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EARLY DETECTION OF OXIDATION OF HDPE GEOMEMBRANES

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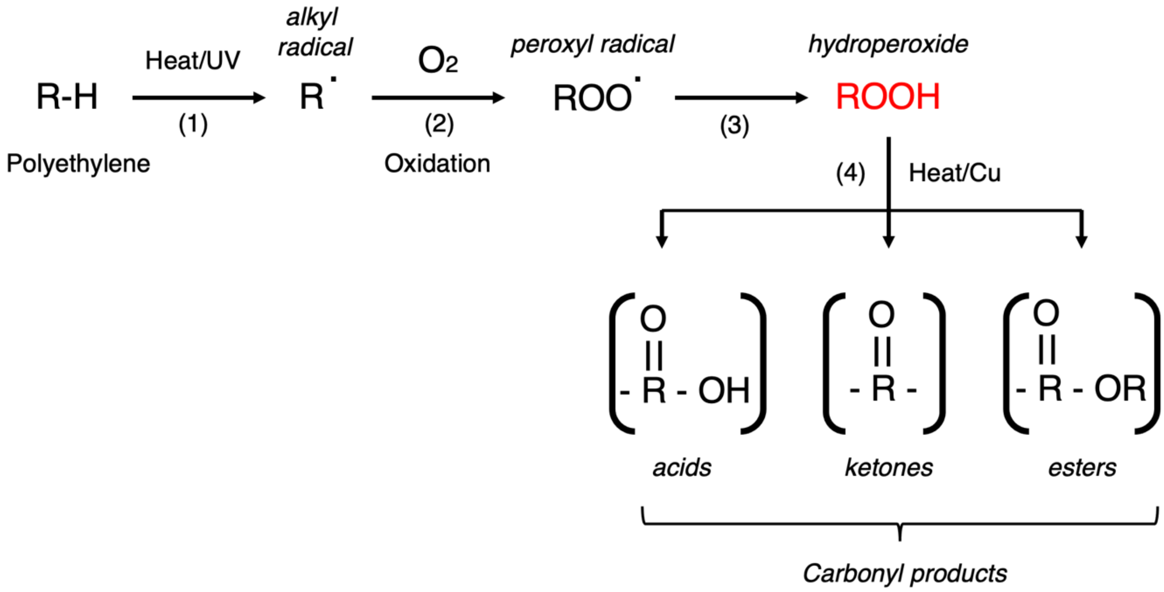
Introduction

There is a need to determine when oxidation of HDPE geomembranes occurs so that measures can be put in place to manage the remaining life and plan for eventual replacement.

Current assessment tools include measuring depletion of antioxidants and stabilizers via S-OIT and HP-OIT respectively, carbonyl index development via FTIR and melt flow rate changes via MFR which collectively can map Stage 1, Stage II and Stage III of the GMB lifetime curve. However there is an important need to identify when the oxidation of the polymer has been triggered once the protective additives have been depleted to low or residual deactivated levels.

A particularly sensitive method of detecting oxidation in HDPE membranes involves tracking the formation of hydroperoxide species. Dr. Scheirs has been involved with the measurement and characterization of hydroperoxides in ageing polyethylenes for over 30 years (see **Annexure A1**).

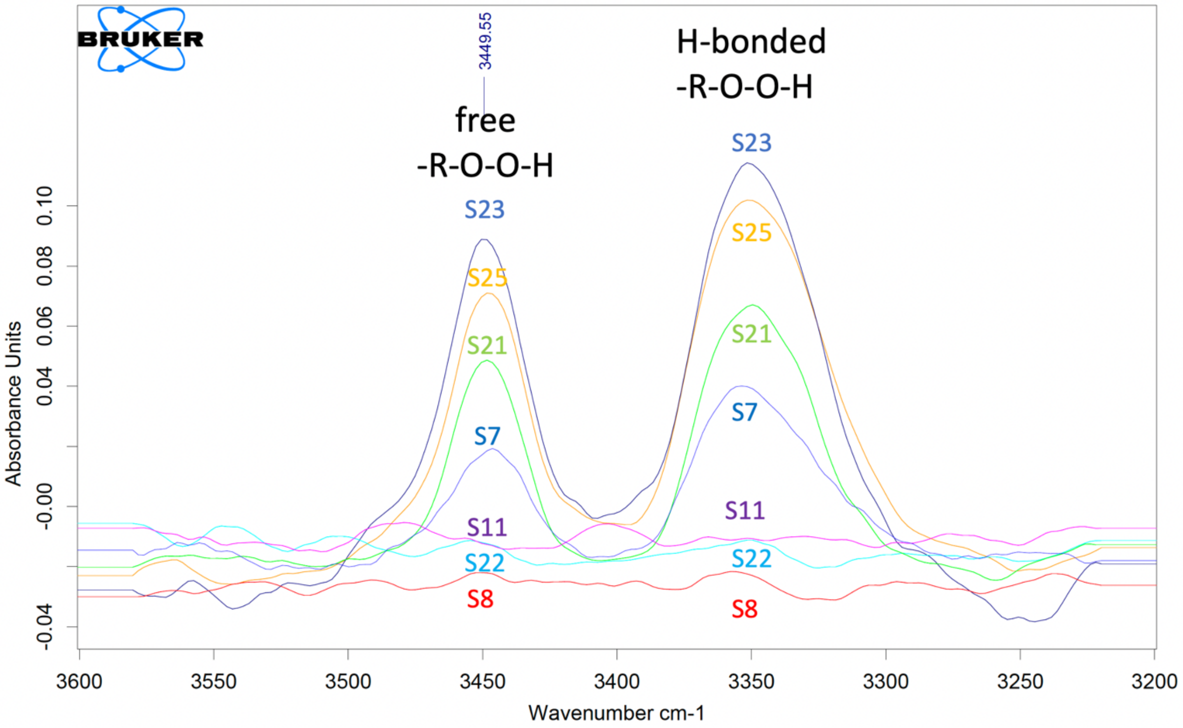
The first stage of oxidation of HPDE is the formation and accumulation of hydroperoxide groups (-R-O-O-H) which are formed in the early stages of oxidation (see steps 2 & 3) in autooxidation reaction scheme below.



