Hydrolytic Aging of Polypropylene Studied by X-Ray Photoelectron Spectroscopy

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) was used to study the hydrolytic aging of polypropylene according to the pHs of degrading buffer solutions and the time of aging. The study was concentrated over periods of 3, 6, and 9 months for values of pH close to the real environments of use of the material (pH of 6, 7, and 8). The polypropylene underwent an oxidation of its polymeric matrix, independently of the range of pH values, by the production of C—OH, C=O, and O=C—O groups. These chemical functions were observed in high resolution XPS spectra around C1s and O1s peaks. Beginning with these results and from mechanisms of (photochemical, thermal, and others) aging proposed in the literature, it was then possible to propose mechanisms of hydrolytic ageing of polypropylene. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3830–3838, 2004

Key words: poly(propylene) (PP); aging; XPS; stabilization

INTRODUCTION

The phenomenon of polymer aging has been known by scientists for years.[1–5] The aging can induce nonreversible chemical transformations in the structure of the molecule. Many agents can start the chemical degradation (light, heat, and flame) and oxidation can occur at the surface of the polymer if the material is in contact with oxygen. The oxidative aging can modify the recycling capability of some thermoplastics. Many studies have tried to find the different ends of the oxidative aging and to explain their formation in different environments.[1,3,6–8]

This paper deals with a kind of environment in which the aging of polypropylene (PP) is not well known: a watery environment. In this work, 1×1 cm^2 PP samples (Appryl, Atofina, France, unspecified purity) floated on KH$_2$PO$_4$–K$_2$HPO$_4$ buffer solutions to study the hydrolytic aging of this material. The surface to be analyzed was downward, in contact with the solution. The periods of aging were 3, 6, and 9 months and the buffer solutions used had pH values of 6, 7, and 8. The choice of the pH values was related to the acidity of water in the environment. The formula of such a polymer is:

$$\text{+\!\!-CH}_2\text{—CH\!-\!+}_n$$
$$\mid$$
$$\text{CH}_3 \qquad (1)$$
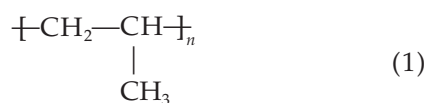
where n is the degree of polymerization.

In this work, X-ray photoelectron spectroscopy (XPS) has been used because the aging of polymers occurs only on the surface of the material ($\sim$ 8–10 nm).[1,8,9] The XPS technique is fully described in the literature.[10–13] Three aspects were analyzed: spectrum surveys of the samples for the study of the atomic concentrations, C1s peak synthesises, and O1s peak synthesises. The first analysis allowed us to determine the nature of the contamination on the samples and the evolution of the presence of oxygen at the surface of samples, which is the most probable contaminant whose concentration can change during aging. The last two points allowed us to study carbon and oxygen atoms with regard to their chemical environment.

EXPERIMENTAL

Table I shows the parameters of aging for all of the samples. The reference samples were in argon atmosphere during the aging period. Each reference sample was associated with a series of degraded samples according to the time of aging. All of the samples were sheltered from light to prevent photodegradation of the material[1,6] and were cleaned with ethanol at the beginning.

The experimental system used for the analysis is a stainless vacuum chamber with a XPS-AES-ISS-SIMS combined system from VG Scientific (UK). The base pressure is of the order of 10^{-11} Torr. The XPS spectrometer is a spherical electrostatic analyzer (150 mm external radius) with electrostatic lenses and one channel detection. The X-ray source is a nonmonochromatic source with an Al/Mg double anode. The 300 W

TABLE I
Parameters of Ageing for Each Sample

Sample	Ageing time (months)	pH of the buffer solution
PP1	3	6
PP2	3	7
PP3	3	8
PP4	6	6
PP5	6	7
PP6	6	8
PP7	9	6
PP8	9	7
PP9	9	8
PP10	3	Reference sample
PP11	6	Reference sample
PP12	9	Reference sample

Mg$K\alpha$ source ($h\upsilon$ = 1,253.6 eV) was used for this study and the take-off angle (the angle between the analyzer direction and the surface normal) was $15°/n$ for all the measurements. The data were analyzed with software (PIXAS) developed in our laboratory for the surface analysis (LAS) based on the code made by Hughes and Sexton.[30] Because of the surface charging of the nonconducting samples, the peaks appeared shifted on the energy scale; the energy calibration was made by setting the C1s peak at 285.0 eV.

RESULTS

Spectrum surveys and atomic concentrations

The XPS surveys of the samples aged for 9 months are shown in Figure 1. The C1s peak at 285 eV is the dominant feature; it can be easily associated with the structure of the polymer. Many contaminants are also found on the surface. The list of the contaminants and their concentration as a percentage are shown in Table II. The atomic concentrations are based on the surface of the peaks in the surveys of the samples.

