Photo-Oxidation of Polymers: Validation of Oxygen Uptake and Relationship with Extent of Hydroperoxidation

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ABSTRACT: In this piece of work we focused our attention on the peroxidation step and alongside considered hydroperoxides as probes for the overall oxidative process. This technique of oxygen uptake actually monitors the amount of oxygen consumed during polymer degradation. Our present work aimed to investigate this technique to evaluate the oxygen uptake during in situ photoirradiation, under controlled atmosphere. Our experimental results clearly elucidate that the oxygen consumption data accounts for a very early stage of aging during the photo-oxidation of polymers and provides us with an accurate and sensitive diagnosis about the formation of hydroperoxides. A straight-line relationship was exhibited under our experimental conditions while observing a relation between oxygen pressure drop and hydroperoxide content in the polymer. This correlation was dependent upon the nature of polymer and of course on the aging conditions (temperature, irradiation, oxidative atmosphere). The impact of environmental atmosphere on aging was particularly kept in mind. To conclude, we emphasized that oxygen uptake is a promisingly powerful tool to identify the impact of the overall environmental parameters on the polymer photoaging. An important implication was on the understanding of atmospheric factors (including pollutants such as O_3, NO_x, etc.), which is usually given minor importance, on the degradation of polymer upon outdoor weathering. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2238–2244, 2006

Key words: oxygen uptake; photo-oxidation; hydroperoxides; degradation

INTRODUCTION

It is well-known that the formation of peroxidic species in the polymer backbone is encountered as the primary step of the oxidative degradation.[1–3] The hydroperoxide groups not only play an important role in inducing both thermal and photo-oxidation of polymers, but are also important intermediates in the overall oxidation reactions. Thus, (hydro)peroxides are the key products in the clear understanding of a mechanism, as well as to gain better insight into correlation between chemical evolution and evolution of the molecular structure (scission/recombination/crosslinking).[4–6] Hence, it becomes utterly important to explore a sensitive method to detect and quantify the presence of even a very low content of peroxidic species.

Oxygen uptake is reported as an absolute, sensitive and a quantitative technique that allows a direct measure of the consumption of oxygen during polymer degradation. The applications of oxygen uptake technique in evaluating polymers' stability have been extensively reviewed including different modification in the device.[7]

The oxygen uptake method was mainly described as an available technique to characterize thermal stability of a large range of polymers.[1,8–10] The wide majority of oxygen uptake studies have been devoted to the thermo-oxidation of polymeric materials at the elevated temperatures. Only few authors reported the usage of this technique during photo-oxidation.[11] However, majority of these studies were conducted on preirradiated polymer samples.[12,13] The oxygen consumption was not monitored under in situ conditions throughout the course of photo-oxidation.

Our aim was to draw attention on this powerful, old and often underestimated technique. The oxygen uptake method was revised i.e., the conventional device has been modified to quantify the oxygen consumption during in situ irradiation under controlled atmosphere. Ethylene–propylene elastomer (EPDM), a dienic polymer (polyoctenamer), and poly(ethylene terephthalate) were selected as test polymers to evaluate the performance of oxygen uptake method during the first step of aging under in situ photo-oxidative conditions.

EXPERIMENTAL

Materials

Polymers used were unstabilized elastomers. Ethylene–propylene terpolymer (EPDM) supplied by Exxon as Vistalon 7500 and polyoctenamer rubber (PO)

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named Vestenamer® 8012, was provided by Cre-anova. Virgin samples were purified twice by precipitation to remove the presence of any possible additives. Films were then prepared by compression molding between two polyester sheets under 100 bar for 1 min, at 120°C and 60°C for EPDM and PO, respectively. Thickness was maintained at around 100 μm.

Unstabilized poly(ethylene terephthalate) (PET) scraps of recycled PET (arise from heterogeneous deposits of various colored post consumer bottles) were kindly supplied by CEREMAP, France. Films were prepared by compression molding between two polyester sheets under 100 bar for 1 min at 260°C (thickness about 100 μm).

