

Parylene Nanospheres, Nanotubes & Nanocoatings for Medical and Electronics Applications

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ABSTRACT

This paper describes Parylene hollow nano & mesospheres and nanotubes with their potential applications. Various types of spheres and particles with different functionality were also explored. The nanospheres are derived from the concept of hollow nanospheres and include non-tubular and non-fiber like surfaces, filled or coated internally and externally that may have different functions; attachment of functional groups that may be metal or non metals. Parylene nanotubes structures were prepared by vapor-phase Parylene coating of electrospun template polymer nanofibers such as polylactide, polyethylene oxide, or polyamide followed by selective removal of the core template fibers. Numerous variations of Parylene nanotubes are possible by loading of the template polymers with other materials or by sequential coating by other materials.

Keywords: Parylene, Medical, Electronics, Hollow-nanospheres, polymer-nanotubes

1. INTRODUCTION

Poly (p-xylylene)s, trade name Parylenes, are exceptional polymers in terms of preparation and properties. The chemical structure of Parylenes is composed by a strictly alternating sequence of phenylene and ethanediylene moieties (Fig. 1). The Parylenes have been classified as thermoplastic polymers that are formed on substrate surfaces using vacuum deposition polymerization. They are polycrystalline and linear in nature, and possess useful dielectric and barrier properties per unit thickness. They are also chemically inert and films are pinhole-free at film-thickness > 700 nm [2]. Parylenes are applied to substrates in a vacuum chamber and have certain similarities with vacuum metallizing. Unlike vacuum metallization, however, which is conducted at pressures of 10^{-5} torr or below, the Parylenes are formed at around 0.1 torr.

Vacuum deposition polymerization begins with the vaporization of a Parylene dimer. The dimer vapor is pyrolytically cleaved at temperatures of 600 to 750°C to form a reactive monomer vapor. The reactive monomer vapor is then transferred to a deposition chamber where the substrates are located. In the deposition chamber, the reactive monomer vapor spontaneously condenses onto the substrates to form a Parylene coating.

The property profile of Gorham-Parylenes can be described by high thermomechanical stability, excellent barrier properties, excellent hydrolytic stability, excellent solvent resistance, excellent insulation properties, excellent biocompatibility, very good transparency, very good oxidative stability, and nicely tailorable friction properties [3]. Parylenes have been utilized for a large variety of applications with different purposes such as protective coatings, insulative coatings, implant coatings and many others.

Parylenes have continuously been finding numerous applications in the protection and reliability enhancement of many nano and micro devices in the medical and electronic fields. Recently Parylenes have drawn considerable interests as a structural material for nano and micro technologies because of their exceptional properties such as stress-free truly conformal deposition, chemical inertness, low dielectric constant, biocompatibility and optical transparency. During the past several years, Parylene polymers have been considered an integral part of micro devices by many biomedical engineering researchers as devices are made of Parylene through MEMs technology.

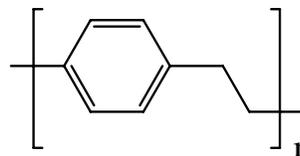


Figure 1: Chemical structure of Parylene

In advancing Parylenes applications further through the above work, Parylene hollow-nanospheres and nanotubes were successfully developed, which opened a variety of new applications, in the medical and electronics areas. Examples include, but not limited to controlled release of drug delivery systems, sensors, separation technology (gases, particle filtration, bacteria etc.) and electronics (piezoelectric shaping, nanoperistaltic pumps etc.).

Parylene nanotubes can be prepared by the TUFT-process (TUFT = Tubes by fiber templates). Very thin electrospun polymer template fibers were coated conformally from the vapor phase by Parylene followed by selective removal of the core template fibers (by pyrolysis or extraction) yielding corresponding Parylene nanotubes. Parylene nanotubes loaded by

different kinds of metal nanoparticles were also prepared by the TUFT process by usage of precursor-loaded template fibers.

This work demonstrate that Parylene nanostructured materials can be obtained, as non woven, from 10 nm to 125 microns in size with excellent electrical insulation, low dielectric constant (< 3), and excellent capability to withstand chemical, mechanical and electrical stresses. Several new commercial applications that will have significant impact in medical, electronics and others areas can now be developed.

