



DEXTER

The Parylene Family

Overview

Summary

Composition, Formation and Advantageous Properties of the Parylene family of coatings

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Parylene C coatings are linear polymers and may be generally referred to as “poly-para-xylylene.” The polymer may contain chlorine, fluorine, or be halogen-free. In addition to Parylene C, there are three other members of the Parylene family, Parylene D, Parylene N, and Parylene HT. All four are based on a poly-para-xylylene backbone, shown in Figure 1 as “polymer” and they vary in their content of chlorine and fluorine. The polymeric Parylene C structure is based on a mono-chlorinated repeating unit.

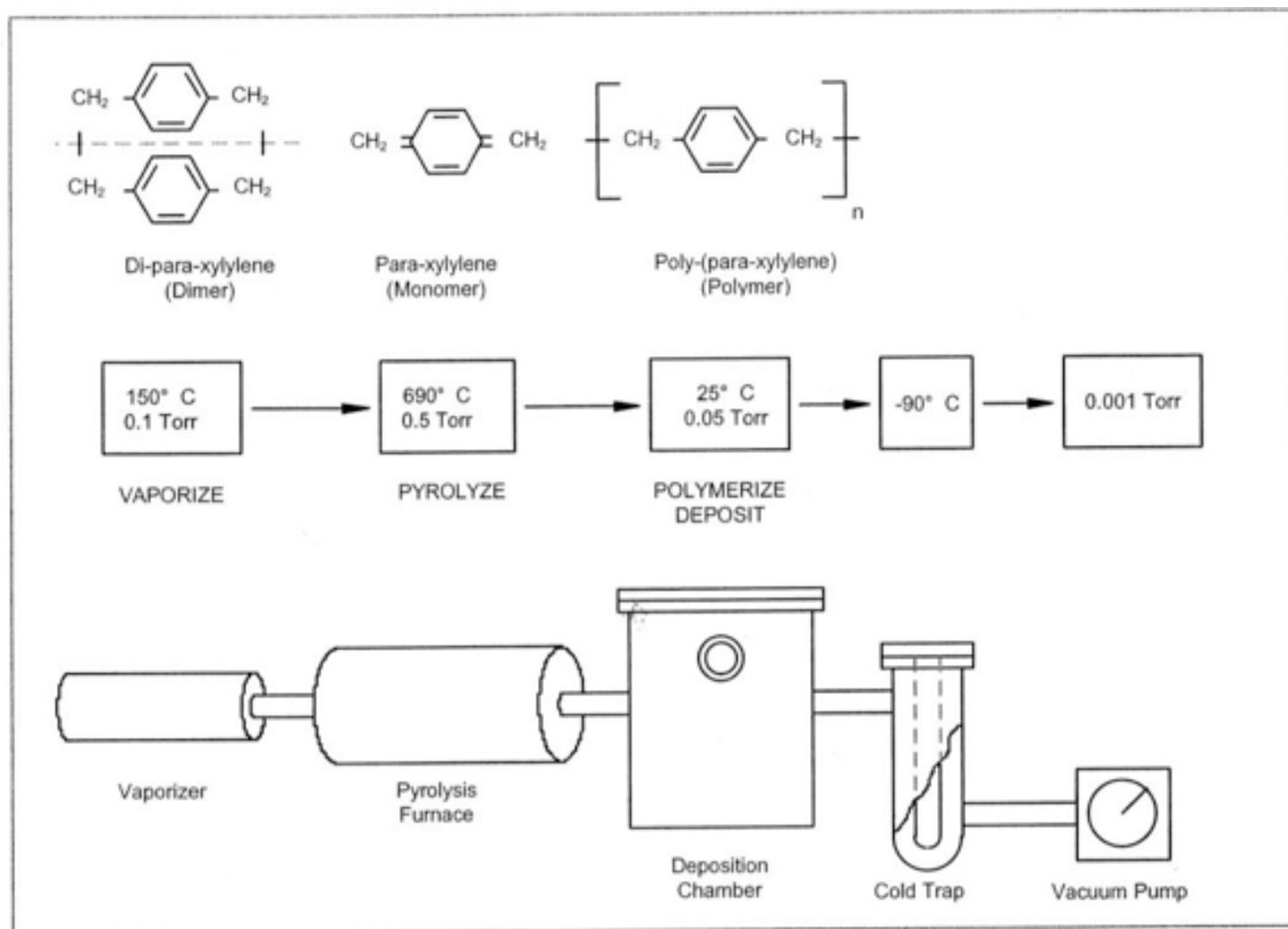
The raw material, from which the Parylene C is made, is typically 92% pure, and, therefore, a variety of side products are generated during the formation process, resulting in a range of polymer sizes, and some chemical structural variation within the polymer composition. For Parylene C, the feedstock raw material is named “DPX-C” and it contains principally 92% di-chlorinated molecules. In addition, about 8% of its contents are trichloro- and poly-chlorinated molecules. During the polymerization, one molecule of the di-chlorinated starting material is cleaved into two mono-chlorinated intermediate molecules, resulting in a repeating polymer unit, with one chlorine. However, because the DPX-C contains up to 8% of poly-chlorinated molecules, the finished linear polymer may contain up to 8% repeating units with more than one chlorine atom.