FTIR spectroscopy

Chemical changes upon oxidation were detected by FTIR spectroscopy in transmission mode, using a Nicolet Impact 400 instrument (Omnic software). The major by-products resulting from oxidation are carbonylated and hydroxylated species, absorbing at about 1710 cm^{-1} and 3400 cm^{-1}, respectively. Since carbonylated species are characterized by high-extinction coefficients (typically around 350 L mol^{-1} cm^{-1}), the absorption band centered at 1710 cm^{-1} results in a high-sensitive parameter, quantitatively related to the amount of oxidation.[14] Hence, as in conventional practice, we concentrated on the carbonyl stretching vibration region (1830–1600 cm^{-1}).

Peroxides titration

Peroxidic species were estimated by iodometric titration[15,16] based on the reduction of (hydro)peroxides by sodium iodide in excess, in acidic medium (acetic acid/isopropanol), as shown in the following reaction:

$$ROOH + 2I^- + 2H^+ \rightarrow ROH + I_2 + H_2O \quad (1)$$

$$I_2 + I^- \rightarrow I_3^- \quad (2)$$
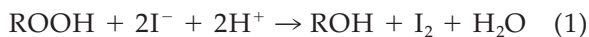
Completeness of the reaction was ensured after 1 h of reflux with fresh reagents. The concentration of the tri-iodide subsequently formed was measured by UV spectophotometry at 362 nm, considering the commonly accepted extinction coefficient of 2.5 $\times$ 10^4 L mol^{-1} cm^{-1}.

Oxygen uptake

The oxygen consumption experiments were carried out in an equipment that was built up in our Laboratory, which was quite similar to other apparatus mentioned in the literature.[7,11,17] Scheme 1 shows this oxygen uptake device. The volume of the whole appa-
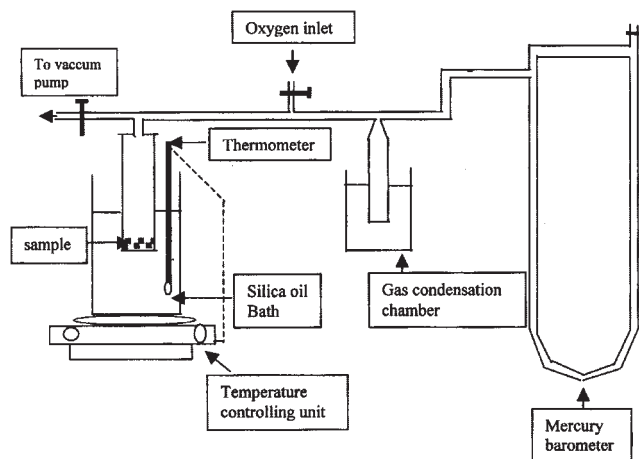
Scheme 1. Oxygen uptake device.

ratus was 153 cm^3. The temperature variation in the oil bath was ± 2°C. The oxygen consumption was measured directly by connecting the reaction chamber to a calibrated-buret type manometer filled with mercury.

To make sure that the sample is under isothermal condition during the ongoing experiment, it was first subjected to the experimental temperature under inert nitrogen. Oxidative atmosphere was then slowly injected in the apparatus while pumping out N$_2$ simultaneously. Oxygen consumption uptake experiments were performed at similar initial pressure of pure oxygen or air, chosen to be about 450 mmHg. Thermooxidation was carried out by isothermally heating the polymer thin films (thickness 100 μm, sample around 250 mg) in the range of 80–150°C.

