

## 전기방전에 의한 폴리에틸렌의 산화

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## Oxidation of Polyethylene in an Electrical Discharge

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**요약 :** 저밀도 폴리에틸렌 필름을 코로나방전으로 처리하면 카르보닐기의 농도가 이중결합 농도보다 빨리 증가하며 이 때의 산화기구는 광산화기구와 비슷하다. 방전처리된 물질을 아황산가스로 다시 처리하여 적외선 분광법으로 확인하면 다른 산화방법에 의해서 고분자물질에 생기는 초기 산화물인 과산화물질이 코로나 방전 처리에서도 생성됨을 알 수 있다. 산소코로나방전처리에 의하면 저밀도 폴리에틸렌의 산화속도는 산화성 물질이 고분자 물질 속으로 확산해 들어가는 속도와 비슷하다. 짧은 방전처리시간 동안은 산화활성화 에너지는 9.0kcal/mol이며 이 값은 오존에 의한 산화활성화 에너지와 거의 같다.

**ABSTRACT:** The production rate of carbonyl groups on a LDPE film treated in an oxygen corona discharge shows faster increase than that of ethylenic double bonds to suggest that the corona oxidation follows closely a photo-oxidation mechanism. The formation of hydroperoxides regarded as the primary step in the production of other oxygen containing groups is confirmed in the oxygen corona treatment by detecting the appearance of a sulfate ester band in IR spectra after treatment of the oxidized film with SO<sub>2</sub> gas. The rate of oxidation by the oxygen corona process seems to be controlled by the rate of diffusion of some active species into the bulk of the polymer. In a short time of oxygen corona treatment, activation energy of the oxidation is 9.0 kcal/mol; the value is in good agreement with the value obtained for ozone-oxidation of LDPE.

### INTRODUCTION

Oxidation products of low density polyethylene (LDPE) have been investigated by several authors using infrared spectroscopy<sup>1-5</sup>. After oxidation, changes in the spectra occur corresponding to the formation of hydroxyl, carbonyl,

unsaturated and ether groups. Formation of hydroperoxide and hydroxyl groups produces absorption bands in the region of 3350-3550 cm<sup>-1</sup> for O-H stretching vibration, and 1150-1200 cm<sup>-1</sup> for C-O vibration. The latter region is also assigned to the ether (C-O-C) linkage. The most obvious change in the infrared spec-

trum of a sample exposed to a discharge is the appearance of a strong band at  $1720\text{ cm}^{-1}$  due to carbonyl groups<sup>4</sup>. The carbonyl band at  $1720\text{ cm}^{-1}$  appears almost as early as the  $\text{-OH}$  band of hydroperoxide groups at about  $3500\text{ cm}^{-1}$ <sup>6</sup>, and infrared absorption of the band at  $1720\text{ cm}^{-1}$  is generally regarded as a measure of the degree of oxidation<sup>3,7</sup>.

In this study we try to prove production of hydroperoxides on a LDPE film treated in an oxygen corona discharge and involvement of different oxidation mechanism in the discharge. We also report some measurements of the rate of corona oxidation and from the results attempts to elucidate the rate-controlling process in the reaction.

### EXPERIMENTAL

The sample used was DFD-0111 of Union Carbide and has density, 0.923 and melt index, 5.0. The film was 0.05mm thick and, in all experiments, the inside surface of LDPE tube formed in a blow extrusion was subjected to the corona discharge.

The corona treatment device has been described in a previous paper<sup>8</sup>. Treatment at 15,000v and 60Hz was carried out in an atmosphere of therapy-type oxygen with purity of 96%. The oxygen flow rate into the cell was 50ml per min. at atmospheric pressure.

Oxidation was followed by infrared analysis using a Wilks model 9 single beam multiple internal reflection attachment (MIR) in conjunction with a Unicam SP 200 G IR spectrometer. Samples were mounted on a KRS-5 reflection plate using a torque wrench in order to obtain uniform and reproducible contact.

### RESULTS AND DISCUSSION

The results in Fig 1 show that there is a general similarity in the oxidation of polyethy-

lene (PE) by corona treatment in air and oxygen. However, some differences are evident. The band around  $1720\text{ cm}^{-1}$  increases much less after treatment in air than after treatment in oxygen while the intensity of the band around  $1640\text{ cm}^{-1}$  is relatively higher after application of the air corona. It is probable that the corona discharge in air may produce less available oxidizing species than in oxygen.

