

The Effects of Substrate Surface Roughness on the Morphology of Plasma-Polymerized Ethylene

It is well known that the vapors of various kinds of organic and organometallic compounds can be polymerized in the plasma created by an electric discharge sustained at low pressures.¹⁻⁴ It has been shown that the surface quality of a plasma-polymerized polymer film is determined by both the reaction conditions (monomer flow rate, pressure, power input, and reactor geometry) and the substrate material on which the film is deposited.^{5,6} The effects of reaction conditions have been interpreted in terms of the concentration of reactive species in the plasma generated by collisions of free electrons with monomer molecules.⁷ The effect of substrate material is, however, more complicated. Thompson and Smolinsky⁸ have noted that the inclusion of a polymer powder in films prepared from organosilicon monomers depends upon the nature of the surface. The present authors⁸ have, on the other hand, pointed out that the roughness of polymer films formed by plasma polymerization of ethylene is closely related to that of the substrate, irrespective of whether it is a metal or a nonmetal. In order to study this problem further, the present investigation undertook an examination of electron micrographs

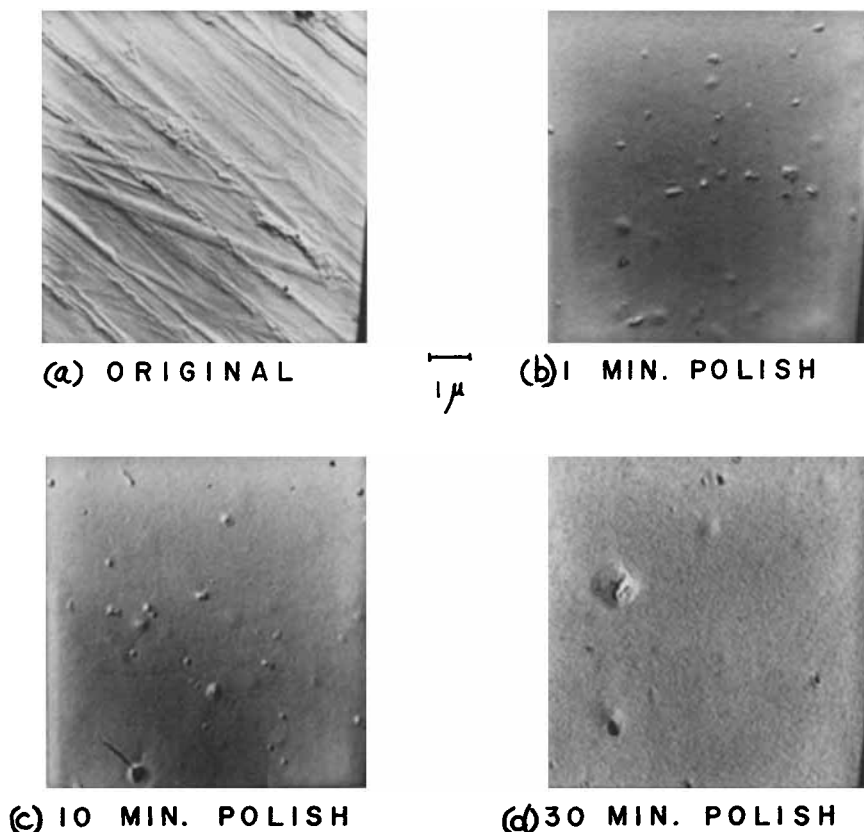


Fig. 1. Electron photomicrograph of aluminum surfaces which are (a) untreated; (b) electropolished for 1 min; (c) electropolished for 10 min; and (d) electropolished for 30 min.

