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Mechanistic Investigations of the Photo- and Thermo-oxidation of Polyethylene

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1.1. Introduction

Polymer materials have been used in many fields due to their excellent performance, such as low weight, easy processing, low cost and inertness. However, one major problem associated with the applications of polymers is their poor stability to weathering (Trozzolo and Winslow 1968; Ranby and Rabek 1975; McKellar and Allen 1979; Allen 1980; Schnabel 1981; Allen and Edge 1992; Halim Hamid et al. 1992; Rabek 1996). Under working conditions, polymers can be permanently subjected to thermal and/or photochemical aging, which can cause irreversible damage to their properties. Consequently, materials may be degraded, resulting in limitations on their effective service life.

Polyethylene (PE) is one of the most common, widespread and inexpensive commodity thermoplastic polymers used for industrial applications as well as medical applications. The photo- and thermo-oxidation of polyolefins have long been of interest to scientists and engineers. Understanding the mechanisms by which

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PE degrades has been the subject of considerable effort in academic and industrial research for the last 50 years. In addition to the interest in understanding the degradation mechanisms, developing and adapting new stabilizers on a rational basis and predicting the lifetime service are most valuable for practical applications.

Thousands of papers have been published over time dealing with the processes involved in photo-oxidation and thermo-oxidation of polyolefins in general, and PE in particular, and their effects on the polymer structure (Ginhac et al. 1981; Lemaire et al. 1983; Arnaud et al. 1984; Fanton et al. 1985; Allen 1980; Allen and Edge 1992; Tidjani and Arnaud 1993; Arnaud et al. 1994; Cruz-Pinto et al. 1994; Costa et al. 1997; Allen et al. 2000; Gardette 2000; Guadagno et al. 2001; Corrales et al. 2002; Oldak et al. 2005; Fayolle et al. 2007; Yang et al. 2006; Guadagno et al. 2001). Most of the investigations concerned various basic aspects: the chemical mechanisms that may explain the oxidative degradation, the basic differences between photo- and thermo-oxidation, the role played by the molecular structure, the polymer morphology (degree of tacticity and crystallinity), the internal impurities and chemical defects, the specimen thickness, the structure of the polymer, the oxidation kinetics, the wavelength sensitivity, the effects of temperature and irradiance, and other climatic conditions, the consequences of chemical degradation (Ginhac et al. 1981; Rapp et al. 2019) at upper scales on both the macromolecular architecture and crystalline morphology and microstructure, with subsequent effects on the mechanical behavior, such as embrittlement.

The aim of this chapter is to review the main results of the literature concerning the thermal and UV degradation PE. A detailed review on the current understanding of the role of free radicals in the oxidation of PE induced by high-energy irradiation (gamma or e-beam) has been published recently (Bracco et al. 2018) and will not be considered here.

The current understanding of stability/degradation is presented and the methods for and elucidating degradation are discussed.

1.2. Oxidative degradation of PE

1.2.1. *Analytical methods for monitoring the oxidation process*

The reaction kinetics of polymer oxidation have been extensively studied and reported in the literature. Expressions that describe the rate of oxygen uptake during photo-oxidation can be derived by considering the mechanistic steps of initiation, propagation and termination, which are shown in the simplified mechanism below:

Initiation $PH + hv \rightarrow P\bullet + H\bullet$

Propagation $P\bullet + O_2 \rightarrow POO\bullet$

$$POO\bullet + PH \rightarrow POOH + P\bullet$$

Termination $2P\bullet \rightarrow$ inactive products

$$2POO\bullet \rightarrow \text{inactive products}$$

During this cycle, the progressive polymer modifications by chain scission or cross-linking result in crack formation in the surface zone and an associated decrease of the mechanical performance.

The accepted mechanisms for photo- and thermo-oxidation of polymers are similar in many respects, but some basic differences exist and will be commented on later.

