Viscoelastic behavior of dental restorative composites during setting
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MODELING OF THE VISCOELASTIC BEHAVIOR OF DENTAL LIGHT-ACTIVATED RESIN COMPOSITES DURING SETTING

Based on the article:

Abstract

The aim of this study is to investigate three mechanical models to describe the viscoelastic behavior of a commercially available light-activated restorative composite during setting. Stress-strain data on Z100 were recorded by a dynamic test method performed on a universal testing machine. The models were tested by matching the model response to experimental data and the material parameters Young’s modulus (E) and viscosity (η) associated with the model were calculated. The universal testing machine generated reliable stress-strain data on the fast setting, light activated resin composite. The high polymerization rate of Z100 had a negative effect on the viscous flow capability of the material. Only a minor proportion of composite shrinkage failed to contribute to stress development in the composite. A predictive model of the viscoelastic behavior of Z100 during setting was carried out, using the Maxwell model for the initial 3 minutes in the setting process and the Kelvin model for the remainder of the process.
Introduction

Shrinkage stresses generated in dental resin composites during setting are among the major problems in adhesive dentistry, because they interfere with the integrity of the restored tooth. For dental restorative applications, light-activated resin composites have replaced chemically activated resin composites, mainly because of their rapid polymerization reaction and the greater freedom in timing the initiation of polymerization. This “cure on command” allows the dentist to place and contour the restorative material with ease. However, it has been demonstrated that under similar test conditions, light-activated resin composites generate higher polymerization shrinkage stress than the analogous chemically activated composites [1]. This striking difference in shrinkage stress development is caused not only by the difference in shrinkage development, but also by the mechanical behavior of the setting composite, which is by nature viscoelastic [2].

In recent years, considerable attention has been given to the use of mechanical models to describe the viscoelastic behavior of dental restorative composites during setting [3-5]. In these studies, several linear viscoelastic models were investigated by applying a modeling procedure to experimental stress-strain data. In addition, the material parameters associated with the model were calculated. The results of these studies contribute to a better understanding of the shrinkage stress problems associated with adhesive composite restoration. Moreover, recent initial modeling studies have shown that both the shrinkage strain, which is associated with the polymerization reaction and is affected by temperature, and the stress field as well, can vary greatly within the restoration preparation [6-7]. Hence, by combining the results from temporal shrinkage strain and mechanical models, the stress field in and around the restoration can be analyzed using Finite Element Analysis (FEA) methods.

All these studies have in common that they have been focused on the viscoelastic behavior of chemically activated resin composites. Through introducing adjustments to the specimen mounting device in a specialized universal testing machine, it is possible to monitor the mechanical behavior of light-activated resin composites during setting [8]. Stress-strain data recorded with a dynamic test method were used to perform a modeling study of the viscoelastic behavior of this type of dental composites.
The aim of this study was to identify a mechanical model for the viscoelastic behavior of light-activated resin composites during setting. Experimental stress-strain data were generated with a dynamic test method in which a vertical oscillatory strain was applied to a commercially available light-activated resin composite. Three linear viscoelastic models (Kelvin, Maxwell, and Standard Linear Solid) were investigated by a validated modeling procedure [5]. On the basis of the modeling and evaluation of results, a suitable model was chosen for light-activated resin composites.

Materials and methods

Dental resin composite

The material utilized in this investigation was a commercially available light-activated resin composite (Z100 MP A3, LOT: 19981009, 3M). According to the manufacturer’s instructions, the resin composite was light cured for 40 s (Elipar Highlight, standard mode, ESPE). The light intensity at the light exit tip was 600 mW/cm² (radiometer, model 100, Demetron).

