

# **Kinetic model for the coupled volumetric and thermal behavior of dental composites**

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Short title: **Kinetic model for dental composites**

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## **Keywords**

Polymerization kinetic, volume model, dental composites, curing shrinkage, thermal expansion

## **Abstract**

Objective: The volume and thermal behavior of dental composites during the curing reaction was analyzed for different modes of initiation using a combination of experiments and models for polymerization kinetics.

Methods: The volume behavior of four dental composites (Venus, Tetric Ceram, Ceram X mono and Filtek Supreme) was studied with buoyancy measurements during the initiation and dark phase of the curing process. The volume and temperature development of the composites were described for different intensities of the photo - initiation with a mathematical model based on the »mixed termination model« for the polymerization reaction.

Results: A good agreement between volumetric data and the model function was achieved. A non-linear regression of the experimental data with the model yields results for the adjustable parameters describing the kinetics of the polymerization reaction which are typical for comparable polymerization reactions. Using kinetic models of the polymerization reaction for analyzing the volume behavior of radically crosslinking curing dental composites, thermal and polymerization-specific components of the overall shrinkage of the composites can be distinguished and compared for different materials.

Significance: With the developed methodology, a more detailed insight into the curing process can be achieved which can contribute to the understanding of the build-up of internal stresses in dental fillings. These stresses can negatively affect the marginal integrity of the filling, which is a relevant precondition of long-term chemical, biological and mechanical stability.

## **Introduction**

Due to their versatility and aesthetic advantages, composite dental materials have found widespread application in restorative dentistry. The material properties of the composites have been improved significantly during the last decades, and a range of products with optimized properties for specific indications like packables for formative applications, specific crack resistive material for load bearing areas and flowables for minimally invasive procedures

have been developed. The material properties of a specific composite are the optimal compromise between ease of handling, superior final material properties, and reliability for the application the composite was designed for. Despite intense research efforts, all currently used materials undergo a certain percentage of volume shrinkage during the curing process. The volume shrinkage of the filling material in the cavity leads to the build-up of internal stresses which can lead to a loss of the marginal integrity of the filling and in turn compromise the mechanical and chemical long-term stability of the restoration, will require further dental treatment, and will possibly result in an earlier loss of the tooth. Therefore, a detailed understanding of the factors which influence the shrinkage process and the build-up of internal stresses is necessary in order to successfully optimize material properties during the development of dental composites.

In the past, a number of studies on the curing behavior of filling materials have been carried out which focus on their polymerization shrinkage. In these studies either clinical aspects [1] or materials science aspects [2-6] have been addressed. The volume behavior is a superposition of the shrinkage caused by the polymerization reaction and the thermal expansion caused by the heat of reaction and the heat input due to the photo-initiation [5]. Both are influenced by the complex chemical and material composition of the material [7] and the handling of the material by the dentist.

The polymerization shrinkage and heat are due to the polymerization reaction which transforms the initially shapeable material via microgelation, macrogelation, and vitrification [8] into a stiff and hard material. A fundamental characterization of the volume behavior can therefore be achieved by examining the polymerization kinetics and by including the processing factors which influence the progress of the polymerization reaction (e.g. the mode of photo - initiation). Several attempts have been made to describe the volume behavior of curing filling materials starting from the microscopic level of the processes, e.g. using percolation - type models [9] or by investigating gelation

and vitrification processes [8]. As a result, the existing dedicated microscopic models are so far of limited use if one aims at clinically relevant conclusions concerning polymerization shrinkage due to different handling techniques or materials. However, the complexity of the microscopic process [10-12] has, up to now, prohibited an established integral description of the entire process, which includes physical, material and processing parameters.

A very promising approach [13] is the macroscopic differential description of the polymerization by the autocatalytic model developed by Kamal. This model is based on the assumption of a changing diffusion processes during the reaction which can be described by two exponents in the differential conversion equation. The model predicts a maximum value of the conversion rate. On the other hand no separation of the quasi steady state phase during initiation and the consuming dark phase is made.

The aim of this paper is to present a macroscopic integral model for the coupled volume and thermal behavior of dental composites during the curing process which is based on the kinetics of the polymerization reaction, and describes the overall thermal and volumetric behavior in a simple mathematical form which might be useful in further investigations of the stress kinetics. The model assumes that each polymerization step results in a specific shrinkage in volume and a release of thermal energy. The kinetics of the reaction is modeled with the so-called »fully integrated mixed termination model« [9] which is one suitable choice for describing the reaction kinetics of curing resins of the radical crosslinking type. In addition to the reaction-specific processes like the polymerization shrinkage and the heat of the polymerization reaction, environmental and processing-specific parameters like the heat entry caused by the photo-initiation and the heat flux from the filling to the environment are considered in the numerical model which describes the thermal and volumetric behavior of the materials.

