Influence of the testing conditions on the efficiency and durability of stabilizers against ABS photo-oxidation

R.M. Santos [a], A. Pimenta [b], G. Botelho [b,*], A.V. Machado [a]

[a] Institute for Polymer and Composites/I3N, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

[b] Centro/Departamento de Química, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal

Keywords:

Weathering
Stabilization
Styrenic polymers
Structure

Abstract

Exploitation of knowledge of the efficiency of stabilizers on acrylonitrile-butadienestyrene stability is very important for appropriate selection of stabilized systems. With the aim of studying the influence of testing conditions on the effectiveness of stabilizers, several compositions were prepared by extrusion and submitted to different weathering conditions. UV/Vis spectroscopy and high performance liquid chromatography were used to assess the durability of stabilizers during the exposure time. Different behaviour was found under natural and accelerated weathering. Although all stabilizers induced a decrease of ABS degradation rate during accelerated weathering, the best results were achieved when combinations of light stabilizers with phenolic antioxidants and trivalent organo phosphorus compounds were used. Natural exposure enhances the degradation process when compared to data obtained in an accelerated chamber under similar light source characteristics. This behaviour suggests that there are other atmospheric parameters that play an important role in the degradation process. The results also showed that a combination of stabilizers and antioxidants induces a decrease of the oxidation

rate in the initial stage of degradation under natural weathering conditions. Nevertheless, this synergetic effect is limited for the degradation time studied.

Introduction

Synthetic polymers are an extraordinarily versatile class of materials, rapidly replacing more traditional materials such as metals, ceramics and concrete in a wide range of technological applications [1].

A common drawback of polymeric materials is their susceptibility to ultraviolet (UV) radiation when used in outdoor applications. This phenomenon is called weathering [2,3] and is defined as an irreversible chemical process induced by atmospheric parameters, which leads to changes in polymer properties [4].

Acrylonitrile-butadiene-styrene (ABS) is an impactmodified polymer used in many technological applications due to its exceptional properties [5]. ABS combines advantageous properties of the different monomers: styrene (S), acrylonitrile (AN) and butadiene (PB). While the *S* component influences the stiffness, processability and gloss, AN influences the rigidity, toughness, heat, chemical resistance and improves the dynamic load-bearing and impact strength [6]. The PB component imparts impact resistance to the brittle thermoplastic matrix at room temperature and, especially, at low temperature since it has a very low glass transition temperature ($Tg \approx -85°C$).

However, ABS is unacceptable for outdoor applications where UV stability is a key issue. The degradation chemistry of ABS under accelerated weathering conditions has been extensively studied over the past few

Table 1
Code, chemical and commercial name, molecular mass, melting range, physical form and amount used in ABS photostabilization.

Code	Chemical name	Commercial name	Mw (g. mol^{-1})	Melting range (°C)	Physical form	Amount (w/w)
UVA	2-(2'-Hydroxy-5'-methylphenyl)benzotriazole	Tinuvin P®	225.4	128-132	Slightly yellow powder	0.10

HALS	1,3,5-triazine-2,4,6-triamine, N,N‴-[1,2-ethanediylbis[[[4,6-bis-[butyl (1,2,2,6,6-pentamethyl-4-piperidinyl) amino]-1,3,5-triazine-2-yl] iminol-3,1-propanediyl]] bis[N′,N″-dibutyl- N′,N″-bis (1,2,2,6,6-pentamethyl-4-piperidinyl	Chimassorb 119FL®	2286	115-150	Granules	0.30
AO_1	Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate)	Irganox 1076 ®	531.0	50-55	White powder	0.15
AO_2	Tris(2,4-di-ter-buthylphenyl)phosphate	Irgafos 168 ®	646.9	183-186	White powder	0.15

decades [7-12] and it is well known that oxidation of the PB phase, by abstraction of allylic hydrogen from the α carbon next to the 1.4 and 1.2 unsaturations, is the main reason for ABS degradation [11,13-19]. Some authors state that photo-oxidative degradation of ABS is confined to the rubbery phase [10], while others state that ABS degradation is a combined phenomenon between acrylonitrilestyrene (SAN) aging and oxidation of the PB component [7,19-21].

As degradation can occur at every stage of the polymer lifetime (manufacturing, processing and end-use), light and thermal stabilizers are introduced into the polymer matrix, in small amounts, to improve its stability. Nowadays, useful data on action mechanisms of several stabilizers and their chemistry have been reported, which is important for appropriate selection and incorporation according to the specified application [22-24].

