Leucopur EGM influence on the surface photooxidation of poly(ethylene terephthalate) and poly(vinyl chloride)

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The surface photooxidation of poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC) has been studied by ESCA in the presence of Leucopur EGM as brightener. The results indicate that in the case of PVC there is no effect of the additive in the photooxidation, while in the case of additivated PET it is possible to observe surface protection for the higher concentrations of brightener used.

(Keywords: Leucopur EGM; brightening agents; photooxidation; photostabilization; surface analysis; ESCA)

Introduction

In the last 50 years, increasing interest has been devoted to the industrial development of fluorescence brightening agents. They are employed in the textile industry, detergent industry, cotton and paper manufacture, fibres and plastics materials production. Their mechanism is based on fluorescent properties and they are characterized by the presence of conjugated double bonds. Modern fluorescent brightening agents are derived from stilbene, benzazol, cumarin and diaryl-pyrazolin.

Leucopur EGM, 7-[2*H*-naphtho-(1,2-*d*)triazol-2-yl]-3-phenyl-2-benzopyrone (Sandoz Huningue S.A.), with structural formula (I) is used as a fluorescence brightener for polymers with very good properties such as excellent thermal stability, excellent chemical stability to oxidizing and reducing agents, excellent lightfastness, excellent polymer solubility, non-toxicity, inertness in polycondensation media, ease of handling.

The additives in plastics and polymeric materials are usually intended to be well distributed throughout the bulk, but in certain circumstances surface segregation

(I)
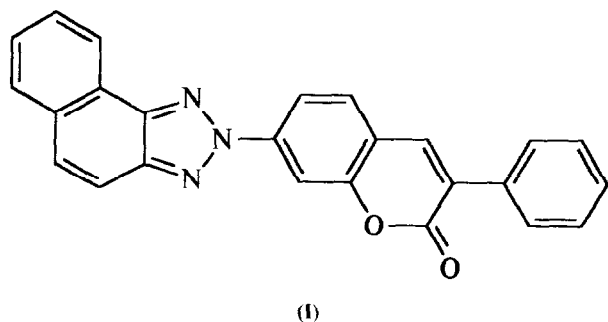
may take place. In addition, their presence could influence thermal photooxidation especially in the surface.

Electron spectroscopy for chemical analysis (ESCA) has been used as a powerful technique to study the surface photooxidation of polymeric materials in the presence or absence of additives[1-10].

We have investigated the effect of Leucopur EGM in the surface photooxidation of PVC and PET by ESCA.

Experimental

PET used for the preparation of samples was semi-opaque, fibre grade (Società Italiana Poliestere), average molecular weight 20 000, containing 0.3% by weight of titanium oxide, while tested PVC was high molecular weight ($K = 70$) Vinnol H 70 DF (Wacker-Chemie). The percentage of Leucopur EGM present in samples 1–7 is reported in *Table 1*.

The fibres were irradiated in a Xenotest 150 S setup for simulated sunlight exposure conditions out-of-doors ($\lambda > 300$ nm) with six i.r. filter plates and one dark u.v. filter glass inserted in the filter lantern. The irradiation was 1030 W m^{-2}. The black panel temperature was 39–40°C and the relative humidity was 62%. The specimen holders turned on their own axis so this resulted in an alternating dark–light cycle.

ESCA spectra were recorded on a VG Instrument electron spectrometer using a Mg K$\alpha_{1,2}$ X-ray source (1253.6 eV). The X-ray source in standard conditions had been working at 300 W, 15 kV and 20 mA. The base pressure of the instrument was 5×10^{-10} torr and operating pressure of 2×10^{-8} torr was typically used. A pass energy of 100 eV, 50 eV, and 20 eV was used for wide scans, narrow scans and for regions required for peak fitting, respectively. The take-off angle of the electrons was 60° with respect to the surface of the sample. This allowed a sampling depth of approximately

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75 Å^{11}. All data analysis (linear background subtraction, peak integration and curve fitting) were accomplished using VGX900x (Version 5) software. Binding energies were referenced to the C–H level at 285.0 eV. The integrated areas were corrected with the appropriate instrument sensitivity factors for the stoichiometries.

Results and discussion

Wide scan analysis revealed the presence of only carbon and oxygen at the surface of PET samples, while carbon, oxygen and chlorine were present at PVC sample surfaces.

The C_{1s} and O_{1s} envelopes were experimentally measured by ESCA for unexposed and exposed PET and PVC. The effect of the X-ray-induced degradation[12,13] can be considered the same for all the samples. The data in *Table 2* relate to the O_{1s}/C_{1s} area ratios. The difference between the experimental and theoretical O_{1s}/C_{1s} area ratio for the unexposed PET sample (from the PET repeat unit formula $O_{1s}/C_{1s} = 0.40$) must be attributed to the presence of a hydrocarbon contaminant present on the surface.

From analysis of the data in *Table 2* it is evident that when Leucopur EGM is present at 0.03–0.04%, the PET samples are protected from photooxidation with respect to the unexposed PET. This fact is more evident in *Figure 1* where the oxygen uptake in PET (sample 1) as a function of the exposure time is compared with that observed for samples 4 and 5.

