

## Surface Morphology of Polyethylene After Treatment in a Corona Discharge

C. Y. KIM and D. A. I. GORING, *Physical Chemistry Section, Pulp and Paper Research Institute of Canada, and Department of Chemistry, McGill University, Montreal, Quebec, Canada*

### Synopsis

Corona treatment of low-density polyethylene in oxygen or oxygen-containing gases produced bumps on the surface, while treatment in nitrogen, hydrogen, argon, or helium caused no detectable surface change. Bumps made by an oxygen corona increased in size with time and temperature of the treatment. The bumps were removed when a treated polymer sheet was dipped into solvents such as  $\text{CCl}_4$ , ethanol, or 0.2% aqueous NaOH. Infrared analysis indicated that most of the oxidized layer was eliminated from the polymer surface by solvent dipping and that the degraded products contained a substantial proportion of  $-\text{CH}_2-$  groups. It is suggested that the bumps are caused by the migration of low molecular weight degradation products to charged areas of the polymer surface.

### INTRODUCTION

Both the printability and the bonding capacity of polyethylene (PE) are improved by exposure of the polymer sheet to electrical discharges.<sup>1-3</sup> The surface of the sheet is known to be changed both chemically and physically by the corona treatment.<sup>1,3-5</sup> In air or oxygen, the main chemical effect is oxidation.<sup>1,4,6,7</sup> In addition, the surface becomes roughened, particularly on prolonged treatment.<sup>3,8</sup> Bailey<sup>8</sup> claims that the surface degradation after prolonged treatment has a deteriorative effect on the printability.

The present work deals with the effect of corona discharges on the surface morphology of PE. Surfaces are examined microscopically before and after treatment. The effect of the temperature of treatment is studied. Several gases are used, but most of the work is done with oxygen in the discharge. In an attempt to characterize the degradation products, the surface is treated with solvent and the materials dissolved are examined. Some tentative explanations are offered concerning the origin of the effects observed.

### EXPERIMENTAL

We are indebted to B. B. Hillary of the Dow Chemical Co. for extruded PE sheets of Dow C.I.L. 220G. The sheets were 0.031 in. thick and had a

density of 0.919 and a melt index of 1.9. Samples were kept scratch free on the surface and were used without pretreatment. Low-density PE 0.002 in. thick was kindly supplied by C. J. Williams of Union Carbide and was used for infrared study and weight loss measurements.

In most experiments, corona treatment was applied in the flat plate device described in a previous report.<sup>3</sup> The power supply was a 15000-V, 60-Hz neon lamp transformer, and the air gap was about 0.12 in. The temperature of the cell was controlled by circulating water from a thermostat bath through the bottom electrode.

A description of the gases used is given in Table I. The inert gases such as N<sub>2</sub>, A, He, and H<sub>2</sub> were purified by passage over a heated copper column (450°C) as described in a previous report.<sup>3</sup> Oxygen and air were demoi-  
sturized using three Dry Ice-acetone traps. The flow rate of the gas into the cell was 50 ml/min.

TABLE I  
Gases Used in Corona Treatment of PE

Gas	Supplier	Purity, %
O <sub>2</sub>	Liquid Air	99.6
N <sub>2</sub>	Liquid Air	99.998
A	Matheson	99.998
He	Matheson	99.995
H <sub>2</sub>	Matheson	99.95
CO <sub>2</sub>	Matheson	99.99

A Reichert Zetopan research microscope was used to photograph the polymer surfaces. Before microscopic examination, the surface was coated with a uniform layer of aluminum using a shadowing angle of 30 degrees. Some electron micrographs were taken with a Cambridge Stereoscan electron microscope.

Infrared spectra of films were obtained on a Unicam SP 200G infrared spectrophotometer with a Wilks Model 9 single-beam multiple internal reflection (MIR) attachment unit with a KRS-5 reflector. Scanning speed was 45 cm<sup>-1</sup>/min and the angle of incidence was 45 degrees. For infrared spectra of soluble materials, a NaCl liquid cell was used with a spacer of 0.01 in.

## RESULTS

As noted previously,<sup>3</sup> corona treatment in air made the PE surface rough, while a similar treatment in nitrogen produced no detectable change on the surface. This effect is shown in Figure 1. Surface roughening similar to that in Figure 1 was obtained when pure oxygen or CO<sub>2</sub> was used instead of air. Corona discharge in gases containing no oxygen such as H<sub>2</sub>, He, A, or N<sub>2</sub> caused no roughness on the surface. Thus, oxidation seems to be a necessary accompaniment to the surface roughening effect.

