) and $t_2$ ($\sigma_f$). The viscosity ($\eta$) was calculated as the mean packing stress multiplied by the persistence time of peak stress as follows:

$$\eta = \left(\frac{\sigma_i + \sigma_f}{2}\right) \times t_p$$

------ (Equation 4.1)

**Figure 4.1**: Schematic diagram showing various parts of the packing stress measurement apparatus.
Figure 4.2: Time-dependent packing stress profile (from $\sigma_i$ to $\sigma_f$) followed by relaxation of stress after the plunger stopped moving.

A total of 108 specimens were examined, divided into 18 groups (n=6). Each material was examined at 23 °C, 30 °C, and 37 °C.

Packing stress and viscosity data among the 18 groups were analysed using One-Way ANOVA (SPSS ver. 16, SPSS Inc., Illinois, USA) ($p < 0.05$). Prior to post hoc tests, data were analysed for equal variances using the homogeneity test ($p < 0.05$). For data of packing stress at 37 °C, and viscosity at 23 °C and 30 °C, equal variances can be assumed, thus Multiple pair-wise comparisons using a Tukey post-hoc test was applied. However, Dunnett’s T3 was applied for data of packing stress at 23 °C and 30 °C, and viscosity at 37 °C as equal variances cannot be assumed. Effect of the temperature on packing stress and viscosity for each material was analysed using t-test for paired data ($p < 0.05$).
4.4 Results:

Table 4.2 and Figure 4.3 summarize mean packing stress (MPa) at 23°C, 30°C, and 37°C of examined resin composites. At 23°C, FXE showed the highest packing stress (2.07 MPa), while GDA showed the lowest stress (1.96 MPa). However, those differences were not statistically significant between examined resin composites (p>0.173), except that between FXE and GDA (p = 0.017). At 30°C, GCK and GRO demonstrated the highest packing stress (1.92 and 191 MPa, respectively) and that were statistically significant from those of GDP and GDA (p<0.006). At 37°C, FXE presented the highest packing stress (1.83 MPa) and those differences were statistically significant from all materials (p<0.022), except for GRO and GCK (p>0.208). Nevertheless, GDA showed the lowest packing stress (1.48 MPa) which was statistically significant from other materials (p<0.003).

All materials demonstrated a lower packing stress at 37°C than 30°C than 23°C. Although all materials showed a statistically significant differences between 23°C and 37°C groups (p<0.022), only GRO and VDD showed a statistically significant differences between 30°C and 37°C groups (p<0.045). All materials showed statistically significant differences between 23°C and 30°C (p<0.012), except for GRO and GCK (p>0.057). The decrease in packing stress with increasing resin composite’s temperature suggested a linear relationship and linear regression gave a negative correlation (r≤-0.94).

Table 4.2: Mean (SD) of packing stress (MPa).

<table>
<thead>
<tr>
<th>Materials</th>
<th>23°C</th>
<th>30°C</th>
<th>37°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>2.06 (0.02)</td>
<td>1.91 (0.04)</td>
<td>1.75 (0.04)</td>
</tr>
<tr>
<td>GCK</td>
<td>2.05 (0.03)</td>
<td>1.92 (0.12)</td>
<td>1.79 (0.04)</td>
</tr>
<tr>
<td>VDD</td>
<td>2.02 (0.01)</td>
<td>1.85 (0.02)</td>
<td>1.70 (0.06)</td>
</tr>
<tr>
<td>FXE</td>
<td>2.07 (0.03)</td>
<td>1.88 (0.01)</td>
<td>1.83 (0.03)</td>
</tr>
<tr>
<td>GDP</td>
<td>1.99 (0.02)</td>
<td>1.71 (0.03)</td>
<td>1.66 (0.02)</td>
</tr>
<tr>
<td>GDA</td>
<td>1.96 (0.07)</td>
<td>1.57 (0.02)</td>
<td>1.48 (0.05)</td>
</tr>
</tbody>
</table>

Different superscript letter indicates significant differences between materials (p<0.05). Within each row beta (β) indicates significant differences between 23°C and 30°C, asterisk (*) indicates significant differences between 23°C and 37°C, and plus (+) indicates significant differences between 30°C and 37°C.
Figure 4.3: Average packing stress at 23 °C, 30 °C, and 37 °C, for six resin composites.

Table 4.3 and Figure 4.4 summarize mean persistence period (s) of packing stress at 23°C, 30 °C, and 37°C of examined resin composites. At 23 °C, FXE showed the highest period (1.03 s), which was statistically significant from other materials (p<0.001) except for GCK and VDD (p>0.393). The lowest value was recorded by GDA (0.43 s), which was statistically significant from other materials (p<0.006) except for GDP (p=0.199). At 30 °C, FXE showed the highest persistence period of packing stress (0.55 s), which was statistically significant from those of other materials (p<0.001) except for GCK and VDD (p>0.267). GDA recorded the lowest period (0.10 s) which was significantly different from other materials (p<0.015) except for GDP (p=0.227). At 37 °C, GCK showed the highest persistence period (0.25 s) which was statistically significant from other materials (p<0.03). However, GDA recorded the lowest value (0.04 s) which was statistically significant from those of other materials (p<0.001) except for GDP (p=0.115). All materials demonstrated lower persistence period of packing stress at 37 °C than 30 °C than 23 °C. These differences were statistically significant between paired groups (p<0.031).
Table 4.3: Mean (SD) of Persistence period (s) of packing stress.

<table>
<thead>
<tr>
<th>Materials</th>
<th>23 °C</th>
<th>30 °C</th>
<th>37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>0.65 (0.026) (^{a})<em>, (^{d})</em></td>
<td>0.29 (0.012)</td>
<td>0.12 (0.013) (^{a})<em>, (^{z})</em></td>
</tr>
<tr>
<td>GCK</td>
<td>0.94 (0.050) (^{b})<em>, (^{c})</em></td>
<td>0.51 (0.085) (^{b})*</td>
<td>0.25 (0.019) (^{b})<em>, (^{c})</em></td>
</tr>
<tr>
<td>VDD</td>
<td>0.93 (0.049) (^{b})*</td>
<td>0.44 (0.064) (^{a})<em>, (^{b})</em></td>
<td>0.14 (0.005) (^{a})<em>, (^{z})</em></td>
</tr>
<tr>
<td>FXE</td>
<td>1.03 (0.038) (^{b})*</td>
<td>0.55 (0.081) (^{b})*</td>
<td>0.20 (0.026) (^{c})<em>, (^{d})</em></td>
</tr>
<tr>
<td>GDP</td>
<td>0.55 (0.064) (^{a})<em>, (^{c})</em>, (^{e})*</td>
<td>0.21 (0.038) (^{c})<em>, (^{d})</em></td>
<td>0.08 (0.007) (^{d})<em>, (^{z})</em></td>
</tr>
<tr>
<td>GDA</td>
<td>0.43 (0.082) (^{e})*</td>
<td>0.10 (0.005) (^{d})*</td>
<td>0.04 (0.008) (^{d})<em>, (^{z})</em></td>
</tr>
</tbody>
</table>

Different superscript letter indicates significant differences between materials \((p<0.05)\). Within each row beta (β) indicates significant differences between 23 °C and 30 °C, asterisk (*) indicates significant differences between 23 °C and 37 °C, and plus (+) indicates significant differences between 30 °C and 37 °C.

Figure 4.4: Average persistence period (from \(t_1\) to \(t_2\)) of packing stress at 23 °C, 30 °C, and 37 °C, for six resin composites.

Table 4.4 and Figure 4.5 summarize mean viscosity (MPa.s) at 23°C, 30 °C, and 37°C of examined resin composites. At 23 °C, FXE demonstrated the highest viscosity (2.14 MPa.s) and this was statistically significant from those of other materials \((p<0.001)\) except for GCK and VDD \((p>0.087)\). However, GDA recorded the lowest viscosity (0.84 MPa.s) which was significantly different from other materials \((p<0.001)\) except for GDP \((p=0.126)\). At 30 °C, FXE showed the highest viscosity (1.02 MPa.s) which was statistically significant from those of other materials \((p<0.001)\) except for GCK and VDD \((p>0.168)\). Although GDA recorded the lowest viscosity (0.16 MPa.s) which was...
statistically significant from those of other materials (p<0.006), it was statistically insignificant from GDP (p=0.207). On the other hand, at 37 °C, GCK showed the highest viscosity (0.44 MPa.s) which was statistically significant from other materials (p<0.016). However, GDA recorded the lowest viscosity (0.06 MPa.s) which was statistically significant from those of other materials (p<0.03).

All materials demonstrated lower viscosity at 37 °C than 30 °C than 23 °C. However, these differences were statistically significant between paired groups (p<0.032). The decrease in viscosity with increasing resin composite’s temperature suggested a linear relationship and linear regression gave a negative correlation (r≤-0.92).

Table 4.4: Mean (SD) of viscosity (η) derived from packing stress (MPa) and persistence period (s).

<table>
<thead>
<tr>
<th>Materials</th>
<th>23 °C</th>
<th>30 °C</th>
<th>37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>1.31 (0.03)</td>
<td>0.54 (0.02)</td>
<td>0.22 (0.01)</td>
</tr>
<tr>
<td>GCK</td>
<td>1.90 (0.10)</td>
<td>0.96 (0.15)</td>
<td>0.44 (0.02)</td>
</tr>
<tr>
<td>VDD</td>
<td>1.89 (0.09)</td>
<td>0.81 (0.11)</td>
<td>0.24 (0.01)</td>
</tr>
<tr>
<td>FXE</td>
<td>2.14 (0.09)</td>
<td>1.02 (0.16)</td>
<td>0.37 (0.04)</td>
</tr>
<tr>
<td>GDP</td>
<td>1.07 (0.12)</td>
<td>0.36 (0.06)</td>
<td>0.13 (0.01)</td>
</tr>
<tr>
<td>GDA</td>
<td>0.84 (0.13)</td>
<td>0.16 (0.01)</td>
<td>0.06 (0.01)</td>
</tr>
</tbody>
</table>

Different superscript letter indicates significant differences between materials (p<0.05). Within each row beta (β) indicates significant differences between 23 °C and 30 °C, asterisk (*) indicates significant differences between 23 °C and 37 °C, and plus (+) indicates significant differences between 30 °C and 37 °C.

Figure 4.5: Viscosity at 23 °C, 30 °C, and 37 °C, for six resin composites.
The temperature dependence of viscosity is given by the Arrhenius equation:

$$\eta = Ae^{\frac{E_a}{RT}}$$

----- (Equation 4.2)

Where $\eta$ is the viscosity; $A$ the pre-exponential factor; $E_a$ the activation energy; $T$ temperature in kelvin, and $R$ the gas constant (8.31451 kJ mol$^{-1}$).

When $\ln \eta$ is plotted against $1/T$, a straight line was obtained (Figure 4.6), the slope was given as:

$$Slope = \frac{E_a}{R}$$

----- (Equation 4.3)

Therefore, activation energy is:

$$E_a = Slope.R$$

----- (Equation 4.4)

**Figure 4.6:** Arrhenius plot of temperature-dependent of viscosity for six resin composites.

When viscosity is plotted against $T$, a straight line was obtained. The slope of that graph is the temperature coefficient of viscosity (C):
Values of activation energy ($E_a$) and temperature coefficient (C) of viscosity are summarized in Table 4.5.

**Table 4.5:** Activation energy ($E_a$) and temperature coefficient (C) of viscosity.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E_a$ [kJ mol$^{-1}$]</th>
<th>C [MPa.s$^{o}$C$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>42.21</td>
<td>-0.078</td>
</tr>
<tr>
<td>GCK</td>
<td>34.39</td>
<td>-0.104</td>
</tr>
<tr>
<td>VDD</td>
<td>48.77</td>
<td>-0.118</td>
</tr>
<tr>
<td>FXE</td>
<td>41.48</td>
<td>-0.126</td>
</tr>
<tr>
<td>GDP</td>
<td>50.11</td>
<td>-0.068</td>
</tr>
<tr>
<td>GDA</td>
<td>62.58</td>
<td>-0.056</td>
</tr>
</tbody>
</table>

The decrease in packing stress with decreasing viscosity suggested a linear relationship and gave positive correlations at 23 °C, 30 °C, and 37 °C ($r = 0.81$, 0.84, and 0.88, respectively)(Figure 4.7).

**Figure 4.7:** Association between viscosity and packing stress at: (a) 23 °C, (b) 30 °C, and (c) 37 °C for six resin composites.
4.5 Discussion:

This study aimed to investigate the handling properties and its temperature dependence of resin composites. Therefore, a set of commercially available resin composites with a range monomer matrix composition and different filler loading were examined at three temperatures; ambient temperature (23 °C), body temperature (37 °C), and intermediate temperature (30 °C). Two of these materials are based on novel monomers; DX-511 in GCK and TCD-DI-HEA in VDD. Additionally, three materials are nanohybrid (GRO, GCK, and VDD), one is nanofilled (FXE), and two are microhybrid (GDA and GDP).

In the current study, packing stress is exhibited by the resistance to plunger’s intrusion, mostly caused by the direct collisions between fillers in the resin matrix [147, 150]. In general, microhybrid resin composites showed lower packing stress than other materials at all applied temperatures. Although FXE demonstrated the highest packing stress at 23 °C and 37 °C, GCK recorded the highest at 30 °C. This could be explained by that FXE is a nanofilled resin composite contains a mix of 20 nm silica nanoparticles and agglomerated nanoclusters that are 0.6-1.4 µm. Thus, the smaller was the filler size; the number of fillers was higher for similar volumes, which led to increase in the surface area and resulted in higher interaction between filler particles. However, GCK is based on DX-511 monomer, which is a urethane methacrylate macromonomer with rigid core [151] and has high molecular weight in comparison to Bis-GMA (895 g/mole vs. 512 g/mole) [145, 152].

A noticeable influence of temperature on packing stress was found for all materials. However, this was more evident when resin composite’s temperature raised from ambient room temperature (23 °C) to the body temperature (37 °C). This is probably due to the fact that resin composite viscosity decreases as the temperature increased [44, 60, 68, 153], resulting in less resistance to the filler mobility within resin composite and leading to less stress during force application. Therefore, the first hypothesis was rejected.