For the purpose of photo-aging, the conventional apparatus has been modified with an irradiation chamber in place of the oil bath. The irradiation chamber has a cylindrical-shaped body with an elliptical base made of highly reflecting aluminum. A "medium pressure" mercury source filtered by borosilicate envelope (Mazda type MA 400), supplying radiation of wavelengths longer than 300 nm, is located along the focal axis. The borosilicate reactor containing the sample film (thickness 100 μm) was set along the other focal axis. The temperature of the sample was controlled by a thermocouple that is connected with a temperature regulator device, which controls a fan. Experiments were carried out at 35°C for elastomers, 60°C for PET. This polychromatic set up was based on the commercial accelerating device (SEPAP 12/24, Atlas)[18] described elsewhere.[14]

The oxygen uptake experiments were performed in a closed system; hence, to take out a sample for analysis, it was necessary to interrupt the oxidation. The oxygen consumption was calculated from the pressure drop measured from the change in the level of mercury meniscus. The data were not corrected for the evolution of gases, a procedure which is not consid-
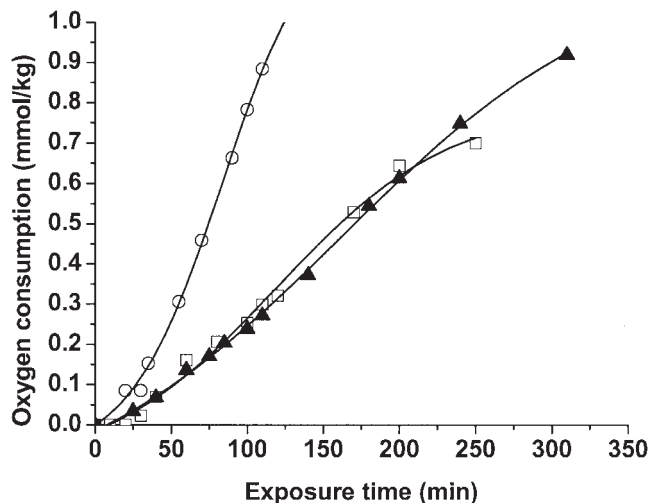
Figure 1 Kinetic oxygen consumption curves recorded for pure EPDM in pure oxygen under thermal treatment at (□) 100°C, (○) 130°C and under irradiation at $\lambda > 300$ nm at 35°C (▲).

ered necessary for all oxygen uptake values below 1800 mmol kg^{-1}.[17] Oxygen uptake data were expressed in moles per kilogram for a polymer.

RESULTS

Oxygen uptake measurements

Oxygen uptake monitors the amount of oxygen consumed during material degradation, thus, revealing a thermo- (or photo) oxidation process. Typical oxygen consumption curve is exemplified in Figure 1. The shape of observed oxygen-uptake profile is usually described as sigmoidal oxidation curve reflecting kinetic parameters. It is well-known that the induction period, process rate, and activation energy strongly depend on the type of polymer, blend ratios, presence of stabilizers, aging conditions etc.[7]

The oxygen consumption curves for unstabilized EPDM undergoing thermal degradation under oxygen atmosphere show an induction period and it is after this time that the oxidation process actually accelerates (see Fig. 1). The induction period ($t_{ind,O2}$) is a critical exposure time, defined as the time-lag during which no pressure drop is detected. Experimentally, this critical exposure time was arbitrary chosen as the time corresponding to a pressure drop (ΔP) of 2 mmHg.

First, an induction period of 40 min is noticed, coming out to be completely reproducible (as the next measured rate of oxygen consumption) and could be considered as an actual characteristic of the sample. Experimental temperature strongly affects induction period as it ($t_{ind,O2}$) was about 40 min at 100°C, 20 min at 120°C, and less than 10 min at 150°C.

Moreover, the oxygen consumption profile for this EPDM sample, which was recorded upon in situ irradiation at $\lambda > 300$ nm, 35°C, and under pure oxygen, looks similar to a typical sigmoid curve. The kinetic parameters were close to those measured under thermal treatment at 100°C. On the contrary, the oxygen-uptake results for polyoctenamer show no induction period. Oxidation starts right from the beginning of the aging exposure (not shown).

