Plasma-Deposited Polymer Films. II. Transmission and Scanning Electron Microscopy

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Synopsis

A transmission electron microscopy (TEM) and scanning electron microscopy (SEM) study of plasma-formed polyethylene and polystyrene is reported. A two-phase structure of spheres embedded in a polymer binder is evident, supporting the predictions of earlier low-angle x-ray scattering data taken of these two plasma-deposited polymers.

INTRODUCTION

In earlier attempts to characterize plasma-deposited polyethylene and polystyrene, the insolubility of these materials as a result of a high degree of crosslinking led to the application of a low-angle x-ray scattering technique which predicted the submicrostructure to consist of nearly spherical globules imbedded in a polymer filler of lower density.

On the basis of the x-ray data, predictions were made as to the size, and shape, and population of the spherical inhomogeneities. Accordingly, it was decided to determine the correctness of the x-ray model by employing TEM and SEM techniques.

EXPERIMENTAL

Problems were encountered in preparing suitable TEM samples. Several replication techniques were performed on fracture edges and surfaces from the same film samples used in the low-angle x-ray scattering method. These were unsuccessful because material from the plasma-deposited films was repeatedly removed and incorporated with the replica.

The next attempt at sample preparation consisted of plasma-depositing polyethylene directly onto a carbon film-coated TEM sample grid. The carbon film provided an electron-transparent surface for the polymer to settle on. This technique was modestly successful provided that deposition times in the rf reactor were shortened to 5 min. Longer time periods deposited films too thick for electron beam penetration. Still, the micrographs obtained from these samples were blurred as if there were a film obscuring the structural features. Suspecting that such a film might arise from reaction of residual trapped free-radical sites with remaining ethylene monomer, the deposition method was al-

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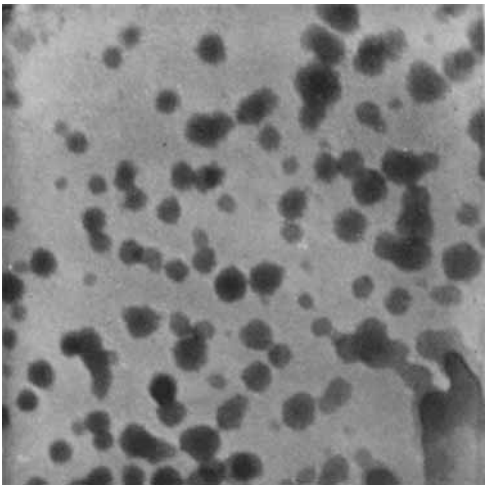

Fig. 1. TEM micrograph of plasma-formed polyethylene. Power level 2 W, partial pressure 10 microns (77,000×).

tered by turning off the ethylene flow 15 sec prior to turning off the rf power. This enhanced the resolution of the anticipated features. All samples for the TEM studies were then prepared in this manner and were not metallized or otherwise enhanced or altered.

The SEM examination of plasma-formed polyethylene was carried out at the Monsanto Research Center in St. Louis. The sample was prepared by depositing polyethylene (5 W, 20 microns pressure) for 28 hr onto a quartz crystal face positioned flush with, and parallel to, the reactor wall. As before, the monomer gas was turned off prior to cutting the power. The film on the crystal was allowed to stabilize under high vacuum within the reactor for three days. The crystal was then marked on the uncoated back side and fractured. A marked fragment was inserted in silver paste at approximately a 45° angle to the horizontal with

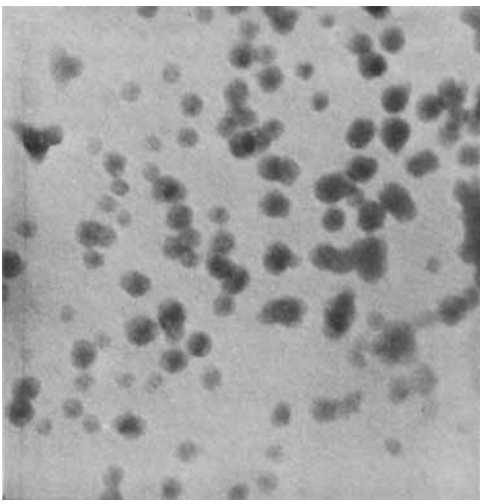

Fig. 2. TEM micrograph of plasma-formed polyethylene. Power level 5 W, partial pressure 10 microns (77,000×).

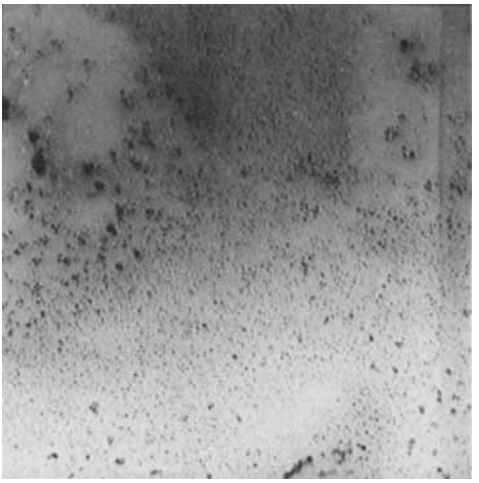

Fig. 3. TEM micrograph of plasma-formed polyethylene. Power level 2 W, partial pressure 20 microns (50,000×).

the fracture edge up across the metallized spot. The polymer surface and fracture edge were lightly gold-metallized.

The microscope was coupled to a contrast-enhancement amplifier. The amplifier increased the photographic apparent resolution but did not alter the calculated resolution of the instrument, which in this study was 150 Å.

