Viscoelastic behavior of dental restorative composites during setting
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Direct restorative resin composites have gained a permanent position on the dental market. Their superior esthetics and consecutive preparation (less destructive than amalgam) have been instrumental in this commercial success. The ideal restoration has a tight seal with the remaining tooth structure, since otherwise bacteria and the toxins they produce can invade and grow in the gap formed, resulting in pulp irritation and even secondary caries. This perfect adaptation must be obtained during setting, and then maintained during thermal and mechanical cycling for the lifetime of the restoration or the patient. Currently, no commercially available resin composite guarantees an intact seal. Because the resin has no anti-microbiological activity, it is important for a restoration to be placed in such a way that the best possible marginal seal is obtained.

There are, however, many side effects that prevent the formation of a perfectly sealed restoration. Most of these effects are related to shrinkage of the restoration during the setting process. As a result of the adhesion to rigid tooth tissue, this shrinkage will be constrained, and this, in combination with the increasing stiffness of the restorative material, will inevitably lead to the development of mechanical stresses in and around the restoration. These stresses are a major problem, since they have a negative influence on the durability of the restoration. While loss of adhesion can occur at any time, the most likely moment is when the magnitude of the shrinkage stress exceeds the strength of the developing restoration-tooth bond. Since most bulk shrinkage takes place within 15 minutes of setting, adhesive failure starts early in the restoration history, occasionally even before the patient has left the dentist’s chair. Although the restoration will probably not fall out of the preparation, it must be replaced in order to prevent adverse biological reactions. If the adhesion survives the mechanical stresses, there may be cusp movement, post-operative sensitivity, cohesive fracture, or tooth fracture.

To gain more insight into the problem of shrinkage stresses, the present research focused on the viscoelastic behavior of dental restorative materials during setting. This mechanical behavior during setting, when the material passes from a liquid to a solid state, is an important factor in the relation between the shrinkage of the restorative material and the stress development in the restoration. When the viscous flow and solidity of the restorative during setting can be quantified, research
into shrinkage stress development can be enriched with numerical analyses and simulation techniques.

The aim of this research project was to use modeling to obtain more information on the viscoelastic behavior of several types of dental composites during the setting process. With the aid of a suitable model, the effect of resin formulation, configuration factor (C-factor), and temperature on the mechanical behavior of resin composites was studied by monitoring the development of viscoelastic parameters during the setting process. In addition, characterization techniques such as infrared spectroscopy, wear, and scanning electron microscopy were performed, in order to provide additional information to support the discussion of these effects on the mechanical behavior.

Chapter 2 reviews the underlying cause of the shrinkage of polymeric restorative materials, and the various factors that influence shrinkage. Some factors affecting stress development are beyond the clinician's control (e.g., composite monomeric and filler formulation); however, the methods used for placement and light-curing can be directly controlled. Chapter 2 stresses the importance of knowing the relation between these manipulative factors and the development of shrinkage stresses. The chapter also addresses the problems involved in weighing a low polymerization reaction rate against the need to obtain a high final monomer conversion value, in order to ensure the clinically adequate properties of the restoration. Allowing a composite to flow prior to reaching the gel point relieves shrinkage stresses, rather than permitting them to build up within the material and at the restoration-tooth interface. Building up a composite in increments helps to reduce the C-factor and minimizes stress development. The exact mechanisms and advantages of stress alteration through the placement of low-modulus liners are still not clear, and the effects of variation in light intensity (the soft-start techniques and the new high-output intensity curing units) have not yet been demonstrated. The influence of water sorption on the stress relaxation of a composite is also addressed here.

The appropriate modeling of the viscoelastic behavior of resin composites during setting requires a good understanding of the mechanical properties of the materials involved. Dynamic tests were necessary to establish the major characteristics of the composites, and to provide the data for the modeling investigation of the linear viscoelasticity of dental composites during setting. Traditionally, dynamic test machines are designed for large amounts of material, in which the structure does not change over time or does so very slowly (physical ageing). As reliable data are crucial to the successful modeling
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of composite behavior, certain aspects of the testing machine and software were improved. **Chapter 3** describes how this optimization process resulted in a versatile testing machine, capable of performing accurate sinus-shaped deformation on the submicrometer level, on small amounts of dental material during setting. The implementation of the software-based dynamic feedback system has proved to be a crucial step in this type of testing. Preliminary experiments on commercially available two-paste and light-activated resin composites have shown that the mechanical behavior of the setting composite is viscoelastic, *i.e.*, part of the deformation applied is recovered spontaneously when the load is removed, while the remaining deformation is permanent.

