Photopolymerizations Center (PC)

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Ultra-Rapid Photopolymerization Method

Fiber optic coatings are one potential use for this technology.

Novel (meth)acrylate monomers for ultra-rapid photopolymerization have been developed by researchers at the Photopolymerizations Center (PC). This program has identified and characterized several new monomers that provide highly photosensitive acrylate compositions with excellent physical and mechanical properties. These materials have potential for the design of improved structural adhesives in engineering applications. One application noted by UCB Chemicals is that of inks used in printing on food packages. Fast-reacting monomers can reduce both cost and food contamination. The fast-reacting monomers result in inks that dry faster and in packaging that is not as slippery, thereby improving the ability to stack packages. These two effects help reduce packaging costs. These materials have also been demonstrated to improve properties when used as dental restorative materials.

An added benefit to the fast-drying ink is that it does not seep through the packaging and therefore does not contaminate food contained in the package with chemicals.

Economic Impact: The economic impact of this project is significant in several respects. First, the enhanced understanding of the formation-structure-property relationships in monomers has been critical in designing formulations. This approach dramatically reduces the experimental evaluation necessary to develop photopolymerizable formulations for new applications, enhancing their penetration into new markets. Further, the existence of new monomers developed by this project that have enhanced characteristics will improve coating performance. Through improved performance, the solventless photopolymerization process, which has improved economics and environmental compatibility, will be able to penetrate markets that could not be reached otherwise, particularly in automotive or other outdoor applications.

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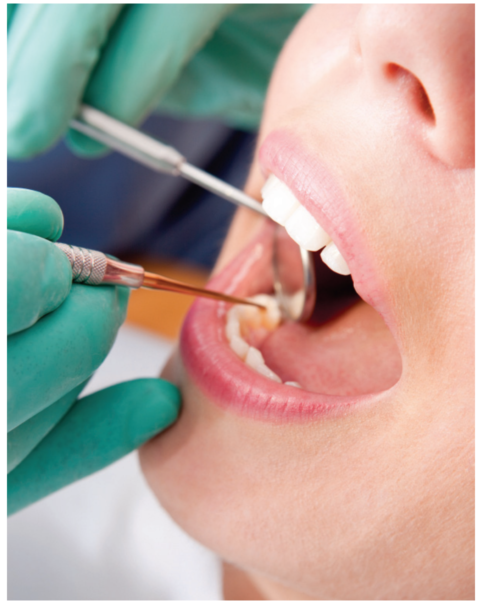
Covalent Adaptable Networks (CANS)



Dental companies benefits from this technology.

PC researchers have developed Covalent Adaptable Networks (CANS), which are polymer networks that are adaptable and have reversible structures with concomitant abilities to reduce stress and change shape after polymerization. These networks have the unique combination of being covalently bonded polymer networks that maintain an ability to change their bonded state. This capability enables materials to alleviate stress, change their shape, become adhesive (or debond), or even to heal fractures and cracks.

Two different classes of CANs exist, those that utilize radical-mediated addition fragmentation and those that utilize thermoreversible Diels-Alder reactions as the activatable bond. In a series of papers, we have demonstrated that the addition-fragmentation based CANs enable three critical advantages: reduction of polymerization shrinkage stress, photoactuation and light induced shape changes, and a novel mechanically assisted photolithographic process that enables a single light exposure to achieve complex topography. The thermoreversible CANs have also been demonstrated to be of significant value through three key developments as well: the ability to heal cracks, the ability to be remotely actuated and manipulated through radiofrequency exposure, and an ability to form complex, custom 3D objects simply through a thiol-ene based photofixation process.

Economic Impact: These materials present an entirely new and functional class of thermosets. Thermosets resins represent a multi-billion dollar market that has exclusively focused on polymer networks that are permanent and unalterable. Here, for many applications, nearly all of the same advantages can be achieved with this CANs approach, with the added benefit of numerous additional and desirable properties such as reduced stress, the ability to heal and mend cracks and defects, and the ability to be recycled more easily. Because the technology has such broad reaches across industries from adhesives to composites to 3D prototyping and photolithography, there has been significant interest from companies. Several invention disclosures have already been submitted spanning applications from conventional composites to dental material to 3D prototyping, to photolithography and adhesives. Dental companies involved in 3D prototyping and adhesive companies have expressed interest or have already optioned the technology in these fields.