Hydroperoxides are unstable intermediates of polyethylene oxidation (Scheirs, 1995 **Annexure A1**). They can be viewed as latent ‘ticking timebombs’ on a molecular level. When hydroperoxides decompose they produce two radicals that propagate further free-radical chain reaction of oxidation. The very first stage of autoxidation of HDPE is therefore the formation of these hydroperoxides (ROOH) which are labile intermediate species that yields free radicals to cause further oxidation of HDPE by free radical processes.

Upon thermal or catalytic decomposition, these hydroperoxide intermediates undergo homolytic cleavage, yielding two alkyl radicals that subsequently participate in additional free-radical chain reactions. The alkyl radicals thus generated, have the capability to propagate the oxidation process of HDPE via free radical mechanisms, leading to further degradation of the polymer (Scheirs, 1995 **Annexure A1**).

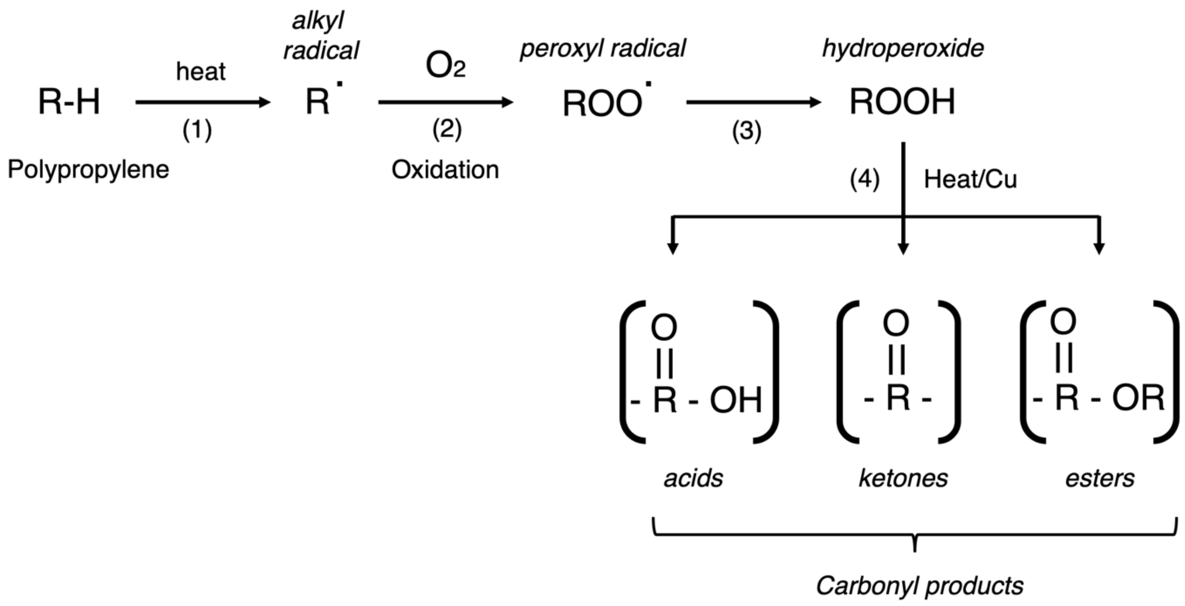
ATR-IR analysis of geomembrane test samples S7, S21, S23 and S25 show the distinctive free and H-bonded hydroperoxide absorption peaks at 3450 cm^{-1} and 3350 cm^{-1} in their IR spectra (see spectra below).



Note the concentration of hydroperoxides on the geomembranes from lowest to highest is as follows S8 ≈ S22 ≈ S11 << S7 < S21 < S25 < S23.

The level of hydroperoxidation of the GMB samples correlates exactly with their reduced antioxidant levels as determine by OIT measurements.

Oxidation of HDPE occurs when the AO levels are significantly reduced (as reflected by OIT results < 3-5 mins) and then hydroperoxide groups form in the polymer which is the first stage of oxidation as indicated below in step 2 & 3 of the autooxidation reaction scheme below. In the later stage of oxidation denoted by step (4) the hydroperoxide groups convert to carbonyl groups. These latter groups are easily detectable by FTIR in the region 1700-1745 cm^{-1}.



“Hydroperoxides are thermolabile compounds that then trigger a chain reaction. The two decomposition reactions of polymer hydroperoxides are shown below.”

Chain branching ROOH → $RO^\cdot + {}^\cdot OH$ 4(a)
2 ROOH → $RO^\cdot + RO_2^\cdot + H_2O$ 4(b)

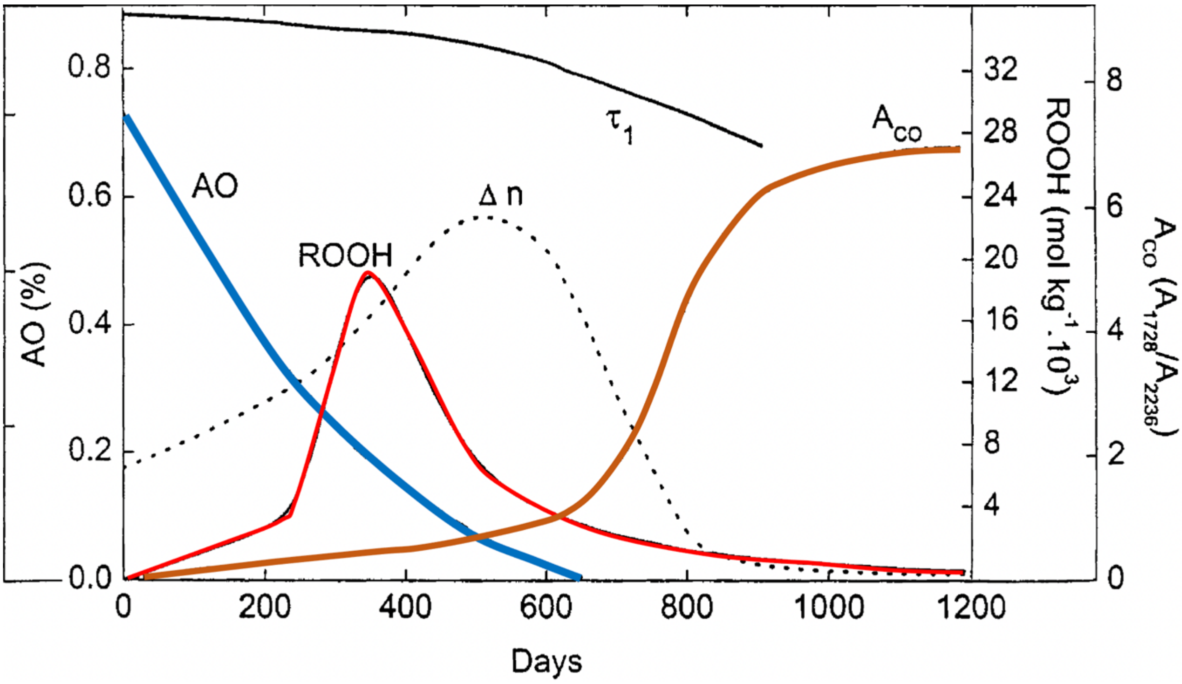
Reactions 4(a) and 4(b) are referred to as ***chain branching reactions***. Chain-branching reactions are reactions with one radical species producing two other radicals every time a reaction event occurs.