Kolawole and Adeniyi [25] studied the influence of a combination of Tinuvin P (UVA) and antioxidant (DBHBT) in thermal and photo degradation of ABS. The results showed that a small amount of Tinuvin P enhances the ABS performance against degradation, and a good synergistic effect was found with both UVA and antioxidant. Kurumada et al. [24] studied the effect of a mixture of HALS/ UVA on several polymers, and a high level of synergy was found for ABS at a mixing ratio of 90/10 (HALS/UVA). Bokria and Schlick [10] studied the photo-oxidative degradation of ABS containing Tinuvin 770 by FTIR-ATR, and the results showed that the degradation occurred within approximately 50μ m of the surface.

This study compares the effectiveness of different stabilization systems on ABS under different testing conditions, natural and accelerated weathering. Although the evaluation of stabilizer consumption during exposure is rather complicated, in this work UV/Vis spectroscopy and high performance liquid chromatography (HPLC) were used to assess

the efficiency of light stabilizers and antioxidants. The influence of the stabilizers on the photooxidative degradation of ABS was also monitored in terms of chemical, physical and mechanical properties.

Experimental procedure

Materials and chemicals

ABS Terluran High Impact- 10® (from BASF, Ludwigshafen, Germany), a high impact grade suitable for injection molding and extrusion, was used as the raw material.

The stabilizers under study are commercially available and are listed in Table 1.

Samples preparation

Samples with different compositions (Table 2) were prepared in a single-screw extruder, (L/D 30) Luigi Bandera. The extruder lay-out and set temperature used to produce a 0.5 mm thick tape are depicted in Fig. 1. The screw speed was 75 rpm . This processing technique was selected to simulate as closely as possible industrial production conditions.

ABS, previously dried in an oven for 1 h at 80°C, was mixed with light or thermal stabilizers or a combination of them in a "home made" rotary mixer. During sample preparation, it was assured that thickness remains unchanged along the material cross-section.

Weathering

ABS samples were submitted to accelerated and natural weathering conditions according to ISO-4892 Plastics Methods of Exposure to Laboratory Light Sources - Part 2: Xenon-arc sources, International Organization for Standardization, 1994 and to ASTM D1435 - Standard Practice for Outdoor Weathering of Plastics, American Society for Testing and Materials, 2005.

Accelerated weathering

Accelerated weathering was performed in a Xenotest 150*S* chamber from Heraeus (Original Hanau) equipped with a filtered Xenon lamp with an intensity of $60 W m^{-2}$. The light below 300 nm was filtered with a UV window combined with six IR filter glasses. The ageing cycle was 120 min (102 ± 0.5 min of dry and 18 ± 0.5 min of rain). The specimens (100 mm × 2.5 mm × 0.5 mm) were exposed for several degradation times.

Table 2
Stabilized ABS samples prepared for weathering studies.

Sample Code	Raw material	Stabilizers			
	ABS	UVA	HALS	AO_1	AO_2
ABS/HALS/UVA	↗	↗	↗	-	-
ABS/AO	↗	-	-	↗	↗

