Viscoelastic behavior of dental restorative composites during setting
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Abstract

This chapter describes a preliminary study on the potential of an experimental low-shrinkage composite for use in restorative dentistry. The shrinkage strain-strain, stiffness development, and tensile strength at different configurations (C-factor) of an oxirane composite were measured and analyzed at room temperature and oral temperature. It was found that the stiffness development was inversely related to the C-factor. Higher temperatures led to increased shrinkage and stiffness, and thus to higher shrinkage stresses. Despite the attractive low-shrinkage, strain-stress behavior, the poor mechanical strength properties of the oxirane composite make this light-activated composite not suitable for use as a posterior restorative material. These poor properties appear to be the result of a weak interaction between filler and oxirane matrix.
Introduction

Resin composites are widely used in dental practice, as they exhibit the appropriate physical and mechanical properties, as well as excellent aesthetic properties. Still, the problem of shrinkage during the setting process has not been solved. Volumetric shrinkage, in combination with the solidification process of the composite, will inevitably lead to development of stress, which may disrupt the restoration bond to cavity walls. The magnitude of the shrinkage stress has been found to be dependent on composite shrinkage [1], the viscoelastic behavior during setting [2], and on the amount of compliance of the substrate material [3-5].

A critical factor in obtaining a leakproof and durable restoration with present-day composites is the practitioner's technique of restoration placement. The choice of restoration design [6-7], filling technique (several increments [8], introducing porosity [9]), and light activation method [10], can reduce the amount of shrinkage stresses in the restoration significantly. These manipulative factors minimized shrinkage stresses by providing the restorative material either more free area (low C-factor) or time (low polymerization rate) to flow during shrinkage.

Obviously, this manipulation will also influence the final material properties. Whereas the effect of restoration design, described by the configuration factor$^1$, on the mechanical properties of the material is assumed to be neglectible, porosities and varying light intensity techniques may influence the mechanical strength of polymerized composites negatively [11-14]. In the choice of an application method or type of restoration, a balance must be found between low shrinkage stress, on the one hand, and a adequate monomer conversion level, on the other [15].

The problems involved with composite shrinkage should not depend on, or in the worst case, solved by the practitioner's technique of making restorations. The use of low-shrinking or even non-shrinking composites would lead to less handling techniques to provide restorations of high quality and long clinical durability. Recently, a dental composite based upon oxirane as monomer system has been developed [16]. A previous study showed that the cationic (ring opening) polymerization of the oxirane composite caused significantly less polymerization shrinkage strain and stress compared with conventional dimethacrylate based composites [17].

$^1$C-factor=ratio bonded (immovable) to unbonded (free) surface of restoration
The aim of this study was to explore the potential of the oxirane composite as dental restorative material by determining the effect of C-factor and temperature on several mechanical properties of the composite during and after setting.

**Materials and methods**

**Experimental composite**

The oxirane composite was prepared by 3M (Pluto, batch EXL546, exp 01/2002 3M). According to the manufacturer’s instructions, the composite was light cured for 60 seconds (Elipar Highlight, standard mode, ESPE) with a light intensity of 600 mW/cm² (radiometer, model 100, Demetron) at the light exit tip (Ø=8.95 cm).

**Dynamic test: oscillatory deformation cycles**

The dynamic stress-strain data were obtained from an oscillatory sinusoidal strain measurement on an automated testing machine (ACTAIntense, ACTA), as specified in chapter 8 of this thesis. The measurements (n=3) on the oxirane composite were performed at four different C-factors (Table 9.1). The effect of the temperature (23±0.5 and 37±0.5 °C) was measured solely at the lowest and highest configuration setting of the composite; i.e., C=1.0 and C=3.85 respectively. The dynamical tests were performed with ACTA application software (version 3.14)

**Table 9.1** Survey of configuration (C) factors (d/2h), their corresponding volumes, and temperature for oxirane composite in the oscillatory deformation tests.

<table>
<thead>
<tr>
<th>Code</th>
<th>Temperature (°C)</th>
<th>C-factor</th>
<th>Diameter [d] steel rod (mm)</th>
<th>Height [h] composite (mm)</th>
<th>Volume (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1-23</td>
<td>23</td>
<td>1.0</td>
<td>3.2</td>
<td>1.60</td>
<td>12.87</td>
</tr>
<tr>
<td>C1-37</td>
<td>37</td>
<td>1.0</td>
<td>3.2</td>
<td>1.60</td>
<td>12.87</td>
</tr>
<tr>
<td>C2-23</td>
<td>23</td>
<td>2.0</td>
<td>4.0</td>
<td>1.00</td>
<td>12.57</td>
</tr>
<tr>
<td>C3-23</td>
<td>23</td>
<td>3.0</td>
<td>4.5</td>
<td>0.75</td>
<td>12.93</td>
</tr>
<tr>
<td>C3.85-23</td>
<td>23</td>
<td>3.85</td>
<td>5.0</td>
<td>0.65</td>
<td>12.76</td>
</tr>
<tr>
<td>C3.85-37</td>
<td>37</td>
<td>3.85</td>
<td>5.0</td>
<td>0.65</td>
<td>12.76</td>
</tr>
</tbody>
</table>
Volumetric shrinkage measurement

