Surface Photostabilization of Polystyrene by Tinuvin 1577

FRANCESCO A. BOTTINO, GIOVANNA DI PASQUALE, ANTONINO POLLICINO, ANTONINO RECCA

Istituto Chimico, Facoltà di Ingegneria, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

ABSTRACT: The effect of a new hydroxyphenyltriazine additive (Tinuvin 1577) on the surface photooxidation of polystyrene films at various concentrations of the additive was studied using ESCA spectroscopy. The accelerated weathering was run in a Xenotest apparatus to mimic outdoor conditions. The presence of Tinuvin 1577 effectively inhibited the surface photooxidation of polystyrene. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 1251–1256, 1998

Key words: polystyrene; surface photostabilization; ESCA; accelerated weathering

INTRODUCTION

The rapid photodegradation of polymers is a serious issue that has economic and environmental implications. [1,2] The outdoor use of polymeric materials is severely limited by their poor stability in sunlight, resulting in environmental problems, as well as considerable consumption of energy and resources due to the necessity of frequent replacement of the materials. Plastics manufacturers recognize that by increasing the resistance of polymers to sunlight the applications of these materials could be extended; this has provided a strong incentive for the development of additives to protect polymers from degradation.

A wide range of photostabilizers [3–18] is available including UV screeners, absorbers, excited state quenchers, and UV stable antioxidants, the choice depending on the polymer and/or related application in which the polymer is used. The more common UV absorbers are based on 2-hydroxybenzophenone (**I**) and 2-hydroxyphenyl-benzotriazole (**II**) classes. Recently a new class of UV absorbers based on hydroxyphenyltriazine (HPT's) was developed; presumably they operate through a mechanism similar to that reported for the **I** and **II** derivatives shown in Scheme 1. Actually, studies reported by Hayoz [19] and Rytz et al. [20] on Tinuvin 1577 (Trademark of Ciba-Geigy), a new UV absorber based on a triazine moiety (**III**), led to the conclusion that Tinuvin 1577 is more efficient than Tinuvin P, a commercial UV absorber based on structure **II.** The better efficiency of Tinuvin 1577 with respect to Tinuvin P has been rationalized in terms of a much stronger intramolecular hydrogen bond and a more suitable geometry.

Applications of HPT UV absorbers include acrylic and methacrylic resins, rigid polyvinylchloride, polyalkylene terephthalates, linear and branched polycarbonates, polyacetal resins, modified polyphenylene ether compounds, polyamides, polyolefins, styrenics, elastomers, adhesives, and various high performance plastics. [21]

The effectiveness of additives in stabilizing polymers has been extensively studied by changing the mechanical properties such as tensile or impact strength. The results have often shown a change in the mechanical performance before any chemical modification has been detected in the bulk of the material. This result can be explained by taking into account that because visible/UV radiation only penetrates a few microns into a polymeric material and because the partial pressure of oxygen is greater at the polymer surface, the photoinduced processes and photooxidation (in particular) are mainly surface phenomena. [22]
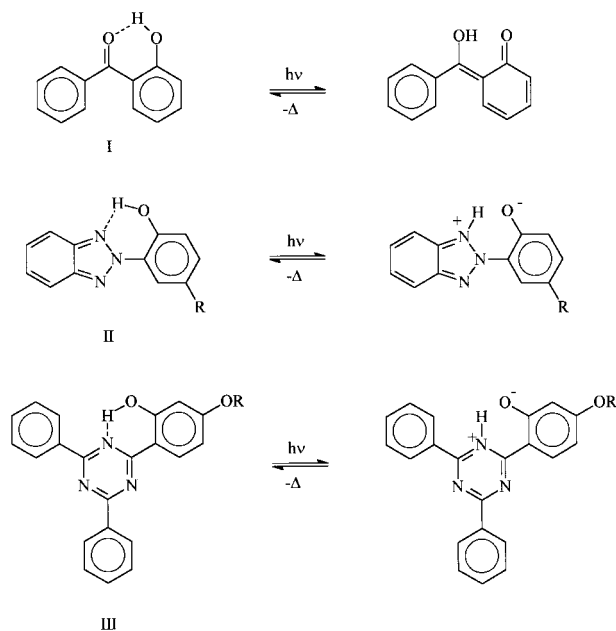
Scheme 1.   UV absorbers **I–III.**