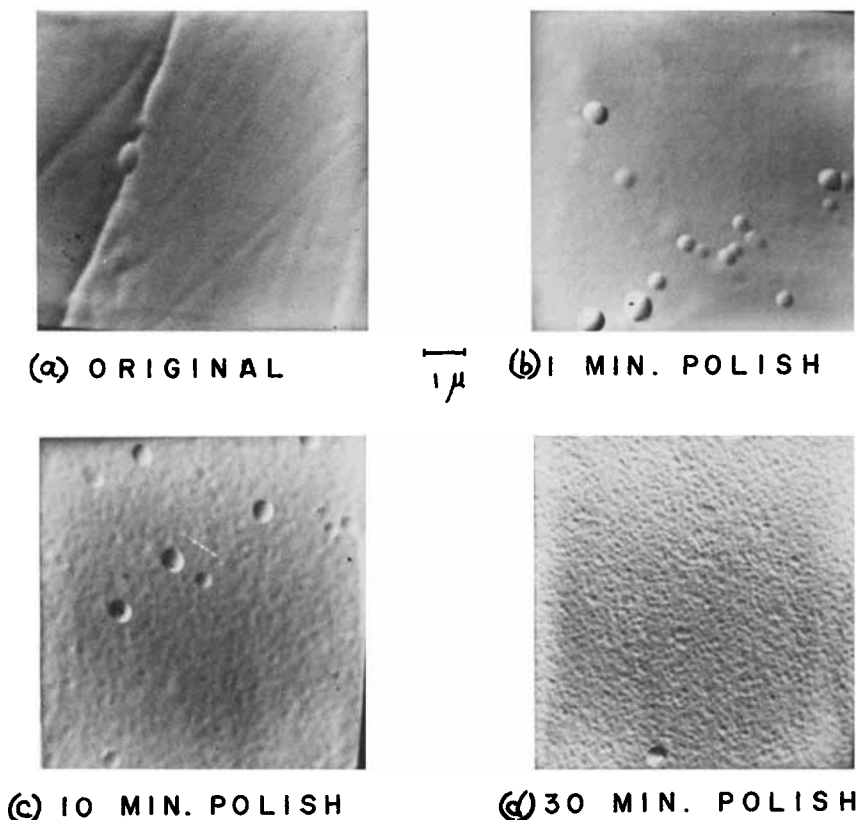


Fig. 2. Electron photomicrographs of plasma polymerized ethylene on (a) untreated aluminum; (b) aluminum after 1 min electropolishing; (c) aluminum after 10 min electropolishing; and (d) aluminum after 30 min electropolishing.

of plasma-polymerized ethylene on electrochemically polished aluminum surfaces with various degrees of surface roughness.

The polishing solution was made of 817 cc orthophosphoric acid (density 1.57), 134 cc sulfuric acid, 156 g chromic oxide, and 40 cc water.⁸ The aluminum plate (2 cm wide, 5 cm long, and 1 mm thick) which was to be polished was made the anode and was placed vertically in the center of the polishing solution kept at 85°C. A cylindrical piece of aluminum foil (radius 10 cm, height 5 cm, thickness 0.1 mm) surrounding the anode in the solution was used as the cathode. The polishing was carried out at 10 V and 0.4 amp for durations extending from 1 to 30 min. Polymerization of ethylene was carried out by using the same apparatus as that described in our earlier studies.⁹ One set of conditions was used for the preparation of all of the samples (pressure of ethylene 2 torr, flow rate 80 cc/min, power 100 W) favorable for the production of smooth polymer films on most substrates.⁶ The reaction period was 10 min, unless otherwise indicated.

A replica of each sample was prepared by transferring the surface features of the sample to an acetyl cellulose film. This film was then shadowed by evaporating a platinum-palladium alloy and backed by a layer of evaporated carbon. The replicas were examined on a Hitachi HU-11 electron microscope at an acceleration voltage of 75 kV.

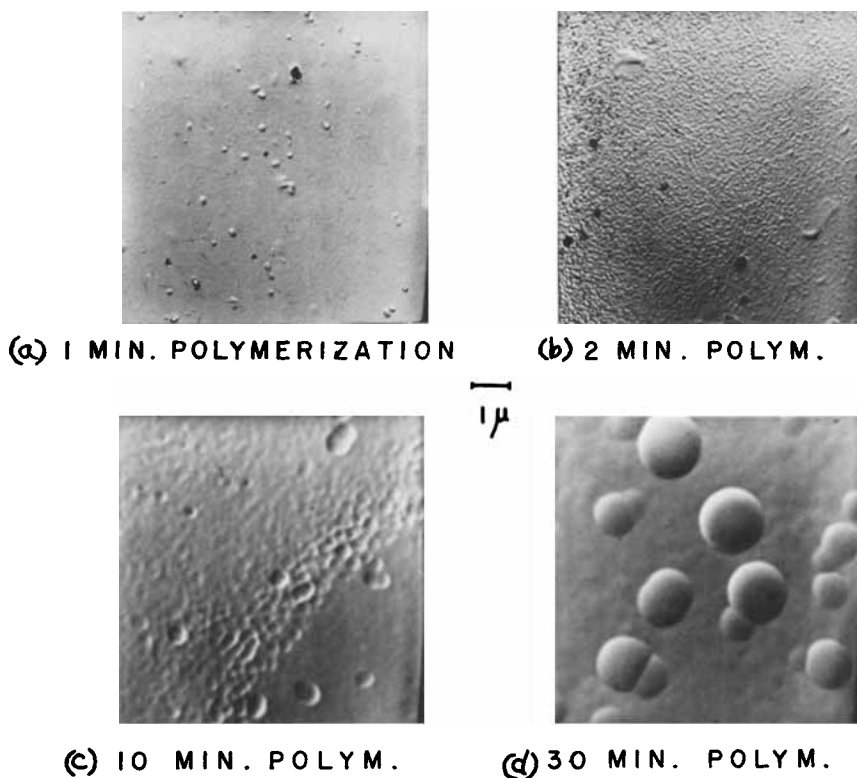


Fig. 3. Electron photomicrographs of plasma-polymerized ethylene on aluminum surface electropolished for 10 min. Durations of plasma polymerization are: (a) 1 min; (b) 2 min; (c) 10 min; (d) 30 min.