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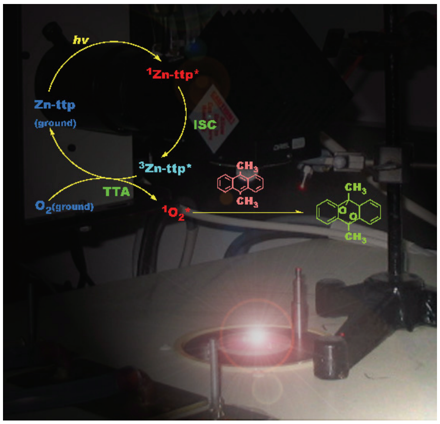
Improvement in Photo-Cured Acrylate Coatings



Increasing the polymerization rate in air environments.

At the University of Iowa's Photopolymerizations Center, (PC) a novel photochemical method to eliminate oxygen inhibition in free-radical photopolymerizations has been developed. This work provides a unique and practical solution to a major problem involving photo cured acrylate coatings, namely, inhibition by air at the coating surface. The advance involves the inclusion of two specially selected components in the reactive formulation: 1) a light-absorbing molecule which interacts with the ground state (triplet) oxygen to produce an excited (singlet) state of oxygen (Zn-ttp in the figure), and 2) a second compound which reacts with the singlet oxygen thereby removing from the system (dimethyl anthracene in the figure). By introducing the near infrared illumination before ultraviolet curing, the combination of singlet oxygen generator and trapper can effectively remove the molecular oxygen dissolved in the system. It therefore significantly increases the polymerization rate in air environments. Unlike the traditional methods to mitigate oxygen inhibition, this new method decouples the oxygen consumption and the polymerization process. The peroxide products formed from the oxidation of trapper have the potential to create new reactive centers upon UV illumination or heating.

Economic Impact: Oxygen inhibition is widely regarded as the most important unsolved problem in acrylate polymerization. Methods to mitigate the problem are generally expensive, ineffective, or undermine the properties of the resulting polymer coating. This breakthrough provides an attractive new alternative for solving this important problem. Because the method is based upon the addition of trace quantities of specially selected additives, it can be applied to any acrylate system with no other modifications to the reactive formulation. Henkel Loctite Corporation expects this technology to be of significant commercial value.

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Improved Understanding of Photopolymerization Using Photobleachable Dyes

Understanding the mechanism of this chemistry helps provide the basis for essential irreversible loss of color in a variety of consumer products. Research at the Photopolymerizations Center (PC) has examined brightly colored photopolymerizable compositions. Research at PC is providing improved fundamental understandings of the photo-induced electron transfer processes that determine the retention or loss of color, as well as the formation of active centers that lead to polymer formation. The work provides direct evidence for conditions required to achieve simultaneous photopolymerization and mechanistic understanding of both reversible and irreversible photobleaching of colored compositions. The work is important for photocurable adhesives in dental and orthodontic materials that provide easy visualization during placement (due to color), then upon light exposure, polymerize and become colorless.

Economic Impact: A fundamental understanding of photopolymerizable systems that possess color has important economic implications for a variety of products. The work has played a key role in the dental industry by in the form of photo-bleachable sealants, orthodontic bracket adhesives, as well as electronic adhesives. It will have significant economic impact in industries that use photopolymers for an array of coatings, dental/orthodontic materials, electronic adhesives, and encapsulants. It has already impacted dental material including photocurable composite fillings, sealants, and orthodontic bracket adhesives.

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Real Time Methods to Examine Photopolymerization Conversion

Researcher have developed real time instrumentation and methodologies to examine and correlate photopolymerization degree of conversion versus shrinkage stress and key mechanical properties. This work at the Photopolymerizations Center has provided results that improve upon 25 years of previously unsuccessful attempts to understand critical relationships involving dental materials and other photocurable, cross linkable systems. Key critical questions relating to shrinkage, stress, degree of conversion, and associated mechanical properties have finally been definitively addressed. These advances have provided definitive proof concerning the polymerization, shrinkage stress, and mechanical properties. Previous efforts failed to address all three relevant aspects resulting in extensive speculation and hand waving arguments.

Economic Impact: A more thorough understanding the relationships among the degree of conversion, the shrinkage stress, and the mechanical properties could impact any product that is based upon crosslinked polymer networks. This advance will have significant impacts in any industries that use photopolymers for a coatings arrays, dental/orthodontic materials, electronic adhesives, and encapsulants. It has already impacted the development of dental material including photocurable composite fillings, sealants, and orthodontic bracket adhesives.

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