

EVALUATION OF DIELECTRIC CURING MONITORING INVESTIGATING LIGHT-CURING DENTAL FILLING COMPOSITES

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Resume

The aim of this study is the evaluation of a dielectric analysis (DEA) method monitoring the curing behaviour of a light curing dental filling material in real-time. The evaluation is to extract the influence of light intensity on the photo-curing process of dental composite filling materials. The intensity change is obtained by measuring the curing process at different sample depth. It could be shown that increasing sample thickness, and therefore exponentially decreasing light intensity, causes a proportional decrease in the initial curing rate. Nevertheless, the results give rise to the assumption that lower illumination intensities over a long period cause higher overall conversion, and thus better mechanical properties. This would allow for predictions of the impact of different curing-rates on the final mechanical properties.

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1. Introduction

Photo-curing dental composite filling materials consist of acrylic resins which are highly filled with glass-ceramic particles. Prior to light curing they have a paste-like consistency. After curing they exhibit a flexural modulus of about 10-15 GPa being close to the elastic modulus of teeth. Several studies show that the polymerisation parameters, e.g. light intensity [1], sample thickness [1-3], exposure time and temperature [2-3], have a notable impact on curing kinetics as well as on the degree of conversion. Thus, the quantification of the influence of these parameters on the curing process is of high interest for dentistry and

composite developers. To find out how light intensity, curing rate and final cross-linking density can be characterised with dielectric analysis (DEA), a high resolution and real-time curing monitoring method was used. The DEA measures the decrease of ion mobility as a function of curing time with a high data acquisition rate, high sensitivity and without any time delay. The curing rate and final ion mobilities of composite samples having different thickness were investigated with DEA.

1.1. Photo-curing of dental composites

The light-curing process of a dental composite is started by light activation of the

curing agent and takes place during the dentist’s direct treatment. The ability to characterise a new filling material composition in its curing kinetics provides the knowledge to recommend the optimal curing light exposure and to optimize the mechanical application properties of the filling. There are several approaches in order to clarify the effects of different illumination strategies on the material processing and application properties [2, 3] (Table 1). None of these strategies like “short and intense”, “soft start” or “weak and long” illumination have yet clearly proven to be the optimal solution [3].

*Table 1
Some examples of different illumination strategies [3]*

illumination strategies	possible benefits	possible drawbacks
short treatment, high intensity ~2000mW/cm ² for 3-5s	short treatment time	high interfacial tension due to high shrinkage rate, high heat release in the tooth
soft start ~300mW/cm ² for 5s followed by 1000mW/mm ² for 35 s	reduced interfacial tension due to smooth initial shrinkage rate	longer treatment time
weak and long illumination ~700mW/cm ² for 60s	reduced interfacial tension due to comparably smooth shrinkage rate	long treatment time

1.2. Dielectric Analysis (DEA)

During the process of DEA dielectric properties of polymers can be investigated as charged ions (e.g. Cl⁻ ions as impurities) and permanent dipoles in the polymer resin are affected by an alternating electrical field. The charged ions tend to move whereas the dipoles are forced to orient in the applied external, alternating electrical field in the DEA measuring device (Fig. 1). Both

processes contribute to an internal electric field which reduces the external one [4]. The energy transferred to the specimen is partly dissipated by internal friction due to ion migration and dipole oscillation in the viscous or viscoelastic polymer resin [5]. This leads to an amplitude loss of the excitation voltage input signal and a phase shift of the response current output signal (Fig. 2). These two characteristic quantities yield the complex dielectric constant which depends both on the polymer viscosity and the measuring frequency [4, 6]. This allows for the precise characterisation of the polymer curing as the viscosity changes drastically shifting all dispersion regions to lower frequencies. The appropriate engineering quantity to trace the curing process is the ion viscosity μ depending reciprocally on the ion mobility u . Equation (1) shows the dependency on the dielectric loss ϵ'' , frequency f and the dielectric constant of vacuum ϵ_0 [4].

$$\mu(f) \sim \frac{1}{u(f)} = \frac{1}{2\pi f \epsilon_0 \epsilon''(f)} \quad (1)$$

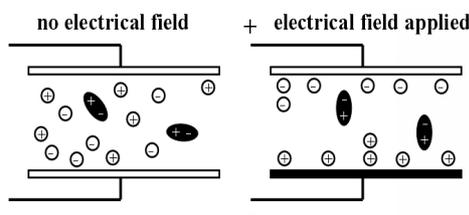


Fig. 1. Dipole orientation and charged ion motion in a polymer due to the external electric field [6]