The development of methodologies for analyzing and evaluating the aging of PE-based materials after natural outdoor or artificially accelerated aging has been the subject that has received the most attention. Differential scanning calorimetry (DSC) can be used for the determination of thermal properties, including the glass transition temperature T_g, melting range, and energies of crystallization and melting. Electron spin resonance spectroscopy (ESR) is a valuable method for the identification of the radicals produced by UV irradiation of stabilized polymers (Kruczala et al. 2005). Density measurements, hardness evaluation, scanning electron microscopy (SEM), measurements of oxygen uptake (Scheirs et al. 1995), chemiluminescence (Billingham and Grigg 2004), thermogravimetric analysis (TGA) (Anthony 1999), UV-Visible spectroscopy, etc., are some of the most cited analytical techniques that allow for the characterization of the consequences of aging on the material properties. The iodometric titration method has been used to measure the hydroperoxide concentration (Mair and Graupner 1964).

Infrared spectroscopy has proven to be a useful and frequently used analytical technique for monitoring the oxidation process of PE and understanding the chemical mechanisms that are involved (Gardette 2000). IR spectroscopy has been widely used to detect and quantify the formation of carbonyl species formed during the oxidative degradation of PE by analyzing the CO stretching frequency range from 1,800 to 1,650 cm^{-1} (Figure 1.1).

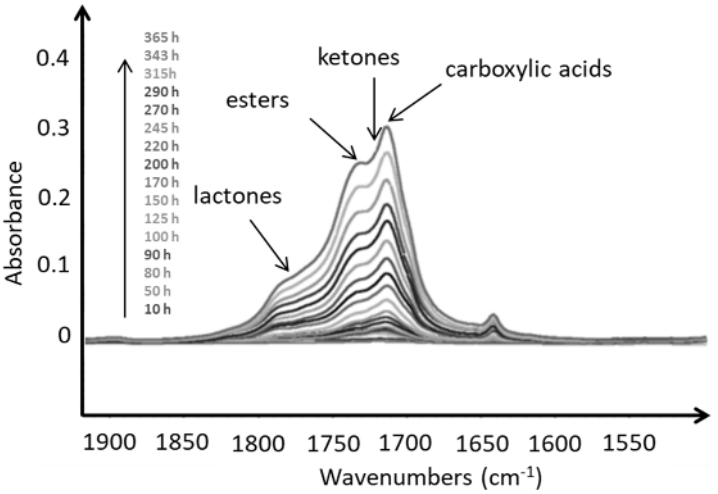


Figure 1.1. *Changes in the infrared spectra of a PE film with irradiation time (SEPAP 12.24–52°C) in the range of carbonyl absorption (film thickness 100 µm) (Gardette and Therias, unpublished results). For a color version of this figure, see www.iste.co.uk/richaud/industrialpolymers2.zip*

However, the bands associated with the different carbonyl compounds strongly overlap. Therefore, it may be difficult to characterize and quantify the various species formed during oxidation. Different strategies have been adopted to overcome this problem. On the basis of the pioneering work by Carlsson and Wiles (Carlsson and Wiles 1969; Carlsson et al. 1988), we can "chemically" deconvolute the complex spectrum in the carbonyl domain in order to highlight the main bands that contribute to the broad absorption of carbonyls. Curve fitting analysis of the IR carbonyl band can also be achieved by direct mathematical treatment of the spectra (Salvalaggio et al. 2006). The resolution of infrared spectrometry can be dramatically extended by employing derivatization reactions. The methods consist of treating the oxidized polymer samples with reactive gas that can specifically convert the oxidation products that have been formed. The result expected from derivatization reactions is a simplification in the interpretation of the infrared spectra resulting from the disappearance of specific bands and the appearance of the absorption bands of the derivated products. Treatment in an atmosphere of ammonia transforms the acidic products, essentially carboxylic acids, into the corresponding ammonium salts. The latter are also detected by IR spectroscopy through their absorbance at 1,550 cm^{-1}. The derivatization method to identify oxidation products was applied to polyolefins (Carlsson et al. 1988; Wilhelm and Gardette 1994) using various reagents. The gases used and the groups quantified included diazomethane