Dynamic test method

Stress-strain data on the light-activated resin composite during setting were obtained with a dynamic test method performed on a home-built automated universal testing machine (ACTAIntense, ACTA). The composite was bonded between a steel disk, which was connected to the cross head with the load cell (1 kN), and a rectangular glass plate (float glass, 50 x 50 x 4 mm, Bakker), which was connected to the stationary part of the framework (Fig. 7.1). To ensure the cylindrical shape of the specimen, the composite was inserted into a lightly greased Teflon mold (d= 3.1 mm, L= 1.6 mm), creating a C-factor for the specimen of 1.0 (d/2L). The steel disk was moved down until it reached the pre-adjusted specimen height. Optimal bonding between the resin composite and the steel disk was achieved by coating the sandblasted surface (Korox® 50 μm, 2 minutes/5 bar pressure, Bego) of the disk with silane (Silicoater, 5 minutes, Kulzer). For the same reason, the glass surface was lightly sandblasted (Korox® 50 μm, 10 seconds/5 bar pressure, Bego), primed (RelyX ceramic primer, 3M), and finally coated with a pressurized air-spread adhesive layer (Scotchbond Multi-purpose, 3M). The submicron-thick adhesive layer was light-cured for 40 seconds (Elipar Highlight, standard mode, ESPE).
Figure 7.1 Experimental setup for light-activated resin composites in dynamic test method. (left) An oscillatory axial strain with amplitude 1.00±0.01 μm and frequency of 1.0 and 0.1 Hz was successively applied to the setting composite around its original height (strain=0 %) in experiment. (right) In the stress response the sinusoidal stress is superimposed on the shrinkage stress.

In the dynamic test method, the upper steel disk performed an oscillating vertical sinusoidal deformation on the setting resin composite around its original height (1.6 mm). The test method was programmed to perform two frequencies with amplitude of 1.00±0.01 μm (0.0625 % strain). First, a frequency of 1.0 Hz was applied for 50 seconds to the fast setting composite, followed by a frequency of 0.1 Hz until termination of the measurement (1 hour). The oscillatory deformation was measured with two displacement probes (Solartron LVDT type AX/1/S, Dimed) at the level of the specimen. The light irradiation process was measured with a custom-made light sensor device. The distance between the light exit tip was equal to the thickness of the glass plate (Fig. 7.1), which was 4 mm. During the measurement, the data (time, load, and displacement signal) were collected simultaneously by a data acquisition console at a rate of 100 points (1.0 Hz period) and 18 points (0.1 Hz period) per second respectively. The measurements were started 5 s prior to the light irradiation process and were repeated three times at room temperature (23±1 °C). One hour after the start of the experiment, the specimen was subjected to tensile loading with a cross head speed of 60 μm/min until fracture. To verify the polymerization efficiency of the resin composite, the cylindrical specimen was fractured and exposed to Astra blue dye test according to the procedure described by De Gee et al. [9].

**Volumetric shrinkage measurement**

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. [10].

Stress-strain data analysis

The data obtained from the dynamic test measurement consisted of an array of load and displacement values for many points in time. The sinusoidal strain ($\varepsilon_{\text{sine}}$) and normal stress ($\sigma_{\text{exp}}$) were calculated using the following equations:

$$\varepsilon_{\text{sine}} = \frac{\Delta L}{L_0} \quad (7.1)$$

$$\sigma_{\text{exp}} = \frac{F}{A} \quad (7.2)$$

in which $\Delta L$ is the displacement value measured by the probes (m), $L_0$ the original specimen height (m), $A$ the cross-sectional area of the specimen (m$^2$), and $F$ the recorded load response of the specimen (N). In addition to the applied sinusoidal strain, the strain caused by axial shrinkage must be taken into account when modeling the stress data as recorded with the dynamic test. The axial shrinkage strain development of the resin composite (C-factor=1.0) was calculated by multiplying the mean volumetric shrinkage strain by a factor of 0.45 (Table 3.1). After spline interpolation of the axial shrinkage strain ($\varepsilon_{\text{shrinkage}}$) fit [11], the obtained axial shrinkage strain data were added to the oscillatory strain (Eq. 7.1) data for all the points in time of the dynamic test measurement, which resulted in the desired strain ($\varepsilon_{\text{tot}}$) for the modeling procedure:

$$\varepsilon_{\text{tot}} = \varepsilon_{\text{sine}} + \varepsilon_{\text{shrinkage}} \quad (7.3)$$

