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PHOTO- AND THERMOOXIDATIVE DEGRADATION OF POLYETHYLENE-POLYPROPYLENE BLENDS: COMPARISON OF OXIDATION PRODUCTS†

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ABSTRACT

The photo- and thermooxidative degradation of various polyethylene–polypropylene (PE–PP) blends (5–80 wt% polyethylene) in air at 60 and 80°C, respectively, have been studied by Fourier-transform infrared spectroscopy. The oxidized samples were reacted with gaseous NH_3, SF_4, and NO for rapid identification and resolution of the various carbonyl species, alcohols, and hydroperoxides. The oxidative degradation results are compared with those of corresponding homopolymers. All the samples gave similar oxidation products but in varying quantities depending upon the composition of the sample. The kinetics of oxidation is presented. The oxidation behavior of PE–PP blends changes gradually from pure PE to isotactic polypropylene. The rate of hydroperoxidation of the blends is an increasing function of the propylene content.

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INTRODUCTION

Many studies on the photodegradation of PE and PP blends by ultraviolet/visible light [1-3] and heat [4,5] have received extensive attention during the past decade. The fundamental and practical aspects of the chemical changes in these polymers in the solid state have been recognized, and it has been observed that the basic reaction in photooxidative degradation is similar to what occurs in thermal oxidative degradation. The photo- and thermooxidative degradation in the solid phase of various heterophasic ethylene-propylene copolymers with different ethylene weight ratio has been described [6-8].

At present, interest is growing in polymer blends due to the feasibility of varying properties of the materials within wide limits that may modify the properties such as tensile strength and impact strength. Numerous papers have appeared in connection with the preparation and mechanical properties of polyolefin blends. However, there appears to be lack of information regarding oxidative stability of ethylene-propylene blends.

In the present investigation the photo- and thermooxidative degradation of various ethylene-propylene blends with different ethylene ratios is described. The oxidation of these blends has been compared with those of their homopolymers. We herein report the use of derivatization techniques using NH_3, SF_4, and NO for a systematic comparison of the oxidation degradative products with the aim of identification of the actual oxidation site in E-P blends.

EXPERIMENTAL

Materials

The ethylene-propylene (E-P) blends were obtained in the form of 100-200 μm thick films from Essochem (Europe). Comparisons are given in Table 1.

Procedure

For photooxidation, the samples were irradiated at 60°C in Sepap 12/24, as described elsewhere [6]. The temperature of the films under irradiation was strictly controlled by using a thermocouple in contact with the samples. The samples were irradiated uniformly on a rotating support. All the samples were irradiated in Sepap 12/24 for 20 hours at 60°C in order to curtail the induction period in thermal

TABLE 1.

Sample	Weight % of ethylene
I	5.0
II	20.0
III	50.0
IV	80.0

exposure. The preirradiated samples were thermally treated in a forced air circulation oven at 80°C for various periods.

The oxidative products were identified with good resolution by Fourier-transform infrared (FT-IR) spectroscopy (Nicolet 5 SX spectrometer). The oxidized films were exposed to each reactive gas at room temperature in a simple flow system that could be sealed off by valves to allow the reaction to proceed. The gases used included NH_3, SF_4, and NO. The NO reaction was performed with films at −20°C. To prevent NO_2 formation from the NO-O_2 reaction, films were swept with nitrogen for about 5 minutes prior to NO introduction. Since SF_4 attacks glass, this reaction was carried out in a Teflon bottle. From changes in FT-IR, it was inferred that reactions were virtually completed in 3 hours for NH_3, 24 hours for SF_4, and 72 hours for NO.

