Viscoelastic behavior of dental restorative composites during setting

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INFLUENCE OF TEGDMA/BISGMA RATIO IN EXPERIMENTAL RESIN COMPOSITES ON SELECTED MECHANICAL PROPERTIES

Abstract

The shrinkage of resin composites, in combination with increasing stiffness, will inevitably lead to stress development in the restoration and its surroundings. One way to relieve the shrinkage stress is by viscous flow of the composite from free, unboned surfaces. This study examines the possibility of stimulating viscous flow by increasing the TEGDMA/bisGMA ratio in the resin of the experimental composites. A series of experimental two-paste composites of varying TEGDMA-bisGMA composition in the resin were used to determine how comonomer composition affects the shrinkage stress-strain, viscoelastic property, and double-bond conversion during setting. In addition, the tensile strength of the composites after setting for one hour, and the wear process over a period of one year were evaluated.

Varying the relative amounts of bisGMA and TEGDMA has a significant effect on the mechanical properties of two-paste composites. It was found that the polymerization rate of bisGMA-TEGDM A composites is an indicative measure of viscoelastic behavior during setting: the higher the reactivity, the higher the stiffness and viscosity. Composites with 50 wt% TEGDMA in the resin displayed the highest maximum polymerization rate. Higher amounts of TEGDMA in the resin resulted in an increased amount of converted double bonds, increased wear, and reduced tensile strength. Higher amounts of TEGDMA resulted in only a moderate increase in the pre-gel viscous flow of composites in the early setting phase, and displayed high shrinkage stresses. The high post-gel shrinkage of this flowable composite is the decisive factor in the high shrinkage stress development in the material.
Introduction

Throughout its lifetime, the interface between a resin composite and the tooth is subjected to the challenge of cyclical thermal and load stresses, which can potentially cause debonding and lead to clinical failure of the restorative treatment. Before the restored tooth is subjected to these stresses, the maturing restoration-tooth interface has first to survive the build-up of shrinkage stress during the setting process of the resin composite. Therefore, the success of a tight sealed restoration after preparation is rooted in minimizing shrinkage stress development in the restoration.

To prevent damage from shrinkage stress, dental literature has given considerable attention to several factors, which reduce shrinkage stress in the restorative material during setting [1]. Some factors are out of the clinician’s control, i.e., resin, filler, and activation system formulation, while others are directly under the clinician’s control, i.e., ratio two-paste system, light-intensity, and preparation geometry (C-factor). These factors not only affect the amount and direction of composite shrinkage, but also the mechanical behavior of the restorative material when it transforms from a fluid substance to a solid [2]. Previous studies showed that the mechanical behavior of resin-based dental materials during setting is viscoelastic by nature [3-5]. Up to the gel-point, the viscous flow property predominates, whereas after the gel-point, the elastic behavior predominates. We shall avoid the word solid for polymerized composites, because the superficial appearance of the composite can be misleading. A composite can look solid and yet achieve flow deformation over a long period of time.

Shrinkage stress development in the restoration can be low when shrinkage is accompanied by predominant (pre-gel) viscous flow of the material [6]. In this way, volume change attributable to shrinkage can be compensated by material flow from the unbonded, outer surface. This chapter is focused on the mechanical properties of experimental composites with different TEGDMA/bisGMA ratio in the resin. Hence, dynamic mechanical, volumetric shrinkage, and wear tests were performed as a function of resin composition. For this purpose, conventional resin formulation is briefly reviewed in the introduction. For a detailed description of the conventional monomer system, we refer to Peutzfeldt [7].

The viscous flow property in dental composites is provided by the resin phase, as it changes from viscous to solid behavior after setting. Many

1viscous flow: polymer chains or isolated cross-linked segments slipping past one another (Fig. 2.4).
2elastic deformation: rotations along the chain backbone of the polymer (Fig. 2.5).
today's commercially available dental resin composite materials utilize bisGMA (Fig. 6.1) as major monomer in the resin. This bulky bifunctional monomer has high reactivity, high molecular weight, undergoes low polymerization shrinkage, and produces a cross-linked, three-dimensional resin network [7].

However, due to presence of intermolecular hydrogen bonding (H-O---H-O) in the monomer [8, 9], bisGMA possesses a very high viscosity. For this reason, the resin phase of dental composites cannot consist purely of bisGMA, because this would lead to poorly filled and tough composite pastes, which handling property is not acceptable in general dental practice. Deviates of bisGMA have been developed by selective replacement of the hydroxyl group by hydrogen or methyl groups [10, 11]. As a consequence, the viscosity of the deviative was lowered, but also the mechanical properties of the polymerized resin, as hydrogen bonding restricts sliding of polymer segments relative to each other [10, 11].

Investigations have been carried out in the use of monomethacrylates as diluent for bisGMA [12, 13]. Some concern can be addressed to the impact this type of diluent may have on the degree of cross-linking in the resin after setting. Monomethacrylates tend to give linear polymers when polymerized by themselves and may still do so in mixtures. Therefore, conventional glycol dimethacrylates, which are cross-linking agents, are used as diluent for bisGMA. The monomer most often used for this purpose is TEGDMA (Fig. 6.1). To put the viscosities in

![Chemical structure of bisGMA and TEGDMA](image)

**Figure 6.1** Chemical structures of bisGMA and TEGDMA.
perspective, the viscosity of water is approximately 1 mPa.s (23 °C), while the viscosity of bisGMA is approximately 1,000,000 mPa.s (23 °C), and that of TEGDMA approximately 10 mPa.s (23 °C) [14].