Oxygen uptake consists of a direct measure of the oxygen consumed during polymer degradation. As we had our attention focused on induction period ($t_{ind,O2}$), the oxygen consumption data accounted for the earliest stage of the oxidation process. Thus, we assume that oxygen uptake is a promising technique to provide an accurate diagnosis about the primary formation of hydroperoxides not only upon thermo-oxidation, but also through photo-oxidation.

Correlation between oxygen uptake and peroxidation

To verify our assumption, chemical evolution of samples was monitored through oxygen consumption measurements. For different pressure drops, samples were removed and characterized by iodometric titration and FTIR spectroscopy simultaneously.

Figure 1 presents the oxygen-uptake curve for EPDM films versus degradation time at 100°C under 100% oxygen. During the induction period ($t_{ind,O2}$), no pressure drop was detected and at the same time, the concentration of peroxydic groups has been checked to be equal to zero. Then, a strong pressure drop was recorded in spite of a very low hydroperoxides content, indicating that oxygen uptake represents a highly sensitive method to evaluate the earliest stage of the oxidative process. The hydroperoxides concentration was still below 10 mmol kg^{-1} when the level of pressure drops to 20 mmHg.

Figure 2 shows the relationship between oxygen-uptake data and concentration of hydroperoxides for pure EPDM (experiment was carried out under 100% O_2 at 100°C). A straight-line relationship was exhibited under the above experimental conditions. Similar trend was observed for Polyoctenamer too, both under the atmosphere of pure oxygen and in air [see Fig. 6(A)]. Hence, oxygen consumption renders information about the primary chemical evolution of polymers through thermo- (or photo-) oxidation, i.e., the initial formation of hydroperoxides. However, this relationship is strictly dependent on the nature of polymer and the aging conditions (temperature, irradiation, oxidative atmosphere, etc.).

The very first stage of oxidative aging of polymers implies to the formation of hydroperoxides as primary by-products, while their subsequent homolysis leads to carbonylated species, as detected by FTIR spectros-
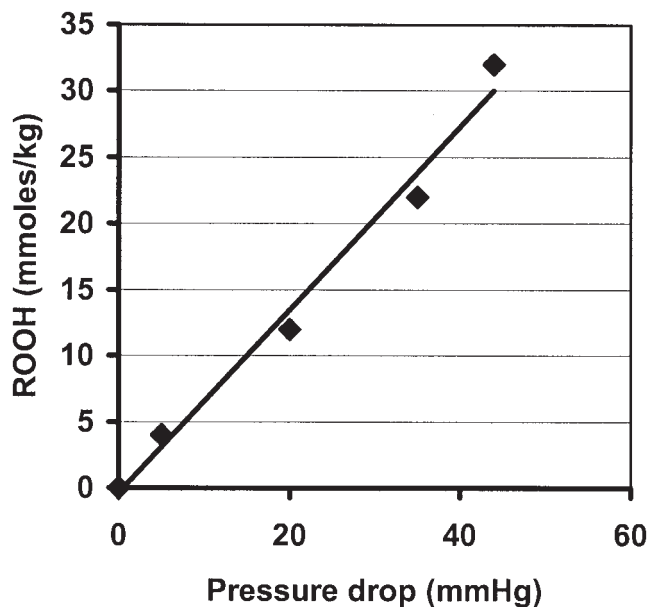
Figure 2 Correlation between oxygen pressure drop through oxygen consumption experiments at 100°C in pure oxygen and hydroperoxides content (based on an iodometric titration) for virgin EPDM sample.

copy. In the case of FTIR analysis, a critical exposure time is defined as an induction period ($t_{ind,IR}$) during which no carbonylated by-product is detected. $t_{ind,IR}$ has conventionally been defined as the exposure time corresponding to a carbonyl absorption value of 0.02 at 1710 cm^{-1}.

