4br Combinatorial Initiated Chemical Vapor Deposition for Polymer Thin Film Discovery

Tyler P. Martin, Kelvin Chan, and Karen K. Gleason

Initiated chemical vapor deposition (iCVD), developed in our lab, is a technique used to synthesize polymer thin films and coatings from the vapor phase *in situ* on solid substrates via free-radical mechanisms. It is a solventless, low-temperature process capable of forming very thin conformal layers on complex architectures. For example, finished, dyed fabrics can be easily coated without affecting the color, breathability or flexibility. Our group has used iCVD to form a range of coatings for diverse applications. These include antimicrobial coatings for fabrics and medical devices, fluorocarbon polymers for superhydrophobic materials, organosilicon films for dielectrics and bio-inert coatings, resist materials for lithography, superhydrophilic materials for thin film gels, and pH sensitive films for controlled release.

Although iCVD is chemically similar to solution-phase free radical polymerization, there are significant differences between them. The iCVD process is heterogeneous, consisting of two phases instead of a homogeneous polymerization. Therefore, two temperatures must be controlled instead of a single temperature, and concentrations of two species in two phases must be controlled. As a result, there are a large number of variables available in the iCVD process, including monomer and initiator choice, initiation temperature, substrate temperature, pressure, etc. making the deposition, characterization and optimization of new materials time consuming. A combinatorial methodology has allowed us to both more widely examine the deposition window for new materials and more quickly move from the initial material deposition optimization to the application phase of study. By implementing a combinatorial approach that examines five initiation temperatures simultaneously, we have realized at least a five-fold increase in efficiency. The deposition of antimicrobial polymer coatings provides a striking example of the gains realized by this system. Despite the lack of prior knowledge on styrene depositions by iCVD, the polymer, poly(dimethylaminomethylstyrene), was rapidly optimized, applied to fabrics and proved highly successful in killing E. coli and S. epidermidis, reducing viable bacteria by 99.9999% according to ASTM E2149-01. Direct synthesis from the vapor phase allows for *in situ* control of film morphology, molecular weight and crosslinking, and the combinatorial system decreases the time required to find the relationship between these interrelated properties. Kinetic examinations of a wide range of vinyl polymerization from the vapor phase now allow us to predict *a priori* the probability of success with a given monomer and intelligently choose appropriate deposition conditions for optimal processing.