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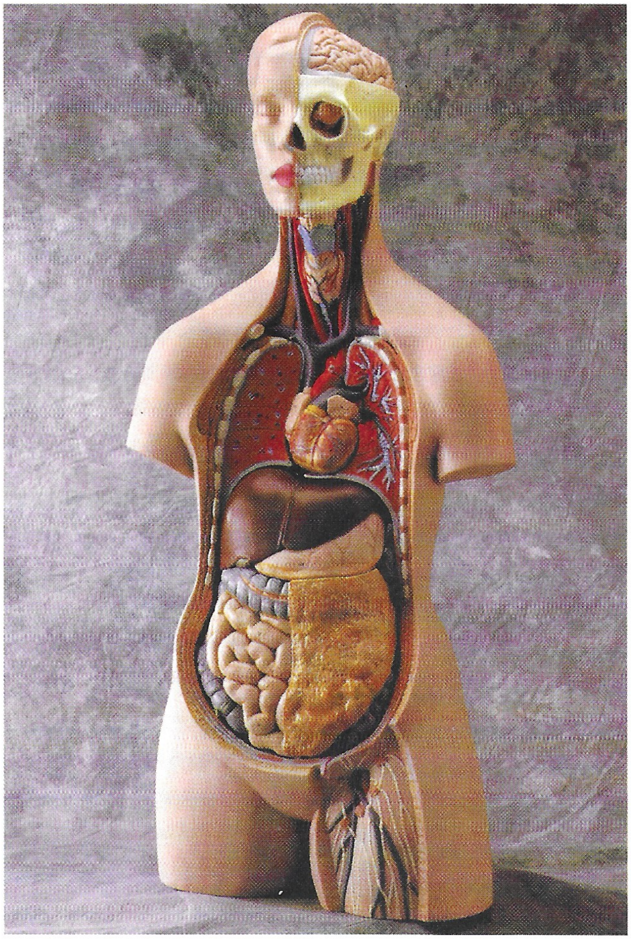

NOVA TRAN LIMITED
PRECISION SURFACE POLYMERS

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Parylene, a conformal polymer film, is being used increasingly in Europe to provide environmental and dielectric isolation. Application areas include electronic circuitry, sensors, and medical substrates. This article describes the variants of parylene and their characteristics, together with the process and applications of parylene coating.

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Parylene has become the generic name for polymers of the poly-para-xylylenes. It is a conformal polymer film that has been commercially available for more than 25 years, but its biomedical use has been limited to the United States (US), for no obvious reason. Only recently has it found increased application in Europe beyond its traditional use in pacemakers. The polymer provides environmental and dielectric isolation in a wide range of applications, including electronic circuits, sensors, and medical substrates. Recently, parylene was selected to preserve remains of Indian burial shrouds in Windover, Florida, USA.

Parylene conformal coatings are used in particular when a combination of protection challenges needs to be solved. They offer uniformity and completeness of coverage in addition to good physical, electrical, chemical, mechanical, and barrier properties. No solvents are released during the coating process and that process is thus not affected by volatile organic compound (VOC) restrictions, or the Montreal Protocol, and other environmental legislation.

Characteristics

Poly-para-xylylenes are thermoplastic polymers that are capable of polymerizing on surfaces from an active monomer gas, without the presence of a liquid. The three commercially available dimer types, Parylene N, C, and D, are shown in Figure 1. Recently, a dimer with eight fluorine atoms has been developed,[1] but its commercial use is reported to be initially restricted to a dielectric layer in chip manufacture and it will take three to five years before it becomes available for more general use.

The polymerization process has several useful features:

- It is effective in thin layers; 10–20 µm is sufficient to protect printed circuit assemblies and electronic components.
- The polymerization process takes place at room temperature and uses no solvents or additives. Outgassing is absent, there are no cure forces that could damage fragile components or coated substrates, and it is effectively stress-free. Parylene is applied from a gas and thus conforms to the topography of the underlying surface. Parylene deposition does not involve a liquid phase, and consequently pooling and bridging will not occur during application. Parylene films have essentially no undesirable physical or mechanical impact on underlying


Courtesy of Nova Tran Ltd.

surfaces, even with large changes in temperature. In contrast, liquid coatings form a dimensional structure that can exert unwanted mechanical force on underlying surfaces, both during the subsequent cure and as a result of thermal cycling.

- Encapsulation. Parylene is free of pinholes even in a thickness of less than 1 µm.
- Parylene is resistant to moisture, hydrocarbons, acids, blood, and many other media.

