

Curing kinetics of visible light curing dental resin composites investigated by dielectric analysis (DEA)

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ABSTRACT

During the curing process of light curing dental composites the mobility of molecules and molecule segments is reduced leading to a significant increase of the viscosity as well as the ion viscosity. Thus, the kinetics of the curing behavior of 6 different composites was derived from dielectric analysis (DEA) using especially redesigned flat sensors with inter-digit comb electrodes allowing for irradiation at the top side and measuring the ion viscosity at the bottom side. As the ion viscosities of dental composites change 1-3 orders of magnitude during the curing process, DEA provides a sensitive approach to evaluate their curing behavior, especially in the phase of undisturbed chain growth. In order to determine quantitative kinetic parameters a kinetic model is presented and examined for the evaluation of the ion viscosity curves. From the obtained results it is seen that DEA might be employed in the investigation of the primary curing process, the quality assurance of ingredients as well as the control of processing stability of the light curing dental composites. © 2014 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved

Keywords:

Visible light curing, Dental composites, Dielectric analysis (DEA), Ion viscosity, Curing behavior, Curing kinetics

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<http://dx.doi.org/10.1016/j.dental.2013.12.013>

1. Introduction

Light curing dental resin composites are used as an alternative to amalgam fillings now for over 40 years. However, in spite of their long availability in dentistry and a lot of research work in optimizing their performance and endurance, the primary curing within the initial stages of irradiation, in particular the curing kinetics, was out of focus for a long time.

Some first attempts to investigate the primary curing process of dental resin (composites) were made in the 90s. It is known that most of the curing process happens within the first 10–20 s after irradiation. In order to obtain reliable data a method having a time resolution of minimum five readings per second is required. Furthermore, the experimental conditions and boundaries should be chosen very close to application procedures in dentistry. The methods employed for real time monitoring of the curing process include (i) optical differential scanning calorimetry (DSC) [1-3], (ii) shrinkage measurements [4-7], (iii) FT-IR spectroscopy in the ATR mode show that in the final cured state remain 20-25% unreacted MA groups [8-10], and (iv) dielectric analysis (DEA) using frequencies in the kilohertz range.

DEA has been used to monitor curing reactions of epoxy resins and optimizing RIM processing of polyurethanes [11,12]. A thorough overview of real-time in situ applications of DEA is given by NAHM [13]. The first applications of DEA to dental resins and resin composites were limited because of the necessity to irradiate through parallel arranged capacitor plates set up to measure the dielectric constant frequency and time dependently. Due to this technical obstacle DEA was considered to be hardly applicable to light curing dental resins and composites [14] and mainly applied to auto-curing resins [15].

The situation changed with the upcoming of small and flat sensors such as

- IDEX-sensors having interdigit comb electrodes with distances of 115 μm , 100 μm and 30 μm and allow for to measure the local curing processes within a layer above the sensor surface having the thickness of the electrode distance [16] and
- monotrode sensors measuring an overall dielectric constant of samples having a thickness of a few millimeters [16,17].

Both sensor types allow for a dentist-like handling of the light curing dental resin composites with respect to procedure and sample mass. In order to gain information of degree of conversion or curing kinetics one requires only the time dependent change of the dielectric constant-more precisely: the change of the conductivity of the sample is the relevant quantity describing the actual curing state. As the sample is irradiated from the top and the DEA measurement is performed at the bottom, it can be investigated how the curing behavior is affected by the initiator content, different monomers and monomer ratios, or the thickness of sample [17-19].

The frequency and time dependent dielectric loss consists of a conductivity part due to the motion of ions in the resin and a dipole part due to the orientation of polar groups of the resin molecules.

$$\varepsilon_r''(\omega, t) = \frac{\sigma_{ion}(\omega, t)}{\varepsilon_0 \omega} + \varepsilon_{dipole}''(\omega, t) \quad (1.1)$$

with dielectric loss the sample ε_r'' , ion conductivity σ_{ion} , dielectric susceptibility ε_0 , frequency ω and dielectric loss of dipoles ε_{dipole}'' . If there are sufficient ions in the resin they dominate the dielectric loss of resins completely. Therefore, the contribution of the dipoles to the dielectric loss is negligible in the phase of primary curing. During curing reactions the dielectric loss changes significantly because the ion conductivity σ_{ion} decreases with the ongoing polymerization and cross-linking. In analogy to the viscosity in rheology one defines the ion viscosity η_{ion}

$$\eta^{\text{ion}}(\omega, t) = \frac{1}{\sigma_{\text{ion}}(\omega, t)} = \frac{1}{\varepsilon_0 \omega \varepsilon_r''(\omega, t) \left(1 - \underbrace{\varepsilon_{\text{dipole}}''(\omega, t) / \varepsilon_r''(\omega, t)}_{\ll 1 \text{ in resins}} \right)}$$

$$\approx \frac{1}{\varepsilon_0 \omega \varepsilon_r''(\omega, t)} \quad (1.2)$$

which is the quantity considered to describe the curing reaction. Investigations of Zahouily et al. [20] showed that the ion viscosity is a function of ion mobility μ , ion concentration c_{ion} and ion charge q .