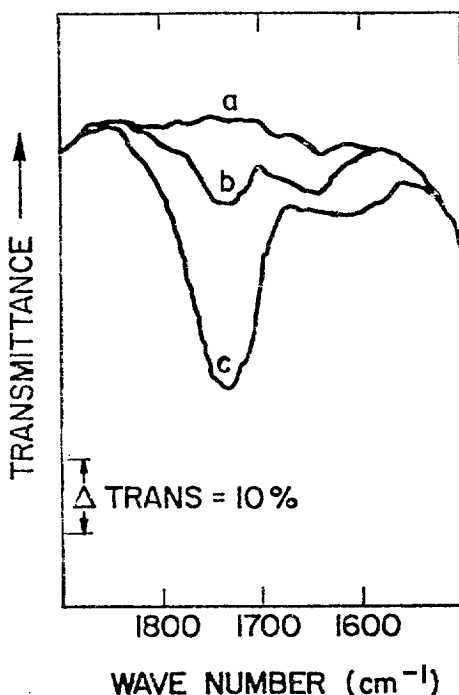
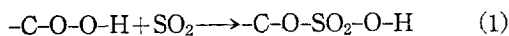


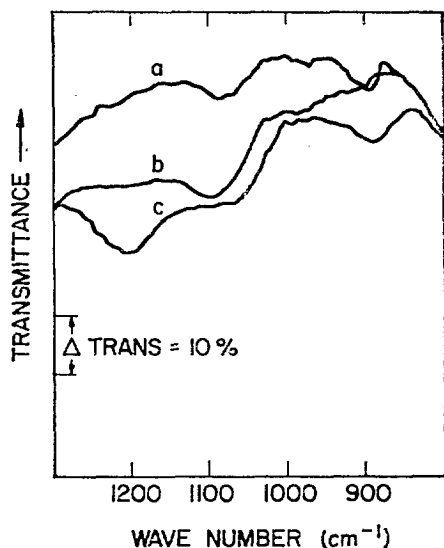
Figure 1. MIR IR spectra of carbonyl and unsaturation stretching regions of PE before and after corona treatment for 60 sec at  $50^{\circ}\text{C}$ , a) untreated control; b) treated in air; c) treated in oxygen.

In one of the important oxidation mechanisms of polymers, the formation of hydroperoxides is regarded as the primary step in the production of other oxygen containing groups<sup>9</sup>. The infrared absorption band at  $3550\text{ cm}^{-1}$  has been used for the detection of  $\text{-O-O-H}$  groups<sup>2,3</sup>.

However, this band is relatively weak and thus is difficult to characterize quantitatively. Mitchell and Perkins<sup>10</sup> demonstrated that hydroperoxide groups in an oxidized polymer could be detected quantitatively by measurement of the band intensity at  $1195\text{ cm}^{-1}$ , (assigned as sulfate ester) after treatment of the oxidized specimen in  $\text{SO}_2$  gas for several hours. The treatment formed sulfate ester as follows:



The method of Mitchell and Perkins was applied in the present work to corona-treated PE in order to confirm the presence of hydroperoxide groups. After treatment in an oxygen corona, the sample was placed in a vacuum desiccator, air was evacuated and then  $\text{SO}_2$  gas was introduced to a pressure of one atm; after 20 hours, the sample was examined in the spectrometer. The spectrum obtained (Fig. 2) shows a distinct band at  $1195\text{ cm}^{-1}$ . Thus it



**Figure 2.** MIR-IR spectra of PE before and after corona treatment for 60 sec. at  $50^\circ\text{C}$ .  
a) untreated control, b) treated in oxygen, c) after exposure of the treated sample to  $\text{SO}_2$  for 20 hr.

seems likely that corona treatment of PE in oxygen produced hydroperoxide groups.

As in Fig 2-b, a general absorption increase of the spectrum background from  $900\text{--}1300\text{ cm}^{-1}$  indicates the formation of oxidation products<sup>2,5</sup>. The intensity of the bands around  $1100\text{ cm}^{-1}$  becomes stronger, which indicates the production of hydroxyl groups by the corona treatment. The increase of the overall intensity of the absorption corresponding to ethylenic double bonds ( $1640\text{ cm}^{-1}$  in Fig. 1)<sup>3,5</sup> with decrease of that of vinylidene groups ( $890\text{ cm}^{-1}$  in Fig. 2-b)<sup>3,5</sup> suggests that the effect of the corona treatment on LDPE has a mechanism similar to that of photo-oxidation rather than thermal oxidation in terms of formation of ethylenic double bonds<sup>1,2</sup>.

Fig. 3 shows the change in the infrared spectrum in the range  $1500\text{--}1900\text{ cm}^{-1}$  produced by treatment in the corona discharge. The band at about  $1720\text{ cm}^{-1}$  is no doubt a composite of many kinds of  $-\text{C}=\text{O}$  groups such as ketones, aldehydes, acids, anhydrides and esters<sup>3,7</sup>.

The absorption at  $1720\text{ cm}^{-1}$  was measured by the base-line technique<sup>11</sup>. In Fig. 4 the increase in absorbance at  $1720\text{ cm}^{-1}$  is plotted against the square root of treatment time at several temperatures. Up to a treatment time of one minute the absorbance,  $A_{1720}$ , seems to follow

$$A_{1720} = k^{\frac{1}{2}}(t - t_0)^{\frac{1}{2}} \quad (2)$$

where  $k$  is the absorption coefficient, and  $t$  and  $t_0$  are a reaction time and an extrapolated zero reaction time of about one second, respectively.

