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Dielectric Analysis of Short-Term and Long-Term Curing of Novel Photo-Curing Dental Filling Materials

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Summary: Highly glass powder filled photo-curing dental filling materials based on acrylic resins are used as an alternative for classical amalgam fillings for almost two decades. To improve the performance of the fillings nowadays nano-particles are introduced in these resins. However, surprisingly less is known about their curing kinetics and how it is affected by the composition of the resin and the kind of the filler. It is shown how the dielectric analysis (DEA) can be used to trace both the short-term photo-curing (Figure 1) as well as the long-term post-curing of such resins when measuring its ion viscosity. Especially if assisted by other thermo-analytical methods the DEA allows for a deeper insight in the processes occurring in the dental filling materials. Long-term measurements over several days using DEA and DMA (dynamic mechanical analysis) exhibit that there are going on significant changes of the properties of the dental material which are relevant for the long-term performance (Figure 2). The DEA is an easy to handle and cost efficient method to investigate the curing kinetic either for dental composite material engineering as well as for quality insurance purposes.

Keywords: dental polymers; dielectric analysis (DEA); differential scanning calorimetry (DSC); dynamic mechanic analysis (DMA); photo-curing of polymers

Introduction

Dental composite filling materials are highly filled acrylic resins having a paste-like consistency. After photo-curing they exhibit a stiffness of 10–15 GPa being close to the elastic modulus of teeth. The polymerisation mechanism of these materials can be separated into two curing phases. In the first phase the light-induced radical polymerisation builds up a rough polymer network within a few seconds consisting of monomers and oligomers. This process is started by a light activation of the curing agent and takes place during the dentist's direct treatment. After this primary curing phase remaining uncured monomers are trapped in the glassy polymer network more or less unable to find radicals as polymerisation partners. In this state the post curing phase begins. Now the curing process is proceeding much slower as it is driven by diffusion and rearrangement processes in the polymer network. The post curing can be described as chemical and physical ageing which occurs after the dentist's treatment during the utilization phase and may go on more than a decade. Due to these processes the composite filling changes its mechanical properties towards equilibrium properties.[1] The ability to characterise a new filling material composition in its primary and post curing kinetics provides the knowledge to recommend the optimal curing light exposure and to predict the life time of the filling.

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Theoretical Background of Dielectric Analysis (DEA)

Dielectric properties of polymers can be investigated using DEA as ions (e.g. Cl^- ions as impurities) and permanent dipoles in their chemical structure contribute to them. The ions are forced to move according to the applied external electrical field in the DEA measuring device while the dipoles are forced to orient (Figure 1, left side). Both processes contribute to an internal electric field which reduces the external one.[2]

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.[3] This leads to an amplitude loss of the excitation voltage input signal and a phase shift of the response current output signal (Figure 1, right side).

These two characteristic quantities yield the complex dielectric constant which depends on the polymer viscosity, the measuring frequency, and the temperature. This allows for the precise characterisation of the curing as the viscosity changes drastically shifting all dispersions 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 how they depend on dielectric loss ε'', frequency f and dielectric susceptibility ε_0.[1]

$$\mu(f) \sim \frac{1}{u(f)} = \frac{1}{2\pi f\, \varepsilon_0\, \varepsilon''(f)} \quad (1)$$

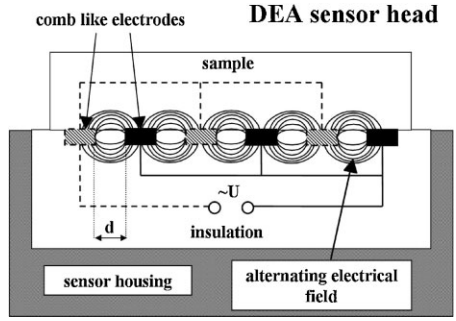

Figure 2.
Schematic design of the DEA sensor device with polymer specimen on top.[4]

Dielectric Analysis (DEA) Measurement Device

To introduce the curing initiating light to the sample not both surfaces can be covered with electrodes. Therefore, flat dielectric sensors consisting of two comb-shaped electrodes embedded in an exactly defined insulating matrix are utilised. On this sensor surface the polymer specimen can be applied as a layer having a thickness of about 1 to 2 mm and can easily be light-cured (Figure 2). The electrical field

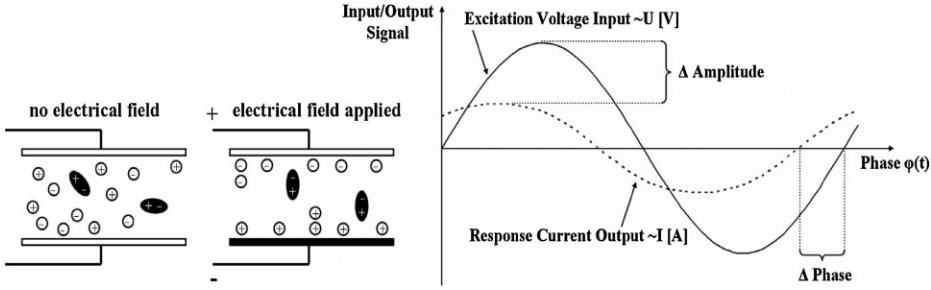

Figure 1.
Dipole orientation and charged ion motion in a polymer due to the external electric field (left).[2] Voltage excitation and current response signal of a dielectric polymer between two electrodes (right).[2]

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. Hence, the chosen electrode distance of the measurement device determines the effectively investigated part of the specimen.