to convert acids and peracids to their respective methylester, sulfur tetrafluoride to convert acids to acyl fluorides, nitric oxide to convert alcohols and hydroperoxides to nitrites and nitrates, respectively, and phosgene to convert alcohol and hydroperoxides to chloroformates. SF_4 derivatization is very informative because there is an important shift between the carbonyl band (C=O stretching vibration) of the acyl fluoride and that of the corresponding acid. The fluorination of organic carbonyl compounds has been reviewed in detail (Wilhelm and Gardette 1994). One of the advantages of SF_4 derivatization is that, depending on the structure of the acyl fluoride, noticeable shifts can be observed. In the case of oxidized PE, SF_4 treatment leads to the generation of a C=O absorption at 1,848 cm^{-1}. This band was attributed to chain-end acyl fluorides. Treatments with a solution of 2,4-initrophenylhydrazine (2,4-DNPH) in methanol allows the identification of aldehydes and ketones as oxidation products. DNPH reacts with aldehyde and ketone groups to give dinitrophenylhydrazones. This product is characterized by infrared absorption bands at 1,618 and 1,594 cm^{-1}, and a strong UV-visible absorption band at 365 nm.

1.2.2. *Photo-oxidation of PE*

Polymers are markedly susceptible to oxidative deterioration when exposed to sunlight. Photo-oxidative degradation is the process which is considered as one of the primary sources of damage exerted upon polymeric substrates at ambient conditions. The absorption of light depends mainly on the polymer structure. For example, saturated hydrocarbons such as polyolefins do not absorb above 250 nm, well below the UV-part of sunlight (290–400 nm) reaching the earth's surface.

Light absorption is necessary to provoke photochemical reactions, although this basic law of photochemistry is sometimes forgotten (Tsuji 2006; Yazdan Mehr et al. 2013). PE is a non-absorbing polymer, which does not contain chromophoric species that can absorb in the range of the solar light (Gardette et al. 2013). The wavelength sensitivity of PE has also attracted much attention (Xingzhou 1997). PE should, in theory, be impervious to photodegradation. It is generally assumed that impurities or chromophoric defects, which absorb UV light, initiate photo-oxidation. These chromophores can vary from one PE to another. There are still major controversies regarding the relative importance of certain types of chromophoric species in this class of polymer (Arnaud et al. 1984; Allen and Edge 1992; Tidjani and Arnaud 1993; Arnaud et al. 1994). The main chromophores can be pigments, additives, impurities, catalyst residues, metal ions (from processing and manufacture) or products from oxidation during processing and use, such as carbonyl groups, double bonds and hydroperoxides. Extensive work has been devoted to the nature of

chromophoric species in general, and it is largely admitted that oxidized species formed during processing, like hydroperoxides (Gugumus 1990) or ketones, are potential candidates.

The starting reaction is always bond scission initiated by the absorption of UV radiation and photooxidative degradation occurs via a free-radical chain mechanism. Irradiation provokes the formation of free carbon radicals (R•) in the polymer by excitation of chromophores, which rapidly combine with oxygen to give peroxy radicals (ROO•). These radicals react by hydrogen abstraction from C-H sites on the backbone to generate hydroperoxide groups (ROOH) (Arnaud et al. 1984) and new carbon-centered radicals, which restart the photo-oxidation cycle. PE types have a few branching, which means a few tertiary carbons. Nevertheless, it is expected that most hydrogen abstraction occurs at secondary carbon atoms, despite the much larger reactivity of hydrogen atoms attached to tertiary carbon atoms (Cheng et al. 1976).

Hydroperoxides are then formed as primary photoproducts and can be chemically titrated. Once formed, they can decompose by the scission of the weak O-O bond, which gives a macro-alkoxy and a hydroxyl radical HO•. The alkoxy macroradical is the key intermediate in the reaction. This radical can react in several ways: β-scission with cleavage of the main chain to form aldehydes, abstraction of hydrogen without cleavage of the chain to form hydroxyls and cage reaction with the pair of the radicals formed, that is, macro-alkoxy radical and hydroxyl radical HO•. The latter reaction produces chain ketones. It is worthy to recall that it has been recently proposed that ketones could be formed by a reaction that does not involve the decomposition of hydroperoxides (Costa et al. 2008). Ketones photochemically react by Norrish type I or type II reactions. Photolysis of ketones by Norrish II processes results in the formation of vinyl-type unsaturations with absorption bands appearing at 909, 991 and 1,640 cm^{-1}, and produces a chain-end ketone, which also reacts by a Norrish II reaction and forms a vinyl unsaturation and acetone. The formation of carboxylic acids, esters and lactones comes from the various reactions involving both the aldehydes and keto radicals formed by Norrish I reactions. The formation of t-vinylenes results from the mesomerism of allylic radicals formed by hydrogen abstraction from the carbon atom in alpha-position to the double bonds of vinyl groups (Arnaud et al. 1984).