ABS/HALS/UVA/AO	↗	↗	↗	↗	↗

Polymer and additives

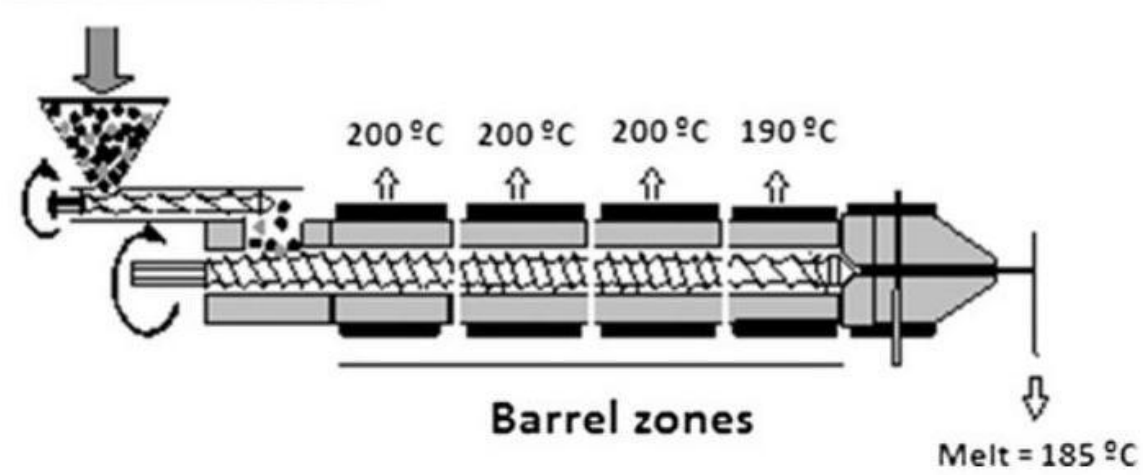

Fig. 1. Extruder lay-out and temperatures to produce *ABS* tape.

Natural weathering

Natural experiments were performed in Arruda dos Vinhos - Lisbon, for 6 months, where the samples were placed on a wood support at an angle of 45° facing south. Natural weathering conditions obtained from a national meteorological institute are presented in Table 3.

Characterization

UV/Vis spectroscopy

UV/Vis spectroscopy was used to follow the behavior of Tinuvin P® in the solid-state and Chimassorb 119FL® in solution during the degradation time, as will be described below.

- Analysis of Tinuvin P® behavior in solid-state

All measurements were carried out with a Shimadzu UV240 apparatus fitted with an integrating sphere in order to avoid the scattered light of ABS samples (0.5 mm thickness). The analyses were performed directly, either on molded discs of the pure compounds or on the degraded surfaces of stabilized samples, without any extraction or refining step, using a barium sulphate disc ($BaSO_4$) as reference.

- Analysis of Chimassorb 119FL® consumption in solution

The analytical procedure used to quantify the Chimassorb 119FL (B) of undegraded and degraded ABS samples involved three steps: a) extraction, b) standard solution preparation to obtain the calibration curve and c) analysis by UV/Vis spectroscopy [9].
a) Extraction of hindered amine light stabilizers (Chimassorb 119FL (8)) from ABS

Undegraded and degraded ABS samples, previously weighed, were placed in a 100 mL flask with 20 mL of chloroform. After 1.5 h under stirring at room temperature, acetonitrile was slowly added to precipitate the polymer. The solution was filtered under vacuum and the supernatant liquid evaporated almost to dryness. The residue obtained was transferred to a 10 mL volumetric flask and chloroform was added to obtain a 10 mL solution.
b) Preparation of standard solutions to obtain the calibration curve

Table 3
Average values of natural exposure.

Month	Maximum temperature / °C	Minimum temperature/ °C	Relative humidity/%	Rain/mm
March	17.6	10.2	68.6	3.4
April	20.8	12.4	67.3	10.1
May	20.4	13.4	71.6	3.4
June	27.4	16.6	60.6	1.7
July	27.9	17.5	62.0	0.0
August	27.4	17.7	64.2	0.0

A 100 ppm stock solution of each UVA/HALS (Tinuvin P® and Chimassorb 119FL®) was prepared in chloroform in order to obtain the calibration curve.

c) Analysis by UV-VIS spectroscopy

All the samples resulting from steps a) and b) were analysed by UV-VIS spectroscopy using a Shimadzu UV $2501-PC$ at 235 nm ; this wavelength minimizes the Tinuvin $P^{®}(\lambda = 341$ nm) interference.

High performance liquid chromatography (HPLC)

HPLC technique was used to evaluate the antioxidant consumption (Irganox 1076 (8) and Irgafos 168 (8)) in ABS samples.

In order to test the method efficiency, initially, nondegraded samples were dissolved, precipitated and the additives were quantified from the extract. Polymer samples were cut into small pieces, 20 mL of propan- 1 -ol was added and kept under stirring at room temperature for 24 h [10]. After this time, acetonitrile was slowly added to precipitate the polymer, the solution was filtered by vacuum and the supernatant liquid evaporated

almost to dryness. The residue obtained was transferred to a 5 mL volumetric flask and propan-1-ol was added to obtain a 5 mL solution.

HPLC was performed using a Jasco-2080 Plus (Japan) model 870 - UV variable wavelength detector ($\lambda = 282$ nm). A reversed-phase column waters Spherisorb 5.0μ m ODS 2 (4.6 mm × 250 m) was used. A ternary mixture of ethyl acetate (500 mL), methanol (380 mL) and water (120 mL) was used as a mobile phase [10]. The injection volume was 20μ L, flow-rate set at 2.0 mL $\cdot$ s^{-1} and a system pressure of 200 MPa .

