

Plasma-Enhanced Parylene Coating

for Medical Device Applications

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Medical devices can benefit from improved surface properties after parylene coating. This article compares traditional parylene coating with plasma-enhanced parylene coating. It explains the processes involved and reports some results.

Beyond functionality

Medical device materials must survive exposure to the harsh environments of the human body. In turn, and more importantly, the body must not be negatively affected by these foreign materials. The compatibility requirement for any material to the various systems of the body has been universally dubbed "biocompatibility," but specific and unique requirements exist for each of the systems of the body. Implantable devices require a range of compatibilities beyond desired functionality, including low intracutaneous reactivity, low systemic toxicity, haemocompatibility and cytotoxicity. Coatings have helped to transform the surface of medical device materials with benefits to patients and industry.

Properties and process

Parylene (poly-para-xylylene) films have unique material properties that can be used to prepare medical device surfaces for use in the human body. These include excellent biocompatibility in terms of low permeability, chemical inertness and extremely low toxicity. In addition, the high dielectric strength of parylene makes it suitable for use as an electrical insulator. These attributes allow the successful implementation of various technologies

such as implantable cardiac rhythm management devices and vascular stenting. Access to these important properties relies on the inherent conformal nature of the surface polymerised film and the adhesion of this film to the device surface.

The parylene deposition process starts with one of several di-para-xylylene dimers. The two most commonly used in medical device applications are type C (mono-chloro substituted on the benzene ring) and type N (no substitutes on the benzene ring). The process is conducted at room temperature in an evacuated chamber at pressures below approximately 100 mTorr. The solid dimer is first vaporised under vacuum at temperatures between 85 °C and 150 °C and then pyrolysed at temperatures above 650 °C to break the methylene-methylene bonds and form the gaseous monomer. The highly mobile monomer enters the process chamber and simultaneously adsorbs and polymerises with like monomers to form a continuous and colourless polymer film. Film quality is controlled by the quality of the starting dimer and, most importantly, by controlling the process pressure. Film thickness can be controlled by one method or a combination of methods, including limiting the amount of dimer, pres-

sure monitoring with feedback control of the sublimation heater and active in-situ film-thickness monitoring such as quartz crystal microbalance. The process is friendly in that any material that can survive exposure to low vacuum (single-digit mTorr range) can be coated.

Limitations of standard parylene

Parylene exhibits relatively poor adhesion to many surfaces because of a lack of chemical bond formation between the polymer film and the substrate material. In the presence of liquids such as those found in the human body any void in the film can allow these liquids to propagate readily into the coating/substrate interface, which results in delamination of the film. Thus, adhesion promoters must be used to bond the parylene film to an intermediate layer that is then bonded to the device surface. However, quite often the parts must first be degreased using solvents before the adhesion promoter can be applied. Typical adhesion promoters are silane-based liquids such as solutions of gamma-methacryloxypropyltrimethoxysilane and vinyl-trichlorosilane, which can be applied in liquid or vapour form. These materials generally require a high degree of safety and handling precaution, because of the

high toxicity of the liquid and vapour phases. In addition, the application of silane-based adhesion promoters is a multistep process of surface preparation, coating and curing that involves moving the parts through various processing chambers. It is only after these critical steps have been completed that the parts can be transferred to a standard vapour phase deposition system for parylene deposition.

The complexity of the standard parylene process has long been accepted as the tradeoff for enjoying the phenomenal performance and applications flexibility of this polymer family. However, a new alternative to standard processing, that of plasma-enhanced parylene, has been developed specifically for medical device applications and is providing enabling solutions for device designers and manufacturers. Plasma-enhanced parylene is allowing designers to consider parylene for applications such as implantable biosensors and neurological implants, where the adhesion of traditional films is often one of the limiting factors in device performance.