RESULTS AND DISCUSSION

Changes in Hydroxyl and Carbonyl Regions

Thermooxidation of preirradiated (20 hour photoirradiated initially) and that of photoirradiated E-P blend films at 80 and 60°C, respectively, led to development of IR bands in the hydroxyl and carbonyl regions. A very broad hydroxyl and hydroperoxide absorption (3700–3200 cm^{-1}) with a maximum centered at 3400 cm^{-1} appeared (Figs. 1 and 2) in all the samples. The changes are very similar in thermooxidative and photooxidative degradation from the point of view of the nature of oxidation products. The broad band at ~3400 cm^{-1} is due to neighboring intramolecular hydrogen-bonded hydroperoxides and alcohols. Hydrogen-bonded

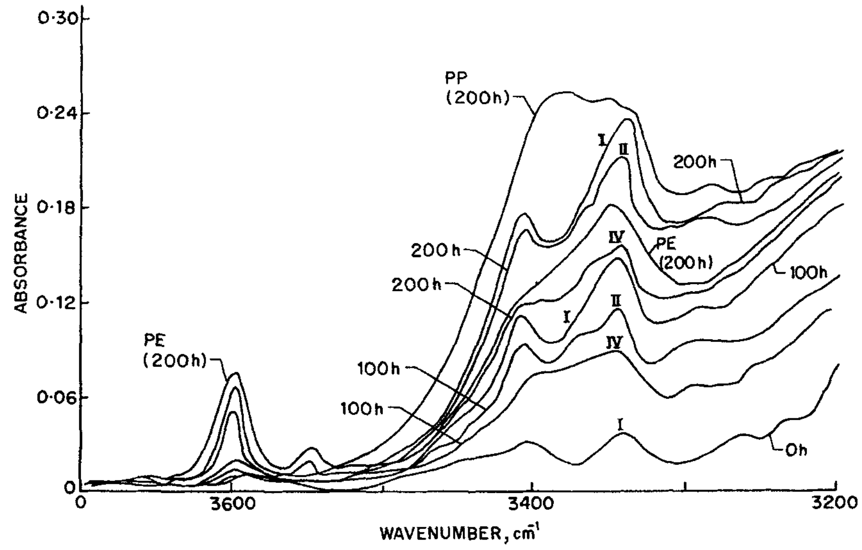


FIG. 1. FT-IR spectral changes in hydroxyl region during thermal treatment of E-P blends at 80°C.

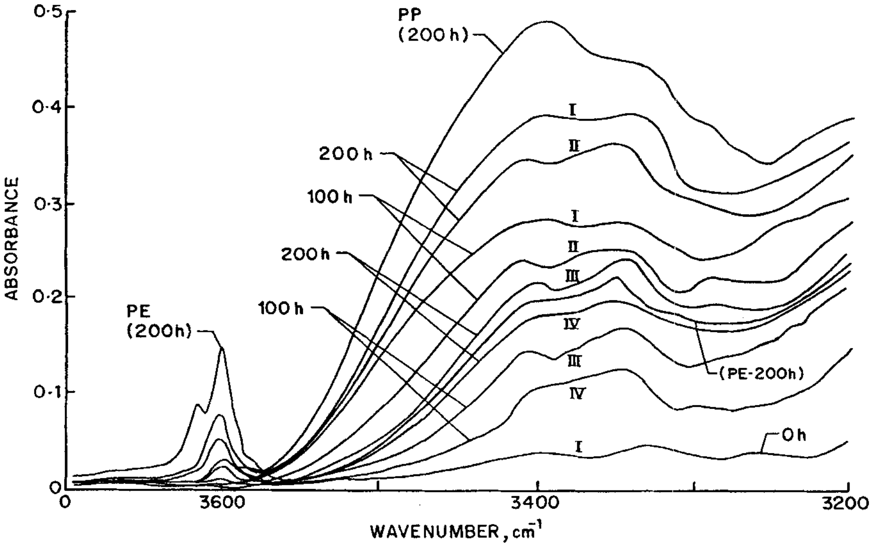


FIG. 2. FT-IR spectral changes in hydroxyl region of polychromatic irradiated E-P blends.

hydroperoxides (3420 cm^{-1}) and associated alcohols (3380 cm^{-1}) were also present. The absorption in the hydroxyl region is wider and more intense in PP, I, and II but comparatively less intense in Samples III, IV, and PE. The intensity of photooxidation is more than thermooxidation in all the samples. An absorption (3552 cm^{-1}) due to isolated hydroperoxides is significant in PE, III, and IV in thermooxidized films. A medium intensity band at 3615 cm^{-1}, due to an isolated hydroxyl band in tertiary alcohol, appeared in thermo/photooxidation but is absent in PP and PE samples. The isolated tertiary alcohols and associated tertiary alcohols indicate the contribution of isolated PP units, whereas associated hydroperoxides are formed on PE segments.

