

CONTRIBUTION TO THE STUDY BY X-RAY PHOTOELECTRON SPECTROSCOPY OF THE NATURAL AGING OF THE POLYPROPYLENE

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In the present work we are concerned in the study, by means of the X-ray Photoelectron Spectroscopy (XPS), of the solar radiation impact (atmospheric environment), on the natural aging of the polypropylene (PP). The study has focused on two periods of aging, 60 and 80 days. Results of the quantitative analysis show an important degradation of the aged material due essentially to the contamination by oxygen, The latter being the main contaminating agent in surface. The solar radiation accelerates the oxidation of the surface of the PP by rupture of the C-H bonds. The decomposition of C1s and O1s peaks has allowed a best comprehension of the chemical reactional mechanisms, in terms of carbon-oxygen bonds (C=O, C-OH and O=C-O) responsible of the photo-oxidation.

Keywords : Polymers ; Polypropylene ; Ageing ; Photo-oxidation ; XPS.

1. Introduction

In the present work, we have been interested in the study, by X-ray photoelectron spectroscopy (XPS), of the solar radiation impact, on the natural aging of the polypropylene (PP), whose chemical formula is represented as follows : - [(CH₂ - CH(CH₃))_n -.

Oxygen constitutes the main agent generating and accelerating the degradation, and notably modifying physical and chemical properties of such materials [1-3]. The phenomenon of oxidation is essentially accelerated by UV radiations (coming from the solar light) whose range of wave lengths includes especially that associated with C-H bonds forming the chemical frame of the polymers [4-7].

Rjeb et al. [4] have studied, by XPS, the effect of a natural aging, during a period of 5 years, on two samples of polypropylene (PP), the first was protected from ambient light, whereas the second was exposed to ambient light. This study

has shown that the oxidative degradation of the surface of the polypropylene samples, is more pronounced in the case of a total exposition to ambient light [4].

Similarly, some members of our group [8], have studied by means of XPS, the non controlled natural aging, of the PP during a year,. This study has focused on two samples one PP partially sheltered from the rain in a sunny place, and the other exposed to an atmospheric environment in a less sunny place. The analysis has also shown that oxygen is the main agent of contamination.

In the present article, we present results obtained by means of XPS, of the oxidative effect on the surface of a series of PP sample under a natural aging. The duration of this aging did not exceed three months (60 and 80 days). The decomposition of the peak corresponding to C1s and O1s permits a best comprehension of the reactional

mechanisms responsible of the photo-oxidation.

2. Experimental Procedure

Sizes of the PP samples studied (size A4, mark Cambridge), manufactured in France, were approximately 2x1 cm². No cleaning of the surface has been practiced prior to the XPS analysis. The experimental apparatus is sufficiently described and commented in references [4,9], We recall here some essential parameters related to the experimental procedure.

We have performed XPS measurements, using a source of radiation Mg Ka, using a VG Escalab MK II system. This system is equipped with an analysis (XPS, AES, SEM), a preparation chamber and a SIMS analysis chamber. The pressure reached in the chamber is around 5x 10⁻¹¹ Torr. The angle as compared to

the normal of the incident radiation, noted θ/n , has been 15°/n. The analysis of data XPS accomplished Summer with the help of a software (PIXAS), based on a code established by Hughes and Sexton [10].

3. Results and discussion

XPS spectra of figure 1 traduce the effect of an atmospheric environment on the degradation of the PP samples, during two periods 60 days (Fig. 1b) and 80 days (Fig. 1c) ; spectra of figure 1a correspond to the non-treated PP sample. These spectra, as well as the results of the analysis of XPS data expressed in percentages of atomic concentrations of the chemical species present on polymer surfaces (Table 1), show that exposition to atmospheric environment affects the state of sample surfaces.

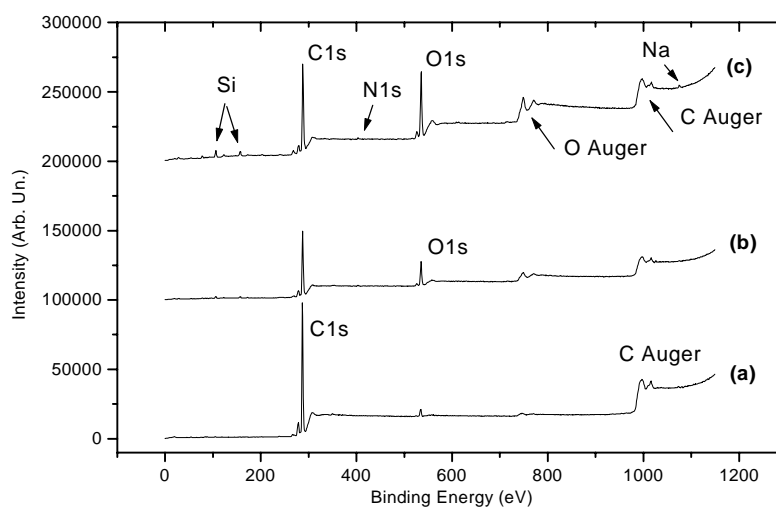


Figure 1 : XPS spectra of the PP samples : aged during 80 days (c), 60 days (b), and non treated sample (a).