Potassium (K2s at 378 eV, K3s at 33 eV, K3p at 17 eV) and phosphorus (P2s at 191 eV, P2p at 134 eV) are present on the surface of all of the samples except for the reference samples (PP10 to PP12). This indicates that these elements come from the buffer solutions used for the study of the hydrolytic aging whose pH values were determined using K_2HPO_4 and KH_2PO_4. For samples PP1 to PP3, the contact of the samples with potassium and phosphorus was of short duration (3 months) and the deposit was nonsignificant, making a concentration too weak to be detectable by XPS; the detection limit of XPS for measurements of the atomic concentrations is between 0.1 and 1%, according to the nature of the element.

The various origins of the other impurities are more difficult to determine because their sources can be multiple and the handling of the samples before re-

ception is unknown. However, some assumptions can be advanced: the contact with the ambient air (N1s at 400 eV), the air pollution [sulphur (S2s at 228 eV), silicon (Si2s at 153 eV, Si2p at 102 eV), sodium (Na1s at 1,072 eV)], the manufacturing method [chlorine (Cl2p at 200 eV), aluminium (Al2p at 73 eV)], etc.[15,16] Other origins can be questioned, in relation to the history of material, such as magnesium (Mg2p at 51 eV).

According to Table I the main contaminant is oxygen and its concentration increases during the aging as shown in Figure 2. The data of the concentrations (as a percentage) shown in Figure 2 have an absolute accuracy of ±0.2%, according to Table II. From the aging period of 3 months to 6 months the oxygen concentration at the surface of the samples increases to a significant degree: 5.8 to 11.1%, 6.5 to 10.1%, and 5.6 to 10.9% for the samples aged in buffer solutions of pH values of 6, 7, and 8, respectively. Also, the oxygen concentration increases between 6 and 9 months, 11.1 to 11.6% (pH 6), 10.1 to 13.4% (pH 7), and 10.9 to 12.8% (pH 8), but the augmentation is less significant than for the first part of the aging period (3 and 6 months).

The increase of the oxygen concentration at the surface of the samples during the different periods of time can be observed by comparing the concentrations for the aged samples and the concentrations for the reference samples. For the aging period of 3 months, the average difference between aged samples and the reference sample is 1.5%. The average difference increases to 6.2 and 5.9% for the periods of 6 and 9 months. The small decrease of the average difference of the concentration of oxygen at the surface of the samples between the two final periods of aging can be explained by the inhomogeneous preliminary oxidation of the samples or by oxidation with residual oxygen in the argon atmosphere.

There is no significant difference in the values of the atomic concentration of oxygen between the samples aged in buffer solutions of different pH values for a same period of degradation, according to Figure 2. In the range of pH values studied, the effect of this parameter cannot be observed.

The C1s spectra

The C1s spectra presented in this paper are the spectra of the samples aged during 9 months in different pHs for the buffer solution (PP7, PP8, and PP9) and the spectrum of the associated reference sample (PP12). The C1s spectra of the other samples are quite similar except for the intensity of some of the synthesized peaks. A Shirley treatment (subtraction of nonlinear background) has been applied to all high-resolution spectra (C1s and O1s).

