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A Critical Comparison of Methods for Hydroperoxide Measurement in Oxidized Polyolefins*

D. J. Carlsson & J. Lacoste‡

Division of Chemistry, National Research Council of Canada,
Ottawa, Ontario, Canada K1A OR6

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ABSTRACT

Hydroperoxide products in solid oxidized polyolefins have been measured by iodometry, Fe^{2+} reaction and by derivatization infrared spectroscopy methods. Polyethylene, polypropylene and elastomers were oxidized by photo, thermal and γ-initiation. The traditional iodometric method appears to be highly reliable within certain constraints of reaction time imposed by sample crosslinking. The Fe^{2+} reaction was found to give values consistently one order of magnitude below the true level because of failure of the reagents to penetrate into the oxidized polymers even after a prior swelling step. Derivatization of hydroperoxides by reaction with nitric oxide produced nitrates which could be measured by infrared spectroscopy with high sensitivity. Total nitrate yields agreed well with iodometric determination of hydroperoxide for reaction conditions under which the nitrates were stable. Different nitrates, and hence hydroperoxides, could be identified and quantified by this method.

INTRODUCTION

Hydroperoxide groups are now widely recognized as key intermediates in the oxidative degradation of many polymers.[1-5] They are present in

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‡ Guest Research scientist, 1989. Permanent address: Université Blaise-Pascal, Clermont-Ferrand, 63177 Aubière, France.

polymers as impurities generated by oxidation during storage, processing or use. Hydroperoxides in polyolefins are thermally labile, even at room temperature, and photolyze very efficiently although they have only a weak absorption in the near ultra violet (UV).[6,7] Free radicals generated by these hydroperoxide decomposition reactions begin new oxidative chain reactions by attack on the polymer matrix (PH) (reactions (1) and (2)) which produce fresh hydroperoxide groups (POOH) with every propagation cycle (reactions (3) and (4)).[1]

$$\mathrm{ROOH} \xrightarrow[\Delta]{h\nu} \mathrm{RO^{\bullet}} + {}^{\bullet}\mathrm{OH} \tag{1}$$

$$\mathrm{RO^{\bullet}},\ {}^{\bullet}\mathrm{OH} + \mathrm{PH} \rightarrow \mathrm{ROH},\ \mathrm{H_2O} + \mathrm{P^{\bullet}} \tag{2}$$

$$\mathrm{P^{\bullet}} + \mathrm{O_2} \rightarrow \mathrm{PO_2^{\bullet}} \tag{3}$$

$$\mathrm{PO_2^{\bullet}} + \mathrm{PH} \rightarrow \mathrm{P^{\bullet}} + \mathrm{POOH} \tag{4}$$

The quantification of the total hydroperoxide level in a polymer is an important analytical parameter required for the study of polymer oxidation and stabilization. Furthermore, the precise identification of hydroperoxide groups (such as from primary, secondary or tertiary C-H abstraction) can be even more informative than the total concentration alone.

Several analytical methods for hydroperoxide determination have been developed over the past 30 years. These include the sensitive but tedious iodometric method adapted from food oil chemistry, SO_2 reaction to give hydrosulfates measured by infrared (IR) or X-ray fluorescence, the $Fe^{2+} \rightarrow Fe^{3+}$ conversion followed by colourimetric determination of Fe^{3+}, high resolution solution NMR and, more recently, NO reaction to give IR-identifiable nitrates.[2,8-11]

We have previously shown that the SO_2 method is only reliable for the simple case of polyethylene (PE) oxidation and misleading for the more complex mix of hydroperoxide species formed from polypropylene.[12] The NMR technique has enormous resolution but relatively low sensitivity. In addition it suffers from the need for long instrument times and the use of high temperatures to dissolve the samples. This leads to decomposition of hydroperoxides and the need to extrapolate data back to zero heating time.[10] In this paper we compare the results from the iodometric, Fe^{2+} and NO methods on PP and PE for total hydroperoxide quantification and explore conditions for NO reaction with hydroperoxides to give reliable estimates of primary, secondary and tertiary hydroperoxides as their corresponding nitrates.