Figure 2 shows that surface morphology changed both with time and temperature of treatment. At constant temperature, the size of the bumps increased with a longer time of treatment. Bump size also increased when

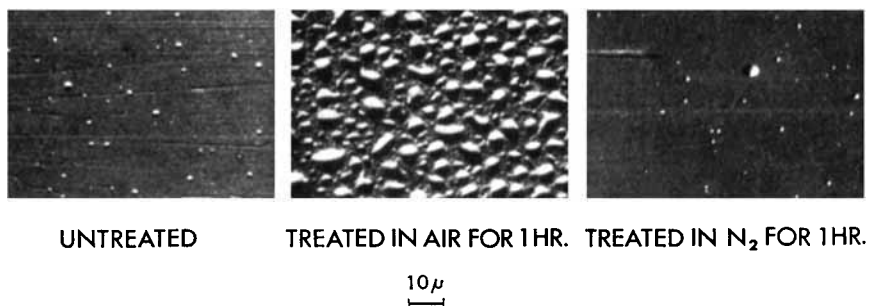


Fig. 1. Surface change of PE before and after 1-hr treatment in corona discharges of air and nitrogen. Aluminum shadowed and photographed in transmitted light.

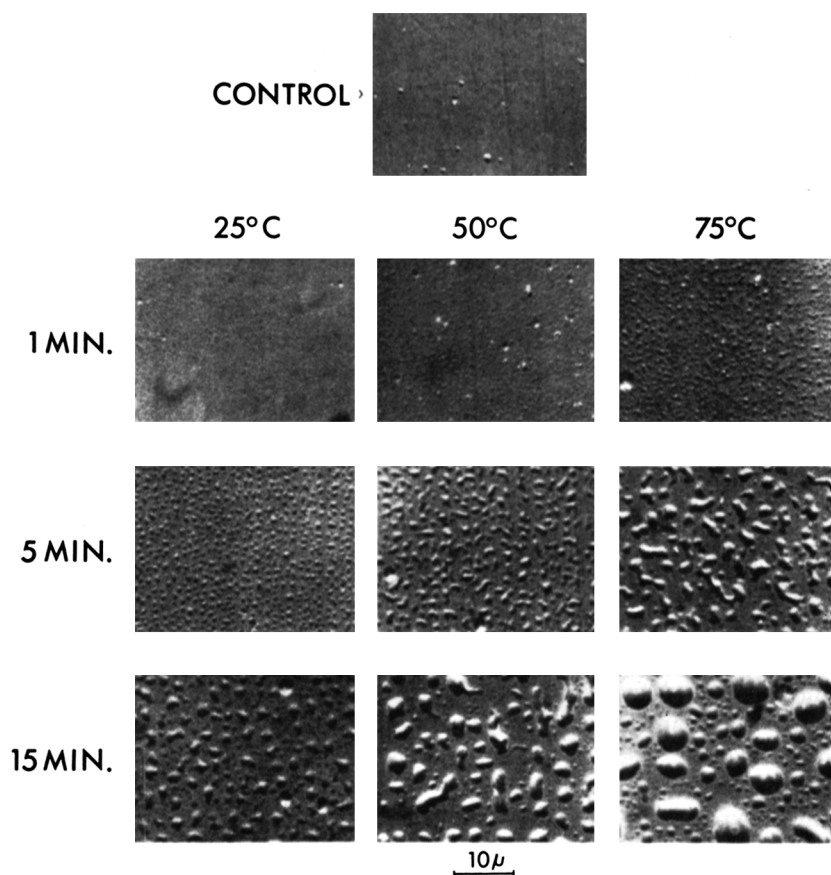


Fig. 2. PE surfaces treated for various times and temperatures in the oxygen corona discharge. Aluminum shadowed and photographed in transmitted light.