The PP7 (pH 6, aging period of 9 months) sample C1s spectrum is presented in Figure 3. In the C1s
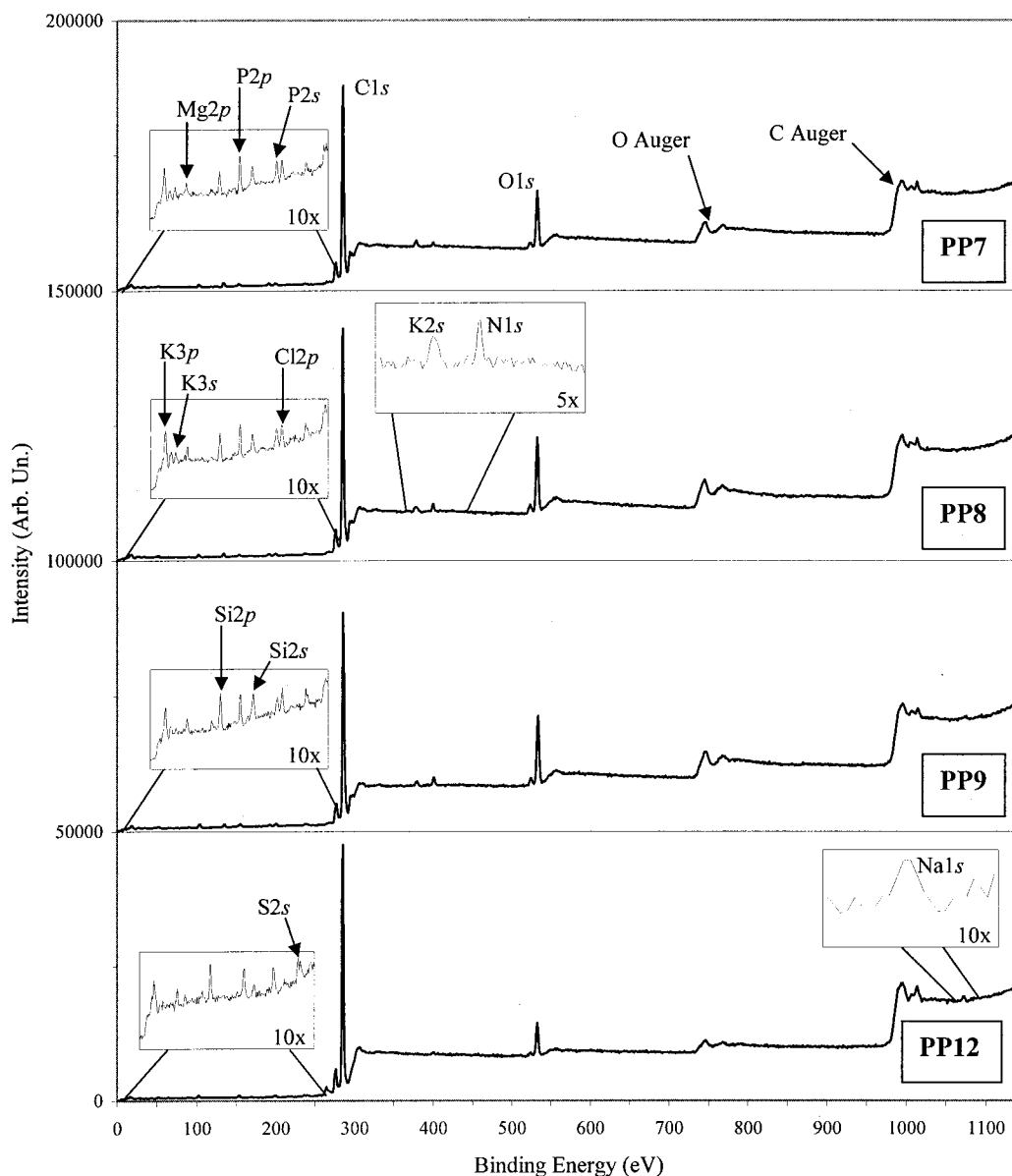
Figure 1 Surveys of the samples PP7 (pH 6), PP8 (pH 7), PP9 (pH 8), and PP12 (reference sample). The aging time for these samples was 9 months. The zeros of the higher spectra were shifted for a better presentation.

spectra of the PP8 (pH 7), PP9 (pH 8), and PP12 (reference) samples, respectively, are presented in Figures 4 to 6. The determination of the accuracy of the analysis of the spectra was considered by taking into account the statistical parameters of the software used (PIXAS), particularly the reduced statistical parameter χ^2 (or χ^2_n), according to the definition found in the literature.[17] An analysis is considered as acceptable when χ^2_n approaches the unit.

All the spectra were shifted to lower energies to consider the charge effect in nonconducting insulators.[1,18,19] The energy shifts are 4.3, 4.5, 5.3, and 4.8 eV for the PP7, PP8, PP9, and PP12 samples, respectively. These energy shifts are considered for all the synthesized peaks energies in Figures 3 to 6.

The dissymmetrical form of the C1s peaks of the PP7, PP8, PP9, and PP12 samples reveals the existence of bindings other than those of pure unmodified polypropylene (C—C and C—H$_n$ at 285.0 eV).[1,20–23] As shown in Table II and Figure 1, the only element present to a significant degree and allowing dissymmetry of the C1s peak by binding with carbon is oxygen. The decomposition of the spectra of Figures 3 to 6 makes it possible to identify atomic functions from the synthesis peaks, by considering that the other bonds between the carbon and the other elements listed in Table II are too weak to be distinguished from the principal peaks and the background. The atomic functions are C—OH / C—O—C (~ 286.4 eV), C=O (~ 287.8 eV), and O=C—O (~ 289.0 eV).[1,14,20–25] The