Parylene coatings can be applied in a single vacuum-coating operation in thicknesses from 0.025 to 75 µm and can be controlled accurately to ±10 per cent of the final thickness. This contrasts with liquid conformal coating where thickness can be controlled to a tolerance of approximately ±50 per cent and is greatly affected by operator skill, relative humidity, viscosity, temperature, and the method of application.

The coating process

Cleaning is an extremely important step in the coating process. This is needed to remove surface contaminants such as oils and ions. As a priming stage, a multimolecular layer of an organosilane is applied to pretreat the parts that have to be coated. This adhesion promoter allows the polymers to be applied to virtually any vacuum-stable material.

Areas that are to remain free of coverage must be masked. Small objects, such as magnets and plastic parts, can be coated in a tumbling process, but for most other applications, parts are usually fixed in a chamber during deposition. The parylene precursor, a granular white powder, is first vaporized at approximately 150°C and 1.0-mbar vacuum. The resultant dimer gas moves slowly towards the pyrolysis chamber and is heated to approximately 680°C at 0.5-mbar vacuum to yield the monomer diradical para-xylylene. This monomer is thermally stable, but kinetically unstable towards homopolymerization.

Next, the highly active monomer gas enters the deposition chamber at ambient temperature and 0.1-mbar vacuum. Here, it simultaneously condenses, adsorbs, and polymerizes on all surfaces to produce a high-molecular-weight polymer. The mean free path of monomer gas molecules is of the order of 0.1 cm and all exposed sides of encapsulated objects are impinged by the gaseous monomer, unlike line-of-sight processes such as vacuum metallization. In contrast to liquid coating, the parylene deposition process cannot entrap air, which can lead to corona problems. Figure 2 illustrates the deposition process.

The coating grows at ambient temperature from the substrate surface outward and the cure cycle occurs during deposition without the need for a subsequent heating step, hence no testing is required to confirm that the parylene has cured fully. The coating grows at approximately 0.2 µm per minute for parylene C and at a slower rate for parylene N. After the deposition cycle, objects are removed from fixtures, demasked, and inspected. The coating thickness is measured using a witness strip or a glass slide.

Quality control of the coating process focuses on a variety of parameters. It starts with chemical analysis of the dimer and monitoring of filtration and cleaning baths with ultraviolet spectroscopy. Temperature and pressure variables must be controlled during the deposition cycle. After coating, careful visual inspection of coated substrates, and adhesion and dielectric testing of coated samples is required.

Poly-para-xylylene variants

There are three common forms of the parylene polymer, parylene C,

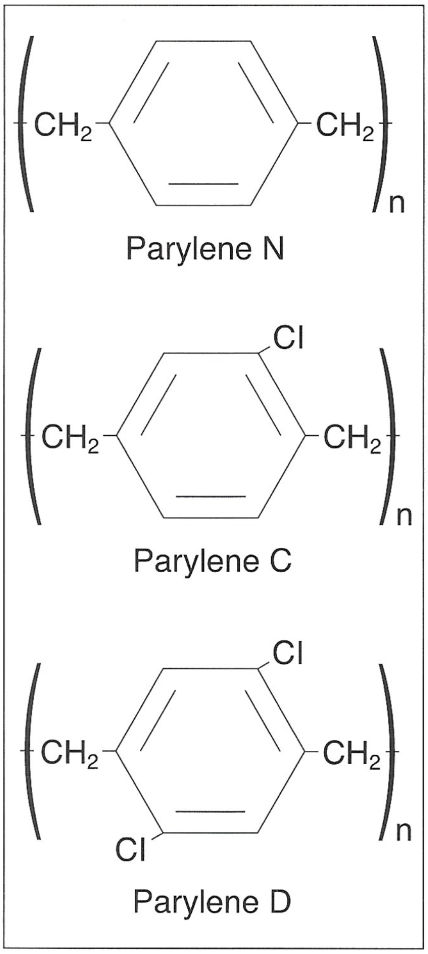

Figure 1: The chemical structures of parylene N, C, and D.