Carbon (C1s, peak at 285 eV) is the main constituent on the surface of the non-treated sample (Fig. 1a). The intensity of the corresponding peak decreases during aging (Figures 3b and 3c), but it remains however the dominant constituent in comparison to the other species. Oxygen, whose peak O1s is located at 532 eV, in

very weak concentration on the surface of the new PP (Table 1), increases during the aging process to the detriment of C1s, its intensity becomes comparable to that of C1s. One observes also on spectra (b) and (c) associated respectively to aged samples during 60 and 80 days, the presence of small peaks located at 102, 153, 400 and

1072 eV, corresponding to Si2p_{3/2}, Si2s, N1s and Na1s respectively. The presence of Si, element whose concentration increases notably with the duration of the aging, could have come from rejects of

factories near the place of samples location ; the main contamination of the surface remaining however essentially due to oxygen.

Samples	Atomic concentrations (%)				
	C1s	O1s	Si	N1s	Na1s
PP non treated	97.32	2.68	-----	-----	-----
PP (60 days)	82.97	13.54	4.50	< 1	< 1
PP (80 days)	68.45	22.77	8.77	< 1	< 1

Table 1 : Atomic concentrations (%) of the different elements constituting the surface of the PP for two duration of the natural aging : 60 and 80 days.

The decomposition of the peaks associated to C1s and O1s, allows a best comprehension of reactional mechanisms, in terms of carbon-oxygen bonding, responsible of the photo-oxidation. This analysis of the peaks C1s and O1s necessitates a numerical processing by means of a software PIXAS [10]. Note however that this processing includes a correction of a charge effect (of 3 to 4 eV) inherent to the insulating nature of the PP samples [11,12].

Figure 2 shows the results of such decomposition of the peaks relative to C1s corresponding to the new sample and to those aged during 60 and 80 days. The peak corresponding to C1s (Fig. 2a) can be decomposed in five peaks located at on 283.2, 285.0, 286.5, 287.7 and 288.9 eV.

On spectra relative to the aged samples appear, together with the three peaks previously mentioned relative to the new sample, two other peaks attributable to C=O and O=C-O bonds respectively. Indeed, there is formation of tertiary alkyls radical by cleavage of C-H bond [13] ; the formation of these radicals occurs after the extremely rapid combination with oxygen [20,21] followed by a release of hydrogen from the polymer chain. The effect of the duration of the aging gives rise to an evolution of the peaks intensity associated with all these bonds (Fig.2).

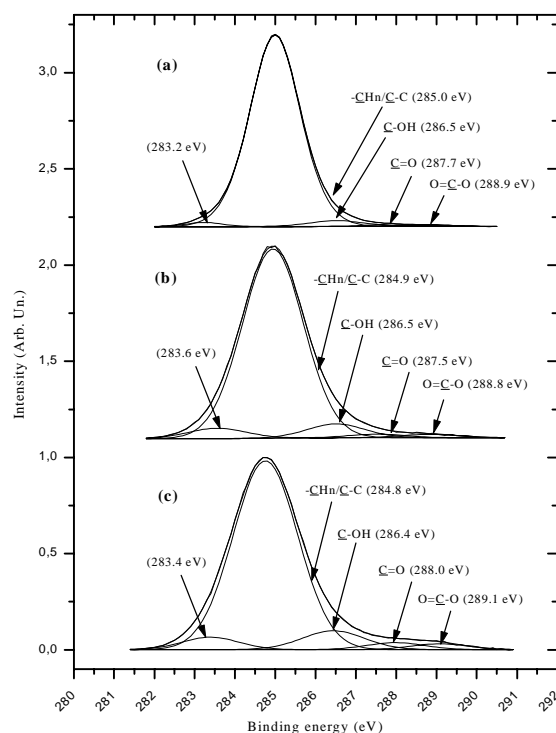


Figure 2 : XPS spectra, centered on the C1s level of the PP samples, aged during 80 days (c), 60 days (b), and non treated (a).

