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The Oxidative Degradation of Ethylene/Vinyl Alcohol Copolymers*

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ABSTRACT

The oxidative behavior of ethylene/vinyl alcohol copolymers has been examined after initiation by γ -irradiation. Oxidation products were identified and quantified by infrared spectroscopy after the use of selective derivatization reactions which allowed the resolution of the various alcohol, hydroperoxide and carbonyl species produced. Extensive preferential attack at the $\text{H}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{OH}$ sites was observed to give backbone ketone and probably hydrogen peroxide. The latter was not unambiguously identified or quantified because of its volatility. The derivatization techniques failed at vinyl alcohol levels above 20 wt%, probably because of the low gas permeability of these films. Implications of the observed products to the oxidation of polyethylene are discussed.

INTRODUCTION

The copolymers of ethylene and vinyl alcohol (EVOH) are finding increased application as components of advanced packaging films because of their high oxygen barrier characteristics.¹ The oxidative behavior of the EVOH

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family is of interest both for stability during melt processing and for the long-term durability of the copolymer and its laminates. In addition, the EVOH copolymers represent model structures for the *sec*-alcohol groups detected in partly oxidized polyethylenes.²

In this paper we report on the oxidation of EVOH copolymers after initiation by γ -irradiation. High energy (γ - or e-beam) irradiation is an important route for the production of sterile devices and packages for medical purposes. In addition, it is also a valuable technique for the clean initiation of oxidation for mechanistic studies without the complication of extraneous initiation by impurities, or complexities arising from the instability of the oxidation products.

EXPERIMENTAL

A high vinyl alcohol copolymer (52 mol%, i.e. 14.3 mol/kg in $\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{OH}$ groups) was obtained as pellets from Enron Corporation (Rolling Meadows, IL) and pressed into films with a N_2 blanketed press. Lower vinyl alcohol copolymers were prepared from films of ethylene/vinyl acetate copolymers (6.0 and 18 wt% in vinyl acetate) supplied by CIL (Brampton, Ontario). The vinyl acetate copolymer films (both 25 and 50 μm thickness) were completely hydrolyzed to EVOH films by a 40-h immersion in 20 wt% methanolic KOH at 60°C. Hydrolysis was shown to be complete by the loss of the acetate infrared (IR) absorption (at 1735 cm^{-1}). These EVOH films were respectively 0.70 and 2.1 mol/kg in alcohol groups as shown by direct IR and from IR analysis after derivatization (see below). Polypropylene film (25 μm , Profax Resin) was supplied by Himont (Wilmington, DE) and purified by acetone extraction (48 h) to remove antioxidants and slip agents.

Copolymer films were oxidized in air in a ^{60}Co Gammacell (Atomic Energy of Canada, Model 220) at a dose rate of 0.9 Mrad/h. Ambient temperature in the Gammacell was $\sim 40^\circ\text{C}$, although some samples were irradiated in dry ice (-78°C) or liquid nitrogen (-196°C) for electron spin resonance (ESR) analysis.

Oxidation products were identified and quantified by Fourier transform infrared (FTIR) spectroscopy. Because of the overlap of $-\text{OH}$ absorptions (alcohols and hydroperoxides) at $\sim 3400\text{ cm}^{-1}$ and carbonyl species (ketones, carboxylic acids, esters, etc.) at $\sim 1720\text{ cm}^{-1}$, controlled product derivatization reactions were used to selectively modify certain product groups as described previously.²⁻⁴ Derivatization involved either treatment of the films with SF_4 to convert $-\text{OH}$ and $-\text{OOH}$ species to fluorides and carboxylic acids to acid fluorides, or treatment with NO to convert $-\text{OH}$ to

nitrite and —OOH to nitrate. The SF₄ treatment greatly simplifies the carbonyl region, not only by removing the broad acid absorption but also by eliminating hydrogen-bonding shifts of the carbonyl absorptions, which were attributable to the various —OH species. The organo-nitrates and nitrites have intense IR absorptions and so give increased sensitivity for the IR detection of species. In addition, their absorptions show distinctive shifts which allow the discrimination of primary, secondary and tertiary groups from both alcohols and hydroperoxides.

Most relatively, smooth films give interference ripples in the IR, which interfere with the precise quantification of absorptions. All of our transmission spectra were recorded with a vertically polarized IR beam (Perkin–Elmer gold-wire-grid polarizer) and films tilted at the Brewster angle as suggested by Harrick.⁵ This procedure completely eliminates ripple effects.