The finished polymer coating is continuous, non-porous, and does not contain residual liquids. Parylene C is clear and colorless. The composition of the DPX-C starting material has been steady for decades, so, the process reproducibility is excellent.

Parylene N does not contain any chlorine and is very crystalline. Parylene D contains two chlorine atoms per repeating unit. Parylene HT contains two fluorine atoms per repeating unit.

In the case of Parylene C, the deposited polymer is continuous, amorphous, clear and colorless. It can be deposited as thin as a few microns up to several mils.

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Figure 1. Schematic depiction of Parylene coating process.¹

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The process of applying a Parylene coating occurs when the Parylene intermediate molecule deposits onto the desired substrate directly from the gas phase. After depositing on the substrate, it spontaneously polymerizes to Parylene. **Figure 1** outlines the sequence as the material moves from vaporization chamber, to pyrolysis chamber and finally to deposition chamber, while transforming from dimer starting material to Parylene polymer coating. The deposition process takes place at ambient temperature, so, even delicate substrates can be safely coated without risk of thermal damage.

The substrate to be coated is placed into a deposition chamber at ambient temperature, and the vapor from an elevated temperature zone (pyrolysis chamber) diffuses into the deposition chamber, where it condenses onto the substrate, as well as the walls of the chamber and all other surfaces inside the chamber. The depositing gas phase is initially formed after the starting material evaporates (1200C) in a vaporization chamber and subsequently is pyrolyzed to the reactive intermediate. The thermolysis reaction (~650-7000C) of the starting material occurs in the pyrolysis chamber at low pressure ($P < 100$ millitorr). The pyrolysis chamber has the effect of thermally transforming the starting material into highly reactive monomers, which polymerize when they condense onto the substrate. The starting materials are volatile solids, and easily vaporize at 1200C and diffuse into the pyrolysis zone, where the pyrolysis occurs. Typically, the vacuum pump is protected from the vapors with a cold trap to prevent Parylene from entering it.

Even though the vapors are very hot (~7000C), the latent thermal energy transferred to the substrate is negligible relative to the overall thermal energy of even very small substrates, because the mass rate of deposition is very low. For this reason, substrates that are easily harmed by temperature excursions can be safely coated because the coating process does not elevate the temperature of the substrate. Typical material deposition rates are on the order of 5 microns/hour, so, the heat of the coating material is easily dissipated making the coating essentially a room temperature process, resulting in a process that does not thermally or mechanically load them.² Because the deposition is a gas-phase process that puts minimal thermal load on the substrate, Parylene is effective at coating virtually any non-volatile substrate, making it an extremely versatile option.