Mechanical models

The material properties of the composite are considered to be isotropic. To meet the assumption of isotropic shrinkage, the specimen's height was made as long as possible without exceeding the depth of cure (2 mm) [12]. The mechanical behavior of the resin composite during
setting was considered linear viscoelastic [13], because the strain applied to the specimen was within the limit of linear viscosity of polymer-based materials (<0.5 %). The mechanical models were investigated in one dimension only, because the stress-strain data were monitored in one direction. The models must be kept simple, because by using uni-axial data, only a restricted number of material parameters can be fitted in a unique way. As a consequence, the validity of the qualitative and quantitative viscoelastic behavior studied is confined to the stress and strain range and the strain rate range covered by the experiment. In this study, the Maxwell, Kelvin, and Standard Linear Solid model were investigated. The models are described in detail in chapter 4 of this thesis.

Parameter identification

A validated parameter identification procedure was developed, which is capable of calculating model material parameters - Young's modulus (E) and viscosity (η) - from experimental stress-strain data. The procedure is described in detail in chapter 4, and only a brief description of its application in this study will be given. The procedure was performed on sinusoidal stress cycles isolated from the stress data recorded by the dynamic test method. The time span [1 or 10 s] of the isolated interval was kept small with respect to the rate of polymerization reaction. As a result, the mechanical behavior of the composite can be assumed to be constant during the isolated interval, which justifies the use of simple differential equations for the mechanical models. These equations were solved analytically (appendix A), allowing the stress to be expressed as a function of strain and unknown material parameters, with the known functional form of the strain:

\[ \varepsilon(t) = \varepsilon(t_0) + At + B \sin(\omega t) \]  

in which \( \varepsilon(t_0) \) is the strain at begin interval, \( t \) is time in isolated interval [0-1 or 0-10 s], \( A \) is the slope of the shrinkage strain (s\(^{-1}\)), \( B \) the amplitude, and \( \omega \) the angular frequency (rad.s\(^{-1}\)) of the oscillatory strain. The shrinkage strain in the isolated time interval was assumed to be linear in time. Except for the Kelvin model, the initial condition (\( \sigma(t_0) \)) for the stress equation of the model was taken from the shrinkage stress data, thereby avoiding the extensive computation involved in evaluating the initial stress mathematically. By means of the initial parameter values, a least square method was performed at equidistantly spaced \( k \) points in time of the isolated interval, to assess how well the model stress (\( \sigma_{\text{model}} \)) approximates the experimental stress of the interval (\( \sigma_{\text{exp}} \)).
The search for the final material parameter values was carried out by minimizing the residual ($\delta$) with an optimization routine based on the Levenberg-Marquardt method [14]. The modeling procedure provides (i) the parameters, (ii) the error estimates on the parameters, and (iii) the residual ($\delta$), a quantitative measure of the difference between experimental and model stress. The algorithms for the modeling procedure were implemented in MATLAB (version 5.3, Mathworks) on a desktop computer (Windows® 98 platform).

**Evaluation of the viscoelastic model**

To evaluate the appropriateness of the three mechanical models under shrinkage strain conditions, the measured axial shrinkage stress development of the light-activated resin composite was compared with the model response. In chapter 4 of this thesis, a shrinkage stress procedure to estimate the model response on basis of the input of the axial shrinkage strain and the calculated material parameters, is described. In addition, an evaluation was performed on both 2-parameteric models: Maxwell model for the initial 3 minutes and the Kelvin model for the remainder of the setting process. The shrinkage stress development of Z100 in the experiment was isolated from the recorded stress data (Eq. 7.2), using the standard Fast Fourier Transform (FFT) smoothing filter in Origin (version 5.0, Microcal). The best result was obtained by taking 200 points for smoothing.

