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Effect of Atomic Oxygen on the Surface Morphology of Polyethylene

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ABSTRACT

The chemical species created in a low-pressure electrical discharge in oxygen attack the polymer at the surface, converting it to gaseous products. This process is interesting because: 1) the chemical changes on the resulting surface facilitate the formation of strong adhesive bonds and provide sites for the chemical attachment of other molecules, 2) significant morphological features lying below the surface may be revealed, 3) polymer can be cleanly removed from surfaces which are resistant to oxidation, and 4) dielectric breakdown frequently is preceded by the attack on the polymer of chemical species created in a corona discharge. Atomic oxygen is an important chemical species created in such a discharge. It reacts with organic substances rapidly at room temperature, but lives long enough in the low-pressure gas that it can be separated from many other reactive species created in the discharge. "Titration" with NO_2 provides a straightforward chemiluminescent means for determining the concentration of atomic oxygen to which the sample is exposed. This paper characterizes the attack of atomic oxygen, perhaps in the presence of long lived but less reactive species such as excited O_2 molecules, on polymer surfaces, using electron microscopic observations of known morphological features of polyethylene to observe the changes produced by atomic oxygen. Lamellar polyethylene crystals were attacked both at the edges and the fold surfaces. Layers many microns thick were removed from spherulitic samples and replicas obtained from the surfaces thus exposed. Thick samples were thinned to the point at which they were transparent to an electron beam and interior morphological features were directly observed.

INTRODUCTION

The chemical changes in polyethylene surfaces produced by exposure to a glow discharge generally make the surface form stronger adhesive bonds, make it wet more easily so that printing is facilitated, and leave chemically active bonds which can serve as sites for the chemical attachment of other molecules. Hansen et al. [1] showed that the reactive species in a glow discharge in oxygen converted surface layers of the polymer to volatile products. The remaining surfaces had low contact angles with water and improved adhesion. Dietl [2], using a glow discharge apparatus similar to that described by Aldrian et al. [3], examined the morphological features that were revealed by exposing polymer surfaces to a glow discharge in oxygen. Using replica techniques, he observed features probably connected with the lamellar morphology of nylon 6, polyethylene, and polypropylene. Fischer et al. [4] obtained electron micrographs that showed edges of lamellae on polymer surfaces that had been etched in a glow discharge in an apparatus similar to that described by Aldrian [3]. They showed, by means of optical Fourier transforms of the electron micrographs, that the spacing and orientation of the lamellae thus revealed were consistent with the lamellar structure indicated by low-angle x-ray scattering. Thomas [5] has recently reviewed the use of chemically reactive gaseous plasmas in the preparation of specimens for microscopy. That review contains a comprehensive bibliography. Gillette et al. [6] showed that a glow discharge in oxygen can be used to clean mirrors and other optical devices by the rapid, residue-free, gentle, and complete oxidation of contaminant films. The dielectric breakdown of the polyethylene insulation used in some high-voltage power transmission cables follows deterioration of the polyethylene caused by the chemical attack of reactive gases created by corona discharges. Mayoux et al. [7] studied the effect of low-energy oxygen ions (and ions of other gases) on polyethylene surfaces in connection with the dielectric breakdown problem. Keller, Priest, and co-workers [8-10] have investigated the oxidation of polyethylene crystals by ozone. Kaplan [11] described some of the properties and chemical reactions of a metastable excited state of molecular oxygen (labeled $^1\Delta_g$ in spectroscopic notation) with an excitation energy of 94.2 kJ/mole (22.5 kcal/mole). Trozzolo and Winslow [12] have proposed a mechanism for the photodegradation of polyethylene that involves oxygen molecules in this excited state. Herron and Schiff [13] used mass spectrometric techniques to observe the longer lived atomic and molecular species that are present in oxygen activated in an electrical discharge similar to that used here. They found about 10% of the oxygen molecules in the metastable $^1\Delta_g$ state. Atomic oxygen, which has a heat of formation of 249 kJ/mole (59.5 kcal/mole) [14], was present in concentrations of 4 to 12 mole %. The higher concentrations were found when trace amounts of water were present. The ozone concentrations found were less than 0.02%. The authors [15] previously described some of the effects of electrical discharges in low-pressure gases on the morphology of polyethylene crystals. The present paper describes further efforts to characterize the chemically active species created in a glow discharge in oxygen and their attack on polymer surfaces so that the processes by which interesting morphological features are revealed can be controlled and the results interpreted.