## Materials and methods

### Materials

The materials used in this study were commercially available, light - activated resin composites (see table 1). For the photo-initiation, the halogen light sources Vivadent Astralis 10 (Ivoclar Vivadent, Schaan, Liechtenstein) in »high power mode« with an output of 1200 mW/cm<sup>2</sup> and Translux (Kulzer GmbH & Co. KG, Hanau, Germany) with an output of 400 mW/cm<sup>2</sup> were employed. In order to attenuate the light intensity of the Translux light source, calibrated neutral optic filters (Schott Glas, Mainz, Germany) were used. The specimens were positioned 1cm from the tip of the light source.

Table 1: Composite resins used in this study

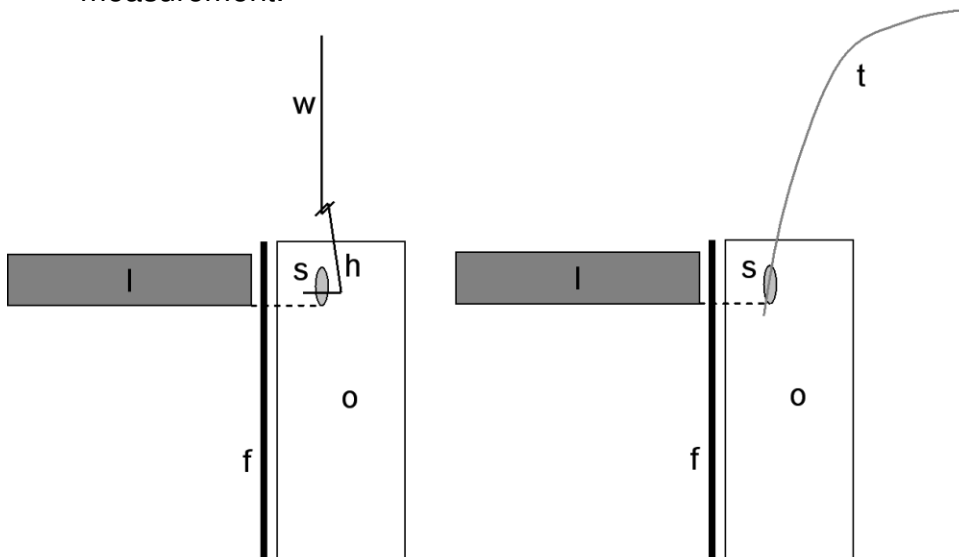
Material	Code	Batch no.	Type	Manufacturer
Tetric Ceram, A3	TC	913067	microfilled hybrid	Ivoclar Vivadent, Schaan, Liechtenstein
Venus, A3	VE	010103	microfilled hybrid	Heraeus Kulzer GmbH & Co. KG, Hanau, Germany
Filtek Supreme, A3	FT	3910A3B	nanofilled hybrid	3M ESPE AG, Seefeld, Germany
Ceram X mono, M5	CX	0405000911	ormocer-nanofilled hybrid	Dentsply AG, Konstanz, Germany

### Experimental procedures

The free volumetric shrinkage was measured by the buoyancy method [14, 15, 16]. The measurements were carried out with a Sartorius MC5 semi-microbalance. Transparent silicone oil (Wacker AK 350) was used for buoyant liquid. Disk-shaped specimens (height 2 mm, diameter 5 mm) were attached to thin steel wires and were submerged in the buoyant medium (fig. 1). In order to obtain stable readings, the measurements were done in a temperature

stabilized room ( $T=25\text{ }^{\circ}\text{C} \pm 1\text{ }^{\circ}\text{C}$ ) and protected from air draft and electrostatic influences. In contrast to earlier measurements which focused on the final value of the polymerization shrinkage, the technique used here aims to describe the development of the volume of the samples during the entire curing period.

Fig. 1. The experimental setup was chosen similar for the buoyancy and the temperature measurements. The specimen (**s**) was submerged in a transparent cuvette filled with silicon oil (**o**). The light tip (**i**) was positioned 1 cm from the specimen. If a filter (**f**) was used, it was positioned perpendicular to the light beam. For the buoyancy measurements, the specimen was connected with a holder (**h**) and a wire (**w**) to the balance. For the temperature measurements, the specimen was positioned at the tip of the thermocouple (**t**) positioned similar to the buoyancy measurement.



The heating-up of the samples due to the heat of the polymerization reaction and the heat entry caused by the photo-initiation was measured by a repeated submerging of the specimen in silicon oil in separate experiments under similar conditions as in the buoyancy measurements. Thermocouples of »type K« with a diameter of 0.5 mm were positioned in the center of the samples in order to monitor the development of the temperature. These thermocouples were chosen since they combine the required mechanical sturdiness with a sufficient measuring sensitivity. The observation of a cooling rate which was significantly faster than the heating rate during the photo-initiation indicates that the

response time of the thermo-couples was sufficient in order to study the relevant thermal behavior.