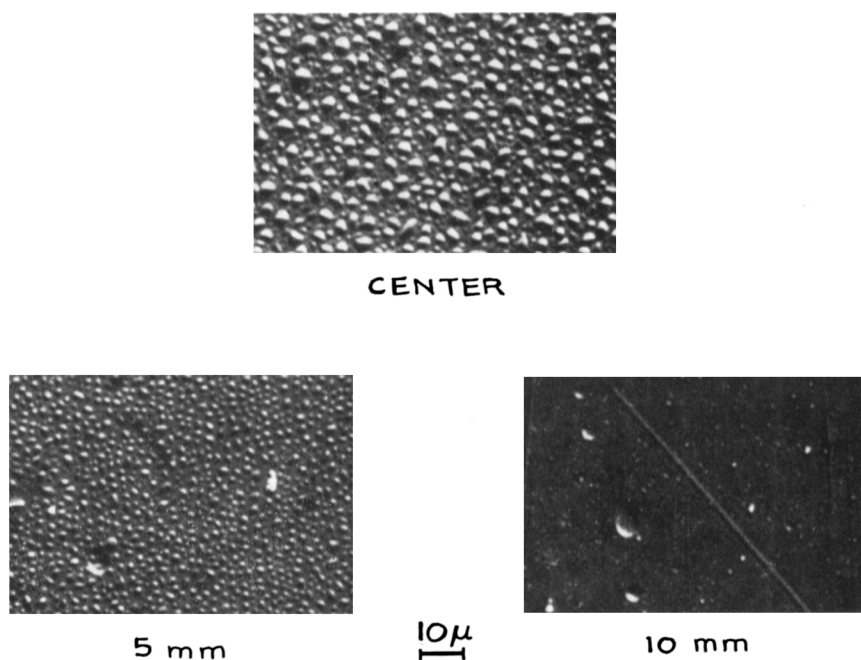


Fig. 3. Decrease in the size of bumps with increase of distance from the needle electrodes for 30-min treatment at room temperature. Aluminum shadowed and photographed in transmitted light.

the temperature was raised for a constant time of treatment. Bumps of about  $1\ \mu$  in diameter were created by a 1-min treatment at  $50^\circ\text{C}$  while treatment for 15 min at  $75^\circ\text{C}$  produced  $10\ \mu$  bumps.

Experiments were then carried out in which the flat plate electrodes of the corona device were replaced by two "needle" electrodes. The purpose of these experiments was to study the effect of restricting the discharge to a small, readily observable area. The needle electrodes were pieces of 0.125-in. copper rod mounted in line, with sharpened ends 0.125 in. apart. When the PE sheet was treated in an oxygen discharge between the electrodes, the physical changes on the surface were similar to those found for the flat plate corona. However, bumps were formed only where the discharge struck the polymer surface, and, as shown in Figure 3, the size of the bumps decreased with increase of the distance from the electrodes. This suggests that the formation of bumps is in some way associated with the corona discharge itself and is not due only to the reaction of an active gas with the polyethylene surface.

An unexpected result was that the bumps on a treated surface were easily removed by dipping the sample into  $\text{CCl}_4$ , ethanol, or 0.2% aqueous  $\text{NaOH}$ . This effect is shown in Figure 4. At low resolution, the solvent-dipped surface appeared to be similar to the untreated surface. However, with high resolution, the treated and ethanol-dipped surface appeared

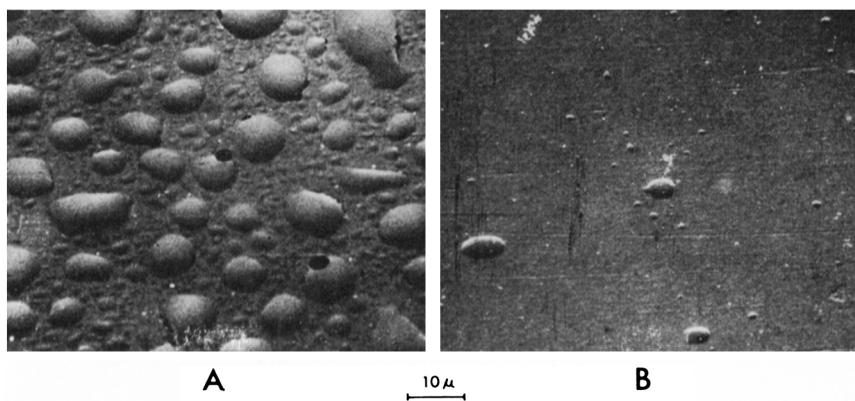


Fig. 4. Scanning electron micrographs of low-density PE surface treated in the oxygen corona for 15 min at 50°C and dipped in ethanol for 12 hr. (A) before dipping in ethanol; (B) after dipping in ethanol.