Total hydroperoxide content in oxidized films was measured by iodometry in *iso*-propanol.² This method also responds to peracids and hydrogen peroxide.

Free radicals produced by γ -irradiation of the copolymer films were measured by ESR spectrometry (Varian E4, X-band, 100 kHz modulation, with double integration of the derivative spectra on an Apple II+).⁶ Absolute radical concentrations were obtained by reference to a dilute dispersion of cupric acetylacetonate in KCl powder. The Cu²⁺ standard was chosen to calibrate the ESR spectrometer because it follows a good Curie law relationship over the temperature range used (–196 to 25°C). The Cu²⁺ standard was adjusted to occupy the same location in the cavity as the irradiated film scrolls. Films were transferred into the ESR tubes after irradiation to avoid the problem of signal generation in irradiated glass. Film transfer was effected at –196°C in liquid nitrogen to minimize radical decay.

The ESR spectrometer was usually operated at 0.5 mW power to prevent saturation of some of the observed signals.

RESULTS

Oxidation of polyolefins leads to a mixture of hydroperoxides, alcohols and carbonyl products.^{2–4,6} In EVOH copolymers, the detection of several of these species by FTIR is complicated by overlap with the strong —OH absorption of the unreacted *sec*-alcohol groups. In addition, hydrogen bonding between these groups and carbonyl products leads to peak broadening and frequency shifts. FTIR changes for γ -oxidized EVOH films containing 0.07 mol/kg of *sec*-alcohol groups are shown in Fig. 1. Spectral

Fig. 1. FTIR spectra of EVOH films (0.70 mol/kg, 50 μ m film). (a) Direct transmission spectra; (b) spectral subtraction (16 - 0 Mrad).

subtraction of the spectrum of the non-oxidized polymer from that of each oxidized sample is not particularly helpful (Fig. 1(b)).

The use of gaseous NO and SF₄ derivatization allows some of the oxidation products to be identified and quantified (Fig. 2). The SF₄-treated films clearly show the sharp 1845 cm⁻¹ absorption typical of chain-end acid fluorides [$\text{—CH}_2\text{—C(=O)—F}$] (Figs 2(b) and 3).⁴ The residual, sharp carbonyl absorption at 1718 cm⁻¹ after SF₄ treatment is identical to that produced from γ -oxidized, high density polyethylene (HDPE) and is assigned to backbone ketone groups [$\sim\text{CH}_2\text{—C(=O)—CH}_2\sim$].²

The NO treatment of the oxidized copolymer films produces several intense new absorptions and loss of the —OH absorption (Fig. 2(a)). Spectral subtraction (Fig. 3) highlights the new products from oxidation followed by NO treatment as well as loss of original groups. The peaks in Figs 2(a) and 3 can be identified and quantified from the previously published assignments and extinction coefficients.^{3,4} The negative peaks at 1645 and 778 cm⁻¹ are indicative of *sec*-nitrite groups which originated from the reaction of NO with *sec*-alcohol groups originally present in the EVOH copolymers. The decrease in *sec*-alcohol concentration implies that these sites are being destroyed during the oxidation process. The positive peaks at $\sim$ 1631, 1276 and 859 cm⁻¹ imply the formation of *sec*-nitrates from NO reaction with *sec*-hydroperoxide groups.^{3,4} These products were also detected in NO-treated, oxidized HDPE and found in the EVOH copolymer after exposure to a HNO₃/H₂SO₄ mixture for 4 days at room temperature. The isolated sharp peak at 1276 cm⁻¹ is consistent with the presence of only *secondary*

Fig. 2. FTIR spectra of EVOH films after derivatization (0.70 mol/kg, 50 μ m film). (a) After exposure to NO (160 h); (b) after exposure to SF₄ (15 h).

Fig. 3. FTIR spectra of EVOH films after derivatization (0.70 mol/kg, 50 μ m films). (a) NO exposed films after spectral subtraction (16 - 0 Mrad) (NB: both films NO treated before subtraction); (b) SF₄ exposed after spectral subtraction (16 - 0 Mrad).

—OOH groups and no other types of stable —OOH species (*tertiary* —OOH, α -hydroxyhydroperoxides, etc.).