TABLE II
Concentration (%) of the Elements of the Samples of PP

Sample (months)[a]	C1s	O1s	Al	Cl	K	Mg	N	Na	P	S	Si
PP1 (3)	91.4 ± 0.3	5.8 ± 0.2	<1	<1	—	<1	—	—	—	—	1.7 ± 0.2
PP2 (3)	90.7 ± 0.2	6.5 ± 0.2	<1	<1	—	<1	—	—	—	—	1.8 ± 0.2
PP3 (3)	90.9 ± 0.3	5.6 ± 0.2	—	<1	—	<1	<1	—	<1	<1	<1
PP4 (6)	82.3 ± 0.5	11.1 ± 0.3	—	<1	—	2.1 ± 0.4	2.1 ± 0.4	—	<1	—	1.2 ± 0.2
PP5 (6)	84.2 ± 0.4	10.1 ± 0.2	—	<1	<1	<1	2.2 ± 0.3	—	<1	—	<1
PP6 (6)	82.0 ± 0.4	10.9 ± 0.2	—	<1	1.2 ± 0.3	<1	2.3 ± 0.3	—	<1	—	1.4 ± 0.1
PP7 (9)	83.1 ± 0.3	11.6 ± 0.2	—	<1	1.4 ± 0.3	<1	<1	—	1.4 ± 0.1	<1	1.2 ± 0.1
PP8 (9)	80.7 ± 0.3	13.4 ± 0.2	—	<1	1.4 ± 0.2	<1	1.9 ± 0.1	—	1.1 ± 01	<1	1.1 ± 0.1
PP9 (9)	80.6 ± 0.2	12.8 ± 0.2	—	<1	<1	<1	2.2 ± 0.2	—	<1	<1	2.0 ± 0.1
PP10 (3)	93.2 ± 0.2	4.5 ± 0.2	<1	<1	—	<1	—	—	—	<1	1.2 ± 0.1
PP11 (6)	91.6 ± 0.5	4.5 ± 0.2	—	<1	—	1.4 ± 0.3	<1	—	—	—	1.5 ± 0.2
PP12 (9)	90.2 ± 0.3	6.7 ± 0.2	—	<1	—	<1	<1	<1	—	<1	1.3 ± 0.1

[a] The time of degradation of the sample is in parentheses.

inhomogeneous charge peak (~ 283.5 eV) is an artificial peak appearing on all the spectra that come from the inhomogeneous charging on the polymer surface due to the insulating nature of the material.[1,18]

The O1s spectra

Figures 7 to 10 present the O1s spectra (532 eV) of PP7 (pH 6), PP8 (pH 7), PP9 (pH 8), and PP12 (reference) samples, respectively. The O1s spectra of the other samples are quite similar except for the intensity of some of the synthesized peaks. A subtraction of the nonlinear background was made for all the high-resolution spectra by a Shirley treatment and all spectra were analyzed with the software PIXAS. The accuracy of the synthesis was evaluated by the consideration of the parameter χ_n^2. The charge effect energies are 4.6, 4.7, 5.4, and 4.9 eV for the PP7, PP8, PP9, and PP12 samples, respectively.[1,18,19]

The spreading out of the O1s peak supposes the existence of several types of bonds. All the spectra give a synthesis of four peaks. The first peak (~ 530.4 eV) is associated with the charging effect due to the nonconducting state of the material.[1,18] The three other peaks are related to oxygen bonds with carbon, considering that the other possible bonds between the oxygen and the other elements of Table II are too weak to be distinguished in the spectra. The analysis of the spectra makes it possible to identify the following chemical functions: C=O (~ 531.7 eV), C—OH
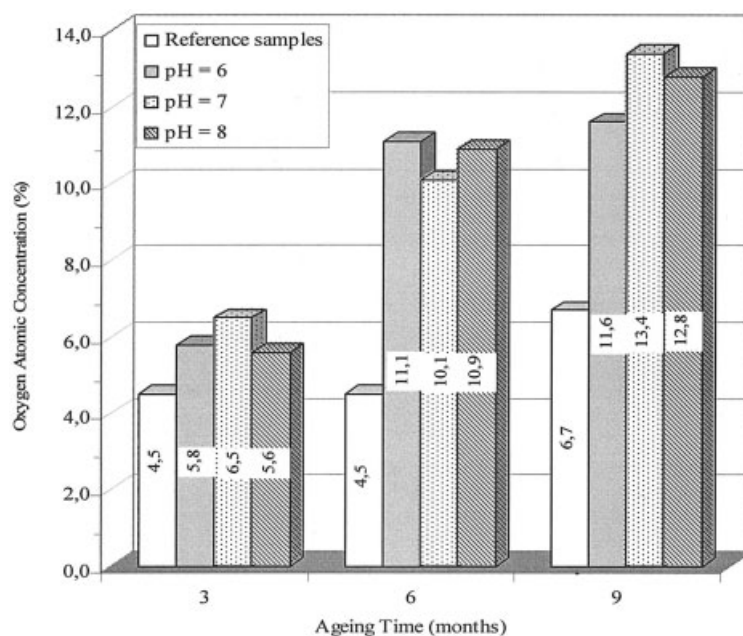