The carbonyl region (1900–1600 cm^{-1}) showed several overlapping absorption bands (Figs. 3 and 4). This region is broad for PP, I, and II but sharp and narrow for PE, III, and IV samples. The absorptions at 1712, 1723, 1740, and 1785 cm^{-1} have been assigned to carboxylic acid, ketone, ester, and γ-lactone, respectively. Vinylidene-type unsaturation, resulting from disproportionation during decomposition of PP units, was detected at 1640 cm^{-1} for longer exposure times. A negligible γ-lactone formation was found in PE, III, and IV in thermooxidation, but this band was easily detected in photooxidation [9]. The carbonyl region increases with time in both thermo- and photooxidation, but the development is faster in photoirradiation. It is evident from infrared spectra that the samples do not behave differently in many aspects. The degradation is maximum in PP and minimum in PE in both types of degradation under similar conditions, while the other samples showed intermediate behavior.

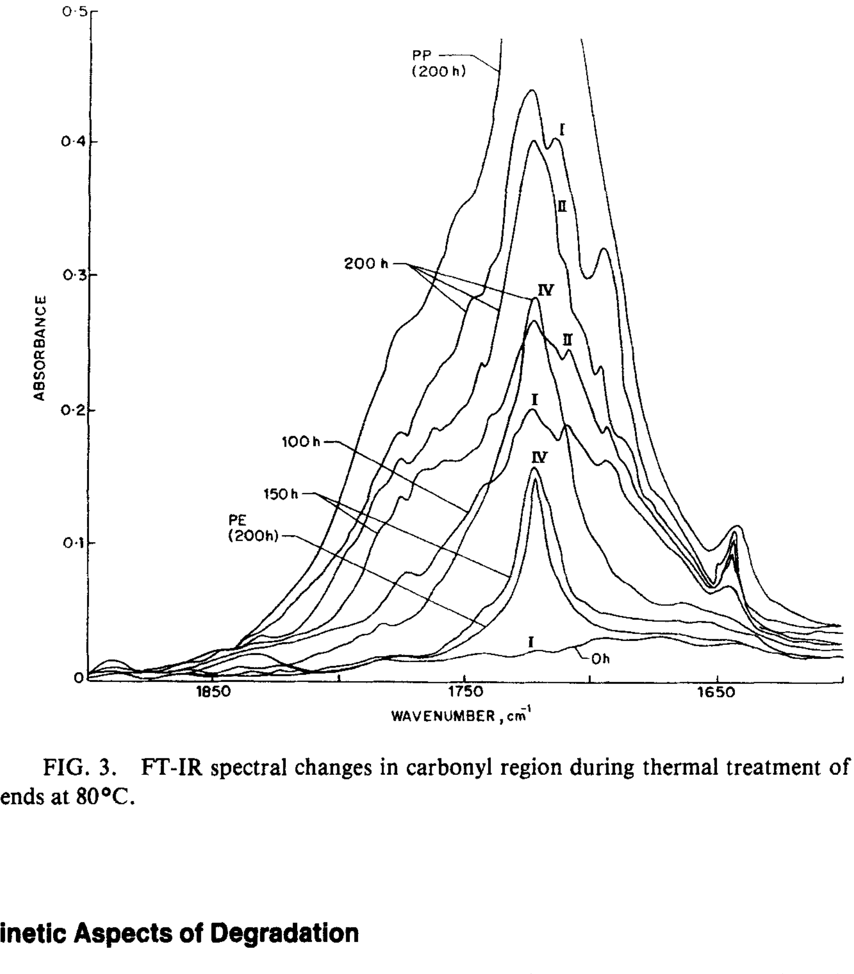


FIG. 3. FT-IR spectral changes in carbonyl region during thermal treatment of E-P blends at 80°C.