$$\eta^{\text{ion}}(\omega, t) = \frac{1}{\mu_{\text{ion}}(\omega, t) * c_{\text{ion}}(t) * q_{\text{ion}}(t)} \quad (1.3)$$

A change of the measured ion viscosity is caused either by a change of the ion mobility due to an increase of the viscosity of the curing resin or by further reactions affecting the ion concentration or ion charge, respectively. This also indicates that ion viscosity measurements become problematic if the ion concentration in the resin is very small, e.g. in the case of very pure resins. The presence of filler particles affects the ion viscosity in two ways:

1. Decrease of the ion viscosity The filler particles increase the ion concentration of the cured resin during the mixing process due to ionic impurities and makes the DEA functioning.
2. Increase of the ion viscosity The filler particles represent inert material and therefore they dilute the resin due to the volume content.

The rheological viscosity of particle filled liquids shows a significant increase with the filler content. It is obvious that the mobility of ions is only affected by the viscosity of the pure liquid in which the ions move driven by an alternating electric field as long as there are no side reactions, e.g. adsorption of initiator and accelerator molecules on the filler surface.

Up to now there has been no attempt to link the ion viscosity measured by DEA to the curing reaction in a quantitative manner. Therefore, this paper focuses on the question if the time dependent ion viscosity is able to provide information of the curing process and how it is linked to the degree of conversion.

2. Theoretical considerations of the reaction kinetics

The samples are irradiated from the top with a very high intensity. This leads to a very fast activation of almost all camphor quinone molecules (CQ) and subsequently amine co-initiator molecules after a certain initiation time. As the molecules of the initiator system are homogeneously distributed in the resin, there is a mean distance between them determined by their concentrations. From an amine ion radical or an amine radical the polymerization reaction starts and the macromolecule is growing in a random walk. This means that two neighboring polymer chains have to grow to a certain length before cross-linking can take place. Therefore, one has to distinguish clearly between the polymerization process at the beginning and the later occurring cross-linking process. The polymerization at the beginning is an "undisturbed chain growth" during the first steps. It is obvious that the phase of ucg comes to an end if the glass transition temperature of polymer chain exceeds the temperature of sample. There are two processes increasing the glass transition temperature (T_g):

1. gradual increase of the glass transition temperature T_g : the polymerization continuously increases the molecular weight of the macromolecule and, as a consequence, the glass transition temperature.

2. sudden increase of glass transition temperature T_g . Cross- linking typically doubles the molecular weight of the macromolecule and generates sudden increases of T_g .

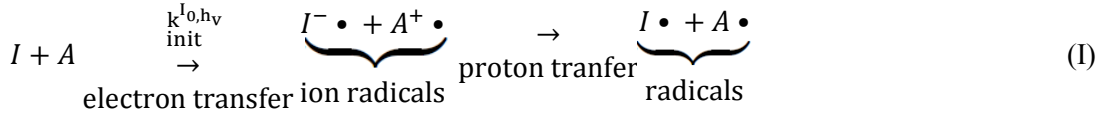
If the glass temperature T_g of the resin surmounts the sample temperature T_{sample} the chains can only grow in a diffusion controlled manner. Then the polymerization rate as well as the cross-linking processes slow down significantly.

The rheological viscosity of polymers depends linearly on molecular mass as long as the chain lengths are too short to form entanglements indicated by the critical molecular weight M_{crit} . The ion viscosity η^{ion} can be considered as a measure of the mobility of a charged probe on the molecular level in a viscous surrounding. Therefore, it has to be proportional to the rheological viscosity η^{rheo} after the initiation phase and to the molecular mass M of the growing chains [21] as long as the resin is above T_g and the molecular weight does not exceed the critical molecular M_{crit} .

$$\eta^{\text{ion}}(t) \sim \eta^{\text{rheo}}(t) \sim M(t) \quad (2.1)$$

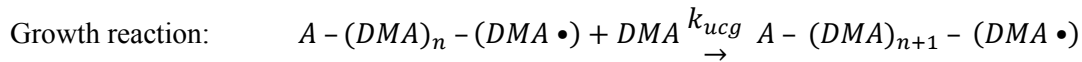
with η^{ion} ; ion viscosity, η^{rheo} ; viscosity of melt or monomer liquid, M ; molecular mass.

The initiator molecule is partly brought to an excited long living triplet state which allows for a reaction to radicalize the non-light sensitive co-agent molecule:



The kinetics of all possible initiation reactions is described in detail by [22]. For our purpose it is sufficient to assume an instantaneous generation of radicals for the first approximation which only depends on the depth due to the intensity reduction caused by absorption and scatter of light. Then the relevant initiation time is very short and can be considered as a reaction delay.

The undisturbed chain growth reaction is started either by an amine ion radical $A^{+\cdot}$ or an amine radical A^{\cdot} , which reacts with neighboring dimethacrylate monomers (DMA):



with k_{start} ; reaction constant of amine radicals, k_{ucg} ; reaction constant of undisturbed chain growth.