**Chapter 4** describes an engineering approach for the analysis of axial stress-strain data by mechanical models. Two 2-parametric models (Kelvin and Maxwell) and one 3-parametric model (Standard Linear Solid) which are possible candidates for describing the viscoelastic behavior of dental restorative material during setting are presented. The modeling technique was kept relatively simple. The state of stress-strain of the composite was assumed to be axial, in which case the model can be described by ordinary differential equations. This equation was solved analytically, and treated in modeling procedures. A procedure was developed by which the material parameters could be identified by a least square fit of the model's stress response on experimental stress data. In addition, an evaluation procedure was developed to calculate the model's response on axial shrinkage strain only. The validation results showed that the parameter identification procedure implemented in MATLAB was free of error. On the basis of sinusoidal stress-strain data, the procedure was capable of finding the two parameters associated with the Maxwell and Kelvin model with a good degree of accuracy. As regards the identification of the viscosity parameter of the Maxwell model, the procedure was relatively sensitive to noise in the stress data. At a signal-to-noise ratio of less than 2, the calculated viscosity value of the Maxwell model must be regarded as questionable. To obtain an accurate prediction of the three material parameters of the Standard Linear Solid model, the stress to be modeled must be generated by a multi-wave strain. The addition of linear strain with slopes larger than 0.0003 %/s to the sinusoidal strain proved adequate for this purpose.

One of the factors thought to reduce early shrinkage stress build-up (Chapter 2) is the ability of the material to undergo viscous flow during the early phase of setting. In a restorative material with increased flow capacity, the volume change attributable to shrinkage is compensated by the material flow from the unbonded, outer surface, ultimately resulting
in lower stress. One way to increase the ability of the material to flow without damaging its internal structure is by lowering the polymerization rate. The dental literature has demonstrated that, under the same conditions, two-paste composites generate lower polymerization shrinkage stress than the analogous light-activated composites. **Chapter 5** deals with the search for a mechanical model for the quantification of the viscous and elastic behavior of a commercially available two-paste resin composite during setting. Uni-axial stress-strain data on Clearfil F2 during setting were obtained by a pulse sinusoidal test method and by mercury dilatometry. The stress-strain relation was analyzed by means of three mechanical models (Maxwell, Kelvin, and the Standard Linear Solid model). Using an identification procedure, the elastic modulus (E) and viscosity (η) values at several setting times were calculated. On the basis of the modeling and evaluation results, a model for describing the viscoelastic behavior of the shrinking resin composite was selected. It is clear from the modeling results that the viscoelastic behavior of Clearfil F2 during setting, as elicited by the conditions of the dynamic test, cannot be described by a single mechanical model. Up to 30 minutes into the setting process, the best prediction was achieved by the Maxwell model, while during the remainder of the setting process the Kelvin model was used to describe the viscoelastic behavior of the two-paste resin composite.

In recent years a new class of low-viscosity resin composites known as “flowable composites” have been added to the range of commercial products for restorative dentistry. This flowability is achieved either by reducing the filler content or by increasing the amount of diluent (TEGDMA) in dimethacrylate composites. In general, flowability is regarded as a desirable property when it comes to reducing shrinkage stresses in the setting restoration. **Chapter 6** describes the results of a study focusing on the possibility of stimulating viscous flow by increasing the TEGDMA/bisGMA ratio in the resin of experimental composites. The setting process was monitored and characterized by dynamic tests, dilatometry, infrared spectroscopy, and mathematical modeling. In addition, the tensile strength of the composites after one hour of setting was evaluated, together with the wear process over a period of one year. It was found that a large amount (70 wt%) of TEGDMA in the resin prolonged the predominant - pre-gel - viscous flow property of the flowable composite to only a moderate degree, and displayed high shrinkage stresses. This is due to the considerable differences in the role of the two monomers in the setting process. The flexible TEGDMA controls the mobility of the dimethacrylate system and the composite shrinkage, whereas the stiff BisGMA largely controls the reactivity of the polymerization reaction. The excellent diluent
properties of TEGDMA with respect to bisGMA play a significant role in the polymerization rate, viscosity, and stiffness development of the composite. A composite containing 50 wt% TEGDMA in the resin displayed the highest maximum rate, the greatest stiffness, and the lowest viscosity. The high shrinkage stress in flowable composites – in spite of the lower stiffness and viscosity - is ascribed to the relatively high post-gel shrinkage, as a result of the presence of a large amount of TEGDMA in the resin. In view of the high shrinkage stress, the high degree of wear, and the low tensile strength, we discourage the use of flowable composites for high-stress applications in restorative dentistry. For the predictive modeling of the viscoelastic behavior of bisGMA-TEGDMA composites based on the two-paste benzoyl peroxide-amine initiator system, the Maxwell model proved most effective during the first 15-20 minutes of the setting process.