In addition, although the total amount of chemical change can be small, in the surface layers such variation may be extensive, causing profound changes in the optical, electrical, or mechanical properties of the polymer. Moreover, the kinetics of the polymer reaction with oxygen or of the formation of functional groups provides a valuable and often rapid means of following resistance to the oxidation. Hence, the determination of polymer surface oxidation could be a particularly convenient way of studying the effects of stabilizers, because their primary function is to interfere with the oxidation process.

The aim of this work was to study the surface photooxidation of polystyrene films containing Tinuvin 1577.

ESCA is a very useful technique for the analysis of polymer surfaces,[23–29] and it was used in this work to determine the changes at the polystyrene surface during accelerated weathering.

EXPERIMENTAL

The additive was supplied by Ciba–Geigy Limited (Switzerland) and was purified by chromatography on a silica gel column using chloroform as the eluent.

ESCA spectra were recorded on a VG instrument electron spectrometer using an Mg $K_{\alpha,1,2}$ X-ray source (1253.6 eV). The X-ray source in the

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 the operating pressure was typically 2×10^{-8} torr. A pass energy of 100, 50, and 20 eV was used for wide scans, narrow scans, and curve 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 75 Å.[30] All data analysis (linear background subtraction, peak integration, and curve fitting) were accomplished using VGX900x (version 6) software. Binding energies were referenced to the C—H level at 285.0 eV. The samples were studied as films in all cases.

Polystyrene (molecular weight, MW, 45,000; Aldrich) was purified by dissolving in toluene, precipitating in methanol, and then drying under a vacuum. Solutions of 5% (w/w) polystyrene containing 0, 0.005, 0.025, 0.05, 0.1, and 0.2% (w/w) of Tinuvin 1577 were prepared in chloroform. Samples 1–6 were obtained that contained, respectively, 0, 0.1, 0.5, 1, 2, and 4% of Tinuvin 1577. The films were cast from the solution on a flat glass dish, and the chloroform was removed under a vacuum (10^{-3} torr) for 24 h.

The polymer films were irradiated in a Xenotest-150S setup for simulated sunlight exposure conditions ($\lambda > 300$ nm) with six infrared filter plates and one dark UV filter glass inserted in the filter lantern. The irradiance 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, which resulted in an alternating dark/light cycle.

RESULTS AND DISCUSSION

Polystyrene films containing different percentages of Tinuvin 1577 (samples **1–6**) were irradiated for different periods. Figure 1 shows the C$_{1s}$ core-level spectra for the unirradiated and irradiated films related to polystyrene (**1**) and samples **4** and **6.** The C$_{1s}$ envelope for the unexposed film shows a photoionization peak centered at 285.0 eV relative to carbon not bonded to oxygen with a little shoulder at higher binding energy arising from the carbon–oxygen environment. A $\pi \rightarrow \pi^*$ shake-up satellite diagnostic of the aromatic ring in the polymer is also present at a binding energy of about 291.6 eV.[31]