The concentration of radicalized initiator molecules $c_0^{\text{initiator}}$ is small compared to the DMA monomers concentration. For high light intensities it is depth dependent but not time independent. Then the undisturbed chain growth reaction is almost completely determined by the reaction constant k_{ucg} . Under this condition the reaction rate is given by a linear differential equation in terms of c^{DMA} :

$$\frac{dc^{\text{DMA}}(t)}{dt} = -k_{\text{ucg}} * c_0^{\text{initiator}}(x) * c^{\text{DMA}}(t) \quad (2.2)$$

with c^{DMA} , concentration of DMA monomers; $c_0^{\text{initiator}}$, concentration of radicalized initiator molecules.

Solving (2.2) yields the time dependent decrease of the DMA monomer concentration:

$$c^{DMA}(t) = c_0^{DMA} * e^{-k_{ucg} * c_0^{initiator}(x) * t} \quad (2.3)$$

Then the time dependent degree of conversion DC(t) is given by:

$$DC(t) = \frac{c_0^{DMA} - c^{DMA}(t)}{c_0^{DMA}} = 1 - \frac{c^{DMA}(t)}{c_0^{DMA}} = 1 - e^{-k_{ucg} * c_0^{initiator}(x) * t} \quad (2.4)$$

This corresponds to a linear relationship in a semi-logarithmic representation:

$$\log(1 - DC(t)) = -k_{ucg} * c_0^{initiator}(x) * t \quad (2.5)$$

with increasing DC the molecular mass of the polymer chains in the matrix is to grow linearly. The consideration of the boundary conditions allow for to link DC and ion viscosity:

$$\text{For } t = t_{init} \quad n^{ion}(t \leq t_{init}) = \eta_{0,init}^{ion} \Leftrightarrow \alpha DC(t = t_{init}) = 0 \quad (2.6)$$

$$\text{For } t = \infty \quad n^{ion}(t \rightarrow \infty) = \eta_{\infty}^{ion} \Leftrightarrow \alpha DC(t \rightarrow \infty) = 1$$

with the time dependent ion viscosity $n^{ion}(t)$, the initial ion viscosity $\eta_{0,init}^{ion}$ and the final ion viscosity η_{∞}^{ion} . Taking into account the exponential time dependency from Eq. (2.4) one gets:

$$n^{ion}(t) = \eta_{\infty}^{ion} - (\eta_{\infty}^{ion} - \eta_{0,init}^{ion}) * e^{-(t-t_{init})/\tau_{reac}} \quad (2.7)$$

where τ_{reac} is the reaction time constant. As the focus of interest is the ion viscosity in the short time range the exponential in Eq. (2.8) is expanded:

$$\eta^{ion}(t) \underset{t \rightarrow t_{init}^+}{\approx} (n^{ion} - n_{0,init}^{ion}) * \left(1 - \frac{t-t_{init}}{\tau_{reac}}\right) = n_{0,init}^{ion} + \frac{\Delta\eta_{max}^{ion}}{\tau_{reac}} * (t - t_{init}) \quad (2.8)$$

During the first seconds after irradiation the ion viscosity should increase linearly with time with the slope B.

$$n^{ion}(t) = \eta_{0,init}^{ion} + \frac{\Delta\eta_{max}^{ion}}{\tau_{reac}} * (t - t_{init}) = \eta_{0,init}^{ion} + B * (t - t_{init}) \quad (2.9)$$

The slope B contains the kinetics of curing reaction. Comparison of Eqs. (2.4) and (2.7) yields

$$\tau_{reac} \Leftrightarrow \frac{1}{k_{ucg} * c_0^{initiator}(x)} \quad (2.10)$$

and allows for the determination of the reaction constant k_{ucg} :

$$k_{ucg} = \frac{B}{\Delta\eta_{max}^{ion} * c_0^{initiator}(x)} \quad (2.11)$$

However, in order to quantify the reaction constant k_{ucg} the knowledge of the final ion viscosity η_{∞}^{ion} is necessary which is not determined in a short term experiment over a few minutes. Furthermore, long term DEA measurements show that the final ion viscosity is not reached after 3 days yet.

3. Experimental

3.1. Methods and materials

3.1.1. Dielectric analysis (DEA)

The DEA-measurements were performed with a dielectric analyzer using comb sensors and a LED light curing unit, **Table 1**. These sensors allow for to irradiate the sample on the top and to perform the DEA-measurement at the bottom. According to the manufacturer the penetration depth of the electric field is identical to the distance of the interdigit comb electrodes. Therefore, the curing process is measured only in the layer above the sensor having a thickness equal to the penetration depth. This gives the possibility to trace the curing process depth dependently in another investigation.

Table 1 - Components of the DEA-setup.

Type	Name	Manufacturer
Dielectric analyzer	DEA 231	Netzsch Gerätebau
Comb sensor	Mini-IDEX, 6 mm x 4 mm electrode distance: 100 μ m	Netzsch Gerätebau
Light curing unit	Celalux LED	VOCO

Fig. 1 shows a scheme of the experimental setup. The Mini- IDEX sensor is glued on the sample support of the oven with a double sided adhesive together with a microscope slide left and right of the sensor for constant sample thickness. The sample thickness can be changed by adding further microscope slides or cover slides, respectively. The position of the light tip is fixed over the center of the measuring field of the sensor. For these investigations the light tip had direct contact with the microscope slide covering the sample which is mainly used to compress the sample to the desired thickness. This also affirms a constant distance of the sample surface to the light tip of 1 mm.