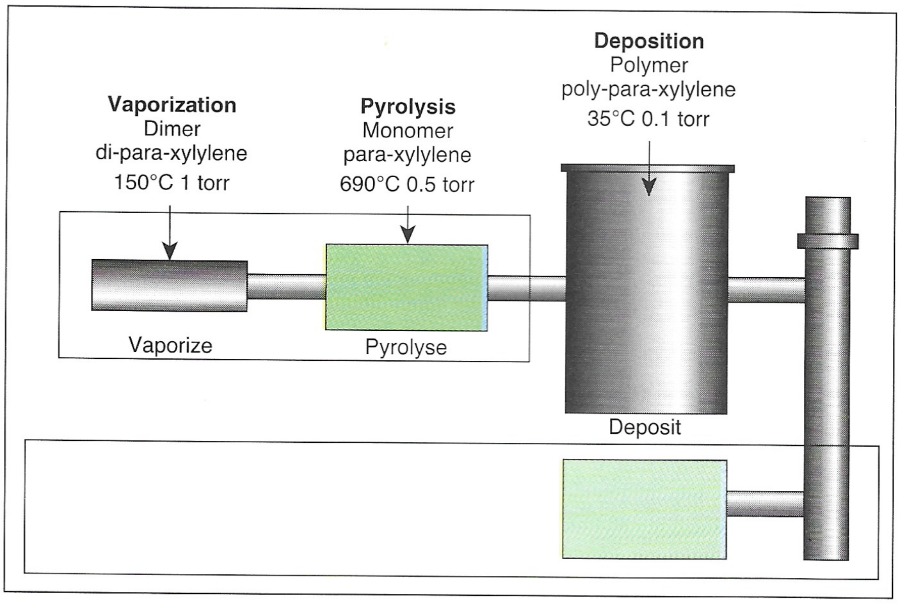

Figure 2: The parylene deposition process.

parylene N, and parylene D, each has unique properties that suit particular coating applications.

- Parylene C has one chlorine atom on the benzene ring, and modified electrical and physical properties. Low permeability to moisture and corrosive gases is most significant. The deposition rate is substantially faster than Parylene N, but its crevice penetration is consequently reduced.
- Parylene N has the greatest penetrating power, with the ability to coat deep recesses and blind holes because of its high molecular activity in the monomer state. It features a low dielectric constant that is independent of frequency. It also has a low dissipation factor and is ideal for high-frequency applications where the coating is in a direct radio-frequency field.
- Parylene D, with two chlorine atoms on the benzene ring, possesses superior physical and electrical properties at high temperatures and has the highest degree of thermal stability of the three variants.

These polymers compare favourably in critical performance categories with other coating materials. Table I reviews the properties of the different polymers. Static and dynamic coefficients of friction are in the range of 0.25 to 0.33, which makes the coating only slightly less lubricious, or slippery, than Teflon. Dry-film lubricity is a useful attribute in some conformal coating applications. An interesting application is that of the coating to silicone keypads and tubing to reduce wear and friction and increase the life of its printed lettering.

The bulk electrical properties of the parylenes make them good candidates for electrical and electronic coating applications. Dielectric-constant and hence dielectric-loss values are low, and are unaffected by absorption of moisture. High surface resistivity results from its hydrophobicity and low surface tension. High bulk resistivity values are attributed to the polymer's high purity, low moisture absorption, and freedom from trace ionic impurities.

Parylene coatings can be selectively removed from surfaces to permit repair. This is particularly useful for costly assemblies or devices. A variety of removal methods are available, and the process selected depends on the location and nature of the repair work. Methods include plasma etching, air abrasion, rotary abrasion, heat softening, and laser etching. Recoating is possible after cleaning has taken place.

Unlike conventional liquid conformal coatings, parylene's properties are uniquely useful for a combination of protection challenges. Electrical insulation and environmental isolation requirements can be combined on extremely delicate substrates. Low applied mass, pinhole-free barriers, and high dielectric strength per unit thickness are possible. Insulation can be consistently applied with minimal dimensional impact on the underlying substrate.

Medical coating applications

Long-term resistance of components against corrosive body fluids, electrolytes, proteins, enzymes, and lipids is required when foreign objects or materials come into direct and prolonged contact with human body tissues. A protective conformal coating on a biomedical surface may be needed to provide

- physical isolation from moisture, chemicals, and other substances
- immobilization of microscopic particles
- passivation of a surface
- electrical insulation
- reduced friction.