Viscosity of resin composites is a complex phenomenon, especially when heat is introduced as a factor. Resin components and filler particles, and their interactions can play a marked role on resin composites viscosity [59, 68]. Although FXE, GCK, and VDD demonstrated a significant higher viscosity than other materials at 23 °C and 30
°C, viscosity of VDD at 37 °C was not significant from GRO. FXE contains UDMA and Bis-EMA monomers, while GCK and VDD contain UDMA, which are of a higher viscosity than the TEGDMA in GRO. Furthermore, these resin composites contain nanofillers, which may contribute to its higher viscosity than that of GDA and GDP. Lee et al [60] studied experimental composites composed of an identical resin matrix of Bis-GMA and TEGDMA and contained different types and fractions of fillers. They reported that, for similar filler volumes, the viscosity increased as the filler size decreased. GDP has higher filler loading than that of GDA; this may contribute to the higher viscosity exhibited by GDP.

Results of the current study showed that temperature has a prominent effect on the viscosity of investigated resin composites. Hence, viscosity decreased exponentially as the temperature of resin composites increased. This is in agreement with previous studies [44, 60, 68]. The temperature dependence of viscosity is given by the Arrhenius equation:

\[ \eta = Ae^{\frac{E_a}{RT}} \]

Therefore, where \( \eta \) is the viscosity and A the pre-exponential factor with \( E_a \) the activation energy and T temperature in kelvin and R the gas constant (8.31451 kJ mol\(^{-1}\)); this relation could explain the decreased in viscosity in accordance to the increase in temperature. Thus, the second hypothesis was rejected.

Analysis of the temperature coefficient of viscosity demonstrated negative correlation with viscosity at 23 °C, 30 °C, and 37 °C (\( r = -0.99, -0.95, \) and \(-0.80, \) respectively). Thus, the lower the temperature coefficient of viscosity, the more the changes in viscosity over the temperature range.

Results of the current study showed that there were positive correlations between the viscosity and packing stress at applied temperatures. Therefore, as the viscosity decreased, the packing stress decreased. Additionally, the present study showed that heating up the highly filled resin composites such as GRO to 37 °C provided viscosity lower than that of the medium filled GDA at room temperature.
4.6 Conclusions:

Within the limitations of this study, it can be concluded that:

(1) Temperature has a prominent effect on the handling properties of resin composites, i.e., as temperature increases the packing stress and viscosity decreases.

(2) Monomer matrix composition and filler loading have an effect on handling properties of resin composites.

(3) Magnitude of the temperature coefficient of viscosity governs the changes in viscosity over the temperature range, i.e., the lower the temperature coefficient of viscosity, the more the changes in viscosity over the temperature range.
Chapter 5

Temperature-dependent degree of conversion of resin-composites

A. A. Alnazzawi, N. Silikas, D. C. Watts
5.1 Abstract:

Objectives: To examine a set of dimethacrylate resin composite formulated with a range of monomers matrix composition and the effect of composition on degree of conversion and its temperature dependence.

Methods: Six commercially available resin composites that incorporate a range of different matrix monomers were selected. The degree of conversion at 23 °C and 37 °C was measured using FTIR spectroscopy with an attenuated total reflectance (ATR) sampling accessory having a heated ZnSe crystal performance plate. Measurements were done immediately (0h), and one hour (1h) after irradiation for 40 s at 550 mW/cm² (energy density = 22 J/cm²). Three specimens (n=3) were used at each temperature per material.

Results: Degree of conversion at 23 °C ranged from 32.19 % to 42.39 % and 43.19 % to 52.93 % for 0h and 1h after photo-activation, respectively. GRO showed the highest value in 0h group, while VDD showed the highest degree of conversion value and the highest increase in degree of conversion (57.6 %) after 1h. Degree of conversion at 37 °C ranged from 50.85 % to 56.84 % and from 53.92 % to 66.05 % for 0h and 1h after photo-activation, respectively. VDD showed the highest degree of conversion at both times, while the highest increase after 1h recorded by GCK (16.5 %). All materials demonstrated higher degree of conversion at 37 °C than 23 °C.

Significance: Photo-activation of resin composites at elevated temperature (37°C) resulted in higher degree of conversion than ambient room temperature (23 °C).
5.2 Introduction:

Demands for resin composites increased recently due to improvements in its mechanical and aesthetic properties. Set resin composites composed of a complex cross-linked organic matrix reinforced by inclusion of inorganic fillers sometimes blended with organic one [70]. However, polymerization of resin composites exhibits partial conversion of carbon double bonds, leaving a considerable amount of unreacted methacrylate groups [46, 71, 72]. This is believed to be due to restrictions on the mobility of reactive species caused by the rapid development of the polymeric network after photo-activation [71, 73]. Inadequate levels of the degree of conversion may compromise mechanical properties, wear resistance and colour stability of resin composites. Additionally, residual monomers and initiators may leach from resin composites, jeopardizing the biocompatibility. On the other hand, maximizing degree of conversion to improve those properties may lead to increased polymerization shrinkage and establish brittle resin composites [75].

Currently, most of the commercially available resin composites are based on dimethacrylate monomers such as 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (Bis-GMA), Urethane dimethacrylate (UDMA) or their variations, typically diluted with a lower molecular weight monomer such as triethylene glycol dimethacrylate (TEGDMA) [74]. Resin composites based on these monomer showed a degree of conversion ranged from 40 % to 73 % [46, 71]. Recently, two novel modified urethane monomers were introduced; these are DX-511 by Dupont and Bis-(acryloyloxymethyl) tricycle [5.2.1.02,6] decane (TCD-DI-HEA). DX-511 monomer found in GCK has a high molecular weight (895 g/mole). Additionally, it has a long rigid core to decrease polymerization shrinkage and flexible arms to increase its reactivity [152]. TCD-DI-HEA found in VDD (Kulzer) is a low viscosity monomer, according to the manufacturer, and has three linked rings in its central portion [154].

The degree of conversion of resin composites can be monitored by various techniques. These techniques include halogenation of residual carbon double bonds, differential scanning calorimetry, differential thermal analysis (DTA), infrared spectroscopy, and Fourier-transform infrared (FTIR) [71, 74]. Among these techniques, FTIR spectroscopy has been widely used as a reliable, relatively easy, and non-destructive technique to determine the degree of conversion of resin composites. It is based on the
absorption of infrared radiation owing to the molecular vibrations of the polymer’s functional groups.

The aim of the current study was to determine the degree of conversion immediately (0h), and one hour (1h) after photo-activation of a range of commercially available resin composites with varying matrices at different temperatures. The specific objectives were: (i) to measure degree of conversion at 23 and 37 °C (0h and 1h) using FTIR technique, (ii) to calculate the percentage of increase in degree of conversion between 0h and 1h for both temperatures.

The null hypotheses were (1) temperature has no effect on the degree of conversion, (2) there is no difference in the degree of conversion of the investigated materials based on various matrix monomers, and (3) the degree of conversion values at 1h are not different from those of 0h.
5.3 Materials and Methods

Six commercial photo-activated resin composites were selected on the basis of their matrix monomers composition and filler loading (Table 5.1).

Table 5.1: Investigated resin-composites.

<table>
<thead>
<tr>
<th>Code</th>
<th>Resin composites</th>
<th>Filler loading</th>
<th>Resin matrix</th>
<th>Lot no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>Grandio</td>
<td>87, 71.4</td>
<td>Bis-GMA, TEGDMA</td>
<td>581793</td>
<td>Voco, Cuxhaven Germany</td>
</tr>
<tr>
<td>GCK</td>
<td>G C Kalore</td>
<td>82, 69</td>
<td>DX-511, UDMA and dimethacrylate co-monomers</td>
<td>0906021</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
<td>81.2, 64</td>
<td>TCD-DI-HEA UDMA</td>
<td>010035</td>
<td>Heraeus Kulzer</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
<td>78.5, 63.3</td>
<td>BIS-GMA, BIS-EMA (6), TEGDMA, PEGDMA and UDMA</td>
<td>N147105</td>
<td>3M ESPE Germany</td>
</tr>
<tr>
<td>GDP</td>
<td>Gradia Direct Posterior</td>
<td>77, 65</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0910191</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>GDA</td>
<td>Gradia Direct Anterior</td>
<td>73, 64</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0909021</td>
<td>GC America Inc.</td>
</tr>
</tbody>
</table>

*Manufacturer data.

The degree of conversion (DC %) at two temperatures namely 23 °C and 37 °C, was measured using FTIR spectroscopy (Avatar 360, Nicolette Analytical Instrument, Thermo Electron Corp., Cambridge, UK) with an attenuated total reflectance (ATR) sampling accessory having a heated ZnSe crystal performance plate (PIKE Technologies, Cottonwood Drive, Madison, USA). Specimen’s temperature was controlled by a PIKE temperature control module (PIKE Technologies, Cottonwood Drive, Madison, USA) (Figure 5.1). The peaks of absorbance of the specimens before and after curing were obtained at a resolution of 4 cm⁻¹ and 32 scans in the range of 4000-400 cm⁻¹. Each specimen was photo-activated for 40 s using a visible light curing unit with an irradiance of 550 mW/cm² (energy density = 22 J/ cm²), (Optilux 500 – Kerr, Orange, CA, USA).

The degree of conversion of each specimen was determined from the ratio of absorbance intensities of aliphatic C=C at 1637 cm⁻¹ against the internal reference before and after photo-activation. The aromatic C=C (peak at 1608 cm⁻¹) was selected as the internal
reference of the Bis-GMA based resin composites which are GRO and FXE (Figure 5.2). On the other hand, the secondary amide (peak at 1537 cm\(^{-1}\)) was selected as the internal reference for the UDMA based resin composite [74, 155, 156] which are GC, VDD, GDP and GDA (Figure 5.3). The degree of conversion (%) was calculated as follows:

\[
DC\% = \left[1 - \left(\frac{AC_{\text{aliphatic}}}{AC_{\text{IR}}} / \frac{AU_{\text{aliphatic}}}{AU_{\text{IR}}}\right)\right] \times 100
\]  \hspace{1cm} \text{(Equation 5.1)}

Where \(AC_{\text{aliphatic}}\) is the absorbance peak at 1637 cm\(^{-1}\) of the cured specimen, \(AC_{\text{IR}}\) is the absorbance peak for the internal references (either 1608 cm\(^{-1}\) or 1537 cm\(^{-1}\)) of the cured specimen, \(AU_{\text{aliphatic}}\) is the absorbance peak at 1637 cm\(^{-1}\) of the uncured specimen and \(AU_{\text{IR}}\) is the absorbance peak for the internal references of the uncured specimen. The degree of conversion of the same material was calculated at two stages: immediately after curing (0h) and then after one hour (1h).

![Figure 5.1: FTIR spectrometer with ATR sampling accessory and connected to temperature control module.](image)

A total of 36 specimens were examined, divided into 12 groups (n= 3). Each material was examined at two different temperatures 23°C and 37°C. Additionally, for each temperature degree of conversion was measured at two different times (0h and 1h after curing).
Figure 5.2: Representative spectra of FXE (Bis-GMA based). Uncured (a), 0h after curing (b), and 1h after curing (c).

Figure 5.3: Representative spectra of GDA (UDMA based). Uncured (a), 0h after curing (b), and 1h after curing (c).

Statistical software (SPSS ver. 16, SPSS Inc., Illinois, USA) was used, and data were analysed by One-way analysis of variance (ANOVA). Prior to post hoc tests, data were analysed for equal variances using the homogeneity test (p < 0.05). For data of degree of conversion at 23 °C and 37 °C, equal variances can be assumed, thus Multiple pair-wise comparisons using a Tukey post-hoc test were conducted to establish homogenous subsets at p=0.05. Differences between groups for temperature and time effects were assessed using a paired t-test.
5.4 Results:

Table 5.2, and Figure 5.4 and 5.5 summarize mean values of degree of conversion (%) for 0h and 1h at 23°C and 37°C. At 23 °C and 0h after curing, GRO showed the highest degree of conversion (42.39 %), and that was statistically significant from other materials (p≤0.011). GCK demonstrated the lowest degree of conversion (32.19 %) and that was statistically insignificant from other materials (p≥0.296) with the exception from that of GRO (p<0.001). On the other hand, VDD exhibited the maximum degree of conversion (52.93 %) at 23 °C and 1h after curing. This value was statistically significant from those of other materials (p≤0.002). Additionally, GCK presented the lowest degree of conversion (43.19 %) and that was statistically significant from other materials (p≤0.023) except that of GDP (p=0.376).

<table>
<thead>
<tr>
<th>Materials</th>
<th>0h At 23 °C</th>
<th>1h</th>
<th>0h At 37 °C</th>
<th>1h</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>42.39 (0.76)</td>
<td>a,A*</td>
<td>47.65 (1.11)</td>
<td>a,B+</td>
</tr>
<tr>
<td>GCK</td>
<td>32.19 (1.42)</td>
<td>b,A*</td>
<td>43.19 (1.44)</td>
<td>b,B+</td>
</tr>
<tr>
<td>VDD</td>
<td>33.59 (1.83)</td>
<td>b,A*</td>
<td>52.93 (1.30)</td>
<td>c,B+</td>
</tr>
<tr>
<td>FXE</td>
<td>35.70 (2.79)</td>
<td>b,A*</td>
<td>47.28 (1.83)</td>
<td>b,B+</td>
</tr>
<tr>
<td>GDP</td>
<td>35.43 (2.73)</td>
<td>b,A*</td>
<td>45.38 (1.30)</td>
<td>b,b,B+</td>
</tr>
<tr>
<td>GDA</td>
<td>34.95 (1.11)</td>
<td>b,A*</td>
<td>47.50 (0.54)</td>
<td>a,B+</td>
</tr>
</tbody>
</table>

Within each column different superscript small letter indicates significant differences between materials (p<0.05).
Within each temperature different superscript capital letter in the same row indicates significant differences in the same material (p<0.05).
Within same time and different temperature, asterisk (*) and plus (+) superscript in the same row indicates significant differences in the same material (p<0.05).

At 37 °C, VDD demonstrated the highest degree of conversion 0h and 1h after curing (56.84 % and 66.05 %, respectively). Those values were statistically significant from other materials (p≤0.009 and p≤0.002, respectively). In contrary, GCK showed the lowest degree of conversion 0h after curing (50.85 %). However, this was statistically insignificant from those values of other materials (p≥0.847) with the exception from that of VDD (p=0.001). Whereas, GRO exhibited the lowest degree of conversion (53.92 %) 1h after curing and that was statistically significant from other materials (p≤0.016) except GDP (p=0.559).