Similar analyses of the C1s peak have been realized on those of O1s. Figure 3 shows the results of this decomposition. For the new sample (Fig. 3a), the O1s can be decomposed in four elementary peaks located at 530.1, 531.9, 532.4 and 534.0

eV associated respectively with the charge effect in the polymer surface, and to C=O, C-OH and O=C-O bonds.

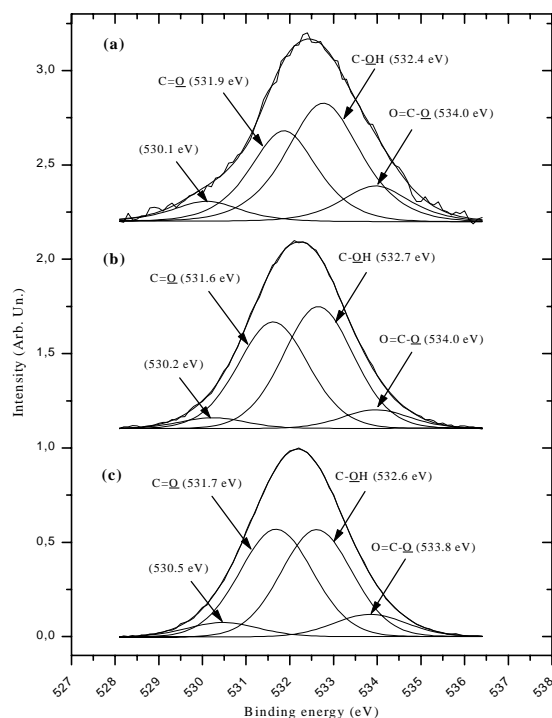
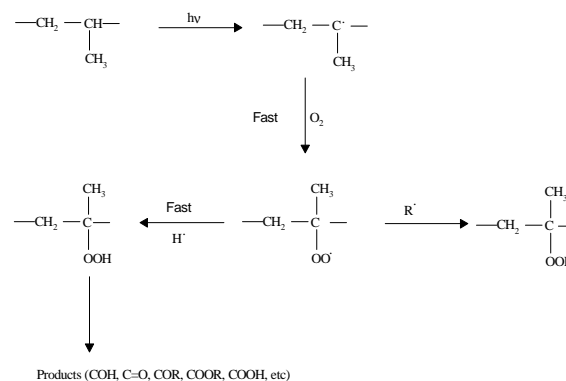


Figure 3 : XPS spectra, centered on the O1s level of the PP samples : aged during 80 days (c), 60 days (b), and non treated (a).

During aging, the intensity of the peaks associated with C-OH and O=C-O bonds decreases at the expense of that corresponding to the C=O bond. The phenomenon of oxidation can be explained by the fact that UV rays contained in the solar radiation spectrum, whose have lengths range between 290 and 400 nm, can especially break C-H bonds, corresponding to a wave length of 290 nm [6,8]. A reactional mechanism of oxidation has been proposed for the purpose to interpret the existence of the different bonds formed by oxygen. The diagram following illustrates a such mechanism [4,5].



Taking account of a such diagram and of the relative intensities of the peaks coming from the decomposition of C1s and O1s peaks (Figures 2 and 3), several reactional mechanisms, which may stabilize the polymer structure, can take place. The first, and the most probable, comes from the neutralization of a state occupied by a proton, leading to the formation of the C-OH bond. The second gives rise to the formation of the C=O bond. Mechanisms involving O=C-O groups seem to be less probable. These mechanisms take place by the appearance of the Ketone form in a monomer and a breakage in the polymeric chain can occur ; the creation of O=C-O bonds stabilizes the material, with the formation of esters or carboxyl acids.

4. Conclusion

XPS spectroscopy has been used to study the natural aging (atmospheric environment), of the polypropylene (PP), during two periods, 60 and 80 days. This study shows an important degradation of the surface state due essentially to the contamination by oxygen. Indeed, quantitative analysis results have shown that oxygen is the main agent of contamination. The peak corresponding to O1s increases and its intensity becomes comparable to that of C1s. The atomic concentration percentage of oxygen increases to the detriment of that of carbon, pointing out that the photo-oxidation is all the more important that the sample is more aged.

The mechanism of the photo-oxidation [4,5] shows that UV rays accelerate the oxidation of the surface of the PP, by rupture of the C-H bond. In addition to the effect of UV rays, atmospheric environment (humidity, rain) contributes to the increase of this oxidation.

The decomposition of C1s and O1s peaks has allowed a best comprehension of chemical reactinal mechanisms, in terms of carbon-oxygen bonds (C=O, C-OH and O=C-O) responsible of the photo-oxidation, and the formation of oxidation products : aldehydes, ketones, esters, acids, etc.

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