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HWCVD of polymers: Commercialization and scale-up

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ABSTRACT

GVD Corporation specializes in process development and equipment design for the production of ultra-thin polymer coatings using hot wire chemical vapor deposition (HWCVD, also known as initiated chemical vapor deposition, iCVD). HWCVD allows many coating compositions to be produced, including fluorocarbon and silicone polymers, copolymers, and vinyl hydrocarbon polymers. It is especially valuable for creating ultra-thin layers of insoluble, infusible polymers which are hard to process by conventional means, such as polytetrafluoroethylene (PTFE, Teflon®). HWCVD PTFE coatings are chemically robust, comprised of essentially 100% CF_2, resistant to solvents, conformal to complex surface geometry, and have excellent adhesion to a wide range of substrates. Since the part to be coated remains at room temperature, fragile materials like plastics and fabrics can be coated with ease. GVD has focused on scale-up of the process equipment and has developed several standard coating systems, which will be discussed in this paper. These include laboratory-scale batch coating systems, a medium sized production batch coating system, a large scale custom batch coater, and a pilot scale roll-to-roll web coater. All of GVD's systems are complete with fully automated, computer based control systems and include options for effluent monitors and an exhaust scrubber.

1. Introduction

Across multiple industries, there is a critical need for a simple, scalable, low-cost polymer coating technology for surface modification. In applications ranging from biomedical implants to portable electronics to aerospace structures, ultra-thin coatings with tunable properties are required. The use of conventional wet-coating methods is common [1], but is often complicated by the need for solvents. That is, the selection, purchase, processing, removal, and disposal of solvents add substantially to total coating complexity, cost, and time to market. Particularly when large manufactured goods are being wet-coated (e.g., as in application of release coatings for molds), worker exposure to harmful volatile organics is an undesirable consequence. In addition, solvent–substrate incompatibility may damage the part being coated or prevent adequate wetting, resulting in a non-uniform coating.

Non-uniformity is exacerbated when the part being coated has a complex topology. In many cases, small features (microns or below) are obscured or overcoated when the solvent is driven off. Coating of nanoscale surface roughness is called for in many emerging applications, and wet processes often do not provide a satisfactory solution. Further, on drying, wet coatings tend to cause aggregation of nanoparticles (e.g., carbon nanotubes, ceramic fillers, etc.) due to strong liquid surface-tension forces and increasing polymer viscosity during drying. This creates liquid bridges that bind the particles together, a problem made even worse when particles are ≤100 μm in size [2]. The capillary action of liquid media can also damage micron-scale substrate features and prevent conformal coating. Hence, there is a great need for an all-dry polymer coating approach.

2. Initiated chemical vapor deposition (iCVD) of polymer coatings

To address this need, GVD Corporation is commercializing a novel HWCVD technology for manufacturing pure polymer coatings. This technology is referred to as iCVD, or "initiated chemical vapor deposition". The iCVD process was invented at MIT by Prof. Karen Gleason, and accommodates a wide range of off-the-shelf monomers and precursors. iCVD coatings can be used in applications requiring lubrication, hydrophobicity/-philicity, environmental protection, biocompatibility, anti-microbial activity, etc. Well-known examples of polymers which iCVD can produce include PTFE (polytetrafluoroethylene, also known as Teflon®), PMMA (poly methylmethacrylate, sold as Plexiglas®), and PHEMA (poly hydroxyethylmethacrylate, used in contact lenses) [3]. iCVD coating thicknesses in the 25 nm to 10 μm range are typical, and deposition rates of up to 1 μm/min or more are achievable for PTFE (Fig. 1).

Notably, and unlike many high-energy plasma CVD processes [4,5], iCVD preserves the original functionality of the monomer in the resulting polymer. For example, iCVD acrylate polymers having

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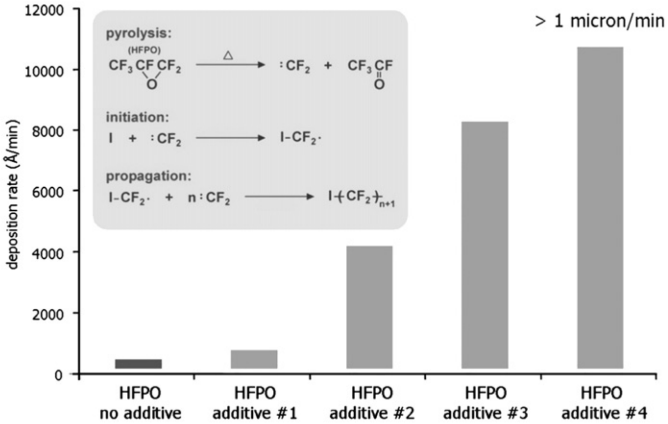

Fig. 1. iCVD polymerization mechanism for PTFE (polytetrafluoroethylene, Teflon®) coatings starting from the HFPO precursor (HFPO = hexafluoropropylene oxide). The use of vapor-phase initiators significantly increases the PTFE deposition rate.

