# *Oxidative Degradation of Polyethylene in Nitrogen Dioxide**

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The oxidative degradation of polyethylene in the presence of oxygen has been studied by several investigators[1,2]. Oxygen has been reported to react with polyethylene to form hydroperoxide in the early stages of the process. However, the degradation of polymers by reagents other than oxygen has scarcely yet been studied. Only Beachell and Nemphos[3] have studied the degradation of polyethylene in ozone and in fuming nitric acid. They have reported that, at low temperatures, the effect of nitric acid is principally the molecular chain scission, as is seen from the appearance of the C=C stretching band at 1645 cm$^{-1}$ in the infrared region, while at high temperatures nitration becomes the principal reaction. However, it is questionable whether or not it is correct to assign 1645 cm$^{-1}$ to the C=C stretching band as they have done.

The present author's experiments were made on the oxidative degradation of polyethylene in nitrogen dioxide. The oxygenated groups which were produced in polyethylene were identified by the use of infrared absorption spectrometry. Oxidation mechanisms will also be discussed.

## Experimental

The sample used was high pressure polyethylene, a relatively highly-branched polyethylene called Yukalon which is produced by the Mitsubishi Yuka Co., Ltd. Its molecular weight has been determined by viscosity measurement to be 34000. The sample contained no antioxidant.

Nitrogen dioxide was prepared by heating mixtures of lead nitrate and sand at 300°C; it was then dried by passing it through phosphorous pentoxide.

The infrared spectra were recorded with a Perkin-Elmer Model 13, a Perkin-Elmer Model 112, or a Hitachi EPI-S infrared spectrometer equipped with either a sodium chloride prism or a potassium bromide prism for the 4000∼400 cm$^{-1}$ region.

A film specimen, about 0.015 mm. thick and 20×45 mm. in area was prepared by hot moulding, mounted on a glass plate, and placed in a Pyrex cylindrical reaction vessel, 26 mm. in diameter and 22 cm. in length. One-third of the atmospheric nitrogen dioxide gas, free from air, was put into the reaction vessel, and this vessel was heated in a silicone bath controlled at 100±0.05°C. After heating, a thin polyethylene film was peeled off and its spectrum was recorded at room temperature within 3 min. after it had been taken out from the vessel.

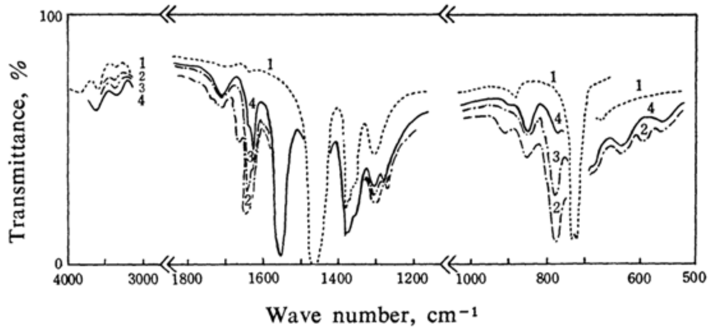

Fig. 1. Infrared spectra of the oxidized polyethylene and their spectral change with the left time in the atmosphere.
1 Original polyethylene
2 Oxidized polyethylene within 3 min. after removal from vessel
3 After 24 hr. in the atmosphere
4 After 2 months in the atmosphere

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[1] F. M. Rugg, J. J. Smith and R. C. Bacon, *J. Polymer Sci.*, **13**, 535 (1954).

[2] J. P. Luongo, ibid., **42**, 139 (1960).

[3] H. C. Beachell and S. P. Nemphos, ibid., **21**, 113 (1956).

## Results

The experimental results are summarized in Table I, while the characteristic spectra of the oxidized polyethylenes and their spectral changes in accordance with the time they were left in the atmosphere are shown in Fig. 1. According to the spectral changes, the observed bands of oxidized specimens can be divided into four categories, i. e., A, B, C and D.