In order to study the influence of different photo - initiation modes and to verify the chosen kinetic model that differentiates between initiation and dark phase, the samples were exposed to different light intensities. The parameters for the photo-initiation were chosen such that the model for describing the reaction kinetics remains applicable, e.g. the applied dosage of light did not lead to a depletion of activator molecules. The highest intensity was achieved with the Astralis – lamp, a modern, fast curing light source with a focusing light tip. The Translux – lamp which operates at lower light intensity and provides an only slightly diverging beam was used with different optical filters to attenuate the light intensity. The reduced intensity of the light was compensated by a longer duration of the exposure time such that the total energy input stayed constant. Six photo - initiation modes were tested: 20 s exposure with the Astralis lamp and 40 s exposure at 100% transmission, 80 s exposure at 50% transmission, 160 s exposure at 25% transmission, 320 s exposure at 12% transmission, and 900 s exposure at 4.4% transmission respectively with the Translux lamp.

Modeling the coupled volumetric and thermal behavior of curing composites assuming a linear relationship between the »relevant« monomer conversion  $[M(t)]$  and volume shrinkage  $\Delta v$

$$1 - [M(t)] \propto -\Delta v ; \Delta v(t) = \frac{V(t)_{specimen} - V(0)_{specimen}}{V(0)_{specimen}} . \quad (1)$$

the development of the volume during the curing process can be linked to the progress of the curing reaction. The maximum relevant monomer conversion reaches 100% when the material-specific maximal degree of conversion of ~ 60%, is achieved. The »fully integrated mixed termination model« yields an analytical description of  $[M(t)]$ . The evolution of the relevant monomer conversion  $[M]$  and the »radical-activated centers«  $[P]$  is determined by the

initiation, propagation and termination steps. The propagation-rate  $R_p$  is given by

$$R_p = -\frac{d[M]}{dt} = k_p [P][M]. \quad (2)$$

with the rate-constant  $k_p$  which describes the conversion of monomers. The termination rate  $R_t$  includes contributions from two termination mechanisms, the monomolecular termination with the rate constant  $k_t^m$  (corresponding to the immobilization of an activated polymer in the evolving structure), and the bimolecular termination with the rate constant  $k_t^b$  (corresponding to the reaction of two activated centers). The coefficients  $k_p$  and  $k_t^b$  are diffusion-controlled, and change during the polymerization process, in particular due to the change in weight between different diffusion processes (translational diffusion, segmental diffusion and reaction diffusion). However, their ratios remain nearly constant during the relevant part of the polymerization [9] that can be used by integrating models.

$$R_t = 2k_t^b [P]^2 + k_t^m [P] \quad (3)$$

During the initiation phase (i.e. the time  $0 < t < \tau$  when the composite is exposed to the light source), the model assumes a steady-state between initiation (described by the rate constant  $R_i$ , the absorption probability  $\phi$  and the light intensity  $I$ ) and termination:

$$R_i = R_t = \phi I \quad (4)$$

Assuming that  $k_p$  remains constant during the initiation period [9], the development of  $[M]$  during the initiation is

$$[M(t)] \underset{\text{light}}{\approx} \left\langle [M]_0 \exp(-k_p [P]_0 t) \right\rangle^{\text{theoretical}} \approx \left\langle \exp\left(\frac{\ln\{[M]_\tau\} t}{\tau}\right) \right\rangle^{\text{simplified}} \quad (5)$$

$$[P]_0 = \left( \sqrt{\left(\frac{k_t^m}{2k_t^b}\right)^2 + \frac{\phi I}{k_t^b}} - \frac{k_t^m}{4k_t^b} \right)$$

The assumption of a steady-state is a simplifying approach for the complex initial phase. An in-detail description of the kinetics in the initiation phase – e.g. in order to describe a maximum of the polymerization rate due to gelation effects – would require a more sophisticated model. The steady state



approximation is used as a working hypothesis for a basic description of the shrinkage and temperature kinetics, where the main focus of our study is the dark phase. A more dedicated approach would include e.g. a detailed description of the heterogeneous microscopic evolution of the polymerization and a distinction between reaction steps which result in a shrinkage (i.e. propagation) and those which do not result in a change in volume (i.e. termination, inhibition, immobilization, etc.).

After the photo-initiation, in the »dark phase«  $t > \tau$ , its development follows

$$[M(t)]_{\text{dark}} = [M]_{\tau} \left( 1 + \frac{2k_t^b}{k_t^m} [P]_0 \{1 - \exp(-k_t^m(t - \tau))\} \right)^{\frac{k_p}{2k_t^b}} \quad (6)$$

The subscript 0 refers to the initial state  $t=0$  at the beginning of the light initiation,  $\tau$  refers to the time  $t=\tau$  at the end of the initiation period.

The volume behavior of the sample is furthermore governed by its thermal expansion due to the heat of polymerization  $dE_M$  ( $dE_M / d[M] \cdot d[M] / dt \cdot dt$ ) and the heat input  $I \cdot dt$  caused by the polymerization lamp. The thermal expansion of the sample is influenced by the transfer of heat to the environment which is determined by the thermal surface conductivity  $\alpha$  and the sample surface  $A$ . A homogeneous temperature  $T$  within the sample was assumed for the modeling of the temperature development. Measurements with thermocouples at the outer and inner part of the specimen did not show any significant differences in temperature.

$$T(t + \Delta t) = \left\{ T(t) + \frac{\Delta t}{mc} \left[ I + \frac{dE_M}{d[M]} \cdot \frac{\Delta[M]_t^{t+\Delta t}}{\Delta t} \right] \right\} \cdot \exp\left(-\frac{\Delta t \alpha A}{mc}\right) \quad (7)$$