Color measurements

The colour difference, given by ΔE, is explained by the following equations [26]:

$$\Delta E = [(\Delta l^2) + (\Delta a^2) + (\Delta b^2)]^{\frac{1}{2}} \quad (1)$$

where the coordinates represent:
ΔE - colour difference;
$\Delta l = l - ls$
1 - luminosity in a scale from 0 (black) to 100 (white) for exposed sample and ls for unexposed sample (standard);
$\Delta a = a - as$
a - ratio between red and green, assuming positive values for the red colour and negative for the green, for exposed sample and as for unexposed sample (standard);
$\Delta b = b - bs$
b - ratio between yellow and blue, assuming positive values for the yellow and negative for the blue for exposed sample and bs for unexposed sample (standard).
$l = 16(y/yo)^{\frac{1}{3}} - 16$
$a = 500\left[(x/x0)^{\frac{1}{3}} - (y/y0)^{\frac{1}{3}}\right]$
$b = 200\left[(y/yo)^{\frac{1}{3}} - (z/zo)^{\frac{1}{3}}\right]$
The total colour difference between the standard and the samples collected along the photodegradation process was measured with a Datacolor 650 TM spectrometer, using a D65 light source and 10° viewing angle. Colour changes, specially yellowing, was obtained by CIE tristimulus values (L^*, a^* and b^*), according to the CIELAB colour system.

Mechanical properties

The mechanical performance of the degraded samples was evaluated using a universal testing machine - Miniature Materials Tester (MINIMAT) from Polymer Laboratories, with a 200 N load cell. The stress-strain data were obtained with a deformation velocity dl/dt = 0.2 mm/min in the direction perpendicular to the machine orientation, at room temperature. For each composition and sample submitted to a specific degradation time, six specimens were tested and sample dimensions were measured with a Mitutoyo Pachymeter with uncertainty of 0.025 mm .

Results and discussion

UV/Vis spectroscopy

Evaluation of Tinuvin *P*® (UVA) consumption during accelerated and natural weathering conditions

UV/Vis spectra of the unstabilized and stabilized ABS samples are depicted in Fig. 2. It can be observed that the UV/Vis spectrum of undegraded ABS sample without any stabilizers shows an absorption maximum in the region of 230 – 280 nm, related to $\pi \rightarrow \pi^*$ transition of the benzene ring of the styrene [2]. Stabilized ABS samples with Tinuvin P® exhibits a strong absorption around 347 nm , attributed to a $\pi \rightarrow \pi^*$ charge-transfer state, and an absorption at 300 nm due a local transition within the benzotriazole [3].

The absorption spectra of the ABS stabilized with UVA and HALS (Chimassorb 119FL®) and UVA, HALS with antioxidant (Irgafos 168® and Irganox 1076®) submitted to accelerated and natural weathering conditions are shown Fig. 3. As the irradiation times increases, all samples exhibited an absorbance increase at 400 nm , indicating that conjugated carbon-carbon double bonds were formed and are responsible for polymer yellowing [4]. Moreover, it can be noted that the color development of samples submitted to accelerated weathering is lower than in samples exposed to natural conditions, as will be shown in further yellowness index results.

