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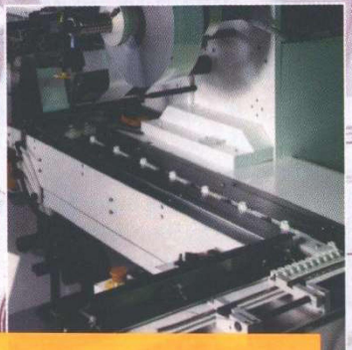

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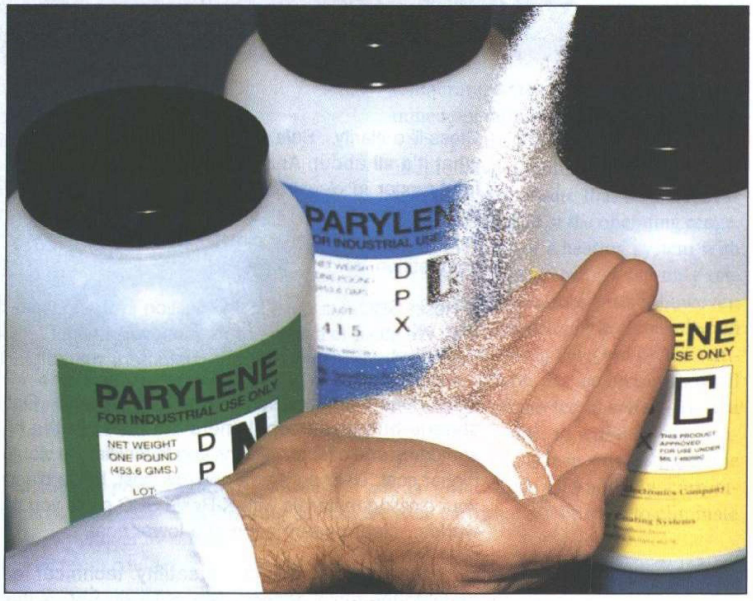
Assessing the Effects of Sterilization Methods on Parylene Coatings

Results of laboratory tests provide insight to the poststerilization characteristics of this common device-coating material.

Lonny Wolgemuth

PARYLENE HAS BEEN USED in a wide range of medical device and component applications since the 1970s. These include catheters and mandrels, stents, needles, cannulae, cardiac assist devices, prosthetics, and electronic circuitry.

The need to sterilize such products raises a number of questions regarding the poststerilization characteristics of the coating material. This article describes a series of laboratory tests that were conducted to determine the effects of common sterilization methods on selected parylene coatings used for medical device applications.[1]



The raw material for parylene films is a powder known as dimer.

PARYLENE FILM AND THE USE OF STERILIZATION

Certain medical components require a protective coating to isolate them from contact with moisture, gases, corrosive biofluids, or chemicals. Coatings are also used to protect patients from contact with surgical items or implanted devices that may not be biocompatible. Vacuum-deposited parylene is often the protective medical coating of choice. Additionally, parylene may be used to deliver other functional properties, such as electrical insulation, particulate tie-down, or increased lubricity.

The thin, transparent polymer film is characterized by pinhole-free coverage of both planar and irregular surfaces. Because it is deposited from a gaseous state, parylene provides uniform coverage across a substrate, even on corners, edges, and in crevices. (See sidebar on p. 48 for a description of parylene variants and the vacuum coating process.)

Sterilization is intended to destroy all microbial contaminants on the surface of a medical device, and the process can be accomplished by a number of chemical or physical means. The challenge in sterilization is to render a surface sterile without degrading the function or useful life of either the sterilized item or its coating.

STERILIZATION TEST METHODS AND SAMPLE MATERIALS

To measure the effects of each sterilization process on a parylene-coated object, it was necessary to compare quantitative test results for coated and sterilized samples with similarly coated samples that had not been sterilized.

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PARYLENE COATING TECHNOLOGY

Transparent parylene film is applied to substrates in a vacuum chamber by means of vapor deposition polymerization. A dry, powdered precursor known as dimer is converted by heat in the coating system to form a dimeric gas, and heated further to generate a monomer gas that is passed to a deposition chamber. Within the chamber, it polymerizes at room temperature as a conformal film on all exposed substrate surfaces.