Within same temperature, all tested materials showed higher values of degree of conversion at 1h after curing than those measured 0h after curing. However, these
differences were statistically significant for both temperatures (p≤0.036), with the exception of that of GRO at 37 °C (p=0.118).

Within the same time, all tested materials demonstrated a higher degree of conversion’s value at 37 °C than those at 23 °C. These differences were statistically significant at both times 0h and 1h after curing (p≤0.012 and p≤0.021, respectively).

![Figure 5.4: Degree of conversion at 23 °C and 37 °C (0h and 1h after curing).](image-url)
Figure 5.5: Time-dependence of degree of conversion at ambient room temperature (23 °C) and oral temperature (37 °C)
5.5 Discussion:

FTIR is a relatively easy and non-destructive technique that has been recognized as a useful instrument for observing degree of conversion in resin composites [74]. This technique is based on the detection of C=C stretching vibrations before and after polymerization of resin composites. In the current study, degree of conversion was monitored at two temperatures (23 °C and 37 °C) and two different times (0h and 1h after photo-activation). The variation in the degree of conversion of the examined resin composites within each temperature and at the same time can be explained on the basis of their chemical composition differences, mainly the resin monomer functionality [77].

At 23 °C, the obtained mean values of the degree of conversion for examined materials ranged from 32.19 % to 42.39 % and 43.19 % to 52.93 % for 0h and 1h after photo-activation groups, respectively. On the other hand, at 37 °C mean values were from 50.85 % to 56.84 % and from 53.92 % to 66.05 % for 0h and 1h after photo-activation groups, respectively. Previous studies [46, 71], reported that the conversions of photo-activated resin composites ranging from 40 % to 73 %, which are higher than degree of conversion values of the current study. This can be explained by that specimens examined in the current study which were inspected immediately and one hour after photo-activation by the ATR technique while those of previous studies were examined by transmission technique typically, 24 hours after photo-activation. Therefore, the first hypothesis was rejected.

At 23 °C and 0h after photo-activation, GRO showed the highest degree of conversion (42 %), which was statistically significant from those of other examined materials. Moreover, it showed the lowest increase in the degree of conversion after 1h (12.41 %) compared to other examined materials (≥28.09 %). Resin matrix of GRO formulated from Bis-GMA/TEGDMA monomers. Bis-GMA is a highly viscous resin due to the presence of stiff bisphenol A core, and two pendant hydroxyl groups which are capable to form strong hydrogen bond. Therefore, TEGDMA with much lower viscosity is added as an efficient diluent in resin composites [93]. Sideridou et al [78] studied the effect of addition of TEGDMA to Bis-GMA on the polymerization rate. They reported that this mixture demonstrated a maximum rate from the beginning of photo-activation and higher polymerization reactivity than that of Bis-GMA alone. Thus, the addition of TEGDMA to dilute the Bis-GMA in GRO leads to more rapid propagation of the
polymerization reaction. In this case, most of the conversion took place immediately after photo-activation, leading to reduced post-cure polymerization.

At 23 °C and after 1h, VDD demonstrated the highest degree of conversion (52.93 %), and that was statistically significant from those of other examined materials. Additionally, it exhibited the highest increase in degree of conversion after 1h (57.60 %). TCD-DI-HEA the main monomer present in VDD is a low viscosity monomer, according to the manufacturer, and has three linked rings in its central portion [154]. The presence of these rings decreases the monomer flexibility and may retard polymerization due to steric hindrance [110]. Additionally, UDMA contained in VDD may enhance its degree of conversion[93]. UDMA is more reactive and has a lower viscosity than Bis-GMA [157]. This could be explained by the greater flexibility and weaker intermolecular bonds promoted by UDMA than Bis-GMA. Also, this increase in the degree of conversion was evident in other materials that contained UDMA, namely; GCK, FXE, GDA and GDP. All these materials showed an increase in the degree of conversion after 1h (ranged from 28.09 % to 35.9 %), and that was higher than that of GRO (12.41 %). Therefore, the second hypothesis was rejected.

At 37 °C, VDD showed the highest degree of conversion at both 0h and 1h after photo-activation (56.84 % and 66.05 %, respectively), which was statistically significant from other examined materials. However, all materials showed an increase in their degree of conversion values at 37 °C compared to those at 23 °C. This could be explained by increases in the number of collisions of reacting molecules caused by decreased viscosity, increased additional free volume and increased molecular mobility due to temperature’s rising of resin composite [72]. Moreover, the increase in temperature may lead to delay in alteration of the termination process of polymerization from diffusion-controlled to reaction-diffusion-controlled due to improved flexibility of the polymer chain [97, 158].

Results of the present study showed that specimens with initially low degree of conversion (0h) after photo-activation tended to have more increase in degree of conversion after 1h. This was obvious by the increase of more than 28 % for all materials at 23 °C with the exception of the GRO. Therefore, greater amounts of degree of conversion occur when the reaction is advancing slowly. On the other hand, at 37 °C all materials demonstrated an increase in degree of conversion of less than 17 % with a
degree of conversion 0h after photo-activation of more than 50 %. Thus, in the initially highly polymerized composites, it is hard for the residual unpolymerized species to be involved in further free-radical reaction due to increase in viscosity [73, 159]. Thus, the third hypothesis was rejected.

5.6 Conclusions:

Within the limitations of this study, it can be concluded that:

(1) Matrix monomers composition of resin composites has an effect on the degree of conversion.
(2) Temperature has a noticeable effect on the degree of conversion, i.e., as the temperature increases the degree of conversion increases.
(3) Magnitude of initial degree of conversion (0h) has an effect on the final degree of conversion (1h), i.e., as the initial degree of conversion is low, percentage of increase in the degree of conversion after 1 h is high and vice versa.
Chapter 6

Simultaneous determination of polymerization shrinkage, exotherm and thermal expansion coefficient for dental resin-composites.

A. A. Alnazzawi and D. C. Watts
6.1 Abstract:

**Objectives:** To measure shrinkage strain, exotherm, and coefficient of thermal expansion (CTE), simultaneously for a set of representative resin composites.

**Methods:** Six commercially available resin composites with different filler loadings were selected. A modified bonded-disk instrument that includes temperature-monitoring apparatus was used to measure simultaneously: shrinkage strain, exotherm, and CTE. Shrinkage strain and temperature of disk specimens (n =3 / materials) were monitored for 1 h after irradiation for 20 s at 1200 mW/cm² (energy density = 24 J/cm²). Disks were irradiated for a second time 60 min after the first irradiation. Axial expansion strain and temperature were monitored for 3 min. Exotherm was obtained from differences between temperature rise during 1st and 2nd irradiations. CTE was calculated from disk axial expansion due to irradiation heat (ΔL) and rise in temperature (ΔT) during the second irradiation.

**Results:** The final shrinkage strain values ranged from 1.7 to 2.34 %, exotherm values ranged from 4.66 to 9.43 °C, and CTE ranged from 18.44 to 24.63 (10⁻⁶/°C). Negative correlations were found between filler loading and shrinkage strain, exotherm, and CTE. Positive correlation was apparent between shrinkage strain and CTE.

**Conclusions:** The modified bonded-disk instrument could be used to measure simultaneously shrinkage strain, exotherm, and CTE of resin composites.

Keywords: resin composite; shrinkage strain; exotherm; thermal expansion; bonded-disk; polymerization.
6.2 Introduction:

Increased desire for aesthetics has led to growing demands on resin composites. Resin composites and their application techniques have undergone significant progress since their first introduction to dentistry by Bowen [145]. Photo-activated resin composites are polymerized through an addition reaction [160]. Inevitably, their polymerization is accompanied with polymerization shrinkage. Current resin composites including flowable types exhibit a volumetric polymerization shrinkage ranging from less than 1 to 6 % [26, 27]. Shrinkage may create stress at the restoration tooth interface and may lead to restoration failure [161]. Also, resin composites after placement in teeth are subjected to dimensional changes due to thermal variations of the oral environment, which can be expressed by their coefficient of thermal expansion (CTE) [135]. CTEs of enamel and dentin are 17 (10⁻⁶/°C) and 11 (10⁻⁶/°C), respectively [137]. Therefore, it is ideal if the CTE of resin composites are in the range of enamel and dentin to help preserve the tooth-restoration bond.

Halogen lights, plasma arc lamps, argon ion lasers, and light emitting diodes (LED) have been used for photo-activation of resin composites [162]. However, owing to several advantages, LED light curing units (LCUs) have gained in popularity relative to quartz tungsten halogen (QTH) units. These advantages include higher efficiency, lower consumption of energy, no need for external cooling, and remarkably long lifetime without a significant loss of intensity [13, 35, 162]. Progress in LED technology has led to the availability of high power LED LCUs. However, their high light intensities of up to 2000 mW/cm² lead to heat generation that may harm the pulp and gingiva [29, 31, 162]. This means a reduction in one of the important characteristics of previous LED versions, which was low heat generation [163].

The polymerization of resin composites is an exothermic reaction. Temperature rise during photo-activation of resin composites is a result of light source energy and the polymerization reaction [28-33]. Some previous studies reported temperature rises of more than 20 °C during photo-activation of resin composites [34, 35]. Theoretically, transmission of heat through dentin can damage pulpal tissues. Zack and Cohen, in their animal study in 1965, demonstrated that an intra-pulpal temperature rise of 5.5 °C is damaging [164]. Later, Lloyd et al argued against the Zack and Cohen methodology and suggested that greater rises in temperature than 5.5 °C may be necessary before any
pulpal damage occurs [165, 166]. Additionally, dentin could protect the pulp against any thermal shock if it is sufficiently thick [31, 162].

The aims of the current study were: (a) to determine simultaneously the shrinkage strain, exotherm, and CTE of a range of representative resin composites; (b) to explore the role of filler loading on shrinkage strain, exotherm, and CTE. The specific objectives were to: (i) measure shrinkage strain and temperature changes using the bonded-disk instrument, (ii) calculate the exotherm, and (iii) calculate the CTE.

The null hypotheses were: (1) there are no correlations between filler loading and shrinkage strain, exotherm, and CTE, and (2) there is no correlation between shrinkage strain and CTE.
6.3 Materials and Methods:

Six representative photo-activated resin composites were selected on the basis of their matrix resin composition and filler loading (Table 6.1).

<table>
<thead>
<tr>
<th>Code</th>
<th>Resin composites</th>
<th>Filler loading wt.%* vol.%</th>
<th>Resin matrix</th>
<th>Lot no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>Grandio</td>
<td>87</td>
<td>Bis-GMA, TEGDMA</td>
<td>581793</td>
<td>Voco, Cuxhaven Germany</td>
</tr>
<tr>
<td>GCK#</td>
<td>G C Kalore</td>
<td>82</td>
<td>DX-511, UDMA and dimethacrylate comonomers</td>
<td>0906021</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
<td>81.2</td>
<td>TCD-DI-HEA UDMA</td>
<td>010035</td>
<td>Heraeus Kulzer</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
<td>78.5</td>
<td>BIS-GMA, BISEMA (6), TEGDMA, PEGDMA and UDMA</td>
<td>N147105</td>
<td>3M ESPE Germany</td>
</tr>
<tr>
<td>GDP#</td>
<td>Gradia Direct Posterior</td>
<td>77</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0910191</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>GDA#</td>
<td>Gradia Direct Anterior</td>
<td>73</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0909021</td>
<td>GC America Inc.</td>
</tr>
</tbody>
</table>

*Manufacturer data; # contain pre-polymerized filler particles.

The bonded-disk instrument [96, 104] was used in this study to measure shrinkage strain kinetics (Figure 6.1). Un-set resin composite of standardized mass of 0.12g was manipulated as a ball and placed centrally within a 16 mm internal diameter and 1mm thick brass ring bonded onto a glass plate 74 x 25 x 3mm in dimension. A flexible microscope cover-slip of 22 x 22 mm area and 0.1mm thickness (Size 0, Chance-Propper Ltd., Warley, UK) was placed over the specimen and pressed gently by another glass plate until it become flattened and evenly contacting both the specimen and brass ring. A type-K thermocouple was passed beneath the brass ring, along a previously drilled groove extending from the edge of the glass plate toward its center, and carefully inserted within the resin composite paste disks. The glass plate, brass ring, specimen, cover slip and thermocouple assembly were mounted in the bonded-disk instrument. This instrument included an aluminum stand to which a Linear Variable Displacement Transducer (LVDT) was attached. The LVDT was connected to a signal-controlling unit (E309, RDP Electronics, Wolverhampton, UK) then to a personal computer via data-loging system hardware and software (ADC-20 multi-channel unit
and PicoLog software; Picotech, Cambridge, UK). After mounting the glass plate assembly in the bonded-disk instrument, the LVDT was positioned to lightly touch the center of the cover-slip. As shrinkage took place, this cover-slip was pulled downwards and its movement recorded by the LVDT. Free ends of the thermocouple wires were connected to a type-K thermocouple amplifier (TCK-4, Audon Electronics, Nottingham, UK) then to the ADC-20 unit.

![Diagram of the bonded-disk instrument](image)

**Figure 6.1:** Modified bonded-disk instrument.

A LCU with an irradiance of 1200 mW/cm² (Elipar S10, 3M ESPE, St. Paul, MN, USA) was used to irradiate the specimen from beneath the glass plate for 20 s (energy density = 24 J/cm²). Polymerization shrinkage strain and temperature of samples were monitored for 60 min. Samples were irradiated for a second time 60 min after the first irradiation. Expansion strain and temperature of samples were monitored for 3 min.

The temperature rise during the first irradiation is caused by the reaction heat (exothermic heat) and by heat due to irradiation itself. However, after 60 min most of the polymerization was already completed and any observed heat would be predominantly from irradiation. The rise in temperature as a function of time (the exotherm $\Delta T(t)$) caused by exothermic heat could be calculated by subtracting the integrated rise in temperature $\Delta T(t)$ during the second irradiation from the first one (Figure 6.2) [35, 165, 167]. Additionally, a value for the coefficient of thermal
expansion (CTE) was calculated from the sample expansion ($\Delta L$) due to irradiation heat, related to the rise in sample temperature ($\Delta T$) during the second irradiation as follow:

$$CTE = \frac{\Delta L}{\Delta T \times L_0}$$

----- (Equation 6.1)

Figure 6.2: Superposition of rise in temperature due to 1st and 2nd irradiations, and exotherm.