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In the case of Parylene C, a single feedstock material, trade-named "DPX-C," is used for its production, which is typically a one-step batch process. The production process for the raw materials has remained constant for decades, which translates into high consistency of properties over many years. DPX-C is a di-chlorinated dimeric starting material that undergoes pyrolysis to create a gas-phase monomer which polymerizes upon contact with the desired substrate surface. Figure 1 shows the raw material labelled "dimer." The deposition process occurs at reduced pressure, e.g. $P < 100$ millitorr, which is a very conveniently achievable pressure. The DPX-C (granular solid) is loaded into a vaporization chamber, which is heated moderately (~1200C). Upon heating and lowering pressure, the DPX-C dimer sublimates and diffuses into the pyrolysis chamber, (650-7000C) where it forms a monomer that polymerizes upon striking the substrate surface. No post-deposition processing is required. The coating is completed in the deposition chamber.

Fixturing is generally an important parameter for any coating process. If the requirement is to deposit the Parylene coating on 100% of the substrate surface area, then, a tumbling approach may be implemented in order to expose all surface area. Tumbling allows all surfaces of the substrate to be accessed by the gas phase deposition process. Depending on the implementation of the tumbling process, parts may abrade each other during the coating process. If the parts can be mounted in a stationary fixture, the coating thickness will be more even and less likely to be damaged during the process. Stationary fixtures may also be placed on moving stages that operate inside the coating chamber, to minimize shadowing and enhance the likelihood of uniform Parylene deposition. However, in most cases, fixturing will obstruct deposition at the point where the fixture touches the substrate, and requires careful management.

The decision to fixture or tumble depends on the coating thickness required and the performance requirements of the finished parts. Thicker coatings on smaller parts will endure tumbling better than thinner coatings, but, will likely show scratches or abrasions resulting from parts sliding over each other during tumbling. In some cases, the scratches or abrasions may be acceptable for the application.



The Parylene Family Formation Process

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Whether parts are fixtured or tumbled in the coating process, the coating is always deposited from the gas phase, so the coverage is diffusion-dependent, not line-of-sight dependent. Parylene is a true conformal coating. This dynamic of the coating process allows the coating material to reach all surfaces of substrates with complex or small form factors.

Conversely, in some applications, it may be desirable to limit the access of the Parylene to some parts of a substrate. Masking techniques may be applied to achieve selective deposition of the Parylene on a substrate. Masking may include mechanical overlays, photoimageable films, tape, etc. Any material that does not cause outgassing is a potentially effective mask material, and should be chosen based on the requirements of the application.



The Parylene Family Advantageous Properties

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Parylene coatings have been used commercially since the 1960s for medical, electronic, automotive, optical, industrial, and aerospace applications on many different substrates.^{3,4,5,6} Parylene is MIL-I-46058C, Type XY, and FDA approved. Parylene coatings derive their value from their virtual inertness to chemical attack, as well as their ability to coat complex three-dimensional form factors.⁷ They are not biodegradable, and therefore find application as coatings on implantable and dental devices. In electronic devices, the Parylene coatings increase mean time between failures, primarily as a barrier to water, significantly retarding electrolytic processes that result in shorts on electronic assemblies.

Parylene has been demonstrated in a "water proof cellular phone."⁸ Likewise, the moisture barrier also retards corrosive processes in electronic assemblies.⁹ For example, in relative terms, the Water Vapor Transport Rate (WVTR) of common epoxies, silicones and polyurethanes are all about 10x the water vapor transport rate of Parylene C.¹⁰ Typical units for WVTR are g-mm/m²-day. The high WVTR performance of the Parylene C provides the same performance as much thicker coatings of other materials. Parylene offers advantage relative to epoxy/silicone/polyurethane in weight sensitive applications such as aerospace due to its performance at much lower thicknesses.