Kinetic Aspects of Degradation

The rate of hydroperoxidation increases with time of exposure, but the increase in hydroperoxide group concentration is maximum in PP and decreases with increasing ethylene content (Fig. 5). The same behavior was also observed in the amount of carbonyl group formation (Fig. 6). This is because the hydroperoxide/hydroxyl and carbonyl group formation are minimum in PE and maximum in PP. On prolonged exposure, hydroxyl/carbonyl regions reach a stationary concentration in both types of degradation. It is also apparent from the curves that the saturation limit is not reached in PP samples under our experimental conditions.

It is concluded from these observations that I and II show an oxidation behavior similar to that of PP whereas III and IV resemble PE. Thus the oxidation behavior changes with ethylene content in E-P blends.

Derivatization Reactions

The complex nature of the carbonyl envelope was simplified, separated, and analyzed by derivatization reactions with polymeric acids. In a series of reactions,

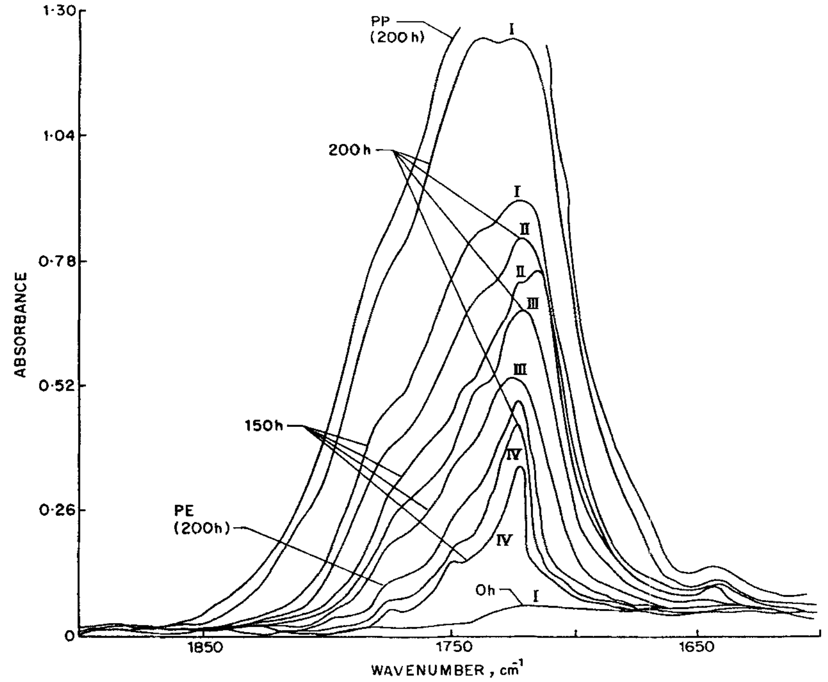
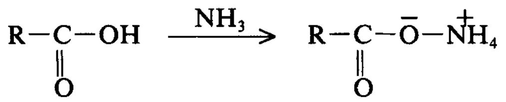


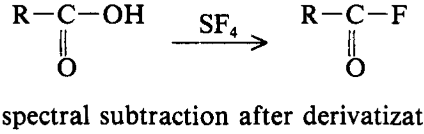
FIG. 4. FT-IR spectral changes in carbonyl region of polychromatic irradiated E-P blends.

gaseous ammonia reacted with oxidized film, and the ammonium carboxylate formation [10] was observed at 1555 cm^{-1}:



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-OH \xrightarrow{NH_3} R-\underset{\underset{\displaystyle O}{\|}}{C}-\bar{O}-\overset{+}{N}H_4$$

The ammonium salt formation (Fig. 7) is quantitative, i.e., maximum in I and minimum in IV. However, these absorptions are very broad, and the method is inferior to acid measurement by SF$_4$ derivatization. The SF$_4$ exposure of the oxidized films causes complete loss of all hydroxyl absorptions and generates acyl fluorides at 1840–1848 cm^{-1}:



$$R-\underset{\underset{\displaystyle O}{\|}}{C}-OH \xrightarrow{SF_4} R-\underset{\underset{\displaystyle O}{\|}}{C}-F$$

The spectral subtraction after derivatization is much more informative and shows the loss and formation of species.