EXPERIMENTAL

High density polyethylene (HDPE, 25 μm, Union Carbide), linear low density polyethylene (LLDPE, 100 μm, Dupont Sclair) and polypropylene (PP, 25 μm, isotactic, Himont Profax) films were Soxhlet extracted with acetone for 48 h to remove process antioxidants. Thin, unfilled films (20–150 μm) of polybutadiene (Buna CB 35NF from Bayer), polyisoprene (Natsyn from Goodyear) and polychloroprene (Neoprene from Dupont) were cast from chloroform solutions.

Films were oxidized by exposure to γ-irradiation in air (AECL, Gammacell 220, dose rate ~0·8 Mrad/h) or to an Atlas xenon arc WeatherOmeter (2500 W Pyrex inner and outer filters, silver and black panel temperatures 60°C and 85°C respectively, ambient humidity). The WeatherOmeter was equipped with an integrating light monitor, set to measure the arc's output at 313 nm. This wavelength is probably of greatest importance for the photo-oxidative degradation of polyolefins based upon the UV absorptions of their oxidation products. Photo-oxidation data are presented in terms of incident energy at 313 nm, rather than simply hours of exposure, to correct for the time-dependent changes in arc output with ageing. For comparison, 100 kJ/m^2 is roughly equivalent to 400 h exposure. A few films were irradiated with a laboratory accelerated weathering (SEPAP) system which uses a medium pressure mercury lamp described previously.[13] Sample temperature was measured by thermocouples, during irradiation. The γ-oxidized samples were analyzed after ~20 h at room temperature following irradiation; photo-oxidized samples were analyzed immediately after irradiation.

The hydroperoxide yields in each sample were determined by iodometry (refluxing in 10:1 isopropanol/acetic acid with excess sodium iodide, spectrophotometric determination of I_3^- at 350 nm, extinction coefficient, $\varepsilon = 25\,000$ litres/mol/cm).[8] Some oxidized polyolefins (especially photo-oxidized) gave colloidal suspensions after reflux, presumably from partly soluble chain scission products extracted from the films. To eliminate this complication to spectrophotometric measurement, solutions after reflux with NaI were quickly filtered under nitrogen through a 5 μm filter (Millipore, Teflon) just before absorbance measurement. Reagent blanks were also handled the same way. Other oxidized samples were swollen in benzene for 24 h, and then hydroperoxide determined by reaction with ferrous ammonium sulfate in methanol to give the intensely coloured ferric thiocyanate anion when ammonium thiocyanate in methanol was added (spectrophotometric determination at 510 nm, $\varepsilon = 16\,800$ litres/mole/cm).[2] Both methanolic solutions were stored under N_2 prior to use. Samples of ferrous ammonium sulfate free of ferric contamination were employed.

Even so reagent blanks were usually quite high and dependant on reaction time after mixing. All ferric thiocyanate spectra were recorded 15 min after mixing, with storage in the dark. For both iodometric and $Fe^{2+} \rightarrow Fe^{3+}$ analyses, film samples were chosen to be in the 10–50 mg range, with the larger samples being used for the less strongly oxidized polymers.

Additional samples were exposed to gaseous NO in the absence of O_2 to convert hydroperoxide groups into their corresponding nitrates.[11,14] These nitrates were identified and quantified by Fourier Transform infrared (FTIR) spectroscopy (Perkin Elmer 1500, gold wire grid polarizer, films inclined at the Brewster angle to eliminate interference ripples).[14] The NO reactions were carried out for various times and temperatures to establish the optimum reaction conditions and the stability of the various nitrate products. For weakly oxidized samples up to four film thicknesses of NO-treated film were used for FTIR to increase the sensitivity of the measurements.