Figure 2 Evolution of the oxygen concentration according to the time of aging and to the pH of the buffer solutions.
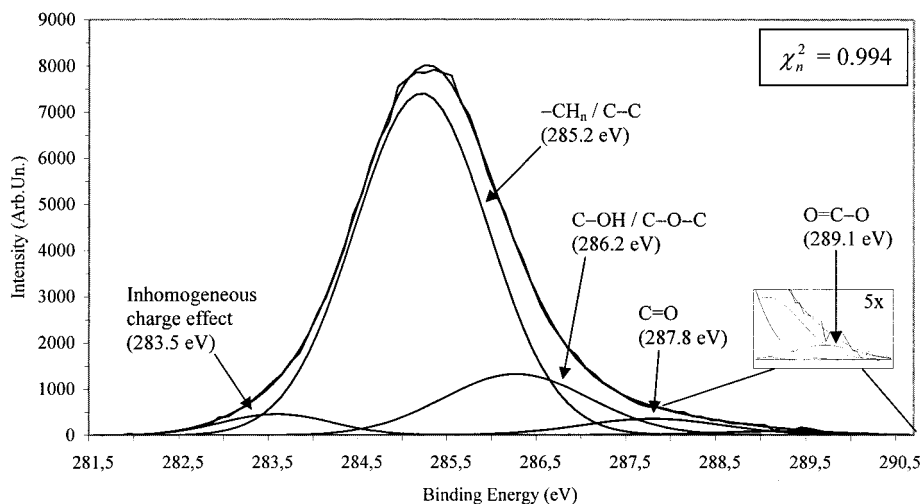
Figure 3 PP7 sample C1s spectrum.

($\sim$ 532.8 eV), and O$=$C$-$O ($\sim$ 533.8 eV).[1,14,18–23] For the peak at $\sim$ 533.8 eV, the oxygen simply bonded to the carbon atom produces mainly this peak. These analyses confirm the studies of C1s spectra by obtaining the same chemical functions on both sides.

Depth profiling

XPS measurements were taken with two angles of photoelectron exit (15°/n and 70°/n) to obtain a depth profiling of oxidation of the material. The analysis of the data was based on the hypothesis of Sheng et al.[26] The assumption of the authors is an oxidation with a constant oxygen concentration as far as depth d in the material. From the depth (d), the material is considered as not oxidized. The results of calculations show that oxidation occurs with an average depth between

9 and 10 nm. This result agrees with other studies that give depths of oxidation of 5–10 nm.[1,8,9]

DISCUSSION

Figure 11 summarizes the possible reactions that lead to the chemical groups identified by XPS in Figures 3 to 10. The principal phenomenon of aging of the PP, based on the literature,[1,3,6–8] is an oxidation of material following the loss of a proton (H$^+$) on the level of the second carbon atom of the monomer unit. Oxidation can follow from various mechanisms of stabilization, of which the most common produce the following functional groups, causing or not chain scissions: alcohols (C$-$OH), ketones (C$=$O), hydroperoxides (COOH), esters [$-$(CO)$-$OR$-$], aldehydes ($-$CH$=$O), and carboxylic acids [$-$(CO)$-$OH]. These assump-
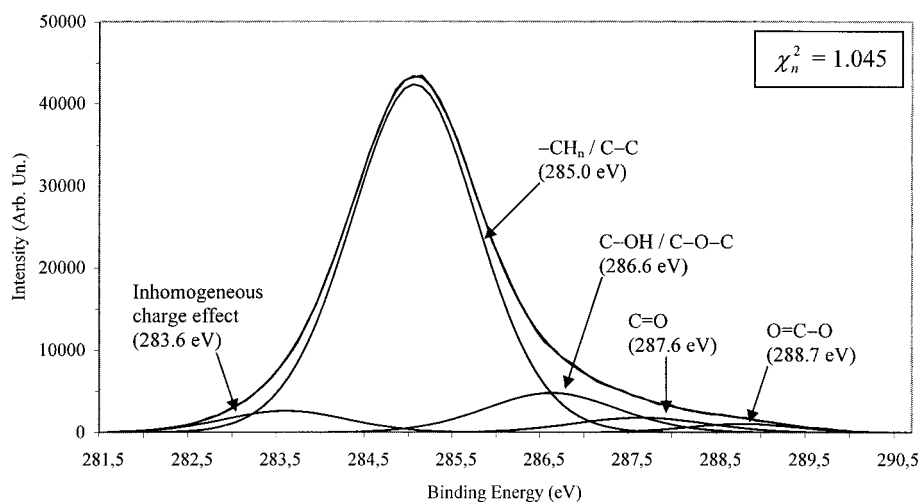