The temperature development was calculated according to eq. 7 which is a combination of an analytical description of the heat transfer to the environment and a discrete description of the effect of the two heat sources. This analytical - discrete description was chosen in order to obtain a numerical algorithm for the non-linear regression of the experimental data which is stable for the transitional description between initiation and dark phase.  $c$  denotes the specific heat of the material,  $m$  is the mass of the sample, and  $t$  and  $\Delta t$  refer to the time and the

time steps. The temperature increase which develops during polymerization leads to a thermal expansion

$$\Delta V = a\Delta T \quad (8)$$

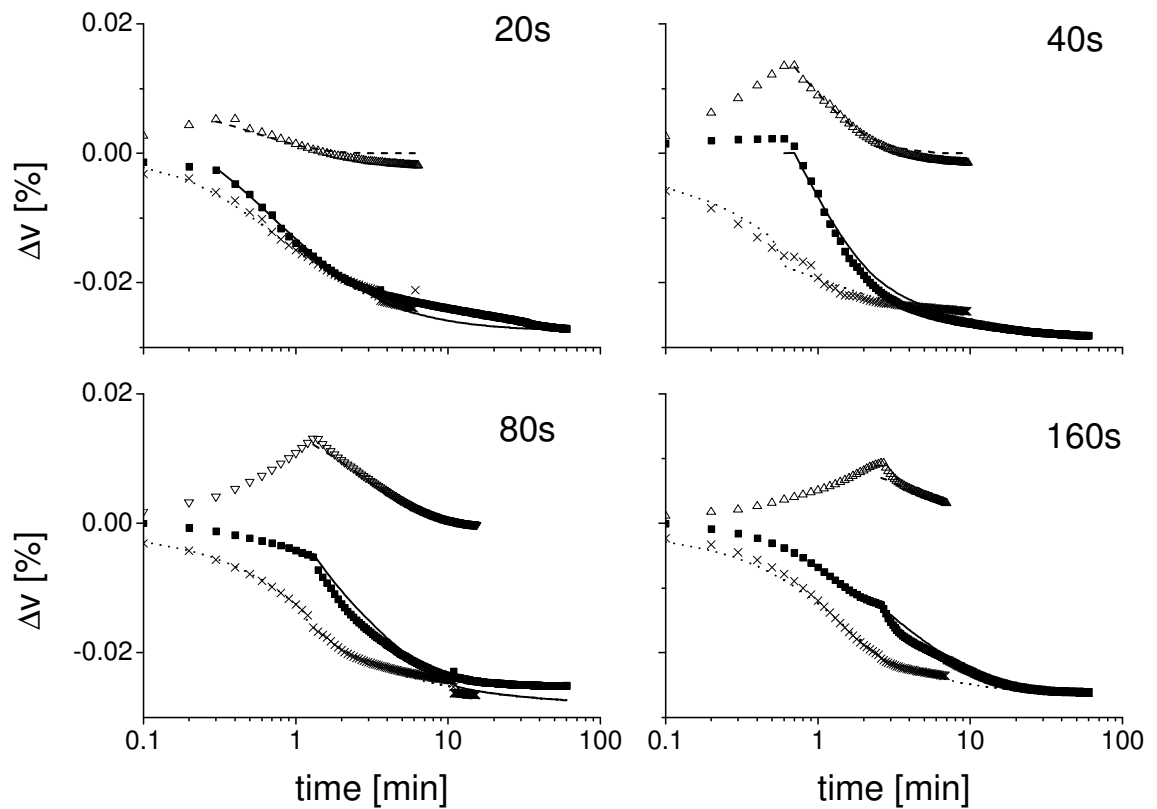
of the material, where  $a$  denotes the volume expansion coefficient. Equations 1 and 8 are used in order to describe the volume behavior of light-curing dental composites which is a combination of the thermal expansion and the polymerization shrinkage.

#### Processing of the experimental data

The parameters of the model which are relevant for describing the polymerization reaction can be most readily obtained from data which describe the volume change of the dental composites which is purely due to the polymerization shrinkage (i.e. without the influence of the thermal effects on the volume measurements). These data can, in principle, be obtained by subtracting data points originating from a measurement of an already cured sample from data points originating from the measurement of a polymerizing sample - provided one takes into account all thermal effects which influence the measurement of the volume. However, since the temperature development which an already cured sample experiences is different from the temperature development of a polymerizing sample, a simple subtraction of the two data sets does not yield satisfactory data for determining the parameters of the polymerization kinetics. The effect of the different temperature development in the two types of experiments on the volume of the sample and the heat transfer to the buoyancy medium has to be taken into account.

The warming-up of the sample due to the heat-entry of the lamp and the heat of the polymerization reaction during the initiation phase leads to a warming-up of the buoyant liquid in the direct vicinity of the specimen since thermal conduction in silicon oil is a faster process than convection. The resulting »bubble« of warm oil surrounding the sample experiences buoyant forces due to its lower density. As a result, one observes temporarily an »apparent« change in the sample volume  $\Delta V_{\text{app}}$  (see fig. 2).