However, TEGDMA has been shown to adversely affect the properties of the resin by increasing the water sorption and polymerization shrinkage [15, 16]. The increase in polymerization shrinkage is a consequence of the fact that TEGDMA is a small molecular dimethacrylate molecule, which delivers more vinyl (C=C) groups per volume unit to the resin system. Because of the relationship between double-bond conversion and polymerization shrinkage strain [1], increasing the amount of double-bond conversion increases volume shrinkage during setting of the resin, under assumption of similar reactivity. However, the relative ease of flow of these resin composites may cause a lower polymerization shrinkage stresses.

To examine this potential advantage of material flow, we determined the mechanical behavior during setting of composites with different TEGDMA/bisGMA ratio in the resin. In addition, the double-bond conversion during setting and the wear property after setting of the composites were studied to understand the effect of TEGDMA concentration in the resin.

### Materials and methods

#### Preparation of chemically activated resin composites

In this study, three chemically activated resin composites, with different bisGMA-TEGDMA composition in the resin, were evaluated. The ingredients for the preparation of the composites were used as received. BisGMA and TEGDMA, purchased from Röhm (Appendix B), were inhibited with 200 ppm Topanol O° and 100 ppm HQME³ respectively. The trade designations, abbreviations, and sources for all materials are given in Table 6.1.

TEGDMA was added to bisGMA in proportions of 30, 50, and 70 % by weight. The monomer mixes were prepared by weighing the components into glass vials and rotating horizontally at room temperature until homogeneous. The mixtures were degassed for 15 minutes under vacuum prior to determine the density by pycnometry. The volume of the pycnometer was determined with deionized water (23 °C).

For preparing the composite, each monomer mixture was divided into

---
³HQME = monomethyl ether of hydroquinone
Chapter 6  |  Influence bisGMA/TEGDMA ratio in two-paste composites

Table 6.1 Materials used for preparation of two-paste resin composites.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Abbreviation</th>
<th>Supplier (appendix B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bisphenol-A-glycidyl dimethacrylate</td>
<td>bisGMA</td>
<td>Röhm</td>
</tr>
<tr>
<td>Triethylene glycol dimethacrylate</td>
<td>TEGDMA</td>
<td>Röhm</td>
</tr>
<tr>
<td>Benzoyl peroxide (25 % H₂O)</td>
<td>Initiator</td>
<td>Aldrich</td>
</tr>
<tr>
<td>N,N-bis(2-hydroxyethyl)-p-toluidine</td>
<td>Accelerator</td>
<td>Fluka</td>
</tr>
<tr>
<td>Butylated hydroxytoluene</td>
<td>Inhibitor</td>
<td>Fluka</td>
</tr>
<tr>
<td>Silanated glassfiller⁣ (LAB7373, [17]) (\rho=2.64\text{g/cm}^3) (23 °C), (\text{dp}=1.53\text{μm}), BET=5.00 m²/g</td>
<td>Filler</td>
<td>SCHOTT</td>
</tr>
</tbody>
</table>

₁⁣ 50 wt% SiO₂, 20 wt% SrO, 15 wt% B₂O₃, 15 wt% Al₂O₃, and 1 wt% BaO

two portions. The activator was dissolved in one part (base resin) and the initiator was dissolved in the other part (catalyst resin). Finally, an inhibitor was added to both resins. The amounts of activator, initiator and inhibitor were chosen to mimic, as close as possible, commercially available conventional dimethacrylate composites (Table 6.2). Finally, all resins were loaded with silanated glass filler (mean particle size about two portions. The activator was dissolved in one part (base resin) and the initiator was dissolved in the other part (catalyst resin). Finally, an inhibitor was added to both resins. The amounts of activator, initiator and inhibitor were chosen to mimic, as close as possible, commercially available conventional dimethacrylate composites (Table 6.2). Finally, all resins were loaded with silanated glass filler (mean particle size about

Table 6.2 Composition of the resins for the 3 two-paste composites.

<table>
<thead>
<tr>
<th>Compound</th>
<th>30 wt% TEGDMA</th>
<th>50 wt% TEGDMA</th>
<th>70 wt% TEGDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Base resin (wt%)</td>
<td>Catalyst resin (wt%)</td>
<td>Base resin (wt%)</td>
</tr>
<tr>
<td>bisGMA</td>
<td>69.05</td>
<td>69.05</td>
<td>49.32</td>
</tr>
<tr>
<td>TEGDMA</td>
<td>29.60</td>
<td>29.60</td>
<td>49.32</td>
</tr>
<tr>
<td>Initiator</td>
<td>1.33</td>
<td>1.33</td>
<td>1.33</td>
</tr>
<tr>
<td>Activator</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Inhibitor</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>(\rho) (g/cm³)</td>
<td>1.134±0.002 (23.6 °C)</td>
<td>1.119±0.002 (23.1 °C)</td>
<td>1.098±0.001 (24.5 °C)</td>
</tr>
<tr>
<td>Total C=C (mol/cm⁹)</td>
<td>5.473·10⁻³</td>
<td>6.088·10⁻³</td>
<td>6.660·10⁻³</td>
</tr>
</tbody>
</table>

⁴Mean density value \((n=3)\) of base resin is statistically similar to catalyst resin \((p<0.05)\).