Reaction 4(a) has higher activation energy than 4(b) and is favoured at higher temperatures, whereas the ***bimolecular decomposition*** 4(b) is favoured by the accumulation of hydroperoxides to critical concentrations.

The hydroperoxides are accumulated during the first part of the oxidation and will then decrease in number, when they decompose to radicals forming carbonyls as end products.

Hydroperoxides are thus an important intermediate in the oxidative degradation of polyethylene, but since they are formed first their formation is of great interest to track polymer oxidation at an early stage.

The progression of oxidation of HDPE is presented schematically below.
Firstly the AO levels are slowly reduced due to consumption and leaching (as shown by the blue curve by decreasing OIT values). Then hydroperoxides start to accumulate as radical reactions occur with oxygen as represented by the red curve. When hydroperoxide reach a critical concentration, they start to decompose by bimolecular decomposition and produce carbonyl groups (as shown by the evolving brown line).



Annexure A1

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A REVIEW OF THE METHODS FOR DETECTING AND CHARACTERIZING HYDROPEROXIDE GROUPS IN OXIDIZED POLYOLEFINS

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BACKGROUND

Hydroperoxide groups are widely believed to be critical intermediates in the oxidative degradation of many polymers, especially commodity

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polyolefins [34, 51–53]. Trace amounts of hydroperoxides in polyolefins such as polyethylene (PE) may be formed inadvertently during polymerization and processing. It is found that hydroperoxides are formed almost quantitatively from the oxygen absorbed by the polymer during its induction period [26, 27, 44]. Moreover, it has been suggested that the stability of articles made from polyolefins depends largely on the concentration of hydroperoxides formed during storage of the nascent polymer before any stabilizer is added [70].

Hydroperoxides are unstable and may undergo thermal, photochemical, or catalytic [31] decomposition to generate free radicals which propagate the oxidative process and ultimately lead to the formation of alcohol and/or carbonyl groups in the polymer [51]. In particular, hydroperoxide decomposition leads to some degree of backbone scission, the direct origin of polymer embrittlement. Certain classes of stabilizers, such as the phosphites and thio compounds, are able to destroy hydroperoxide groups during processing or storage. Other types of stabilizers, such as hindered piperidinyl compounds, require oxidative conversion to an active stabilizer intermediate and this conversion is driven primarily by hydroperoxide decomposition.

The concentration of hydroperoxides during photo- and thermal oxidation increases and may reach a maximum or a plateau level corresponding to a dynamic equilibrium [7, 52, 53]. However, Gugumus [39] has proposed that the photooxidation of PE does not necessarily involve the photolysis of secondary hydroperoxide groups, but rather an oxygen–polymer charge transfer complex. Nevertheless, hydroperoxide species do form and accumulate during the photooxidation of PE and these are suggested to play a major role in free-radical formation [52, 53].

If hydroperoxide groups are produced in sufficient numbers and are stable enough to accumulate to high concentrations, they may be detected by various methods. Highly sensitive methods for hydroperoxide detection based on chemiluminescence have been developed recently [72]. Other techniques such as sulfur dioxide staining/heating [71] for detecting the spatial distribution of hydroperoxide groups in PE films and powders are refinements of older methods [69]. Analytical methods for the detection and quantification of polymer hydroperoxides have been discussed by several authors [5, 18, 34, 47] and some comparisons of these have been made [18, 34]. However, several new methods have been prepared in recent years and a critical survey of their strengths and/or limitations is appropriate.

DIFFICULTIES IN DETECTING POLYMER HYDROPEROXIDES

Although there are usually no problems with the determination of hydroperoxides in polymers soluble at low temperatures, complications arise if the polymer is insoluble or soluble only at high temperatures where significant thermal decomposition of hydroperoxides occurs [7, 18, 25, 70]. For example, hydroperoxides in polyamides are particularly difficult to quantify because of their thermal instability [4, 34]. However, the dissolution of these polymers can be achieved at room temperature using fluoroalcohols such as tetrafluoropropanol.

The quantitative determination of hydroperoxides in high-density polyethylene (HDPE) is complicated by the fact that this polymer is not soluble below 100°C. Furthermore, the concentration of hydroperoxides in HDPE is often very low compared with, for example, polypropylene (PP). Indeed, very few methods of hydroperoxide analysis are sufficiently sensitive to measure the very low concentrations of hydroperoxide found in processed polymers [3].

COLORIMETRIC METHODS

Iodometric Methods

A method based on the oxidation of the iodide ion by hydroperoxide is the most widely used of all techniques for hydroperoxide analysis and accounts for approximately 70% of reported methods of hydroperoxide determination in polymers. The iodometric method was first described by Heaton and Uri [40] and later refined by Mair and Graupner [57] and Carlsson and Wiles [11] to remedy earlier deficiencies.