The bands at 1730, 1300, 900 and 1681 $cm^{-1}$ belong to group A and disappear within 24 hr. when the oxidized film is left in the atmosphere. The bands at 1640, 778 and 600 $cm^{-1}$ belong to group B and disappear within two months. On the other hand, the bands at 3400 and 1713 $cm^{-1}$, which belong to group C, gradually increase in intensity. The bands at 1554, 1365, 629, 562, 1635, 1280, 852 and 675 $cm^{-1}$, which fall into group D, did not change. However, when the oxidized film was heated in nitrogen

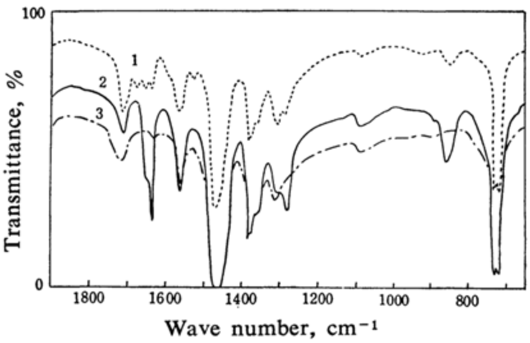

Fig. 2. Infrared spectra of the oxidized polyethylene.

1 Oxidized in fuming nitric acid at room temperature
2 Oxidized in 60% nitric acid at room temperature
3 After the oxidized polyethylene was heated in nitrogen at 200°C.

TABLE I. OXIDATIVE DEGRADATION OF POLYETHYLENE*

| Group | Band** $cm^{-1}$ | Spectral change in the atm. at room temp. | Spectral change in $N_2$ at 200°C | Oxidation in $HNO_3$ at room temp. | Oxidation in fuming $HNO_3$ at room temp. | Oxidation in the air at room temp. | Assignment |
|---|---|---|---|---|---|---|---|
| A | 1713 | Disap. within 24 hr. | Disap. | — | — | — | $HNO_3$ |
| | 1300 | | | | | | $HNO_3$ |
| | 900 | | | | | | $HNO_3$ |
| | 1681 | | | | | | Nitrite ester group trans N=O str. |
| B | 1640 | Disap. within 2 months | Disap. | — | — | — | Nitrite ester group cis N=O str. |
| | 778 | | | | | | Nitrite ester group trans N-O str. |
| | 600 | | | | | | Nitrite ester group cis O-N=O bend. |
| C | 3400 | Increase | Increase | App. | App. | App. | Hydrogen bonded O-H str. |
| | 1713 | | | | | | C=O str. |
| $D_1$ | 1554 | Stable | Stable | App. | App. | — | Nitro group $NO_2$ asym. str. |
| | 1365 | | | | | | Nitro group $NO_2$ sym. str. |
| | 629 | | | | | | Nitro group $NO_2$ bend. |
| | 562 | | | | | | Nitro group $NO_2$ bend. |
| $D_2$ | 1635 | Stable | Stable | App. | App. | — | Nitrate ester group $NO_2$ asym. str. |
| | 1280 | | | | | | Nitrate ester group $NO_2$ sym. str. |
| | 852 | | | | | | Nitrate ester group N-O str. |
| | 675 | | | | | | Nitrate ester group $NO_2$ bend. |

* Abbreviation: atm. atmosphere, tem. temperature, disap. disappear, app. appear, str. stretching vibration, bend. bending vibration, asym. asymmetric, sym. symmetric

** Observed bands in the polyethylene oxidized by nitric dioxide at 200°C for 20 min., the bands in group A and group B and some of those in group D, namely, 1635, 1280, 852 and 675 cm$^{-1}$, disappeared. Therefore, group D can be subdivided into group $D_1$, which did not disappear upon heating, and group $D_2$, which disappeared upon heating. When polyethylene was aged in nitric acid (more than 60% concentration) at room temperature (Fig. 2), the bands in groups C and D were observed, but those in groups A and B were not.