Fig. 2. Experimental results on the volume behavior of VE for different initiation times and light intensities and results of the non-linear regressions of the data with the model. The symbols ( $\square$ ) denote measurements on polymerizing samples (fit: -); the symbols ( $\Delta$ ) denote measurements on already cured samples (fit: ...). The symbols (x) denote the resulting volume development purely due to polymerization shrinkage (fit: ). All measurements on the already cured samples were carried out 1h after the initial polymerization. The initiation duration and intensity of the Translux lamp was varied such that an identical total energy input was achieved. Initiation times: Astralis: 20 s; Translux: 40 s; 80 s; 160 s.



This effect was confirmed by calculating the development of the temperature and density of the sphere of warmer oil during the experiment. In order to do this, the structure of the sphere of heated oil was approximated by ten concentric »shells« of oil, whose temperature decreased from the center to the outer shell. The experimental input into the calculation of the temperature of the shells and the sample is the average temperature of the sample during the light initiation phase and the development of the volume in the dark phase. Based on these data, the temperature development of the individual shells and the sample was calculated. The temperature development of the oil and its heat expansion coefficient was used in order to calculate and confirm for the apparent change in the sample volume  $\Delta V_{\text{app}}(t)$  for the buoyancy measurements on the polymerizing sample and the cured sample.

The data processing procedure described above was implemented by carrying out a simultaneous non-linear regression of two types of data (temperature and volume development of a polymerizing sample and a cured sample) and the results of the weighed subtraction of the volume - curves with the mathematical model by minimizing the sum  $\sigma^2$  of the squared deviations. The development of the volume of the polymerizing and already cured samples in the dark phase was used in order to optimize the individual weighed subtraction of both volume curves by validating the weighing with the shell model. The resulting curve represents the true polymerization shrinkage and is the main input into the regression for the determination of the parameters of the mixed termination model. Since the focus of the study lies on the volume behavior of the composites, the deviation of the volumetric data were weighed more strongly in the non-linear regressions than were the deviation of the temperature data ( $\sigma_{\text{total}}^2 = 10^5 \cdot \sigma_{\text{volume}}^2/\text{mm}^3 \cdot \sigma_{\text{temperature}}^2/^\circ\text{C}$ ).

The model characterizes the thermal and volumetric behavior of the composites with 16 parameters (see table 2). The modeling of the heat transfer from the sample into the buoyancy medium requires four additional parameters. The majority of the parameters describe materials or system properties (like the

specific heat, the thermal expansion coefficients  $a$ , the heat transmission coefficient, the inhibition time etc.). These parameters can be determined by separate measurements or are available as literature data, and therefore do not need to be optimized in the nonlinear regression. Finally, there remain eight parameters to optimize, and only three of them describe the variations of the kinetics of the curing process caused by different modes of initiation:  $k_p/2k_t^b$ ,  $2k_t^b/k_t^m[P]_0$ , and  $[M]_\tau$ .

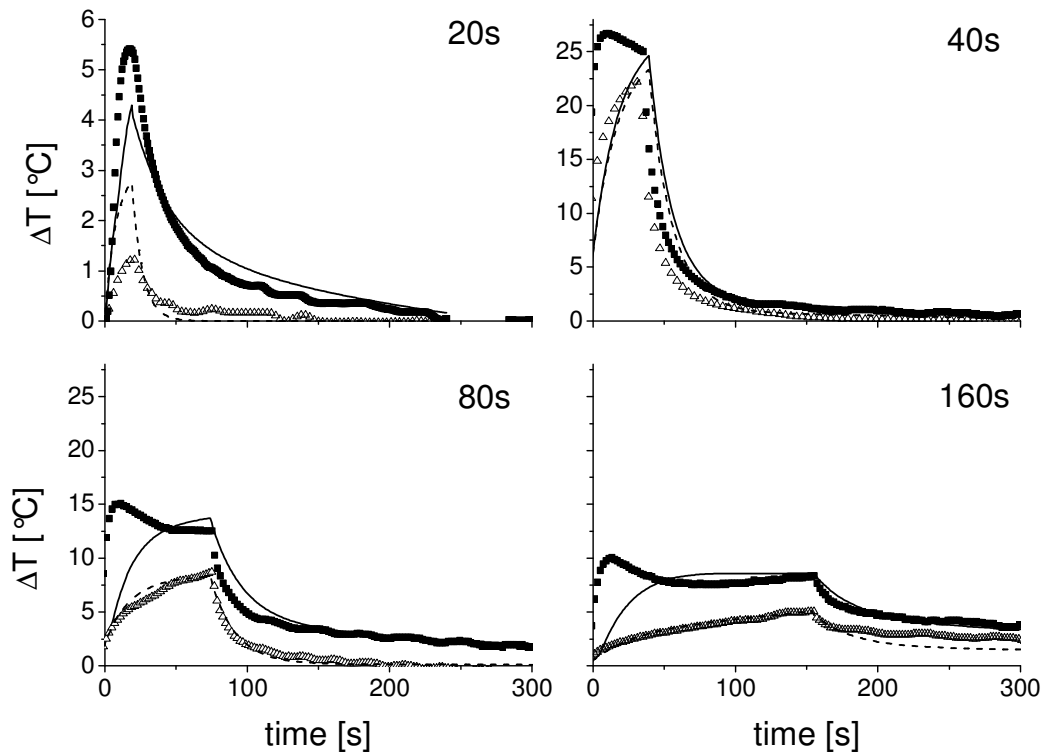
Table 2: Parameters used in the mathematical model

