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ADVANCES IN BASIC AND APPLIED ASPECTS OF MICROWAVE PLASMA POLYMERIZATION.

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ABSTRACT

Variation of certain fabrication parameters during microwave plasma polymerization of organosilicones allows one to produce deposits with controlled characteristics. This paper describes the effect of substrate temperature, T_s, on various properties related to potential applications.

1. INTRODUCTION

Plasma polymerization of thin solid films using a microwave processe has became on important technique for preparing uniform, pinhole-free, strongly adhering coatings for a variety of applications. This paper is intended to illustrate that controllable changes in fabrication parameters can lead to large changes in the structure and chemical composition of the resultant polymer film. These changes, in turn, give rise to dramatic changes in several physical properties.

In particular, organosilicone monomers hexamethyldisiloxane (HMDSO) and hexamethyldisilazane (HMDSN) are used to demonstrate that variation of the substrate temperature during plasma polymerization, T_s, can lead to systematic changes in polymer morphology, density, refractive index, moisture permeability, adhesion, etc. As a particular application example, effects of these structural changes on anticorrosion barrier properties are discussed.

2. EXPERIMENTAL

A large volume microwave plasma apparatus (LMP) operating at 2.45 GHz has been described in detail previously (1). The microwave power ($0 \leqslant P \leqslant 2.5$ kW) is fed into the plasma by means of one or several slow wave applicators. The reactor chamber, made of fused silica, is equipped with a heated ($25^o \leqslant T_s \leqslant 800^oC$) substrate holder as shown in fig. 1. A cylindrical reactor vessel is "sandwiched" between two microwave applicators; and the substrate holder is rotated around the axis at about 10 rpm in order to assure uniformity of the deposit. Apart from the power density in the plasma P, and the substrate temperature T_s, other important deposition variables are the gas flow rate and pressure. The monomer vapor was introduced continuously through a micrometric needle valve while gaseous reaction products are removed by a two-stage mechanical pump. Pressure is controlled by a throttling valve and measured using a capacitive manometer (MKS Baratron, type 310); generally a pressure close to 0.2 Torr is used.

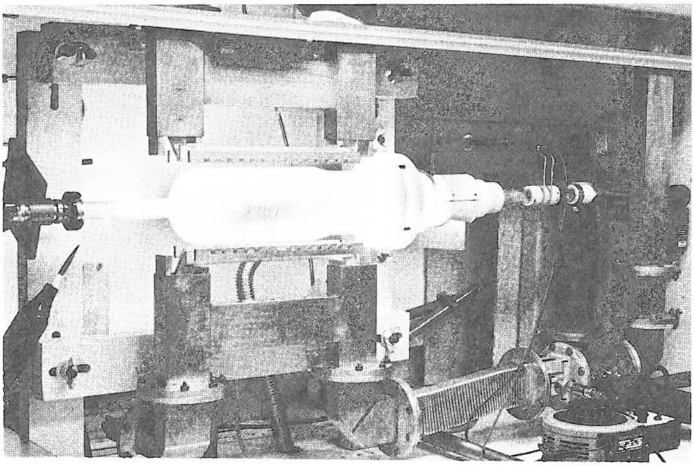

Fig. 1. Microwave deposition system

3. RESULTS AND DISCUSSION

Fabrication conditions have a very significant effect on film morphology, as illustrated by a series of scanning electron micrographs, figures 2 (a) - (c). The plasma polymerized film was deposited on glass at various substrate temperatures T_s, while other fabrication parameters were kept constant.

Fig. 2 (a) shows the edge of a sample deposited at $T_s = 25^{\circ}C$. The film consists of an agglomerate of spheroidal particles. This type of morphology is quite common for plasma polymer films (2, 3). However, as can be seen from figs 2 (b) and (c), significant morphological changes result from higher substrate temperatures during deposition. In addition, the interfacial adhesion changes dramatically as T_s is raised: the low temperature film, fig. 2 (a), actually peeled off the glass substrate after some time, whereas the films made at higher T_s adhered tenaciously. We feel that this change in adhesion is due to a combination of various effects such as relaxation of internal stresses by annealing and enhanced chemical bonding at the interface. Figure 2 (b) shows a substantially reduced number of spheroidal particles; still higher T_s almost completely eliminates the occurence of particles, as seen in 2 (c).