Dielectric Results of the Curing Process

The two curing phases, primary photo-curing and post curing have to be investigated with two different measuring techniques. The photo-curing process requires only a few seconds to transfer the acrylic resin to a rough polymer network. Hence, the dielectric measurement device needs to collect data for about 1 minute with a sampling rate of 10 to 20 data points per second. The post-curing process takes place in a time range lasting from several days to some years due to slow diffusion and rearrangement processes in the polymer network. The investigation of the post-curing process requires a very sensitive device to detect the small changes in the dielectric behaviour of the polymer specimen over a long time.

Experimental Results of the Primary Photo-Curing

During the photo-curing of a dental composite material the dielectric analysis (DEA) shows a rampant increase in ion viscosity directly after exposing to light. After approximately 8 seconds, the drastic increase of the ion viscosity has reached saturation. The primary photo-curing phase is finished by the cross-linking of a rough polymer network. In Figure 3 the time dependent ion viscosity is compared to a DSC-measurement (Dynamic Scanning Calorimetry) of the corresponding curing reaction heat flow.

The DSC-curve shows a minimum of the exothermal heat flow 8 seconds after the exposure. This can be interpreted in the way that the heat flow release due to the curing reaction has come to an end and that the relaxation of the heat flow to the base line is due to simple cooling. The DEA and the DSC measurements indicate that the saturation of ion viscosity or ion mobility coincides with the end of heat generation in the sample.

Experimental Results of the Post-Curing-Phase

After the photo-curing process dental composite materials show a slowly proceeding increase in stiffness. The time dependent elastic modulus measured by Dynamic Mechanic Analysis (DMA) shows that the stiffness rises approximately by 30% during 2 days (Figure 4, right side). In this post-curing phase the dielectric analysis (DEA)

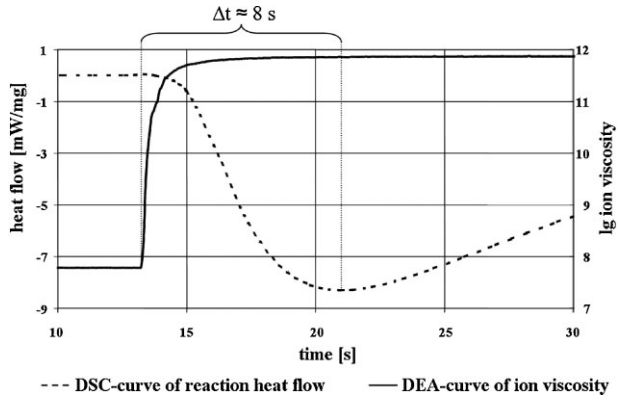

Figure 3.
Comparison of DEA and DSC measurement of the photo-curing process of a dental composite material.

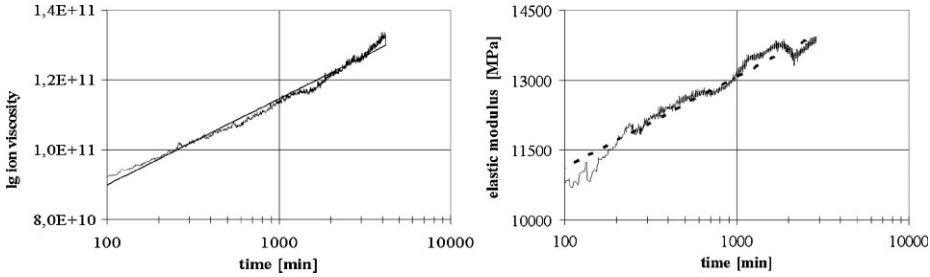

Figure 4.
Comparison of DEA (left) and DMA (right) measurements of the post-curing process of a dental composite

shows also a similar continuous increase of the ion viscosity after the exposure (Figure 4, left side).

In the first approximation the time dependency of stiffness and ion viscosity, respectively, can be described by following equations

$$E(t) = E_0 + \Delta E \log t \quad (2)$$

$$\mu(t) = \mu_0 + \Delta\mu * \log t \quad (3)$$

with the initial modulus E_0, the change of modulus ΔE, the initial ion viscosity μ_0, and the change of the ion viscosity $\Delta(\log\mu)$. For the investigated dental composite material one gets the stiffness constants to $E_0 = 7200\,\text{MPa}$ and $\Delta E = 850\,\text{MPa}$ and the ion viscosity constants to $\mu_0 = 4^{*}10^{10}$ and $\Delta\mu = 1^{*}10^{10}$. Both DEA and DMA measurements show a linear dependency of the post cure kinetics in the logarithmic time scale. This indicates in principle that the post-curing process will never come to an end.

Conclusion

Hence, the DEA method allows for a precise and detailed view both on the short-term and long-term curing processes. It provides characteristic data for the engineering of dental composite polymers and others with respect to curing light exposure conditions, minimal illumination times, life time predictions, and effects of resin components. Furthermore, the DEA is an easy to handle and cost efficient method to investigate curing kinetics of dental composite fillings and a powerful tool if assisted by other thermo-analytical methods.

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