The glass filler was silanated by Heraeus Kulzer by means of a dry-blending process [17]. In this process, the glass was grinded in a ball mill for about half an hour. The volume proportion between glass and balls should be nearly 50/50. The silane coupling agent \(\gamma\)-methacryloxypropyltrimethoxysilane (MPS) was added 50 % in excess to the theoretically necessary amount for covering the glass surface fully with one layer of silane obtaining a monolayer and the milling continued for three hours. This mixture was heated four hours at 100 to 104 °C in an oven. Finally, the glass was sieved by 200 μm.
1.5 µm) to a content of 70 wt%. This filler content, 50.4±0.4 % in volume, is characteristic for commercially available flowable composites [18]. The resin was mixed with filler using the following procedure. The resin was spread over a Teflon plate and a small fraction of the glass filler amount was spread as a thin layer over the resin. The filler and resin were gently mixed by shearing the mixture between a Teflon spatula and the Teflon plate until homogeneous. Again, the mixture was spread over the Teflon plate and the next small fraction of the glass filler amount was spread as a thin layer, and mixed with the same shear movement by the Teflon spatula. After mixing the mixture with the final glass filler fraction, the composite was degassed for 15 minutes in an excicator. The composite was stored for 2 days at room temperature. Finally, the composite was mixed again on the Teflon plate, degassed for 15 minutes, and finally stored in a refrigerator at 6 °C.

Except for the wear experiments, the amount of composites was kept constant (0.114 cm$^3$) and the measurements were performed under dry condition at room temperature (23±1 °C).

Dynamic test: oscillatory sinusoidal cycles

The viscoelastic property of the resin composites during setting was measured using the oscillatory sinusoidal strain test on an automated universal testing machine (H10KM, Hounsfield). Details of the testing machine are described extensively in chapter 3 of this thesis. The freshly mixed resin composite (1:1 w/w) was bonded between opposing steel disks with diameter (d) of 5.4 mm and separated by a distance (h) of 5.0 mm, creating a C-factor of 0.5 (=d/2h). During the measurement, the upper disk performed an oscillating sinusoidal deformation with amplitude of 1.0 µm (=0.02 % strain) and frequency of 0.1 Hz around the original height of the specimen (Fig. 6.2).

One hour after the start of the experiment, the resin composite was subjected to tensile loading (5 µm/min) until fracture. The measurements were repeated 3 times at room temperature (23±1 °C). During the measurement, the data (time, load, and displacement signal) were collected simultaneously at a sample rate of 18 points per second. All measurements were started within 2 minutes after mixing the composites.

Volumetric shrinkage

During the dynamic test measurement, the axial shrinkage strain of
the specimen was not measured, because the oscillatory deformation was performed around the original height of the specimen. However, the displacement caused by axial shrinkage must be taken into account when modeling the stress data recorded by the dynamic test method. For this reason, volumetric shrinkage measurements (n=3) were performed by a mercury dilatometer at 23±0.1 °C, using the procedure described by De Gee et al. [19]. All measurements were started within 2 minutes after mixing the composites.

Parameter identification on stress-strain data

For this investigation, it was assumed that the mechanical properties of the composite are isotropic (the same in all directions), and that the viscoelastic behavior of the composites in the early stage of setting can be described by the Maxwell model [20]. The load and displacement data from the oscillatory strain measurement were converted to normal stress (σ) and strain (ε) data by using Equation (6.1) and (6.2) respectively:

\[
\sigma = \frac{F}{A} \quad (6.1)
\]

\[
\varepsilon_{axial} = \frac{\Delta L}{L_0} \quad (6.2)
\]

in which A is the cross-sectional area of the cylindrical specimen (m²), F the recorded load response of the specimen (N), ΔL is the displacement recorded by the LVDT transducers (m), L₀ the height of the specimen.
before setting (m). The shrinkage and dynamic component in the stress data were isolated with the standard Fast Fourier Transform (FFT) smoothing procedure in Origin (version 5.0, Microcal).

The Maxwell’s material parameters ($E$=Young’s modulus and $\eta$=viscosity) were determined by applying the parameter identification procedure, as described in chapter 4, on small time intervals (ten seconds) in the stress-strain data. The strain for the small time intervals was calculated by adding the oscillatory strain of the dynamic experiment to the shrinkage strain, which was considered as a linear function:

$$\varepsilon(t) = \varepsilon(t_0) + At + B\sin(\omega t)$$  \hspace{1cm} (6.3)

in which $\varepsilon(t_0)$ is the strain at begin time interval, $A$ is the slope of the shrinkage strain (1/s), $B$ the amplitude, and $\omega$ the angular frequency (rad/s) of the applied oscillatory strain. The shrinkage strain was obtained from the free volumetric shrinkage data by the conversion factor provided by Feilzer and co-workers (Table 3.1).