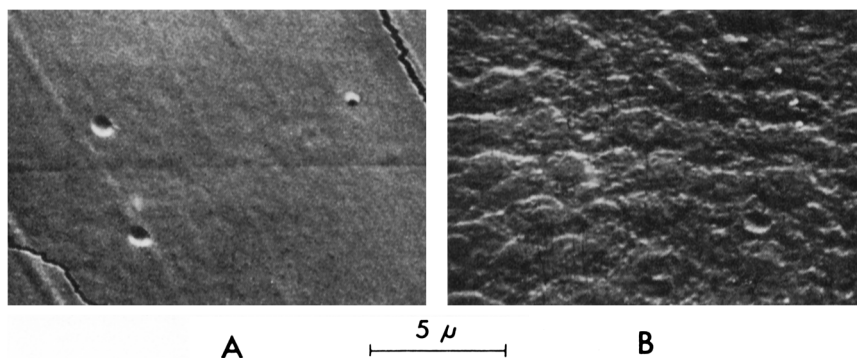


Fig. 5. Scanning electron micrographs of low-density PE surface: (A) untreated control; (B) treated in the oxygen corona for 15 min at 50°C followed by dipping in ethanol for 12 hr.

rough and textured compared with the original surface (Fig. 5). Perhaps the oxygen corona attacked the amorphous regions preferentially, thus causing etching which became visible when the degradation products were removed.

MIR infrared analysis of surfaces treated in air or oxygen gave the well-known strong absorption of  $\text{—C=O}$  groups at  $1720\text{ cm}^{-1}$ . However, after solvent dipping, the  $\text{—C=O}$  peak decreased as shown in Figure 6. Apparently, the oxidation produced by the corona treatment resides largely in the material which is removed by the solvent.

The infrared spectrum of the material removed by solvent is shown in Figure 7. As expected, carbonyl groups were evident ( $\nu\text{ C=O} = 1720\text{ cm}^{-1}$ ). However, a considerable amount of  $\text{—CH}_2\text{—}$  ( $\nu_a\text{CH}_2 = 2922\text{ cm}^{-1}$ ,  $\nu_s\text{CH} = 2857\text{ cm}^{-1}$ ,  $\nu_s\text{CH}_2 = 1464\text{ cm}^{-1}$ ) is indicated as well as a smaller proportion of  $\text{—CH}_3$  ( $\nu_a\text{CH}_3 = 2959\text{ cm}^{-1}$ ,  $\nu_s\text{CH}_3 = 2875\text{ cm}^{-1}$ ).<sup>9</sup>

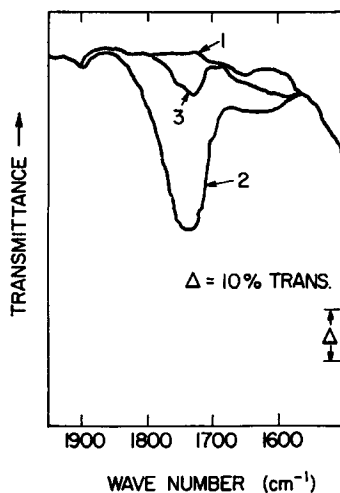


Fig. 6. MIR infrared spectra of (1) control; (2) treated in the oxygen corona for 1 min at 75°C; (3) after corona treatment, sheet dipped in CCl<sub>4</sub>.

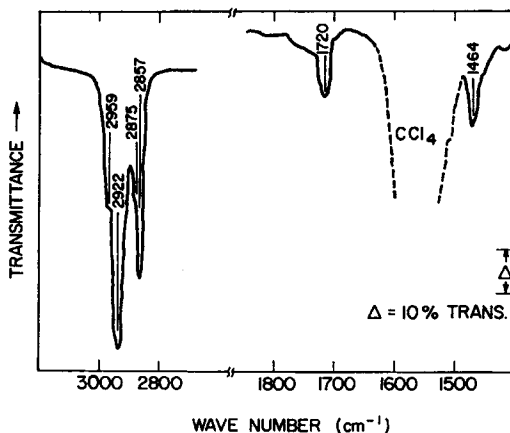


Fig. 7. Infrared spectrum of the solution collected after dipping the corona-treated PE in CCl<sub>4</sub>.