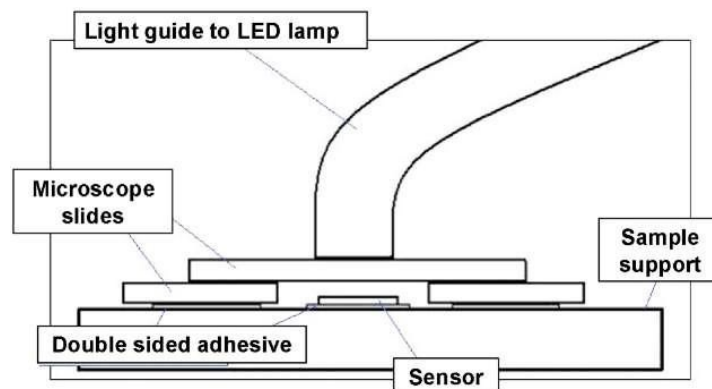


Fig. 1 Scheme of DEA-setup.

The DEA measurements were performed in the following way:

- highly viscous or paste-like sample material is placed on the sensor
- the sample is compressed to a thickness of 1 mm using a microscope slide
- the light tip is centered above the sensor
- data collection from the DEA analyzer is started to determine the ion viscosity of the uncured material
- after typically 10 s the LCU is switched on starting the curing process
- the data collection lasts until a saturation level is reached.

A minimum of three measurements were performed on each composite. For the investigated composites the time of irradiation was 160 s to affirm an almost constant level of the ion viscosity in the cured state. As these composites cure very quickly, a high sampling rate of the data is necessary. Therefore, a frequency of 1 kHz was chosen in the experiments at a temperature of 23 °C.

3.1.2. Materials

In order to demonstrate the capability of the DEA to monitor fast curing processes, six light curing dental composites were investigated, **Table 2**. These composites are well defined with respect to their composition, e.g. filler content, matrix monomers, initiator system, and inhibitor system. All composites were cured with the battery driven LCU Celalux LED from VOCO. To achieve reproducible results it is important to affirm well charged batteries.

3.2. Evaluation of kinetic parameters

3.2.1. Direct evaluation of the DEA curve

The ion viscosity of light curing resin composites depends strongly on the actual degree of conversion. Depending on their composition the ion viscosity may change several orders of magnitude-typically between one and three-during the curing process. A typical curve is shown in **Fig. 2**. The uncured composite has a constant ion viscosity. After illumination one observes a small decrease of the ion viscosity due to the generation of ion molecule radicals or exciplexes [22,23]. This is very quickly antagonized by the polymerization reactions leading to a significantly higher final ion viscosity. In order to characterize the curing process, the ion viscosity curves were evaluated with respect to:

- ion viscosity of the uncured material $\eta_{0,init}^{ion}$
- time to reach the minimum ion viscosity t_{min}
- drop of ion viscosity $\Delta\eta = \eta_0 - \eta(t = t_{min})$
- reaction time constant $\tau_{reaction}$ of the ion viscosity
- ion viscosity of the cured composite η_{∞}^{ion}

Table 2 - Investigated light curing dental composites; composition

Product name	Producer	Filler content	Monomers
Filtek XT	3 M ESPE	65%	BisGMA TEGDMA BisEMA
CeramX	Dentsply	88%	DMAs MA modified polysiloxane
DynactX	Dentsply	72%	UDMA TEGDMA TCB
SDR	Dentsply	68%	UDMA Bifunctional cross-linker
Arabesk	VOCO	77%	BisGMA UDMA TEGDMA
Grandio	VOCO	86%	BisGMA TEGDMA

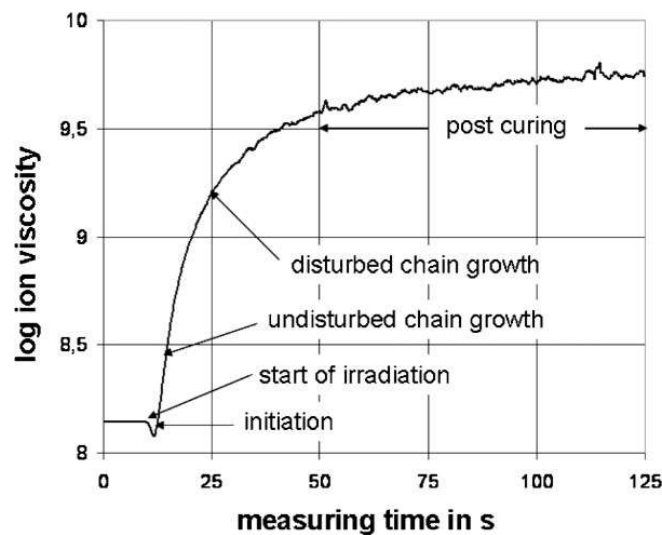


Fig. 2 Schematic ion viscosity curve with characteristic points and ranges (logarithmic scale).