Light-activation of dental restorative materials has become a “way of life” for the average clinician, as it makes it possible to obtain immediate, direct, and highly esthetic results with minimal loss of patient time. However, the absence of internal porosities and the higher rate of polymerization contribute to the increase in stress development, since the restoration is less able to flow permanently. As we strive for a better understanding of the stress development of light-activated composites, it is important to know more about the viscoelastic behavior during setting. Chapter 7 deals with a modeling study focusing on the visco-elastic behavior of a commercially available composite during setting. Stress-strain data on Z100 were recorded by means of a dynamic test method performed on a universal testing machine. Three models (Kelvin, Maxwell, and Standard Linear Solid) were tested by matching the model response to experimental data; the viscoelastic parameters associated with the model were calculated. The high polymerization rate of Z100 had a negative effect on the flow capability of the material. Only a small proportion of composite shrinkage failed to contribute to stress development in the composite. The experimental conditions were insufficient to model both the viscoelastic liquid and solid behavior of Z100 during setting using 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.

A straightforward way to reduce, or even prevent, shrinkage stress is by developing a non-shrinking or low-shrinking resin system for dental restorative composites. Photo-polymerization of this type of composite with no limitations as regards depth of cure would be ideal, because it would provide a high-quality bulk-filled restoration, with all the
benefits of a "cure-on-command" restorative. **Chapter 8** describes a modeling study focusing on the viscoelastic behavior of a new class of low-shrinkage dental restorative composites during setting. The setting behavior of the experimental oxirane composite was investigated by analyzing stress-strain data with the aid of 2-parametric mechanical models. The experimental data were obtained by means of a dynamic test method, in which the light-activated composite was continuously subjected to sinusoidal strain cycles during setting. The material parameters and the model's predictive capacity were analyzed using validated modeling procedures. The light-activated oxirane composite displays attractive mechanical properties for application as restorative material. In addition to shrinkage delay, it also undergoes lower polymerization shrinkage strain and stresses than conventional (dimethacrylate) light-activated composite. Unlike experimental stress-strain data observation, the Maxwell model cannot predict the viscoelastic behavior of the oxirane composite during setting. The high level of the noise carried by the low stress signal has a decisive influence on the value of the viscosity parameter associated with this model. On the other hand, the elastic part of the Maxwell model does predict the stiffness development of the composite during setting with a good degree of accuracy.

**Chapter 9** describes a preliminary study on the potential of the oxirane composite as direct restorative composite. The shrinkage stress-strain, stiffness development, and tensile strength at different C-factors of the low-shrinkage composite were measured and analyzed at room temperature and oral temperature. The configuration and temperature of the composite affect the axial shrinkage strain and axial shrinkage stress, as well as the stiffness development of the composite during setting. It was found that the stiffness development was inversely related to the C-factor. Higher temperatures led to increased shrinkage, stiffness, and increased shrinkage stresses. Despite the attractive low shrinkage strain-stress behavior, its poor mechanical strength and slow setting process make the low-shrinkage oxirane composite yet unsuitable for posterior restorative work.
Conclusions

From this research the following conclusions can be drawn.

- The dynamic test system developed for testing dental restorative material proved capable of generating reliable stress-strain data on two-paste and light-activated restorative materials.

- Dental restorative composites show viscoelastic behavior during setting. The composite is transformed from a pre-gel structure, in which the viscous flow behavior predominates over the elastic behavior, into a post-gel structure, in which the elastic behavior predominates over the viscous flow behavior. The time of crossover -the so-called sol-gel or gel point - is not a hard material property, as it is influenced by the conditions of polymerization activation and dynamic testing.

- The validated parameter identification procedure is capable of identifying the material parameters associated with a mechanical model on the basis of axial stress-strain data with a good degree of accuracy. When performing the modeling procedure on stress data with a high level of noise (Signal-to-Noise ratio < 2), the calculated viscosity value must be regarded as questionable.