In an evaluation procedure, the Maxwell model was loaded with the calculated parameters and shrinkage strain of the composite, to determine up to where in setting time the model simulates the real behavior of the composite. Details of the evaluation procedure are described in chapter 4 of this thesis.

**Stress relaxation time**

A number of constraints must be placed on the Maxwell’s model parameters. All parameters have to be positive, and must increase monotonically over time. Stress relaxation is an important material property, involving the time-dependent decrease in stress at constant strain by viscous flow. A measure of stress relaxation under constrained conditions is the so-called stress relaxation time ($\tau$). This material property, defined as $\eta/E$ for this model, is the time required for the stress to decrease to 1/e ($\approx$37%) of its initial value.

**Infrared spectroscopy**

The infrared measurements were performed on a Biorad 165 FT-IR spectrometer, equipped with a DTGS-detector, and controlled by Win-IR software (version 2.04, Biorad) on a Pentium (200 MHz) desktop computer (Windows© 98 platform).
Table 6.3 Infrared measurement protocol for two-paste resin composites.

<table>
<thead>
<tr>
<th>Type</th>
<th>Number of scans</th>
<th>Resolution (cm⁻¹)</th>
<th>Time (s)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Background scan</td>
<td>16</td>
<td>2</td>
<td>40</td>
<td>Background</td>
</tr>
<tr>
<td>Insertion individual paste</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Static scan</td>
<td>64</td>
<td>2</td>
<td>160</td>
<td>No conversion spectrum performed 1 time</td>
</tr>
<tr>
<td>Insertion mixed pastes</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kinetic scan</td>
<td>4</td>
<td>2</td>
<td>10</td>
<td>Conversion spectrum performed 385 times</td>
</tr>
</tbody>
</table>

All specimens were measured in a Teflon mold (d=5.4 mm, h=5.0 mm) placed directly on a Golden Gate (Single Reflection Diamond ATR, 10500 series, Graseby). The top of the cylindrical specimens was covered with a greased glass slide. Absorbance spectra were taken before and during the setting of the resin composites, according to the measurement protocol as specified in Table 6.3. The kinetic scan was started within 60

Figure 6.3 Peak of methacrylate double-bond stretch vibration (1636 cm⁻¹) and 1,4-disubstituted phenylene stretch vibration (1582 cm⁻¹) as internal reference [21]. The baseline (dotted line) for the methacrylic peak is drawn from approximately 1655 to 1590 cm⁻¹.
seconds after mixing the composites. The double-bond conversion ($\xi$) for each spectrum was determined by the following equation:

$$\xi = 1 - \frac{c_t}{u}$$  \hspace{1cm} (6.4)

where $c_t$ is the ratio of the peak height of the methacrylate double-bond stretch vibration at 1636 cm$^{-1}$ to the peak height of the internal reference (Fig. 6.3) at time $t$, and $u$ is the same (mean) ratio for the individual pastes. The static and kinetic scans were measured 3 and 5 times respectively.

**Wear**

The erosive wear performance of the experimental composites was tested by three-body wear tests in the ACTA wear machine (ACTA, The Netherlands), shown in Figure 6.4. This wear test mimics the clinical condition in which the occlusal surface of the restoration is exposed to stresses and relative motions associated with chewing and a third-body medium. The third-body medium contains components resembling those, which are present in natural food. A detailed description of the wear machine and its functioning has been given by Pallav et al. [22-24].

Each compartment in the sample wheel was filled with freshly hand mixed (1:1 wt%) composite material, covered by a matrix, and polymerized at room temperature. The sample wheel accommodates three specimens of each composite material. The commercially available dental resin composite Z100 was also included, to serve as reference. This light-activated composite, covered by a matrix, was polymerized for 180 seconds in a halogen light curing cabinet (Dentacolor XS, Kulzer) at room temperature. After one hour, the specimens were glued onto the sample wheel with cyanoacrylate, and ground with a diamond wheel (grit 600), to obtain a uniform cylindrical outer surface. The starting profile on the specimen surfaces was obtained in the wear machine, by cycling the wheel 25,000 cycles in used (old) slurry. After being finished, the specimens were maintained at room temperature and kept wet at all times.

The wear of the composites was tested once at a set time intervals after preparation of the specimens: after 1 day, 3 days, 1 week, 1 month, 4 months, and 1.4 years respectively. Each wear test run consists of 200,000 cycles of the sample wheel at a rotational speed of 1 Hz (chewing frequency). The entire process lasts approximately 55 hours. After each
wear test, the third-body medium, consisting of a slurry of white rice and millet seeds shells, was renewed. Before and after each wear test, ten separate surface profiles of each specimen in the axial direction of the sample wheel were recorded in an automated profilometer set up. As can be seen from Figure 6.4, the surface profile includes of two unworn reference planes flanking the worn area. The average depth of the worn surface relative to the reference planes represents the wear in microns (vertical loss of substance). By taking the reference areas outside the wearing area, yet still on the material itself, any swelling by water sorption is canceled out in the measured wear.