While recognizing that measurement of the concentration of atomic oxygen created in an electrical discharge does not provide enough information to characterize all the species that may attack polyethylene, in this work we concentrated on atomic oxygen because: 1) it attacks polyethylene rapidly at room temperature, 2) it can be separated from many short-lived species created in the discharge simply by placing the sample downstream, and 3) its concentration can be measured by straightforward procedures.

EXPERIMENTAL

The apparatus used is shown in Fig. 1. Oxygen at a pressure of around 133 N/m^2 (1 Torr) was pumped through the glass tube at a measured rate. A 5 to 10 mA direct current discharge was established in the curved part of the tube between a copper electrode and the metal part of the glass-to-metal seal where the gas was admitted to the apparatus. The purpose of the curved segment was to reduce the intensity of the light from

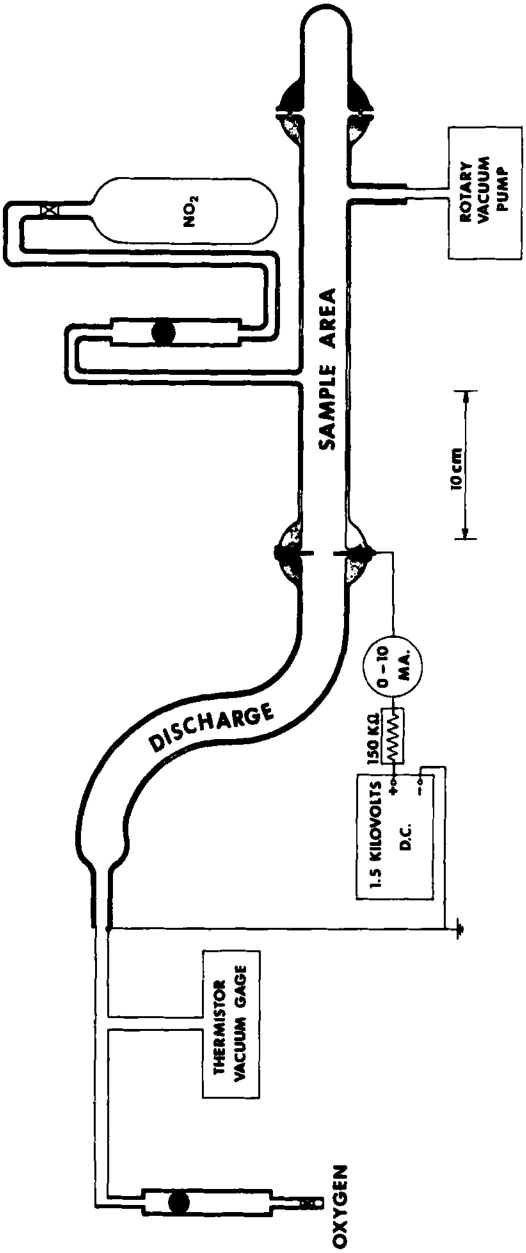

FIG. 1. Glow discharge apparatus used to expose polyethylene to atomic oxygen.

the discharge that reached the sample area. The concentration of O atoms in the sample area was measured by a NO_2 titration method described by Kaufman [16, 17]. Accordingly, NO_2 was admitted at an adjustable and measured rate. At low concentrations, NO_2 reacts very rapidly with O to form NO which in turn reacts more slowly with O to form an excited state of NO_2, which then decays with the emission of a greenish yellow light. Relative concentration of O_2 and NO_2 were adjusted by controlling the flow. Flow rates were measured with flowmeters of the type in which the flowing gas lifts a ball in a vertical variable area tube. As the concentration of NO_2 increased, the intensity of the greenish yellow light first increased and then, at the concentrations at which the fast reaction between NO_2 and O consumed all the O, the light disappeared. This sharp end point established the amount of NO_2 required to equal the concentration of O.

The rate of attack was established by subjecting a small sheet of polymer to the active oxygen and measuring the weight loss as a function of exposure time. Etching rates were around 0.5 μm/hr, similar to that observed by Hansen et al. [1] at O atom concentrations of 10^{14} to 10^{15} oxygen atoms/cm^3. The etching rate was about 5 times higher in the region immediately adjacent to the electrode and decreased to the above rate at a point 5 cm downstream from the electrode.