After prolonged NO or SF₄ treatment, weak absorptions were still detectable at 3400 cm⁻¹. For the film initially 0.70 mol/kg in *sec*-alcohol groups, roughly 15% of these groups were not derivatized. The alcohol-NO reaction is quite slow and prolonged reaction times (100–150 h) were required previously for oxidized HDPE.² However, the failure to achieve 100% conversion with SF₄ is surprising since it reacts extremely quickly with oxidized polyolefins and model alcohols. This implies that the unreactive

$\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{OH}$ groups are inaccessible to SF₄, possibly because they are incorporated in crystalline domains. For the film initially 2.1 mol/kg in $\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{OH}$, roughly 25% of these groups were unreactive towards both SF₄ and NO. Reaction was so limited with the 14.3 mol/kg copolymer that the methods could not be applied.

It should be mentioned that the 0.70 mol/kg EVOH copolymer contains roughly equal levels of both free (non-hydrogen bonded) and associated —OH groups which absorb at 3630 and ~3400 cm⁻¹ respectively. The 3630 cm⁻¹ peak can be seen only after spectral subtraction because of overlap with the sharp 3640 and 3608 cm⁻¹ peaks present in all ethylene-based polymers. The free —OH groups react with SF₄ and NO, and decrease during oxidation in the same manner as the bonded —OH species.

Based on extinction coefficients for model acid fluorides, nitrates and nitrites in hydrocarbons, the concentrations of oxidation products can be calculated.^{3,4,6} The growth of these products with increasing γ -dose is shown in Fig. 4. Also shown is the total concentration of peroxidic species estimated by iodometry. The use of extinction coefficients to calculate concentrations from absorbance peak heights is a convenient technique, but in polymers is subject to problems caused by peak broadening. The concentration values quoted in Fig. 4 were derived from known concentrations of model compounds in hexane solutions but using peak areas to correct for the broadening effects of the polymer environment. For

example, the 1631 cm⁻¹ $\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{ONO}_2$ peak has a width at half height of 6 cm⁻¹ for the model compound in hexane but is 12 cm⁻¹ in the oxidized polymer, whereas the 1276 cm⁻¹ peak of this same species is 14 cm⁻¹ wide for both the hexane solution of the model and in the oxidized polymer.

The data presented in Figs 1–4 all relate to the copolymer with the lowest vinyl alcohol content (0.70 mol/kg). Similar data were obtained for 20 and

Fig. 4. γ -Oxidation effects on C_2H_4 /vinyl alcohol copolymer (0.70 mol/kg VA, 50 μ m film). ●, Ketone from 1718 cm^{-1} absorption (extinction coefficient $\epsilon = 300\text{ kg/mol cm}$) after SF_4 treatment; ▽, total hydroperoxide species from iodometry; △, $H-C-OOH$ measured as its nitrate (at 1276 cm^{-1} , $\epsilon = 470\text{ kg/mol cm}$) after NO exposure; □, $\sim CH_2-C(=O)-OH$ measured as its acid fluoride at 1845 cm^{-1} ($\epsilon = 650\text{ kg/mol cm}$) after SF_4 treatment; ○, $H-C-OH$ measured as its nitrite (at 778 cm^{-1} , $\epsilon = 410\text{ kg/mol cm}$) after NO exposure.

40 μ m films of the 2.1 mol/kg copolymer, and are shown in compressed form in Table 1. Both film thicknesses gave identical product yields, which implied that O_2 diffusion was not rate controlling. For the high vinyl alcohol films (14.3 mol/kg), only partial reaction with NO and SF_4 was possible, which severely limited the quantification of products. One clear result was the unexpectedly low rate of ketone formation, roughly comparable to the rate of production from the 2.1 mol/kg copolymer.

From a study of the ESR spectra of the 0.70 and 2.1 mol/kg EVOH copolymers and HDPE, identical signals were found after γ -irradiation under vacuum at -196°C (Fig. 5). Upon admission of oxygen and warming to -78°C all of these irradiated samples rapidly (10–20 s) converted virtually quantitatively to the anisotropic signal typical of peroxy radicals.⁷ Identical signals and concentrations (within $\pm 15\%$) resulted from irradiation at -78°C in air. Upon warming to room temperature rapid decay of the peroxy signal occurred (Fig. 5C). This decay is too rapid to allow the quantification of the peroxy radicals, but this problem was overcome by

TABLE 1
Oxidation of 'Substituted Polyethylenes'. (Product concentration (mol/kg $\times 10^3$)^a)