Coatings are conformal and pin-hole free, and remain flexible when applied thin ($t < 75$ microns). In this case, "conformal" means that the coating thickness is uniform on all contours of the part. Because the Parylene coatings can be applied very thin, the weight added to protect the substrate is very small relative to spray or dip processes. Since no solvents are involved in the Parylene deposition process, volatile organic compound environmental restrictions do not apply and Parylene deposition does not violate the Montreal Protocol for ozone depletion.¹¹

The three-dimensional coating ability is enabled because during the coating process, a gas phase material is generated which diffuses in all directions and deposits and polymerizes wherever it collides with the substrate. Unlike many spray-coating processes, there is no "line of sight" limitation to the Parylene coating process. The gas phase process allows the Parylene coating to be deposited into extremely small openings, so that spaces that are difficult to reach with sprays or bath processes are accessible by the gas phase deposition.



The Parylene Family Advantageous Properties

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Even the smallest mechanical openings (e.g. micron-sized pinholes or slots) found on commercial parts, are many orders of magnitude larger than the dimension of a gas molecule, making passage of such molecules through these small openings possible in the coating process. The Parylene coating material is easily passed through even the tiniest of openings.

Of the four members of the Parylene family, Parylene C has the highest Young's Modulus, ($Y = 400,000$ psi) which means it is the most difficult to deform under mechanical load. By comparison, polycarbonate has $Y=377,000$ psi, and polyethylene has $Y=116,000$ psi, and epoxies are commonly $Y=430,000$.¹²

All four have very low moisture absorption, $<0.1\%$ after 24 hours. The Parylene forms a layered polymer structure, which, combined with the inherent hydrophobic nature of the Parylene, makes the coatings excellent barriers against aqueous ionic solutions.¹³ In addition, Parylene has a low dynamic coefficient of friction (~ 0.29), making a naturally lubricious surface. Consider the dynamic coefficient values of the following materials commonly used for their low friction properties for comparison: ice ~ 0.1 , polytetrafluoroethylene (TeflonR) ~ 0.04 , graphite ~ 0.1 , and nylon ~ 0.4 .¹⁴ At the level of 0.29, Parylene C is considered an excellent dry film lubricant.

Parylene C has a dielectric breakdown voltage rating of nearly 7000 volts/mil. This compares favorably with common printed circuit board dielectrics, like polyimide film or FR4 laminate. By comparison, polyimide dielectric breakdown voltage is typically rated at about 6300 volts/mil¹⁵, and FR4 is rated at 1600 volts/mil.¹⁶ Because Parylene coatings are truly conformal, they have excellent barrier properties, inhibiting passage of moisture and gases to the underlying substrate.

The inertness of Parylene enables the coating to pass biocompatibility tests, as well as perform well as a barrier in harsh conditions, including salt spray, elevated humidity, and caustic or acidic exposure.¹⁷ Parylene does not respond to organic solvents up to 1500C. Furthermore, the Parylene coatings are not damaged by sterilization techniques including autoclave, radiation and ethylene oxide treatment. Parylene is widely regarded as an excellent corrosion barrier.¹⁸