**Figure 6.4** Schematic representation of the various steps in the wear test. **Upper left:** sample wheel with some specimens polymerized and glued onto the wheel. **Middle:** (1) sample wheel and (2) antagonist wheel rolling over each other in a slurry of rice and millet seed shells for three-body (erosive) wear. The antagonist wheel is pressed against the sample wheel by a spring force of 15 N, and the surface velocity has been adjusted to obtain slip rates of 15 % for occlusal contact-free wear. The rotational speed of the sample wheel was fixed at 1 Hz (chewing frequency). **Upper right:** surface tracings from one unworn reference to the other across the worn surface for wear measurements [22].
Results and discussion

Shrinkage stress-strain data

The material properties of dental resin composites depend on several factors, related to the initiation system, the resin, the filler particles, and the coupling between filler and resin. It is often difficult on the basis of the published literature to know what has caused measured differences in material properties, because the investigated materials were different in several aspects. In this study, only one factor was varied, i.e., the weight composition of bisGMA and TEGDMA in the resin.

Figure 6.5 shows the shrinkage strain and shrinkage stress development during setting for the experimental composites with various bisGMA-TEGDMA weights in the resin. The more bisGMA was replaced by TEGDMA, the higher the composite shrinkage strain development. This observation is in agreement with expectation, because the increase of TEGDMA results in the increase of double-bond content in the resin (Table 6.2). From the shrinkage results presented in Table 6.4, we may notice a doubling of shrinkage during the pre-gel phase of the composite at each increment step of TEGDMA. Although the presence of more TEGDMA in the resin leads to more flowable composites, as noticeable during handling, it does not provide the desired prolonged predominant viscous state for the composite. At maximum flowability, only 20% of the total shrinkage had been completed before a stress response was registered.

The stress-strain results show that bisGMA-TEGDMA composites reveal a linear relation between the amount of post-gel shrinkage strain and the amount of shrinkage stress after one hour setting. The effect of TEGDMA

<table>
<thead>
<tr>
<th>Resin composition</th>
<th>Pre-gel shrinkage (vol%)</th>
<th>Post-gel shrinkage* (vol%)</th>
<th>Total shrinkage (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 wt% TEGDMA</td>
<td>0.3</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>50 wt% TEGDMA</td>
<td>0.6</td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>70 wt% TEGDMA</td>
<td>1.1</td>
<td>4.6</td>
<td>5.7</td>
</tr>
</tbody>
</table>

* Post-gel shrinkage = part of the overall shrinkage wherein a shrinkage stress on the composite is recorded.
on the polymerization rate, stiffness, and viscosity development of the composites will be presented and discussed in the next sections.

**Figure 6.5** (a) Volumetric shrinkage strain and (b) axial shrinkage stress development (—measured, ▲ Maxwell model) of experimental resin composites (C-factor=0.5) during setting. The onset in shrinkage stress (=gel-point) for the 30, 50, and 70 wt% TEGDMA composite was 192, 180, and 190 s respectively.

**Infrared spectroscopy**

The infrared results summarized in Table 6.5 provide valuable information about the effect of resin composition on the dynamics of the composite’s polymerization reaction. The double-bond conversion rate was determined from the time derivative of the mean conversion-time data.

**Table 6.5** Summary of the infrared results for two-paste composites in which the weight composition of bisGMA-TEGDMA in the resin was varied.

<table>
<thead>
<tr>
<th>Composition (wt % TEGDMA)</th>
<th>Maximum conversion rate (%/s)</th>
<th>Setting time at maximum conversion rate (s)</th>
<th>Conversion at maximum rate (%)</th>
<th>Conversion after one hour (%)</th>
<th>Converted C=C (mol/cm³)</th>
<th>Unreacted C=C (mol/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>0.47 (0.03)</td>
<td>143</td>
<td>27.0 (2.4)</td>
<td>57.3 (2.3)</td>
<td>1.937x10⁻³</td>
<td>1.443x10⁻³</td>
</tr>
<tr>
<td>50</td>
<td>0.53 (0.02)</td>
<td>163</td>
<td>25.5 (1.9)</td>
<td>56.3 (3.8)</td>
<td>1.723x10⁻³</td>
<td>1.338x10⁻³</td>
</tr>
<tr>
<td>30</td>
<td>0.41 (0.03)</td>
<td>186</td>
<td>15.1 (2.1)</td>
<td>44.2 (3.2)</td>
<td>1.208x10⁻³</td>
<td>1.525x10⁻³</td>
</tr>
</tbody>
</table>

*Conversion is not significant different from each other (p<0.05)*
The increase of TEGDMA in the resin phase resulted in higher double-bond conversion of the composite. This is in agreement with the literature [12, 25]. The conversion after one hour setting was limited to values below 60%. A hundred percent conversion is practically not feasible, due to the formation of a high cross-linked polymer network, which limits the mobility of reacting species. Studies on light-activated dental dimethacrylate resins revealed final double-bond conversions in the range of 55-80% [26, 27].