Figure 3 depicts the evolution of carbonylated by-products and the formation of hydroperoxides versus oxygen consumption data while polyoctenamer was irradiated in pure oxygen atmosphere at 35°C. We pointed out that oxidation starts from the very begin-
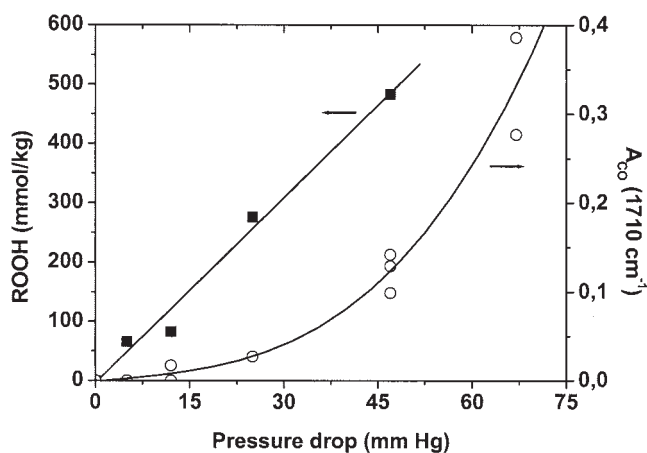

Figure 3 Correlation between oxygen consumption drops recorded for pure polyoctenamer under irradiation at λ > 300 nm at 35°C in pure oxygen and (■) hydroperoxides concentration, and (○) carbonyl formation.
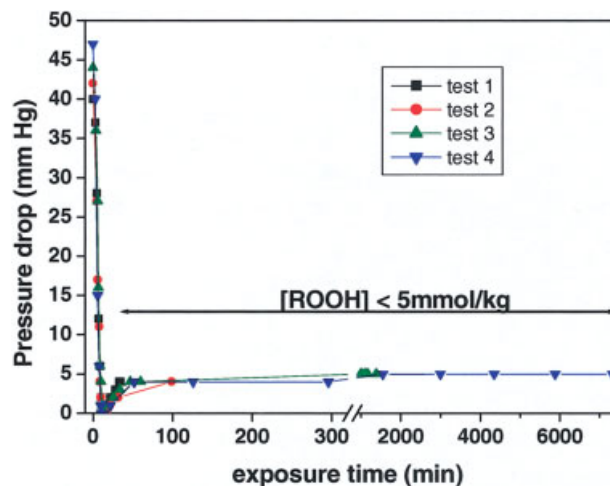

Figure 4 Kinetic oxygen consumption curves recorded for PET in pure oxygen under irradiation at λ > 300 nm at 60°C. Measurements were performed four times. [Color figure can be viewed in the online issue, which is available at www. interscience.wiley.com.]

ning of UV exposure and no induction period was thus detected while measuring oxygen consumption ($t_{ind,O2}$ value equals zero). Hydroperoxides titration was in good agreement, as a significant level of peroxidic species was quantified right from the commencement of irradiation. On the other hand, an actual induction period was revealed by FTIR analysis, which was about 50 min. This induction time ($t_{ind,IR}$) value pertains to the formation of carbonylated photoproducts. At this point, we could clearly say that even though we did not observe any changes in IR, we could detect an appreciable level of hydroperoxides (about 100 mmol kg^{-1} at $t_{ind,IR}$) and a subsequent pressure drop (about 20 mmHg) while performing oxygen consumption. This indicates that iodometric titration (as oxygen-uptake method) gives a diagnosis about the first stage of oxidative process, i.e., the peroxidation step.

Finally, Figure 4 displays the oxygen consumption curves detected upon irradiation of PET films at 60°C. Although a typical shape of oxygen consumption curve is recorded under thermo-oxidation (not shown), as already described by Gijsman and coworkers,[4] an unusual but quite reproducible behavior too was observed during photoirradiation. To check the reproducibility of the oxygen-uptake measurements, PET sample was tested several times in quite similar photoaging conditions. A drastic pressure increase was first observed during the first 10 min of irradiation because of the thermal expansion of the gas. Henceforth, there was a drop in pressure for about 40 min, which later stabilizes and reaches a plateau at a constant value of 5 mmHg. This value remains undeterred throughout for the next 125 h of exposure.

