Action of water in the degradation of low-density polyethylene studied by X-ray photoelectron spectroscopy

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Abstract. Industrial low-density polyethylene (LDPE) was aged in stagnant distilled water during one year. Two types of this material were studied. The first one was without additives and the second type was doped with 4% of hindered-amine light stabilizers (HALS). Using X-ray photoelectron spectroscopy (XPS), the evidence that an oxidation occurs was demonstrated for the two types of LDPE (with and without HALS). One objective was to observe the chemical groups resulting of the ageing and to propose a mechanism of hydrolytic degradation for LDPE. The analysis of C1s spectra shows that the main oxidation products are C–O and C=O groups. Unlike the hydrolytic degradation of polypropylene, there is no presence of O=C–O groups, which suggests that there is no oxidative chain scission during hydrolytic ageing of the LDPE. The other objective of the study was to observe if the HALS can have an influence in the hydrolytic ageing of the LDPE. The values of the atomic concentration of the oxygen for the two types of samples show that the HALS could slightly slow down the oxidation of the LDPE.

Keywords: damage mechanism, low-density polyethylene, hydrolytic degradation, X-ray photoelectron spectroscopy, oxidation

1. Introduction

Polyethylene is one of the most used polymers in modern society. Unfortunately, the polymers, like polyethylene, undergo ageing and this phenomenon can induce non reversible chemical transformations in the structure of the macromolecules that can modify the recycling capability of some thermoplastics. Many agents can start the chemical degradation and an oxidation can occur in the polymer if the material is in contact with oxygen. Many studies proposed different chemical mechanisms to explain the processes of degradation of polyethylene, like degradation by light [1, 2], heat [1, 3] or weathering conditions [4, 5].

The action of water on polymers is another source of degradation of polymers. Many studies were done on the subject, but only concentrations of oxidation or macroscopic characteristics were measured, like lifetime for mechanical failure [6], tensile strain [7] or crystallinity percentage [8]. These experiments were mainly done at high temperatures [6–8]. In the authors' knowledge, the influence of water during ageing from a chemical point of view is not reported at room temperature. The aim of this work is then to determine if water is an important factor in the ageing of additive-free low-density polyethylene (LDPE) and HALS-stabilized LDPE at the chemical level by studying the chemical

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bonds after ageing in distilled water during one year, and to propose a mechanism of degradation of the polymer.

2. Experimental section

The industrial LDPE samples were made by ENIP (*Entreprise Nationale des Industries Pétrochimiques*), Algeria (trademark: PEBD B21 ENIP, Skikda). The samples were received in the form of film made by extrusion blow moulding. The density and the melt flow index of the received material are 0.923 g/cm^3 and 0.019 g/min , respectively. Four samples, of about 2 cm by 2 cm, were used; two of them are unstabilized LDPE and the two others are LDPE stabilized with 4% of HALS from Ampacet™. All the samples were immersed in distilled water during one year at room temperature. Also, two unaged samples (one unstabilized and one 4% HALS stabilized) were analyzed by XPS as reference. The two kinds of LDPE samples used in this experiment came from the same source to make sure that the properties of the polymer were similar; the use of two identical samples is to ensure the validity of the results. After the ageing period, the samples were dried with compressed air.

XPS measurements were carried in a Kratos Axis-Ultra system in a UHV chamber with an electrostatic-magnetic hybrid lens and a 300 W monochromatic AlK α X-ray source (20 mA, 15 kV). The analysed surface was approximately $400 \mu\text{m}$ by $800 \mu\text{m}$. The angle of the X-ray beam is 60° with respect to the sample normal ($60^\circ/\text{n}$) and the take-off angle was $0^\circ/\text{n}$ for all the measurements. The data analysis was done with the software CasaXPS provided with the XPS setup. XPS surveys and C1s spectra were analyzed in this work. Because of the surface charging of non-conducting samples [9, 10], the peaks appeared shifted on the energy scale; the energy calibration was done by setting the C1s peak at 285.2 eV for the Csp3 peak. During the peak synthesis, a Shirley background subtraction [11] was used and the Gaussian/Lorentzian shape ratio was 40 for all the spectra.

