NEW PHOTOINITIATING SYSTEMS FOR DENTAL MATERIALS

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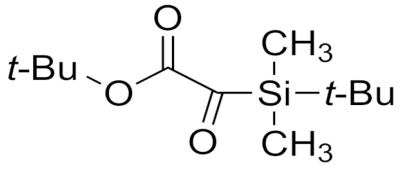
In dental restorative materials, the camphorquinone (CQ)/amine photoinitiating system (PIS) is clearly the most well-established reference system for the free radical photopolymerization of methacrylates due to its visible light absorption properties in the 400-500 nm spectral region. Ethyl-4-(dimethylamino)benzoate (EDB) is a very efficient hydrogen donor and is largely used in combination with CQ in dental materials. However, the presence of tertiary aromatic amines in (meth-)acrylate containing compositions can cause yellowing (discoloration) of the resulting photocured materials. Furthermore, the use of tertiary aromatic amines gives more and more rise to toxicological concerns. Therefore, the development of amine-free PISs is of great interest for dental manufacturers.

In this presentation, different amine-free photoinitiating systems will be presented. For example, Silyl glyoxylates (e.g. DKSi in Scheme 1) are proposed here as a new class of high performance photoinitiators for the polymerization upon Near UV or Blue Light Emitting Diodes (LEDs). Remarkably, they can be used in the presence of an iodonium salt DPI (or a germane Ph_3GeH) or added to CQ/DPI/EDB or CQ/DPI/Ph_3GeH combinations. Thin adhesives and thick highly filled composites can be easily obtained.

The silyl glyoxylates-based photoinitiating systems exhibited excellent polymerization performance under blue LED (477 nm) with exceptional bleaching properties compared to CQ systems.

FTIR experiments are used to monitor the polymerization profiles. The involved chemical mechanisms are investigated by ESR spectroscopy, laser flash photolysis and steady state photolysis experiments. Molecular orbital calculations were carried out in addition. The overall excited state processes and chemical mechanisms involved in the initiation step are detailed.

Other Phoinitiating systems based on sulfinates or originally designed H-donors will be also presented.



Scheme 1. Structure of DKSi.

[1] EP 15 188 969.8 (2015), J.E. Klee, F. Szillat, M. Maier, C.P. Fik, H. Ritter, J. Lalevee, J.P. Fouassier, F. Morlet-Savary, C. Dietlin (invs.)

[2] M Bouzrati, J Kirschner, CP Fik, M Maier, C Dietlin, F Morlet-Savary, JP Fouassier, JM Becht, JE Klee, J Lalevee, *SilylGlyoxylates as a New Class of High Performance Photoinitiators: Blue LED Induced Polymerization of Methacrylates in Thin and Thick Films*, Macromolecules, **50**, 6911-6923 (2017)