Polymer	Peroxyl radical	Total OOH ^b	After NO reaction				After SF ₄ reaction	
			Hydroperoxide		Alcohol		Ketone	$\begin{array}{c} \text{O} \\ \parallel \\ \sim\text{C} \\ \backslash \\ \text{OH} \end{array}$
			Sec.	Tert.	Sec.	Tert.		
HDPE	30	20	19	0	7	0	30	18 ^c
<i>C₂H₄/vinyl alcohol</i>								
0.70 mol/kg	42	42	35	0	—54	0	54	10 ^c
2.1 mol/kg	50	54	24	0	—77	0	86	16 ^c
14.3 mol/kg	52 ^d	ND	ND	ND	ND	ND	~90	ND
PP	42	205	35	156	2	9	120	~5 ^c (17) ^d

^a After 10 Mrad dose.

^b From iodometry.

^c Chain-end acid groups.

^d Probably $\sim\text{CH}_2-\dot{\text{C}}(\text{OH})\text{CH}_2\sim$ radicals.

^e Pendant acid groups.

Fig. 5. ESR spectra of γ -irradiated polymers (0.5 Mrad exposure, 24 mg film). A, HDPE or 0.70 mol/kg EVOG or 2.1 mol/kg EVOH; irradiation at -190°C under vacuum, ESR measured at -190°C ; B, as for A but irradiation in air at -78°C , ESR measured at -78°C ; C, as for B but after warming to 22°C for the times shown; all spectra at the same gain, ESR measured at 22°C ; D, 14.3 mol/kg EVOH; irradiation at -190°C under vacuum, ESR measured at -190°C ; E, as for D but irradiation in air at -78°C , ESR measured at -78°C ; F, as for B but after warming to 22°C for the times shown; gain values in parentheses, ESR measured at 22°C .

Fig. 6. Decay of radicals in polymer films. All films irradiated at -78°C in air to a dose of 0.5 Mrad. Decays measured after warming to 22°C at time zero. ○, Polypropylene; □, HDPE; ▼, 0.70 mol/kg EVOH; △, 2.1 mol/kg EVOH; ●, 14.3 mol/kg EVOH.

periodically quenching the decay process by cooling the samples in liquid nitrogen. This allowed the measurement by double integration of the (now stable) peroxy level and the data are collected in Fig. 6 and Table 1.

The 14.3 mol/kg EVOH copolymer displayed a very different ESR behavior. Radicals generated by γ -irradiation of film cooled in liquid nitrogen were found to convert very slowly (but irreversibly) at -78°C in air to a new, very stable signal (Fig. 5). This same signal (Fig. 5E) resulted both from irradiation at -78°C and also from irradiation at ambient temperature in air. This signal saturated at low microwave power (~ 0.5 mW), which implies the species is not peroxy which saturates at ≥ 10 mW. In addition, this signal (Fig. 5E and F) decays very slowly in air at room temperature in comparison with peroxy radicals from HDPE or the other EVOH copolymers (Fig. 6).

DISCUSSION

Vinyl acetate copolymers are usually believed to be random because of the similarity in the ethylene and vinyl acetate reactivity ratios.⁸ Consequently all of our vinyl alcohol/ethylene copolymers must also be random as all are derived from vinyl acetate precursors. These precursors are known to be

quite highly branched because of chain transfer during polymerization. The vinyl alcohol copolymers also contain these same branch sites, as shown by the strong CH_3 chain-end absorption at 1378 cm^{-1} (see Fig. 1(a)). From this absorption and the FTIR spectral subtraction method we have described previously, branch concentrations were found to be 1.4 mol/kg (0.70 mol/kg copolymer) and 1.8 mol/kg (2.1 mol/kg copolymer).² Equivalent levels of *tertiary* C—H sites must exist at these branch sites, and are comparable to the level found in LDPEs. We have previously shown that *tertiary* C—H sites at this level are insignificant contributors to the γ -initiated oxidation of LDPEs.²

The discrepancy between total peroxidic species in the copolymers as measured by iodometry and *secondary* —OOH levels from nitrate formation (Table 1) is too large to attribute to experimental error. For both of the copolymers, appreciable I_3^- was produced at room temperature, even before the normal 5 min reflux of the reagents had begun. In contrast, for oxidized PE or PP, the yellow I_3^- is observed to develop only during reflux. This implies the presence of an extremely unstable peroxidic product in the irradiated copolymers.

The loss of H—C—OH , extensive formation of >C=O and formation of a very unstable peroxidic species can all be rationalized in terms of Scheme 1.

