# HIGHLY EFFICIENT POLYMERIZATION INVOLVING REDOX-ASSISTED PHOTOINITIATION OF ONE-PART FORMULATIONS WITH EXTENSIVE DARK CURE

Kangmin Kim, Jasmine Sinha, Charles B. Musgrave, Jeffrey W. Stansbury

Chemistry/Chemical and Biological Engineering,
University of Colorado, Boulder, CO USA

The use of photoinitiated radical polymerization is widespread but could potentially be made more reliable or extended to additional application areas if photo-curing limitations associated with significant light attenuation or nonuniform light access could be addressed. This applies to thick materials, even in cases of photobleaching initiators, highly filled and/or pigmented materials, as well as samples that present curved or otherwise irregular surfaces that promote substantial local variability in incident irradiance. The goal here is to offer an autonomous self-correcting photopolymerization process that effectively assures full conversion throughout a sample if light activation is halted prior to the polymer reaching complete polymerization. Examples of both UV and visible light active chromophores that photolyze to release both initiating radicals and tertiary aromatic amine compounds have been developed. By inclusion of benzoyl peroxide (or other oxidants) as a component of the initiator package in these shelf-stable, one-part resin formulations, rapid light-activated polymerization can be augmented by an amine-peroxide redox initiation process that provides latent polymerization at controllable rates to near the vitrification limit even if photocuring is interrupted at just 20 % conversion in conventional (meth)acrylate resins. The design of these initiators was facilitated by computational chemistry input, which was also applied to elucidate the complex mechanistic pathways that yield multiple active radicals per photon absorbed. As examples of the utility of this approach, in dental composites that present considerable light attenuation as a function of depth, this photo-activated dark cure initiation route means that the surface of the composite does not need to be over-irradiated in order to achieve a complete and uniform cure throughout the restoration. In an analogous manner for 3D printing applications, the significant conversion gradients present across printed layers can be programmed to undergo spontaneous post cure only within patterned regions that limits uncontrolled monomer migration during printing.