A crucial issue for producers of medical implants and surgical components is chemical inertness. Mechanical performance requirements may be troubled with biostability issues. Medical materials that are not intrinsically biostable must be protected by an isolating material. A process that does not degrade their functionality and preserves mechanical tolerances and critical performance characteristics is needed. Products such as bone pins, needles, medical probes, cochlear-implant catheters, cardiac pacemakers, and prosthetic hardware must be biostable to prevent substrate degradation and their medical efficacy being compromised.[2,3,4]

Some solvent-based liquid conformal coatings, such as silicones, acrylics, epoxies, and urethanes are available in high-percentage solid form. All these materials exhibit liquid properties, such as pool formation and menisci, that may make them unsuitable for some medical coating applications. In addition, liquid coatings may not meet toxicity and/or biocompatibility requirements, and cannot be applied with precise control.

It is often difficult to meet all the requirements of a medical coating because they are varied and precise and depend on the structure and purpose of the substrate. For example,

- cannulae require dielectric insulation and precise control over coating thickness
- medical seals demand lubricity and inertness with minimum change to dimension and durometer values
- guidewires and stylettes require lubricity and inertness and a coating that will not flake off
- catheters need a consistent coating thickness over widely varying geometry to safeguard lubricity and inertness
- stents require minimal impact on dimensions and physical or mechanical properties with a biocompatible surface
- blood-pressure transducers require precise coating thickness across their 1–2-mm dimensions.

Formed from a pure molecular precursor (a monomer gas), the transparent parylene film has no contaminating inclusions and the film forms an effective barrier against passage of contaminants from a coated substrate to the body or surrounding environment. A material with low thrombogenic properties and low potential to trigger an immune response is hence obtained.

The most prevalent parylene medical-coating applications are summarized by type in Table II. Usually, parylene N is selected in instances where lubricity and high crevice penetration are required. Parylene C is suitable for most coating applications because of its moisture-barrier properties and low gas permeability. With a dielectric strength of 5000–6000 V over a 25-µm thickness, parylene C is used for laproscopic devices to prevent uncontrolled arcing on the surgeons hands as well as the body tissue. Parylene coating of screws and nuts used with temporary bone pins and plates can prevent seizing, corrosion, and metal fragmentation. The hydrophobic and lubricious nature of parylene coatings can minimize residual fluid buildup on the inner and outer surfaces of needles and other medical components. It is capable of sealing metals that could otherwise trap and retain contamination. Parylene D is limited to industrial applications where mechanical toughness and thermal stability are of highest concern.

Documentation

Drug and device master files have been lodged with the US Food and Drug Administration (FDA) for

Table I: Parylene properties by polymer type.

Properties	Parylene N	Parylene C
Crevice penetration	Best	Good
Molecular activity	Highest	Good
Coating uniformity	Best	Good
Hardness	Least	Moderate
Physical toughness	Least	Moderate
Moisture resistance	Moderate	Best
Cost effectiveness	Moderate	Best
Dielectric strength	Best	Good
Dielectric constant	Lowest	Higher
Gas permeability	Good	Best
Chemical resistance	Good	Excellent
Elongation to break	Lower	Best
Thickness control	Good	Best
Masking complexity	Greatest	Moderate
Thermal stability	Moderate	Moderate
Coating speed	Lowest	Moderate
Dissipation factor	Lower	Higher
Lubricity (coeff. of friction)	Best	Good

Table II: Primary parylene coating functions for selected medical substrates.

Application	Parylene N	Parylene C
Catheter mandrels	Lubricity	–
Feeder tubes	Crevice penetration	–
Laproscopic devices	–	Dielectric strength
Catheters/stylettes	–	Lubricity
Cardiac assist devices	–	Barrier/dielectric
Orthopaedic hardware	–	Biocompat. barrier
Pressure sensors	–	Dielectric/barrier
Prosthetic components	–	Barrier/lubricity
Stents	–	Biocompat. barrier
Electronic circuits	–	Dielectric/barrier
Ultrasonic transducers	–	Biocompat. barrier
Bone-growth stimulators	–	Biocompat. barrier
Cochlear ear implants	–	Barrier dielectric
Brain probes	–	Biostability
Blood-handling components	–	Biostability
Needles	–	Biostability
Cannulae	–	Biostability
Bone pins	–	Biostability
Analytical lab trays	–	Biostability

parylene polymers and can be referenced in support of any applications to the Administration. Data on the body tissue and blood compatibility of parylene have been obtained in studies in several US-based institutes such as Battelle Memorial Institute, (University of North Carolina, Chapel Hill, North Carolina, USA); Johns Hopkins Hospital (Baltimore, Maryland, USA); University of California, (San Diego, California, USA); Carnegie Mellon University (Pittsburg, Pennsylvania, USA); and University of Michigan (Ann Arbor, Michigan, USA).[5,6]