**Results and discussion**

**Stress-strain data**

Figure 7.2 shows the applied strain and stress response of Z100 during the initial 75 seconds of the setting process at room temperature. The positive strain of the sinusoidal cycles represents the cross head displacement away from the specimen, while the negative strain represents the cross head displacement towards the specimen. As the oscillatory strain was performed around the original specimen height, the stress response on the oscillatory strain was superimposed on the continuous shrinkage stress development of the specimen.
**Figure 7.2** (a) Strain and (b) stress data of Z100 with C-factor=1.0 collected with the dynamic test method. For clarity, only the initial 75 seconds of the setting reaction is shown. The dotted lines represent the initiation and termination of the irradiation process of the light unit.

There was no premature debonding from either the glass plate or the steel disk, because subsequent to tensile loading the fracture always occurred in the glass plate, at a stress level 1.5 times the maximum stress (18 MPa) measured in the test method. The choice of the light source, the duration of light irradiation process, and the distance between the light exit tip to the specimen was found to be adequate for the complete polymerization of Z100, because the Astra blue dye tests on the specimens revealed no visible staining inside the semi-cylindrical surface of the resin composite.

The mean axial shrinkage strain, as calculated from the volumetric measurements, is shown in Figure 7.3a. The shrinkage rate curve shown in Figure 7.3c is a good estimate for the polymerization rate of Z100, because shrinkage is associated with polymerization of the monomers. Figure 7.3b shows the shrinkage stress obtained after smoothing the recorded stress data (Fig. 7.2b).

An interesting feature of Z100 is that in the initial 2 seconds of the setting process, the material undergoes 15% of the measured axial shrinkage strain without generating shrinkage stress. The relationship between shrinkage stress and shrinkage strain displayed by this dental composite contrasts with that of a chemically activated composite where, under closely similar experimental conditions and up to 4 minutes after the start of polymerization, a large proportion of composite shrinkage (50% or more) failed to contribute to stress development in the material [4]. Although the chemical composition of these commercially available resin composites differs, it may be concluded that, in general, an increase in the polymerization rate of resin composites has a negative effect on the viscous flow capability of the material.
Figure 7.3 (a) Mean axial shrinkage strain and (c) its derivate with time for Z100 at C-factor=1.0. (b) Shrinkage stress curve of Z100 after smoothing the experimental stress data (Fig. 7.2b) with a Fast Fourier Transform. The strain data used for the parameter identification procedure consisted of oscillatory strain (Fig. 7.2a) superimposed on the axial shrinkage strain curve (Fig. 7.3a). The dotted lines represent the initiation and termination of the irradiation process of the light unit.

Parameter identification

Table 7.1 and Figure 7.4 show the calculated material parameter values for the three models for several stress intervals of one experiment. The viscosity (η) values of all models, as calculated by analyzing the stress cycles by the identification procedure, were all positive and developed according to the spring-dashpot arrangement in the model with setting time. The Young’s modulus (E) values were also positive and increased monotonically with the setting time.

The Young’s modulus of Z100 after one hour setting (approximately 6.5 GPa) is not in agreement with the value of 13 GPa provided by the manufacturer. It is known that factors such as the choice of mechanical model, test methods (bending, shear, compression, tension), conditions of the test method (strain rate, setting time, temperature), and light
Table 7.1 Material parameters for several cycles during one measurement of Z100 during setting with standard deviation in parenthesis. Material parameters: $E(x)=$Young's modulus, $\eta=$viscosity, and $\delta=$quantitative measure of the difference between experimental and model stress.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Kelvin model</th>
<th>Maxwell model</th>
<th>Standard Linear Solid model</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (GPa)</td>
<td>$\eta$ (GPa.s)</td>
<td>$\delta$</td>
<td>E (GPa)</td>
</tr>
<tr>
<td>4.6</td>
<td>0.24 (0.03)</td>
<td>0.02 (&lt;0.01)</td>
<td>0.746</td>
</tr>
<tr>
<td>10.6</td>
<td>1.96 (0.02)</td>
<td>0.07 (&lt;0.01)</td>
<td>0.387</td>
</tr>
<tr>
<td>20.6</td>
<td>3.55 (0.01)</td>
<td>0.11 (&lt;0.01)</td>
<td>0.173</td>
</tr>
<tr>
<td>40.6</td>
<td>4.70 (0.05)</td>
<td>0.11 (&lt;0.01)</td>
<td>2.87</td>
</tr>
<tr>
<td>302</td>
<td>5.45 (0.01)</td>
<td>0.75 (&lt;0.01)</td>
<td>0.374</td>
</tr>
<tr>
<td>1202</td>
<td>6.32 (0.05)</td>
<td>0.60 (&lt;0.01)</td>
<td>0.770</td>
</tr>
<tr>
<td>3352</td>
<td>6.57 (0.01)</td>
<td>0.56 (&lt;0.01)</td>
<td>0.496</td>
</tr>
</tbody>
</table>