### Assignment

Rigg⁴⁾ identified nitroalkanes, alkyl nitrates and alkyl nitrites as reaction products by means of the infrared analysis of an irradiated mixture of *n*-dodecane and nitrogen dioxide. Brand and Stevens⁵⁾ also identified nitro alkanes and alkyl nitrates as products in the reactions between nitrogen dioxide and olefins, e. g., cyclohexene and cyclopentene.

As, however, the data obtained above were insufficient for the intended assignment, several compounds were synthesized whose infrared spectra were measured for the assignment. On the basis of these findings, together with changes of observed bands upon various treatments, the assignments of the observed bands were determined as follows:

**$D_2$ Group.**—The infrared spectrum of 2-ethylhexyl nitrate, which had been prepared from 2-ethylhexyl alcohol⁶⁾, was observed (Fig. 3). The bands other than those due to 2-ethylhexyl alcohol were regarded as bands due to the nitrate group. The locations of the oxygenated groups of polyethylene were compared with those of alkyl nitrate, and it was shown that the bands which belonged to the $D_2$ group are to be assigned to the nitrate ester group. This assignment is shown in the last column of Table I, with reference to the results on alkyl nitrates given by Brown⁷⁾ and by Brand and Cawthon⁸⁾.

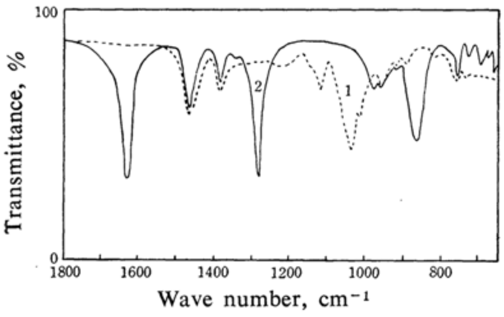

Fig. 3. Infrared spectra of 2-ethylhexyl alcohol (1) and 2-ethylhexyl nitrate (2).

**$D_1$ Group.**—By comparison with the data on various types of nitroalkanes reported by Smith et al.⁹⁾ and by Pierson et al.¹⁰⁾, the bands in the $D_1$ group were assigned to the nitro group.

**C Group.**—The bands at 3400 and 1713 cm$^{-1}$ were also observed when the oxidation of polyethylene was carried out in the presence of oxygen (Fig. 4). The band at 3400 cm$^{-1}$ was assigned to hydrogen-bonded hydroxyl group by reference to the data on low molecular weight compounds¹¹⁾. Rugg et al.¹⁾ and Loungo²⁾ also assigned these bands to the hydroxyl group and carbonyl group respectively.

**A and B Groups.** — The infrared spectra of low-molecular-weight alkyl nitrites were measured. These compounds had various types of branches, ranging from ethyl nitrite to octyl nitrite. They were prepared by the ordinary synthetic method from alcohols. It was shown that the band at 1681 cm$^{-1}$ in A group and the bands in B group are to be assigned to the nitrite ester group, as may be seen in the last column of Table I, by reference to the data of Tarte¹²⁾, Haszeldine and Mattinson¹³⁾ and Bellamy et al.¹⁴⁾

Beachell and Nemphos³⁾ assigned the band at 1640 cm$^{-1}$ to the C=C stretching band. When the thermal degradation of polyethylene was carried out at 350~370°C for 20 min. in nitrogen, the C=C stretching band was observed at 1640 cm$^{-1}$. At the same time, four strong bands which were attributable to C–H out of plane vibrations were observed at 900~1000 cm$^{-1}$ (Fig. 4), whereas when the oxidative degradations were carried out in nitrogen dioxide, the bands at 900~1000 cm$^{-1}$ were not observed. Similarly, the bands at 900~1000 cm$^{-1}$ were not observed in the oxidative degradations in fuming nitric acid or in 60% nitric acid at room temperature (Fig. 2). Moreover, when those double bonds of the polyethylene which had been produced by the thermal degradation were brominated, the bands at 1640 cm$^{-1}$ and 900~1000 cm$^{-1}$

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4) T. Rigg, *Nature*, **187**, 933 (1960).

5) J. C. D. Brand and I. D. R. Stevens, *J. Chem. Soc.*, **1958**, 629.