3. Results and discussion

The XPS surveys of all the unstabilized LDPE samples and of all the 4% HALS stabilized LDPE samples studied are presented in Figures 1 and 2, respectively. The zeros of the higher spectra were

Figure 1. XPS survey spectra of the unstabilized LDPE samples

Figure 2. XPS survey spectra of the 4% HALS stabilized LDPE samples

Table 1. Atomic concentration^a [%] of the elements in the samples of LDPE

Sample	C1s	O1s	N1s	Contaminants (<1%)
Unstabilized LDPE (unaged sample)	99.1	0.7	0.1	–
Unstabilized LDPE (aged sample 1)	87.4	9.3	2.7	Ca, Cl, Cu, Na, S, Si
Unstabilized LDPE (aged sample 2)	87.9	8.6	1.6	Ca, Cl, Cu, Mg, Na, S, Si
LDPE w/4% HALS (unaged sample)	90.8	1.8	6.7	Al, Cl, Na, S, Zn
LDPE w/4% HALS (aged sample 1)	87.5	7.0	4.8	Al, Ca, Cl, Na, S, Si
LDPE w/4% HALS (aged sample 2)	87.2	6.7	4.7	Al, Ca, Cl, Na, S, Si, Zn

^aThe error of the concentrations is estimated at $\pm 0.1\%$

shifted for a better presentation for both Figures. Three major peaks are observed on the survey spectra. These peaks are C1s at 285 eV, which is associated to the polymer, O1s at 532 eV which seems to indicate an oxidation of the polymer, and N1s at 400 eV, which is attributed to HALS that contain amines. The hypotheses for the origin of the presence of the two last peaks are that oxygen is mainly observed in degraded samples and that nitrogen is observed mainly in 4% HALS stabilized samples. An interesting fact for nitrogen is a decrease of N1s for the 4% HALS stabilized aged samples that is probably due to the loss of the additive with the time [8, 12, 13], as shown in Table 1. An increase of N1s is observed for the aged unstabilized LDPE samples comparing to the unaged sample. This phenomenon was also observed in the study of hydrolytic degradation of polypropylene [14]. An

assumption of this increase is the presence of gaseous nitrogen coming from dissolved air in water. As time goes by, nitrogen could contaminate the surface of the samples. Other minor peaks are also present and their relative atomic concentrations are given in Table 1. The various origins of these impurities are more difficult to determine because their sources can be multiple; the samples come from industry and their history is unknown. The atomic concentrations are based on the surface of the peaks in the XPS surveys.

To be sure that the presence of oxygen in the survey spectra is due to oxidation of the polymer samples and not simply the insertion of water molecules in the polymer matrix, C1s spectra were analysed by peak synthesis. Results of the analysis of the unstabilized and 4% HALS stabilized samples are shown in Figures 3 and 4, respectively. All the peak syn-

Figure 3. Results of the synthesis of the C1s spectra of the unstabilized LDPE samples **Figure 4.** Results of the synthesis of the C1s spectra of the 4% HALS stabilized LDPE samples

theses were done with a maximal residual standard deviation of 1.38157 or less (data given by the software CasaXPS), and all the spectra were shifted to higher energies to consider the inhomogeneous charge effect in non-conducting insulators [9, 10] by setting the *Csp3* peak at 285.2 eV. The peak synthesis of the C1s spectrum of the unstabilized unaged sample gives two resulting peaks that are associated to *Csp3* (285.2 eV) and *Csp2* (284.9 eV) hybridizations [15, 16]. The origin of the two peaks is probably due to the industrial processes of polymerization that can induce some imperfections in the structure of the material. For the case of the 4% HALS stabilized unaged sample, the C1s peak is clearly asymmetric, as seen in Figure 4. The atomic concentrations shown in Table 1 suggest that nitrogen is the only element present that can be bonded with carbon to a significant degree to cause this shape of the C1s peak. The peak synthesis of the spectrum gives four peaks at 284.9 eV (*Csp2*), 285.2 eV (*Csp3*), 286.1 eV (C–N) and 287.5 eV (C=N) [15–17]. The last two peaks are probably associated with the HALS incorporated in the polymer matrix.

The asymmetric shape of the C1s peaks of the degraded samples reveals the existence of bonds other than those of pure not modified LDPE. As shown in Table 1, oxygen is the main element present to a significant degree that can cause asymmetry of the C1s peak for the aged unstabilized samples by binding with carbon atoms. Considering that contaminants listed in Table 1 cannot make bonds observable by XPS with carbon due to their low atomic concentration, the atomic functions found by decomposition of C1s spectra of unstabilized LDPE samples (Figure 3) are *Csp2* (~284.9 eV), *Csp3* (285.2 eV), C–O (~286.5 eV) and C=O (~288.4 eV) [14–16, 18, 19]. Under the same assumptions and considering that bonds between nitrogen and carbon can be detected by

XPS due to the significant intensity of the N1s peak (Figure 2 and Table 1), the results of the decomposition of the C1s spectra of the 4% HALS stabilized LDPE samples are Csp2 (~284.9 eV), Csp3 (285.2 eV), C–O/C–N (~286.5 eV) and C=N (~287.7 eV) and C=O (~288.3 eV) [14–19]. Due to the proximity of the C–O and C–N peaks, there is no possibility to separate these two peaks. The approximated values listed above are an average of the results of the C1s spectra decomposition.

