

Parylene coatings on biological specimens

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Properties

ABSTRACT

Purpose: of this paper is show how parylene coatings can protect biological specimens.

Design/methodology/approach: Parylene technology is a process, in which a thin polymer film of a very uniform thickness is deposited onto the entire surface of any object placed in the reactor. The polymer, either poly-para-xylylene or one of its ring substituted derivatives, is characterized by excellent mechanical and dielectric [1] as well as barrier [2] properties, at the same time being transparent in the entire visible range of radiation. The process takes place at room temperature, which permits to use virtually any material as substrate.

Findings: The following work reports results of parylene application to the conservation of such natural objects, as *Pieris brassicae* butterflies, *Pygocentrus pirania* pirania fish and *Quercus L.* oak leaves. The number of specimens was always divided in two, of which one part was coated with 4 micrometers of Parylene C while the other remained uncoated as a reference sample. All the specimen were then placed on the surface of garden soil and kept there at constant temperature of 37°C and constant humidity of 75%, where their disintegration was followed by means of optical microscopy. After several months of staying under these conditions all the coated specimens were intact remaining their full integrity and colors. In contrast to that, the uncoated fish began to decompose after nine days, the uncoated butterflies after twenty one days and uncoated leaves after three months.

Practical implications: A very tight deposition, at room temperature of such a coating onto practically any object obviously focuses an attention of conservators of both natural and cultural human heritage [3-6]. Probably the most important advantage of this technology is its extraordinary penetration ability. When coating a fabric, for instance, this feature allows one to deposit parylene film onto single fibers, leaving open space in-between and simultaneously reinforcing the knots. This is the reason why parylene technology is most often used in the conservation of paper [5] and silk [6].

Originality/value: The originality of present investigation is in application of parylene coatings. The method should be interest for the conservation applications.

Keywords: Parylene coatings; Parylene process; Parylene technology; Conservation

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1. Introduction

Since the parylene technology constitutes a unique CVD process it appears appropriate to present its brief description together with the description of the starting compounds, the intermediate compound and the final polymeric product poly-p-xylylene.

1.1. The monomer

In contrast to typical polymerization processes, in the parylene technology the monomer and namely p-xylylene is not the process starting material, but an unstable intermediate compound instead. P-xylylene is stable only under such conditions when collisions between its molecules are infrequent, i.e. in the gas phase under reduced pressure [7] or in dilute solutions under low temperatures [8]. Upon condensation on surfaces it polymerizes rapidly with a formation of thin polymer film. These are a principal reason why other compounds, which produce p-xylylene as a result of the thermal decomposition are used as starting materials. Historically, the first such compound was p-xylene [7]. Since, however, the temperature of thermal cleavage of p-xylene was very high (up to 1150°C) and the process yield never exceeded 26% [9] other starting had to be found. It turned out that one of the byproducts of p-xylene based synthesis of the polymer, namely a cyclic dimer di-p-xylylene, was an excellent candidate for the job [10].

1.2. The dimer

Di-p-xylylene also known as [2] paracyclophane, is a crystalline compound, stable at room temperature, which easily sublimates at 100-150°C [11]. This compound is a precursor of the entire group of aromatic hydrocarbons, called cyclophanes, in which benzene rings are placed above each other and bridged with ethylene bonds [12]. In its molecule, presented in Figure 1, there is substantial amount of strain energy stored [13]. Due to the strain energy, cyclophanes possess a number of unique properties, among which an ease of thermal cleavage of methylene bonds has been utilized in the Parylene technology.

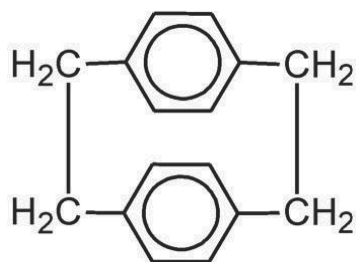


Fig. 1. Structural formula of di-p-xylylene

At temperatures 600-650°C thermal decomposition of di-p-xylylene results in the quantitative formation of monomer

[10]. The process has been utilized by Union Carbide Co., which on its basis formulated the Parylene technology [14].

1.3. The technology

The Parylene technology is a thin film technique belonging to the category of chemical vapor deposition (CVD). It differs from typical CVD processes, usually used to deposit inorganic oxides, carbides or nitrides, in its two principal aspects. First of all, its product is a linear ultrahigh molecular weight organic polymer. The second difference consists in a reversed thermal arrangement. While typical CVD processes are realized under cold gas hot substrate conditions, Parylene is deposited in a hot gas - cold substrate system.