In the presence of acid, polymer hydroperoxides oxidize iodide ions to iodine [Eq. (1)]. The intensely colored triiodide species is subsequently formed via the reaction between iodine and excess iodide [Eq. (2)] during refluxing. The concentration of triiodide can be measured

$$\mathrm{ROOH + 2I^- + 2H^+ \longrightarrow I_2 + H_2O + ROH} \qquad (1)$$

$$\mathrm{I_2 + I^- \rightleftharpoons I_3^-} \qquad (2)$$

by titrimetry [8, 24, 26, 27, 40, 57, 68, 74] or by ultraviolet (UV)/visible spectrophotometry [1, 6, 11, 35, 75]. Spectrophotometric determination of triiodide is usually carried out at a wavelength of 362 nm where the molar extinction coefficient [36] of the triiodide species is 2.530×10^4

M^{-1} cm^{-1}. Wavelengths of 352, 360, 425, and 460 nm have also been used to detect the triiodide species [1, 6, 35]. Carlsson and Wiles [11] found that if 1-cm absorption cells are used, the iodometric method is capable of determining hydroperoxide concentrations down to 1×10^{-4} mol kg^{-1}. The method can be effectively used for oxidized polymeric films of thickness less than 200 μm, where it purportedly has a lower detection limit of about 30 ppm hydroperoxide [41].

The reflux times adopted by various workers who have used iodometric methods vary considerably from 3 min to 18 h [1, 8, 11, 27, 30, 57, 58, 62, 66]. The loss of hydroperoxide during refluxing is generally considered negligible. For example, Decker et al. [27] found that after 1-h refluxing, the hydroperoxide level detected in polyolefins is equal to 93% of the value obtained after a 3-min reflux. A 5-min reflux period is normally required to produce a quantitative yield of triiodide in hydroperoxide determinations on nonsoluble polymers in the absence of diffusion effects. However, the production of triiodide from some polymers may be limited by the slow diffusion of reagents into the sample and so a reflux period of 30 min is necessary for 40 μm thick films, especially if crosslinking has occurred as in the case of γ-initiated oxidations [11]. For highest sensitivity, low reagent blanks are required. These may be achieved by the use of very pure sodium iodide and peroxide-free (HPLC grade) propan-2-ol solvent. The latter, however, peroxidizes itself upon standing once opened to the air.

Gardette and Lemaire [34] explored the reliability of the iodometric method for a wide range of oxidized polymers. It was concluded that the method is not quantitative if the hydroperoxide groups are unstable at the reflux temperature (approximately 80°C), as is the case for oxidized polyamides. The solubility of polyamides in fluoroalcohols enables iodometric determinations to be performed at temperatures close to room temperature [4] but it is difficult to cross-check the completeness of reaction against other methods. Gijsman et al. [37] used room-temperature iodometry after a prolonged preswelling to measure peroxides in thermally oxidized PP. Despite the long reaction times used (50 h under oxygen-free conditions), it is possible that reaction had only occurred at the polymer surface. Complete quantification of hydroperoxide should ideally be confirmed by comparison with other methods such as infrared (IR) analysis.

Despite its high sensitivity and linearity of response, the iodometric technique is subject to certain interferences. For instance, any species which can oxidize iodide or reduce iodine will interfere. In oxidized

PE, oxidation products such as carboxylic acids may react with the liberated iodine and cause rapid bleaching [33]. Holtz et al. [42] reported that iodometric hydroperoxide determination in oxidized PE is unreliable due to interfering reactions from olefinic functional groups. Although subsequent researchers have established that the presence of double bonds does not appear to interfere with the method, peroxidic compounds such as peracids, peresters, and some dialkylperoxides can oxidize iodide and produce erroneously high results [11, 66]. Furthermore, products from some stabilizer systems, such as nitroxides from piperdinyl compounds, can also lead to erroneous results obtained from the iodometric method.

The use of excess iodide in the reaction mixture causes the iodine–triiodide equilibrium [Eq. (2)] to lie far to the right. Consequently, the almost complete conversion of iodine to the nonvolatile and photostable triiodide species in the presence of excess iodide ensures that the loss of iodine from the system is minimized.

Iodometric Methods for Total Peroxide Determination

During the oxidation of polyolefins both hydroperoxides (ROOH) and dialkylperoxides (ROOR) are formed [26, 27, 53, 62, 74]. It is claimed that these species can be distinguished by iodometric analysis either by changing the temperature at which the titration is performed [41] or by changing the nature of the acidic medium [57, 62, 68]. Shilov and Denisov [74] and Cicchetti et al. [24] determined the total peroxide concentration in PE by iodometry using hydriodic acid as a reagent which produces stronger reducing conditions than acetic acid [24]. However, caution should be applied in using strong acids in quantitative work because of drifting end points and extremely high reagent blanks.

Rapoport et al. [68] and Niki et al. [62, 63] described iodometric methods in which the hydroperoxides in PE are determined using acetic acid as the acidic medium and the total peroxide content (ROOR and ROOH) is determined using hydrochloric acid as suggested by Mair and Graupner [57]. The concentration of ROOR may thus be determined from the difference between the total peroxide concentration and the concentration of ROOH. The concentration of ROOR in the presence of ROOH has also been determined for oxidized PP film by treating the sample with SF_4 to remove all of the hydroxyl groups [11]. Since SF_4 does not attack dialkylperoxides, the concentration of these can be estimated by the iodometric method after the SF_4 treatment.

Ferrometric Methods

The ferrometric methods for the determination of hydroperoxides exploit the stoichiometric oxidation of ferrous ions by hydroperoxides [Eq. (3)]. The concentration of Fe^{3+} ions formed during the reaction

$$2Fe^{2+} + ROOH + 2H^+ \longrightarrow 2Fe^{3+} + ROH + H_2O \tag{3}$$

can be determined colorimetrically by complexing these with thiocyanate (SCN^-) ions to produce the highly colored $Fe(SCN)_6^{3-}$ complex (molar extinction coefficient of $1.34 \times 10^4\ M^{-1}\ cm^{-1}$ at 512 nm). Alternatively, the decrease in the concentration of Fe^{2+} ions can be determined colorimetrically via its complex with 1,10-phenanthroline.

Thiocyanate Complexing of Ferric Ions

The method involving the thiocyanate complexation of Fe^{3+} produced from the oxidation of Fe^{2+} by hydroperoxides ("ferric thiocyanate" method) was first applied to polymers by Zeppenfeld [78] and has since been refined by a number of workers [20, 34, 38, 42, 50, 59, 65, 66, 73]. Scott et al. [3, 20, 73] have used the ferrous ion titration method routinely for estimating the growth and decay of hydroperoxides during the photo- and thermal oxidation of PE.