6) R. L. Shriner and E. A. Parker, *J. Am. Chem. Soc.*, **55**, 766 (1933).

7) J. F. Brown, ibid., **77**, 6341 (1955).

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10) P. H. Pierson, A. N. Fletcher and E. S. C. Cantz, *Anal. Chem.*, **28**, 1218 (1956).

11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", 2 nd Ed., John Wiley & Sons, Inc., New York (1958).

12) P. Tarte, *J. Chem. Phys.*, **20**, 1570 (1952).

13) R. N. Haszeldine and B. J. Mattinson, *J. Chem. Soc.*, **1954**, 691, 4172.

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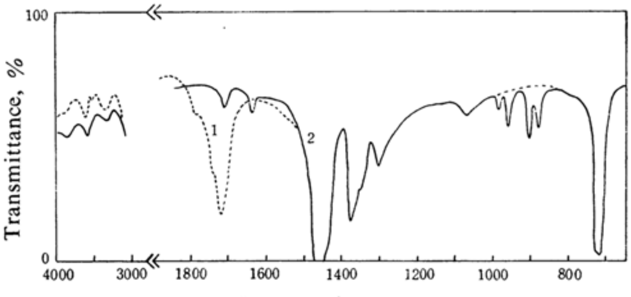

Fig. 4. Infrared spectra of oxidized polyethylene.
1 Thermal oxidation in the air (at 150°C)
2 Thermal degradation in nitrogen (at 350°C)

disappeared and a new band appeared at 573 cm$^{-1}$. This new one is attributable to the C–Br stretching band(11). However, when the polyethylene which had been oxidized in nitrogen dioxide was brominated, the band at 1640 cm$^{-1}$ disappeared, but the new band did not appear. Therefore, it would be erroneous to assign the band at 1640 cm$^{-1}$ to the C=C stretching band, as was proposed by Beachell and Nemphos(3).

In the case of low-molecular-weight alkyl nitrites, the intensities of the trans N=O stretching at 1681 cm$^{-1}$ are stronger than those of the cis N=O stretching at 1620 cm$^{-1}$, as may be seen in Fig. 5, but the reverse is true of the nitrite ester groups in polyethylene (Fig. 1). By preservation of oxidized products in a vessel cooled by a mixture of dry ice and *n*-heptane, the bands at 1730, 1300, 900 and 1681 cm$^{-1}$ in group A could be preserved for more than a week before they disappeared (Fig. 6). When they were kept in a vacuum desiccator with phosphorous pentoxide, the band at 1681 cm$^{-1}$ did not disappear until after more than a week, but the bands at 1730, 1300 and 900 cm$^{-1}$ went away within 24 hr., as when the samples were left in the atmosphere. The prevention of the disappearance of the band at 1681 cm$^{-1}$ was greater in a cool place.

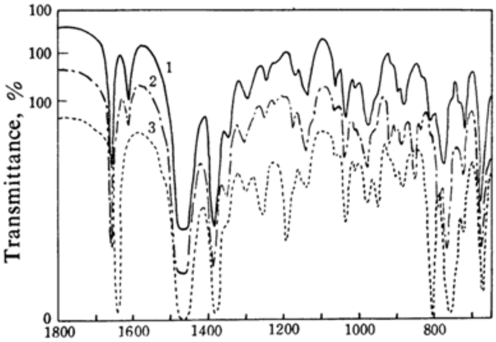

Fig. 5. Infrared spectra of alkyl nitrites.
1 *n*-Butyl nitrite
2 *sec*-Butyl nitrite
3 *tert*-Butyl nitrite