Schematic representation of the parylene process is presented in Figure 2. The entire process is carried out under reduced pressures, with the substantial pressure gradient between both ends of the equipment. First, the dimer is sublimated at temperatures 150-200°C and its vapours are introduced into the pyrolysis furnace. In the furnace, a decomposition of the dimer with the quantitative formation of the monomer, p-xylylene, takes place. The monomer is then directed into the deposition chamber where it condenses on every surface available with the simultaneous formation of thin polymer films on each of these surfaces. Deposition of poly-p-xylylene usually takes place at room temperature. Due to extremely high penetration ability of monomer molecules the vacuum pumps of the system have to be protected against damage stemming from the possibility of parylene deposition on their inner surfaces. This is done an application of the cold trapping operation, usually performed with the liquid nitrogen cold trap.

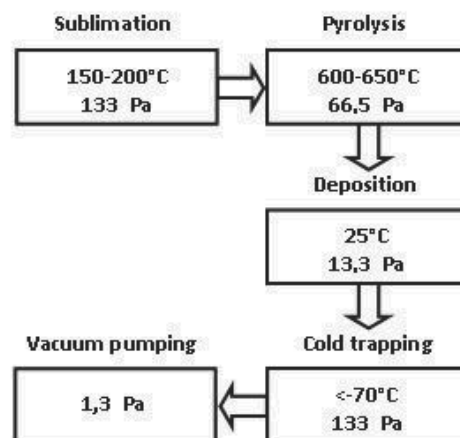


Fig. 2. Schematic diagram of parylene deposition

The Union Carbide Co. reserved the trade name of Parylene, which is used with respect to poly(p-xylylene) and its derivatives, obtained in the process described above. The company also introduced letters referring to the different ring substituents. Parylene N refers to an unsubstituted polymer, whereas the substituted products are marked in the following way, presented in Figure 3 below :

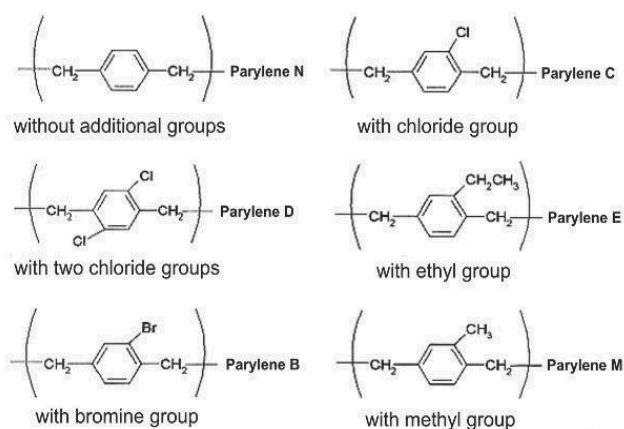


Fig. 3. Structural formulae of different types of parylene

1.4. The polymer

Poly(para-xylylene) and its derivatives obtained in the parylene process possess a number of unique properties. First of all, the deposition process itself has several advantages. Two major benefits of the process consist in the conformity (meaning even thickness on every surface including concave, convex ones as well as sharp edges) of the coating, and the extraordinary penetration ability, enabling coating of deep and very narrow crevasses. The physical properties of the parylene films are also extremely advantageous compared to other thin polymer film materials. These materials are characterized by high mechanical strength [1], large elongation at break, high dielectric strength and low dielectric dissipation factor [1], very low gas and ion

permeability [2], a nearly complete chemical inertness and clear optical transparency.

As far as the chemistry of the polymerization process is concerned, it is a radical chain propagation reaction with two radical centers at both ends of the growing chain (see Figure 4). The most important factor of the entire process is the fact that it is self-initiated by a monomer molecule. This makes the resulting polymer completely free of material other than the monomer, i.e. free from external initiator material. It is then the extreme purity of the polymer that is responsible for some of the extraordinary properties (such as low dissipation factor or chemical inertness). Parylene materials are also high crystalline polymers, which additionally contributes to their practical benefits.