2. NANOSPHERES, NANOTUBES & NANOCAOTINGS

The nano spheres and particles are made from polymeric materials and metals and are produced using vapor phase polymerization processes involving scaffold, foaming, spraying and various types of chemical reactions. To prepare the hollow spheres that include both closed and open structures, it is necessary to have scaffold materials that are to be removed after final structures of spheres are formed. Processes involved in manufacturing of nano and meso structured scaffold materials include colloidal precipitation, spray (liquid, plasma, laser ablation/shock/vaporization), nebulized (ultra sonic), electro-spray, electro-spinning and planar templates. There are two processes involved in electrospinning to prepare scaffold materials; one is through electrical modulation and other involving multi-axial spinning. A carbohydrate, particularly sugar was used to create initial scaffold materials for producing the nano & meso spheres. However, there are other materials as well that will be used including soluble polymers and compounds, natural products, radiation active compounds (both metallic and non-metallic), and ice, moisture, heat and light sensitive materials.

The process of making hollow spheres involves creating solid spheres using the techniques described above with the diameter range from 1 nm to 100 microns and then applying another layer of materials over the solid spheres using PVD, CVD, liquids, copolymerization and in combination there of. The scaffold materials are finally removed either by heat, radiation or through chemical reactions that could also include solubilization to produce hollow nano & meso spheres of 10 nm to 125 microns diameter range. Hollow spheres are then functionalized based on individual applications, which include ultracapacitors, active and passive thermal management systems, electromagnetic shielding materials, radiation dosimeter, timed drug released systems, catalysts, nanotextiles, various types of membranes, rheology modifier, air purification systems, drug therapy, and displays. Functionalization is achieved through co-polymerization, plasma attachment and grafting and gas phase/liquid attachment.

Scaffolding materials for nano & mesotubes, shown in Fig 2, were prepared to be rod-shaped by hot-melting sucrose. The sucrose granules were heated to a temperature in a range of about 185° to about 220° C until the granules were transformed into a liquid state. The hot-melted sugar was spun at a rate in a range of about 1,000 to about 3,000

rpm to create fine solid fiber structures. The spun solid fiber structures were allowed to cool to about room temperature. Scaffolding materials for nano & mesospheres as shown in Fig 3 were prepared by granulation of hot-melting sucrose into substantially spherical-shaped particles.

The formed scaffolding materials were then coated by vapor phase deposition polymerization (utilizing a PDS system available from Specialty Coating Systems, Indianapolis, Indiana) of a Parylene precursor, dimer (DPXC) to create a polymeric layer of Parylene. Vaporization was performed at a temperature of about 150° C at a pressure of about 1 torr. Pyrolyzation was performed at a temperature of about 680° C at a pressure of about 0.5 torr. Deposition was performed at a temperature of about 25° C with a chamber vacuum pressure of about 0.1 torr.

Following vapor phase coating, the samples were exposed to hot water at near boiling point, having a temperature in a range of about 80° to about 90° C. The hot water solvent was replaced about every twelve hours. After about four days, the mesoscaled structures were dried under vacuum, of about -25 psi, in an oven at a temperature of about 60° C.

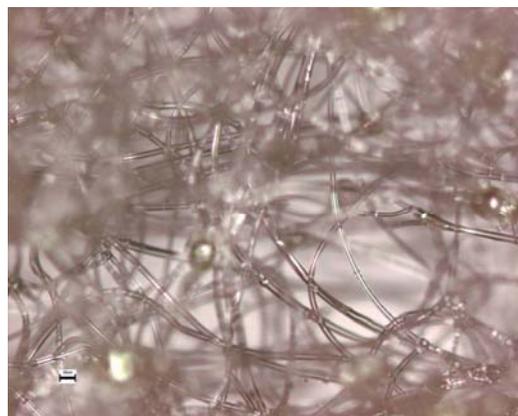


FIG. 2: Parylene mesoscale tube structures.

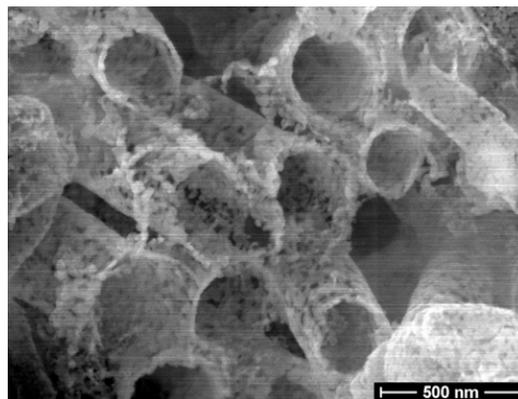


FIG. 2A: Parylene Nanotubes

Functionalization of nano & mesotube structures was carried out by deposition of metal on Parylene surface. Copper was deposited on the outer surface of the Parylene mesostubes by utilizing electroless copper

coating techniques to produce a copper layer with a thickness of about 0.2 to about 0.3 μm (Figure 4).