The variation of  $1720\text{ cm}^{-1}$  absorption with the square root of the time suggests that the formation of  $-\text{C}=\text{O}$  is a diffusion-controlled process<sup>12,13</sup>. The Arrhenius plot of  $k$ , in Fig. 5 gives a reasonable straight line and the activation energy is  $9.0\text{ kcal/mol}$ . This is in good agreement with the value of  $9.2\text{ kcal/mol}$  reported

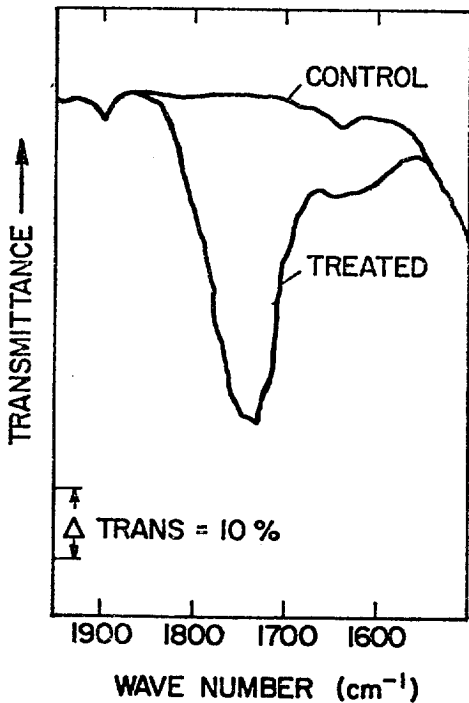


Figure 3. MIR-IR spectra of PE before and after corona treatment for 60 sec at 50°C.  
a) untreated control, b) treated in oxygen.

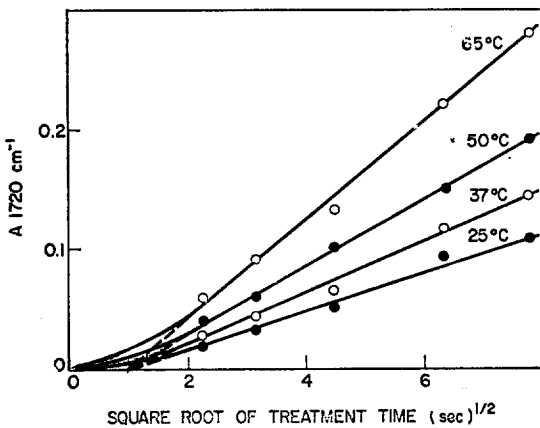


Figure 4. Rate of increase of intensity of the 1720cm⁻¹ band in PE treated in the corona discharge against square root of treatment time.

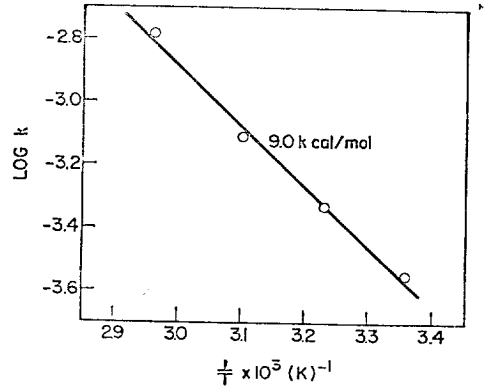


Figure 5. Arrhenius plot of formation of oxidized groups.

by Beachell and Nemphos<sup>6</sup> for ozone catalyzed polyethylene oxidation. The activation energy from Fig. 5 also agrees with the fig of 9.8 kcal/mol for the permeation of oxygen in LDPE

The origin of the one-second induction period is uncertain. Similar induction periods have been noted previously in the oxidation of PE<sup>15,16</sup>. The induction may be related to the time required to build up the concentration of active species in a 60-Hz corona<sup>17</sup>. The results therefore indicate that after an induction period of about one second, the rate of the oxidation process seems to be controlled by rate of diffusion of some active species into the bulk of the polymer. However, this conclusion is probably only valid for times of treatment shorter than a few minutes. For longer treatment times, surface migration of degradation products occurs and some low molecular weight fragments are lost by evaporation<sup>18</sup>. Under such conditions the relationship shown in Fig. 4 will not be obtained.

In conclusion, the corona treatment of LDPE in oxygen follows a mechanism similar to that of photo-oxidation and proceeds by the production of hydroperoxide groups on the treated sample. There is one-second induction period

in oxidation of a LDPE film in the oxygen corona treatment but the origin is uncertain. The rate of the oxidation process seems to be controlled by rate of diffusion of some active species into the bulk of the polymer.

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