Figure 3 is a composite plot, showing the variation of several important physico-chemical characteristics of PPHMDSO and PPHMDSN films deposited at different T_s. From top to bottom are shown the chemical composition of PPHMDSN, the optical refractive index, the density (for both types of films), and the moisture permeation coefficient (for PPHMDSO).

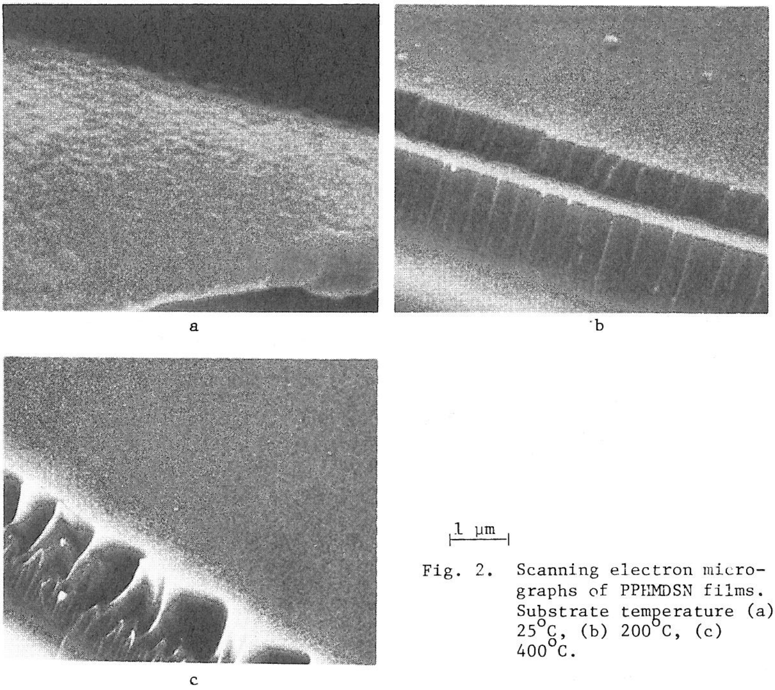

Fig. 2. Scanning electron micrographs of PPHMDSN films. Substrate temperature (a) 25°C, (b) 200°C, (c) 400°C.

The high density (1.7 to $\sim$ 1.9 g cm^{-3}) of these films has been interpreted (4) as being due to their very high crosslink density, and their lower "organic content" compared to those of conventional organosilicone polymers. The latter characteristic, which is further enhanced by raising T_s, is clearly shown in the top (composition) portion of figure 3: whereas films deposited at T_s = 25°C do not differ very substantially from the monomer in the relative concentrations of constituent elements, films produced at high T_s are almost carbon-free. In other words, the initially "organic" films become increasingly "inorganic" as T_s is raised. It should be pointed out that the analytical technique used here did not permit us to measure the oxygen content in the PPHMDSN films. From our own (ESCA and AES) studies and published results (5), it is known that several atomic % oxygen are also present in these films.

Not surprisingly, these changes in density and chemical composition result in systematic changes of other physical and chemical characteristics, two of which are illustrated in figure 3: the optical refractive index is seen to rise in a similar manner as the density. In a recent paper (6) we have analysed the observed behaviour in terms of the Lorenz-Lorentz relation.