A total of 18 samples were examined, divided into 6 groups (n = 3).

Statistical software (SPSS ver. 16, SPSS Inc., Illinois, USA) was used, and data were analyzed by One-way analysis of variance (ANOVA). Multiple pair-wise comparisons using a Tukey post-hoc test were conducted to establish homogenous subsets at p=0.05.
6.4 Results:

Integrated temperature/time profiles were calculated for each material (Table 6.2; units: °C.min) then plotted graphically (Figure 6.3). High correlations were evident between peak temperatures and integrated temperature/time profiles for total temperature rise ($r = 0.998$), LCU contribution ($r = 0.988$), and exotherm ($r = 0.968$) (Figure 6.4).

**Table 6.2: Integrated temperature/time profiles (mean): Units: °C.min.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Total rise</th>
<th>LCU contribution</th>
<th>Exotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>5.36</td>
<td>3.46</td>
<td>1.89</td>
</tr>
<tr>
<td>GCK</td>
<td>7.11</td>
<td>4.76</td>
<td>2.35</td>
</tr>
<tr>
<td>VDD</td>
<td>6.67</td>
<td>3.16</td>
<td>3.51</td>
</tr>
<tr>
<td>FXE</td>
<td>5.12</td>
<td>2.72</td>
<td>2.40</td>
</tr>
<tr>
<td>GDP</td>
<td>7.45</td>
<td>3.90</td>
<td>3.16</td>
</tr>
<tr>
<td>GDA</td>
<td>8.32</td>
<td>4.77</td>
<td>3.43</td>
</tr>
</tbody>
</table>
Figure 6.3: Temperature/time profiles for resin-composites: (a) total rise, (b) LCU contribution, (c) exotherm.
Figure 6.4: Correlations between peak temperatures and integrated temperature/time profiles: (a) total rise, (b) LCU contribution, and (c) exotherm.

Representative time-dependent curves of shrinkage strain and temperature for FXE for 60 min and 3 min are presented in Figures 6.5 and 6.6, respectively. Table 6.3 and Figures 6.7 to 6.9 summarize mean shrinkage strain (%), exotherm (°C) and CTE (10−6/°C) of examined materials. Mean values of final shrinkage strain ranged from 1.70 % to 2.34 %. The lowest value was recorded for GCK (1.70 %), which was statistically significant from the other materials (p<0.004) except GRO (p=0.422). GDA showed the highest value (2.34 %), which was statistically significant from other materials (p<0.013). Furthermore, shrinkage strain data correlated negatively with filler loading (r = -0.89) (Figure 6.10a).
**Figure 6.5:** Time-dependence of shrinkage-strain and temperature for 60 min for FXE resin-composite.

**Figure 6.6:** Time-dependence of shrinkage-strain and temperature (expanded for the first 3 min) for FXE resin-composite.
Table 6.3: Mean (SD) values of polymerization shrinkage-strain (%), exothermic heat (°C) and CTE (10⁻⁶/°C).

<table>
<thead>
<tr>
<th>Resin composites</th>
<th>Shrinkage-strain</th>
<th>Exotherm (°C)</th>
<th>CTE (10⁻⁶/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>1.80 (0.08) a,b</td>
<td>4.66 (0.89) a</td>
<td>18.44 (1.08) a</td>
</tr>
<tr>
<td>GCK</td>
<td>1.70 (0.03) a</td>
<td>5.48 (1.02) a</td>
<td>21.61 (0.38) b,c</td>
</tr>
<tr>
<td>VDD</td>
<td>1.95 (0.05) b,c</td>
<td>8.37 (0.29) b</td>
<td>21.07 (1.02) a,c</td>
</tr>
<tr>
<td>FXE</td>
<td>2.05 (0.05) c,d</td>
<td>5.48 (0.21) a</td>
<td>21.97 (1.19) b,c,d</td>
</tr>
<tr>
<td>GDP</td>
<td>2.13 (0.09) d</td>
<td>8.44 (0.92) b</td>
<td>21.69 (0.94) b,c</td>
</tr>
<tr>
<td>GDA</td>
<td>2.34 (0.04) e</td>
<td>9.43 (1.15) b</td>
<td>24.63 (1.10) d</td>
</tr>
</tbody>
</table>

Within each column; different superscript letter indicates significant differences between materials (p<0.05).

Figure 6.7: Mean and standard deviation of shrinkage-strain for resin-composites.

Figure 6.8: Mean and standard deviation of peak temperatures: (a) total rise, (b) LCU contribution, and (c) exotherm.
Mean exotherm peak temperature rises were from 4.66 °C to 9.43 °C. GRO had the lowest value (4.66 °C), which was statistically significant from other materials (p<0.002) except GCK and FXE (p>0.821). The highest value was with GDA (9.43 °C). This was significantly different from other materials (p<0.001) except for VDD and GDP (p>0.634). Generally, as the filler loading increased, the exotherm value decreased. A negative correlation was evident (r = -0.77) (Figure 6.10b).

Mean values of CTE ranged from 18.44 (10^-6/°C) to 24.63 (10^-6/°C). The lowest CTE was recorded for GRO, which was statistically significant from other materials (p<0.019) except VDD (p=0.059). Although GDA showed the significantly highest CTE among all examined materials (p<0.031), this difference was insignificant statistically from that of FXE (p=0.055). The decrease in CTE values with increasing filler loading suggested a linear relationship and linear regression gave a good correlation (r = -0.95) (Figure 6.10c).
Figure 6.10: Linear correlations between: (a) shrinkage-strain, (b) Exotherm, (c) CTE – all versus filler loading, and between (d) shrinkage-strain and CTE.
6.5 Discussion:

In the present study, the bonded-disk instrument was modified to measure simultaneously polymerization shrinkage strain and temperature of six representative resin composites. A carefully drilled groove on the glass plate was created so that thermocouple could be passed beneath the brass ring without disturbing the cover-slip or specimen. Thus, the disk-specimen configuration, a crucial aspect of the bonded-disk technique, was maintained.

Simultaneous plotting of shrinkage strain and temperature for the first three minutes after the commencement of photo-activation (Figure 6.4) showed a characteristic transition point in the strain that occur in concurrence with a sudden drop in temperature. This phenomenon happens immediately after the end of irradiation. The sudden drop in temperature leads to thermal contraction that adds to the shrinkage strain. Hofmann et al. [35] compared the effect of LED and QTH irradiation on shrinkage strain kinetics, temperature rise, and hardness of photo-activated resin composites. Although this phenomenon was evident in the QTH irradiated group, they concluded that its absence for the LED group was due to a small temperature change. However, a LED LCU with higher energy density (24 J/cm²) was used in the current study. The maximum shrinkage strains, ranging from 1.70 % to 2.34 %, are in broad agreement with previous studies [26, 27, 93, 168-171]. GC and GRO demonstrated the lowest shrinkage strain, while GDA exhibited the highest shrinkage strain. Results demonstrated a strong negative correlation between shrinkage strain and percent filler loading (r = -0.89). In general, as the filler load increased, the shrinkage strain decreased [88, 89, 91, 92, 172].

The polymerization of resin composites is an exothermic reaction. Temperature rise during photo-activation of resin composites is a result of light source irradiance and the polymerization reaction [28-30]. Results showed that the mean temperature rises during the first irradiation ranged from 8.91 to 15.35 °C. Previous studies reported temperature rises up to 20 °C during photo-activation of resin composites [34, 35]. Hofmann et al. [35] recorded a temperature rise of 8.2 to 12.4 °C during photo-activation of resin composites by a LED curing unit. However, the higher values obtained in the current study could be explained by the application of higher irradiance [163]. On the other hand, temperatures rises during the second irradiation ranged from 5.44 to 9.75 °C. As
most of the polymerization was already completed during the second irradiation, this rise in temperature is caused by the photon energy of irradiation. Asmussen and Peutzfeldt [163] compared the relationship between light intensity of different LED and QTH LCUs and the rise in temperature in already cured resin composites. They found that the high intensity LED caused a rise in temperature of 9.4 °C. This is comparable to the finding of the current study.

A negative correlation (r = -0.77) was found between the exotherm magnitude and the filler content of the examined resin composites. This arises from the decrease in number of C=C double bonds from decreased monomer content. That is, increasing the filler loading reduces the exothermic response by dilution of the reactive groups and also from the filler acting as a heat sink [173].

The critical temperature that leads to pulp damage is a controversial. Zach and Cohen reported that an increase of 5.5 °C in pulp temperature of Macaca Rhesus monkeys was damaging [164]. However, Lloyd et al. [165] questioned the methods of Zach and Cohen and concluded that the critical temperature rise, before onset of pulpal damage, may be higher than 5.5 °C. In their clinical study, Baldissara et al. [166] evaluated the effect of pulp temperature rises from 8.9 to 14.7 °C. They reported that temperature rise up to 11.2 °C did not harm the pulp. In any case, the duration of the temperature stimulus would be crucial. Although the highest temperature rise in the present study was 15.35 °C, from an ambient baseline of 23 °C, clinically the actual temperature increase transferred to the pulp would be much lower. Intra-orally, more resin composite surface area is in contact with tooth tissues, therefore, excess heat is dissipated easily. Additionally, owing to its low thermal conductivity, dentin could insulate and protect pulp tissue from thermal shock. Finally, the oral temperature baseline is lower than 37 °C especially with rubber dam application [35]. Plasmans et al. [174] reported that with application of rubber dam the oral cavity temperature was lowered to 25.1 °C.

The numerical values of the coefficients of thermal expansion (CTE) obtained via the bonded-disk measurement should be interpreted with care. Normally, such coefficients can be defined for a temperature change ΔT either on a linear or a volumetric basis, respectively, by the following equations:
\[ CTE_{\text{Linear}} = \frac{\Delta L}{L_0 \Delta T} \]  \hspace{1cm} -----(Equation 6.2)

\[ CTE_{\text{Volumetric}} = \frac{\Delta V}{V_0 \Delta T} \]  \hspace{1cm} -----(Equation 6.3)

In the case of isotropic materials:

\[ CTE_{\text{Volumetric}} = 3 \times CTE_{\text{Linear}} \]  \hspace{1cm} -----(Equation 6.4)

This may be established by the following standard argument relating linear and volumetric strain, which also applies to considerations of linear and volumetric shrinkage.

A cubical volume \( V_0 \) that undergoes isotropic expansion (strain: \( \varepsilon \)) to volume \( V \) is given by:

\[ V = V_0 + \Delta V = V_0 (1 + \varepsilon_v) \]  \hspace{1cm} -----(Equation 6.5)

But for a unit cell, \((1 + \varepsilon_v) = (1 + \varepsilon_x)(1 + \varepsilon_y)(1 + \varepsilon_z)\)  \hspace{1cm} -----(Equation 6.6)

If the Unit cell is isotropic \((1 + \varepsilon_v) = (1 + \varepsilon_L)^3 = 1 + 3\varepsilon_L + 3\varepsilon_L^2 + \varepsilon_L^3\) -----(Equation 6.7)

Hence \( \varepsilon_v = 3\varepsilon_L + 3\varepsilon_L^2 + \varepsilon_L^3 \approx 3\varepsilon_L \)  \hspace{1cm} -----(Equation 6.8)

However, if the specimen does not behave isotropically, then for such anisotropic materials equation 3 no longer holds.

Several lines of evidence converge on the conclusion that the strain measured axially in a bonded-disk experiment is far from isotropic and indeed is close to, or in some cases identical with the volumetric strain value. This evidence may be summarised by the following points:

- The lower surface of the disk specimen bonded to the glass plate experiences a constraint in the radial direction (or x, y plane), such that \( \varepsilon_x = \varepsilon_y \approx 0 \). Hence \( \varepsilon_{\text{vol}} \approx \varepsilon_z \).

That is shrinkage occurs either mainly or even wholly in the axial (z) direction.
Since the shrinkage of 100% methylmethacrylate (MMA) is 21 %, [175] for a 3:1 PMMA/MMA dough system, the theoretical volumetric shrinkage 
\[ \varepsilon_{\text{vol}} = \frac{21}{4} = 5.25 \text{%} \]. Experimentally [176] \( \varepsilon_{\text{bonded\_disk}} = 5.4(0.2) \text{%} \)

For a number of resin composites [27, 177], the bonded-disk value of shrinkage strain has been found to be very close to the volumetric value, as determined by dilatometry or Archimedes principle.

It follows that the CTE \( \varepsilon_{\text{bonded\_disk}} \) is expected to be closer to the CTE \( \varepsilon_{\text{volumetric}} \) value, rather than the CTE \( \varepsilon_{\text{linear}} \) value, even though it is measured in the linear axial direction.

Clinically, it is desirable for the CTE of resin composites to match those of tooth structure in order to maintain the bond between tooth structures and restoration. In the present study, recorded values of CTE are greater than those of enamel and dentin: 17 (10\(^{-6}\)/oC) and 11 (10\(^{-6}\)/oC), respectively [137]. However, a strong negative correlation (r = -0.95) was found between CTE and filler loading. This is in broad agreement with previous studies [135, 138, 140-142]. The literature shows that the CTE of filler particles ranges from 0.5 to 6 (10\(^{-6}\)/oC), and that of the resin matrix ranges from 110 to 190 (10\(^{-6}\)/oC) [138, 139]. Therefore, as the percent filler loading increases, the effect from the high CTE resin matrix is lowered leading to lower composite CTE. Additionally, a good positive correlation was demonstrated between shrinkage strain and CTE (r=0.75). Thus, materials of low shrinkage strain exhibited lower CTE on account of their higher filler loading (Figure 6.10d). Baek et al. [143] demonstrated a similar trend in their study. Therefore, the null hypotheses were rejected.