- The viscoelastic behavior of conventional - dimethacrylate - composites as elicited by the conditions of the test method cannot be predicted by a single mechanical model. Good predictive modeling can be carried out by using the Maxwell model in the early phase of setting and the Kelvin model during the remainder of the setting process. The mode of polymerization activation significantly affects the time period of permanent viscous flow, and thus influences the time period in which the Maxwell model is valid. For composites based on the two-paste benzoyl peroxide-amine initiator system, the Maxwell model proved most effective for the first 15-20 minutes of the setting process. In the case of composites based on the light-sensitive camphorquinone-amine initiator system, this model is only valid for a number of minutes when polymerized with a conventional quartz tungsten halogen light unit under standard light-activation conditions (600 mW/cm² for 40 s).

- Permanent viscous flow of the composite during shrinkage is effective in lowering the ultimate stress level of the restoration. Low polymerization rates have a positive effect on the viscous flow
capability of dental resin composites, permitting the setting composite to shrink considerably during the permanent viscous flow state. In this light, two-paste resin composites are preferable to their light-activated analogues for direct restorative applications.

- Elastic modulus development in a bonded resin composite depends of:
  - the temperature of the composite;
  - the C-factor of the composite;
  - the strain rate applied on the composite.

- Varying the TEGDMA/bisGMA ratio in the resin has a significant effect on the mechanical properties of two-paste composites. It was found that the polymerization rate of bisGMA-TEGDMA composites is an indicative measure of the viscoelastic behavior during setting: the higher the reactivity, the greater the development of stiffness and viscosity. Composites with 50 wt% TEGDMA in the resin displayed the highest maximum polymerization rate. A large amount (70 wt%) of TEGDMA in the resin prolonged the predominant - pre-gel - viscous flow property of the flowable composite to only a moderate degree, and displayed high shrinkage stresses. The relatively high post-gel shrinkage of flowable composites is the decisive factor in the development of high shrinkage stress.

- Low-shrinking composites can be developed using oxirane monomers. The light-activated oxirane composites exhibit intrinsic 'soft start', undergo 45% less shrinkage strain than commercially available light-activated resin composites, and generate very low shrinkage stresses. However, the mechanical properties of the oxirane composite cannot yet compete with those of the resin composites currently available.

**Recommendations**

Some recommendations for future work related to the viscoelastic behavior and shrinkage stress relief of dental restoratives are presented below.

- The use of one model for describing both the viscoelastic liquid and solid behavior of setting composites is to be preferred. The inability of the Standard Linear Solid model to do so is due to the fact that the experimental conditions of the dynamic test method are not good enough for predictive modeling with this 3-parametric model.
Summary

Modifications to the application software of the test system would make it far better suited for the identification of three parameters in the Standard Linear Solid model. It is advisable to perform sinusoidal deformations with different frequencies simultaneously; i.e., as a multi-sine. If care is taken not to exceed the strain limitation for linear viscoelasticity (0.5%), this would result in better predictive modeling with the Standard Linear Solid model.

- Several other improvements to the dynamic test system would make it possible to extend the scope of research into the viscoelasticity of setting composites. Incorporation of the load signal in the feedback loop for the crosshead movement, in combination with a more sensitive load cell (250 N or lower), would enhance the axial shrinkage strain measurements of bonded composites. In addition, implementation of an optical device in the specimen mounting device would make it possible to measure the lateral shrinkage strain of the bonded composite during setting, and to calculate the Poisson’s ratio of the material. Alternatively, the Poisson’s ratio could be determined indirectly by performing additional shear loading tests on setting dental materials. In order to obtain reliable shear stress-strain data, the rotational test device should meet the requirements set for dynamic testing in the tension-compression direction.

- The low shrinkage behavior of the oxirane composite is promising, in view of the restorative materials currently available. The use of this composite would fundamentally alter the resin composites, expand their indications, diminish the demands on dentin-bonding agents and clinical handling techniques. Therefore, efforts must be undertaken to improve the filler-oxirane matrix bond, which would appear to be the weakest link among the mechanical properties of this composite. Besides these mechanical aspects, also carcinogenic risks to humans by oxirane exposure must be studied.

- In this research project we have dealt with the viscoelastic behavior of resin composites at room temperature and oral temperature. It would be of clinical value to study the mechanical behavior of restoratives in the presence of water. This is of importance, in particular for the oxirane composites, because water sorption after setting could frustrate the high expectations of this low-shrinking composite.

- It would be interesting to incorporate the models and their parameter values into a finite elemental analysis package, in order to simulate the shrinkage stress development in different cavity preparation
designs. To achieve this goal, close collaboration with the mathematical profession is required. To avoid mathematical over-kill, the dental profession must test these cavity preparation designs in a clinical setting.