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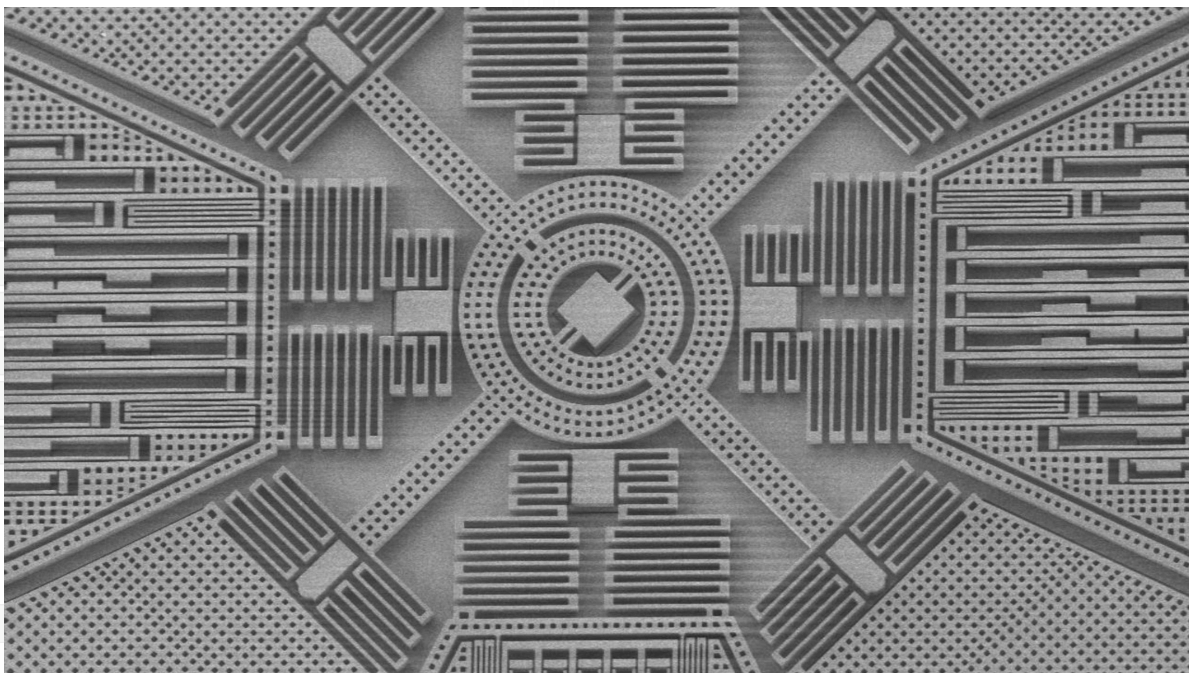
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Parylene N has excellent electronic properties, including low dissipation factor, high dielectric strength, and low dielectric constant. These properties are beneficial for applications involving printed circuit boards and signal transmission. The extra chlorine in Parylene D results in slightly higher operating temperature for Parylene D relative to Parylene C.

Parylene C is rated for 800°C continuous operating temperature, and Parylene D is rated for 1000°C continuous operating temperature. Parylene HT has a continuous operating temperature of 350°C.¹⁹ The relatively higher operating temperature of the fluorinated Parylene HT might be expected, given that many fluoro-carbon polymers have very high continuous operating temperatures, e.g. PTFE (Teflon®) which is rated for 260°C.²⁰

Since the 1990s, these properties have made Parylene an important component of a variety of MEMS devices such as microfluidic valves²¹, circular micromirrors and cantilever actuators²², beam seismometer²², peristaltic pumps²⁴, to name a few. In addition, NdFeB magnets have been coated with Parylene to fabricate energy harvesting devices²⁵, which convert environmental vibrations into electrical energy.



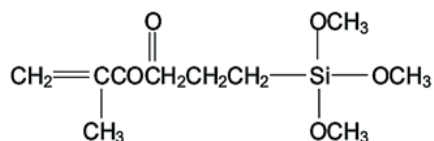
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When considering any coating, adhesion and durability are key performance properties. In the case of Parylene C, it has been well established that application of surface treatments prior to applying the Parylene coating process significantly enhances adhesion.²⁶ Common commercial method includes application of "SCS A-174," an alkoxy silane called gamma-methacryloxypropyltrimethoxysilane. SCS A-174 readily hydrolyzes in organic solution with water, and is applied directly to the surface at ambient temperature. The activated alkoxy silane bonds quickly to the substrate surface resulting in a new surface chemical composition that bonds well to the Parylene coating. The A-174 has been demonstrated on many metal and metal-hydroxide surfaces. The A-174 is effective with many surfaces, however, other kinds of alkoxy silanes may be chosen to optimize performance for a specific application. The gamma-methacryloxypropyltrimethoxysilane forms a chemical bond with the Parylene as shown in the drawing below, taken from Gao et. al.^{27 21}. The end group, (-CH₂=CH₂) is called a vinyl group. Generally speaking, vinyl groups are highly reactive with other vinyl groups. For example, CH₂=CH₂ is called ethylene and it reacts with itself to form well-known polyethylene by converting the carbon-carbon double bond to carbon-carbon single bonds and forming a long chain as seen in the chemical equation below.