Allen et al. have reported similar changes in the hydroperoxides' concentration during irradiation of

PET bottle material. During the early stage of degradation, there was an initial rapid rise in concentration followed by a plateau.[2]

To ensure the reliability of the oxygen-uptake data, hydroperoxides determination (through titration) was carried out at different exposure times ranging from 50 min to 125 h. Very low hydroperoxide content (less than 5 mmol kg^{-1}) was titrated by iodometry and was comparable with the value indicated by Allen et al.[2] This low hydroperoxides level was in agreement with the value measured during oxygen consumption ($\Delta P \leq 5$ mmHg). This confirms that oxygen uptake directly reflects the hydroperoxidation stage.

In addition, changes were parally observed in the FTIR spectra as a function of irradiation time starting from 1 h of exposure. In hydroxyl region, an absorption band at around 3265 cm^{-1} accounts for the formation of carboxylic acids.[19] Simultaneously, the strong initial C=O stretching vibration band between 1750 and 1700 cm^{-1} was observed, getting enlarged at both extremities. Thus, oxygen-uptake measurement makes it quite evident that hydroperoxides play an important role in inducing the oxidation of PET. The low concentration of primary hydroperoxides formed undergoes a photolytic process leading to the formation of IR absorbing oxidation products. Hence, photolytic process is a main process under photo-oxidation of PET during which other minor photo-oxidative reactions intervene.

We conclude that oxygen uptake is an interesting method, which could be considered as a direct measure of oxidation. The oxygen consumption data accounts for a very early stages of the photo- (as well as thermo-) oxidation of polymers and provide fundamental information about chemical changes, especially concerning the formation of hydroperoxides. Oxygen consumption measurements combined with other standard techniques (as iodometric titration and FTIR) allow the acquisition of a clear picture of oxidation mechanism of an aging polymer.

Moreover, this technique offers a complete control on the overall environmental parameters. These parameters not only include temperature and type of aging, but also atmospheric parameter, as there is always a possibility of manipulating the composition of mixture of the oxidative gas in use.

Impact of oxidative environmental atmosphere

Figure 5 displays the oxygen consumption data obtained through in situ irradiation of polyoctenamer in pure oxygen as well as the results obtained in air.

As expected, the oxidation occurs with different rates depending upon the oxidative atmosphere. Although in both cases, no induction time was observed ($t_{ind,O2}$ equals zero), the oxygen consumption rate was higher in pure oxygen than in air. A number of re-
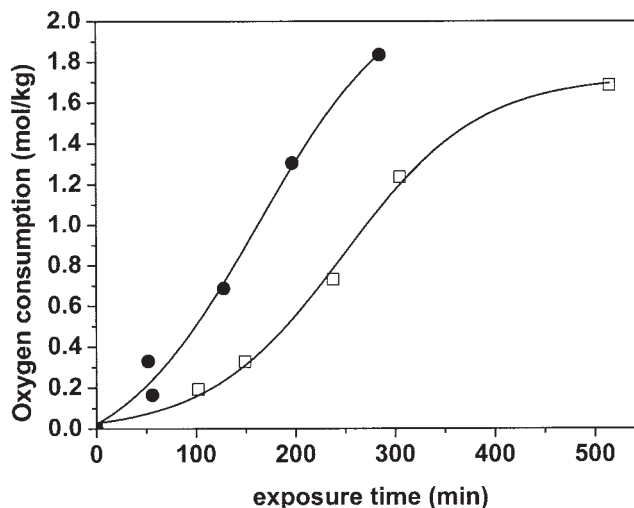