The thermo- and photooxidized samples give rise to distinctly different acyl fluoride absorption as shown in the subtraction of the spectra for nonoxidized film from that of SF$_4$-treated oxidized film in Fig. 8. The absorbance of III and IV after treatment lies at 1848 cm^{-1}. This is attributed [6] to chain-end acid fluoride on the PE backbone:

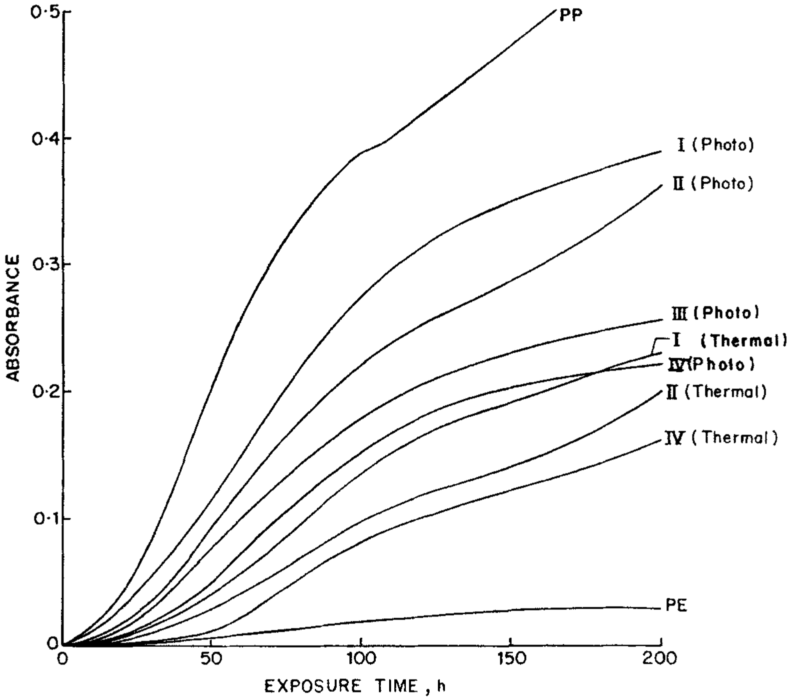


FIG. 5. Rate of hydroxyl group formation during thermal-polychromatic irradiation.

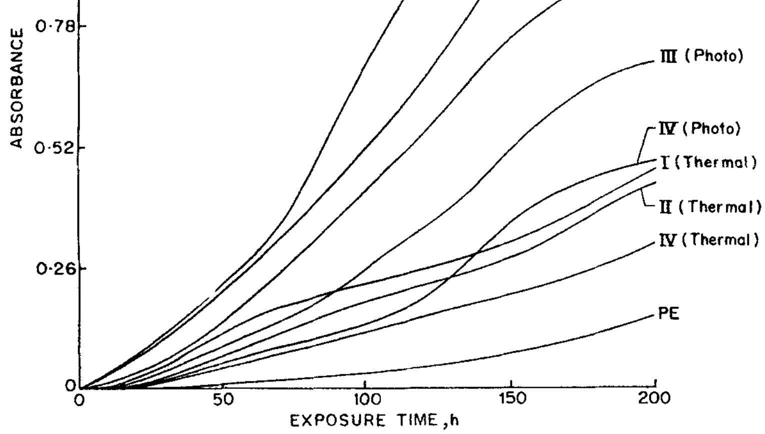


FIG. 6. Rate of carbonyl group formation with time during thermal-polychromatic irradiation.