The method assumes that hydroperoxides are stoichiometrically reduced in the oxidation of Fe^{2+} to Fe^{3+}, and that the Fe^{3+} ions are quantitatively complexed by SCN^- [Eq. (4)]. The concentration of hydroperoxides can be calculated by spectrophotometrically determining

$$Fe^{3+} + 6SCN^- \longrightarrow Fe(SCN)_6^{3-} \tag{4}$$

the concentration of the colored $Fe(SCN)_6^{3-}$ complex or by titrating the hydroperoxides with a ferrous ammonium thiocyanate solution [50] in benzene. The ferric thiocyanate method is suitable only for easily reduced peroxides such as hydroperoxides, peracids, and diacylperoxides. This makes the method particularly well suited for unstable hydroperoxides, but complete solubilization of the polymer is required [34]. The accuracy of the ferric thiocyanate method depends strongly on temperature and the suppression of side reactions such as the one shown in Eq. (5).

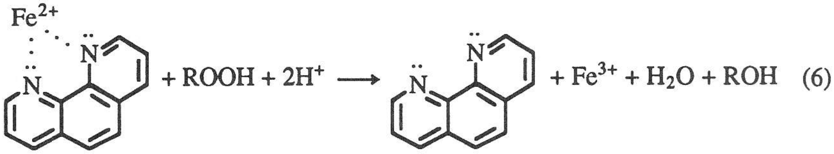
$$RO^{\cdot} + Fe^{2+} + H^+ \longrightarrow ROH + Fe^{3+} \tag{5}$$

Despite its limitations, the method is reported to be quite sensitive [66] and is capable of detecting hydroperoxides at levels as low as 10^{-3} mol kg^{-1} polymer [78]. Petruj et al. [66] reported that the reproducibility of the colorimetric ferric thiocyanate method when applied to low-density polyethylene (LDPE) is excellent, taking into account the heterogeneous character of oxidation in the polymer. However, this conclusion has been challenged by Carlsson and Lacoste [18], who compared hydroperoxide levels as measured by both the ferric thiocyanate and iodometric methods on polymer samples that were oxidized under identical conditions. The latter method produced values consistently 10 times greater than the room-temperature ferric thiocyanate method for preswollen samples of both PE and PP film. The nitric oxide method (see below) was also applied to these samples and confirmed the iodometric values. The shortcomings of the ferric thiocyanate method were attributed to the failure of the reagents to fully penetrate the oxidized polyolefins, even after preswelling in benzene.

It has been established [66] that the presence of phenolic antioxidants such as butylated hydroxytoluene, thioesters such as dilaurylthiodipropionate, or benzophenones such as Tinuvin P, do not interfere with the ferric thiocyanate method even at concentrations far in excess (i.e., 500 times) of that of the hydroperoxides. However, the presence of hindered amine light stabilizers does interfere strongly with the ferric thiocyanate method [66].

Complex of Ferrous Ion with 1,10-Phenanthroline

Bocek [9, 10] developed a method of hydroperoxide quantification in atactic PP which involves first treating the hydroperoxides with the complex formed between Fe^{2+} and 1,10-phenanthroline [Eq. (6)]. The



(6)

method is purported to have a lower hydroperoxide detection limit of 10^{-3} mol kg^{-1} in polymer samples of suitable size. As the method relies on the decreased absorbance of the Fe^{2+}/phenanthroline complex that results from the oxidation of Fe^{2+}, its main disadvantage is that the strongest coloration is observed at zero concentration of hydroperoxide. Thus, in the case of very low hydroperoxide concentrations, quantification involves the subtraction of two comparatively high absorbance values, which reduces significantly the accuracy of the determination [66]. In contrast, the ferric thiocyanate method produces a coloration that increases with increasing hydroperoxide concentration and, as such, is better suited for the analysis of low levels of hydroperoxides in polymers amenable to this method.

Amin et al. [3] suggested that the Fe^{2+}/phenanthroline method is not reproducible when applied to PE because the phenanthroline complex is unstable at the wavelength (510 nm) used for its measurement. Furthermore, there is only a slow penetration of the phenanthroline complex into PE films and the recommended reaction time of 15 min is insufficient for constant stoichiometry to be achieved. An extended reaction time of 2 h is necessary to increase the penetration of the complex into PE [3].

Solvents for Colorimetric Hydroperoxide Determinations

The application of colorimetric methods for the analysis of hydroperoxides in polymers is possible only if the polymer can be dissolved or if the reactants can diffuse significantly into the polymer matrix. Diffusion is enhanced by using solvents, or solvent mixtures, which are capable of swelling the polymer by penetrating its amorphous regions. Solvents frequently used in the determination of hydroperoxides in synthetic polymers include benzene, toluene, xylenes, chloroform, and propan-2-ol.

Citovicky et al. [25] compared the effectiveness of various solvents frequently used in the iodometric determination of PP hydroperoxides in the presence of glacial acetic acid and potassium iodide. Chloroform was found to be the solvent that is most effective at penetrating the polymer matrix. The next most effective is carbon tetrachloride, followed by benzene, *n*-heptane, and propan-2-ol. Interestingly, an equivolume mixture of chloroform and *n*-heptane proves to be more effective than chloroform [25].

Petruj et al. [66] suggested that in order for the determination of trace levels of hydroperoxides in PE to be accurate, the reaction medium must be completely nonoxidizable so as to prevent background interferences. In this regard, benzene has been recommended as a swelling reagent for polyolefins since it is relatively inert towards oxidation. The addition of 4% (v/v) methanol to benzene increases the polarity of the solvent system and improves the accuracy in the determination of organic hydroperoxides in degraded polyolefins.

Use of Inert Atmospheres

For some hydroperoxide determinations it is necessary to blanket the reaction mixture with an inert gas such as nitrogen during the swelling and refluxing stages. This is because alkoxyl radicals in the presence of atmospheric oxygen can produce additional hydroperoxides [65]. Furthermore, in the iodometric method of hydroperoxide analysis, rapid aerobic oxidation of iodide ions tends to occur if acetic acid is used as the catalyst but this problem can be avoided by using acetic anhydride instead [64]. It has also been reported [57] that the use of propan-2-ol as the solvent imparts high oxidative stability to iodide ions and eradicates the need for nitrogen blanketing.