RESULTS

Since the morphology of lamellar polyethylene crystals precipitated from dilute solution is well known [18], the morphological changes produced by active oxygen attack can be recognized. The relative thickening of the edges of lamellae sometimes observed when the sample was immersed in the discharge [15] is shown in Fig. 2. This phenomenon was not observed in samples subjected to atomic oxygen outside the discharge. Instead, the polyethylene was cleanly removed, both from the edges and the fold surfaces of the crystals. Attack on the fold surfaces penetrated two or three lamellae before the attack on the original and newly exposed edges resulted in the complete elimination of the lamellae. Figure 3 shows a multilayer polyethylene crystal almost completely eliminated by a prolonged attack. The radiating lines in Fig. 3 are the remains of wrinkles (a similar wrinkle is shown in Fig. 2) that formed when the hollow-pyramidal crystal collapsed onto the substrate. The length of these wrinkles shows that the original width of the crystal was 3 or 4 times the width of the remaining part.

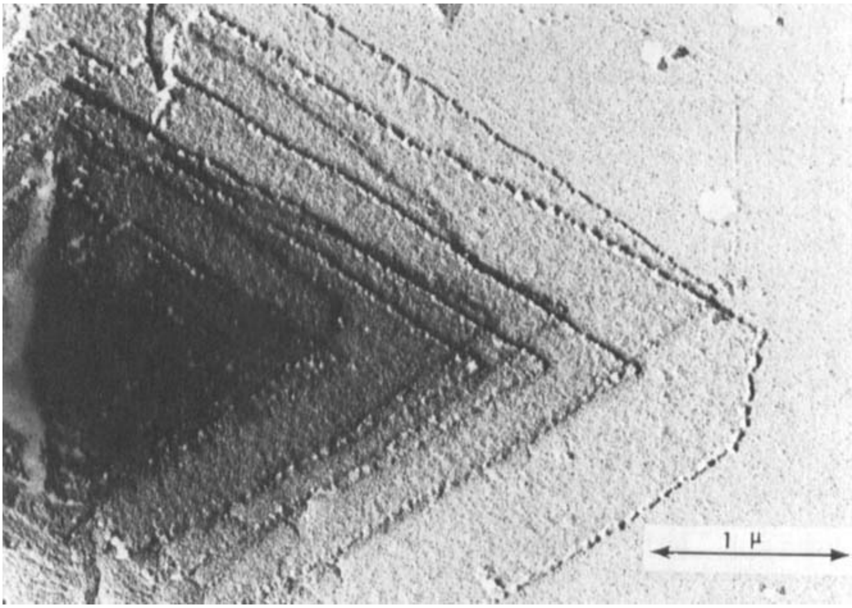

FIG. 2. Relatively thick edges of the lamellae in a polyethylene crystal exposed to atomic oxygen while immersed in the discharge [8].

Observation of the morphology produced at the surface of solid polyethylene by active oxygen attack is complicated by the fact that it is difficult to obtain replicas of the surface because the replicating material adheres so tightly to the chemically changed surfaces. Figure 4 shows a replica obtained from a high molecular weight linear polyethylene replica obtained from a high molecular weight linear polyethylene sample that contained well developed ringed spherulites. Several micrometers of polymer were removed from this surface before the surface was shadowed with a platinum palladium alloy. The metal replica was then pulled off the sample with a dried drop of polyacrylic acid-polyvinyl alcohol mixture, which forms a tight bond to the replica. The replica separated from the polymer cleanly in the regions where the lamellar crystals were nearly perpendicular to the surface, but pieces of polymer several lamellae thick were pulled off the sample at places where the lamellae were nearly parallel to the surface. This served to decorate the replica so that the rings of the spherulite are evident, particularly in the lower left quadrant of Fig. 4. In high magnification photographs of this sample, the edges of 10 nm thick lamellae