In experiments by the US National Heart, Lung, and Blood Institute (Bethseda, Maryland, USA), inert parylene has been used to coat and anchor experimental fabrics used as linings for circulatory-assist devices.[7] In vitro tissue culture studies show that human cell types (such as Chang liver cells and Wish amnion cells), as well as bovine and ovine fibroplasts, readily proliferate on parylene-coated surfaces to produce thin, adherent layers of morphologically normal tissue.[8] Furthermore, deposition of a thin film of parylene over a toxic surface has been shown to render it atraumatic to cells.[9]

Successful in vivo cell-growth studies with parylene-coated objects have also been carried out in animals.[10] The minimal perturbance of cells growing in the vicinity of the coating can be ascribed to the high purity of the coating and its ability to impede impure species that may otherwise diffuse out of a substrate material. The corrosive biological environment does not affect parylene, which cannot be hydrolytically degraded.

Parylene C polymer has been evaluated in blood-compatibility tests at the University of North Carolina. In these in vitro tests, it was ranked thirteenth of 57 materials. Materials ranked significantly lower include polyhydroxyethyl methacrylate, tetrafluororethylene- and fluoroethylbenzene-fluorinated polymers, polydimethylsiloxane, and polyvinylpyrrolidone. Stypven and partial thromboplastin times were employed to measure thrombogenic activity. The release rates of haemoglobin and adenine nucleotide were also measured.[11]

Parylene-coated semiconductor devices (CMOS operational amplifiers) have been shown to be operable when completely immersed in saline solutions for more than 300 days with no change in input bias when compared to dry operation.[12]

Conclusion

It is apparent that the parylene family of polymers will continue to find increased use in critical biomedical applications for two main reasons:

- The inertness and purity of the end product makes the parylenes a logical choice from functional and safety aspects.
- The capability to make the polymers from a molecular state suggests that the parylenes will be able to solve the coating problems related to the increased complexity and shrinking geometry of devices.

References

1. J. Wary, R.A. Olsen, and W.F. Beach, "Vacuum-deposited Parylene AF4, a thermally stable low dielectric constant for interlayer use," Proc. of UMIC Conference 18–20 June 1996, p. 143.
2. A. Thornton, *Conformal Coatings for Pacemaker Applications,* NBS Spec Publ., pp. 400–450 and pp. 109–113 (1979).
3. D. Devanathan and R. Carr, "Polymeric Conformal Coatings for Implantable Electronic Devices," *IEEE Trans Biomed. Engin. BME* **27**(11), 671–675 (1980).
4. "Component Coatings for Use on Recognized Printed Wiring Boards," Underwriters Laboratory E94133(N), 7 July 1995. For use in equipment where the acceptability of the combination is determined by Underwriters Laboratories Inc., Northbrook, Illinois, USA, (held by SCS/Nova Tran).
5. F.G Yamagishi, "Investigation of Plasma Polymerized Films as Primers For Parylene C Coatings on Neural Prosthesis Materials," *Thin Solid Films* **202**, 39–50 (1991).
6. S.M. Christopher, R.C. Myers, and B. Ballantyne, "Acute Toxicological Evaluation of Di-chloro-di-p-xylylene. *J. Am. Coll. Toxicol.* **12**(6), 580 (1994).
7. Contract No. 1-HV-8-1388, National Heart, Lung and Blood institute, Division of Heart and Vascular Diseases, Bethseda, Maryland, USA.
8. F.R. Tittman and W.F. Beach, *Synthetic Biomedical Polymers: Concept and Applications,* M. Szycher and W.J. Robinson, Eds., (Technomic Publishing Co. Inc., Westport, Virginia, USA, 1980), pp. 117–132.
9. R.H. Kahn and W.E. Burkel, "Propagation of pseudo-intimal linings of vascular prostheses," *In Vitro* **8**(6), 451 (1973).
10. S.G. Eskin et al., "Growth of cultured calf aortic smooth muscle cells on cardiovascular prosthetic materials," *J. Biomed. Mater. Res.* **10**(1), 113–122 (1976).
11. H.K. Yasuda, M.O. Bumgarner, and R.G. Mason, "Improvement of Blood Compatibility by Discharge Polymerization," ACS ORPL prepar. **34**(1), 574–577 (1974).
12. M.F. Nichols and A.W. Hahn, "Functional Hermetic Encapsulation of Integrated Circuits," Proc. of 28th Rocky Mountain Bioengineering Symposium, pp. 331–338 (1991). ❑

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