TRIPHENYLPHOSPHINE METHOD

Triphenylphosphine reduces polymer hydroperoxides to alcohols which, in some cases, can be subsequently analyzed by gas chromatography [42, 50, 60]. This method has been used as an independent means of checking the results of iodometric determinations on low molecular weight hydroperoxides [50, 60]. However, macroalcohols originating from hydroperoxide groups in polymers cannot be analyzed by gas chromatography and only the triphenylphosphine oxide reaction product can be conveniently detected in such cases.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

The quantification of polymer hydroperoxides by direct spectroscopic techniques is often limited either by the sensitivity or by the resolution of the technique. Nuclear magnetic resonance (NMR) spectroscopy on dissolved samples has superb resolution but modest sensitivity in the detection of polymer hydroperoxides. Despite this limitation, polymer hydroperoxides have been identified and quantified by high-resolution solution NMR [19, 45].

Although almost every conceivable oxidation product of the polymer can be identified by NMR spectroscopy, the method suffers from several disadvantages. A very long time is usually required for the acquisition of data with adequate signal-to-noise ratio. Even when this is achieved the method can only detect oxidation products that are present at quite high levels (≥ 0.1 mol kg^{-1}) where the polymer is highly degraded. In addition, the dissolution of polyolefins occurs only at temperatures where hydroperoxide groups decompose rapidly. This makes the NMR spectra dependent upon the heating period required to dissolve the sample and necessitates the back-extrapolation of the data to zero heating time if a reliable quantification is to be achieved.

INFRARED METHODS

Direct Infrared Methods

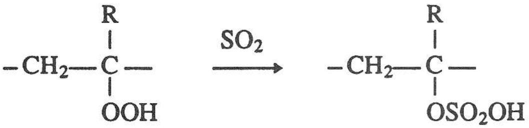
Weak IR absorptions due to polymer hydroperoxides occur at 3550–3555 cm^{-1} for isolated hydroperoxides and about 3400 cm^{-1} for hydrogen-bonded hydroperoxides. Jellinek [46] and Luongo [55, 56] reported that the 3555 cm^{-1} absorption, generally attributed to isolated hydroperoxides [75], is particularly diagnostic for the detection of hydroperoxides in polyolefins but fails to quantify hydrogen-bonded hydroperoxide groups. Although this absorption is measurable in LDPE it is extremely weak in linear low-density polyethylene (LLDPE) and HDPE. Despite the low sensitivity, IR methods can be used to give a cross-check on the broad level of hydroperoxide groups in a polymer sample.

The IR absorption at ca. 3400 cm^{-1} has been used to monitor the buildup of hydrogen-bonded hydroperoxides during the thermal oxidation of HDPE, LLDPE, and PP [48, 52, 53]. The small quantity of hydroperoxides which is formed is difficult to detect because the extinction coefficient, ϵ, of the hydroperoxide group ($\epsilon \approx 90$–70 M^{-1} cm^{-1}) [75] is considerably lower than that of the carbonyl group ($\epsilon \approx 300$–675 M^{-1} cm^{-1}) [43] at this wavenumber. Hydrogen-bonded alcohol groups also absorb at around 3400 cm^{-1} and IR measurements will thus produce an overestimate of the hydroperoxide level, unless the alcohol level can be shown to be insignificant by, for example, the nitric oxide method [14]. Moreover, attempts to identify differing hydroperoxide groups in oxidized polyurethanes based on vague features that appear on the broad hydroxyl absorption in the IR region seem to be suspect because of severe shifts caused by hydrogen bonding [54].

Indirect Infrared Methods

Sulfur Dioxide Method

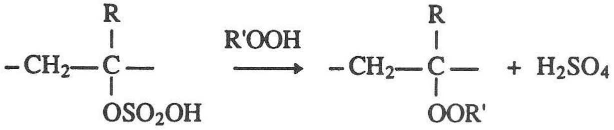
The sulfur dioxide method relies on the derivatization of hydroperoxide groups in order to overcome their weak IR absorptions. Mitchell and Perkins [61] showed that polymer hydroperoxides can be transformed into alkyl hydrosulfates by treatment with sulfur dioxide [Eq. (7)]. Alkyl hydrosulfates absorb at a well-defined position in the IR spectrum (1195 cm^{-1}) compared with bound hydroperoxide groups, which give a weak band that overlaps with the broad alcohol absorption band.



$$-CH_2-\overset{\overset{R}{|}}{\underset{\underset{OOH}{|}}{C}}- \xrightarrow{SO_2} -CH_2-\overset{\overset{R}{|}}{\underset{\underset{OSO_2OH}{|}}{C}}- \qquad (7)$$

The high sensitivity of modern Fourier transform infrared (FTIR) spectrophotometers enables the detection of hydroperoxide levels down to 10^{-3} mol kg^{-1} [34]. However, the claim [61] that 0.1 ppm hydroperoxide in PE should be detectable at 1195 cm^{-1} after treatment with SO_2 has been regarded as highly suspect [41]. Even in the case of heavily oxidized LDPE, the reaction between SO_2 and polymer hydroperoxides [Eq. (7)] is not quantitative and so this technique can produce erroneous results for hydroperoxide determinations [13, 16].

Tabankia et al. [75] compared the sulfur dioxide method with the iodide method for the detection of polymer hydroperoxides. It was found that differences between the results obtained by the two methods reflect the differences in the accessibility of the reagents to deeper regions within the polymer samples. Furthermore, Carlsson and Wiles [11] found that the sulfur dioxide method does not work satisfactorily for oxidized PP because the expected IR band at 1195 cm^{-1} is largely masked by the IR absorption of H_2SO_4 produced in the highly hydroperoxidized domains found in oxidized PP [Eq. (8)] [13].