The prevalence of —CH<sub>2</sub>— suggests that the degraded material consisted of short PE chains produced by oxidation and cleavage of the parent polymer. The degradation reaction may occur in many ways, one of which could be the decomposition of hydroperoxides at tertiary carbon atoms.<sup>10</sup>

Samples usually gained between 0.1 and 0.3% in weight after a 30-min corona treatment in oxygen. Increased time of treatment produced no further weight change. However, oxidation as detected by infrared analysis continued for times of treatment much longer than 30 min. Thus it seemed likely that some degraded material evaporated from the sample and thereby compensated approximately for the weight gain due to oxida-

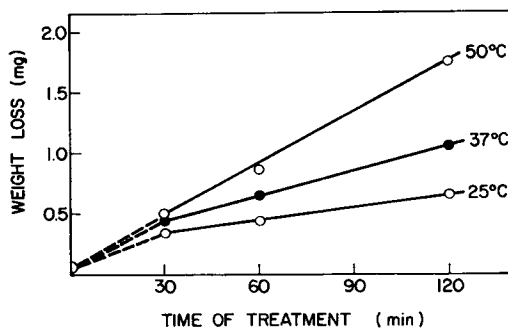


Fig. 8. Net weight loss, after ethanol dipping, against time of treatment in an oxygen corona at various temperatures. Samples were circles 6 cm in diameter cut from the 0.002-in. PE film.

tion of the surface. At higher temperatures and after long times of treatment, waxy materials were deposited on the surface of the glass covering the upper electrode.

After being dipped in solvent, the oxygen-treated samples lost weight. The net weight loss was obtained by subtracting from the weight of the original sheet the weight of the solvent-dipped sample. As shown in Figure 8, the net weight loss increased regularly with time and temperature of treatment in an oxygen corona.

Schonhorn and co-workers<sup>11-13</sup> have pointed out the importance of crosslinking at the surfaces of polymers treated in discharges to increase adhesion. Gel fractions were measured by Soxhlet extraction with toluene for 72 hr using a porous crucible (pore size = 25  $\mu$ ). The crucible was dried in vacuo at 50°C and the gel fraction determined from the weight of the residue retained. For a sample treated in oxygen at 50°C for 1 hr, the gel fraction was only 0.75%. Similar results were obtained for a control sample and also for a sample treated for shorter times. Apparently, therefore, under the conditions used in the present work, crosslinking was a minor reaction in the corona discharge.

## DISCUSSION

Two possible explanations of the corona-induced changes in surface morphology have occurred to us. The first explanation is that the polyethylene possesses an inert skin on its surface which is not much attacked by the active species in an oxygen-containing corona. Degradation of the polymer occurs below this skin and a certain amount of gas is evolved. This may cause the skin to blister and thus give rise to the bumps observed. However, there is no apparent reason why the skin should be removed so cleanly when the treated surface is dipped into ethanol (Fig. 4) or other solvents.

The second explanation was conceived during a careful examination of photomicrographs of the type shown in Figure 2. With increase in the time or the temperature of treatment, the bumps appeared to grow by

migration of bump-forming material rather than by coalescence of several smaller bumps to give a bigger bump. It therefore seemed possible that the bumps consisted of the low molecular weight degradation products which are not linked covalently to the surface and which can migrate to give the characteristic patterns shown in Figure 2. The question then arises as to what is the cause of the surface migration. In a forthcoming report,<sup>14</sup> evidence is presented that treatment in the corona discharge produces long-lived electrical charges on the surface of the polymer. It is likely that such charges are heterogeneously distributed on the surface. Perhaps the degraded material migrates under the influence of electrostatic attraction to the points on the surface where the charge centers are located. With increased time of treatment or at higher temperature of treatment, the pattern of charge distribution may change in such a way that there are fewer but stronger charge centers. This will give rise to fewer but more pronounced bumps. Bumps may also tend to grow because of the electrostatic attraction between the degraded material and the opposite electrode. When the treated sheet is dipped into a suitable solvent, the bumps disappear because the degraded material is removed. Bumps are not produced by corona treatment in nitrogen (or H<sub>2</sub>, He, and A) because no degradation of the surface occurs in these gases.

Of course, the above suggestions are speculation, and further work is required to test which, if either, of the mechanisms proposed is correct. A useful approach would be to devise a method of measuring the surface charge over an area of a few square microns. If charge distribution could then be correlated with bump distribution, this would support the concept that the bumps are produced by the migration of degraded material to charge centers on the surface of the polymer.

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