Rosentritt's evaluation [19] is supplemented by the reaction time constants τ_{reaction} defined as the time required generating a $(1 - 1/e)$ change of the total change of the ion viscosity (not its logarithm). The reaction time constant represents a measure of the reaction rate.

3.2.2. Evaluation of the DEA curves with respect to reaction kinetics and fitting procedure

During the curing process the ion viscosity may change in a range of several decades. Therefore, the measured data is represented logarithmically. In order to evaluate and fit the data the following procedure is performed:

- transforming the data to the ion viscosity curves and representing them in a manner that they can be evaluated according to Eq. (2.8)
- rescaling the time axis to coincide time zero with the start of irradiation

- calculating the initial ion viscosity $\eta_{0,init}^{ion}$ as the average over nine seconds before irradiation
- calculating the final ion viscosity η_{∞}^{ion} as the average over 20 s in the range of constant final ion viscosity, typically between 90 and 110 s. The long irradiation time is to provide sufficient curing to affirm a DC close to the maximum DC.
- Fitting of the measured curves in their linear range which begins 1-5 s and ends 10-20 s after the start to the irradiation (depending on the composite) using a least square fit and the excel solver
- calculating the reaction time constants τ_{reac} and the initiation times t_{init} for each measurement
- calculating the averages and standard deviations of $\eta_{0,init}^{ion}$, η_{∞}^{ion} and t_{init} out of three measurements for each composite.

4. Results and discussion

During the curing process the ion viscosity of all investigated light curing dental composites increases typically by a factor of 10-100. Therefore, the ion viscosity data is usually represented in a logarithmic scale, **Fig. 2**. The direct evaluation of the ion viscosity curves shows significant differences with respect to initial ion viscosity η_0^{ion} , final ion viscosity η_{∞}^{ion} and reaction time constant $\tau_{reaction}$, while the time to minimum ion viscosity t_{min} is for all composites close to 1 s, **Table 3**. Especially, the final ion viscosities may exhibit big scatter, e.g. for Dyract X it is almost the same as the mean value. Of course, this also affects the corresponding reaction time constant determined from the final ion viscosity according to Eq. (2.8).

Table 3 - Direct evaluation of the ion viscosity curves

Material	η_0^{ion} ($10^6 \Omega \text{ cm}$)	η_{∞}^{ion} ($10^6 \Omega \text{ cm}$)	t_{min} (s)	$\tau_{reaction}$ (s)
Filtek XT	4.06 ± 0.42	1150 ± 150	0.75 ± 0.07	38.4 ± 2.1
CeramX	910 ± 87	0730 ± 310	0.93 ± 0.15	16.9 ± 6.3
DyractX	56.4 ± 4.5	$11,770 \pm 9800$	0.63 ± 0.06	64.9 ± 45.1
SDR	512 ± 44	7720 ± 2940	0.78 ± 0.16	71.9 ± 44.8
Arabesk	171 ± 4	$11,570 \pm 1840$	1.05 ± 0.21	53.2 ± 2.8
Grandio	89 ± 6	$10,450 \pm 1920$	0.67 ± 0.06	88.4 ± 4.2

Although all composites are composed in a similar way, the time dependency of the polymerization and curing process differ with respect to initiation time and initial reaction rate (slopes of the corresponding curves) after the initiation phase, **Fig. 3**. Filtek XT exhibits an ion viscosity being significantly lower even in the long time range, whereas Ceram X reaches the state of reduced ion mobility already after 5 s.

An important point is the reproducibility of the ion viscosity. Samples taken from the same tube show a good reproducibility during the phase of undisturbed chain growth, **Fig. 4**. This is important as this time range may be used to evaluate the reaction constant if the concentration of radicalized initiator molecules is known. It was also found that measurements made with samples from different tubes are not entirely reproducible. This behavior was more pronounced for samples from different batches. The reason for this may be not attributed to the DEA method itself but to differences in the composites compositions. The filler content of these highly filled composites is in the order of 75-90%. A few verification measurements using thermo-gravimetric analysis (TGA) show that two batches may differ in their filler contents in the order of 3%. For such highly filled composites this corresponds to changes of the resin content between 10 and 30%, and thus to changes in the measured ion viscosity curves.