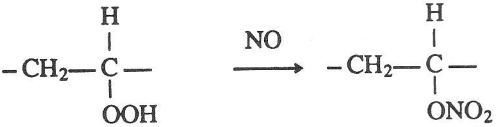


$$-CH_2-\overset{\overset{R}{|}}{\underset{\underset{OSO_2OH}{|}}{C}}- \xrightarrow{R'OOH} -CH_2-\overset{\overset{R}{|}}{\underset{\underset{OOR'}{|}}{C}}- + H_2SO_4 \qquad (8)$$

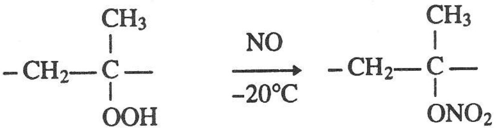
A variation of the sulfur dioxide method has been reported by Gardette and Lemair [34] where, instead of measuring the sulfate peak (1195 cm^{-1}), the hydroperoxides that are not hydrogen bonded are measured by the diminution of their hydroxyl stretching peak (3555 cm^{-1}). Moreover, Henman [41] has used the extremely high sensitivity of X-ray fluorescence to monitor atomic sulfur remaining in the oxidized polymer after SO_2 exposure. Although this method should be reliable for detecting hydroperoxides in oxidized PE, it may suffer from the variable stoichiometry in the reaction between SO_2 and polymer hydroperoxides [Eq. (7)].

Nitric Oxide Method

The efficient reaction of SO_2 with hydroperoxide sites results from the ease of reaction of each hydroperoxide group with a small gas molecule which can diffuse through the solid polymer. This concept has been extended by the use of nitric oxide (NO). By careful control of the reaction conditions, quantitative reaction between NO and polymer hydroperoxides occurs to produce nitrate groups which are readily measured by their IR absorption [Eqs. (9) and (10)] [14]. This technique



$$-\mathrm{CH_2}-\underset{\mathrm{OOH}}{\overset{\mathrm{H}}{\mathrm{C}}}- \xrightarrow{\mathrm{NO}} -\mathrm{CH_2}-\underset{\mathrm{ONO_2}}{\overset{\mathrm{H}}{\mathrm{C}}}- \qquad (\mathrm{IR}\ 1276\ \mathrm{cm}^{-1}) \tag{9}$$



$$-\mathrm{CH_2}-\underset{\mathrm{OOH}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}- \xrightarrow[-20^{\circ}\mathrm{C}]{\mathrm{NO}} -\mathrm{CH_2}-\underset{\mathrm{ONO_2}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}- \qquad (\mathrm{IR}\ 1290\ \mathrm{cm}^{-1}) \tag{10}$$

has several advantages, including its ability to quantify hydroperoxide groups in the presence of alcohols and, most importantly, its ability to discriminate between primary, secondary, and tertiary hydroperoxides. The latter results from the sharp IR absorptions of the respective nitrate products which can be deconvoluted, for example, in some oxidized samples of PP. The poor thermal stability of tertiary nitrate groups at room temperature means that the reaction between oxidized PP and NO should be carried out at $-20°C$. The reaction is believed to be quantitative up to modest degrees of peroxidation (ca. 0.3 mol kg^{-1}), as shown by the correlation between total hydroperoxide level as determined from NO reaction, iodometry, and direct IR measurement assuming all of the 3400 cm^{-1} absorption results from hydroperoxide, which is the case for γ-oxidized PP.

In γ-, photo-, and thermally oxidized PP, tertiary and secondary hydroperoxide groups have been quantified and found to be present in a ratio of about 10:1 [53]. The frequently reported differences in PE oxidative sensitivity result from the varying levels of initiating impurities required to drive photo- and thermal oxidations. Identical rates of secondary hydroperoxide formation were found in HDPE, LDPE, and several LLDPE materials that were oxidized using γ-initiation [15]. Even in the case of highly branched LLDPE containing three tertiary carbon–hydrogen branch sites per 100 carbon atoms, only secondary hydroperoxide groups can be observed [15].

COMPARISON OF HYDROPEROXIDES IN POLYPROPYLENE AND POLYETHYLENE

Oxidized PP contains a much higher concentration of hydroperoxides than PE oxidized under identical conditions. In isotactic PP, long sequences, or "blocks," of tertiary hydroperoxides are usually formed when the polymer is oxidized [38, 46]. In contrast, the hydroperoxide groups in PE are generally isolated from each other, although these may be hydrogen bonded to other oxidation products. This difference in the patterns of oxidation stems from the lower rate of attack of peroxyl radicals on secondary carbon–hydrogen sites as compared with their attack on tertiary carbon–hydrogen sites, the latter being about 10 times more reactive [17]. In addition, self-reaction of tertiary peroxyl radicals is very slow (and often not chain terminating) whereas secondary peroxyl radicals terminate much more rapidly. Even in LDPE and LLDPE the concentrations of tertiary carbon–hydrogen sites (at the branch points) are still very low. Oxidation at these branch sites has, however, been observed using high-resolution NMR and IR derivatization techniques [15, 19].

The oxidation of polymers having regular, reactive, tertiary carbon–hydrogen sites along the backbone can give rise to three types of hydroperoxide sites. These are: (i) isolated hydroperoxides that are not hydrogen bonded; (ii) runs of adjacent, hydrogen-bonded hydroperoxides that are formed by the sequential intramolecular propagation of peroxyl radicals and that occur at alternate positions along the backbone; and (iii) hydroperoxides that are hydrogen bonded to oxidation products such as other hydroperoxides, ketone, or carboxylic acid functionalities and that occur on adjacent chain segments.

Infrared spectroscopic studies of some oxidized PP and PE samples show the presence of isolated hydroperoxides as a sharp absorption at about 3550 cm^{-1} [17]. These can be clearly differentiated from isolated alcoholic hydroxyl groups (3650 cm^{-1}) and all other hydrogen-bonded alcohol and hydroperoxide groups (ca. 3400 cm^{-1}). However, the hydrogen-bonded species usually dominate.

Chien et al. [22] attempted to confirm the presence of hydroperoxide runs in oxidized PP. To do this, a series of reactions was used that was believed to quantitatively convert the hydroperoxide groups first to alcohol and then to carbon–carbon unsaturation. The lengths of the conjugated unsaturation sequences were established from the UV absorption spectrum of the final, treated polymer, and the initial hydroperoxide runs were inferred to be 60% adjacent tertiary hydroperoxides, 20% trihydroperoxides, and a further 10% distributed in runs of up to eight adjacent groups.