An assumption of the mechanisms of the degradation of LDPE by water is presented in Figure 5. The first step of the degradation, based on the literature [1, 3], is a loss of a proton (H^+) due to the polarity of the water molecules or the ionic potential of the negative ions present in the water (e.g. OH^-) by charge transfer complexes (CTCs) [20]. The rupture of the C–H bond occurs by electrostatic attraction of the proton [14, 21]. An oxidation of the polymer can follow the loss of a proton as showed in Figure 5, resulting in the formation of alcohol (C–OH) groups by association of the macroradical and an OH^- group produced in water, or the oxidation of the macroradical by O_2^- originated in water. The last case is not stable in time and can stabilize by two ways. The first way is the formation of an alcohol group by the association with a proton. The second one is the formation of ketone (C=O) by the loss of the second proton bonded to the carbon atom that is bonded to oxygen (Figure 5). One should note that C–O groups in Figures 3 and 4 could not be associated to hydroperoxides (C–OOH) because of the weak enthalpy of dissociation of the O–O bond (35–40 kcal/mol) [22–24]. The hydroperoxide groups are often cited in the LDPE oxidation [1, 3].

Chemical conversions can occur between the various chemical groups because the stability of the chemical species is inversely proportional to their enthalpy of dissociation (potential energy of disso-

Figure 5. Proposed mechanisms for the hydrolytic degradation of the LDPE

ciation) [25]. By comparing the enthalpy of dissociation of chemical groups C–OH (383 kJ/mol) and C=O (178 kJ/mol) at a temperature of 25°C, a tendency of stabilization toward alcohols is present augmenting the probability of the presence of alcohols [14]. Another interesting point is the possibility that LDPE does not undergo chain scission during hydrolytic degradation. After the ageing time, the degraded samples do not show any cracking or loss of flexibility in comparison with unaged samples. This observation and also the absence of the O=C–O groups in Figures 3 and 4, suggest that the hydrolytic degradation of LDPE does not break macromolecular chains, unlike the hydrolytic ageing of polypropylene [14].

As shown in Table 1, the atomic concentration of oxygen is higher for the unstabilized LDPE degraded samples than for the 4% HALS stabilized LDPE samples. The presence of HALS can decrease the oxidation of LDPE by scavenging oxygen present at the surface of the polymer [26]. It is evident that HALS contribute to a certain degree to the retardation of oxidative degradation of LDPE in water, but the efficiency of the HALS for hydrolytic ageing is less than the ageing in air [6].

4. Conclusions

Unstabilized and 4% HALS stabilized industrial LDPE samples were aged in stagnant distilled water during one year to observe how the degradation of the polymer occurs. Using XPS technique, the evidence that an oxidation occurs was demonstrated for all LDPE samples by formation of C–O and C=O groups. These groups were determined by analysis of the C1s spectra. It was then possible to propose mechanisms of degradation that suggest that there is no chain scission during hydrolytic degradation of the material. This assumption is based on the fact that there is no presence of O=C–O groups in the analysis of XPS measurements. The influence of HALS was also studied by comparing the oxygen atomic concentration of the samples. The lower values for the 4% HALS stabilized LDPE samples suggest that the HALS could slow the oxidation of the LDPE, but the difference of oxygen atomic concentrations between unstabilized and 4% HALS stabilized samples suggest that HALS are not the most efficient additives for slowing the hydrolytic degradation.