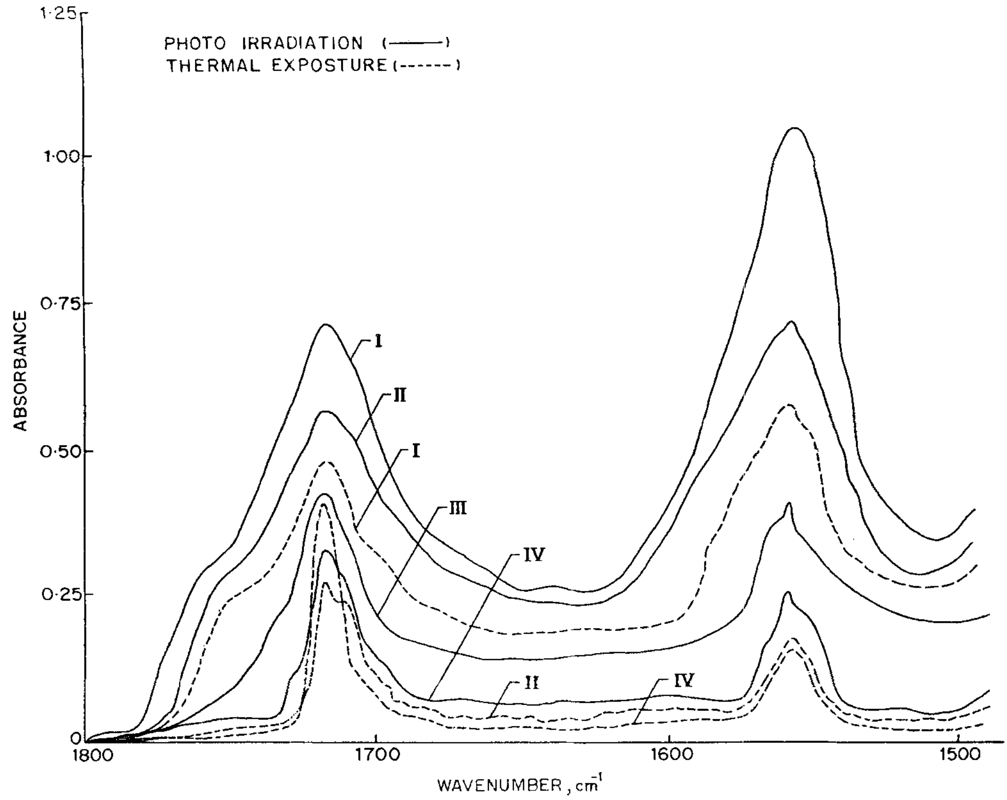
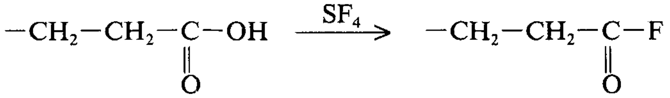
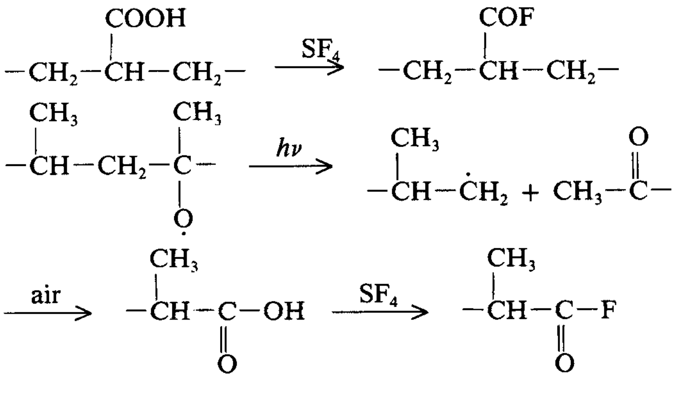


FIG. 7. Changes in carboxylate ion concentration of 200 hours thermal-photooxidized E–P blend films after ammonia treatment.



$$-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{SF_4} -CH_2-CH_2-\underset{\underset{O}{\|}}{C}-F$$