6.6 Conclusions:

Within the limits of this study, it can be concluded that:

(1) Shrinkage strain, exotherm, and a value for CTE can be measured simultaneously for resin composites by using the modified bonded-disk instrument.
(2) Increased filler loading reduces shrinkage strain, exotherm, and CTE.
(3) There was a positive correlation between shrinkage strain and CTE for the resin composites studied.
Chapter 7

Temperature-dependent polymerization shrinkage strain kinetics of resin-composites

A. A. Alnazzawi, N. Silikas, D. C. Watts
7.1 Abstract:

Objectives: To examine a set of resin composites formulated with a range of monomer matrix compositions mostly of dimethacrylate structures and the effect of composition on shrinkage strain and its temperature dependence.

Methods: Six commercially available resin composites that incorporate a range of different matrix monomers were selected. Some of these matrices included pre-polymerized filler particles. The percentage of organic phase was determined by combustion of specimens at 800 °C for 1 h. The shrinkage strain kinetics at 23 °C and 37 °C was measured using the bonded-disk instrument. Measurements were monitored for 1 h after irradiation for 40 s at 550 mW/cm² (energy density = 22 J/cm²). Three samples (n=3) were used at each temperature per material.

Results: The final shrinkage strain values ranged from 1.79 to 2.36 % at 23 °C and from 2.11 to 2.45 % at 37 °C. A negative correlation was found between the percent filler loading (wt. %) and shrinkage strain at 23 °C and 37 °C (r=0.93 and 0.72 respectively). A strong, positive, correlation was found between activation energy for the shrinkage kinetics and percent organic phase calculated from combustion (r=0.86).

Significance: A representative range of resin composites exhibited a significant variation of shrinkage strain which correlated negatively with the total filler loading or positively with the proportion of organic matrix phase. However, for most formulations the shrinkage magnitudes were also dependent upon the ambient temperature of cure, increasing significantly as this was raised to oral temperature (37 °C). This temperature dependence should be considered during clinical handling.
7.2 Introduction:

Since their introduction in 1960s, resin composites have undergone several changes to improve their properties. Resin composites are heterogeneous materials with three main constituents (phases); the resin matrix (continuous phase), the filler particles (dispersed phase) and coupling agent (interfacial phase) [1, 2]. During setting, they undergo a polymerization reaction which is a chemical process involve the linking of smaller monomer molecules to create a cross-linked network. As a result of polymerization, resin composite shrinks because of the conversion of inter-molecular distances, typically Van der Waals bond (0.3-0.4 nm) into intra-molecular covalent bond (0.15 nm) [3-5]. In general, the larger the monomer unit, the fewer the number of covalent bonds that are needed to build the final polymer network. As a result, higher polymerization shrinkage is associated with utilization of low molecular weight monomers. Contemporary resin composites show a volumetric polymerization shrinkage ranging from less than 1 to 6 % [6, 7]. However, polymerization shrinkage is affected by many factors, including functionality of monomer, average molecular weight, degree of conversion, curing conditions and amount of filler loading [4, 8-14].

Over the last decades, numerous enhancements have been attained in physical and mechanical properties of resin composites. Modifications in fillers and matrix were the main area of researches that led to these enhancements. Fillers are incorporated in resin composites to improve their properties [15]. This improvement was achieved by altering the filler composition, particle size, distribution, and percent of filler loading. Indeed, percent of filler loading is known to have a strong influence on polymerization shrinkage of resin composites. Increasing the percent of filler content in resin composite decreases its polymerization shrinkage [9-12, 14, 16]. This relation holds true for a relatively high level of filler loading. Thereafter, the percentage of low molecular weight monomer has to be raised to reduce the increased viscosity caused by high filler loadings. In summary, a balance in relative amounts between constituents of resin matrix during formulation of resin composites is paramount, and this leads to trade-offs between viscosity, mechanical properties, and degree of conversion [1].
Most of commercial resin composites utilize Bis-GMA or UDMA mixed with a lower molecular weight monomer such as TEGDMA to lower their high viscosity [15]. Recently, several novel monomers have been introduced; among these are DX-511 by Dupont and TCD-DI-HEA. DX-511 monomer found in GCK is a modified UDMA and has a high molecular weight in comparison to Bis-GMA (895 g/mole vs. 512 g/mole) [15, 17]. TCD-DI-HEA, as found in VDD (Kulzer), is described as a low shrinkage monomer with low viscosity [15, 18].

The objective of the current study was to determine, for a set of representative resin composites, the extent to which increasing specimen temperature from ambient (23 °C) to body temperature (37 °C) affects the setting process as assessed by shrinkage kinetic measurements. The specific objectives were: (i) to determine organic phase % by the combustion technique, and (ii) to measure shrinkage strain at 23 and 37 °C using the bonded-disk instrument.

The null hypotheses were (1) shrinkage strain has no correlation with filler loading, (2) temperature has no effect on shrinkage strain, and (3) there is no correlation between activation energy for shrinkage kinetics and the resin matrix proportions in resin composites.
7.3 Materials and Methods:

Six commercial photo-activated resin composites were selected on the basis of their matrix resin composition and filler loading (Table 7.1).

Table 7.1: Investigated resin-composites

<table>
<thead>
<tr>
<th>Code</th>
<th>Resin composites</th>
<th>Filler loading wt. %</th>
<th>Resin matrix</th>
<th>Lot no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>Grandio</td>
<td>87</td>
<td>Bis-GMA, TEGDMA</td>
<td>581793</td>
<td>Voco, Cuxhaven Germany</td>
</tr>
<tr>
<td>GCK</td>
<td>G C Kalore</td>
<td>82</td>
<td>DX-511, UDMA and dimethacrylate co monomers</td>
<td>0906021</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
<td>81.2</td>
<td>TCD-DI-HEA UDMA</td>
<td>010035</td>
<td>Heraeus Kulzer</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
<td>78.5</td>
<td>BIS-GMA, BIS-EMA (6), TEGDMA, PEGDMA and UDMA</td>
<td>N147105</td>
<td>3M ESPE Germany</td>
</tr>
<tr>
<td>GDP</td>
<td>Gradia Direct Posterior</td>
<td>77</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0910191</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>GDA</td>
<td>Gradia Direct Anterior</td>
<td>73</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0909021</td>
<td>GC America Inc.</td>
</tr>
</tbody>
</table>

*Manufacturer data.

Filler contents:

To allow for the fact that some resin composites contain organic content other than matrix monomers, two sets of data were obtained:

1. The percentages of filler loading (total fillers) were taken from manufacturers.

Therefore, the weight percentage of resin content (matrix organic) was calculated as follows:

\[
\text{Matrix organic (wt.%) = 100} - \text{Total fillers (wt.%) \quad \text{(Equation 7.1)}
\]

2. The percentages of inorganic fillers and organic content (total organic) by weight \((n = 3)\) were determined by combustion of 0.5 g of each material at 800 °C for 1 h. The weight of each specimen was measured before and after combustion with a precision balance (E400D, Ohaus, Brooklyn, USA) with accuracy of 0.1 mg. By comparing the weight differences, the percentage of
inorganic fillers by weight were calculated. Additionally, by subtracting those values from 100, the percentages of total organic by weight were determined.

\[
\text{Total organic (wt.\%) = 100 - Inorganic fillers content (wt.\%)} \quad \text{(Equation 7.2)}
\]

**Shrinkage kinetics measurements:**

The bonded-disk instrument [19-21] was used in this study to measure shrinkage strain kinetics (Figure 7.1). Un-set resin composite of standardized weight of 0.12g was placed centrally within a 16mm internal diameter and 1mm thick brass ring bonded on a glass plate of 74 x 25 x 3mm in dimension. A flexible microscope cover-slip of 22 x 22mm in dimension and 0.1mm in thickness was placed over the specimen and pressed gently by another glass plate until it become flattened and evenly contacted both the specimen and brass ring. The glass plate, brass ring, specimen and cover-slip assembly was mounted in the bonded-disk instrument. This instrument has an aluminum stand to which a Linear Variable Displacement Transducer (LVDT) was attached. The LVDT was connected to a signal-controlling unit then to a personal computer via data-logging system hardware and software. After mounting the glass plate assembly in the bonded-disk instrument, the LVDT was positioned-lightly touching the center of the cover-slip. As shrinkage took place, this cover-slip was pulled downwards and its movement recorded by the LVDT. Shrinkage plots were obtained as a function of time.

![Figure 7.1: Bonded-disk instrument](image-url)
A light cure unit, specially provided with straight curing tip, with an irradiance of 550 mW/cm², (Optilux 500 – Kerr, Orange, CA, USA) was used to irradiate the specimen from beneath the glass plate for 40 s (energy density = 22 J/cm²). Polymerization shrinkage strain was monitored for 60 min. The temperature of the specimen was controlled by an adjustable power supply unit connected to the metal base beneath the specimen-glass plate assembly. Temperature changes were monitored by a digital thermometer inserted into a hole drilled into the metal base.

A total of 36 specimens were examined, divided into 12 groups (n= 3). Each material was examined at two different temperatures 23°C and 37°C.

Statistical software (SPSS ver. 16, SPSS Inc., Illinois, USA) was used, and data were analysed by One-way analysis of variance (ANOVA). Prior to post hoc tests, data were analysed for equal variances using the homogeneity test (p < 0.05). For data of shrinkage strain at 23 °C and 37 °C, equal variances can be assumed, thus Multiple pairwise comparisons using a Tukey post-hoc test were conducted to establish homogenous subsets at p=0.05. Differences between groups for temperature effects were assessed using a paired t-test.

**Analysis of the rate of shrinkage via time constant:**

Activation Energy ($E_a$) of the shrinkage kinetics was calculated from time constants ($\tau$) of shrinkage strain as follow:

Shrinkage (%) can be re-expressed as ‘Normalized Shrinkage’ [$S_N$] by dividing each measured shrinkage value (data-point) by the Maximum shrinkage observed (at 60 min). The Normalized Shrinkage data-points then vary between Zero and One. Then by fitting to a simple exponential growth curve, the mathematical equations can be expressed in terms of a time constant ($\tau$) as follows:

$$S_N = 1 - e^{-t/\tau}$$

------ (Equation 7.3)

However, the time-constant $\tau$ corresponds to the time-point at which:

$$S_N = 1 - (1/e) = 0.632$$

------ (Equation 7.4)
Thus, the time constant is the time value corresponding to 63.2% of the maximum shrinkage (Figure 7.2). The time constant is the reciprocal of a rate-constant ($k$). The temperature dependence of chemical rate constants is generally expressed by the Arrhenius Equation.

$$k = 1/\tau = Ae^{-E_a/RT} \quad \text{------ (Equation 7.5)}$$

Here, $A$ is the ‘pre-exponential’ factor, $E_a$ is the Activation Energy per mole, $R$ is the Gas Constant = 8.3145 JK$^{-1}$ mol$^{-1}$, $T$ is the absolute (Kelvin) temperature. By taking the natural logs of both sides of the above equation:

$$\ln k = \ln \tau^{-1} = \ln A - E_a/RT \quad \text{------ (Equation 7.6)}$$

By plotting $\ln \tau^{-1}$ versus $1/T_{\text{Kelvin}}$ (Figure 7.3), the negative slope was given as:

$$-\text{Slope} = (E_a/R) \quad \text{------ (Equation 7.7)}$$

$$E_a = |\text{Slope}| \cdot R \quad \text{------ (Equation 7.8)}$$

![Figure 7.2: Time-dependent plotting of normalized shrinkage.](image)
Figure 7.3: Graph of $\ln \tau^{-1}$ versus $1/T_{\text{Kelvin}}$
7.4 Results:

Table 7.2 summarizes total filler loading (wt. %), inorganic filler (wt. %), matrix organic (wt. %), and total organic (wt. %) of the investigated resin composites. GRO had the highest weight percentage of inorganic fillers (84.4 wt. %) followed by VDD (76.75 wt. %). GDA had the lowest weight percentage of inorganic fillers followed by GDP (54.25 wt. % and 42.49 wt. %, respectively).

Table 7.2: Summary of total fillers (wt. %), inorganic fillers (wt. %), matrix organic (wt. %), and total organic (wt. %).

<table>
<thead>
<tr>
<th>Resin composites</th>
<th>Total fillers (wt. %)</th>
<th>Inorganic fillers (wt. %)</th>
<th>Matrix organic (wt. %)</th>
<th>Total organic (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>87</td>
<td>84.44 (0.06)</td>
<td>13</td>
<td>15.56 (0.06)</td>
</tr>
<tr>
<td>GCK*</td>
<td>82</td>
<td>70.52 (0.13)</td>
<td>18</td>
<td>29.48 (0.13)</td>
</tr>
<tr>
<td>VDD</td>
<td>81.2</td>
<td>76.75 (0.07)</td>
<td>18.8</td>
<td>23.25 (0.07)</td>
</tr>
<tr>
<td>FXE</td>
<td>78.5</td>
<td>72.82 (0.03)</td>
<td>21.5</td>
<td>27.18 (0.03)</td>
</tr>
<tr>
<td>GDP*</td>
<td>77</td>
<td>57.51 (0.17)</td>
<td>23</td>
<td>42.49 (0.17)</td>
</tr>
<tr>
<td>GDA*</td>
<td>73</td>
<td>45.75 (0.05)</td>
<td>27</td>
<td>54.25 (0.05)</td>
</tr>
</tbody>
</table>

# contain pre-polymerized filler particles.

Table 7.3 columns 2 &3 and Figure 7.4 summarize mean shrinkage strain (%) at 23°C and 37°C of the examined materials. At 23°C, the lowest shrinkage was recorded for GRO, which was significantly lower than the other materials (p<0.006) with the exception of GCK (p=0.708). GDA showed the highest shrinkage (2.36%), which was significantly greater than the other materials (p<0.001).

Table 7.3: Mean (SD) values of maximum polymerization shrinkage-strain (%) at 1h, time constants $\tau$ (min) at 23°C and 37°C, and activation energy ($E_a$) [kJ mol$^{-1}$].