RESULTS AND DISCUSSION

Selected micrographs obtained by TEM are shown in Figures 1–4. The micrographs show the nearly spherical globules postulated from prior low-angle x-ray analysis. In Figures 3 and 4, the spherical diameters are of the order of the minimum 330 Å dimension reported in the preceding paper for a polyethylene film produced under identical reactor conditions but for a longer time period.

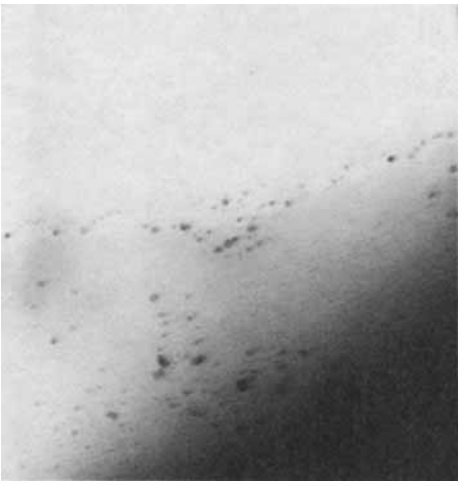

Fig. 4. TEM micrograph of plasma-formed polyethylene. Power level 5 W, partial pressure 20 microns (77,000×).

In the other micrographs, the diameters lie between the predicted maximum and minimum dimensions. There are insufficient data to attempt a reliable correlation of power and pressure with spherical diameter. However, the trend in dimensions is that smaller particles are produced with higher powers. This trend is in agreement with that observed by Thompson for plasma-formed polystyrene and reported by others.[1-5]

Two problems exist in interpreting the TEM micrographs. There is little doubt that the electron beam (~100 kV) attacked the polymer. This would be especially true because the TEM samples were not metallized as were the SEM samples.

The fact that the TEM micrographs still provided evidence of spherical particles despite thermal attack of the polymer can be explained on the basis of thermal gravimetric analysis (TGA). TGA has shown that plasma-formed polystyrene films have a high degree of thermal stability, with about 40% of the original mass remaining at temperatures of 700°C.[1,3] The mass remaining was of a carbon matrix form consistent with the crosslinked plasma-formed polymer structure. It has also been shown that conventional polystyrene and the soluble portion of the plasma-formed polystyrene are completely thermally degraded at temperatures of 600°C.[1,3] This TGA investigation has been extended recently to plasma-deposited polyethylene where 50% of the original mass remains at 450°C.[6] Clearly, the thermal stability of the plasma-formed polymers is greater than that of their conventional analogues.

It appears reasonable therefore to assume that a degradation process similar to that involved with TGA occurred in the TEM beam—a burning away of the lower-density material and carbonizing of the higher-density spheres—to leave a TEM-resolvable structure. Carbonized particles produced in this manner resting on a carbon film would project a low but resolvable contrast image on the viewing screen and micrograph negative.

Since the low-angle x-ray data suggested a distribution of spheres throughout the film volume and because the TEM replication techniques on cross sections

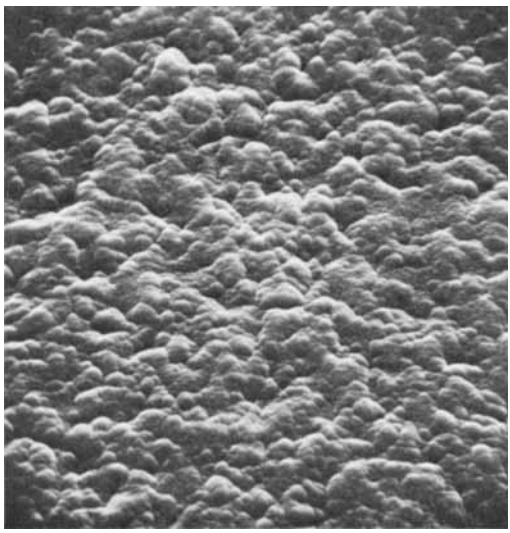

Fig. 5. SEM micrograph of plasma-formed polyethylene. Power level 5 W, partial pressure 20 microns (2000×).

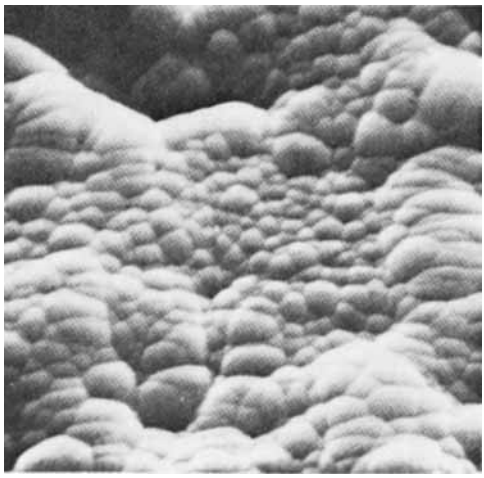

Fig. 6. SEM micrograph of plasma-formed polyethylene. Power level 5 W, partial pressure 20 microns (9800×).

had been unsuccessful, it was decided to employ high-resolution SEM methods.

The SEM micrographs for plasma-deposited polyethylene are shown in Figures 5–7. An agglomeration of globules is evident in Figure 5. The smaller globules in Figures 6 and 7 are approximately 0.2 micron in diameter. The larger spheres are about 2.0 microns in diameter but appear to be clumps of smaller globules. It should be pointed out that, since the clumps appear to have interfaces between smaller globules that persist toward the interior, resulting x-ray scattering will provide spectra of these smaller spheres.

On the basis of the TEM and SEM studies, the two-phase polymer model used to treat the low-angle x-ray data appears to be not only reasonable but consistent with the experimental observations.

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Fig. 7. SEM micrograph of plasma-formed polyethylene. Power level 5 W, partial pressure 20 microns (49,000×).

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