Irradiation procedure (light intensity, duration time) have a considerable effect on the ultimate Young's modulus value of the composites. The Young's modulus of viscoelastic materials generally decreases with a decreasing strain rate [15], as evident in the strain rate transition from 1.0...
Figure 7.5 Modeling results for two stress cycles of Z100 during setting at (a) time=4.58 s and (b) time=10.59 s for the (top) Maxwell model, (middle) Kelvin model, and (bottom) Standard Linear Solid model.

Hz to 0.1 Hz (Fig. 7.4). For a valid comparison between Young's modulus values, the variables described above must be the same. Any difference between these variables will make comparisons between Young's moduli impossible.

The graphic results of the parameter identification procedure on two stress intervals isolated from one dynamic test experiment are shown in Figure 7.5. The continuous black line represents the measured stress, while the dots represent the values computed by the model, using the material parameter values as calculated by the modeling procedure (Table 7.1).

All models failed to predict the experimental stress in the early stage of setting (4.58 s). The lack of modeling capability is not caused by the low Signal-to-Noise Ratio (SNR=2.40) of the experimental stress data. A previous study showed that when the viscoelastic behavior of the resin composite was exactly the same as that of a model, then it was possible to model very precise experimental stress data with practical SNR
values as low as 2.20 [5]. All models failed to predict the stress a few seconds after the initiation of polymerization, because the material parameters were kept constant over the time interval, whereas in reality the material stiffness increases noticeably, as indicated by the asymmetrical sinusoid around the shrinkage stress line (Fig. 7.5a). Better modeling results should be obtained by isolating smaller time intervals in the stress data, i.e., 0.50 s or less, or by using differential equations for the model in which material parameters vary in time. For further studies, the former is recommended, since solving partial differential equations involves intensive computation work.

Model evaluation

The Maxwell stress curve at setting time 10.59 s is a poor approximation of the stress response of the dental composite. This is clear not only from the graphical fit, but also in the $\delta$ parameter (Table 7.1) - the quantitative measure of the difference between experimental and model stress – which is the highest value of all models. The phase lag between the model stress curve and the experimental stress curve indicates that the model predicts more viscous flow than the material actually undergoes. As a result, the Maxwell model predicts for the first 3 minutes of setting a lower shrinkage stress development than Z100 actually undergoes. (Fig. 7.6a).

![Figure 7.6 Axial shrinkage stress development (--- measured ■ Kelvin model ▲ Maxwell model ◆ Standard Linear Solid model ● Maxwell & Kelvin) during (A) the initial 10 minutes and (B) one hour setting of Z100. Error bars indicate the relative standard error in the calculated mean (n=3).](image)

This result is essentially different from chemically activated resin composites, where the Maxwell model predicts the shrinkage stress
better and for a longer period in setting time (up to 11 minutes) [5]. Obviously, high polymerization rates reduce the ability of the composite to flow permanently. This may explain why light-activated resin composites generate higher polymerization shrinkage stresses than analogous chemically activated composites [1], because composite shrinkage is less compensated by permanent viscous flow from the unbonded, outer surface of the material. In the remainder of the setting process, the Maxwell model predicts too much stress relief, which is obviously not the case for Z100 in the experimental situation (Fig. 7.6b).