The increase of the double-bond conversion rate to a maximum, even though the amount of monomer is diminishing, is quite common in multifunctional dimethacrylate systems, and is known as auto-acceleration, gel effect, or Trommsdorff-Norrish effect [28]. This effect is attributed to the growth of polymer, which results in an increase of viscosity. This, in turn, has an adverse effect on the diffusion process of radicals to terminate (Fig. 2.1), resulting in an increase in the concentration of free radicals [29]. At a certain point in the reaction time, the mobility of the monomer becomes even lower, and propagation (Fig. 2.1) also becomes diffusion-controlled, along with termination. This phenomenon, known as autodeceleration, causes the rate of reaction to fall off substantially.

Inspection of the maximum conversion rates in Table 6.5 reveals that an increase of TEGDMA in the resin causes the maximum conversion rate to shift significantly (p<0.05) to higher values, with an optimum for the composite with 50 wt% TEGDMA in the resin. This observation is in agreement with that of Lovell et al. [27], who found the highest maximum rate for experimental light-activated resins in the range of 25 to 50% in weight TEGDMA. The researchers attribute the occurrence of a maximum rate at this specific bisGMA-TEGDMA composition to the excellent diluent property of TEGDMA, and the high reactivity of bisGMA [30, 31]. In this specific resin composition range, sufficient TEGDMA is present to reduce the initial viscosity of the composite, and thereby increasing the mobility of the reactive bisGMA. When the composite contains too much TEGDMA in the resin, then the less reactive TEGDMA dominates the reaction, resulting in a slower polymerization reaction.

It is striking that the setting time for maximum conversion rate is not related to the polymerization rate, but to the amount of TEGDMA in the resin. The explanation for this observation may be that the composites did not had the same inhibition period. The monomers were stabilized with different amounts of inhibitor. As the monomers were used as received (Table 6.1), the inhibitor concentration decreased when bisGMA was replaced by TEGDMA, resulting in shorter inhibitor time periods.
Examination of the setting time for maximum conversion rate (Table 6.5) with the start of shrinkage stress development (Fig. 6.5) reveals that the transition of the auto-acceleration to autodeceleration occurs in the pre-gel setting phase of the composite. It was after 200 seconds, in which 17 % or more of the measured double-bond conversion had been completed, that a stress response was registered. From statistical calculations it is known that during the early stage of polymerization, monomers are mainly converted into polymeric chains [32]. It may be expected that up to 17 % double-bond conversion, some cross-linking of the polymer chains may have occurred, since both TEGDMA and bisGMA are cross-linking agents. The fact that the composite structure is still capable to flow predominantly up to 17 % double-bond conversion indicate that the build up of the resin network proceeds with the formation of isolated cross-linked polymer segments, which can slip along one another (Fig 2.4).

Maxwell model

The evaluation results of the Maxwell model reveals that even in the post-gel phase of setting, the composites can still flow permanently for a considerable period in time. An explanation for viscous flow during post-gel setting, wherein double-bond conversion is mainly consumed for cross-linking, may be that the cross-linking reaction proceeds faster in polymer segments than between polymer segments. Cross-linking between growing polymer segments proceeds slowly with time, due to diffusion limitations. As a result, the polymer segments can still slip along one another. As soon as all polymer segments are connected to each other, viscous flow is highly restricted to processes, such as local rearrangement in the polymer network, movement of the unreacted vinyl groups, and to porosity in the composites, introduced by mixing and formation of carbon dioxide (Fig. 2.1). From this point in setting time, the Maxwell model is no longer valid, because it predicts permanent viscous flow. In this study, this point in setting time is reached at approximately 15-20 minutes (Fig. 6.5b), wherein 40 % or more double-bonds have been converted. On future studies, it might be usefull to follow the setting process of dental composites with Nuclear Magnetic Resonance (NMR). This technique may be considered as a type of chemical microscope, by which the bisGMA and TEGDMA units during the polymerization process can be monitored [33].
Material parameters

The Maxwell parameters $E$ (Young’s modulus) and $\eta$ (viscosity) were examined up to 15 minutes after mixing, because the Maxwell model had been proved valid during this setting phase (Fig. 6.5b). Table 6.6 summarizes the calculated values for several points in setting time of one measurement.

Maximum double-bond conversion is obtained when the amount of TEGDMA in the resin is increased. The student’s $t$ test with pooled variance ($p<0.05$) demonstrated that the maximum amount of double-bond conversion after one hour setting, was similar for the 50 and 70 wt% TEGDMA composite. As the viscosity and Young’s modulus development with setting time differs significantly (Table 6.6), one may conclude that the effect of TEGDMA on the viscoelastic property is not solely due to the degree of conversion. Probably, the amount and nature of the TEGDMA and bisGMA subunits in the polymer network also plays a role in the viscoelastic behavior of the composites. The aromatic bisGMA molecule is relative stiffer than TEGDMA. The aromatic group in the central part of the molecule (Fig. 6.1) causes much larger barriers to rotation about the bonds. TEGDMA is more flexible, because the ether (C-O-C) linkages of the molecule give rise to only slight barriers to free rotation about the bonds. Furthermore, bisGMA molecules are capable of forming hydrogen bonding, which restricts sliding of polymer chains, thereby increasing the viscosity of the system. The highest Young’s modulus and viscosity development with setting time for the 50 wt% TEGDMA composite can be explained by the fast polymerization reaction, in combination with the build of an optimum bisGMA and TEGDMA monomer ratio in the polymer network, and the low concentration of unreacted double-bond in the resin (Table 6.5). Too much TEGDMA in the resin results in a slower polymerization rate, a more flexible polymer network, and more unreacted double-bonds in the resin. As a result, the stiffness and viscosity development with setting time is lower.