Figure 5 Kinetic oxygen consumption curves recorded for pure polyoctenamer under irradiation at $\lambda > 300$ nm at 35°C (●) in pure oxygen and (□) in air.

searchers have reported a dependance of the rate of oxygen uptake on the partial pressure of oxygen.[7,13,20] Moreover, on the basis of FTIR analysis, the photo-oxidation proceeds more rapidly in pure oxygen than in air. Carbonylated by-products are detected for an exposure time three times higher in air than in oxygen ($t_{ind,IR}$ equals 50 min and 150 min in air and in pure oxygen, respectively). The kinetic parameters are correlated with the external oxygen pressure.

On the other hand, we observed an unexpected result while following chemical changes in oxidized samples at different level of drop in the pressure. Figure 6 depicts the relationship between the hydroperoxides content (or the formation of carbonyl groups) and oxygen uptake, which was found to be dependent upon the atmospheric composition. Although peroxidation rate was clearly lower in air, the steady-state level of peroxide was surprisingly higher in air atmosphere than in pure oxygen for a defined pressure drop over the entire course of irradiation [see Fig. 6(A)]. From the earliest stage of oxidation process, for a fixed oxygen uptake indicating the amount of oxygen consumed upon the peroxidation stage, the level of hydroperoxides are shown to be related to the external pressure of oxygen.

Similarly, the conversion of oxygen into IR detectable products depends on the specific UV-degradation conditions used. The induction period for formation of carbonylated by-products ($t_{ind,IR}$) was observed at a fixed pressure drop of about 20 mmHg, regardless of the environmental atmosphere. Furthermore, after this critical exposure, less oxygen was necessary under air than under 100% O$_2$ to obtain the same level carbonyl absorbance.

From our preliminary experimental results, for a fixed oxygen uptake, the level of stationary peroxides
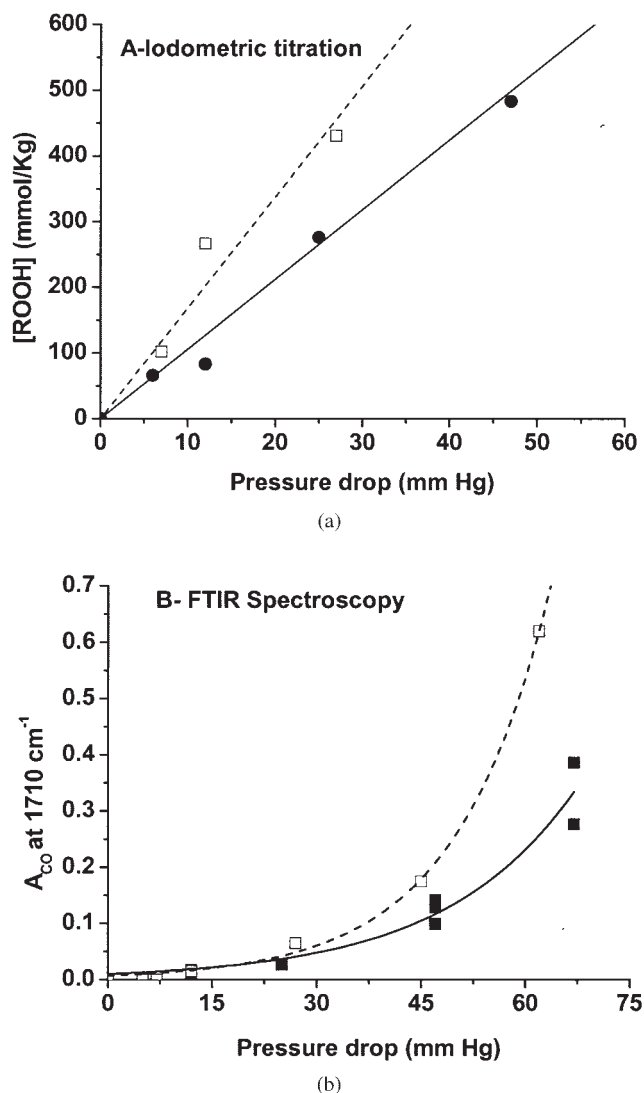
Figure 6 (A) Hydroperoxide concentration from iodometric titration and (B) carbonylated by-products from FTIR spectroscopy versus pressure drop upon oxygen uptake measurements through irradiation at $\lambda > 300$ nm at 35°C for a virgin polyoctenamer sample. Experiments were performed (empty symbols) in air and (filled symbols) in pure oxygen.