The formation of the various oxidation products provokes dramatic modification of the infrared spectra in the carbonyl domain, which reflects the formation of ketones (1,720 cm^{-1}) in the initial steps, and carboxylic acids (1,713 cm^{-1}), esters (1,735 cm^{-1}) and lactones (1,780 cm^{-1}) form in secondary processes. We also observe the formation of isolated double bonds (1,640 cm^{-1}).

Product	Conjugated ketone	Carboxylic acid	Ketone	Ester	Peracid	Lactone
Absorption maximum (cm^{-1})	1,695	1,713	1,720	1,735	1,765	1,785
Molar absorption coefficient ($M^{-1}cm^{-1}$)		680 (Carlsson and Wiles 1969)	350 (Carlsson and Wiles 1969)	500 (Carlsson and Wiles 1969)		720 (Lacoste 1992)

Table 1.1. *Infrared characteristics of the main oxidation products formed in PE*

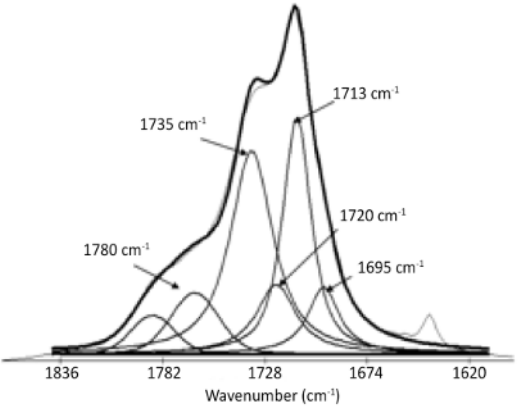
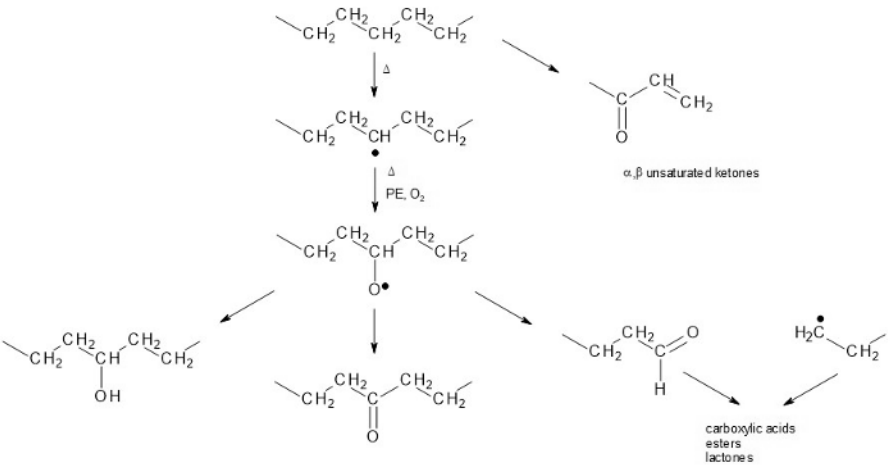


Figure 1.2. *Deconvoluted FTIR spectrum in the absorption range of carbonyl groups for a PE film (film thickness 100 µm) recorded after exposure to UV light (SEPAP 12.24–52°C) (deconvolutions performed using Spectracorr (OMNIC 8.1) software from ThermoOptek)*

In the range of hydroxyl frequencies, a broad band with a maximum at 3,420 cm^{-1} and a sharp absorption band at 3,550 cm^{-1} appear in the spectrum. These bands are known to come from the formation of monomeric hydroperoxides (3,550 cm^{-1}) and hydrogen-bonded alcohols and hydroperoxides (3,420 cm^{-1}). The intensities of both bands remain very low, confirming that the stationary concentrations of hydroperoxides are rather small under the conditions of photo-oxidation (Arnaud et al. 1984). The mechanism of photo-oxidation accounting for the main routes of photo-oxidation of PE can be summarized as shown in Scheme 1.1.