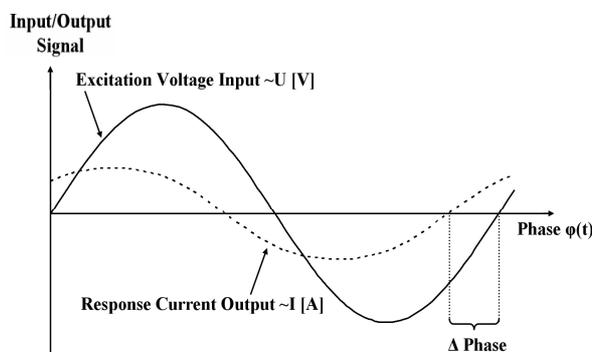


Fig. 2. Voltage excitation and current response signal of a dielectric polymer between two electrodes [6]

1.3. DEA-curve evaluation

In a DEA-curve the logarithm of the investigated ion viscosity is plotted over the curing-time. Fig. 3 shows a typical DEA-curve of a light-curing process of dental composites. After the start of illumination at the time t_0 the curve firstly shows a decrease in ion viscosity. After a few seconds the curve exhibits a minimum, $\log \mu_{min}$, followed by a rapid increase. At longer curing times the measured ion viscosity approaches a saturation level $\log \mu_{\infty}$. Important values characterising the curing process are the step height $\Delta \log \mu$ between the minimum and the saturation level and the reaction time constant τ indicating the time at which the log ion viscosity reaches approximately $(1-e^{-1})$ of the total step height $\Delta \log \mu$. The corresponding value is $\log \mu_{\tau}$.

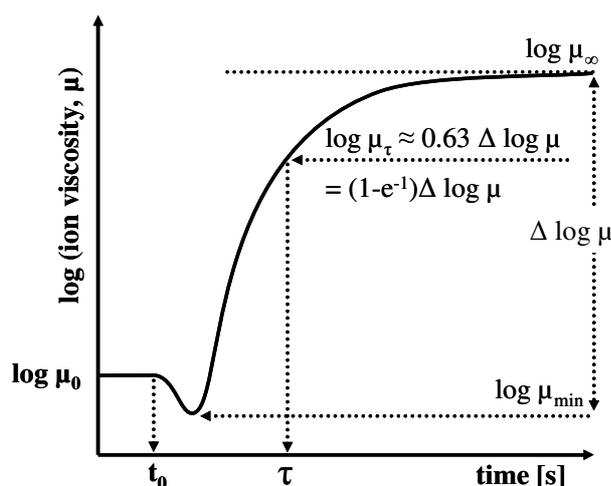


Fig. 3. Typical characteristics and specific values of the DEA-curve of a light-cured dental composite.

2. Method and materials

2.1. DEA measuring device

All measurements were performed with a dielectric cure analyser (DEA 231/1 Epsilon®, Netzsch-Gerätebau, Selb, Germany) using a measuring frequency of 1000 Hz. To introduce the curing initiating light to the sample only one surface can be covered with electrodes. Therefore, flat dielectric sensors (Mini IDEX®, Netzsch-Gerätebau) consisting of two comb-shaped interdigitated electrodes embedded in an exactly defined insulating matrix are utilised. On this sensor

surface the specimen can be applied as a layer having a thickness up to 2 mm and easily light-cured (Fig. 4). The electrical field between the electrodes has a finite reach into the sample and penetrates the specimen to a depth being more or less identical to the electrode distance [6]. Hence, the chosen electrode distance of the measurement device determines the effectively investigated part of the specimen.

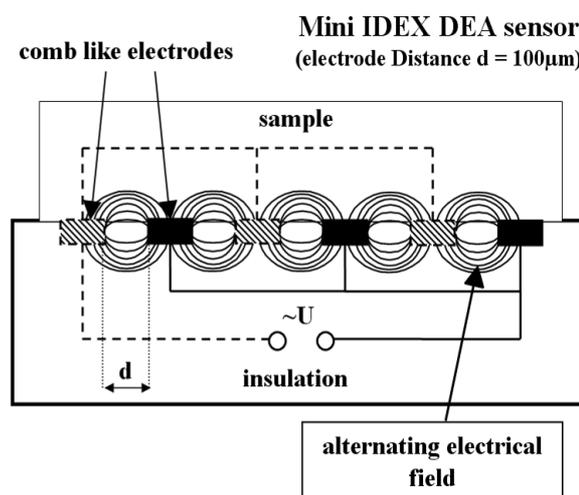


Fig. 4. Schematic design of the DEA sensor device with polymer specimen on top [7]