Figures 1a-d show the surface of the aluminum after different lengths of polishing. Figure 1a is the original surface. It contains many striations whose widths range from 400 to 4000 Å and whose height is about several hundred angstroms. After 1 min of polishing, almost all the striations were removed, as seen in Figure 1b. Prolonged polishing produced tiny etch pits of about 100 Å in diameter. The diameter of these pits becomes larger as the polishing time is lengthened (Figs. 1c and 1d).

Figure 2a shows the surface of a polymer film deposited on the unpolished aluminum surface shown in Figure 1a. Although the surface now looks smooth, striations of the original surface are still clearly discernible. The surface of the polymer deposited on the 1-min-polished aluminum appears extremely smooth, as seen in Figure 2b, although a number of submicron particles are present. By contrast, polymer films deposited on the 10-min-polished aluminum exhibit a rougher surface (Fig. 2c). This tendency is enhanced in Figure 2d in which polymer was deposited on the 30-min-polished aluminum. These surfaces seem to be made of a flock of merged semispheres which, however, are to be distinguished from the larger spherical particles.

The micrographs shown in Figures 2a-d suggest that a rough polymer surface will be produced on aluminum surfaces which are highly etched. Surface irregularities in the aluminum which are larger than about 100 Å, however, do not appear to contribute to

producing a rough polymer surface. Thus, the surfaces in Figures 2a and 2b are smooth, whereas those in Figures 2c and 2d are rough. Since large surface irregularities in the aluminum are covered over but not obliterated (viz, Figs. 1a and 2a) when the polymer film is relatively thin, it may be concluded that in order to produce a uniformly smooth polymer surface, the substrate should be free of both large irregularities and small etch pits.

In order to clarify the difference between the large ($\sim 1 \mu$) and small spherical features observed in Figures 2a-d, polymerization of ethylene was carried out for 1, 2, 10, and 30 min. The substrates used in this series of experiments were polished for 10 min. In Figure 3a, which shows a film after 1 min of polymerization, spheres of about 0.2μ in diameter are seen. Whether the distribution of these spheres is random is not known. The size of the spheres is slightly larger ($0.2\text{--}0.3 \mu$ dia.) after 2 min of polymerization, as shown in Figure 3b. In this micrograph, the spheres appear as black particles since they were transferred to the replica film during replication and blocked the passage of the electron beam. The substrate surface is also covered by small irregular-shaped polymer lumps, the diameters of which are $400\text{--}1000 \text{ \AA}$. These lumps seem to grow larger until their growth is ceased by mutual coalescence. For longer polymerization times, the film becomes smoother as more polymer is deposited between the coalesced lumps. This trend can be seen in Figures 3c and d, which show 10- and 30-min-polymerized surfaces, respectively. The larger spherical features continue to grow as reaction proceeds. Their diameter is about 0.5μ at 10 min of polymerization (Fig. 3c) and about 1.5μ at 30 min (Fig. 3d). Since these features are always found on the surface of a polymer film, it suggests that they are due to spherical particles grown in the gas phase which have fallen onto the substrate surface at the end of the polymerization period.

From these experiments, it is possible to postulate that the small semispherical features observed in Figures 3a-c are small lumps of polymer which with time grow together to form a continuous film. The formation of such semispherical features appears to depend upon the extent to which the surface is covered by the small etch pits (compare, for example, Figs. 2b and c). It is possible that these pits act as nucleating centers for the formation of the small semispheres. The larger spheres seen in Figures 3c and d appear on the topmost surface of the polymer film. Thus, it appears likely that they are formed in the gas phase and then fall onto the film surface at the end of the polymerization period. This interpretation would be consistent with our previous observations⁶ of the formation of powder particles in the gas phase whose diameters are comparable to those of the larger spherical features observed in the micrographs presented here.

This work was supported in part by the Advanced Research Projects Agency of the Department of Defense, monitored by the Office of Naval Research under Contract No. N00014-69 A-0200-1053.

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Received January 11, 1974