<table>
<thead>
<tr>
<th>Resin composites</th>
<th>Maximum shrinkage-strain (%)</th>
<th>$\tau$ (min)</th>
<th>$\tau$ (23°C) / $\tau$ (37°C)</th>
<th>$E_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 23°C</td>
<td>At 37°C</td>
<td>At 23°C</td>
<td>At 37°C</td>
</tr>
<tr>
<td>GRO</td>
<td>1.79 (0.03)$^{a*,ab}$</td>
<td>2.14 (0.05)$^{c,e}$</td>
<td>0.199</td>
<td>0.152</td>
</tr>
<tr>
<td>GCK</td>
<td>1.82 (0.03)$^{a,b*,*}$</td>
<td>2.11 (0.06)$^{a}$</td>
<td>0.351</td>
<td>0.213</td>
</tr>
<tr>
<td>VDD</td>
<td>1.90 (0.06)$^{b,c,e}$</td>
<td>2.31 (0.05)$^{c,d,e}$</td>
<td>0.331</td>
<td>0.192</td>
</tr>
<tr>
<td>FXE</td>
<td>1.96 (0.02)$^{e}$</td>
<td>2.35 (0.04)$^{d,e}$</td>
<td>0.250</td>
<td>0.183</td>
</tr>
<tr>
<td>GDP</td>
<td>2.16 (0.02)$^{d}$</td>
<td>2.18 (0.01)$^{a,c,d}$</td>
<td>0.284</td>
<td>0.183</td>
</tr>
<tr>
<td>GDA</td>
<td>2.36 (0.01)$^{e}$</td>
<td>2.45 (0.13)$^{d}$</td>
<td>0.299</td>
<td>0.181</td>
</tr>
</tbody>
</table>

For shrinkage strain within each column; different superscript letter indicates significant differences between materials (p<0.05). Within each row asterisk indicates significant differences between the paired groups (p<0.05).
At 37°C, the lowest shrinkage was obtained with GCK (2.11%), which was significantly lower than the other materials (p<0.031) except GRO and GDP (p>0.783). However, the highest shrinkage was for GDA (2.45%), which was statistically greater than the other materials (p<0.003) except VDD and FXE (p>0.165).

All materials showed a statistically significant increase in shrinkage between 23°C and 37°C (p<0.05), except for GDA (p=0.363) and GDP (p=0.288) (Table 7.3). The decrease in shrinkage with increasing filler loading gave linear regression relationship with a strong correlation at 23°C (r=0.93) and a lower correlation at 37°C (r=0.72) (Figure 7.5).
Figure 7.5: Linear correlation between shrinkage-strain (%) and filler loading (wt%) at 23°C and 37°C, for six resin composites.

Table 7.3 columns 4-6 summarize time constants at 23°C and 37°C and their ratios for the investigated materials. All materials had a shorter time constant at 37 °C than at 23 °C. GRO had the shortest values at 23°C and 37°C (11.9 s and 9.1 s, respectively) and also the lowest ratio of time constants among the examined materials (1.31). GCK recorded the longest values at 23°C and 37°C (21.1 s and 12.8 s, respectively). However, the highest ratio of time constants was found for VDD (1.72).

Table 7.3 column 7 summarizes activation energies for shrinkage kinetics. GRO had the lowest activation energy for shrinkage kinetics followed by FXE (15.4 and 20 kJ mol⁻¹, respectively). The highest activation energy was recorded for GDA followed by GCK and GDP (42.2, 33.8, and 33.7 kJ mol⁻¹, respectively). In general, as the weight percent of organic content increased, the activation energy increased (Figure 7.6). There was a positive correlation between activation energy and total organic weight percent \( r = 0.86 \) and a positive correlation between activation energy and matrix organic weight percent \( r = 0.75 \).
**Figure 7.6:** Linear correlation between activation energy $E_a$ (kJ mol$^{-1}$) and organic content (wt.%), $r = 0.75$ and $0.86$ for matrix organic and total organic, respectively.
7.5 Discussion:

A set of resin composites formulated with a range monomer matrix composition mostly of dimethacrylate, and with different filler loadings were examined. Some of these materials incorporated pre-polymerized filler particles (GCK, GDP, and GDA). Measurements were made of: (1) shrinkage strain, at two temperatures (23 °C and 37 °C), and (2) percentage of organic content in these resin composites, both utilizing established techniques [10, 14, 20-24].

In the current study, a combustion technique was applied to calculate the percentages of organic phase by weight. It is a widely used method, is relatively straightforward and provides reproducible results. In the current study, specimens were combusted at 800 °C, while other researchers applied different temperatures ranging from 400 to 900 °C [12, 22, 25-28]. Sabbagh et al [22] applied two methods: Thermogravimetric Analysis (TG) and ashing in air (combustion) to determine the percentages of inorganic fillers by weight. They demonstrated stable patterns of the TG curves after 750 °C, which mean no further loss of mass after this temperature.

In the current study, differences were found between the weight percentages of total fillers (given by manufacturers) and those calculated from the combustion technique (inorganic fillers). This could be explained by differences in thickness and amount of coupling agent applied to fillers. Additionally, manufacturers have their own unique methods of silanization, and they apply different techniques for calculation of filler loading by weight. On the other hand, greater differences were found with three materials, which are GCK, GDA and GDP. These materials included pre-polymerized fillers in their filler system. The combustion technique destroys the organic part and measures only the inorganic constituents of those fillers.

Shrinkage strains at 1h, at both 23 °C and 37 °C, ranging from 1.79 to 2.45%, are in agreement with previous studies [6, 7, 14, 24, 29-31]. GRO and GCK exhibited the lowest shrinkage strain, while GDA showed the highest shrinkage strain. Results of the current study demonstrated a good negative correlation (Figure 5) between shrinkage strain and filler loading at both 23 °C and 37 °C (r = 0.93 and 0.72 respectively). This inverse relationship between shrinkage strain and filler loading has been found in previous studies [10-13, 32]. Therefore, the first hypothesis was rejected.
The mean shrinkage strains at 37 °C were numerically and significantly greater (p<0.05) than those at 23 °C for all cases except GDA and GDP. As a result, the second hypothesis was partially rejected. This trend is in agreement with a previous study [33], which showed that increasing temperature affects (a) the maximum shrinkage and (b) the shrinkage rate, i.e. as the temperature increased the maximum shrinkage and shrinkage rate increased. This increase could be linked to the effect of elevated temperature on monomer degrees of conversion [13], which is generally accepted [34, 35]. Many factors could cause this phenomenon. Raising resin composite temperature reduces its viscosity, increases additional free volume and enhances molecular mobility. All these factors lead to increase in the rate of movement of reacting molecules, resulting in additional monomer conversion [34]. The two materials GDA and GDP which did not showed this trend are micro-fine hybrid resin composites with pre-polymerized fillers. Furthermore, they share the same resin matrix which is composed of UDMA and Dimethacrylate co-monomer.

Results showed a positive strong correlation between activation energy of shrinkage strain and the percentage of total organic material calculated from the combustion technique (r = 0.86). Thus, the third hypothesis was rejected. Furthermore, three resin composites showed higher activation energy values than other materials. These are; GCK, GDP, and GDA. These resin composites have pre-polymerized fillers incorporated in their formulations.

Activation energy is a subtle chemical concept such that it is difficult to predict or explain how it might vary with changing composition of a composite system. Moreover, the fact that we have found certain correlations between this and compositional factors does not mean that there is a direct causal relationship between them.
7.6 Conclusions:

Within the limits of this study, it can be concluded that:

(1) Increasing percent filler loading (from 73 wt. % to 87 wt. %) reduces shrinkage strain of the examined resin composites (by up to 0.57 %).

(2) Temperature rise from 23 °C to 37 °C cause increase shrinkage strain by up to 0.41 %, i.e., as the temperature increases the shrinkage strain increases.

(3) As the total organic content increased (from 15.56 wt. % to 54.25 wt. %) the activation energy increased (from 15.4 kJ mol\(^{-1}\) to 42.2 kJ mol\(^{-1}\)). Thus the kinetic (shrinkage rate) become progressively more sensitive to temperature increase.
Chapter 8

Temperature-dependent polymerization
shrinkage stress kinetics of resin-composites

A. A. Alnazzawi, N. Silikas, D. C. Watts
8.1 Abstract:

**Objectives:** To examine a set of resin composites formulated with dimethacrylate monomer matrix and the effect of composition on shrinkage stress kinetics and its temperature dependence.

**Methods:** Six commercially available resin composites with a range of resin matrix were selected. Two of them were considered as low shrinking resin composites, which are GCK and VDD. The shrinkage stress kinetics at 23 °C and 37 °C was measured continuously using the Bioman instrument for 60 min. Stress was evaluated at two times 2 min and 60 min. Specimens temperature was controlled by a newly designed heating device. Measurements were monitored for 1 h after irradiation for 40 s at 550 mW/cm² (energy density = 22 J/cm²). Three specimens (n=3) were used at each temperature per material.

**Results:** Shrinkage stress at 23 °C ranged from 2.93 MPa to 4.71 MPa and from 3.57 MPa to 5.42 MPa for 2 min and 60 min after photo-activation, respectively. The lowest stress rate was recorded by GCK and VDD (0.34 MPas⁻¹), whereas the highest was recorded by FXE (0.63 MPas⁻¹). At 37 °C, shrinkage stress ranged from 3.27 MPa to 5.35 MPa and from 3.36 MPa to 5.49 MPa for 2 min and 60 min after photo-activation, respectively. GCK demonstrated the lowest stress rate (0.44 MPas⁻¹), whereas FXE recorded the highest (0.85 MPas⁻¹). At both temperatures, GCK showed the lowest stress, while the highest was recorded by FXE. All materials showed a higher stress at 37 °C than 23 °C with the exception of GCK and VDD, where they recorded lower stress at 37 °C. A positive correlations were found between shrinkage stress and stress rate at 23 °C and 37 °C (r=0.70 and 0.92, respectively).

**Significance:** Investigated resin composites polymerized at elevated temperature (37 °C) showed an ability to compete stress build up after 60 min compared to those at ambient room temperature (23 °C).
8.2 Introduction:

Resin composites were developed and introduced commercially in the late 1950s to restore the appearance and function of biological tooth tissues [87, 111]. Since that time, it has undergone extensive research resulting in improvements in mechanical and physical properties. However, polymerization shrinkage and subsequent shrinkage stress that occur during polymerization are still significant disadvantages [110]. This may lead to deleterious clinical complications, such as post-operative pain, marginal discolouration, recurrent caries, cusp deflection and enamel micro-cracks [111, 112].

Shrinkage stress is the result of confining the dimensional changes of resin composites due to shrinkage by bonding to cavity walls. During the early stage of the polymerization reaction, resin composites may flow and relax any developing stress. However, there is a very short time period before the material becomes stiff and unable to deform, and consequently stress starts to build up [111]. Thus, material properties, geometry, and boundary conditions are contributory factors that interact with each other to determine the resulting stress.

The degree of conversion, polymerization rate, shrinkage strain, elastic modulus, pre-gel flow, and post-gel shrinkage are among material factors that play a role in stress development [87, 114-117]. Previous studies have proposed different ways to reduce shrinkage and its accompanying stress, comprising incremental placement technique, placement of stress absorbing liners, soft-start light curing, and redesigning of materials [110, 111]. Recently, several low shrinking resin composites have been commercially introduced; among these are GCK and VDD. GCK is based on novel monomer (DX-511), which is a modified UDMA and has a high molecular weight in comparison to Bis-GMA (895 g/mole vs. 512 g/mole) [145, 152]. On the other hand, VDD is based on TCD-DI-HEA monomer which is described as a low shrinkage monomer with low viscosity [110, 145].

Previous studies showed that the testing temperature has effects on different properties of resin composites, such as degree of conversion [72, 97], rate of polymerization [97], shrinkage strain and its rate [88, 89], and elastic and viscous moduli [183, 184]. Increasing resin composite temperature decreases its viscosity, increases additional free volume and improves molecular mobility. All of these may lead to an increase in the degree of conversion and consequently increases in shrinkage strain. Furthermore,
higher temperature may assist polymer chain movement which can result in greater compliance and lower elastic modulus [184]. Many studies have taken place that explores the polymerization stress phenomenon. However, most or all of them were conducted at ambient room temperature.

The objective of the current study was to investigate the effect on shrinkage stress kinetics of increasing specimen temperature of a range of resin composites from room temperature (23 °C) to body temperature (37 °C). The specific objectives were to study a range of resin composites (two of them are low shrinking) using the Bioman instrument including a newly designed specimen heating device in order to:

- Compare shrinkage stress at 23 °C and 37 °C.
- Compare shrinkage stress at 2 min and 60 min.

The null hypotheses were (1) temperature has no effect on shrinkage stress, (2) there is no difference in shrinkage stress at 2 min and 60 min, and (3) there is no relation between shrinkage stress and stress rate.
8.3 Materials and Methods:

Six commercial photo-activated resin composites were selected on the basis of their matrix monomer compositions and filler loading (Table 8.1).

<table>
<thead>
<tr>
<th>Code</th>
<th>Resin composites</th>
<th>Filler loading</th>
<th>Resin matrix</th>
<th>Lot no.</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>GRO</td>
<td>Grandio</td>
<td>87</td>
<td>Bis-GMA, TEGDMA</td>
<td>581793</td>
<td>Voco, Cuxhaven Germany</td>
</tr>
<tr>
<td>GCK</td>
<td>G C Kalore</td>
<td>82</td>
<td>DX-511, UDMA and dimethacrylate co-monomers</td>
<td>0903171</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>VDD</td>
<td>Venus Diamond</td>
<td>81.2</td>
<td>TCD-DI-HEA UDMA</td>
<td>010035</td>
<td>Heraeus Kulzer</td>
</tr>
<tr>
<td>FXE</td>
<td>Filtek Supreme XTE</td>
<td>78.5</td>
<td>BIS-GMA, BIS-EMA (6), TEGDMA, PEGDMA and UDMA</td>
<td>N147105</td>
<td>3M ESPE Germany</td>
</tr>
<tr>
<td>GDP</td>
<td>Gradia Direct Posterior</td>
<td>77</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0905201</td>
<td>GC America Inc.</td>
</tr>
<tr>
<td>GDA</td>
<td>Gradia Direct Anterior</td>
<td>73</td>
<td>UDMA and dimethacrylate co-monomers</td>
<td>0901134</td>
<td>GC America Inc.</td>
</tr>
</tbody>
</table>

*Manufacturer data.