RESULTS AND DISCUSSION

Iodometry

Extensive studies with model compounds have clearly shown that the iodometry method is quantitative for hydrogen peroxide and all model hydroperoxides.[8] Dialkyl peroxides usually do not react with NaI/isopropanol in the absence of a very strong acid. Decker *et al.*[15,16] have found that the iodometric methods can accurately measure hydroperoxides in solid, γ-irradiated polyolefins because total oxygen uptake agreed well (within 5–10%) with total analyzed oxidation products (predominantly hydroperoxides).

For photo-oxidized PP or HDPE films (25 μm), all hydroperoxide was converted to I_3^- during a 5 min reflux in our experiments. Completeness of reaction was shown by repeating successive 5 min refluxes with fresh reagent but on the same film sample: negligible further I_3^- generation occurred. For thicker photo-oxidized films and for all γ-irradiated films (which may be partially cross-linked), up to 60 min reflux was required for complete hydroperoxide reaction to give I_3^-. Within these experimental limitations of reaction time, the iodometric method appears to be a reliable, quantitative measure of total hydroperoxide in oxidized polyolefins. Total hydroperoxide increased linearly with γ-irradiation dose for both PP and HDPE (Fig. 1). HDPE and LLDPE oxidize at identical rates under γ-irradiation.[17] Photo-oxidations follow the usual sigmoidal curve (Fig. 2).

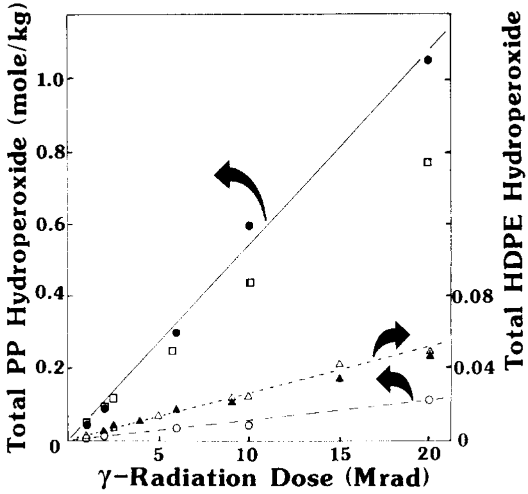

Fig. 1. Total hydroperoxide estimations for γ-oxidized polyolefins. Films irradiated in air at ambient temperature (~40°C) in the Gammacell. PP film: (●) from iodometry (60 min reflux); (□) from NO exposure at −20°C for ≥70 h; (○) from Fe^{2+}/thiocyanate after swelling in benzene (15 h). HDPE: (△) from iodometry (60 min reflux); (▲) from NO exposure at ambient for ≥20 min.

Ferrous → Ferric method

Quantitative yields of ferric thiocyanate were formed from liquid tertiary butyl hydroperoxide standards (2 moles of ferric ions per mole of hydroperoxide). However, solid, oxidized polyolefin samples gave little reaction with methanolic ammonium thiocyanate and acidified ferrous

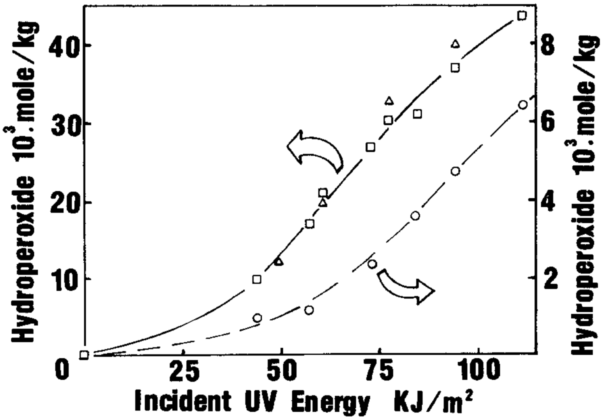

Fig. 2. Total hydroperoxide estimations for photo-oxidized LLDPE. Films Xe arc irradiated in air. (□) from iodometry, (60 min reflux); (○) from Fe^{2+}/thiocyanate after swelling in benzene (24 h); (△) from NO exposure at −20°C. Total of secondary and tertiary nitrates observed.