Fig. 2. GVD's 40 in. × 20 in. commercial iCVD coating tool. This system is currently used to deposit PTFE coatings, but can be adapted for deposition of many other iCVD polymer coatings, as needed.

reactive epoxy side groups can be formed. The side groups survive iCVD polymerization, and can then engage in subsequent reactions (e.g., protein attachment) after the coating is deposited. GVD's coatings are highly-conformal to substrates with complex topologies, including molds, nanofibers, foams, membranes, and particles. Whereas plasma CVD processes tend to produce crosslinked polymer coatings, iCVD produces flexible coatings composed of linear polymer chains. (As desired, crosslinked coatings can also be produced by iCVD.) iCVD silicone coatings have survived under physiological saline soak and DC electrical bias for >4 years [6]. No coating cracks, pinholes, or other failure manifestations have developed over this time period. At the time of writing, the electrical resistance of these silicone coatings remains in the 10^{12}–10^{13} Ω range.

GVD has focused on commercial development of infusible, insoluble polymer coatings such as PTFE using iCVD. PTFE is a widely-used polymer that has unique properties including hydrophobicity, lubricity, excellent release characteristics, and unsurpassed chemical resistance. As a bulk material, however, it is insoluble (does not dissolve) and infusible (does not melt), such that very thick coatings are typical [7]. Conventional coating approaches require emulsification of a PTFE powder, followed by spraying/dipping and an aggressive cure (300 °C or higher) [8]. This makes coating of temperature-sensitive substrates, such as fabrics and plastics, very difficult. Thick, porous coatings often result due to sintering of the PTFE powder, and adhesion is poor unless a primer is used. This conventional approach is impractical for the PTFE coating of particles, for example. In contrast, GVD's iCVD approach allows a thin, smooth PTFE coating to be produced on particles, membranes, etc. without any need for a cure. iCVD therefore represents a very promising method for applying uniform, well-controlled coatings.

Currently, GVD's adherent, room-temperature PTFE coatings and large-batch deposition chambers constitute the company's most mature product offerings. GVD has scaled up production of its PTFE coatings from a 10 in.-diameter R&D-scale reactor in 2002 to a 40 in. × 20 in. commercial coating tool in 2006 (Fig. 2). Volumetrically, this represents a 100× scale-up. GVD is working with other industrial, consumer product, semiconductor equipment, and military equipment manufacturers on numerous high-value PTFE applications. A detailed description of the underlying iCVD process used in these applications follows.

2.1. Overview of the iCVD Process

iCVD combines the clean, all-dry character of CVD with the versatility of radical chemistry techniques used in bulk polymer processing [9]. Fig. 3 shows a schematic of an iCVD coating system. iCVD is well-suited to coating both porous, high-surface-area substrates and planar, non-porous substrates. By thermally activating a polymerization initiator in the vapor phase and introducing monomer vapor, a polymerization reaction is induced on the surface of the substrate. If a porous medium is to be iCVD-coated, for example, the reactive vapors infiltrate the porous structure, forming a thin polymer coating on contact and “shrink-wrapping” the medium. The open-pore structure of the medium is thus preserved. Many different iCVD polymer compositions have already been developed, and a partial list is shown in Table 1 [10].

When iCVD PTFE coatings are to be formed, for example, a gaseous, commercially-available precursor (hexafluoropropylene oxide, HFPO) decomposes as it passes over heated metal filaments. Suitable filament materials include highly resistive metals such as tantalum, tungsten, stainless steel, and nickel–chromium, among others [10]. The thermal energy from the filament array splits off individual difluorocarbene (CF_2 monomer) units from the precursor (see Fig. 1).

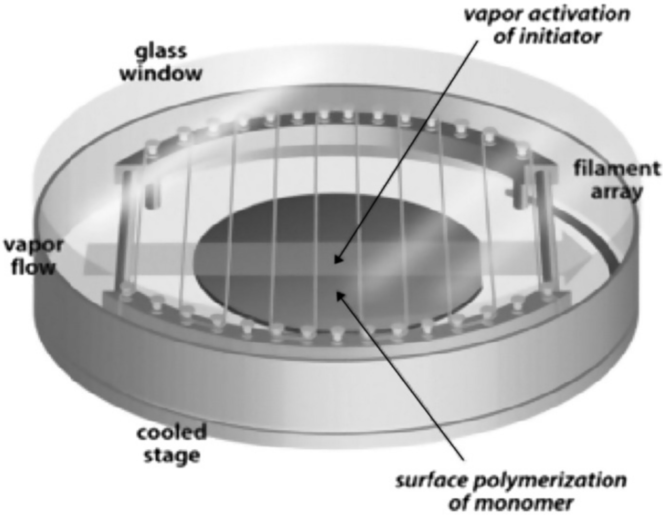

Fig. 3. Schematic of an iCVD system. The vapor-phase monomer and initiator flow parallel to an array of heated filaments. The substrate on which the polymer coating is desired sits below the filaments. Initiator and monomer are thermally activated by the filaments, forming reactive species which adsorb to and polymerize on the substrate surface. The substrate is cooled through contact with a water-cooled stage, and the top viewport is glass for inline monitoring.