The Bioman instrument [121, 126] was used in this study to measure shrinkage stress kinetics (Figure 8.1) at 23 °C and 37 °C. This instrument is composed of a cantilever load cell with a compliant end and attached firmly to a 2 cm thick stainless steel base-plate. The compliant end has an integral clamp holding a circular steel rod (10 mm in diameter, 22 mm long) in a vertical and perpendicular orientation to the load cell axis. Resin composite specimens were placed between two surfaces, the lower surface of the rod and a glass plate surface. These two surfaces were lightly sandblasted to promote bonding of the composite specimens. The glass plate (3 mm thick) was held tight by an aluminium clamp and a hollow cylindrical bolt. This hollow cylindrical bolt allows for passage of a straight light curing guide to contact the glass plate. The gap between the rod and glass plate was adjusted with the aid of a feeler gauge to 0.8 mm. Resin composite paste of standardised weight (0.12 - 0.15 g) was introduced into this gap to form specimen disk of 10 mm diameter and 0.8 mm thickness (configuration factor = 6.25). The specimen was then photo-activated from below, through the glass plate across its thickness.
During polymerization, the stress created within resin composite causes displacement of the compliant end of the load cell. The load signal from the cantilever load cell was detected with a strain gauge. This signal was amplified by a wide-range strain indicator (Model 3800, Vishay, Measurements Group, Raleigh, NC, USA) then connected to a personal computer via data-logging system hardware and software (ADC-20 multi-channel data acquisition unit and PicoLog software; Picotech, Cambridge, UK). The stress value in MPa is then obtained from the recorded load divided by the specimen disk area.

A newly designed heating device which contained a heating element and connected to a power supply (Farnell E20-28, Farnell instruments LTD., Wetherby, Yorkshire, England) was used to provide a heat source for stress measurements at 37°C (Figure 8.2). The power supply was set at 5.00 Volts to heat up the heating element to 75°C and resin composite specimen to 37°C. The resin composite specimen temperature reached 37°C after 30 min then stabilized for the next 60 min (Figure 8.3).
Figure 8.2: Heating device above the glass plate, shown in the retracted position.

Figure 8.3: Graph of temperature vs time of heating element and resin composite specimen.

A light cure unit, with a modified straight curing tip and delivering a calibrated irradiance of 550 mW/cm², (Optilux 500 – Kerr, Orange, CA, USA) was used to irradiate the specimen from beneath the glass plate for 40 s (energy density = 22 J/cm²). Polymerization shrinkage stress was monitored for 60 min.

Statistical software (SPSS ver. 16, SPSS Inc., Illinois, USA) was used, and data were analysed by One-way analysis of variance (ANOVA). Prior to post hoc tests, data were analysed for equal variances using the homogeneity test (p<0.05). For data of shrinkage stress at 23 °C and 37 °C, equal variances can be assumed, thus Multiple pair-wise comparisons using a Tukey post-hoc test were conducted to establish homogenous subsets at p=0.05. Differences between groups for temperature and time effects were assessed using a paired t-test.
8.4 Results

Data of shrinkage stress at 23°C and 37°C for all materials were plotted graphically as time-dependent curves in Figures 8.4 and 8.5, respectively. Table 8.2 summarizes mean values of shrinkage strain (MPa) for 2 min and 60 min, and stress rate at 23°C and 37°C.

![Figure 8.4](image)

**Figure 8.4:** Time-dependence shrinkage stress at 23 °C, up to 2 min and 60 min for six resin composites, irradiated for 40 s at 550 mW/cm².

![Figure 8.5](image)

**Figure 8.5:** Time-dependence shrinkage stress at 37 °C, up to 2 min and 60 min for six resin composites, irradiated for 40 s at 550 mW/cm².
Table 8.2: Shrinkage stress (MPa) and stress rate (MPas\(^{-1}\)) at 23°C and 37°C.

<table>
<thead>
<tr>
<th>Materials</th>
<th>At 23 °C</th>
<th></th>
<th>At 37 °C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 min</td>
<td>60 min</td>
<td>Rate</td>
<td>2 min</td>
</tr>
<tr>
<td>GRO</td>
<td>3.29 (0.10)(^{a,A*})</td>
<td>3.80 (0.12)(^{a,B})</td>
<td>0.44 (0.042)</td>
<td>3.79 (0.09)(^{a,A*})</td>
</tr>
<tr>
<td>GCK</td>
<td>2.93 (0.15)(^{b,A})</td>
<td>3.57 (0.16)(^{a,B})</td>
<td>0.34 (0.035)</td>
<td>3.27 (0.04)(^{b,A})</td>
</tr>
<tr>
<td>VDD</td>
<td>3.68 (0.15)(^{c,A})</td>
<td>4.54 (0.17)(^{b,B+})</td>
<td>0.34 (0.012)</td>
<td>3.62 (0.09)(^{b,B})</td>
</tr>
<tr>
<td>FXE</td>
<td>4.71 (0.08)(^{d,A*})</td>
<td>5.42 (0.09)(^{c,B})</td>
<td>0.63 (0.004)</td>
<td>5.35 (0.11)(^{c,A*})</td>
</tr>
<tr>
<td>GDP</td>
<td>3.69 (0.16)(^{c,A*})</td>
<td>4.39 (0.17)(^{b,B})</td>
<td>0.42 (0.006)</td>
<td>4.21 (0.21)(^{d,A})</td>
</tr>
<tr>
<td>GDA</td>
<td>4.03 (0.04)(^{c,A*})</td>
<td>4.76 (0.11)(^{b,B})</td>
<td>0.40 (0.036)</td>
<td>4.58 (0.18)(^{d,A})</td>
</tr>
</tbody>
</table>

Within each column different superscript small letter indicates significant differences between materials (p<0.05).

Within each temperature different superscript capital letter in the same row indicates significant differences in the same material (p<0.05).

Within same time and different temperature, asterisk (*) and plus (+) superscript in the same row indicates significant differences in the same material (p<0.05).

At 23 °C and 2 min after photo-activation, the lowest shrinkage stress was recorded by GCK (2.93 MPa) which was statistically significant from the other materials (p≤0.026). The highest value was seen with FXE (4.71 MPa) which was statistically significant from other materials (p<0.001). On the other hand, at 23 °C and 60 min after photo-activation, GCK demonstrated the lowest shrinkage stress (3.75 MPa) which was statistically significant (p<0.001) except GRO (p=0.361). Moreover, FXE showed the highest shrinkage stress (5.42 MPa) which was statistically significant (p<0.001).

At 37 °C and 2 min after photo-activation, GCK showed the lowest shrinkage stress among all examined materials (3.27 MPa) which was statistically significant (p≤0.012) with the exception of VDD (p=0.065). Also, the highest shrinkage stress was seen with FXE (5.49 MPa) which was statistically significant from other examined materials (p<0.001). In contrast, the lowest shrinkage stress after 60 min was recorded by GCK (3.27 MPa) which was statistically significant from other materials (p≤0.05). Furthermore, FXE demonstrated the highest shrinkage stress among all examined materials (p≤0.002).

All materials showed a higher shrinkage stress at 60 min compared to those at 2 min for both temperatures. Although this difference was statistically significant at 23 °C (p≤0.007), it was statistically insignificant at 37 °C (p≥0.112).
The lowest rate at 23 °C was recorded by GCK and VDD (0.34 MPas⁻¹), while the highest was recorded by FXE (0.63 MPas⁻¹) (Figure 8.6). On the other hand, at 37 °C GCK demonstrated the lowest rate (0.44 MPas⁻¹), whereas FXE demonstrated the highest rate (0.85 MPas⁻¹) (Figure 8.7). All materials showed higher shrinkage stress rate at 37 °C compared to 23 °C (Figure 8.8).

**Figure 8.6:** Time-dependent shrinkage stress-rate at 23 °C.

**Figure 8.7:** Time-dependent shrinkage stress-rate at 37 °C.
The increase in shrinkage stress with increasing stress rate proposed a linear relationship and linear regression gave a positive correlation at 23 °C and 37 °C (r = 0.70 and 0.92, respectively) (Figure 8.9).

Figure 8.9: Association map of maximum shrinkage stress (at 60 min) and maximum stress rate (at 3-5 s) for a series of resin composites at 23 °C and 37 °C.
At different temperatures and 2 min after photo-activation, all materials demonstrated a higher shrinkage stress at 37 °C with the exception of VDD. Although, this difference was statistically significant for all materials (p≤0.028), it was statistically insignificant for GCK and VDD (p=0.068 and 0.687, respectively). There were negative correlations between shrinkage stress and filler volume fraction of examined materials at 23 °C and 37 °C (r = -0.94 and -0.80, respectively) (Figure 8.10).

![Figure 8.10: Early shrinkage-stress at 2 min versus filler loading (vol%) at 23 °C and 37 °C for six resin composites.](image)

After 60 min all materials demonstrated almost the same shrinkage stress at both temperatures, except for GCK and VDD. Both of them are demonstrated a lower shrinkage stress at 37 °C. Though only VDD was statistically significant (p=0.006). There were negative correlations between shrinkage stress and filler volume fraction of examined materials at 23 °C and 37 °C (r = -0.97 and -0.82, respectively) (Figure 8.11).
Figure 8.11: Maximum shrinkage-stress at 60 min versus filler loading (vol%) at 23 °C and 37 °C for six resin composites.
8.5 Discussion:

Shrinkage stress is a local physical condition resulting from the interaction of material properties, geometry, and boundary conditions. Although numerous methods have been proposed to measure shrinkage, the principle underlying each of these methods is similar [111, 115]. However, results for the same material may differ greatly between methods due to differences in testing configuration and instrument compliance. The Bioman instrument used in the current study uses a beam of fixed compliance and proved to be convenient, and gave reproducible results [126]. The heating device was carefully designed to provide heat locally. Therefore, specimen’s temperature may increase without change in the temperature of load cell.

In the current study, recorded final shrinkage stress ranging from 3.54 to 5.42 MPa and from 3.27 to 5.49 MPa (at 23 °C and 37 °C, respectively). Even at body temperature (37 °C) the measured stress levels for examined materials were less than the bond strength of good dental adhesives. The bond strength of the adhesive has been found to be typically in the range of 15-30 MPa for fully cured resin composites when bonded to enamel [185-187], and in the range of 13-23 MPa when bonded to dentin [187, 188].

GCK demonstrated the lowest shrinkage stress among all examined materials at both temperatures and both times. Additionally, it showed lower stress rate than other examined materials at both temperatures. These could be explained by the high molecular weight of the base monomer within GCK; DX-511(895 g/mole vs. 512 g/mole for Bis-GMA), which allow GCK to have fewer reactive sites. Thus, for equal mass, GCK may undergoes a lower number of reactions during polymerization compared to other dimethacrylate resin composites [189]. Moreover, this monomer has a long rigid core and two flexible side arms [151]. Previous studies showed that GCK has a lower shrinkage strain and low modulus in comparison to conventional resin composites [117, 190]. Therefore, the lower stress recorded by GCK may be explained by its lower shrinkage, polymerization rate, modulus and possibly degree of conversion compared to other materials.

On the other hand, FXE showed the highest shrinkage stress and stress rate among all examined materials at both temperatures and both times. Probably, this high stress may be explained by the higher polymerization rate and faster attainment of stiffness which
may lead to less ability of flow to relieve stress. Takahashi et al. [191] investigated the effects of shrinkage strain, shrinkage stress, and Young’s modulus of resin composites on marginal adaptation. They concluded that resin composites with low shrinkage strain, low shrinkage stress, and low stiffness resulted in superior cavity adaptation.

Shrinkage stress in resin composites is produced by interplay of several factors: such as degree of conversion, shrinkage strain, reaction rate and elastic modulus [111]. Polymerization of resin composites at higher temperature compared to room temperature is accompanied by an increase in degree of conversion, shrinkage strain, and polymerization rate [72, 97]. Although most of the examined materials showed a higher stress after 2 min at 37 °C compared to that at 23 °C, VDD recorded a lower magnitude. Additionally, differences in GCK were not significant. On the other hand, after 60 min and at 37 °C, GCK and VDD showed the ability to compete the growing stress and eventually recorded lower stress than those at 23 °C. Nevertheless, all materials showed this ability, but it was more obvious in VDD. This may be explained by the effect of raising the temperature in elastic and viscous moduli of examined materials [183, 184]. Thus, the first hypothesis was partially rejected.

Photo-activation of resin composites characterised by fast reaction rate which reduces the time allowed for material to flow [111]. Thus, stress starts to increase instantly after photo-activation and continue to increase with time. In the current study, all materials showed higher stress at one hour after photo-activation than that at 2 min for both temperatures. At 23 °C, examined materials showed increases in stress of more than 15 %, whereas less than 6 % observed at 37 °C. However, increases in stress at 37 °C were not statistically significant. This may be explained by the fact that a higher temperature leads to expansion of resin composites and increasing its free volume, which may facilitate polymer chain movement and result in greater compliance of the polymers. Previous studies [183, 184] reported that the elastic modulus and viscous moduli are dependent on testing temperature and concluded that increasing resin composite temperature leads to a decrease in elastic modulus, and an increase in viscous modulus. Therefore, the second hypothesis was partially rejected.

In the present study, the analysis of shrinkage stress rate showed positive correlations with shrinkage stress at both temperatures. Previous studies reported that the polymerization rate imposes shrinkage strain rate, and the rate of increase in elastic
modulus. As a result, the shrinkage stress rate is directly affected by the polymerization rate [111, 192]. Thus, the greater the stress rate the higher shrinkage stress and, therefore, the third hypothesis was rejected.

8.6 Conclusions:

Within limitations of this study, it can be concluded that:

(1) Polymerization shrinkage stress behaved differently at different temperatures.
(2) Even at oral temperature (37 °C) the measured stress for examined materials was less than the bond strength of good dental adhesives.
(3) VDD recorded lower stress at 37 °C compared to that at 23 °C.
Chapter 9

General discussion, Conclusions and Future Work Recommendations


9.1 Introduction:

Resin composites are composed of inorganic fillers coated with coupling agent dispersed in an organic resin matrix [37]. In their precured state, they are paste type viscoelastic materials and are positioned intermediately between viscous and elastic materials. However, these materials are changed rapidly to a hardened mass after photo-activation [91].