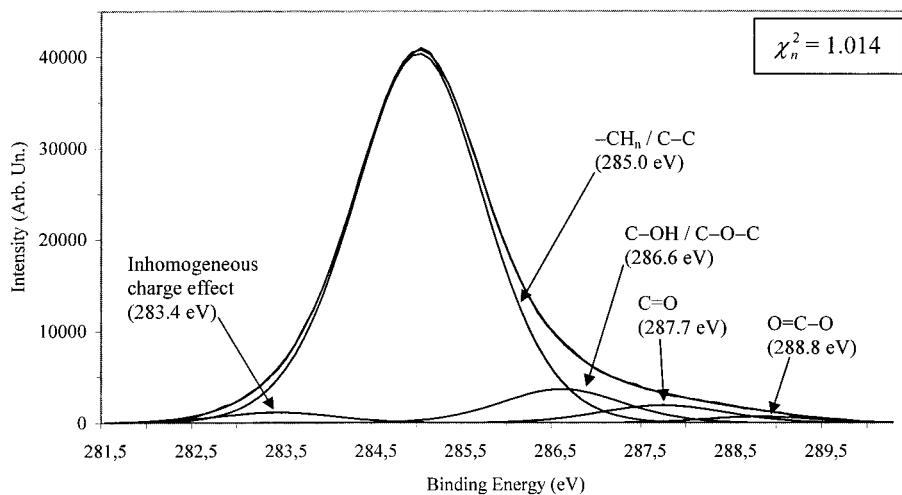**Figure 4** PP8 sample C1s spectrum.

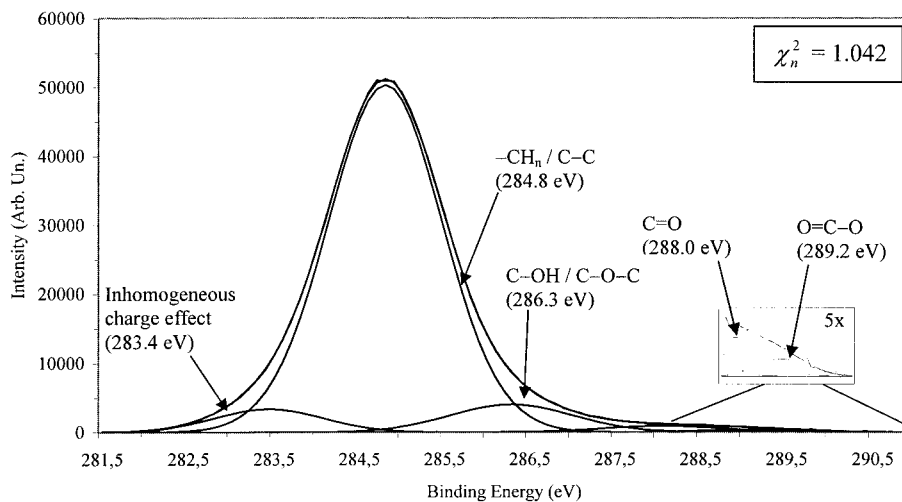**Figure 5**   PP9 sample C1s spectrum.
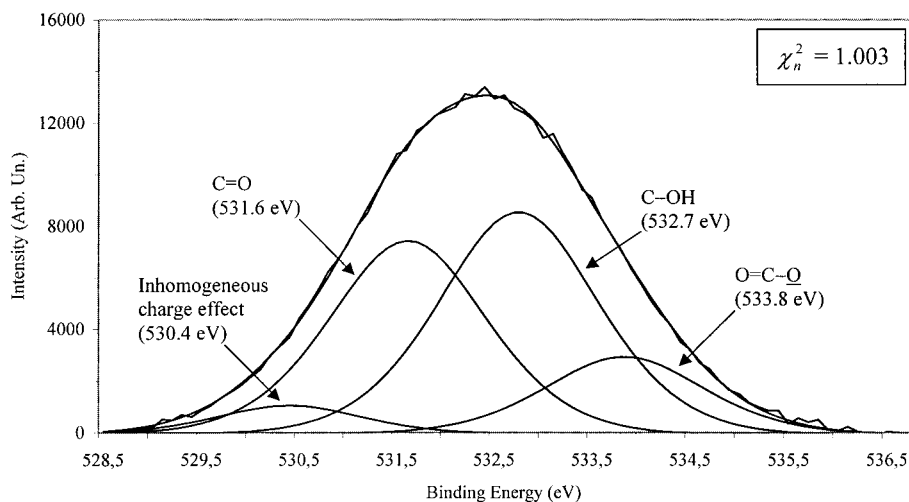

Figure 6   PP12 sample C1s spectrum.