During the dynamic test, the axial shrinkage strain of the specimen was not measured, because the height of the specimen during setting was kept constant. However, the displacement caused by axial shrinkage must be taken into account when modeling the stress data. For this reason, volumetric shrinkage measurements (n=3) were performed with a mercury dilatometer at 23±0.1 and 37±0.1 °C, using the procedure described by De Gee et al. [18].

Scanning electron microscopy

The fractured surface of the composites was examined in a Philips 20 XL scanning electron microscope at an accelerating voltage of 20 kV.

Stress-strain analysis

The stress-strain data obtained from the oscillatory deformation measurement were analyzed as described in chapter 8 of this thesis. The data obtained from the volume shrinkage measurement were averaged, and the axial shrinkage strain (axial) of the oxirane composite at the chosen configuration was calculated from the volumetric shrinkage strain (ε_vol) by the conversion factors in Table 3.1. In this approach, we assumed that the shrinkage behavior of the oxirane composite was similar to the conventional dimethacrylate composites, as measured by Feilzer and co-workers. [19]. For the identification of the Young's modulus, the functional expression of the obtained axial shrinkage strain with time was calculated by a cubic spline fit, and added to the oscillatory strain for all the points in time of the dynamic test measurement (Fig. 8.7e).

Young's modulus identification

A previous study showed that the stiffness development, denoted by the elastic or Young's modulus E, of the oxirane composite during setting can be identified by analyzing isolated stress-strain data with the Maxwell model (Fig. 8.9). Due to the high level of noise carried by the stress data, we were not able to predict realistic viscosity values with the Maxwell model [17]. The identification procedure for the Young's modulus on stress-strain data of small time intervals (approx. 10
seconds) is described in chapter 8 of this thesis. The parameter identification procedure was performed with Matlab (version 5.3, Mathworks) on a desktop computer (Windows® 98 platform).

**Results and discussion**

**Effect of configuration factor**

Polymerization shrinkage has three fundamental aspects, namely magnitude, direction and time-dependence. The magnitude and direction (or vector character of shrinkage) are influenced not only by material composition, but also by the geometry of the host environment, normally the shape and size of the preparation being restored. To a first approximation, this is governed by the C-factor, the ratio of bonded (immovable) to unbonded (free) surface of the material. In this study, we could not determine the effect of the C-factor on the axial shrinkage.

![Graphs](image_url)

**Figure 9.1** (a) Axial shrinkage strain for the oxirane composite at several C-factors at room temperature. The horizontal line in the figure represent the level of volumetric shrinkage strain after 6000 seconds setting as measured with the dilatometer. (b) The shrinkage stress development of the oxirane composite bonded at several specimen configurations at room temperature. (c) The Young's modulus development as predicted by the Maxwell model. Error bars indicate the relative standard error in the calculated mean (n=3).
behavior of Pluto with a linometer [20-22], because the test conditions of the linometer are insufficient to measure the slow and low shrinkage process of Pluto on a reproducible and reliable basis.

The shrinkage strain of the experimental composite was determined indirectly with mercury dilatometry by the conversion factors provided by Feilzer et al. [19]. Figure 9.1a shows the shrinkage curves derived from dilatometry. As was found by Feilzer and co-workers, the composite shrinkage, which is normally distributed in three dimensions, was gradually converted into one direction, approaching the magnitude of volumetric shrinkage when the C-factor of the composites was increased.

Figure 9.1b shows the increase of shrinkage stresses with increasing the C-factor of the oxirane composite. This shrinkage stress dependency on the C-factor was also observed for conventional dimethacrylate composites by Feilzer et al. [7]. Contrary to that study, none of the oxirane composite specimens fractured spontaneously. This may not be a surprise by the look at the slow and low shrinkage stress development, which was in magnitude twenty times lower than measured by Feilzer and co-workers under similar test conditions. The low shrinkage stress development of the oxirane composite puts a low demand on oxirane based bonding agents [23]. For the clinical practice, it may be expected that the dentin-oxirane composite interface in a bulk filled Class V preparation will survive the shrinkage stress when light cured for 60 seconds. A clinical handling, which often results in poor marginal sealing with conventional dimethacrylate composites [24].