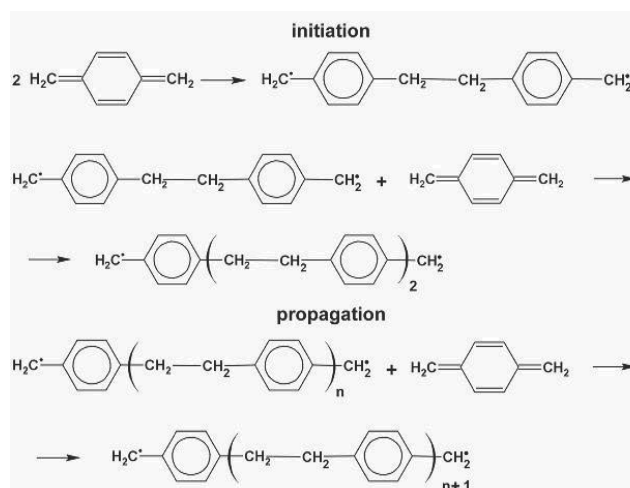


Fig. 4. Polymerization reaction of p-xylylene

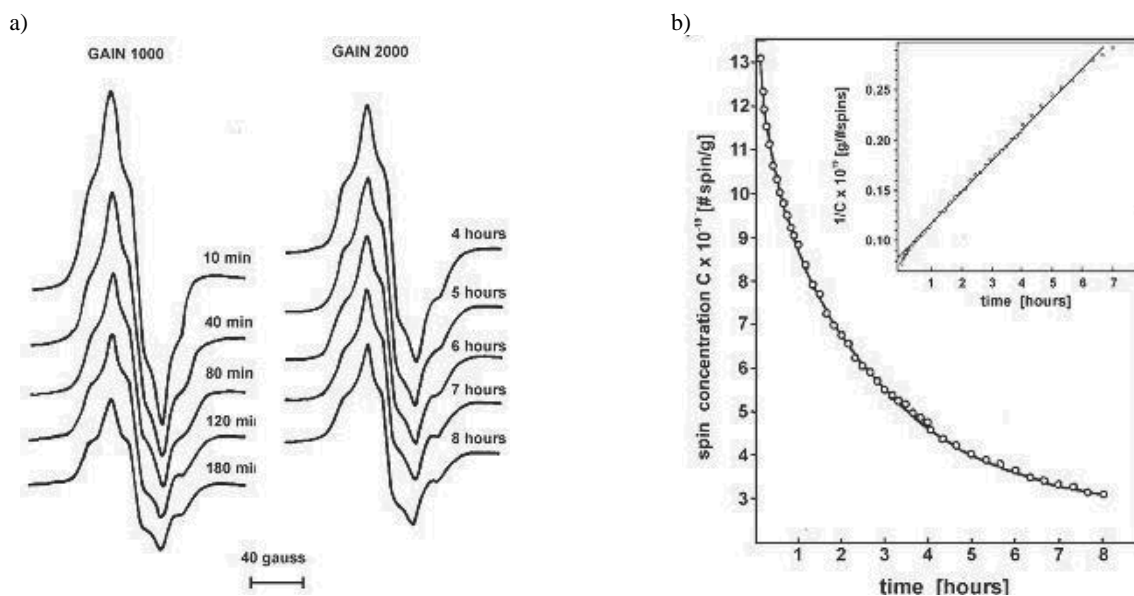


Fig. 5. A decay of EPR signal of poly(p-xylylene) under vacuum

The radical mechanism of the polymerization reaction has been confirmed by the results of the measurement of the decay of a number of unpaired electrons in the system, using the electron paramagnetic resonance (EPR) technique [15]. These results, presented in Figure 5, show a second order kinetic relationship to time (see the window in the Figure 5b) with respect to the spin concentration. The results presented in Figure 5 have been collected under vacuum conditions, which assured that the decay was exclusively due to the recombination of the end radical species. The unchanged character of the EPR signal, presented in Figure 5a, makes a direct proof of the correctness of this claim.

2. Sample preparation

Deposition of parylene coatings were carried out using a self-designed parylene equipment, presented in Figure 6.



Fig. 6. Parylene equipment in the laboratory of the Institute of Materials Science and Engineering



Fig. 7. *Pieris brassicae* butterfly

Samples used in testing of parylene application to the conservation were such natural objects, as *Pieris brassicae* butterflies (see Figure 7), *Pygocentrus piranya* pirania fish (see Figure 8) and *Quercus L.* oak leaves (see Figure 9). All the samples we coated with 4 μm thick coating of Parylene C.

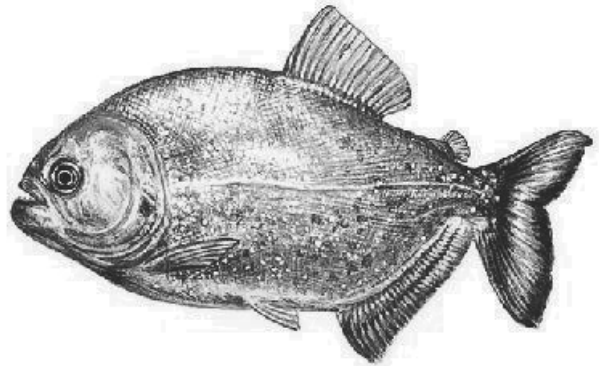


Fig. 8. *Pygocentrus piranya* pirania fish



Fig. 9. *Quercus L.* oak leaves



Fig. 10. Garden soil witch sample before the test

3. Testing

The number of specimens was always divided in two, of which one part was coated with Parylene C, while the other remained uncoated as a reference sample. All the specimen were then placed on the surface of garden soil (Figure 10) and kept there at constant temperature of 37°C and constant humidity of 75%, where their disintegration was then followed by means of both macroscopic inspection and optical microscopy. Since the

macroscopic results better illustrate differences between the coated and the reference samples, they are presented below to show the effects of the coating.