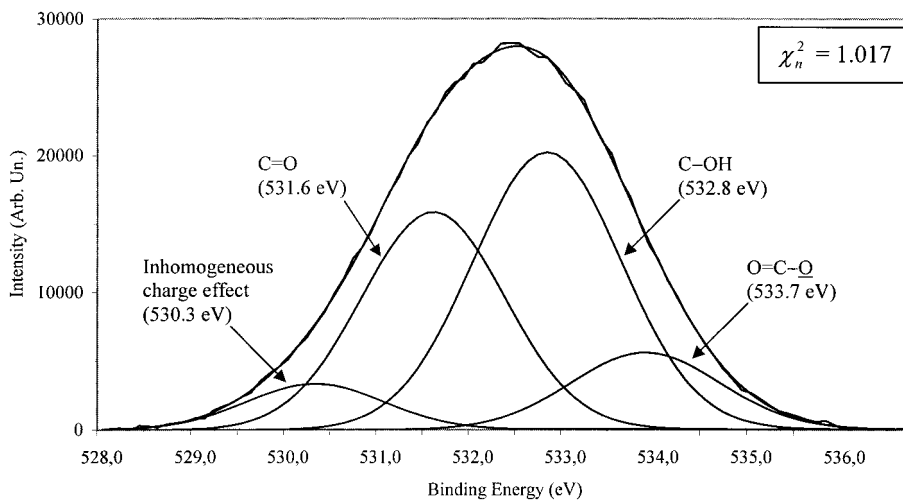**Figure 7**   PP7 sample O1s spectrum.

Figure 8 PP8 sample O1s spectrum.

tions of aging are based on various experiments of degradation.[1,3,6-8]

The first phenomenon of aging (loss of the proton) is based on the weakness of the bond between the second carbon of the monomer and its associated hydrogen atom compared to the other bonds in the monomer.[1,3,6,7] The scission of the C—H bond can be made by the ionic potential of the various negative ions of the solution (OH^-, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) or by the polarity of the water molecules. The rupture of the bond or of the polymeric chain occurs by the electrostatic attraction of the proton.[27,28] The solvent can also fit through the polymeric matrix by dividing the interactions between the chains, to establish stronger polymer–solvent interactions.[27,28]

The possibilities of stabilization of the free bond respect the nature of the various ions and molecules present in significant concentration in the aqueous solution (H^+, OH^-, O^{2-}). As shown in Figures 7 to 10, the presence of bonds between two oxygen atoms is negligible compared to the possibilities of stabilization of the oxidized polymer, because the enthalpy of dissociation of the O—O bond is weak and can be easily broken (125.6–146.5 kJ/mol) compared to approximately 414 kJ/mol (4.3 eV) for a C—H bond. The possibility of an oxidation by an oxygen molecule is also shown in Figure 11 but, as the O_2 concentration is weaker than the concentration of the ions of the solution and as the enthalpy of dissociation of a O—O bond is weak, the probability of this mechanism of stabilization is weak.

As shown in Figure 11, chemical conversions can occur between the various chemical groups because the stability of the chemical species is inversely proportional to their enthalpy of dissociation.[29] By comparing the enthalpy of dissociation (binding energy) of
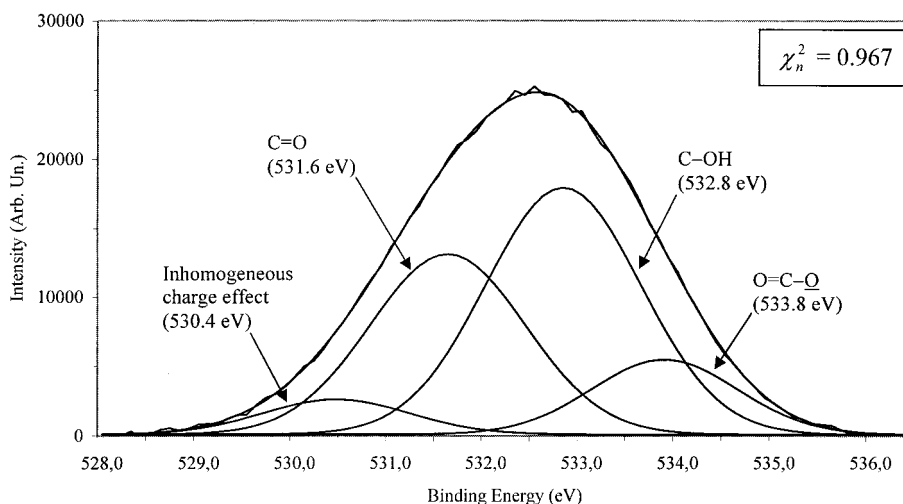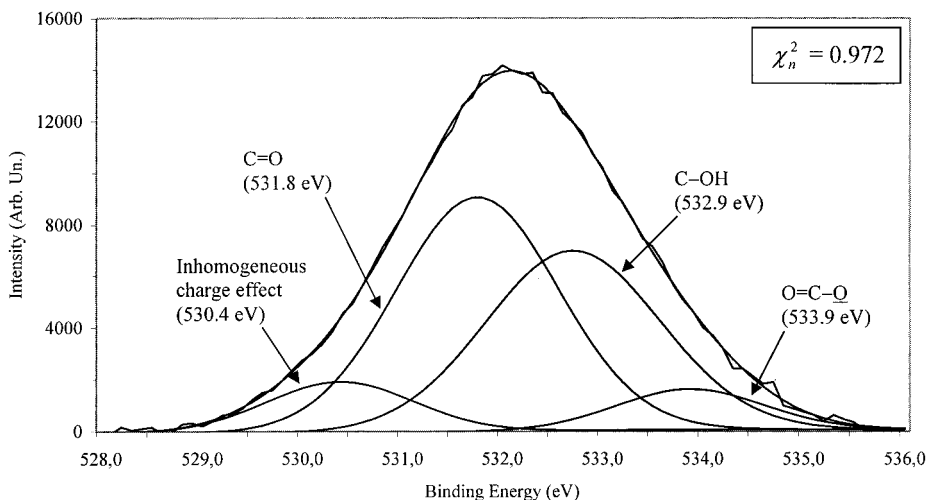

