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Report of the Ph.D. Thesis

Entitled “Real-time Investigation of Curing Mechanisms of Thermoset Resins for Medical and Technical Applications” by Johannes Steinhaus

Johannes Steinhaus' doctoral thesis focuses on the dielectric analysis (DEA) in terms of the quantity “ion viscosity” and its applications to monitor the curing behavior and reaction kinetics of thermoset based materials. The DEA method was not yet applied to fast reacting visible light curing resin based dental composites having typical curing time of 10 to 20 s or slowly reacting resins used as hardeners for three dimensional printing in additive manufacturing with curing times of 30 minutes or more, respectively. Therefore, new experimental setups and evaluation methods had to be developed.

In the thesis an engineering approach is chosen. Both kinds of resin based thermosets were supplied by industrial companies what affirmed practical relevance for materials developers as well as deeper insights for the clinicians. The scientific aspects were clearly demonstrated by the fact that three publications in peer reviewed journals were published, a fourth was accepted and a fifth was already submitted. The focus of the thesis was laid on the following questions:

- How can DEA be applied to dental composites and is it possible to “see” differences in the depth dependent curing behavior? (Paper 1)
- Is it possible to apply reaction kinetics approaches to DEA data in order to extract kinetic quantities out of time dependent ion viscosities curves on one hand and to characterize the curing behavior of the dental composites on the other hand? (Paper 2)

- Are there other methods such as NMR to monitor the depth dependent curing behavior of dental composites – especially at low irradiances - which also provide curing information that can be compared to DEA data? (Paper 3)
- How can DEA be applied to resin based hardeners used for three dimensional printing and what curing information does it provide? Furthermore, is it possible to apply DEA in a production facility? (Paper 4)
- How does the quantity “ion viscosity” correlate to the “shear viscosity”? Where are similarities and differences, and why? (Paper 5)

The five papers show the highly scientific approach to the mentioned questions as well as their practical relevance. In paper 1 a well adapted experimental setup is developed and applied to measure DEA data. The results clearly demonstrate that the curing behavior differs significantly with depth. Furthermore, it is shown that the slope of the linear range can be used as a measure for the reaction rate. It also allows for estimating the depth of cure of light curing composites.

In paper 2 Johannes Steinhaus invested a lot of efforts to describe the curing kinetics by deriving a solution for the differential equation of the reaction kinetics, to transfer it to the quantity “ion viscosity” and to apply it to six different light curing dental compo-sites. A nice result is that the curing state can be described by the dielectric reaction time constants as a characteristic quantity. In the thesis the results of paper 2 are supplemented and reinforced by further – so far unpublished – results dealing with a time dependent reaction constant taking into account that the reaction rate slows down if the viscosity of the resin increases due to polymerization and the solution of the rate equation of the curing kinetics of the hardener system for the three dimensional printing process.

Paper 3 deals with the question if NMR as an alternative method is able to detect differences of the curing kinetics in large depths at low light intensities. It is clearly shown that the character of the curing process changes if there is only a small rate of radical generation what makes the radical concentration a time dependent quantity. In that respect the NMR results are consistent with the DEA data in depths of 2 mm and more.

Paper 4 shows that the curing behavior of the hardener is very complex and can change due to aging significantly. Furthermore, a “strange” and not yet understood frequency dependency was found for HEMA and VXP1-old binders. A real high-light is that Johannes Steinhaus demonstrated that only small modifications are required to enable the DEA equipment to monitor the curing process under manufacturing conditions in a production plant.

In paper 5 Johannes Steinhaus determined “ion viscosity” and “shear viscosity” of uncured dental resin composites for different filler contents. He showed that the ion viscosity is a more complex quantity as it also depends on the ion concentration which may differ for different resins due to their chemical purities. The finding that the temperature dependencies of both quantities are identical within the experimental error is a surprise. However, it states the assumption that ions can be considered as moving “spheres” driven by the electric field. In that respect the ion viscosity is sensing a rheological property. He also showed that rheological models can be applied to describe the effects of the filler particles as long as the filler content is not exceeding 30%. The assumption that the filler does only reduce the concentration of mobile ions provides a new approach which shows deviations between the theoretical description and experimental data. The measured ion viscosities are higher for low filler contents and lower for high filler contents than the predictions. This indicates that further processes are involved if this assumption is valid.

Johannes Steinhaus has performed a very thorough experimental and theoretical work in the field of describing the curing behavior of resin based thermoset systems as well as the transfer of reaction kinetics based considerations to evaluate the corresponding ion viscosity curves. However, there are some open points attached in the appendix of this review which should be addressed in the discussion of the final exam to further clarify the topic.

Congratulations to this excellent thesis.

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Appendix: Questions for the final exam

1. Figure 5 of paper 1 shows how the radical concentration changes with depth. How does this change of radical concentration affect the structure of the network or polymer chains?
2. In paper 2 the reaction time constant τ_{reaction} is used to characterize the different dental composites. Can you give a graphic explanation of the meaning of the reaction time constant?
3. Why was NMR used only for deep depths and low irradiances and not close to the surface?
4. In figure 6 of paper 4 one can see a very different curing behavior for a frequency of 10 Hz on one hand and 1,000 or 10,000 Hz on the other. What can be the reason for this?
5. In paper 5 the filler content dependent ion viscosity is described using an approach based on the mixture rule. For low filler contents the measured ion viscosity is higher than the prediction while it is lower for higher filler contents. How can these deviations be explained?