fixed, measured or literature data	$k_t^m$	$\tau = t_{\text{light}}$	$t_{\text{inhibition}}$	$m$
	$0.015 \text{ h}^{-1}$	x s	5 s	110 mg
fixed, technical data	$c_{\text{oil}}$	$\lambda_{\text{oil}}$	$\rho_{\text{oil}}$	$a_{\text{oil}}$
	1.55 J/gK	0.15 W/Km	0.968 mg/mm <sup>3</sup>	0.000925 °C <sup>-1</sup>
varied	$k_p/2k_t^b$	$2k_t^b/k_t^m[P]_0$	$[M]_\tau$	$A^*\alpha$
	x	x	x	55.4 mm <sup>2</sup> * x W/m <sup>2</sup>
varied	$dE_M/d[M]$	$l$	$\Delta V_{\text{therm,cured}} /$ $\Delta V_{\text{therm,curing}}$	$\alpha_{\text{apparent}} / \alpha$
	x J	x W	x	x

## Results

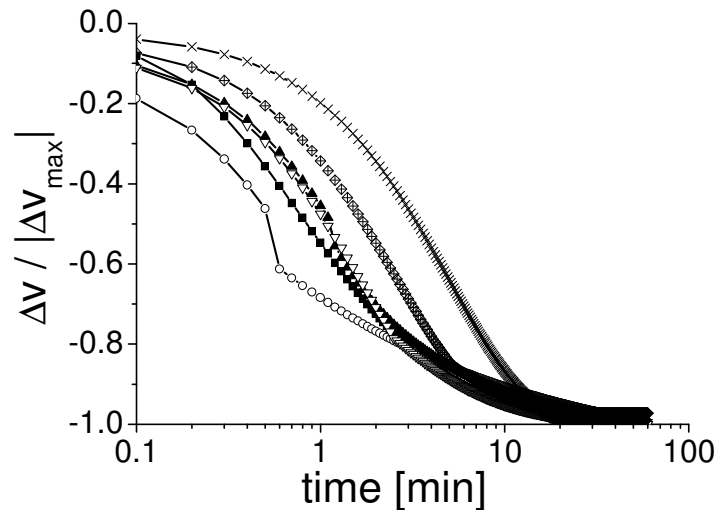
The development of the volume of polymerizing and already cured samples of the composite »Venus« for different modes of photo - initiation is displayed in figure 2. In addition, the changes in volume  $\Delta V_{pol}$  which are purely due to the polymerization shrinkage are shown. A good agreement between the experimental data for the volume development and the model function for the thermal - volumetric behavior of the composites is generally observed. The experimental data show that the reaction kinetics can be influenced by the duration of the initiation time, and the model is able to describe the development of  $\Delta V_{pol}(t)$  for all initiation times. The temperature development of a Venus sample for different modes of initiation is shown in figure 3.

Fig. 3. Experimental results on the thermal behavior of VE for different initiation times and light intensities and results of the non-linear regressions of the data with the model. The symbols ( $\square$ ) denote measurements on polymerizing samples (fit: -); the symbols ( $\Delta$ ) denote measurements on already cured samples (fit: ---). The measurements were carried out submerged in silicon oil, with samples positioned in the same way as for the buoyancy measurements. All measurements on the already cured samples were carried out 1h after the initial polymerization. The initiation duration and intensity of the Translux lamp was varied such that an identical total energy input was achieved. Initiation times: Astralis: 20 s; Translux: 40 s; 80 s; 160 s.



The model agrees well with the experimental data for the already cured samples and the polymerizing samples in the dark phase. In the initiation phase of the polymerizing samples we generally observe a small temperature peak around approximately 15 - 20 s, which disagrees with the temperature development predicted by the mixed termination model. Figure 4 shows the development of the volume of VE for different intensities and different durations of the photo initiation.