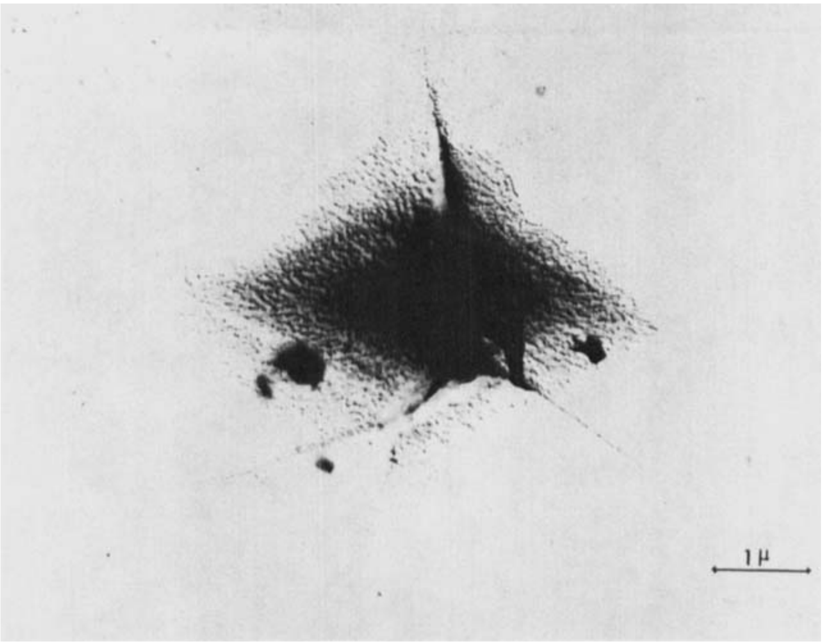

FIG. 3. Remains of a large multilayer polyethylene crystal subjected to prolonged exposure to atomic oxygen.

were discernible near the centers of spherulites and in the rings where the lamellae were nearly normal to the surface. The networks of fibrous material on Fig. 4 are a small amount of debris, some of which seems to accumulate during the exposure to atomic oxygen, and some of which was produced by mechanical drawing of small regions when the metal replica was pulled off the sample.

The attack of the atomic oxygen is so gentle and well controlled that it is possible to reduce the thickness of samples to a few hundred angstroms without overheating or mechanical deformation. Such thinned regions are transparent in an ordinary transmission electron microscope. Figure 5 shows a sample of polyethylene originally about 100 μm thick which was thinned by atomic oxygen attack from both sides until small holes were formed. The lamellar nature of the polyethylene is clearly evident in the thin transparent regions surrounding the small holes. Figure 6 shows another polyethylene sample which was thinned in a similar way. The selected area electron diffraction pattern from the marked triangular area is shown in the inset. The sharp diffraction spots show that this region contained

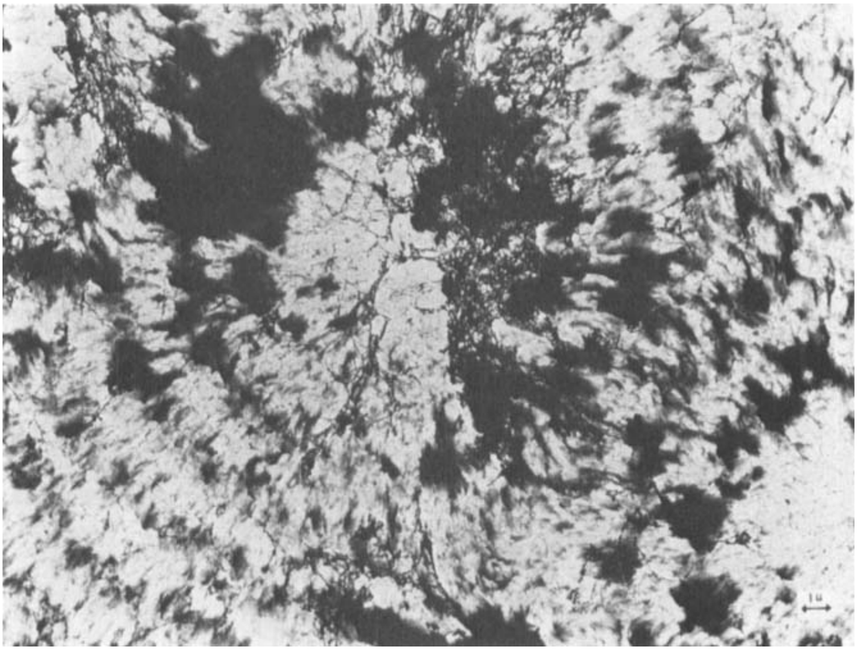

FIG. 4. Metal replica with adhering polymer fragments from a surface revealed by atomic etching of a spherulitic sample of polyethylene. Several micrometers of polymer were removed.

several polyethylene crystals with somewhat different orientations as would be expected in a spherulitic polyethylene sample. This result indicates that the crystal structure of the region was not disrupted by the thinning treatment.