Scheme 1.1. *Simplified photo-oxidation mechanism of polyethylene*

1.2.3. *Thermo-oxidation of polyethylene: comparison with photo-oxidation*

Much work has been carried out on the analysis of thermally induced oxidation of PE (Lacoste 1992; Pimentel Real and Correia 2012; Reano et al. 2018; Rapp et al. 2019). It is generally known that, like in the case of photo-oxidation, thermo-oxidation has consequences at upper scales and affects both macromolecular architecture (Khabbaz et al. 1999; Hoang et al. 2006) and crystalline morphology and microstructure (Weon 2010; Chabira et al. 2011; Ferhoum 2013; Maryudi et al. 2013; Imane et al. 2015), with subsequent effects on the mechanical behavior such as, for instance, embrittlement (Fayolle et al. 2007).

In the case of cross-linked PE, thermal oxidation leads to a decrease in the gel fraction resulting from a chain scission process (Figueroa 1987; Celina and George 1995; Perthue et al. 2016) and an increase in the overall crystallinity ratio (Boukezzi et al. 2007), which is usually ascribed to chemi-crystallization and/or annealing phenomena. Some changes in the physical properties, such as discoloration, volume shrinkage and brittleness, have also been observed (Boukezzi et al. 2006). Thermal aging also leads to the deterioration of electrical and mechanical properties (Kim et al. 2006; Nedjar 2009).

Generally, the literature reports studies performed at elevated temperatures in order to increase the oxidation rate of the polymers and then use the obtained data to extrapolate material performance and predict its lifetime. This method requires that the mechanisms occurring during accelerated aging are the same as those during aging in service conditions. Thermo-oxidation leads to dramatic modifications of the infrared spectra, with absorption bands at frequencies similar to those reported above for photo-oxidation (1,718, 1,713, 1,735 and 1,780 cm^{-1}), which indicates that the same products are formed. However, the shape of the complex carbonyl band strongly differs, which reflects dissimilar relative concentrations of the products formed by thermo- and photo-oxidation, respectively. It is important to note that the main absorption maximum is observed at 1,720 cm^{-1} (see Figure 1.3), which is characteristic of ketones, whereas it appeared at 1,713 cm^{-1} in the case of photo-oxidation. Ketones are then the main products formed by thermal oxidation.