TABLE 1
Comparison of Total Hydroperoxide Determinations in Photo-oxidized Chloroprene[a]

Photo-oxidation time (h)	*Hydroperoxide level (10^3 mole/kg)*	
	I_3^-	Fe^{2+}
0	<1·0	0·3
3·0	75·6	5·5
5·0	130	8·1
10·0	146	6·8

[a] SEPAP system. Sample temperature = 35°C, 150 μm films.

ammonium sulfate solutions as reported previously.[2] Pre-swelling the oxidized films in benzene for 15 h resulted in some reaction with the ferrous solution. However, hydroperoxide estimated from the ferric thiocyanate complex measured at 510 nm ($\varepsilon = 16\,800$ litres/mole/cm) was only about 1/10 of the hydroperoxide concentrations measured by iodometry (Figs 1 and 2). This is most likely attributed to the failure of the methanolic reagents to penetrate into the partly swollen polymer.[3,5] This method appears to be reliable only for polymers which can be completely dissolved prior to analysis.[3] Low total hydroperoxide values were also obtained from thermally oxidized polyolefins when the Fe^{2+}/thiocyanate method was used.

A brief study of total hydroperoxides in a photo-oxidized rubber showed again a large deficiency in the Fe^{2+} method (Table 1). After only 3 hours' exposure in the SEPAP system, films were extensively crosslinked (completely insoluble) which presumably exacerbated Fe^{2+} penetration.

Previous reports of reproducible estimation of hydroperoxides in thermal and γ-oxidized LDPE films and pellets must be serious underestimations of the true level.[2,18] For example, ~0·01 mole/kg of hydroperoxide was reported after ~7 Mrad dose for LDPE film, whereas we find ~0·1 mol/kg at this dose (Fig. 1). In addition our dose rate was over 200 times greater than in the reports of Petruj *et al.*[2,18] and oxidation levels decrease with increasing dose rate for a given total dose.

NO method

FTIR spectroscopy can indicate the presence of hydroperoxide and/or alcohol groups from the broad absorption at 3400 cm^{-1} in oxidized polyolefins (Figs 3 and 4). However, this hydrogen bonded absorption cannot be used to discriminate between these species or to differentiate

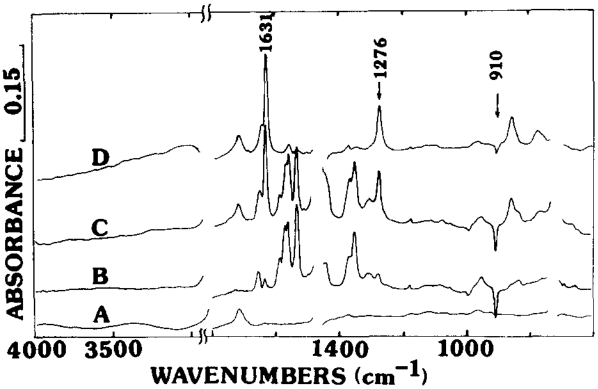

Fig. 3. IR spectra of HDPE films. All spectra are obtained by first subtracting the spectrum of the non-oxidized film. Spectra recorded on four thicknesses of 25 μm film. (A) after 2 Mrad irradiation in air; (B) non-oxidized film after ≥30 h NO exposure at 22°C; (C) after 2 Mrad irradiation in air followed by 48 h NO exposure at 22°C; (D) after 2 Mrad irradiation in air followed by 20 min NO exposure at 22°C or ≥40 h NO exposure at −20°C.

various OOH groups, except possibly in very specialized cases such as oxidized polyurethanes.[4] It is possible to differentiate between free (non hydrogen bonded) alcohol (3650 cm^{-1}) and hydroperoxide (3550 cm^{-1}) groups as compared to the composite hydrogen-bonded absorption (~3400 cm^{-1}). A small amount of free hydroperoxide is visible in Fig. 4 (curve A).