Parylene nanotubes were also prepared, using the TUFT-process, by coating of electrospun [4] polymer nanofibers according to the so-called TUFT-process [5]. According this straight-forward process Parylene nanotubes were obtained by vapor-phase Parylene coating of electrospun template polymer nanofibers such as polylactide (PLA), polyethylene oxide (PEO), or polyamide (PA) followed by selective removal of the core template fibers. Numerous variations of Parylene nanotubes are possible by loading of the template polymers with other materials or by sequential coating by other materials.

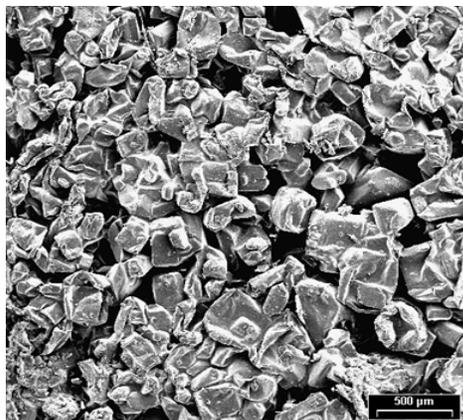


Figure 3: Parylene Hollow-spheres or structures

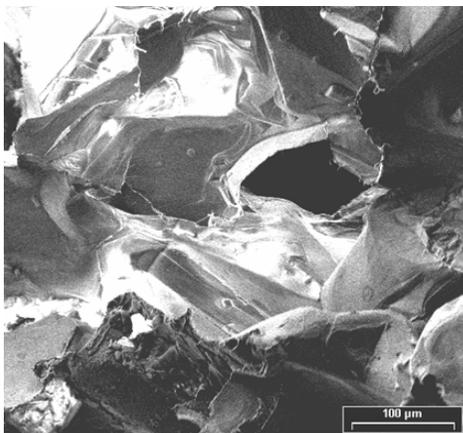


Figure 3A: Parylene hollow-shape structures

It is important in the context of the template materials for the preparation of tubes by coating of heat degradable template fibers that the melting point of Parylene is 420°C and that it shows a very good thermal stability. This makes Parylene a perfect material to withstand thermal degradation conditions to which the PLA template fibers have to be subjected. Coating of the PLA template fibers with Parylene by CVD yields Parylene/PLA core-shell fibers. Subsequent annealing of these fibers above 250°C in vacuum results in the degradation of the PLA-core, which leads to Parylene tubes (Figure 5). The length of the tubes is

$> 100 \mu\text{m}$. The inner tube diameter can be adjusted between 10-2000 nm depending on the diameter of the PLA template fibers. The wall thickness of the tubes is in the range of several 100 up to 1000 nm depending on the feed of [2.2] paracyclophane.

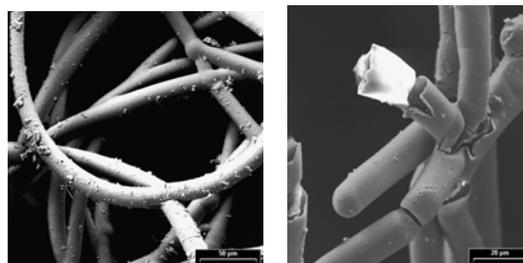


Figure 4: Copper coated Parylene mesotube structures

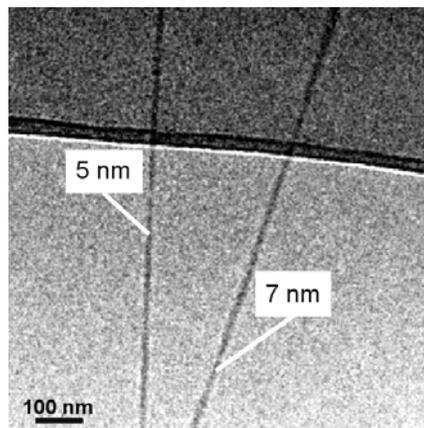


Figure 5: TEM of electrospun PLA nanofibers

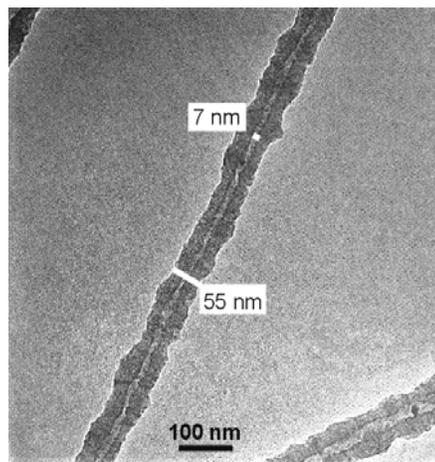


Figure 5A: TEM of Parylene nanotubes obtained using electrospun PLA nanofibers (Figure 4A) according to the TUFT-process [6].