depends on the environmental parameters, where only hydroperoxides are formed under our accelerated photo-aging conditions.[21] Thus, we assume that photodegradation chemistry strongly depends on environmental conditions such as oxygen pressure. We believe that the balance in the formation/homolysis of hydroperoxides seems to be controlled by the oxidative atmosphere composition.[21]

Gijsman and Sampers reported similar results for polyethylene.[22] The relationship between the formation of carbonyl groups or the decline in mechanical properties and the oxygen uptake was found to be dependent on the type of weathering, especially on the temperature and the oxygen pressure. However,

the authors claimed that the influence of oxygen pressure is negligible at low temperatures (about 30°C).

The first stage of photo-oxidation of polymers implies the formation of hydroperoxides as primary by-products over the induction period $t_{ind,IR}$, while their subsequent homolysis leads to carbonylated species, as detected by FTIR spectroscopy. We believe that hydroperoxides has to be considered as probes of the oxidative process. Thus, the study of the nature and reactivity of peroxidic species formed upon the first step regarding different aging conditions is assumed to give better insights about the impact of less obvious factors in outdoor weathering of polymers (as environmental parameters, concentration of oxidative components, etc.).

The oxygen consumption data account for the very early stage of the photo-oxidation of polymers and provide an accurate diagnosis about the primary formation of hydroperoxides. Hence, in situ oxygen-uptake measurements upon irradiation could be considered as a promising method to identify the impact of the overall weathering factors, including both climatic and atmospheric ones, on the polymer photoperoxidation upon aging, since this technique offers a complete control of the composition of oxidative gas mixture.

CONCLUSION AND PERSPECTIVES

Oxygen-uptake technique monitors the amount of oxygen consumed during polymer degradation revealing a thermo- or photo-oxidation process. The possibilities offered by this method to evaluate the stability of polymers were widely reported for thermo-oxidation. The present work proposed to revise this old technique to evaluate the oxygen uptake through in situ irradiation under controlled atmosphere.

Our experimental results exhibit that the oxygen consumption data account for the very early stage of the photo-oxidation of polymers and provide a clear picture about the primary formation of hydroperoxides. Oxygen-uptake method represents a relevant procedure to investigate the peroxidation process, considering different aging conditions, since this technique offers a complete control of the overall environnemental parameters including atmospheric ones as the composition of oxidative gas mixture.

Hence, oxygen uptake could be considered as a promising methodology to identify the impact of the overall environmental parameters on the polymer photoaging. An important implication is in the understanding of atmospheric factors (including pollutants such as O_3, NO_x, etc.), usually considered of minor importance on polymer degradation upon outdoor weathering.

We point out that the correlation between the results in accelerated test devices and outdoor weather-

ing is still problematic. Only a few studies have been published that attempted to explain unexpected differences between two well-known exposure sites with apparent similar climatic conditions.[12,23] It is note worthy that in all cases, results were discussed on the basis of photodegradation rates according to the formation of carbonylated by-products detected by FTIR. Hence, in further developments, we will focus our attention on the impact of environmental factors on the nature and reactivity of (hydro)peroxides to correlate the lifetime of polymers in different outdoor weathering locations for a similar climatic site. Oxygen uptake will be a powerful tool for us to reach our goal.

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