The better modeling results achieved with the Kelvin and Standard Linear Solid model confirms that the behavior of light-activated resin composites is more viscoelastic solid-like (reversible flow) than viscoelastic liquid-like (permanent flow). The slightly better approximation by the Standard Linear Solid model, where the development of $E_2$ indicates reversible flow behavior, can be explained by the extra parameter it contains in comparison with the Kelvin model. A closer look at the sinusoid curve at 10.59 s reveals that the Kelvin model responds somewhat more stiffly in the first section and slightly softer in the second section of the curve than Z100 in the measurement. As stated for the Maxwell model, this can be explained by the fact that the material parameters were kept constant in time, whereas in reality the material increases in stiffness over time. Up to 25 seconds into the light irradiation procedure, the response of the Kelvin model closely resembles the shrinkage stress response of Z100 in the measurement (Fig. 7.6a). After 25 seconds, the model generates higher shrinkage stresses, leading ultimately to a shrinkage stress level that is a factor of two higher than measured for Z100 during the experiment (Fig. 7.6b).

There may be two explanations, one or both of which may be responsible for the failure of the Kelvin model in the remainder of the setting process. First, the flow behavior of light-activated resin composite could be non-Newtonian; i.e., the viscosity is not constant, but depends on the strain rate. For this reason, the viscosity values of the Kelvin model may not be valid in this part of the setting process, where the shrinkage rate is close to zero (Fig. 7.3c), since the parameter values were calculated from experimental stress that depended exclusively on the oscillatory strain. Secondly, the failure of the Kelvin model can perhaps be accounted for by the fact that the material undergoes two deformation processes, namely reversible, by viscous flow as predicted by the model, and permanent, by imperfections in the materials, such as voids, crazes, and microcracks [16, 17]. These imperfections are usually generated when local stress spots in the material exceed inter-atomic bond strength within the polymer and/or polymer-filler interface and are likely to
be present in light-activated resin composite, where high shrinkage stress developed during setting (Fig. 7.6b). It is difficult to develop a model that is capable of taking into account these two processes, which occur simultaneously but are different in origin.

Theoretically, the Standard Linear Solid model is able to describe both the viscoelastic liquid ($E_2 = 0$) and the viscoelastic solid behavior of resin composites during setting. On a practical level, the evaluation results of the model reveal that the viscoelastic behavior of Z100, as excited by the conditions of the dynamic test method, cannot be adequately predicted by this model. It was shown in chapter 4 that a shrinkage strain rate contribution in the total strain is necessarily for proper identification of the three parameters of the Standard Linear Solid model. Validation of artificial strain data revealed that the parameter identification procedure was not able to calculate the parameters of this 3-parametric model exactly when the shrinkage strain rate dropped below $0.0003\%/s$ (Fig. 4.7). The experimental data of Z100 in Figure 7.3c and Figure 7.4c confirm the relationship between the value of the standard error in $E_1$ and $E_2$ and the shrinkage rate profile. As the shrinkage rate rapidly declines, and the contribution of shrinkage strain to the applied strain deteriorates within 20 seconds after start light irradiation, the stress response becomes more exclusively dynamical, i.e., more dependent on the sinusoidal strain of one frequency alone. In this situation, the values of $E_1$ and $E_2$ associated with the Standard Linear Solid model cannot be distinguished from one another, as evidenced by the high error value, because with this type of stress response no more than two independent parameters can be determined. To obtain reliable $E_1$ and $E_2$ values in the remainder of the setting process, the stress to be modeled must be generated by a multi-wave strain, which entails sophisticated dynamic test conditions. This approach requires modifications in the application software, which, however, has not been established.

**Conclusions**

The automated universal testing machine developed for the dynamic testing of dental restorative material proved capable of generating stress-strain data on fast setting light-activated resin composites. An increase in the polymerization rate has a negative effect on the viscous flow capability of dental resin composites. The experimental conditions were insufficient to model both the viscoelastic liquid and viscoelastic solid behavior of Z100 during setting with the Standard Linear Solid model. Adequate predictive modeling of Z100 can be carried out by using the Maxwell model for the initial 3 minutes of the setting process and the Kelvin model for the remainder of the setting process.
Chapter 7  Modeling light-activated resin composites

References

2. See chapter 3 of this thesis.