According to the Lambert Beer law (Eq. 2) the intensity I_0 of light introduced to a transparent or opaque body decreases exponentially with penetration depth d [8]. Here γ is the Napierian absorption coefficient of the sample. Thus the DEA measuring device can be used for the investigation of the curing behaviour of the sample in distinguished illumination depths and the corresponding intensities.

$$I(d) = I_0 e^{-\gamma d} \quad (2)$$

2.2. Measuring procedure

Prior to curing the sample was slightly pressed with a microscope slide (thickness 1.15mm) on the sensor surface to the desired target thickness. The sensor surface ($4 \times 6 \text{ mm}^2$) has to be covered completely. The LED curing device (Celalux®, VOCCO, Cuxhaven, Germany) was assembled with a laboratory stand above the

composite sample pointing directly to the glass slide. The sample was cured with an illumination device intensity of 700mW/mm² for 80s starting 10s after switching on the DEA measurement. This unusually long photo polymerisation time was realized by two 40s sequenced illuminations with the curing device.

2.3. Material composition

- Polymer matrix is based on acrylic resins (approx. 28 weight%)
- Compatibilised glass particle filler (approx. 71 weight%)
- Additives: e.g. initiator, accelerator, stabiliser, colour etc. (approx. 1 weight%)

3. Results and discussion

Within the first seconds after starting the illumination device, the ion viscosity curves show a minimum (Fig. 5). Radicals are formed and react in a first step with daylight stabilizers in the composite [2, 3]. These stabilizers are necessary for the processing of the material itself. The light initiated process leads to a small decrease of ion viscosity. Within 0.5 to 3 seconds (depending on the sample thickness, Fig. 7) the DEA curves reach the minimum value and subsequently show a rampant increase indicating a high rate propagation of the curing process. When reaching the curve minimum all stabilizer is consumed.

At the time τ the $\log \mu_{ion}$ -curves decrease significantly in its slope. At this point the polymer network of the filling composite is assumed to be roughly set accompanied by a drastically reduction in ion mobility. The reaction time constant τ is reached at a $\log \mu_{\tau}$ value of about 9.4 (Fig. 5). The corresponding time constants of all 7 sample thicknesses are plotted in Fig. 6. It was found that τ depends reciprocally on the illumination intensity acc. to the Lambert Beer law (Eq. 2) with an absorption coefficient $\gamma \approx 1.3$.

Another important value characterising the curing behaviour of a filling composite is the slope of the DEA-curves. It decreases

significantly with increasing sample thickness (Fig. 5). This is due to the fact that the DEA measures the ion viscosity directly above the sensor electrodes at the back side of the illuminated sample. Fig. 6 shows that the maximum slopes of the DEA-curves correlate to the light intensity and show the same Lambert Beer behaviour (Eq. 2). Thus the ion viscosity proves as an appropriate measure for the curing rate. After about 80 s of illumination, all curves seem to have reached the saturation ion viscosity $\log \mu_{\infty}$ (Fig. 5).

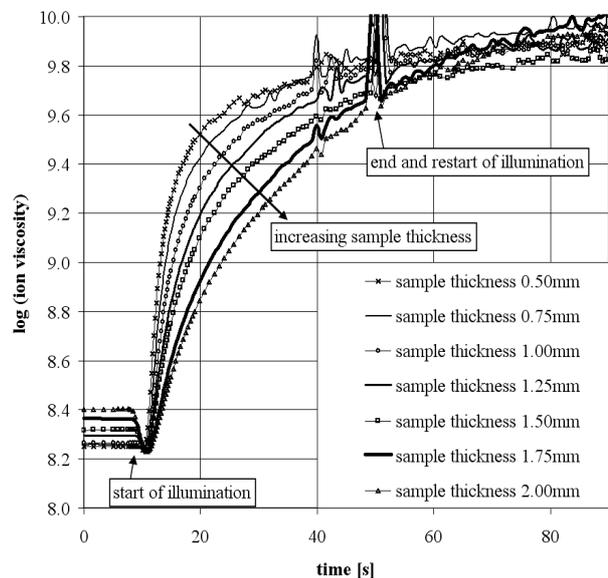


Fig. 5. DEA ion viscosity curves of the photo-curing process measured for various specimen thicknesses ranging from 0.5mm – 2.00mm at room temperature; (each is a mean curve of 3 measurements; all curves are shifted to the same starting minimum)

Due to the experimental conditions before the start of illumination all curves show the same ion viscosity $\log \mu_0$. Nevertheless acc. to Rosentritt *et al.* [2] the difference between the starting minimum-maximum values, $\Delta \log \mu$, may be seen as a significant value for the polymer network density. Therefore, all curves in Fig. 5 are shifted vertically to match all starting minimum values in one point. Thus, the curve shapes of the different sample thicknesses can easily be compared. All curves show nearly the same $\Delta \log \mu$ after about 80 s curing time.