It is interesting that the Young’s modulus development of the composite in relation to the C-factor (Fig. 9.1c) did not coincide with our expectation. Due to the less flow ability of the composite, we expected an increase in stiffness behavior of the composite when polymerized at higher C-factors. The observed relation between the stiffness development and C-factor is not strictly valid for this experimental composite. Preliminary dynamic tests in our laboratory on a commercially available dimethacrylate composite (TetricCeram, Vivadent) revealed the same relation between C-factor and stiffness development.

The relation between the Young’s modulus and C-factor needs further to be discussed. A factor that could have influenced the Young’s modulus negatively at thin composite layers may be the presence of voids or flaws in the specimen upon setting. In general, the effect of voids or flaws is minimized in compression, but show up in tensile mode of the specimen as a reduction in Young’s modulus. Due to shrinkage, the
composite becomes more stretched at high C-factor. As a result, the compression phase; i.e., the cross head movement towards the specimen, in the oscillatory deformations becomes less effective compressive. This could have lead to lower Young’s modulus development at higher C-factors. The structural integrity of the oxirane composite will be discussed in the next paragraph.

### Scanning electron microscopy

Shown in Figure 9.2 are SEM images of the fracture surface produced by axial tensile loading. The fracture surface exhibited many empty, spherical voids in a range of 5-125 μm in diameter. It is observed that more voids were presence on the fracture surface of the composite polymerized at higher C-factors. This observation may explain the lower Young’s modulus development at higher C-factors. Owing to the size of these voids, we conclude that void formation must have started from porosity. The level of voids did surprise us, because not much

![SEM images of fractured surface](image_url)

**Figure 9.2** SEM pictures of fractured surface of the oxirane composite at magnification (a) x15 (C3.85-37), (b) x50 (C3.85-37), (c) x500 (C3.85-37), and (d) x2000 (C1-23) after tensile loading. The framework represents the zoom area for the following picture. The white arrow in (a) indicate the most likely site of fracture initiation.
Oppportunity was given to introduce air in the light-activated composite during specimen preparation. In fact, precautions were taken to avoid air introduction: the composite was pressed slowly out from the wide-open syringe tip, and condensed carefully on the glass plate. The monomer conversion should not be affected by these voids, because the cationic polymerization of oxiranes is not inhibited by oxygen.

The SEM image in Figure 9.2d shows clearly that the adhesion between the filler surface and polymerized oxirane phase is poor. This picture shows clean filler surfaces and smooth filler prints in the dense resin phase, which indicates that the filler was easily separated from the resin phase during tensile loading. A study of the wear property is in progress, to evaluate the resin-filler integrity of this oxirane composite.

**Tensile strength**

Depending on the intended use, the tensile strength and stiffness are important properties for dental restorative composites. Undoubtedly, for some purposes the restorative should be stiff and strong, in other situations flexibility is more important, and strength not a critical factor. To judge whether the oxirane composite can be a potential posterior restorative, its stiffness and tensile strength were compared with Clearfil F2, a commercially available posterior dimethacrylate composite.

The dependence of tensile strength on the configuration of the oxirane composite is visualized in Figure 9.3. The tensile strength of the oxirane composite reaches a maximum value, which was in contrast with the findings of Alster and co-workers, which reported a gradually increase of tensile strength of Clearfil F2 with increasing C-factor [26]. The divergent course in the tensile strength relation with C-factor may be attributed to the structural integrity of the oxirane composite, which becomes weaker at C-factor≥2. No explanation has yet been found why the tensile strength relation with C-factor shows an optimum, and the Young’s modulus with C-factor not (Fig. 9.1)

The relatively weakness of the structural integrity of the oxirane composite with regard to Clearfil F2 is manifest, when the tensile strength (Fig. 9.3) and Young’s modulus of both composites are compared. Both material parameter values of the oxirane composite cannot compete with the values of Clearfil F2 (Young’s modulus = 10 GPa [2, 27]). The low stiffness (appr. 3 GPa) of this experimental composite indicates a low potential as posterior restorative, which is subjected to masticatory forces when in operation. SEM analysis revealed
Chapter 9  Part II: Mechanical properties of low shrinkage composite

that the poor performance of the material properties is mainly related to the weak interaction between the resin phase and filler surface. Considering this aspect, improvement of the resin-filler interphase might enhance the mechanical strength of this oxirane composite significantly.

![Graph showing tensile strength values](image)

**Figure 9.3** Tensile strength values of the oxirane composite after approximately 114 minutes setting. The tensile strength for Clearfil F2 after 60 minutes setting is also incorporated [28]. Error bars indicate the standard deviations of the calculated mean (n=3).