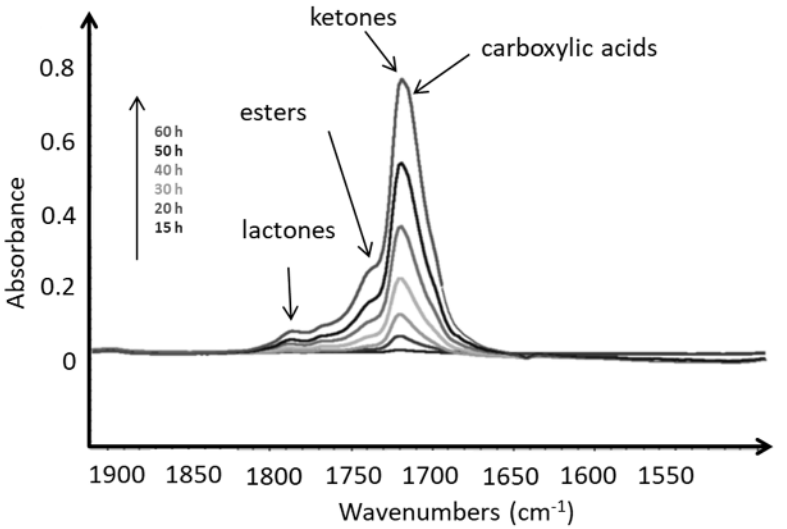
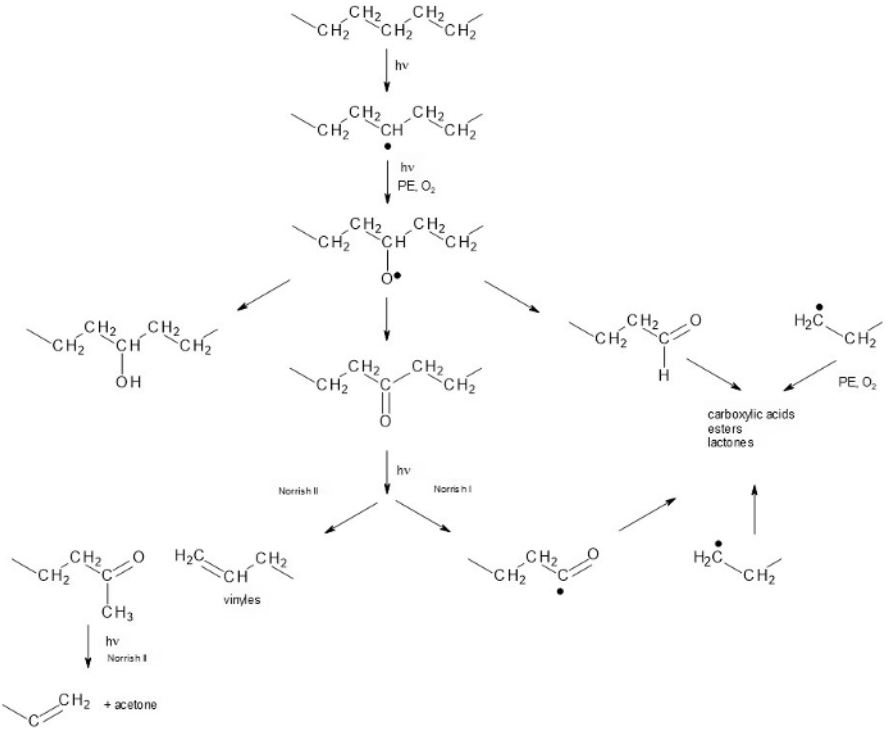


Figure 1.3. *Infrared spectra of a PE film (film thickness 100 µm) in the range of carbonyl absorption spectra as a function of the time of oxidation (100°C). For a color version of this figure, see www.iste.co.uk/richaud/industrialpolymers2.zip*

Although no modification of the UV-visible absorption characteristics was observed during photo-oxidation, some notable changes appear in the spectra as a result of thermal oxidation, with an absorption maximum at 275 nm that develops during the oxidation. This absorption band at 275 nm is characteristic of $\pi\pi^*$

transition in α-β unsaturated ketones, and it indicates the formation of conjugated ketones, as already observed in the case of polyvinylalcohol (PVA) (Gaume et al. 2011). Ketones are not photochemically stable and disappear in only a few hours of exposure of a thermo-oxidized film to UV-light irradiation in the presence of air (Gardette et al. 2013).

The thermo-oxidation of PE occurs in a similar way to photodegradation and produces almost the same oxidation products, but their relative concentrations are different. Ketones and conjugated ketones accumulate during thermodegradation, whereas they disappear to yield new unsaturations in photodegradation. The Norrish reactions that occur in photo-oxidation, but not in thermo-oxidation, are responsible for these differences. Scheme 1.2 represents a simplified mechanism of PE thermal oxidation.



Scheme 1.2. *Simplified mechanism of the thermal oxidation of polyethylene*

1.3. Effects of light intensity and temperature on the photodegradation

Accurate prediction of the durability of polymers and data indicating that the material is capable of fulfilling its expected service requirement safely are of crucial importance. Lifetime prediction of polymers requires accelerated aging based on artificial exposures, which involve an increase in UV light intensity and temperature. As recalled above, polymer oxidation depends on simultaneous chemical and physical reactions. Accelerative conditions add complexity to this phenomenon and the representativeness of artificial aging is still an issue.