After exposure of the polymer films in a Xenotest apparatus, distinct changes in the C$_{1s}$ core-level spectra are observed; in particular the region
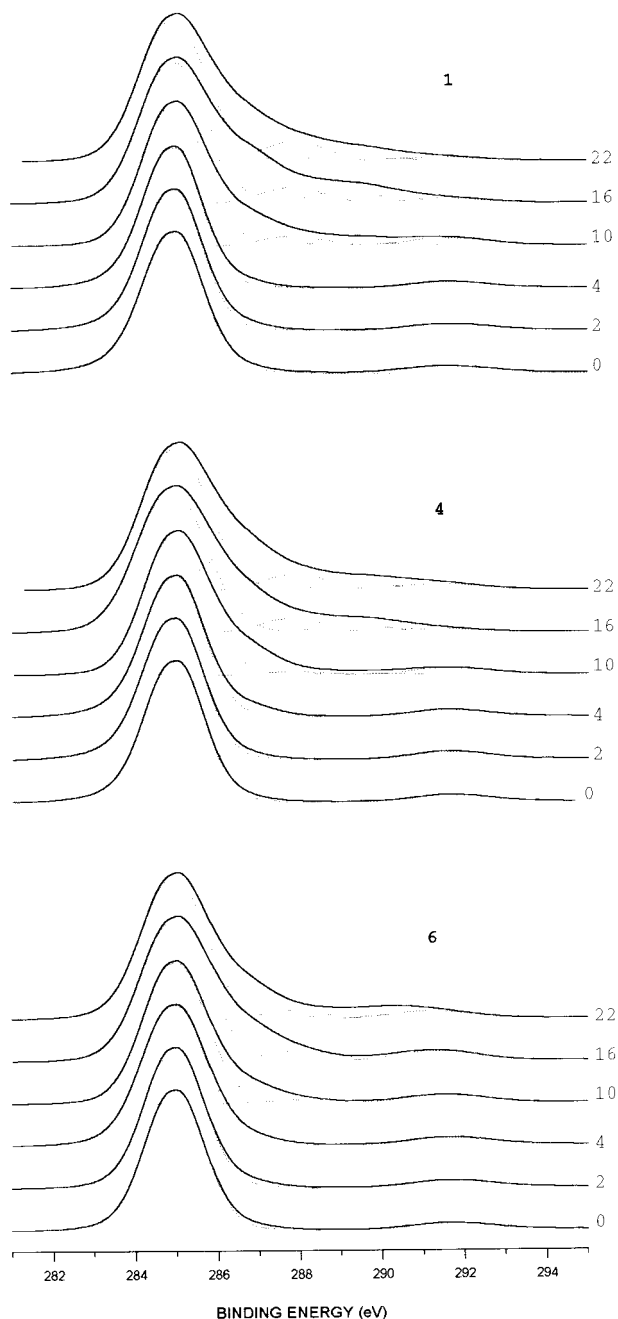
Figure 1 C_{1s} envelopes of the ESCA spectra of unexposed and exposed polystyrene (**1**) and samples **4** and **6** photooxidized for various lengths of time (days).

on the higher binding energy side of the main photoionization peak at 285.0 eV becomes more complex due to the increasing content in C—O functionalities.

Considering first the overall reaction process, the O_{1s}/C_{1s} peak intensity ratio, calculated by taking into account the appropriate instrument sensitivity factors, is very indicative of the oxygen

uptake on the polymer film surface. The values are reported in Table I and plotted in Figure 2 as a function of the irradiation time.