Plasma-enhanced parylene

An alternative to the traditional multistep parylene process is plasma-enhanced parylene deposition. This process combines low-temperature plasma cleaning, surface modification and parylene chemical vapour deposition in a single process chamber without changing the chemical composition or properties of the parylene film. The result is a traditional parylene film with exceptional adhesion (see performance study below) that can be obtained without resorting to the use of liquid-based adhesion promoters. A secondary benefit is that the parts endure considerably less handling and less chemical exposure.

Plasma, which is a highly energised state of matter consisting of electrons, positive ion and neutral species, is traditionally used for surface cleaning and modification. Feed gases are ionised at pressures at or below approximately 2 mTorr to yield highly reactive species. These discrete plas-

mas can etch a surface, deposit a film, add or modify chemical functional groups or simply alter the surface energy to control water management characteristics. Low-temperature plasmas, also called cold plasmas, do not adversely affect the bulk mechanical or electrical properties of polymers, metal alloys, glasses and ceramics. Instead the effect is realised at the surface to provide new and enhanced surface functionality.

Process method

The plasma-enhanced parylene process is fully contained in a parylene reactor that has been modified to include radio frequency plasma technology. Plasma technology is incorporated into the overall process in two steps. The first is brief plasma cleaning using the appropriate gas species to remove organic contamination and create a pristine surface to build upon. The second process step involves surface modification. Specific hydrocarbon gas precursors are plasma polymerised on the substrate to form a well-bonded polymer interlayer with reactive sites. This serves as the anchor for subsequent parylene deposition. The key to the process is that each process step is performed in this single process vessel without breaking vacuum integrity in between steps. This preserves the reactivity of the surface and ensures maximum coating adhesion with minimal handling.

Performance

The adhesion of standard parylene and plasma-enhanced parylene can best be described by evaluating test results in the wet and dry environments. Test articles with both films were exposed to lactated Ringer's (saline) solution at 20 °C and 100 °C and evaluated visually every hour for signs of delamination. The results are shown in Figure 1. Plasma-enhanced parylene outlasted traditional parylene by 22 times when exposed at 20 °C and eight times when exposed at 100 °C. This is significant in that it provides a real measure of the differences in adhesion in the presence of a liquid. In the dry state, tape

Figure 1: Adhesion lifetimes for conventional parylene and plasma-enhanced (PE) parylene films exposed to lactated Ringer's solution at 100 °C and 20 °C.

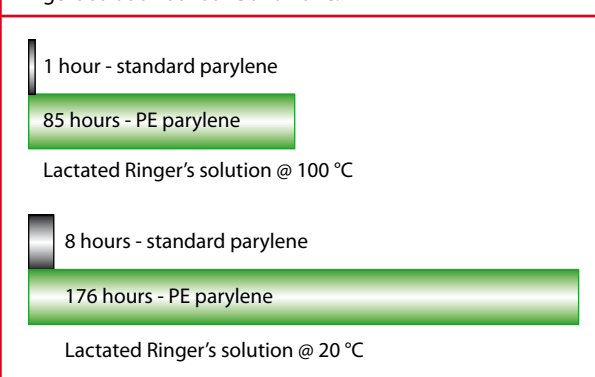


Table I: Adhesion results for conventional parylene and plasma-enhanced (PE) parylene films tested under dry conditions according to ASTM D3359-95a.

	Conventional parylene	PE parylene
X-cut	0 (10 measurements)	5 (31 measurements)
Cross hatch	0 (16 measurements)	5 (16 measurements)

testing was conducted according to ASTM D3359-95a using both X-cut and cross-hatch patterns. Samples were rated per procedure based on the delamination incurred by removal of the tape. The rating scale ranged from 0 (removal of the coating beyond the cut area) to 5 (no film removal). The results are shown in Table I. In these tests, there is a clear and contrasting performance difference between plasma-enhanced and traditional parylene films.

The increased performance of plasma-enhanced parylene films comes without the expected trade off. The films have equal electrical, chemical and barrier performance to traditional parylene films and are used in a number of Food and Drug Administration-approved implantable devices. Sterilisation via ethylene oxide, gamma radiation or electron beam is possible. **mdt**

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