Studies focusing on the influence of temperature on thermooxidative degradation have gained considerable attention for years (Celina 2013) and are well reported in the literature. They will not be considered in this chapter. To summarize, it is often reported that the chemical processes governing thermal oxidation follow Arrhenius behavior, although there is evidence that some polymers show curvature in the Arrhenius plot of oxidation rates (Costa et al. 1997; Khabbaz et al. 1999; Celina et al. 2005). It must also be considered that increasing the temperature of the samples during the experiments can cause heterogeneous degradation due to diffusion-limited oxidation. This issue is also well documented and has been reported in a large number of scientific papers (Clough and Gillen 1992; Pospisil et al. 2006).

In the case of the reactions produced via light exposure, the situation is more complex (Fairbrother et al. 2019). The accelerated aging methods use commercial devices for accelerated weathering or homemade constructed devices. The acceleration of aging is usually obtained by increasing the intensity of the UV light, and simultaneously increasing the temperature of the exposed samples. A careful examination of the literature also shows that sometimes, light sources emitting wavelengths shorter than those of solar light – hence more energetic – are used. This is one of the main sources of misleading and erroneous results. The difference between the energy of short and long wavelengths in the UV and visible domains of the solar radiation spectrum is well understood and documented in the literature (Rivaton et al. 1983; Lemaire et al. 1986), and those light sources emitting short wavelengths, which are not present in sunlight, have to be rejected.

The main question is then the representativeness of the accelerated aging experiments. Testing in accelerated conditions provides useful information in shorter time periods (Lemaire et al. 1986, 1996), but the stresses (light, heat, etc.) and their intensity have to be chosen accurately to avoid unrealistic degradation modes and failure mechanisms not observed in “true” environmental conditions.

There are many sources of misleading and erroneous results. Understanding the sources of errors is mandatory for developing relevant testing methods. Increasing

the intensity of UV light may cause errors when predicting the lifetime. Light sources with excessively high intensities (lasers) should be avoided, since this kind of source may produce biphotonic processes, triplet-triplet annihilation or excessive recombination of radicals, producing results similar to those obtained when using sources with short wavelengths. This causes aging mechanisms not observed in natural conditions. The light intensities used in conventional accelerated weathering devices are, however, well below the level which would cause a significant amount of these processes associated with pulsed lasers. Previous results published some years ago in the case of polypropylene unambiguously showed that the photo-oxidation rate of polymers depends on the light intensity (Philippart et al. 1997, 1999). However, it remains a fact that the effect of irradiance, even in acceptable ranges of light intensity, is still the object of severe debates. Currently, there is a growing interest regarding this issue because of the technical, economic and environmental problems arising from the degradation of polymers. Special attention must be paid to ensure that there is no change between the mechanisms of the accelerated tests and outdoor exposure. Nonlinear oxidative degradation would be expected if diffusion of oxygen into the sample, additive migration, or other thermally controlled reactions become the rate-limiting step. Although this is a well-documented area, the effect of irradiance, even if not producing heterogeneous oxidation and remaining in acceptable ranges of wavelengths and light intensity, is not well understood and is still the subject of severe debates.

The effect of irradiance on the rate of a photochemical process can be characterized by the reciprocity. A material obeys reciprocity if the degradation is a function of the total radiant energy and not a function of the rate at which the energy is applied. The reciprocity law can be described as:

$$I\,t = \text{constant},$$

where I is the irradiance and t is the exposure time.

The rates of photochemical processes as a function of light intensity usually follow the Schwarzschild law (Schwarzschild 1900):

$$k = AI^p$$

where k is the reaction rate, A is a proportionality constant, I is intensity (or irradiance) and p is the Schwarzschild coefficient, which is an experimentally derived number. This may also be written as:

$$I^p\,t = \text{constant}$$

When p = 1, Schwarzschild's law becomes the reciprocity law.

For most polymeric systems (unstabilized, stabilized or pigmented), the literature reports that the p-coefficient ranges between 0.5 and 1 (Martin et al. 2003) for changes in properties, such as color change and yellowing, gloss loss, crystallinity, modulus, elongation at break and mechanical properties. However, the degradation of these properties is not a direct consequence of UV light degradation, and in most cases involves several processes, some of which are not light dependent, which makes many of the published results very questionable. We should study the influence of the extent of the applied stresses (light and temperature) on the most primary detectable events, which are the chemical reactions involved in the degradation of the properties.