From an analysis of the data it seems that an induction period exists before the photooxidation starts; this is shown by the O_{1s}/C_{1s} values after 4 days of accelerated aging that are practically unchanged with respect to the unexposed materials. In a recent article France et al. hypothesized[32] that during this period substantial changes occur in the surface molecular structure of polystyrene, which correspond to loss of aromaticity evidenced by the decreasing of $\pi \rightarrow \pi^*$ shake-up satellite intensity, and that these changes precede any uptake of oxygen. During 10 exposure days the oxygen uptake increased at a rate that is inversely proportional to the amount of additive present in the sample. The O_{1s}/C_{1s} values stay in the range of 0.20–0.11 (samples **1** and **6**, respectively). These differences were still present for the O_{1s}/C_{1s} values after 16 days; at this time the neat polystyrene showed a high oxygen uptake (O_{1s}/C_{1s} 0.33) indicative of a highly oxidized surface, while the stabilizing effect was low in samples **2** and **3** and grew moving from sample **4** to sample **6**. The subsequent leveling off in the O_{1s}/C_{1s} peak area ratio indicates that a steady state was reached after 16 days of irradiation. In this state the rate of evolution of the oxidation product (carbon dioxide, in addition to volatile carboxylic acid products, has been found as a major product in the photooxidation of solid polystyrene[33,34]) is equal to the rate
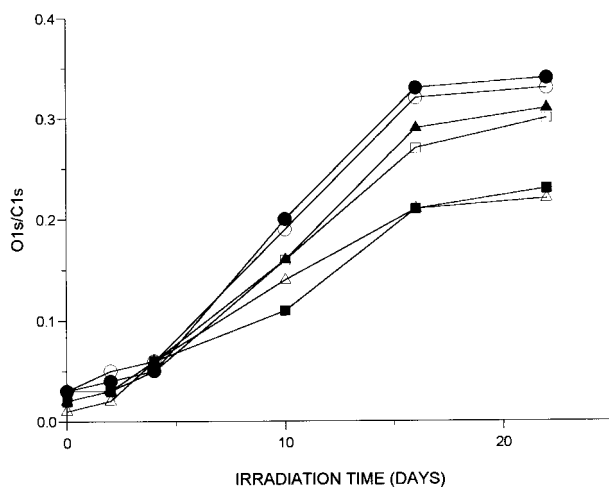

Figure 2 O_{1s}/C_{1s} peak area ratio as a function of irradiation time of (●) polystyrene (PS), (○) PS + 0.1% of Tinuvin 1577, (▲) PS + 0.5% of Tinuvin 1577, (□) PS + 1% of Tinuvin 1577, (△) PS + 2% of Tinuvin 1577, and (■) PS + 4% of Tinuvin 1577.

Table I O_{1s}/C_{1s} Ratio as Function of Irradiation Time

Sample	Unexposed	2 Days	4 Days	10 Days	16 Days	22 Days
1	0.03	0.04	0.05	0.20	0.33	0.34
2	0.03	0.05	0.06	0.19	0.32	0.33
3	0.02	0.03	0.05	0.16	0.29	0.31
4	0.03	0.03	0.06	0.16	0.27	0.30
5	0.01	0.02	0.06	0.14	0.21	0.22
6	0.02	0.03	0.06	0.11	0.21	0.23

of oxidation of the surface of the remaining solid polymer. These results show that the oxygen uptake on the surface of the additive containing samples was lower than the one on the neat polystyrene sample. This trend was maintained after 16 and 22 days with the indication of a photostabilization of the surface induced by the presence of Tinuvin 1577. It seems clear that the additive acted positively at all percentages, but that the best results for the surface protection were obtained for the samples containing more than 1% of the additive (Fig. 2).

Peak fitting of the C_{1s} envelope (Fig. 1) of all unexposed samples shows a principal component at 285.0 eV due to the carbon atoms not bonded to oxygen (C—H or C—C) and a weak peak centered at 286.5 eV arising from carbon atoms single bonded to oxygen, indicating that a low degree of oxidation was present initially.

Upon irradiation in a Xenotest apparatus the C—H component showed a progressive decrease in intensity as the exposure time increased. In addition, the component centered at 286.5 eV increased and new components centered at 287.8 eV (due to ketonic functionalities, C=O), 289.3 eV [due to acidic or anhydride functionalities, C(O)O], and 290.3 eV (due to carbonate functionalities, CO_3^{2-}) appeared.