However, maximum protection is reached after 30 days of irradiation in both cases. A lower percentage of additive (sample 2 and 3) is unsuitable for protection of the surface of PET from photooxidation. In fact, the O_{1s}/C_{1s} ratio increases from 0.335 to 0.513 and 0.282 to 0.507, respectively, very close to the values of pristine PET (0.318–0.470).

Curve fitting analysis of the C_{1s} region of unexposed samples is consistent with the PET repeat unit and shows the presence of four peaks that correspond to $\underline{C}$–H (285 eV), $\underline{C}$–O–C (286.5 eV), O–$\underline{C}$=O (289 eV), and to the $\pi \rightarrow \pi^*$ shake-up (291.4 eV). During accelerated weathering the analysis showed the onset of a fifth

peak centred at 287.8 eV, which grows with exposure. A plot of the percentage of this new ketonic component with respect to the whole C_{1s} envelope as function of the exposure time (*Figure 2*) reveals that its growth is inversely proportional to the surface stability to photooxidation, confirming the action of Leucopur EGM when used at higher concentrations.

In the case of PVC (*Table 2*) there is no evidence of surface stabilization of such a polymer in the presence of additive. In fact, taking into account experimental error, the differences between samples (6 and 7) are very small.

Conclusion

It is evident that Leucopur EGM when used as a brightener for PET and PVC shows very good performance, such as excellent thermal stability, excellent chemical stability to oxidizing and reducing agents, excellent lightfastness, excellent polymer solubility, etc. and does not increase the surface photooxidation of the materials. On the contrary, in the case of PET it is possible to observe surface protection in the case samples treated with 0.03 and 0.04% of Leucopur EGM.
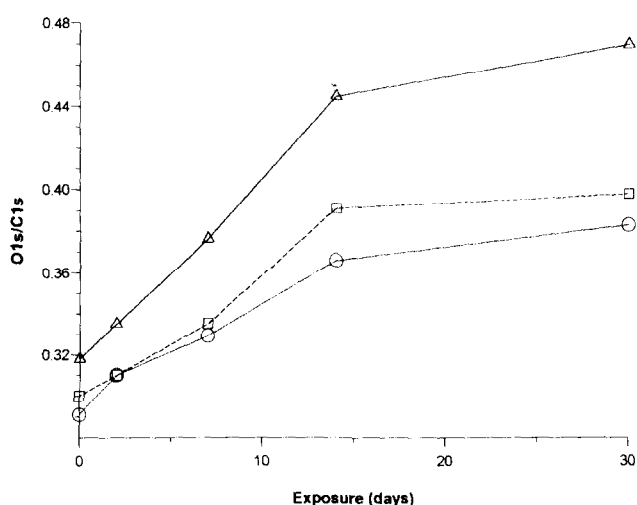
Figure 1 O_{1s}/C_{1s} area ratio for exposed PET: △, no additve; ☐, with 0.03% Leucopur EGM; ○, with 0.04% Leucopur EGM

Table 1

Sample	Polymer	Leucopur EGM (%)
1	PET	0.00
2	PET	0.01
3	PET	0.02
4	PET	0.03
5	PET	0.04
6	PVC	0.00
7	PVC	0.05

Table 2 O_{1s}/C_{1s} area ratio as function of exposure

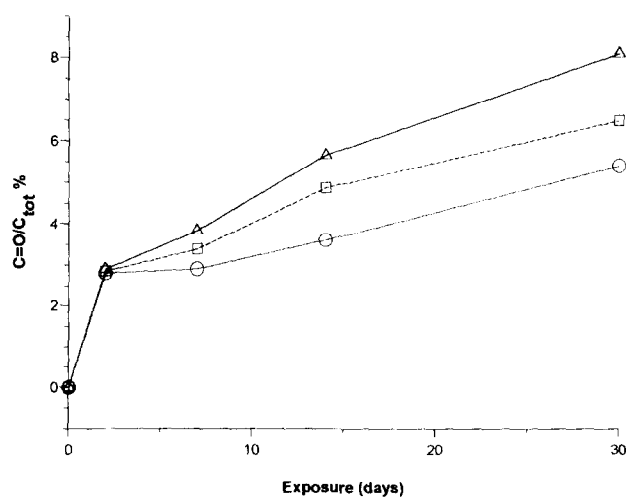| Sample	Unexposed	2 days	7 days	14 days	30 days
1	0.318	0.335	0.376	0.445	0.470
2	0.335	0.334	0.463	0.493	0.513
3	0.282	0.418	0.451	0.446	0.507
4	0.300	0.310	0.335	0.391	0.398
5	0.291	0.310	0.329	0.366	0.383
6	0.165	0.306	0.739	0.786	1.085
7	0.193	0.291	0.308	0.796	0.863

Figure 2 Percentage of carbonyl function (determined by peak fitting) as function of exposure: △, no additive; ☐, with 0.03% Leucopur EGM; ○, with 0.04% Leucopur EGM

In all cases there is no evidence of surface segregation of the additive on the surface.

Studies are in progress to better understand the mechanism of the stabilization action of Leucopur EGM.

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