After exposure to SF_4 gas, the oxidized PP chain absorbs at 1841 cm^{-1}. The carboxylic acid group in this case arises from the free-radical oxidation of the methyl group and β-scission of chain-end alkoxy radicals [11]:



$$-CH_2-\overset{\overset{COOH}{|}}{C}H-CH_2- \xrightarrow{SF_4} -CH_2-\overset{\overset{COF}{|}}{C}H-CH_2-$$

$$-\overset{\overset{CH_3}{|}}{C}H-CH_2-\underset{\underset{\dot{O}}{|}}{\overset{\overset{CH_3}{|}}{C}}- \xrightarrow{h\nu} -\overset{\overset{CH_3}{|}}{C}H-\dot{C}H_2 + CH_3-\overset{\overset{O}{\|}}{C}-$$

$$\xrightarrow{air} -\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{O}{\|}}{C}-OH \xrightarrow{SF_4} -\overset{\overset{CH_3}{|}}{C}H-\underset{\underset{O}{\|}}{C}-F$$

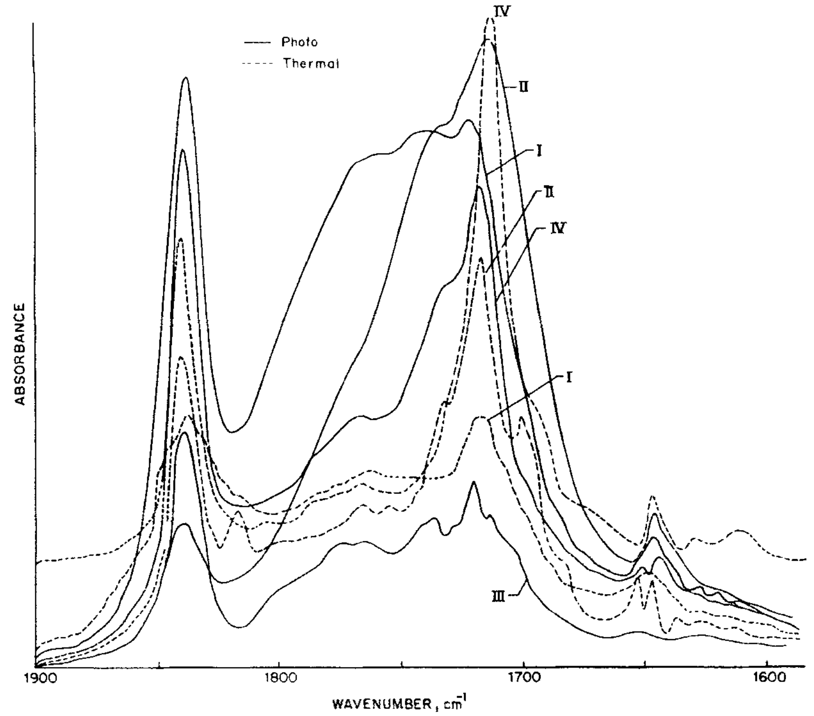
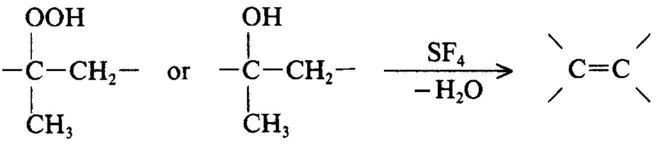


FIG. 8. FT-IR spectral changes upon thermal-photooxidization (200 hours), then SF_4 treated, and the corresponding nonoxidized E-P blend films subtracted.

After SF_4 treatment the carboxyl region reveals the presence of unsaturation at 1640 cm^{-1} due to dehydration of tertiary hydroxyl/hydroperoxide groups:



$$-\overset{\overset{\Large OOH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_2- \quad \text{or} \quad -\overset{\overset{\Large OH}{|}}{\underset{\underset{\Large CH_3}{|}}{C}}-CH_2- \xrightarrow[-H_2O]{SF_4} \;\; >C=C<$$

This unsaturation is more prominent in I and II due to the large content of PP, and therefore the comparatively larger quantities of hydroperoxides and alcohols in these samples. This means that initial oxidation occurs in the PP phase.