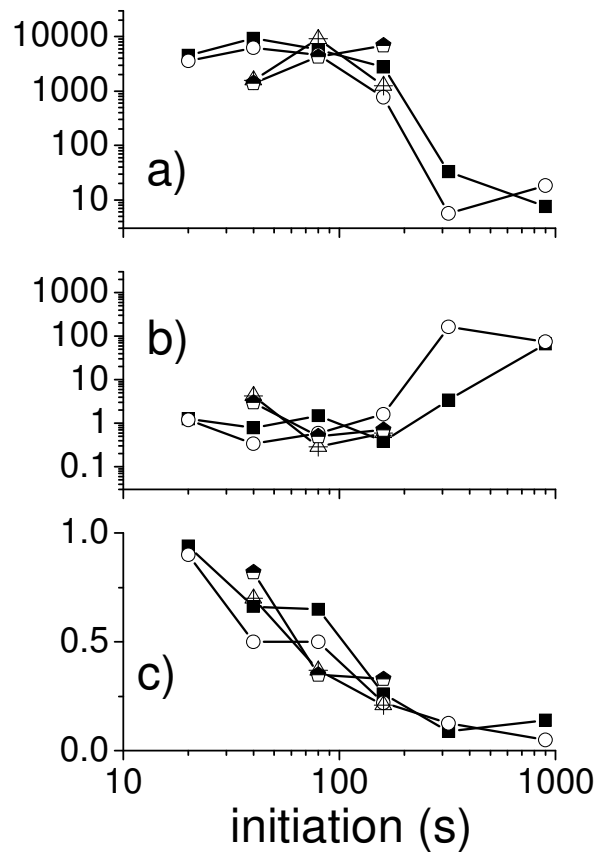
Fig. 4. The results for the volume behavior of VE which is purely due to the polymerization shrinkage. Initiation times: Astralis lamp: 20 s (n); Translux lamp: 40 s (○), 80 s (▲), 160 s (▽), 320 s (⊠) and 900 s (x).





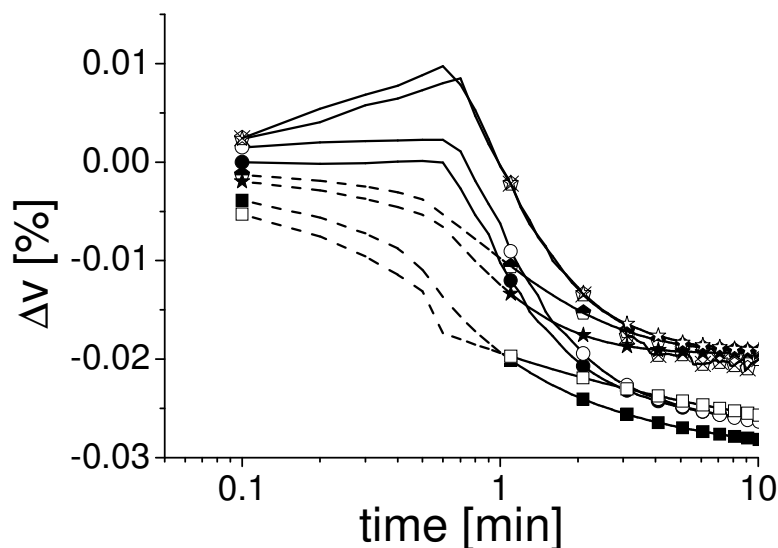
For lower intensities, the development of the volume, and therefore the progress of the polymerization reaction, is slowed down. In figure 5 the development of the adjustable parameters  $k_p/2k_t^b$ ,  $2k_t^b/k_t^m[P]_0$ , and  $[M]_\tau$  as a function of the initiation time is shown.

Fig. 5. The initiation time - dependence of the model - parameters which describe the polymerization kinetics: a)  $2k_t^b/k_t^m[P]_0$ , b)  $k_p/2k_t^b$  and c) the monomer concentration after the initiation phase  $[M]_\tau$ . TC ( $\square$ ), VE ( $\circ$ ), CX ( $\Delta$ ), FT ( $\blacklozenge$ ).



These parameters are used to describe the kinetics of the polymerization reaction. The composites VE, TC, CX, and FT show a qualitative similar development of these parameters. Figure 6 shows the experimental data on the development of the volume of the composites TC, VE, CX, and FT after an initiation time of 40 s with the Translux lamp.

Fig. 6. Measurements of the volume behavior for all four composites during the curing process, with thermal expansion, and the results for of the volume development which was induced by the polymerization, without thermal expansion. Experimental results (-) with thermal expansion: TC (n), VE (□), CX (x), FT (●); volume behavior purely due to polymerization (---): TC (●), VE (○), CX (+), FT (-).



In addition, the contribution of the polymerization shrinkage to the overall volume development of the composites is displayed in this figure. The curves of  $\Delta V_{pol}(t)$  are the result of the non-linear regressions of the experimental data with the model function. The behavior of the nano-filled composites FT and CX differs from the composites VE and TC: FT and CX show a higher thermal expansion during the initiation phase. In addition, the final volume shrinkage of the composites FT and CX is smaller than the shrinkage of the composites VE and TC.