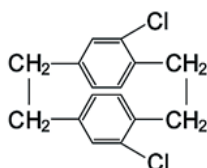


In this case, the gamma-methacryloxypropyltrimethoxysilane and the Parylene both have the reactive vinyl groups as part of their chemical structures. The vinyl groups easily react to form a chemical bond between the two molecules. The net effect of treating the surface with molecules like the A-174 is that the Parylene is now linked to the surface through a series of chemical bonds, which are significantly stronger than typical surface mechanical bonds or Van der Waals bonds. The chemical bond is the strongest mechanism of adhesion possible at a surface.

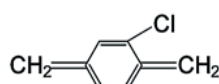
The adhesion and durability of the Parylene coating has been shown to depend upon shape, Parylene coating process parameters, and coating thickness.²⁸ Adhesion may be easily measured using pull- or peel-strength methods.



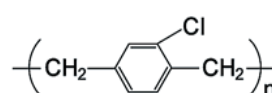
(a) A-174



Dimer Parylene-C

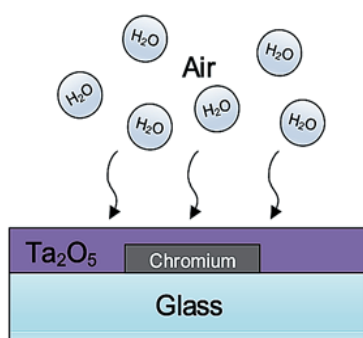


Monomer Parylene-C

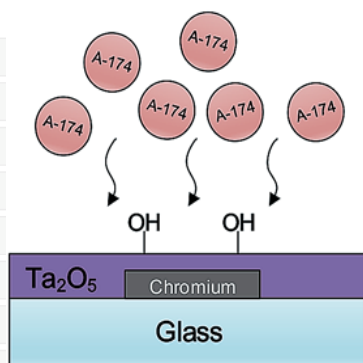


Polymer Parylene-C

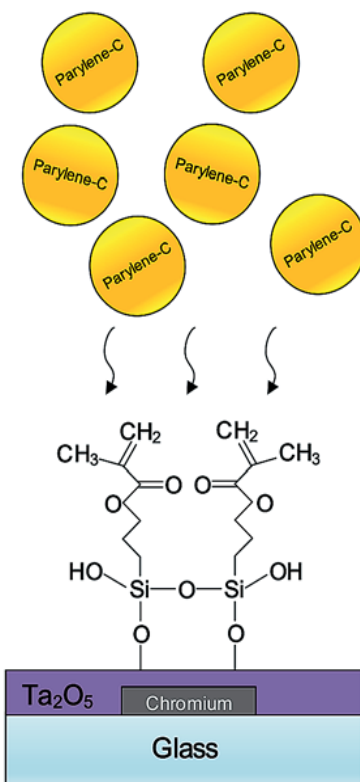
(b) Parylene-C



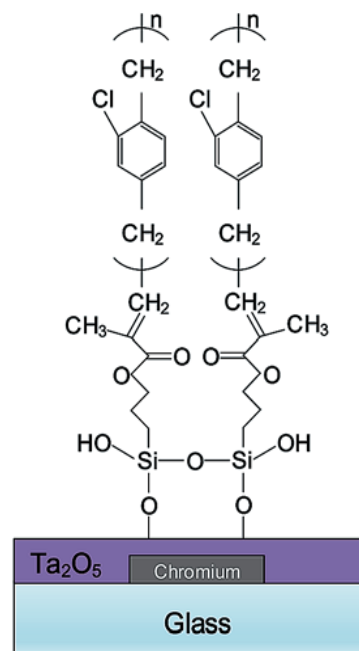
1. Absorb water in air



2. A-174 bonding



3. Parylene-C bonding



4. Final Structure

(c) Processing

Figure 2. Depiction of Parylene adhesion promotion by application of surface bonded gamma-methacryloxypropyltrimethoxysilane.

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