After several months of staying under the above mentioned conditions all the coated specimens were intact remaining their full integrity and colors. In contrast to that, the uncoated fish began to decompose after nine days (Figure 11), the uncoated butterflies after twenty one days (Figure 12) and uncoated leaves after three months (Figure 13).



Fig. 11. *Pygocentrus pirania* pirania fish uncoated and coated after nine days of remaining on garden soil

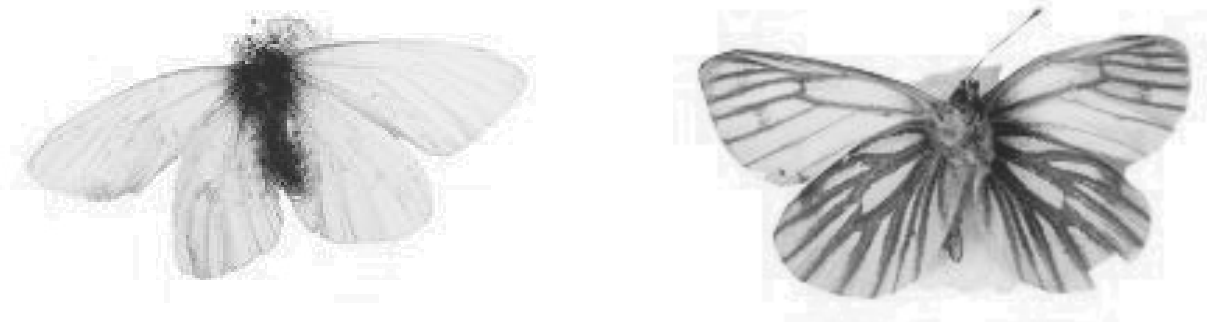


Fig. 12. *Pieris brassicae* butterflies uncoated and coated after twenty one days of remaining on garden soil

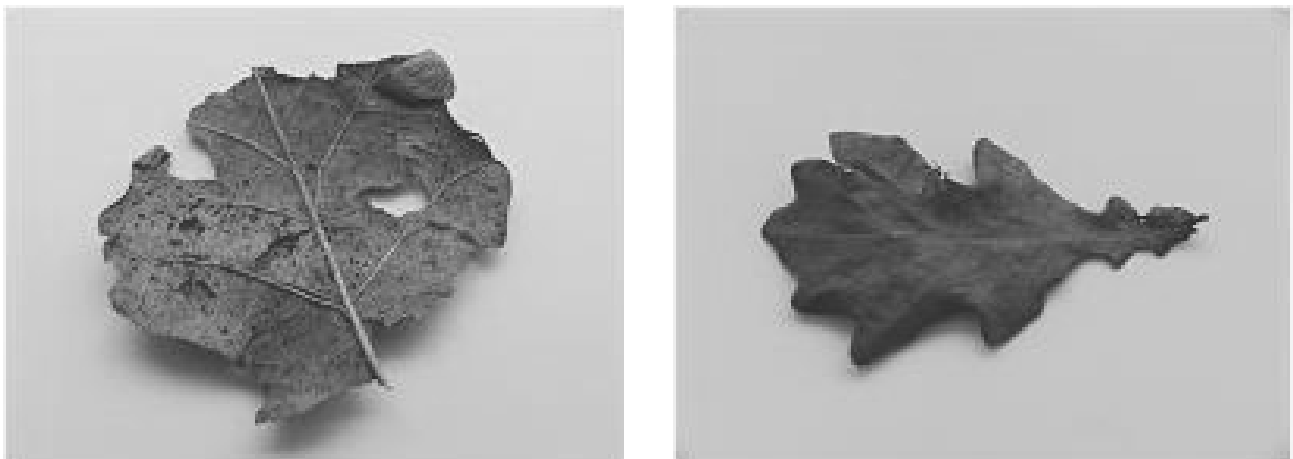


Fig. 13. *Quercus L.* oak leaves uncoated and coated after three months of remaining on garden soil

4. Conclusions

The results of the test show that parylene C layer provides a very good protection to natural objects. Due to its conformity and high penetration ability, parylene process covers all the morphological details of the objects, even those of microscopic dimensions, with a protective layer of even or nearly even thickness. The barrier properties of the coatings keep to minimum the growth of fungus and other microorganisms. High mechanical strength of these coatings provides full integrity as well as resistance to modest mechanical damage forces. Finally, good optical properties of the parylene layer and its high transparency in particular, combined with the relatively low thickness assure an excellent appearance of the objects, comparable to that of fresh ones.

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