The composition and application techniques of resin composites have undergone significant progress since their introduction to practice over fifty years ago. Changes in composition involved both the polymeric matrix and reinforcing fillers, and successfully resulted in improvement of mechanical and physical properties, reduced polymerization shrinkage and polymerization stress [145]. However, current attempts to improve resin composites focused on their polymeric matrix and, therefore, several novel monomers have been introduced to the market. Silorane is an example of a novel monomer and resin composite based on silorane technology showed lower polymerization shrinkage than dimethacrylate based resin composites [27]. Other examples are DX-511 by Dupont and TCD-DI-HEA. DX-511 monomer found in GCK is a modified UDMA and has a high molecular weight in comparison to Bis-GMA (895 g/mole vs. 512 g/mole) [145]. On the other hand, TCD-DI-HEA found in VDD (Kulzer) is described as a low shrinkage monomer with low viscosity [110, 145].

Preheating of the resin composite decreases its viscosity, increases additional free volume and improves its molecular mobility. All of these may lead to an increase in the rate of movement of reacting molecules. Therefore, the material temperature has an effect on the different properties of resin composites, such as the degree of conversion [72, 97], rate of polymerization [97], shrinkage strain and its rate [88, 89], and elastic and viscous moduli [183, 184].

The aims of this research were to explore the extent to which increasing resin composite temperature from the ambient room temperature (23 °C) to the body temperature (37 °C) affects properties before and during the setting process. The six resin composites used in the current research were selected on the basis of their matrix monomers composition and filler loading. Three of them are nanohybrid; GRO, GCK, and VDD. GRO is based on classical matrix monomers (Bis-GMA/TEGDMA), whereas GCK and VDD are
based on novel monomers (DX-511 and TCD-DI-HEA, respectively). FXE is a nanofilled resin composite based on Bis-GMA/TEGDMA, Bis-EMA, and UDMA matrix monomers. Finally, two resin composites (GDP and GDA) are microhybrid and based on UDMA/DMA co-monomers matrix monomers.

Different methodologies were applied in the current research to investigate the temperature dependence of resin composites properties before and during the setting process. At first, temperature dependence of resin composite pastes were examined at precured state (packing stress and viscosity), then during photo-activation (exotherm), after photo-activation and during the polymerization process up to one hour (degree of conversion, shrinkage strain, and shrinkage stress). Additionally, the bonded-disk instrument was modified to measure simultaneously shrinkage strain, temperature, and CTE of the investigated resin composites.

9.2 Temperature-dependent properties before the setting process:

Handling properties of resin composites are a key factor to consider during their selection. Flow, stickiness to hand instruments and tooth, pack-ability, and slumping resistance are associated with ease of placement and shaping, chair time, and success of the restoration \([59-62]\). Clinically, resin composites are subjected to different actions during application and manipulations such as apply and press to pack in the cavity, and sculpt to shape the occlusal anatomy.

Handling properties (packing stress and viscosity) of investigated resin composites were examined using the penetrometer principle at three different temperatures (23 °C, 30 °C, and 37 °C). Results of the packing stress and viscosity for examined materials were presented in Chapter 4. Packing stress is exhibited by the resistance to plunger’s intrusion, mostly caused by the direct collisions between fillers in the resin matrix \([147, 150]\). Therefore, the mean packing stress was calculated from the time-dependent plotting of packing stress (Figure 4.2) as the average packing stress during the persistence period of packing stress. A noticeable influence of temperature on packing stress was found among all examined materials. That is, increasing the temperature of resin composite reduces the packing stress (Figure 4.4). This could be explained by the fact that resin composite viscosity decreases as the temperature increases \([44, 60, 68,\]
153], resulting in less resistance to the filler mobility within resin composite and leading to less stress during force application.

The viscosity of resin composites has a direct impact on most of their handling properties [60, 62-65]. Matrix monomers composition and filler particles, and their interactions can play a marked role on resin composites viscosity [59, 60, 68]. In the current study, values for viscosity of examined materials were derived from the mean packing stress multiplied by the persistence period of packing stress. Temperature has a prominent effect on the viscosity of investigated resin composites; therefore, viscosity follows an Arrhenius equation and decreased exponentially as the temperature of resin composites increased. This is in agreement with previous studies [44, 60, 68].

Results of this study showed that both the packing stress and viscosity were decreased as the material temperature increased. The impact of viscosity on the packing stress suggested a positive linear relationship. This was confirmed by the positive linear correlations between them at 23 °C, 30 °C, and 37 °C (r = 0.81, 0.84, and 0.88, respectively) (Figure 4.9). As the temperature rose from the ambient room temperature (23 °C) to a higher temperature (intermediate temperature 30 °C and body temperature 37 °C) the viscosity decreased exponentially. Therefore, it is easier for resin composite particles to migrate from an area of higher pressure at higher temperature due to decreased viscosity leading to lower packing stress.

This study provided a feasible methodology for quantifying and investigating packing stress and viscosity, and their temperature-dependencies of resin composites.

**9.3 Temperature-dependent properties during the setting process:**

Once photo-activated, resin composites undergo an extremely fast chemical reaction they change rapidly from a paste to a hard material [91, 193]. This process involves a progressive development in degree of conversion, shrinkage strain, elastic modulus, shrinkage stress, and other key viscoelastic properties. Preheating of resin composites reduces their viscosity, increases additional free volume and enhances molecular mobility. Therefore, photo-activation of resin composites at elevated temperature may lead to an increase in the degree of conversion due to increases in the rate of movement of reacting molecules [72]. Additionally, higher temperature may assist polymer chain movement which can result in greater compliance and lower elastic modulus [184].
9.3.1 Temperature-dependent degree of conversion:

The degree of conversion of resin composites plays an important role in determining their physical and mechanical properties [74]. Inadequate levels of the degree of conversion may compromise mechanical properties, wear resistance and colour stability of resin composites. Additionally, residual monomers and initiators may leach from resin composites, jeopardizing the biocompatibility. On the other hand, maximizing the degree of conversion to improve those properties may lead to increased polymerization shrinkage and establish brittle resin composites [75]. Hence the effect of temperature on the degree of conversion of resin composites was investigated in Chapter 5 utilising the FTIR spectroscopy technique at the ambient room temperature (23 °C) and the body temperature (37 °C).

All examined resin composites demonstrated an increase in the degree of conversion at body temperature compared to the ambient room temperature. These differences ranged from 23 % to 69 % at 0h and from 13 % to 37 % at 1h. This could be explained by an increase in the number of collisions of reacting molecules caused by decreased viscosity, increased additional free volume and increased molecular mobility due to temperature’s rising of resin composites [72]. Moreover, increase in temperature may lead to delay in alteration of the termination process of polymerization from diffusion-controlled to reaction-diffusion-controlled due to improved flexibility of the polymer chain [97, 158].

9.3.2 Simultaneous determination of shrinkage strain, exotherm, and CTE:

During setting, resin composites undergo a polymerization reaction which is a chemical process involve the linking of smaller monomer molecules to create a cross-linked network. Inevitably, their polymerization is accompanied with polymerization shrinkage and elaboration of heat. Additionally, resin composites in the oral cavity are subjected to thermal variations, which lead to dimensional changes typically expressed by their CTE. Therefore, the bonded-disk instrument, which is designed to measure polymerization shrinkage strain of resin composites, was modified to determine simultaneously shrinkage strain, exotherm, and CTE (Chapter 6).
The maximum shrinkage strain values ranged from 1.70 % to 2.34 % (Figure 6.7), and are in broad agreement with previous studies [26, 27, 93, 168-171]. However, a LED LCU with irradiance of 1200 mW/cm² was used for photo-activation for 20 s (energy density = 24 J/cm²). A strong negative correlation was demonstrated between shrinkage strain and percent filler loading (r = -0.89) (Figure 6.10a). Therefore, as the percent filler loading increased, the shrinkage strain decreased, which is in agreement with previous studies [88, 89, 91, 92, 172].

Temperature rise during photo-activation of resin composites is the sum of temperature rise caused by light source irradiation and exotherm. This study showed that the mean total rises ranged from 8.91 to 15.35 °C. Hofmann et al. [35] recorded a temperature rise of 8.2 to 12.4 °C during photo-activation of resin composites by a LED LCU (irradiance = 320 mW/cm²). However, a LED LCU with higher irradiance (1200 mW/cm²) was used in the current study. In a clinical and histological study, Baldissara et al. [166] reported that up to 11.2 °C rise in temperature would not harm the pulp. Taking into consideration that oral temperature baseline is lower than 37 °C [174], low thermal conductivity of dentin, and easy dissipation of excess heat from the resin composite filling. Therefore, the actual temperature increase transferred to the pulp would be much lower.

As mentioned earlier the CTE of resin composites represent their dimensional changes due to thermal variations. The recorded mean values of CTE ranged from 18.44 (10⁻⁶/°C) to 24.63 (10⁻⁶/°C), which are greater than those of enamel and dentin. Previous studies showed that there is a negative correlation between CTE and filler loading. The same trend was evident in the current study (r = -0.95) (Figure 6.10c). Therefore, GRO showed the lowest CTE, whereas GDA showed the highest.

9.3.3 Temperature-dependent shrinkage strain kinetics:

Polymerization shrinkage of resin composites is affected by many factors, including functionality of monomer, average molecular weight, degree of conversion, curing conditions and amount of filler loading [18, 86, 88-93]. Temperature of resin composites during the setting process is considered as one of the curing conditions that may affect their degree of conversion and polymerization shrinkage. Results showed that all examined materials had a higher shrinkage strain at body temperature (37 °C) compared to ambient room temperature (23 °C) (Chapter 7). This could be attributed to
the decreased viscosity and increased degree of conversion due to increase in resin composites temperature as seen in Chapters 4 and 5, respectively.

Photo-activation of resin composites with a higher irradiance (1200 mW/cm²) at the ambient room temperature as seen in Chapter 6 resulted in shrinkage strain comparable to that photo-activated with lower irradiance (550 mW/cm²). This could be explained by that both experiments had no much difference in the applied energy densities, which are 24 J/cm² and 22 J/cm² for experiments in Chapter 6 and Chapter 7, respectively.

Time constant (τ) is the time value corresponding to 63.2% of the maximum shrinkage value, and it is the reciprocal of a rate-constant (k) of Arrhenius Equation. Results showed that the time constant is decreased when resin composite temperature increased from the ambient room temperature to the body temperature (Table 7.2). Therefore, 63.2% of the maximum shrinkage strain of examined resin composites occurred in a shorter time at the body temperature than ambient room temperature. In other words, increasing resin composites temperature leads to a decrease in their viscosity (Chapter 4), and an increase in the rate-constant, which manifest in higher immediate degree of conversion at the body temperature compared to the ambient room temperature (Chapter 5).

9.3.4 Temperature-dependent shrinkage stress kinetics:

Polymerization shrinkage and subsequent shrinkage stress are still significant disadvantages of resin composites, which may lead to post-operative pain, marginal discolouration, recurrent caries, cusp deflection, and enamel micro-cracks [111, 112]. Shrinkage stress is the result of interactions between material properties, geometry, and boundary conditions. Among material factors are the degree of conversion, polymerization rate, shrinkage strain, elastic modulus, pre-gel flow, and post-gel shrinkage [87, 114-117]. Resin composites temperature has effects on their different properties, such as degree of conversion [72, 97], rate of polymerization [97], shrinkage strain and its rate [88, 89], and elastic and viscous moduli [183, 184].

Results showed that all materials demonstrated a statistically significant higher stress after 2 min at the body temperature compared to the ambient room temperature, except GCK and VDD. However, VDD recorded a lower shrinkage stress. Additionally, all materials showed an increase in their stress rate when the temperature increased from
the ambient room temperature to the body temperature. On the other hand, after 60 min and at body temperature, all materials showed an ability to compete the growing stress. This phenomenon was more obvious in GCK and VDD, where they recorded a lower stress compared to the ambient room temperature. This could be explained by the effect of temperature on the elastic and viscous moduli. Previous studies [183, 184] reported that the elastic modulus and viscous moduli are temperature-dependent, where the increasing in resin composites temperature leads to a decrease in their elastic modulus and an increase in viscous modulus.

The shrinkage stress starts to increase instantly after photo-activation and continues to increase with time due to the fast reaction rate which is a characteristic of photo-activated resin composites [111]. This was obvious at the ambient room temperature with a statistically significant increase of more than 15 % between shrinkage stress at 2 min and 60 min. On the other hand, at body temperature examined materials showed a less than 6 % of increase, which was statistically insignificant. Increasing resin composites temperature decreases their viscosity (Chapter 4), increases the degree of conversion (Chapter 5) and hence increases shrinkage strain (Chapter 7), and may assist polymer chain movement which can result in greater compliance and lower elastic modulus [184]. That is, shrinkage stress is a result of interactions between these properties and its temperature-dependence is affected by these interactions.
9.4 Conclusions:

Within limitations of this study it was concluded that:

- Temperature has a pronounced effect on the handling properties (packing stress and viscosity) of resin composites. An increase in temperature resulted in lower packing stress and viscosity.

- Matrix monomers composition and temperature of resin composites have a noticeable effect on the degree of conversion at both immediately and one hour after photo-activation.

- As the temperature of resin composites increases the viscosity decreases and immediate (0h) degree of conversion increases.

- The modified bonded-disk instrument could be used to measure simultaneously shrinkage strain, exotherm, and a value for CTE of resin composites. Shrinkage strain, exotherm, and CTE were inversely related with filler loading of resin composites.

- Temperature has a significant effect on shrinkage strain of resin composites. As the temperature increases the shrinkage strain increases.

- Activation energy of shrinkage strain correlates positively with percent resin matrix of examined resin composites. As the percent of resin matrix increases the activation energy increases.

- Shrinkage stress of resin composites is a result of interactions between the viscosity, degree of conversion, shrinkage strain, and elastic modulus. Furthermore, its temperature-dependence is affected by these interactions.

- Although all materials showed an ability to compete the growing stress after 60 min and at body temperature, GCK and VDD (based on novel monomers) recorded lower shrinkage stresses compared to the ambient room temperature.
9.5 Future Work Recommendations:

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

- A study to investigate the temperature-dependence of resin composites properties:
  - At higher temperatures (50-60 °C), which are applied by the preheating device.
  - For a series of model composites with different filler loading.
  - Using different LCUs and curing protocols.

- Further studies on the modified bonded-disk instrument:
  - Performing the same methodological settings presented in this work but at different temperatures.
    - Using different LCUs and curing protocols.

- In vivo study to measure the rise in temperature caused by photo-activation of resin composites.