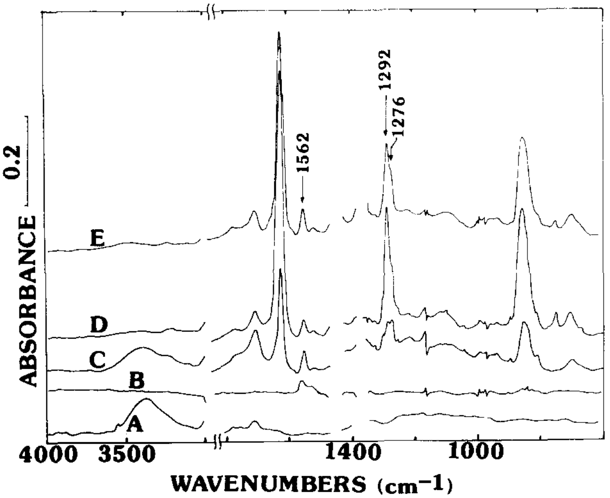

Fig. 4. IR spectra of PP films. Spectral subtract data as in Fig. 2. (A) after 2 Mrad irradiation in air; (B) non-oxidized film after ≥20 min NO exposure at 22°C; (C) after 2 Mrad irradiation in air followed by 80 h NO exposure at −22°C and then 17 days at 22°C in air or NO; (D) after 2 Mrad irradiation in air followed by 80 h NO exposure at −20°C; (E) after 2 Mrad irradiation in air followed by 8 h NO exposure at 22°C.

Nitric oxide reacts with hydroperoxides and alcohols to give, respectively, nitrates and nitrites. It has previously been proposed that the sharp, intense IR spectra of these organo-nitrates and nitritres can be used to differentiate between primary, secondary and tertiary species.[19,20] As well as this ability to discriminate between species, a 4–10 fold jump in IR sensitivity over the 3400 cm^{-1} absorption also results. We have exploited this IR derivatization method to identify and quantify hydroperoxide and alcohol products in oxidized polymers.[11,14] More reliable reaction conditions have now been found for the reproducible quantification of products with a minimum of side reactions and are discussed below.

For LLDPE and HDPE, the NO reaction with oxidation products is very fast and quantitative. The secondary nitrate IR peaks from the secondary hydroperoxide groups are formed quantitatively within ~20 min at room temperature. This is shown for HDPE by the complete loss of the absorption at ~3400 cm^{-1} and the plateauing of the 1276 cm^{-1} absorption from the secondary nitrate group (Fig. 3). The secondary nitrate yield (based on the extinction coefficient of model nitrates) agreed within ±10% with the total hydroperoxide yield from iodometry (Figs 1 and 2). Longer NO treatment times (as are necessary for complete reaction with thick films for example) lead to the progressive growth in absorptions at 1586, 1562, 1536, 1374 and 1354 cm^{-1}. At the same time a progressive loss of the 910 cm^{-1} absorption attributable to vinyl end groups occurs (Fig. 3). The growth of these new absorptions and the loss of the 910 cm^{-1} peak both stop after about 25 h of NO exposure. These same changes occur in both oxidized and non-oxidized samples and can be explained by NO attack on the vinyl unsaturation to give a range of nitro and nitro-olefinic species.[21,22]

Polypropylene can theoretically give rise to at least three different hydroperoxides (primary, secondary and tertiary) upon oxidation. Formation of organo-nitrates should allow the measurement of these three species from a comparison of the IR spectra of model nitrates. From a study of the time dependence of the nitrate peaks produced from oxidized polypropylene, a complex behaviour is evident at room temperature (Fig. 4). The secondary nitrate peak at 1276 cm^{-1} forms quickly as in HDPE and plateaus at ~20 min. The tertiary nitrate peak at 1292 continues to increase up to ~15 h NO exposure time and then decays. This behaviour is shown more clearly in Fig. 5. The maximum total nitrate yield (secondary + tertiary) is only ~50% of the iodometric value for these samples. Oxidized polypropylene film exposed to NO for ~15 h and then stored in air showed the same drop in 1292 cm^{-1} intensity as samples stored in NO. However, the secondary nitrate peak at 1276 cm^{-1} remained constant in both air and NO atmospheres. This implies that only the tertiary nitrate group is inherently unstable at room temperature. Loss of the 1292 cm^{-1} absorption was