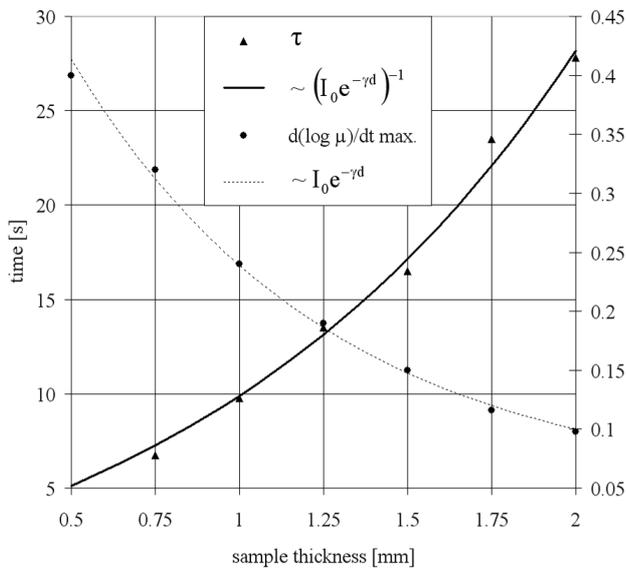


Fig. 6. Reaction time constant τ (s. chapter 1.3.) and maximum slope of the DEA-curves of Fig. 5. vs. sample thickness correlated with either the reciprocal or direct light intensity acc. to Lambert Beer law [8].

All samples reach a similar degree of conversion although the change in initial slope with increasing sample thickness clearly indicates a smaller curing rate in the beginning. So far the focus of the evaluations in this paper is on the curing process of a dental composite. As all dental fillings are equipped with stabilizers the first few seconds after starting the illumination are mainly controlled by the retarding effect of those inhibitors. In Fig. 7. the first 8 seconds after light initiation are plotted. With increasing sample thickness the minimum is more pronounced and occur for longer illumination times (Table 2). In dentistry dental filling thicknesses of 1 to 2mm are quite common. Therefore, the retarding effect of stabilizers as well as the reduced curing-light intensity in material depths of 1mm and more has to be considered for choosing an appropriate illumination strategy.

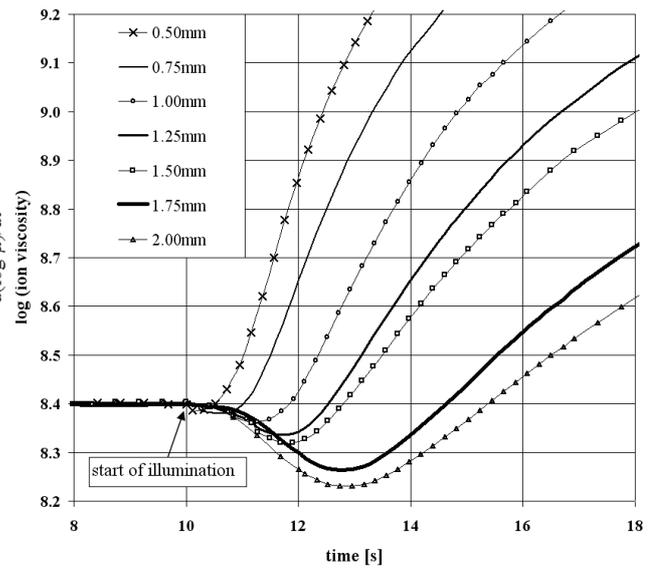


Fig. 7. Magnified minima of the DEA ion viscosity curves of Fig. 5. (all curves are shifted to the same starting ion viscosity)

4. Conclusions

The DEA method allows for a precise and detailed view on the photo curing process of highly filled dental composites. The curing rate and network density can be qualitatively and quantitatively characterised depending on the local illumination intensity. This can be achieved by the evaluation of the reaction time constant τ and the maximum slope of the DEA-curves which are found to correlate with either the reciprocal or direct light intensity acc. to the Lambert Beer law. Furthermore, the time dependency of the two processes “consumption of stabilizers” and “initiation of the photopolymerisation” depend in the initial curing phase significantly on the light intensity.

Evaluation of the curve minima of Fig. 7

Table 2

sample thickness [mm]	0.5	0.75	1.0	1.25	1.5	1.75	2.0
time of minimum after start of illumination [s]	0.2	0.6	1.3	1.7	1.8	2.8	2.9
deviation of minimum from the log start ion viscosity	0.014	0.02	0.036	0.064	0.08	0.137	0.17

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