CONCLUSIONS

Active oxygen extracted from a glow discharge in oxygen attacks solid polyethylene at room temperature and converts it to gaseous products. The rate of attack is reproducible and easy to control. Familiar morphological features of polyethylene are revealed in the interior of thick specimens. The procedures described here show promise as an incisive means to investigate phenomena such as morphology, adhesion, dielectric breakdown, and the distribution of oxygen-resistant particles in polyethylene and other polymers.

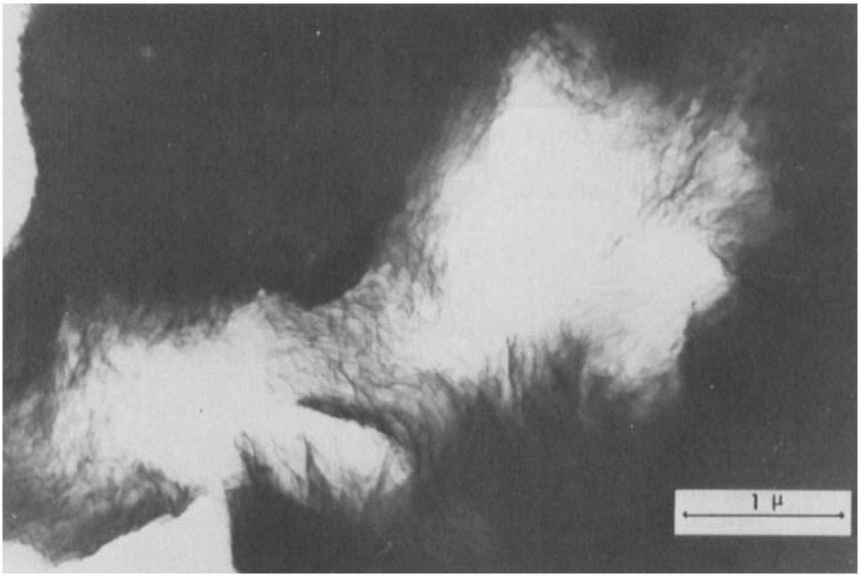

FIG. 5. Polyethylene lamellae exposed by thinning of a thick sample until it was transparent to the electron beam.

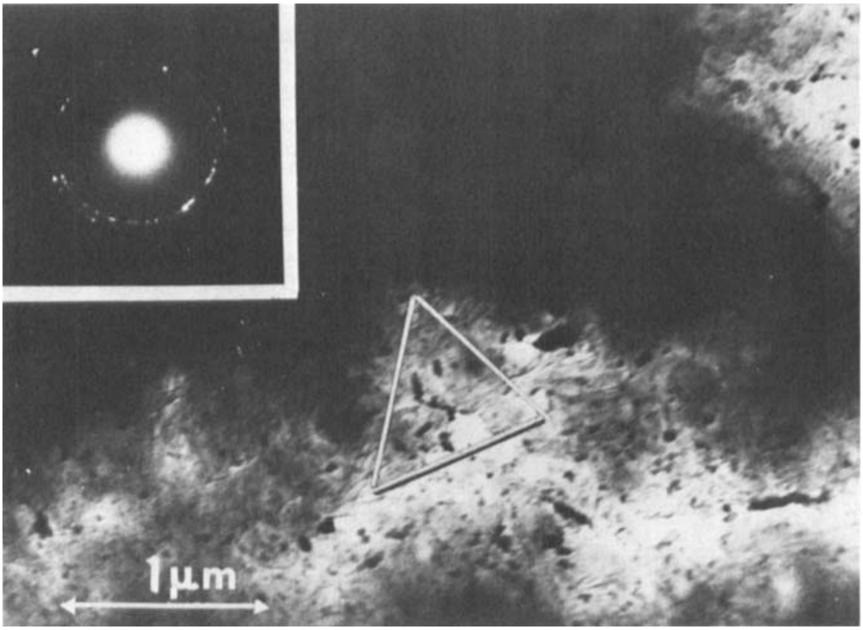

FIG. 6. Electron micrograph of a thinned region in a different sample of spherulitic polyethylene. The inset shows the selected area diffraction pattern from the marked triangular area.

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