Clearly, the polymerization rate of bisGMA-TEGDMA composites is an indicative measure for the stiffness and viscosity development of the composite. This is visualized in Figure 6.6. Instead of plotting the Maxwell parameters individually, the ratio of viscosity to stiffness, the so-called stress relaxation time, is given for each composite. Stress-relaxation is a measure of stress relief under constrained conditions. It represents the time required for the stress to decrease to $1/e$ ($\approx 37\%$) of its initial value. The effect of TEGDMA on lowering the viscous state of the composite, which is similar to the effect of increasing the
### Chapter 6

**Influence bisGMA/TEGDMA ratio in two-paste composites**

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>30 wt% TEGDMA</th>
<th>50 wt% TEGDMA</th>
<th>70 wt% TEGDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E (GPa)</td>
<td>$\eta$ (Pa.s)</td>
<td>E (GPa)</td>
</tr>
<tr>
<td>0</td>
<td>0.230(0.01)</td>
<td>0.13(0.01)</td>
<td>0.85(0.03)</td>
</tr>
<tr>
<td>10</td>
<td>0.230(0.01)</td>
<td>0.13(0.01)</td>
<td>0.85(0.03)</td>
</tr>
<tr>
<td>30</td>
<td>0.230(0.01)</td>
<td>0.13(0.01)</td>
<td>0.85(0.03)</td>
</tr>
<tr>
<td>60</td>
<td>0.230(0.01)</td>
<td>0.13(0.01)</td>
<td>0.85(0.03)</td>
</tr>
<tr>
<td>120</td>
<td>0.230(0.01)</td>
<td>0.13(0.01)</td>
<td>0.85(0.03)</td>
</tr>
</tbody>
</table>

All values are averages of $n = 3$.

---

*Note: Time relaxation time, defined as $\eta/t$, is the time to decrease the stress to 1/e ($\approx 37\%$) of its initial value.*
Figure 6.6 Stress relaxation (=\eta/E) development of experimental chemically activated resin composites (C-factor=0.5) with different TEGDMA-bisGMA composition. Error bars indicate the standard deviations of the calculated mean (n=3).

temperature, lasted only for the first minute in low stress-relaxation times. After this period, the stress relaxation time development occurs according the polymerization reaction rate, as discussed in the previous section.

De curves in Figure 6.6 and Figure 6.5 show that for the most reactive bisGMA-TEGDMA composites, the post-gel shrinkage is the decisive factor in the shrinkage stress development of the composite. Too much TEGDMA in the resin leads to a higher concentration of double-bond conversion, and thus higher post-gel shrinkage. As the relaxation curve is only slightly lower than for the 50 wt% TEGDMA composite, the ultimate shrinkage stress development is higher.

The composite with the lowest content of TEGDMA undergoes low post-gel shrinkage and develops low relaxation times. As a consequence, the shrinkage stress is favorable low, which allow the bond to the cavity wall a chance to form and remain intact. However, due to the restricted mobility of the bisGMA monomer, less double-bonds are converted. As a result, relatively more unreacted monomer will be present in the composite. The presence of unreacted monomers is of considerable concern, because these monomers will slowly leach into the surrounding
medium, resulting in deleterious effects on the mechanical stability and biocompatibility of the restoration [34, 35]. Further studies with bisGMA-TEGDMA composites should be focused on two aspects, which can reduce post-gel shrinkage of the composite. First, the most reactive bisGMA-TEGDMA composition must be better specified by increasing the TEGDMA in smaller increments. An optimum directed toward the use of less TEGDMA should result in less post-gel shrinkage. Second, the application of diatomites as dental filler must be tested [36]. This high porosity material, with pore size in the range of 1.5-22 μm, allows the formation of an integrated resin-filler system. In this case, shrinkage of the polymer system does not occur solely between filler particles, which, ultimately, should lead to lower post-gel shrinkage.

Young's modulus and tensile strength after one hour setting

Table 6.7 summarizes the elastic modulus and tensile strength of the composites after one hour setting. All composites fractured cohesively, whereby the fracture always started at one side at the periphery of the metal-composite interface, and propagated at a small angle to the other side. The diameter of the fractured surface area did not derivated significantly from the diameter of the paper matrix.

Table 6.7 Material properties of experimental resin composites at a 60-minute setting (mean – SD).

<table>
<thead>
<tr>
<th>Material property</th>
<th>30 wt% TEGDMA</th>
<th>50 wt% TEGDMA</th>
<th>70 wt% TEGDMA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young's modulus (GPa)</td>
<td>6.97 (0.1)</td>
<td>7.24 (0.1)</td>
<td>7.08 (0.1)</td>
</tr>
<tr>
<td>Tensile strength (MPa)</td>
<td>29.3 (5.1)</td>
<td>20.0 (4.0)</td>
<td>17.8 (3.6)</td>
</tr>
</tbody>
</table>

The Young's modulus values are in agreement with the results of Asmussen et al. for experimental light-activated bisGMA-TEGDMA composites [37]. They found also a maximum in the Young's modulus. Due to the smaller increments, the maximum was observed at a 64 wt% bisGMA - 36 wt% TEGDMA composition in the resin. The existence of an optimum bisGMA-TEGDMA composition toward less TEGDMA is favorable, because this will ultimately cause less post-gel shrinkage strain of the material.