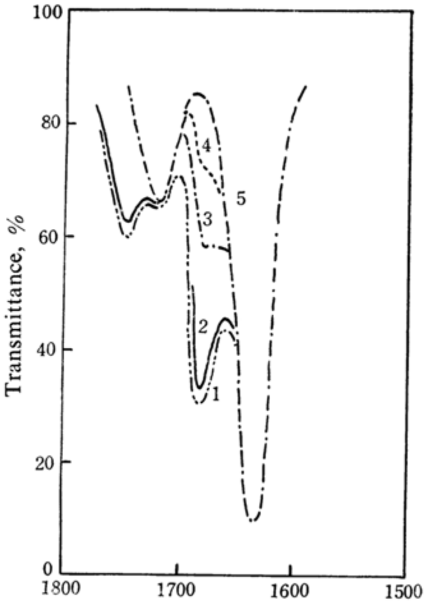

Fig. 6. Spectral change of the band at 1681 cm$^{-1}$.
1 Oxidized polyethylene
2 Kept 8 days at dry ice-*n*-heptane temperature
3 Kept 8 days in vacuum desiccator with $P_2O_5$
4 Left 30 min. in the atmosphere
5 Left 3 days in the atmosphere

The intensities of bands in the A group decreased as the reaction gas or the produced gas was removed from the polymer. As for the band at 1681 cm$^{-1}$, it seemed that the above process was not responsible for its disappearance, because when the oxidized films were left in a desiccator, the band did not disappear. However, the bands at 1730, 1300 and 900 cm$^{-1}$ could be attributed to the production of nitric acid in view of the location of the absorption bands, their relative intensities[15], and the fact that when the products were placed in a desiccator, the bands at 1730, 1300 and 900 cm$^{-1}$ disappeared. It seems that the rate of disappearance of the band at 1681 cm$^{-1}$ depends on the temperature, but it is not clear why the intensity of the trans N=O is weaker than that of the cis N=O in the polymer. This problem should be investigated in the future.

## Discussion

The kinetic studies of polyethylene oxidations in nitrogen dioxide were made on the basis of the identification of the groups which were formed in polyethylene during oxidation and of the rates of formation of groups (Fig. 7). The bands used for the studies were 1554 (nitro group), 778 (nitrite ester group), 852 (nitrate ester group) and 1713 cm$^{-1}$ (carbonyl group). As may be seen in Fig. 7, the nitro group and the nitrite ester group were produced in the early stages; the intensity of the nitro group increased constantly, while that of the nitrite ester group reached its maximum point and even began to level off in five hours. On the other hand, the nitrate ester group and the carbonyl group did not appear in the early stages; they appeared after the nitro group and some of the nitrite ester groups had been formed.

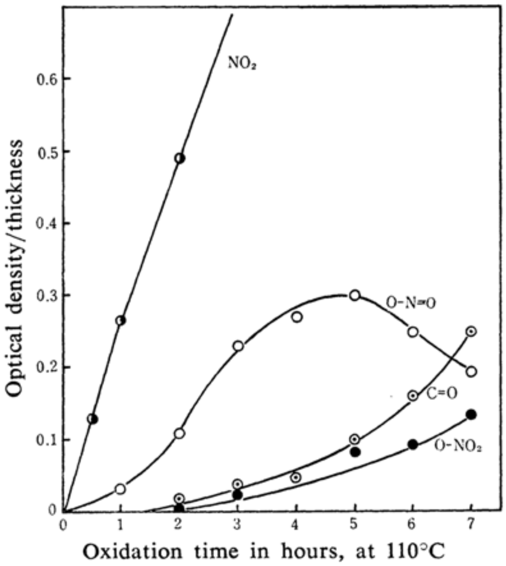

Fig. 7. Rate of formation of oxygenated groups in polyethylene.

As nitrogen dioxide gas has an odd electron structure, it may be expected to combine with radicals easily[4,16]. Therefore, it seems that in the early stages the nitro groups and the nitrite ester groups are produced by the reaction of activated polyethylene with nitrogen dioxide in terms of the $\dot{R}+\dot{N}O_2 \rightarrow RNO_2$ and $\dot{R} + \dot{O}NO \rightarrow RONO$ processes. The carbonyl groups and the nitrate ester groups were produced as decomposition products of the nitro and the nitrite ester groups in the secondary state. Gray et al.[17] have identified aldehyde and ketone as decomposition products of the pyrolyses of alkyl nitro compounds, especially nitroethane, at temperatures between 240 and 800°C. As the intensity of the nitro group did not change when the oxidized products were left in the atmosphere, and as the change in intensity was only a little when the products were heated at 200°C in nitrogen gas, it seems that the nitro group formed in polyethylene is relatively stable. On the other hand, as the intensity of the nitrite ester group decreased when the oxidized products were left in the atmosphere, the nitrite ester group seems to be unstable.