The self reaction of *tert*-peroxyl radicals is a slow process expected to be insignificant in the presence of the *sec*-peroxyl radicals.⁹

Peroxyl radical yields from the copolymers are clearly greater than from HDPE and may be attributed to selective bond scission at the *sec*-alcohol

site.¹⁰ The *tert*-hydrogen of the $\text{H—}\overset{\textstyle \text{}}{\underset{\textstyle \text{}}{\text{C}}}\text{—OH}$ group is expected to be quite labile towards peroxyl radical attack, with a reactivity higher than the *tertiary* C—H groups in polypropylene.⁹ α -Hydroxyhydroperoxides have

been proposed as products from the photo-oxidation of poly(vinyl alcohol) and 2-propanol, but found to be very unstable and to spontaneously break down to ketone and H_2O_2 (reaction (5)).^{11,12} The latter would account for the high reactivity of the oxidized copolymer films in the iodometric analysis. With NO , H_2O_2 may form nitric acid but none was detected in the film spectra. (HNO_3 absorbed in the copolymers produced a 1296 cm^{-1} IR peak.) Iodometric peroxide levels were somewhat reduced (10–15%) by a prior evacuation of oxidized copolymer films, consistent with the presence of a volatile peroxidic species.

Radical termination will involve the fast reactions of *sec*-peroxyl radicals (reactions (7a) and (7b)). These should give equimolar quantities of *sec*-

Scheme 1

alcohol and ketone.¹¹ However, the roughly equivalent levels of $\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{OH}$ loss and ketone formation are consistent with reaction (2a), followed by (3a), (4) and (5) being dominant. From the values for the oxidation of liquid hydrocarbons, $k_{2a} \approx 70k_{2b}$ at 30°C.¹⁰ This ratio leads to a predicted value of $(>\text{C}=\text{O})/(\text{H}-\overset{\text{}}{\underset{\text{}}{\text{C}}}-\text{OOH}) \approx 0.7$ (0.70 mol/kg of EVOH) and ~ 2 (2.1 mol/kg of EVOH), assuming that the copolymers are $\sim 40\%$ crystalline and that most of the *sec*-alcohol groups are in the O_2 -permeable amorphous domains. These values are fairly consistent with the data in Table 1, after allowing for $>\text{C}=\text{O}$ from peroxy termination. The lower yield of *sec*-hydroperoxide from 2.1 mol/kg EVOH as compared with the 0.70 mol/kg

copolymer cannot be easily explained. Furthermore, the slow rate of oxidation of the high EVOH copolymer implies a complex interplay of radical formation and decay with very limited O_2 access.

The ESR changes in Fig. 5 are in general consistent with Scheme 1. The signal from HDPE and the lower EVOH copolymers at -190°C is reported to originate from $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$ with some allyl contribution ($\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}=\text{CH}-\text{CH}_2\sim$).¹³ Rapid reaction with O_2 , even at -78°C , gives the peroxy signal, with hindered rotation at -78°C (anisotropic signal) and free rotation of the radical site at ambient (singlet).⁷ For the 14.3 mol/kg EVOH, the -190°C signal appears to be from pure $\sim\text{CH}_2-\dot{\text{C}}\text{H}-\text{CH}_2\sim$ species, whereas at -78°C and ambient this converts entirely to a signal assigned to $\sim\text{CH}_2-\dot{\text{C}}(\text{OH})-\text{CH}_2\sim$.¹⁴ A weak peroxy signal could be buried under the spectrum of this latter species, but it appears that the O_2 permeability of this copolymer is low enough to prevent peroxy radical build-up.

The observed reactivity of $\text{H}-\overset{\text{\tiny $\left\{ \right.$}}{\underset{\text{\tiny $\left. \right\}}{\text{C}}}-\text{OH}$ sites towards oxidation may be important in the oxidation of LDPE and HDPE homopolymers. The classical (liquid phase) oxidation of linear alkanes should lead to equimolar concentrations of *sec*-alcohol and backbone ketone groups from the self-termination of *sec*-peroxy radicals.² However, the alcohol yield from HDPE is much less than the ketone yield, which in turn is much higher than expected from the peroxy radical yield (Table 1). Due to the localized nature of polymer oxidation in the solid state, radical attack on *sec*-alcohol sites produced from peroxy termination will be much more important than suggested by their low average concentration. Still unresolved is the origin of carboxylic acid end groups, the dominant backbone scission products of polyethylenes. From Table 1, these end groups do not originate from attack on *sec*-alcohol sites.

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