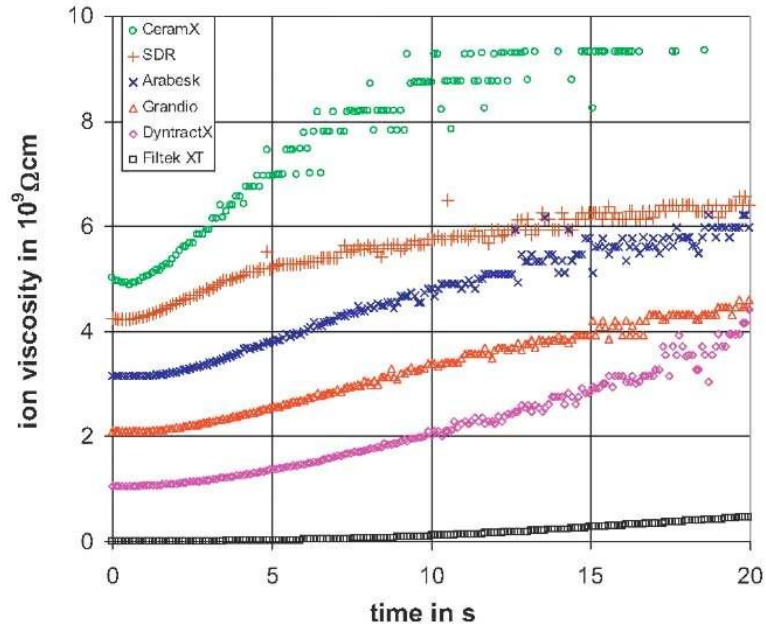


Fig. 3 Comparison of ion viscosity curves of all composites - for clarity reasons curves #3- #6 are shifted in vertical direction by $10^9 \Omega \text{ cm}$ each, curve #1 is Filtek XT.

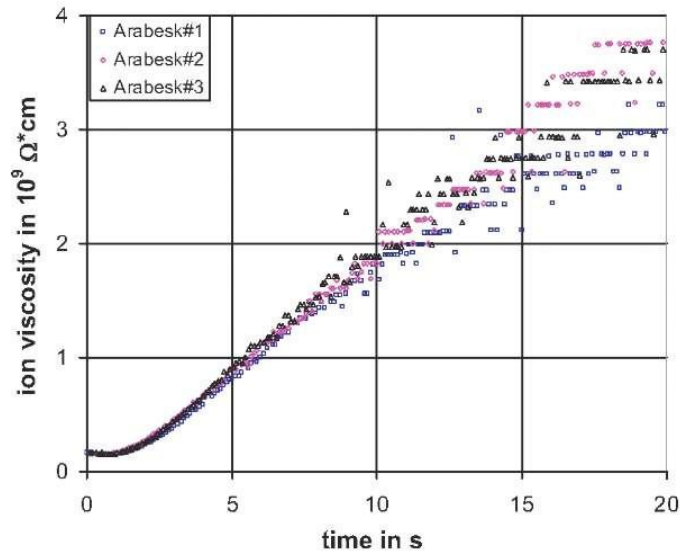


Fig. 4 Reproducibility of ion viscosity curves.

Within the measured time dependent ion viscosity curves one can distinguish the following ranges in **Fig. 2**:

- the constant initial ion viscosity η_0^{ion} of the non-irradiated composites
- the initiation phase with a slight decrease of the ion viscosity
- the linear increase of the ion viscosity
- the degressive increase of the ion viscosity slowly approaching the final state
- the final ion viscosity η_{∞}^{ion} of the fully cured composites.

The constant initial ion viscosity η_0^{ion} depends mainly on the composition of the materials defining the concentration of ions. It was found that the measured initial ion viscosities change between 3 and 10%

within the same batch depending on the composite. Larger changes were found between different batches of the same composite. This means that the DEA is able to indicate changes of the raw composites as well as changes in the composition of the produced dental filling composites.

Immediately after switching on the LCU the irradiation excites a part of the camphor quinone molecules (CQ) to a triplet state from which they can react with co-initiator molecules – so-called accelerators – generating two ion radicals. These ion radicals are clearly responsible for the slight decrease of the ion viscosity measured by the DEA as they increase the ion concentration. The duration of the initiation phase depends on the composition of composites as the resin viscosity defines the mobility of the CQ molecules and the time to generate a reasonable number of ion radicals.

The pronunciation of the decrease of ion viscosity is mainly affected by the filler content as it reduces the global ion concentration. Furthermore, these initiator ion radicals start the polymerization process. In the case of CQ, the co-agent radicals (mostly amines) are the rate determining species [22,23]. This means that there are always two superposing processes during the initiation phase:

1. ion radical generation which decreases the ion viscosity
- and
2. chain growth which increases the ion viscosity.

The linear increase of ion viscosity after irradiation depends on the concentration of radicalized CQ molecules. It is affected by the initial light intensity, the concentration of CQ molecules in the resin and the filler content. This linear increase comes to an end if a certain ion viscosity is achieved as the mobility of the DMA molecules is significantly reduced due to vitrification indicating that the resin is transferred from the liquid state to the solid glassy state.

The subsequent degressive time dependency of the ion viscosity shows that further chain growth and cross-linking become diffusion controlled. If this reaction phase is reached, the molecules in the resin become more and more immobilized. The ion mobility becomes very small while the ion viscosity reaches values close to the resolution limit of the DEA 231 being in the order of 10^{10} - 10^{11} Ω cm. This means that digitizing effects are seen in the measured curves as the data points show constant differences for ion viscosities exceeding 2×10^9 Ω cm, **Fig. 5**. The scatter of the ion viscosity in the long term range is also connected to the filler as it is much more pronounced for the highly filled composites than for pure resins. This may be due to the relaxation of internal stresses, filler matrix debonding,