The derivatization of oxidized E-P blends using nitric oxide (NO) proved to be very informative for product identification. The NO gas reacts with hydroperoxides and alcohols to give nitrates and nitrites, respectively:

$$ROOH \xrightarrow[-20°C]{NO} RONO_2 \text{ (nitrate)}$$

$$ROH \xrightarrow[-20°C]{NO} RNO_2 \text{ (nitrite)}$$

It is essential to work at −20°C to react peroxy radicals smoothly and to identify and quantify tertiary nitrates accurately because they decompose rapidly at

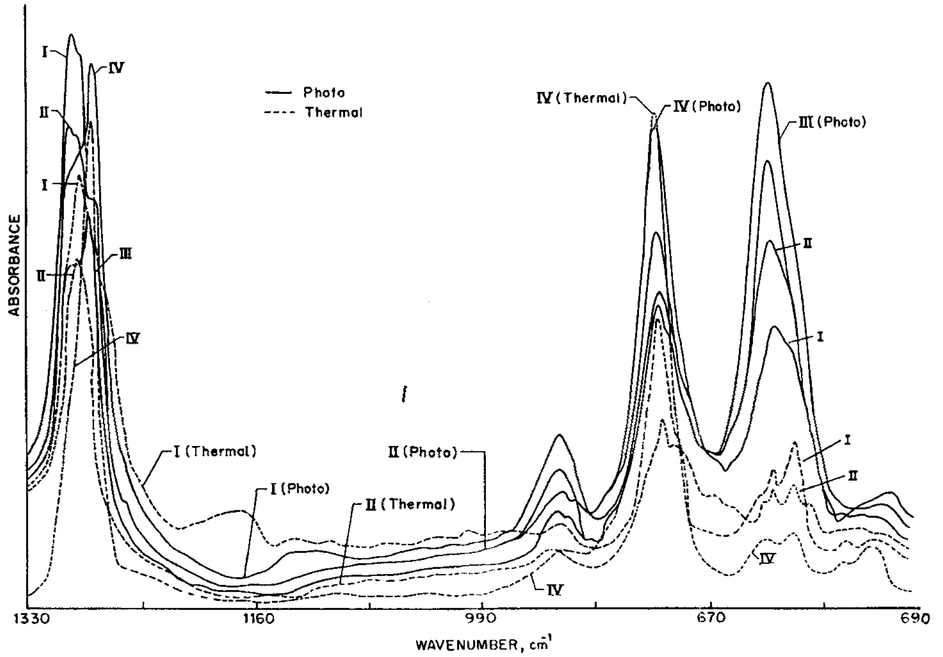


FIG. 9. FT-IR spectral changes of thermal-photooxidized (150 hours) E-P blend films. Spectral substraction of oxidized film from corresponding oxidized and NO treated.

room temperature. Carlsson et al. [10] exploited the sharp and intense IR absorptions arising from derivatization to nitrates and nitrites to differentiate primary, secondary, and tertiary species and to identify precisely the hydroperoxide and alcoholic products in the oxidized blends. The NO-treated oxidized III and IV films show a symmetrical nitrate absorption at 1276 cm^{-1} from secondary hydroperoxide and a small secondary nitrite peak at 778 cm^{-1} from secondary alcohol (Fig. 9). The oxidized I and II films show a much more complex behavior and yield prominent absorptions at 1302 and 1290 cm^{-1} with small absorptions at 760 and 778 cm^{-1}. Carlsson et al. [12] attributed nitrite formation with NO at the chain-end (1302 cm^{-1}) and along the backbone (1290 cm^{-1}) of the PP segment in the blend. The absorptions at 760 and 778 cm^{-1} are due to tertiary and secondary nitrites, respectively. Upon derivatization, I and II show a behavior similar to PP whereas samples III and IV are similar to PE. However, primary hydroperoxide/alcohols were not detected in any of the samples in thermo- and photooxidation.

CONCLUSION

The basic reaction in thermo- and photooxidation is similar from the point of view of the nature of the oxidation products. The extent of degradation in the blend depends upon the ethylene content. The degradation is maximum in Sample I: it contains only 5 wt% ethylene and resembles the results of PP oxidation. The intensity of photooxidation is more than that of thermooxidation in all samples. The derivatization reactions confirm the PP phase as the initial oxidation site.

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