PLASMA-POLYMERIZED TETRAFLUOROETHYLENE AS SEMIPERMEABLE
COATING FILM ON SOLID SUBSTRATE

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ABSTRACT

Thin film of plasma-polymerized tetrafluoroethylene (TFE) was coated on a variety of solid substrates. Uniform coating layer could be deposited on powder materials put in a vibrating vessel, while some permeation of relatively small molecules through the TFE polymer film was observed. The micropores distributed in the polymer matrix were found to be 20-40 Å in diameter. The TFE polymer film functioned as a control barrier to mass transfer at the surface of solid materials.

1. INTRODUCTION

Plasma-coating of solid materials under glow discharge of fluorocarbon monomer is an effective means for suppression of their hygroscopic nature and it was successfully applied to moisture-resistant alkali halide optical crystals (1), preservation of microstructure of ash patterns of biological specimens (2, 3), and a nonhygroscopic surface treatment of calcium pantothenate (4). However, it has been revealed that the plasma-coated materials still retained a low level of moisture uptake for fairly long time, thus suggesting a suppressed rate of moisture permeation through the polymer film. Experiments have been therefore carried out to evidence the mass transfer of small molecules through the polymer film employing gas chromatographic technique incorporated with plasma-coated adsorbents (5) and measurement of the rate of dissolution of plasma-coated pharmaceuticals (6). Micropores distributed in the polymer matrix were also an interesting subject in this research.

2. EXPERIMENTAL

The plasma-coating apparatus was consisted of a glass bell jar (H 30 cm, D 25 cm) and a metal base plate in which a pair of parallel electrodes was installed horizontally as illustrated in Fig. 1. TFE monomer gas was supplied at a flow rate of 3 ml/min(STP) into the drum-shaped upper electrode through a Teflon tube and the gas was diffused downward from a number of nozzles to the lower electrode. A rotary pump of 300 l/min capacity was used to hold the pressure in the chamber at 0.3
Torr. Plasma excitation of the monomer was sustained by relatively low RF power of 5 W (13.56 MHz). Powder materials were coated in a plastic vessel having upward convex bottom which was vibrated by a lateral motion using a 60 Hz electric vibrator. Circulation of the powder was monitored by a colored particle which appeared and disappeared several times within a minute. Film thickness grown on the solid substrates was also monitored by a glass slide which was closely placed by the specimens and plasma-coated at the same condition. Optical interferometry of the film thickness on the glass slide was employed as a measure of the film thickness grown on the substrate tested. Dissolution test of the pharmaceuticals was carried out following the rotary basket method (Japanese Pharmacopoeia) and the rate of dissolution was determined by the UV light absorption of the aqueous phase.

3. RESULTS

Hydrophobic coating of solid materials was first applied in our laboratory to ashed residues of biological specimens which were very hygroscopic in ambient air. In fact, thin sections of animal tissue were ashed on a glass slide in an oxygen plasma and the residual inorganic microstructures were to be microscopically observed. However, the ashed residues contained a large quantity of free phosphoric acid which rapidly absorbed moisture when the glass slide was taken out of the plasma chamber, a short time later forming droplets throughout the area of the ash patterns.

The thin film of plasma-polymerized TFE was therefore subsequently deposited on the shed specimens and the film effectively eliminated the hygroscopicity. The polymer film also showed a good optical transparency throughout the visible light region. Since the polymer film was deposited very gently and uniformly onto the ashed specimens, the fine microstructure of the ash patterns was well preserved on the glass slide on which microscopic investigation could be carried out in detail. It has been found, however, a low level of moisture uptake was still detected even though a thick polymer film was deposited as illustrated in Fig. 2.

A similar attempt was made to suppress the hygroscopicity of calcium pantothenate which is often dispensed in drug prepara-
Fig. 2. Time courses of moisture uptake by ashed lung specimens coated by varying polymer film thickness and exposed in ambient air. Temperature, 25°C; Relative humidity, 54%.

While an effective moisture-proof property was attained with the plasma coating, a low level of moisture uptake was again observed with thick polymer film. The slow permeation of moisture through the plasma-polymerized TFE film suggested semipermeable property for materials having relatively small molecular size.

The gas chromatographic technique was applied to investigate the gas permeation through the TFE polymer. Column packing agents such as silica gel and activated charcoal (50-100 mesh) were plasma-coated and the adsorption chromatography was carried out. The result showed that shorter retention time of chromatogram peaks was generally obtained with thicker coating layer, but chromatographic separation was well preserved suggesting the gas permeation through the polymer film coated on the adsorbents (Fig. 3).

The results raised a question whether the plasma polymer covered all around the surface of individual particle. Porapak Q (polystyrene spherical gel, 80-100 mesh) was therefore plasma-coated and dispersed in methyl methacrylate monomer which was subsequently polymerized by the conventional way. The polymer block was thin sectioned to investigate the profile of plasma-coated layer. A scanning electron micrograph showed highly uniform coating layer around the particle as illustrated in Fig. 4.

**Fig. 3** Gas chromatograms of solvent mixture by using TFE plasma-coated silica gel with varying film thickness

Composition of solvent mixture: 1:1:1 in volume ratio; Injection volume: 0.3 μl; Column condition: Same as Fig. 2; Thickness: (a) 0.3 μm (deposition: 30 min), (b) 1.2 μm (deposition: 2 h), (c) 2.4 μm (deposition: 4 h); Peaks: 1: Carbon tetrachloride, 2: Benzene, 3: Methanol
A further attempt was made to evidence the micropores in the polymer matrix through which relatively small molecules might permeate. The TFE polymer film was thus deposited on porous membrane filters changing the polymer film thickness. High pressure of water was then applied onto the plasma-coated membrane filters (Millipore VS) and the decreasing rate of water flux was observed with thicker polymer film. It was of interest to know that the water flux continued with the thick polymer film by which the surface of the membrane filter was entirely covered with the plasma polymer. Successive experiment was carried out to roughly estimate the size of the micropores distributed in the polymer matrix by ultrafiltration of organic solutes having different molecular sizes (7). Aqueous solutions of lysozyme chloride (40 Å), cyanocobalamine (20 Å), and nicotinic acid (5 Å) were ultrafiltrated and the permeability of the solutes was determined by the absorption spectrometry of the filtrate. Cyanocobalamine and nicotinic acid freely passed with aqueous medium, while lysozyme chloride was perfectly excluded by the plasma polymer as shown in Fig. 5. It seemed therefore that the micropores distributed in the polymer matrix would have average diameter of 20-40 Å.

The semipermeable property of plasma-polymerized TFE was applied to control the rate of dissolution of pharmaceuticals. The work was considered as an approach to slow release of pharmaceuticals from solid drugs. Powders of lysozyme chloride and nicotinic acid were again chosen as model pharmaceuticals having large and small molecular sizes. It has been observed that the rate of dissolution of the pharmaceuticals from the solid drugs such as tablets and granules was fairly well controlled by changing the film thickness of the plasma polymer as shown in Fig. 6 and Fig. 7. It has been also supposed that the lysozyme chloride having large molecular size was not permeable through the thick
coating film but it was released through cracks produced by expansion of the pharmaceutical after absorption of moisture through the coating film, while the nicotinic acid having relatively small molecular size was released not only through the cracks but also through the coating film by permeation.

REFERENCES