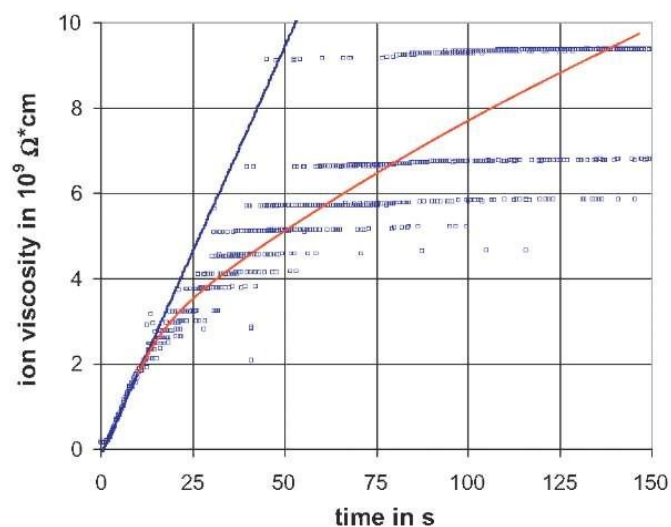


Fig. 5 - Scatter of ion viscosity at large curing times, (data points), straight blue line is the short time fit according to Eq. (2.9)), red line shows the deviation from the linear behavior beyond vitrification. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

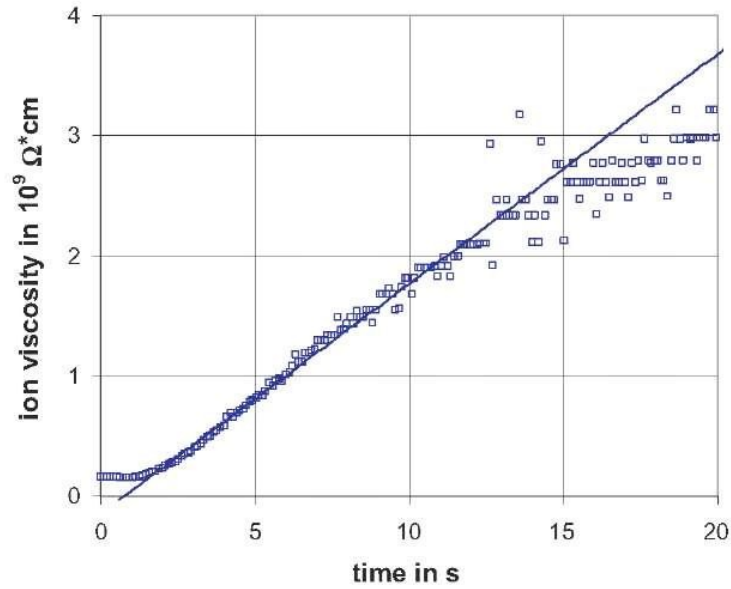


Fig. 6 Evaluation of Arabesk OA2 according to Eq. (2.9).

local composites debonding from the sensor and the reduction of ion concentration in the investigated volume layer due to the filler itself. In spite of the scatter of the ion viscosity data one can "see" the "slow down" of the curing process as shown by the red line.

As the curing kinetics of the undisturbed chain growth is of interest, the data is evaluated with respect to the slopes in the linear time range B , the initiation time t_{init} , the reaction time τ_{reac} and the initiator dependent reaction constant $c_0^{initiator} \times k_{ucg}$. **Table 4** and **Fig. 6**.

The measured ion viscosity approaches the final ion viscosity η_{∞}^{ion} after the primary curing. Long term measurements of the ion viscosity over several days exhibit still a very slow increase [24]. A rough consideration of the curing process shows that one MA group of the DMA molecule is only required for polymerization before cross-links can be formed. The second MA group can only partly contribute to cross-linking and further polymerization as well as termination reactions. With proceeding cross-linking and polymerization the 3D-network becomes more and more immobilized. Thus, a remarkable amount of MA groups has to remain in the composite [10]. This simply means that the state of a fully cured dental composite does not correspond to the full consumption of MA groups but to a state in which all radicals have been vanished.

The curing behavior measured by the change of ion viscosity can be explained with a simple lattice model, **Fig. 7**. Under the assumption of homogeneously distributed initiator and accelerator molecules throughout the resin there is a mean distance \bar{d}_{ia} between initiator and accelerator molecules and a distance \bar{d}_{aa} between the accelerator radicals. This means that the initiation time is the time which is needed for most of the triplet activated CQ molecules to overcome \bar{d}_{ia} in order to find and to react with an accelerator molecule. Because of the high intensities of the LCU most of the initiator and accelerator molecules are radicalized after the initiation time. Every acceleration radical starts a polymer chain to grow in an undisturbed linear way in a random walk. This is called the "phase of undisturbed chain growth". Therefore, the concentration of acceleration radicals determines the kinetics of the polymerization reaction. This explains that the reaction rate depends on initiator concentrations and irradiation intensity. Furthermore, it explains why the reaction rate does not change anymore if the initiator concentration exceeds a certain value. The time of undisturbed chain growth becomes that short

that the only few polymerization steps are possible to reach the vitrification point. Then the curing time is mainly determined by the diffusion controlled disturbed chain growth and cross-linking processes.