Parylene deposition has no liquid phase, uses no solvent or catalyst, and generates no gaseous by-products. Consequently, there are no cure-related hydraulic or liquid surface-tension forces in the coating cycle, and coated objects remain free of mechanical stress. The resulting film is a high-molecular-weight, linear, crystalline polymer with an all-carbon backbone. With the absence of polar entities, and substantial crystallinity, the finished film is stable and highly resistant to chemical attack.

The static and dynamic coefficients of friction for parylenes are in the range of 0.25 to 0.33. This dry-film lubricity is an important chracteristic for certain device applications, such as catheter and guidewire coatings.

Property		Parylene N	Parylene C
Dielectric constant	60 Hz	2.65	3.15
	1 KHz	2.65	3.10
	1 MHz	2.65	2.95
Dissipation factor	60 Hz	0.0002	0.020
	1 KHz	0.0002	0.019
	1 MHz	0.0006	0.013
Secant modulus (psi)		350,000	400,000
Tensile strength (psi)		6000–11,000	10,000
Yield strength (psi)		6100	8000
Elongation to break (%)		20–250	200
Yield elongation (%)		2.5	2.9
Density (gm/cm^3)		1.10–1.12	1.289
Index of refraction (n_D^{23})		1.661	1.639
Water absorption (% after 24 hr)		<0.1	<0.1
Rockwell hardness		R85	R80
Static coefficient of friction		0.25	0.29
Dynamic coefficient of friction		0.25	0.29
Melting point (°C)		420	290
T5 point (°C)		160	125
Gas permeability at 25°C (cm^3(STP)•mil/100 in^2/d•atm)	N_2	7.7	1.0
	O_2	39	7.2
	CO_2	214	7.7
	H_2	540	110
Moisture vapor transmission at 90% RH, 37°C (g•mil/100 in^2•d)		1.5	0.21

Table I. Key physical and mechanical properties displayed by Parylene N and Parylene C.

PARYLENE VARIANTS

There are four primary variants of the polymer: Parylenes N, C, D, and HT. Although they all have the same essential coating properties and are applied in the same manner, each has a unique molecular form that results in specialized performance characteristics. Parylenes N and C are the most commonly used variants in medical coating applications. Table I describes the key properties of these parylenes.

Parylene N offers the highest penetrating power of the variants. Because of its greater molecular activity in the monomer phase, it can be used to coat relatively deep recesses and blind holes. This form of parylene also provides slightly higher dielectric strength than C, and a dielectric constant that is independent of frequency. The lower dissipation factor and dielectric constant of this parylene form enable it to be used for protecting high-frequency substrates where the coating is in the direct electromagnetic field.

Parylene C differs from N in that it has a chlorine atom on the benzene ring, providing a useful combination of electrical and physical properties. Among these are very low permeability to moisture and corrosive gases. Compared to Parylene N, C displays less crevice-penetrating ability.

The physical-property measurements identified for the sterilization tests were tensile strength, tensile modulus, coefficient of friction, moisture vapor transmission, and dielectric strength. Standard statistical tools were used to determine sterilization-related differences (changes) between the control and test samples. The sterilization procedures tested included steam autoclave, gamma and e-beam irradiation, hydrogen peroxide (H_2O_2) plasma, and ethylene oxide (EtO). Three laboratories performed the various post-sterilization tests.

Parylene-coated test samples included borosilicate glass plates and polished 16-gauge 304-stainless-steel coupons. The glass plates were treated with a release agent to allow the film to be separated after sterilization for moisture vapor transmission and tensile strength mea-

Sterilization Method	Parylene N					Parylene C				
	Dielectric Strength	MVT	Tensile Strength	Tensile Modulus	COF	Dielectric Strength	MVT	Tensile Strength	Tensile Modulus	COF
Steam	None	Δ43%	None	Δ12%	Δ38%	None	Δ5%*	Δ17%	Δ9%	None
EtO	None	Δ21%	None	None	Δ33%	None	Δ8%	None	None	None
E-beam	na	None	None	None	None	NA	None	None	None	None
H_2O_2 plasma	None	None	None	None	Δ48%	Δ9%	None	None	None	Δ188%
Gamma	None	None	None	None	None	None	Δ5%*	None	None	None

* 5% values are not likely to be statistically significant. NA=not applicable.