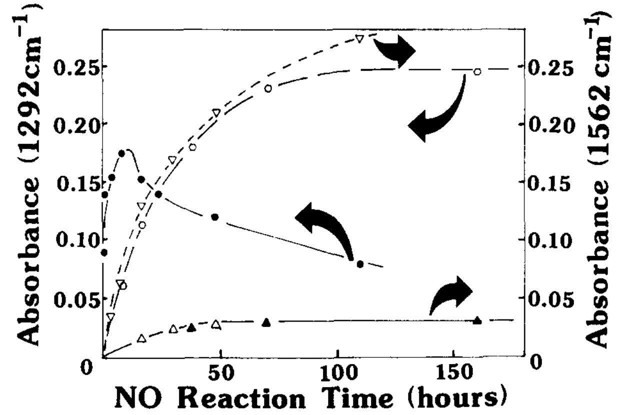

Fig. 5. IR spectral changes for NO exposed PP. (▽, ●) after 2 Mrad irradiation in air followed by NO exposure at 22°C; (▲, ○) after 2 Mrad irradiation in air followed by NO exposure at −20°C; (△) non-oxidized film after NO exposure at −20°C.

accompanied by a slight increase in both the carbonyl absorptions (1750–1710 cm^{-1}) and OH absorptions (~3400 cm^{-1}) and of an absorption at ~1562 cm^{-1}, again attributed to the formation of nitro compounds.

Alcohol groups react with NO to give nitrites.[19,14] Both secondary and tertiary nitrites formed from PP and HDPE were found to be unstable to long term storage, as was shown by the progressive decrease of the (overlapped) 1645 and 775 cm^{-1} absorptions over ~10 days.

NO reactions with oxidized PP were performed under various conditions at or below room temperature in an attempt to find conditions where complete tertiary hydroperoxide reaction occurred and the tertiary nitrate was stable. At −78°C, the tertiary nitrate groups were stable but the reaction times prohibitively long (>200 h). At −20°C, the groups were again stable and reached a plateau concentration at ~60 h (Fig. 5). Under these latter conditions the total nitrate yield agreed well with the total hydroperoxide yield from iodometry at radiation doses up to 5 Mrad (Fig. 1). Only a very weak peak at 1562 cm^{-1} was observed after NO reaction with oxidized polypropylene at −20°C or after prolonged NO reaction with non-oxidized polymer at room temperature (Fig. 4).

At very high PP oxidation levels (≥ ~0·4 mole/kg −OOH from iodometry) the NO method at −20°C gave total nitrate levels below the iodometric values (Fig. 1). However, at these degrees of oxidation the polymer is so brittle as to be useless for practical purposes.

Some NO reactions at −20°C were performed on oxidized LLDPE for comparison with the behaviour of PP. The secondary nitrate peak plateaued at ~40 h with a value identical to that found for ≥20 min NO reaction at 21°C for the same sample. However, for highly photo-oxidized LLDPE samples, a tertiary nitrate shoulder became visible after ~70 hours' exposure to NO at −20°C. This tertiary nitrate was not observed for NO treatment at room temperature or after −20°C/NO treated films had stood at room temperature for ~20 h. Quite good agreement between the iodometric method and the −20°C/NO method was found for photo-oxidized LLDPE (Fig. 2).

In conclusion, the NO method can give reliable quantitative information on —OOH species in oxidized polyolefins with careful selection of the NO reaction conditions. For other polymers, insurmountable problems often arise. For example, polyamides reacted directly with NO, obscuring any products from oxidation of the polymer. Unsaturated polymers such as polybutadiene and polyisoprene also reacted directly with NO even at −20°C, presumably to give nitro-compounds which again interfere with the identification of oxidation products.

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