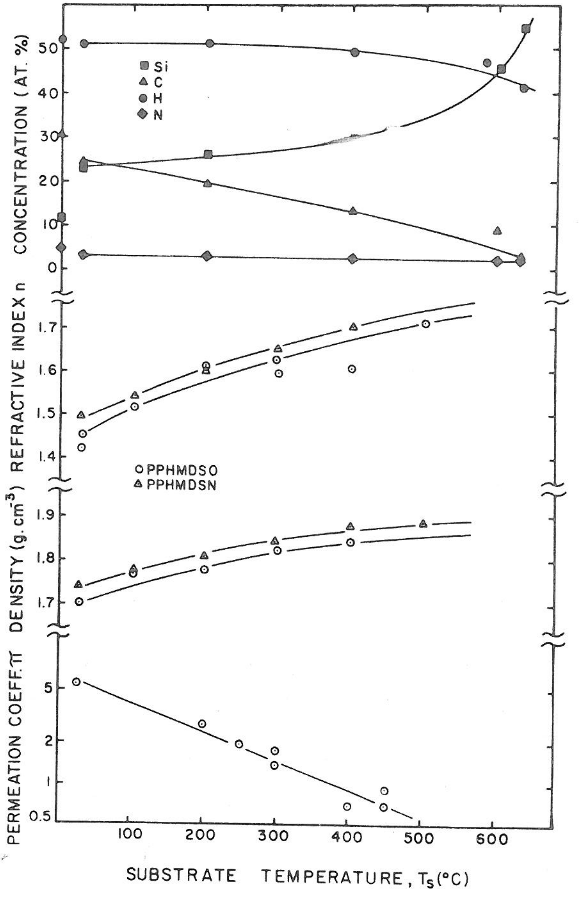

Fig. 3. Variation of chemical composition (PPHMDSN), optical refractive index, density, and moisture permeation coefficient as functions of substrate temperature.

The moisture permeation coefficient, π, (in units of 10^{-8} std cc·cm/cm^2 sec·cm Hg) is seen to decrease almost ten-fold between $T_s = 25^oC$ and 500^oC. The very low π values of PPHMDSO, up to 10^2 x lower than for "conventional" polymers, are felt to be due to their higher density and intense crosslinking; the additional drop in π with rising T_s is related to the reduced ability of films to swell as the structure becomes more "inorganic". This is discussed in detail elsewhere (7).

Clearly, the numerous attractive properties of organosilicone plasma polymers suggest a strong potential for practical applications. We wish to discuss one such application among those we have studied, namely anti-corrosion coatings.

On the basis of the morphological and moisture-permeation data presented above, one would expect PPHMDSO or PPHMDSN films prepared at elevated T_s to give better corrosion protection than films prepared at lower T_s. In order to test this, the following experiments were carried out: a series of glass microscope slides were coated with ∿ 5000 Å thick layers of Al by evaporation under vacuum. The aluminized slides were then overcoated with a constant thickness (∿ 0.1 μm) of PPHMDSO prepared at T_s ranging from 100^oC to ∿ 300^oC. Plasma-coated and control (uncoated) samples were placed in a bath of corrosive household cleaning fluid and periodically removed for visual inspection. Where the fluid contacted the metal directly, for example at a pinhole or other defect in the overcoat, the metal corroded away, leaving a transparent "window" in the structure. Figure 4 shows a collage of such samples: T_s increases from left to right, while immersion time in the corrosive bath increases from top to bottom.

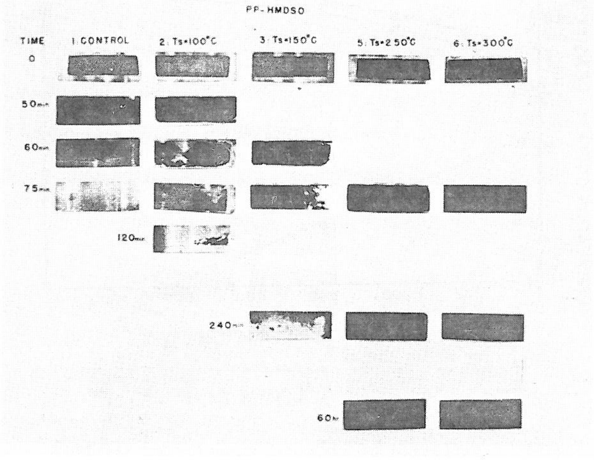

Fig. 4. Corrosive attack by household cleaning fluid on overcoated aluminized substrates: Effect of substrate temperature on degree of protection given by PPHMDSO overcoats.

Control samples, or samples coated at $T_s = 100^\circ C$ begin to show corrosive attack after less than 60 minutes of immersion, and are almost totally bare after 75 or 120 minutes, respectively. Samples coated at $T_s = 250$ or $300^\circ C$, on the other hand, showed no signs of corrosion, even after several days of immersion. These results confirm our earlier published data on the corrosion inhibition of steel samples (8,9).

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