The hydroperoxide groups in PP can also occur in isolated positions and the proportion of this type as compared with hydroperoxide "blocks" depends on the oxygen pressure during hydroperoxide formation [28, 29]. Isolated hydroperoxide groups appear to form in the early stages of radical-pair propagation. At later stages, when the individual radicals formed from the initiation process are well separated as a result of propagative translation, clusters of hydroperoxide groups seem to result [12].

STABILITY OF HYDROPEROXIDES

The stability of polymer hydroperoxides depends largely on the proximity of neighboring hydroperoxide groups, other oxidation products, the temperature, and the presence of metal ions. Transition metal ions reduce the stability of hydroperoxides because the activation energy of the metal ion catalyzed decomposition of hydroperoxides is much less than that of the bimolecular hydroperoxide decomposition as depicted in the basic autooxidation scheme [46]. However, the alkylperoxyl and alkoxyl radical products are the same in each case. The presence of "blocks" of hydroperoxides in PP favors their bimolecular decomposition as this has a lower activation energy than the monomolecular reaction. Thus the initiation rate associated with hydroperoxide "blocks" is superior to that associated with isolated hydroperoxides.

Under some oxidative conditions, such as high-temperature thermal oxidation, the stationary concentration of hydroperoxides in LDPE may be too low to be measured by conventional techniques, whereas in the case of PP the formation and decay of hydroperoxides can usually be measured accurately [2]. The factors responsible for the relatively low concentration of hydroperoxides in LDPE include its relatively short kinetic chain length of oxidation [5, 47], especially at low oxygen pressures, and the instability of its hydroperoxides to heat and light [16].

Hydroperoxides are readily detected in PE which has been photo- and/or thermally oxidized under conditions as moderate as those imposed by longer wavelength UV from solar simulation or thermal oxidation at temperatures below 100°C [52]. Hydroperoxide formation is particularly striking during the γ-initiated oxidation of PE and PP, where the hydroperoxide concentration increases linearly with dose [52, 53]. This well-behaved formation results from the stability of the hydroperoxide groups over the time scale of the γ-irradiation. However, the γ- (or electron beam)-initiated oxidation of polyolefins is complicated by the slow but steady postirradiation oxidation. This thermal oxidation is driven by the slow decomposition of hydroperoxide groups even at room temperature [51].

Pleshanov and Berlyant [67] noted that the oxidative resistance of partially oxidized PE can be improved by long-term heating in a vacuum at temperatures below the melting point so as to decompose peroxidic impurities. Other workers [58] have found that residual hydroperoxides in PE are removed by 2-h heating at 150°C in an atmosphere of nitrogen because most of the hydroperoxides in PE are readily decomposed at temperatures greater than 100°C. Chien [21] has found that more than 85% of PP hydroperoxides are rapidly decomposed within the temperature range of 100°–135°C. Moreover, the thermal stability of hydroperoxides in PP is particularly low compared to PE and appreciable decomposition occurs at temperatures slightly above 30°C [25].

The anomalous thermal stability of PE and PP hydroperoxides was first reported by Chien and Jabloner [23], who found that at modest temperatures (85°–135°C) in the absence of oxygen, the hydroperoxides undergo decay by dual kinetics. The faster component in the decay was attributed to the decomposition of sequences of adjacent tertiary hydroperoxide groups attached to the backbone at alternate positions. The slower component in the decay was attributed to isolated hydroperoxide groups. Quite recently, Zahradnickova et al. [76, 77] investigated another facet of this phenomenon and concluded that the faster decaying component is due to peracid (—C(=O)OOH) groups. This conclusion supports previous proposals that perester and/or peracid moieties are involved in the decay kinetics [37, 49] and is based on studies of model compounds in the liquid phase which show that dimethylsulfide (DMS) reacts extremely rapidly with peracids but much more slowly with tertiary hydroperoxides. The treatment of oxidized PP films with DMS vapor results in the elimination of the rapidly decaying hydroperoxide component, suggesting that peracids are responsible for the more rapidly decaying component.

Although several authors have proposed the involvement of peracids, no firm, unequivocal identification has been made. Indeed, the conclusion reached by Zahradnickova et al. [76, 77] has been contradicted by the work of Falicki et al. [32] which showed that DMS also reacts with hydroperoxides in the polymer, as confirmed by iodometry and the nitric oxide–FTIR derivatization method. Both tertiary and secondary hydroperoxides in oxidized PP exhibit dual kinetics during their destruction by DMS, as do the secondary hydroperoxides in oxidized PE samples. The latter authors suggested that the faster decaying hydroperoxide groups are those that are hydrogen bonded to carboxylic acid sites.

Moreover, the reaction of an oxidized polymer with gaseous diazomethane can be used to differentiate between peracid and carboxylic acid functionalities [16]. The former yields a methyl perester absorbing in the infrared at 1784 cm^{-1} whereas the latter yields a methyl ester absorbing at 1740 cm^{-1}. Studies using model compounds have shown that the reaction must be carried out at −78°C because reaction at room temperature yields a methyl ester rather than a methyl perester from the peracid. Even under low-temperature reaction conditions, the peracid derivative has not, as yet, been identified in oxidized PP or PE [16].

GLOSSARY

DMS	dimethylsulfide
FTIR	Fourier–transform infrared
HDPE	high-density polyethylene

HPLC	high-performance liquid chromatography
IR	infrared
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
NMR	nuclear magnetic resonance
PE	polyethylene
PP	polypropylene
ROOH	hydroperoxide species
ROOR	alkyl hydroperoxide species
Tinuvin P	2-(2′-hydroxy-5′-methylphenyl)-2*H*-benzotriazole
UV	ultraviolet

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Note Added in Proof. Mielewski et al. [79] have developed a successful iodometric procedure to quantify hydroperoxide levels in weathered automotive paints. These highly crosslinked acrylic copolymers were first cryoground and then swollen in dichloromethane before refluxing with acidified sodium iodide. In addition, these authors were able to overcome the interference by nitroxides generated from HALS photostabilizers in paint film. Iodine liberated by the nitroxide was estimated from the partial changes in nitroxide concentrations, measured by electron spin resonance spectroscopy. Overall iodine yields were then back corrected for the nitroxide generated level.

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