Table I. Effects of various sterilization methods on parylene.

surements. The coated steel coupons were used for voltage breakdown tests.

The steel and glass coupons were prepared in four coating runs (two Parylene N and two Parylene C), with consistent run-to-run fixturing. All of the specifications for each coating run were recorded and provided to researchers. These included such factors as chamber volume, dimer charge, polymer density, deposited mass, and average film thickness.

Dielectric Strength. Breakdown voltage testing was peformed in accordance with ASTM 149, Method A, at a ramp rate of 500 V/sec. Groups of five replicate breakdown voltages were recorded in ac kilovolts, and the results were coordinated with precise film-thickness measurements.

Dielectric strength was defined as the voltage gradient, or electric field strength, at which the breakdown occurs, and was calculated from the raw voltage breakdown data. In most cases, voltage breakdown resulted in a clearly visible puncture hole through the coating, and film thickness at each breakdown point was recorded with an accuracy of ± 0.1 µm.

Moisture Vapor Transmission. Moisture vapor transmission (MVT, also called permeability) calculations on sterilized coating samples followed the provisions of ASTM F1249, a dynamic flow method using a dry gas carrier, with a pressure-modulated infrared detector to measure transmitted moisture.

These measurements were made on 3-in. free-film samples lifted from coated glass coupons. Laboratory results took into account any sample-to-sample variations in coating thickness.

Tensile Properties. Tensile properties were measured in accordance with pull tests as defined by ASTM D882. Tensile tests were made on 1 × 10 in. free-film-strip specimens that were removed from glass plate carriers. This method generated data for peak load (lb), peak stress (psi), Mod E (psi), yield at 10% (psi), and elongation to break (%).

Coefficient of Friction. Coefficient of friction (COF) values for sterilization samples were determined according to ASTM D1894, which involves use of a weighted sled and strain-gauge measurements. The COF is the relation of the frictional force—as measured by the strain gauge of the test apparatus—to the sled weight. Two force values were recorded: starting (static) COF, and sliding (dynamic) COF.

GENERAL TEST RESULTS

Parylene coatings respond to these sterilization methods in a variety of ways (see summary of responses in Table 1). With regard to tensile properties, Parylene N and C were largely unaffected by any of these sterilization techniques. Only steam appears to have had any effect, causing an annealing impact on samples coated with Parylene C, seen as an increase in film crystallinity with a slight change in the tensile properties. Similarly, the tensile modulus property of Parylene N exhibited a minor change.

H_2O_2 plasma sterilization treatment appeared to alter dielectric strength, with a minimal change in Parylene C, and no change in Parylene N.

As with many polymers, parylene subjected to radiation sterilization techniques exhibits an accumulated-dose effect. Consequently, device manufacturers considering E-beam or gamma sterilization should conduct further testing to determine the effects of repeated radiation sterilizations at the anticipated dosage level in the intended application.

There were some subtle differences in the responses of the two parylene variants to these tested sterilization methods. For example, E-beam and gamma irradiation sterilization had no impact on either Parylene N or C tensile properties. H_2O_2 plasma sterilization mildly affected the coefficient of friction value of Parylene N, and the dielectric strength and COF of Parylene C. EtO affected MVT and COF in Parylene N, but only MVT in Parylene C.

In summary, the test results were quite favorable for each type of sterilization method tested. Individual film performance and sterilization impact must be addressed specifically by application.

CONCLUSION

The multilaboratory sterilization test information presented here is an important asset for the continuing development of parylene coating technology for medical device applications. The data generated will be useful for medical manufacturers in the selection of sterilization processes for given products and application settings.

FOOTNOTES

1. Parylene (poly-para-xylylene) is a generic polymer coating. Although several suppliers manufacture proprietary versions of the precursor dimer, di-para-xylylene, these sterilization tests were sponsored exclusively by Specialty Coating Systems (SCS; Indianapolis) and were confined to coated test-film samples made from SCS dimer. Thus, test results should not be regarded as being applicable to the dimer or coated products of other suppliers. ■

A hypertext version of this article will be available on Medical Device Link, http://www.devicelink.com/mddi, by September 1.