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References

- [1] Corrales T., Catalina F., Peinado C., Allen N. S., Fontan E.: Photooxidative and thermal degradation of polyethylenes: interrelationship by chemiluminescence, thermal gravimetric analysis and FTIR data. *Journal of Photochemistry and Photobiology A: Chemistry*, **147**, 213–224 (2002).
- [2] Stark N. M., Matuana L. M.: Surface chemistry changes of weathered HDPE/wood-flour composites studied by XPS and FTIR spectroscopy. *Polymer Degradation and Stability*, **86**, 1–9 (2004).
- [3] Gugumus F.: Re-examination of the thermal oxidation reactions of polymers – 2. Thermal oxidation of polyethylene. *Polymer Degradation and Stability*, **76**, 329–340 (2002).
- [4] El-Awady M. M.: Natural weathering, artificial photo-oxidation, and thermal aging of low density polyethylene: Grafting of acrylic acid onto aged polyethylene films. *Journal of Applied Polymer Science*, **87**, 2365–2371 (2003).
- [5] Pagès P., Carrasco F., Saurina J., Colom X.: FTIR and DSC study of HDPE structural changes and mechanical properties variation when exposed to weathering aging during canadian winter. *Journal of Applied Polymer Science*, **60**, 153–159 (1996).
- [6] Henry J. L., Ruaya A. L., Garton A.: The kinetics of polyolefin oxidation in aqueous media. *Journal of Polymer Science: Part A Polymer Chemistry*, **30**, 1693–1703 (1992).
- [7] Dörner G., Lang R. W.: Influence of various stabilizer systems on the ageing behavior of PE-MD-I. Hot-water ageing of compression molded plaques. *Polymer Degradation and Stability*, **62**, 421–430 (1998).
- [8] Amato L., Gilbert M., Caswell A.: Degradation studies of crosslinked polyethylene. II Aged in water. *Plastics, Rubbers and Composites*, **34**, 179–187 (2005).
- [9] Bryson III C. E.: Surface potential control in XPS. *Surface Science*, **189/190**, 50–58 (1987).
- [10] Barth G., Linder R., Bryson C.: Advances in charge neutralization for XPS measurements of nonconducting materials. *Surface and Interface Analysis*, **11**, 307–311 (1988).
- [11] Shirley D. A.: High-resolution X-ray photoemission spectrum of the valence bands of gold. *Physical Review: B*, **5**, 4709–4714 (1972).
- [12] Haillant O., Lemaire J.: Natural and artificial photo-aging of non-stabilized and pigmented, hindered-amine stabilized propylene-ethylene copolymers. *Polymer Degradation and Stability*, **91**, 2748–2760 (2006).

- [13] Gerlock J. L., Kuchеров A. V., Smith C. A.: Determination of active HALS in automotive paint systems II: HALS distribution in weathered clearcoat/basecoat paint systems. *Polymer Degradation and Stability*, **73**, 201–210 (2001).
- [14] Massey S., Adnot A., Roy D.: Hydrolytic aging of polypropylene studied by X-ray photoelectron spectroscopy. *Journal of Applied Polymer Science*, **92**, 3830–3838 (2004).
- [15] Marcondes A. R., Ueda M., Kostov K. G., Beloto A. F., Leite N. F., Gomes G. F., Lepienski C. M.: Improvements of ultra-high molecular weight polyethylene mechanical properties by nitrogen plasma immersion ion implantation. *Brazilian Journal of Physics*, **34**, 1667–1672 (2004).
- [16] Mähl S., Neumann M., Schlett V., Baalmann A.: Some aspects of the fitting of XPS core spectra of polymers. *Surface and Interface Analysis*, **26**, 204–212 (1998).
- [17] Wang M.-J., Chang Y.-I., Poncin-Epaillard F.: Acid and basic functionalities of nitrogen and carbon dioxide plasma-treated polystyrene. *Surface and Interface Analysis*, **37**, 348–355 (2005).
- [18] Rjeb A., Letarte S., Tajounte L., El Idrissi M. C., Adnot A., Roy D., Claire Y., Kaloustian J.: Polypropylene natural aging studied by X-ray photoelectron spectroscopy. *Journal of Electron Spectroscopy and Related Phenomena*, **107**, 221–230 (2000).
- [19] Clark D. T., Cromarty B. J., Dilks A.: Theoretical investigation of molecular core binding and relaxation energies in a series of oxygen-containing organic-molecules of interest in the study of surface oxidation of polymers. *Journal of Polymer Science: Part A Polymer Chemistry*, **16**, 3173–3184 (1978).
- [20] Chien J. C. W.: On the possible initiation of photooxidation by charge-transfer excitation. *Journal of Physical Chemistry*, **69**, 4317–4325 (1965).
- [21] Verdu J.: *Vieillissement des plastiques*. AFNOR Techniques, Paris (1984).
- [22] March J.: *Advanced Organic Chemistry* 4th edition. Wiley and Sons, New York (1992).
- [23] Guillet J. E., Dhanraj J., Golemba F. J., Hartley G. H.: Fundamental processes in the photodegradation of polymers. *Advances in Chemistry Series*, **85**, 272–286 (1968).
- [24] Carlsson D. J., Wiles D. M.: Photooxidative degradation of polypropylene. 1. Photooxidation and photoinitiation processes. *Journal of Macromolecular Science C – Reviews in Macromolecular Chemistry and Physics*, **14**, 65–106 (1976).
- [25] Solomons T. W. G., Fryhle C. B.: *Organic chemistry* 7th edition. Wiley and Sons, New York (2000).
- [26] Basfar A. A., Ali K. M. I.: Effect of various additives on tensile properties of polyethylene films irradiated in air, water, N₂, and vacuum. *Polymer-Plastics Technology and Engineering*, **43**, 389–405 (2004).