It is well known that the Schwarzschild coefficient p may vary from one given polymer to another. Moreover, it may also vary for a given polymer depending on the stability of the material brought by stabilizers. Recent results have shown that in the case of unstabilized low-density PE exposed to light with irradiance between 300 and 415 nm fixed at 90 or 300 $W.m^{-2}$, no acceleration of the photo-oxidation was observed (Therias et al. 2021), which means that the Schwarzschild coefficient was equal to 0 in this range of irradiances (Figure 1.4). For lower levels of irradiance, the Schwarzschild coefficient p was always below 1 and approached 0.5 at irradiances below 50 $W.m^{-2}$.

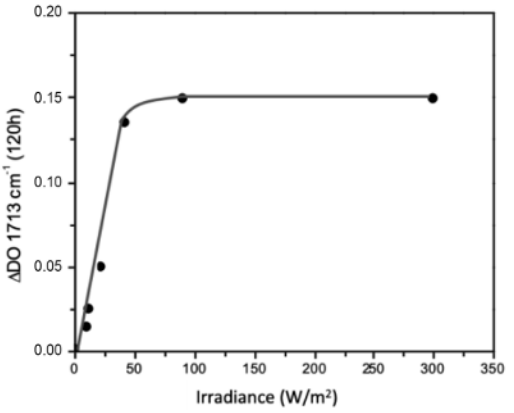


Figure 1.4. *Absorbance after 120 h of exposure as a function of the irradiance (PE films 100 µm) (Gardette and Therias, unpublished results)*

This had been explained by the fact that recombination and/or disproportionation are faster than propagation as a result of excessive free radical generation resulting from light absorption when the irradiance level is above 50 $W.m^{-2}$. It has been

observed that reducing the rate of photo-oxidation when using efficient stabilizers allows for increasing this limiting irradiance, and acceleration factors around 2 could be obtained when passing from 90 to 300 $W.m^{-2}$. It is, however, worth noting that the value of 3.3, which corresponds to p = 1, is never reached. These results obtained in the case of PE highlight the issue of lifetime prediction.

1.4. Conclusion

The photo- and thermo-oxidation of PE have been largely studied and reported in the literature. There is a good agreement between researchers about the causes and consequences of weathering, and the mechanisms that are involved are fairly well understood. A free radical mechanism of oxidation has been proved for years, which is similar to the mechanism of oxidation of low molecular weight compounds, but the relative importance of the various steps involved in the chain reaction is different. This is mainly due to the close vicinity of reactive groups in polymers and the restricted mobility of macroradicals in a rigid matrix.

The oxidation of the macromolecular chains results in a reduction in the molecular weight, a higher crystallinity and the loss of mechanical properties. The development of methodologies for analyzing and evaluating the aging of PE-based materials after natural outdoors or artificial accelerated aging has been the subject that has received the most attention. The analytical methods for monitoring the oxidation process have made significant progress, with the development of chemical treatments and the intensification of the use of many analytical techniques in the academic and industrial research centers.

The thermo-oxidation of PE and photo-oxidation produce almost the same oxidation products, but their relative concentrations are different. The main differences between photo- and thermo-oxidation are attributed to the Norrish reactions. Ketones and conjugated ketones accumulate during thermo-oxidation, whereas they disappear to yield new unsaturations in photo-oxidation. The Norrish reactions that occur under light exposure are responsible for these differences.

The problem now is not to know why polymers degrade, but when. Accurate prediction of the durability of polymers is of crucial importance. Testing in accelerated artificial conditions provides useful information in shorter time periods. However, because polymer oxidation depends on simultaneous chemical and physical reactions, accelerative conditions add complexity to this phenomenon and then the representativeness of artificial aging is still an issue. In the case of PE, there are limits to the acceleration that occurs for relatively moderate irradiances. Attention should be paid to some issues in the future: ultrasensitive tests for chemical or

mechanical damage should be investigated, in combination with more severe testing conditions, which should be as representative as possible of outdoor conditions, but with a faster degradation rate.

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