## Discussion

The general good agreement of the experimental data on the volume development (see fig. 2) of the composites with the model function indicates that the fully integrated mixed termination model can be used in order to describe the volumetric behavior of the composites. In addition, the order of magnitude of the adjustable parameter  $k_p/2k_t^b$  (see fig. 5) agrees well with literature data:  $k_p/2k_t^b \approx 0.1 - 1$  [9]. However, the applied model is of limited use if one attempts to simulate the observed temperature development of the composites in the early stages of the initiation phase (see fig. 3). The temperature peak which is observed after 10 s – 20 s of the initiation phase [17] is most likely a result of the more complex reaction process which e.g. also includes inhibitors and stabilizers, which are not accounted for in the mixed termination model, and a non linearly related development of coefficients  $k_p$  and  $k_t$  which limits the accuracy of the fully integration technique. The analysis of the experimental data with the model for the thermal and volumetric behavior of the composites enables us to estimate the magnitude of the different factors - polymerization shrinkage, thermal expansion, and local heating of the buoyancy medium - on the experimental results of the buoyancy measurements. The polymerization shrinkage and temporary the local heating of the buoyancy medium strongly influence the outcome of the buoyancy measurements. The thermal expansion of the sample plays a smaller role. In addition, a significant decrease of volume due to an accelerated propagation of the reaction during the initial temperature peak is not observed, i.e. the peak is possibly due to reactions (e.g. inhibition) which are not directly related to the macroscopic shrinkage. This explains why we could achieve a good agreement of the model with the volumetric data despite the discrepancies between experimental thermal data and the corresponding model for the temperature development at the beginning of the initiation phase. The effect of the temperature peak at the beginning of the initiation phase on the thermal expansion of the sample is relatively small. Its effect on the local heating of the buoyancy medium only becomes apparent under extreme experimental conditions (e.g. very long photo - initiation times at low intensity), since the oil reacts sluggishly towards short-

term temperature variations. Under typical experimental conditions, the contribution of the smaller initial temperature peak with an intensity independent maximum at 15s - 20s is difficult to separate from the contributions by the heat input of the lamp and the remaining heat of reaction to the additional buoyant forces caused by the local heating of the buoyant medium.

The light intensity has a clearly visible, dominant influence on the progress of the polymerization reaction and the development of the volume (see fig. 4) [18-19]. Lower initiation intensities result in a slower development of the volume shrinkage of the composites. Since the lower light intensity is compensated with a longer duration  $\tau$  of the initiation period, the percentage of the polymerization shrinkage which occurs in the initiation phase nevertheless increases for the lower light intensities.

This can also be seen in the results for the parameters of the model. We observe a decreasing level of resident monomer concentration at the end of the initiation period  $M(\tau)$  with increasing duration  $\tau$  of the initiation period (see fig. 5). Regarding the agreement of model and experimental data on volumetric and thermal development of the composites in the dark phase, we conclude that the working hypothesis of a steady state required for the fully integrated mixed termination model is a viable approach. The changes in the ratios of rate constants  $k_p$ ,  $k_t^m$ , and  $k_t^b$  of the reaction - and therefore changes in the level of the steady state between initiation and termination - are for initiation periods up to 160 s not so significant that the slower dynamics of the reaction could not be partially compensated with a longer duration of the initiation period. The ratios of rate constants  $k_p/2k_t^b$  and  $2k_t^b/k_t^m[P]_0$  remain, for initiation times up to 160 s, relatively constant. Obviously, in this case there is only a limited change in the diffusive microscopic processes compared to the drastically changed initiation conditions.

In principle, the rate constants can be influenced by the mode of initiation. A low light intensity can e.g. lead to the creation of fewer activated centers which can

result in a different structure of the evolving polymer network. In turn, this will influence the diffusion processes of the reactants and the rate constants of the reaction. A significant change of the ratios of rate constants  $k_p/2k_t^b$  and  $2k_t^b/k_t^m[P]_0$  can be observed for very low light intensities and long initiation times  $\tau > 160s$ . A large percentage of the polymerization reaction occurs for those initiation intensities during the initiation period. In addition, we observe a decreasing maximal volume shrinkage of the composites only at these long light initiation times with low light intensities. A possible explanation for this result is that the polymerization reaction does not progress to the full extent, as it does for the exposure times with higher light intensities, since activated polymers are trapped in the evolving structure.

The continuous buoyancy measurements and the subsequent analysis of the experimental data with the model for the thermal - volumetric behavior of the composites offers the opportunity to discriminate between the factors influencing the development of volume and temperature of dental composites during the curing reaction. The results on the volume - development of four different composites TC, VE, CX, and FT show that the heat of reaction of the composites CX and FTK leads to an initial thermal expansion which can temporarily reduce their overall shrinkage during the beginning of the curing reaction if thermal conduction is low. This can partially prevent stress relaxations which can occur in the early stages of the curing process by viscous flow of the not yet fully cured material. These relaxation processes can reduce the shrinkage stresses by 90% [20]. The thermal contraction of the composites at a later stage in the curing process will result in additional internal stresses. For a concluding assessment of the thermal effects on the volume development and - ultimately - the build-up of shrinkage stresses, one has to take the thermal conductivity of the system consisting of tooth and filling into account.

Using a combination of continuous buoyancy measurements and models for polymerization kinetics appears to be a promising approach in order to describe and analyze the volume- and temperature behavior of different dental

composites. In addition, the influence of different initiation modes and light sources on the development of the volume and the temperature of the composites during the curing reaction can be evaluated. Future work will focus on the development of the mechanical properties of dental composites during the curing reaction in order to describe the complex interplay of increasing stiffness, decreasing viscosity, and volume shrinkage which determines the build-up of internal stresses [21].

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