Phillips[18] has identified methyl alcohol, formaldehyde and hydrogen cyanide as the decomposition products of the pyrolysis of methyl nitrite. Levy[19] has identified not only isopropyl alcohol and acetone, but also such chain scission products as acetaldehyde and hydrogen cyanide as the thermal decomposition products of isopropyl nitrite, while for ethyl nitrite he has identified acetaldehyde and ethyl alcohol. Gray and Williams[20] and Pollard et al.[21] have suggested that alkyl nitrate is produced by the pyrolysis of alkyl nitrite in the presence of nitrogen dioxide. From the present analyses of the infrared spectra of the oxidized products, the carbonyl, hydroxyl and nitrate ester groups have been identified and it seems that these are mainly the decomposition products of the nitrite ester group, because the nitrite ester group is unstable, as has been mentioned above.

On the basis of the mechanisms which have been proposed by several investigators for the pyrolyses of alkyl nitrite[18,19,22] and alkyl nitrate[20] and for the photolysis of alkyl

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nitrite[23], the following mechanisms may be considered:

$$\mathrm{RH} \xrightarrow{\text{activated}} \dot{\mathrm{R}} + \dot{\mathrm{H}} \quad \mathrm{RH}\text{; polyethylene}$$

In early stages:

$$\dot{\mathrm{R}} + \dot{\mathrm{N}}\mathrm{O_2} \rightarrow \mathrm{RNO_2}\text{; nitro group}$$

$$\dot{\mathrm{R}} + \dot{\mathrm{O}}\mathrm{NO} \rightarrow \mathrm{RONO}\text{; nitrite ester group}$$

In secondary stages:

$$\mathrm{RONO} \rightarrow \mathrm{R}\dot{\mathrm{O}} + \dot{\mathrm{N}}\mathrm{O}\text{; O–N fission}$$

$$\mathrm{R}\dot{\mathrm{O}} + \dot{\mathrm{N}}\mathrm{O_2} \rightarrow \mathrm{RONO_2}\text{; nitrate ester group}$$

$$\left.\begin{array}{lll} \mathrm{R'CH_2}\dot{\mathrm{O}} & \rightarrow \mathrm{R'CHO} & + \dot{\mathrm{H}} \\ \mathrm{R''R'''CH}\dot{\mathrm{O}} & \rightarrow \mathrm{R''R'''CO} & + \dot{\mathrm{H}} \\ \mathrm{R''R'''CH}\dot{\mathrm{O}} & \rightarrow \mathrm{R''CHO} & + \dot{\mathrm{R}}''' \end{array}\right\} \begin{array}{c}\text{carbonyl}\\ \text{group}\end{array}$$

$$\mathrm{R}\dot{\mathrm{O}} + \dot{\mathrm{H}} \rightarrow \mathrm{ROH}\text{; hydroxyl group}$$

$$\mathrm{RONO_2} \rightarrow \mathrm{R}\dot{\mathrm{O}} + \dot{\mathrm{N}}\mathrm{O_2}$$

In our study no decision was made whether the nitro group or the nitrite ester group was produced in the greater amount, for the absolute intensity of the nitrite ester group has not yet been obtained.

## Conclusion

From analyses of the infrared spectra of polyethylene oxidized in nitrogen dioxide, the formation of the nitro, nitrite ester, nitrate ester, carbonyl and hydroxyl groups have been identified. In early stages, the nitro group and the nitrite ester group were produced by the addition of nitrogen dioxide to the activated position of polyethylene. The nitrate ester, carbonyl and hydroxyl groups were produced as decomposition products of the two aforementioned groups, mainly the nitrite ester group.

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