556a Investigation of Chemical Composition and Physical Properties of Photopolymerized Hybrid Resin Coatings

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Photopolymerization is a method in which liquid monomer is cured by light-initiated chain reaction. The advantages of using light to initiate the reaction rather than heat include the significant savings in energy costs, processing space and time, environmentally friendly solvent-free systems, and easy reaction control. Photopolymerization initiation schemes include free-radical and cationic active centers. Free-radical photopolymerization is the most popular and well studied scheme. Cationic photopolymerizations are relatively newer and less used industrially. There are many monomers and initiators available for free-radical photopolymerization systems, which exhibit high reaction rates and result in durable products for different applications. However, the applications in thin films and coatings are limited to systems with nitrogen blanketing or require special photoinitiators when cured in air since free radicals are inhibited by oxygen and exhibit high shrinkage. In comparison, cationic photopolymerizations have lower reaction rates, humidity inhibition problems, smaller monomer selection, and less efficient initiators. However, they are not sensitive to oxygen and show less shrinkage, and the development of new monomers and initiators has also improved the curing speed. To address the limitations existing in the above systems, hybrid systems, in which a combination of two functional groups cured by two different and independent reaction mechanisms, have arisen in recent years. These systems exhibit lower sensitivity to oxygen and moisture and offer advantages such as increased cure speed and improved film-forming properties. This research investigates hybrid resin systems based on formulations that contain both an epoxide moiety, which undergoes cationic ring-opening photopolymerization, and an acrylate moiety, which undergoes free-radical photopolymerization. Studies are underway to characterize the fundamental kinetics of these hybrid resin systems and to determine the chemical distribution of the two moieties and physical properties in the resulting polymers. The hybrid monomer, 3,4-epoxy-cyclohexyl-methyl methacrylate, which contains both acrylate C=C double bond and epoxide ring moieties, was initiated by free-radical and/or cationic photopolymerization to produce a thin coating. The effect of formulation and atmosphere upon surface quality and chemical composition was investigated. The chemical composition map of the surface and at different depths was obtained by Raman confocal microscopy. The surface property of the resulting coating was tested by the pencil hardness test based on ASTM D3363. In the confocal Raman experiments, oxygen inhibition of acrylate C=C double bonds decreases with increasing depth. The inhibition effects were observed up to 10 microns below the surface. Systems containing both free-radical and cationic photoinitiators result in a cross-linked polymer and exhibit less atmospheric sensitivity and better surface properties compared to systems initiated by only free-radical photoinitiator. The average conversions of both functional groups from chemical composition study are in agreement with bulk conversion measurements from real-time reaction studies using Raman spectroscopy. Results from this research will be used to investigate the interactions between the two polymerization systems; to determine the relationship among formulation, reaction variables and product properties; and to provide guidance that will aid in the design of these reaction systems for the radiation cure industries. These hybrid photopolymers are well-suited for coating materials, adhesives and dental restoratives due to better adhesion, flexibility and less shrinkage.