Figure 9 PP9 sample O1s spectrum.

Figure 10 PP12 sample O1s spectrum.

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, thus breaking the double bond between carbon and oxygen.

CONCLUSION

Twelve samples of industrial polypropylene were put in KH₂PO₄–K₂HPO₄ buffer solutions at different pH values (6, 7, and 8) for different periods of aging (3, 6, and 9 months). XPS measurements on a range of 0 to 1150 eV (MgKα) allowed the determination of the changes in the nature of the surface of the studied samples, by an observation of the evolution of the presence of the main impurity of PP: oxygen. This study made it possible to determine that the polypropylene oxidizes at the surface (9–10 nm depth) during the hydrolytic aging. The oxidation is a function of the time of aging, but seems independent of the range of pH values used for buffer solutions. XPS studies around the C1s peak (285 eV), confirmed by those of the O1s peak (532 eV), made it possible to know the nature of oxidation by determining the principal chemical groups formed by the polymer and the ions of the buffer solution: alcohols, ketones, aldehydes, esters, and acids. It was then possible to propose mechanisms of degradation in accordance with the literature about similar studies (photodegradation,
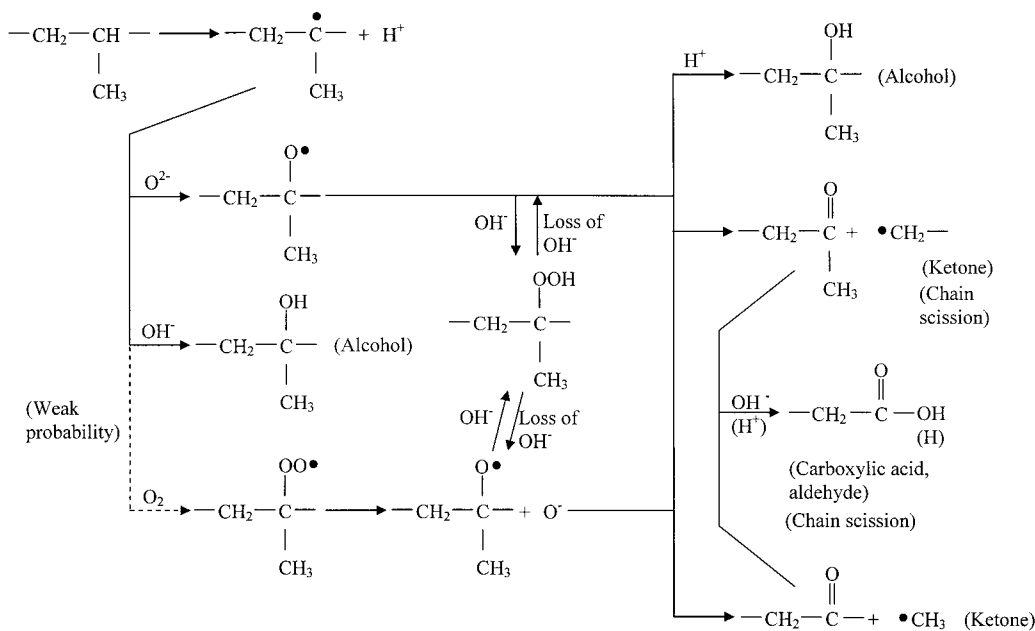

Figure 11 Proposed mechanisms for the hydrolytic aging of the PP.

flame, heat, etc.). The main exception from the literature is the case of the hydroperoxides, which dissociate to give an ion OH^- and a free bond to the level of the first oxygen atom.

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