The relationship between tensile strength and monomer composition contrasts with the findings of Asmussen and co-workers. They observed an increase of tensile strength with the amount of TEGDMA, while in this
Figure 6.7 Tensile stress-strain behavior of the experimental resin composites at one hour setting. Specimens were prepared during dynamic testing, and, therefore, differs in shrinkage stress history (notice stress value at strain=0 %).

In this study, the opposite relation is observed. Many factors (methodology, specimen preparation, initiation system, etc.) may contribute for the difference in observation. The most decisive factor, probably, will be the specimen preparation, as this affects the structural integrity, and, therefore, the tensile strength of composites severely. In the study of Asmussen et al., specimens of light-activated composites were prepared in a mold, under (shrinkage) stress free conditions. In this study, specimens of chemically activated composites were prepared during dynamic testing. In this test, the composite was loaded with shrinkage stress (Fig 6.7). It is known that internal stresses stimulate microvoid formation in the composite structure [36]. For this reason, it may be expected that the composites in this study contain microvoids. The higher the shrinkage stress, the more microvoids may be expected. In addition, hand mixing of composites introduce porosity, another source of microvoids formation. High amount of microvoids weakens the composite; i.e., the difference between the real (bulk) value and measured value becomes greater. By stretching the composite until fracture, the microvoids may grow substantially until they reached the critical size, and initiated the fracture process. The higher the amount of microvoids, the more the measured value deviates from the bulk material. This might be the case in our study, while Asmussen and co-workers measured more likely the bulk property of the composites.
This observation of the tensile strength dependence on the shrinkage stress is of clinical relevance in dentistry.

The reason for the good agreement between the Young’s modulus in this study with Asmussen and co-workers is that the values for the Young’s modulus were determined from the initial (straight) stress-strain portion of the tension curve. In this region, the elongation of the composites, and, therefore, the growth of the microvoids was relatively small. As a result, the measured moduli are representative for the bulk material.

Wear

An increase of TEGDMA in the resin phase results in a higher concentration of converted double-bonds in the composite (Table 6.5). This benefits the adhesion between the resin and the filler, because more converted double-bonds could contribute to bind the resin to the filler, leading to increased wear resistance. The results of the erosive wear test (Fig. 6.8) confirms this statement; the higher the TEGDMA concentration, the lower the wear; i.e., higher wear resistance. The

![Figure 6.8](image)

**Figure 6.8** The effect of maturation on occlusal contact-free wear for experimental two-paste resin composites in comparison with reference (Z100) at 15 % slip and 15 N force (in m/200,000 cycles). Each sample wheel, which accommodates three specimens of each composite material, was tested once. All means (n=3) were significantly different (p<0.05).
experimental composites show a significant decrease in wear over time. Similar behavior was observed for the composite Z100, and is commonly seen in composites [38]. This phenomenon, which last for four months, has been attributed to internal stress relief [39]; however, a continued conversion of double-bonds also contributes to the increased wear resistance [40].

The sudden increase of wear after one year is a phenomenon that can be observed only when wear is measured with a single measurement. Usually, subsequent measurements should reveal several microns less wear for the same material. This effect is attributed to surface softening caused by the prolonged exposure to water, and seems to be related to hydrolysis and subsequent resin-filler debonding [41].

The thickness of the softened layer, however, is much less than the amount of wear, which occurs clinically in the same time period. This means that the rate at which the surface softens is much less than the rate at which it wears off, and, therefore, it is unlikely that this softening has any clinical significance.

**Conclusions**

This research shows that the relative amounts of bisGMA and TEGDMA in the resin affect the maximum polymerization rate and mechanical properties of experimental composites. It was found that, in general, bisGMA controls the reactivity of the polymerization reaction, whereas TEGDMA controls the mobility of the reacting dimethacrylate system and the composite shrinkage. Composites with 50 wt% TEGDMA in resin displayed the highest polymerization rate and the highest viscoelastic parameter development during setting. Although large amounts of TEGDMA in the resin resulted in a higher number of converted double bonds, it also increased wear and reduced tensile strength. Substituting bisGMA for TEGDMA prolonged the predominant - pre-gel - viscous flow property of composites to only a moderate degree. At a high TEGDMA/bisGMA ratio, the relatively high post-gel shrinkage is the decisive factor in shrinkage stress development. The Maxwell model is able to predict the viscoelastic behavior of two-paste bisGMA-TEGDMA composites up to 15-20 minutes into the setting process.
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References

1. See chapter 2 of this thesis.
17. Private communication with dr AJ Erdrich and dr A Grundler of Heraeus Kulzer GmbH & Co. KG, D-61273 Wehrheim, Germany, Germany (1999).


20. See chapter 5 of this thesis.


Chapter 6  

Influence bisGMA/TEGDMA ratio in two-paste composites


Influence bisGMA/TEGDMA ratio in two-paste composites