- I. initiation and activation,
- II. start of undisturbed chain growth with short chains,
- III. start of undisturbed chain growth with long chains,
- IV. cross-linking becomes possible

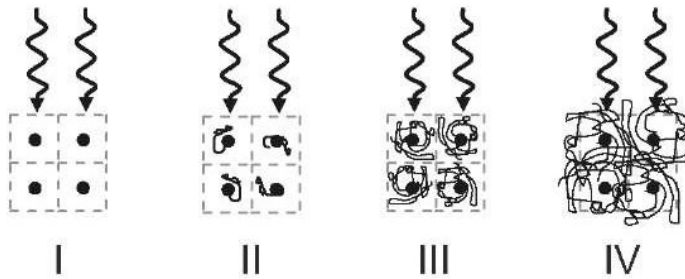


Fig. 7 – Model of the curing process of light curing dental composites.

Table 4 – Evaluation of DEA curve according to Eq. (2.9).

Material	Fit range (s)	Slope B ($10^6 \Omega \text{ cm s}^{-1}$)	t_{init} (s)	τ_{reac} (s)	$\times k_{ucg} (= \text{slope } b) (10^{-3} \text{ s}^{-1})$	$C_0^{\text{initiator}}$
Filtek XT	13-20	29.1 ± 9.3	7.35 ± 1.00	41.7 ± 12.4		25.3 ± 6.4
CeramX	1-5	559 ± 20	1.38 ± 0.13	17.6 ± 1.0		56.9 ± 3.4
DyractX	5-15	138 ± 21	2.46 ± 0.66	83.6 ± 66.4		16.9 ± 9.4
SDR	1-5	333 ± 192	0.91 ± 0.25	24.0 ± 8.1		44.7 ± 13.0
Arabesk	2-10	204 ± 12	1.62 ± 0.50	56.1 ± 9.1		18.1 ± 2.7
Grandio	3-13	143 ± 16	2.18 ± 0.42	73.7 ± 20.5		14.3 ± 3.7

Only if the end-to-end distance of the chains exceeds \bar{d}_{ia} , cross-linking reactions can occur in a significant number leading to a further increase of glass transition temperatures. The resin undergoes a very quick change from the liquid to the solid glassy state. In the glassy state further polymerization and cross-linking reactions depend on the diffusion and mobility of radicals and double bonds in the almost cured resin which are very slow. Therefore, the further increase of the ion viscosity becomes negligible. With respect to the kinetics this can be considered as the final ion viscosity η_{∞}^{ion} . The phase of "disturbed chain growth" starts if the ion viscosity deviates from linear behavior. In the long term the post-curing reactions are dominated by termination reactions of CQ radicals. This leads to only small absolute changes of the ion mobility. However, these small changes may cause big changes of the "final" ion viscosity as it is inversely linked to the ion mobility.

5. Conclusion

The time dependent ion viscosity measured by DEA during light curing of resin based dental composites is considered as an appropriate way to investigate the kinetics of the curing processes due to its significant changes and little scatter. After an initiation time of typically 1-3 s, the linear increase of the ion viscosity states the assumption that most of the photo initiator molecules are activated due to the high light intensity of the LCU. This allows for the determination of the curing rate and of the reaction constant of the curing process if the amount of activated initiator concentration is known. As the final

ion viscosity η_{∞}^{ion} plays a relevant role in the determination of the reaction time constant – not for the determination of the reaction rate - the reasons of the significant scatter has to be investigated very thoroughly. The scatter for sure deals with the fact that the "fast" Netzsch DEA 231 has a significantly lower resolution limit than the "slow" DEA 230, which exhibited much less scatter in our post-curing investigations [24]. May be this problem will be overcome by the new DEA 288 Epsilon.

The ion viscosity curves show nicely the ionic character of the initiation reaction between photo-initiator and accelerator molecules as the ion viscosity exhibits a small decrease immediately after irradiation. This decrease can mainly be explained by an increase of the ion concentration in the resin due to its instantaneous character. The temperature increase due to the photo-thermal effect is estimated with 0.1-0.2 K in the depth of 1mm after 1-2 s of irradiation. Therefore, significant temperature effects are expected either immediately in a thin layer close to the surface or after 10-20 s in depths over 1 mm.

The ion viscosities of the investigated uncured dental composites differ significantly because the initial ion concentration depends mainly on the composition of the resin. Changes of the ion viscosity indicate changes in the composition. Therefore, the DEA is an easy-to-perform and reliable method for quality control of the ingredients introduced to the composites. The DEA measures only the ion viscosity in a layer having the thickness of the distance of the IDEX electrodes. Therefore, it becomes possible to investigate the curing behavior of light curing dental composites at different depths as the sample thickness can be freely changed. This will lead to a better understanding of the global curing behavior of such composites as the light absorption significantly affects the generation of activated CQ molecules.

Acknowledgements

The authors thank the Federal Republic of Germany, Ministry of Education and Research for financial support due to the FHProfUnt project, VOCO GmbH for providing the composites, and Netzsch for experimental support. The author B.H. acknowledges the support of Operational Program Research and Development for Innovations co-funded by the European Regional Development Fund (ERDF) and national budget of Czech Republic, within the framework of project Center of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111).

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