**Effect of temperature**

Figure 9.4 depicts the volumetric shrinkage performance of oxirane composite during setting at room temperature and oral temperature. The curves reveal that temperature affects the rate of the cationic polymerization positively. This is noticeable by the shorter delay in shrinkage, and the higher slope at each point in time of the shrinkage curve at 37 °C. The higher amount of shrinkage suggests a higher degree of monomer conversion at oral temperature. Attempts to monitor the oxirane conversion by infrared spectroscopy failed, because no characteristic peak of the C-O-C bond stretching was observed on the spectrograph at the range of 1050-1175 cm⁻¹ [29]. Raman spectroscopy might be helpful for this purpose.
Figure 9.4 Volumetric shrinkage of the oxirane composite at two temperatures and two different time-scales: (a) 100 seconds and (b) 100 minutes. Error bars indicate the relative standard error in the calculated mean (n=3). The light signal represents the initiation and termination of the irradiation process of the light unit.

The results shown in Figure 9.5a, however, confirm indirectly, the positive effect of temperature on the degree of monomer conversion. As the composition of the oxirane composite was kept constant, the increase in stiffness with temperature can only be caused by an increase in monomer conversion. Degree of conversion should not be interpreted as degree of cross-linking, because other mechanisms, such as polymer chain length distribution, and bonding polymer to filler, may play a role. Considering the effect of temperature on shrinkage and stiffness, it may not be a surprise that composite setting at oral temperature results in a higher shrinkage stresses (Fig. 9.5b). To mimic the clinical situation in future studies as close as possible, the oxirane composite must be exposed to water during setting. Besides the effect of water sorption on material properties [30], it will also be of interest to find out if the rate of the cationic polymerization reaction is affected by water uptake.

It is interesting to see that the stiffness curves of the oxirane composite at C-factor=3.85 converge to one single stiffness value. From this observation alone, one may conclude that temperature affects only the rate of monomer conversion, and not the amount of monomer conversion, because the same value of stiffness is reached. However, the shrinkage curve reveals more shrinkage at higher temperature, so more monomer conversion must have been taken place. An explanation for this phenomenon is not as simple as one would expect. The complexity lies in the dual role of temperature during setting. On one hand, the input of thermal energy increases monomer conversion, and as a result, the stiffness of the composite. On the other hand, an increase of thermal
energy decreases the stiffness, because the segmental mobility of the polymer chains is increased [31]. The dual role of temperature might explain the course of the stiffness curve at oral temperature. It can be argued that at the early 1200 seconds of setting, the temperature effect on the monomer conversion predominates, and in the remainder part of the setting process, wherein the rate of monomer conversion is low, the temperature effect on the polymer mobility predominates.

The convergence of the stiffness curves is not restricted to C-factor=3.85 solely. Extrapolation of both curves of C-factor=1 revealed that they tend to converge at 200 minutes setting. An explanation for this slow converge rate might be that the actual temperature of this thick layered composite is lower due to the existence of a temperature gradient across the specimen height; i.e., the distance between the heated glass plate and the head of the steel rod.

**Figure 9.5 (a)** The Young’s modulus development, as predicted by the Maxwell model, and (b) the shrinkage stress development of the oxirane composite at two specimen configurations and two temperatures. Error bars indicate the relative standard error in the calculated mean (n=3).

In the previous section, we discussed the stiffness and tensile strength property of the oxirane composite at 100 minutes setting. The slope of the stiffness curve C1-37 in Figure 9.5a indicate that maturation of the oxirane composite structure still proceeds after this time period of setting, which is characteristic for (living) cationic polymerization reactions [31, 32]. The continuation of the setting reaction after 100 minutes leads to improved stiffness. However, this begs the question how the practitioner knows when this composite has properly set for clinical function. In dentistry, up to 30 minutes as maximum setting time is considered to be acceptable, whilst several hours would
obviously be unacceptable. Therefore, in the development of the oxirane composite to become a restorative material, better material properties must be gained with shorter setting time.

Conclusions and recommendations

Several conclusions can be drawn from this explorative study of an experimental oxirane composite. The configuration and temperature of the composite affect the axial shrinkage strain, the axial shrinkage stress, and the stiffness development of the composite during setting. It was found that the C-factor was inversely related to the stiffness. Its poor mechanical strength and slow setting process make the low-shrinkage oxirane composite unsuitable for posterior restorative work. The mechanical properties can be improved if a strong bond is formed between filler and oxirane matrix. If the properties of this experimental composite can be improved, an attempt can then be made to study how water sorption affects the filler-matrix bonding process, the polymerization reaction, and the shrinkage of this composite.

References


17. See chapter 8 of this thesis.


28. See chapter 3 of this thesis.