Using template fibers with a porous surface, one is able to fabricate tubes displaying a structured inner surface (Fig. 6 & 6A). Such highly structured surfaces are of great interest for applications related to large surface/volume ratios.

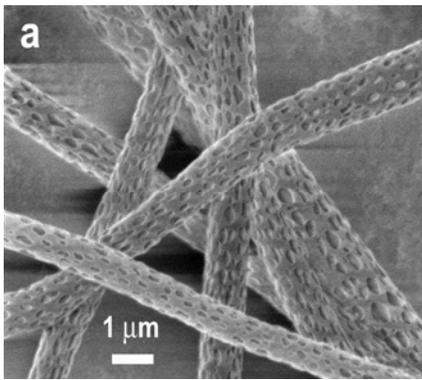


Figure 6: Scanning electron microscopy (SEM) micrograph of porous electrospun PLA nanofibers



Figure 6A: Scanning electron microscopy (SEM) micrograph of Parylene nanotubes obtained using electrospun PLA nanofibers (Figure 6) according to the TUFT-process.

Electrospinning of a solution of poly (L-lactide) (PLA) and metal compounds such as palladium diacetate (PdOAc), silver acetate or copper acetate in dichloromethane (e. g. 3 weight % each) resulted in PLA-metal acetate composite fibers. Coating of these composite nanofibers by Parylene and subsequent annealing resulted in the formation of Parylene tubes doped with corresponding metal nanoparticles (Figure 7) [6, 7].

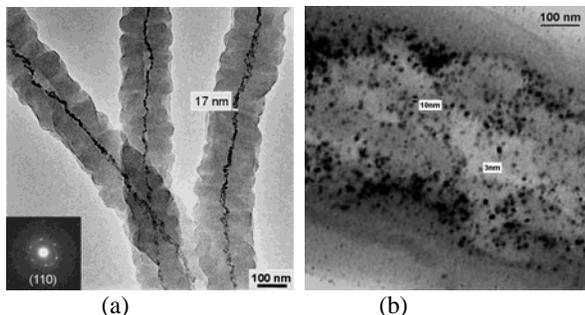


Figure 7: Transmission electron microscopy (TEM) image of Parylene-Pd composite tubes (a) and a high resolution TEM of Parylene-Pd composite tubes (b)

The sizes of these Pd-nanoparticles as well as their positions depend significantly on the processing parameters. For example, annealing of cutted PLA-PdOAc-Parylene

composite fibers for five hours in vacuum resulted in the formation of Parylene-Pd-composite nanotubes with Pd-nanoparticles also on the outside of the tubes (Figure. 8).

3. MEDICAL AND ELECTRONICS APPLICATIONS

Applications of nano & meso structures include, but not limited to:

- Separation Technology - gases, particle filtration, bacteria, viruses, ion exchangers in dialysis and desalination for water.

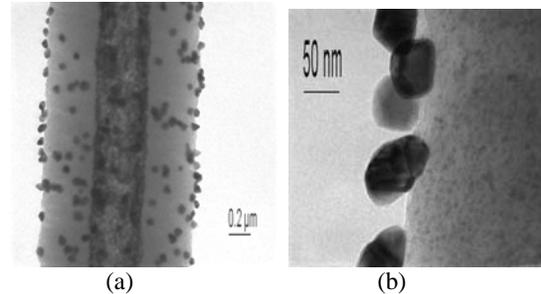


Figure 8: TEM of Parylene-Pd composite tubes (a) and high resolution TEM of Parylene-Pd composite tubes (b)

- Sensor Technology - solvent, gas, moisture and controlled release of drug delivery.
- Electronics, Optics and Energy Recovery - wire, cables or capacitors, micromachines (e.g. piezoelectric shaping, nanoperistaltic pumps or for the shaping of photo addressable polymers), microreactors, in chip technology as flexible devices, interlayer dielectrics.
- Fuel cell, batteries, and electro-chemical reactions.

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