Table II shows how the percent contribution of all these components to the C_{1s} envelope changes as a function of the irradiation time in samples **1, 4,** and **6.**

In the case of neat polystyrene the analysis of the data shows that, of the components arising from carbon bonded to oxygen, the one centered at 286.5 eV, arising from hydroperoxides, alcohols, and ethers groups, increased in intensity rapidly in the 4–10 day exposure period and leveled off after about 16 days of irradiation. The rapid increase in the intensity of this peak probably reflects a buildup of hydroperoxides at the surface, because these groups initiate the photooxidation process. The subsequent leveling off in the

intensity of the 286.5 eV peak may be due to saturation of surface sites readily susceptible to hydroperoxide formation. The other functionalities centered at 287.8, 289.3, and 290.3 eV, respectively, were detected starting from the 10-day exposure. By increasing the exposure time a high degree of surface oxidation was reached, as indicated by the increase of all these functionalities, while the C—O component remains almost constant. Moreover, a decrease in intensity of the shake-up satellite was observed. This decrease is indicative of the degradation of the aromatic rings.

The presence of Tinuvin 1577 affects the polystyrene surface photooxidation. A stabilizing effect was revealed from the O_{1s}/C_{1s} ratios, which are lower for samples **3–6** with respect to sample **1.** For correlative exposure time, the component analysis also reveals some interesting features. Table II shows the results obtained from the curve fitting analysis for samples **4** and **6.** Looking at the component arising from the carbon atoms not bonded to oxygen (C—H or C—C), it is evident that its intensity was higher on increasing the amount of stabilizer present in the sample. At 10-day exposure the jump of the amount of the component arising from carbon single bonded to oxygen was less pronounced in sample **6** with respect to the other samples; in this latter sample it leveled off at a lower level. At the same time the increase of ketonic, acidic, and carbonate functionalities was very reduced, particularly for sample **6.** In fact, it can be noted that in this sample at 10- and 16-day exposure, carboxylic and carbonate components were absent and they appeared after 22 days, only reaching values that are lower than those found for neat polystyrene (sample **1**). These data could suggest that the Tinuvin 1577 acts by decreasing the amount of ketonic functions that can originate from the further oxidation of C—O groups, that is, by deactivating the peroxidic and/or radical functions. Moreover, because the more oxygenated functions can also derive from the attack of oxygen on the

Table II Comparision of C_{1s} Components of Samples 1, 4, and 6 as Function of Irradiation Time

Sample	Time (Days)	C—H	C—O	C=O	O—C=O	CO_3^{2-}	$\pi \to \pi^*$
1	0	91	3	—	—	—	6
	2	90	4	—	—	—	6
	4	90	5	—	—	—	5
	10	73	14	5	3	1	4
	16	66	18	7	5	1	3
	22	63	18	8	6	3	2
4	0	91	3	—	—	—	6
	2	91	3	—	—	—	5
	4	90	6	—	—	—	5
	10	77	15	2	1	1	4
	16	70	16	6	4	1	3
	22	65	19	7	4	2	3
6	0	92	2	—	—	—	6
	2	91	3	—	—	—	6
	4	89	5	—	—	—	6
	10	81	10	2	—	—	6
	16	74	15	5	—	—	6
	22	70	16	4	3	2	5

aromatic moiety, and taking into account that the shake-up in this sample remains almost unchanged, this could be indicative that the Tinuvin 1577 could also act by protecting the aromatic ring from oxidative attack.

CONCLUSIONS

In conclusion, ESCA studies on the surface photooxidation of polystyrene containing different percentages of Tinuvin 1577 demonstrate that the presence of additive effectively inhibits the surface photooxidation of polystyrene.

Moreover, examination of the functionalization of the surface, as expressed by changes in the line shape of the C_{1s} region, revealed the presence of an induction period. Then alcohol/hydroperoxide groups appeared before carbonyl and carboxyl functions could be detected. It is suggested that Tinuvin 1577 acts in two ways: in the stage during which hydroperoxide species formed react to give the other oxygen containing functional groups, and by protecting the aromatic rings from oxidation.

Surface photooxidation studies on other systems containing HPTs alone or in combination with phenolic antioxidants or hindered amine light stabilizers are in progress.

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