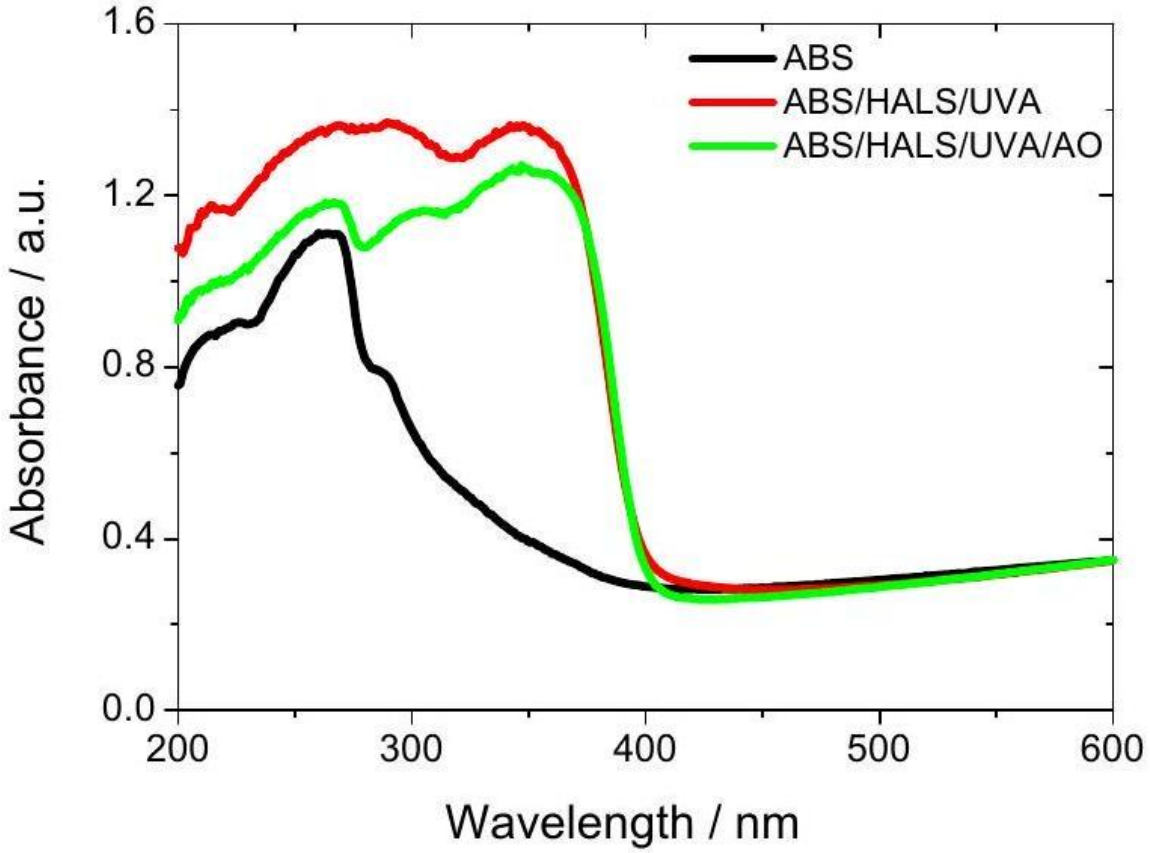

Fig. 2. UV/Vis spectra of undegraded ABS, ABS/HALS/UVA and ABS/HALS/ UVA/AO samples.

Fig. 3a shows that up to 100 h of exposure, a change in the absorbance spectra range occurs for samples containing a combination of Tinuvin P® and Chimassorb 119FL®. Suggesting

that UVA was partially consumed [27]. Although combination of Tinuvin P® and Chimassorb 119FL (8) enhances the ABS photostability during accelerated weathering experiments, the best results were achieved with combinations of these with phenolic antioxidants (Irganox 1076 (a)) and trivalent organo phosphorus compounds (Irgafos 168®), as can be observed in Fig. 3c. The spectra of stabilized ABS samples remained almost unchanged until 100 h of exposure, supporting that a synergistic effect occurred, which can be explained taking into account the action mechanism of each stabilizer. Whereas Irganox 1076 (8) acts as a labile Hdonor in competition with the polymeric hydrogen abstraction, Irgafos 168® converts hydroperoxides into stable products, such as phosphates and alcohols, competing with the propagation step of photo-oxidative degradation.

Differences between accelerated and natural weathering experiments can be noted. No significant advantages were found when combinations of light and thermal stabilizers were used. Fig. 3b and d exhibit a similar trend, i.e. the peaks at 300 and 347 nm , characteristic of the UVA, disappeared only after one month of exposure, indicating that Tinuvin P® was consumed and/or that physical loss by evaporation, leaching or blooming occurred [28].

These results indicate that there are other atmospheric parameter that play an unpredicted role under natural exposure, and enhanced the degradation process, even under lower intensity of UV radiation when compared with the accelerated chamber [29].

Evaluation of Chimassorb 119 FL (B) (HALS) consumption during accelerated and natural weathering conditions

The amount of Chimassorb 119FL(8) in ABS samples containing Tinuvin P and in combination with Irganox 1076® and Irgafos 168® submitted to accelerated and natural weathering conditions is depicted in Fig. 4.

All samples submitted to accelerated weathering conditions present a reduction of Chimassorb 119FL® as a consequence of interactions with reactive species formed

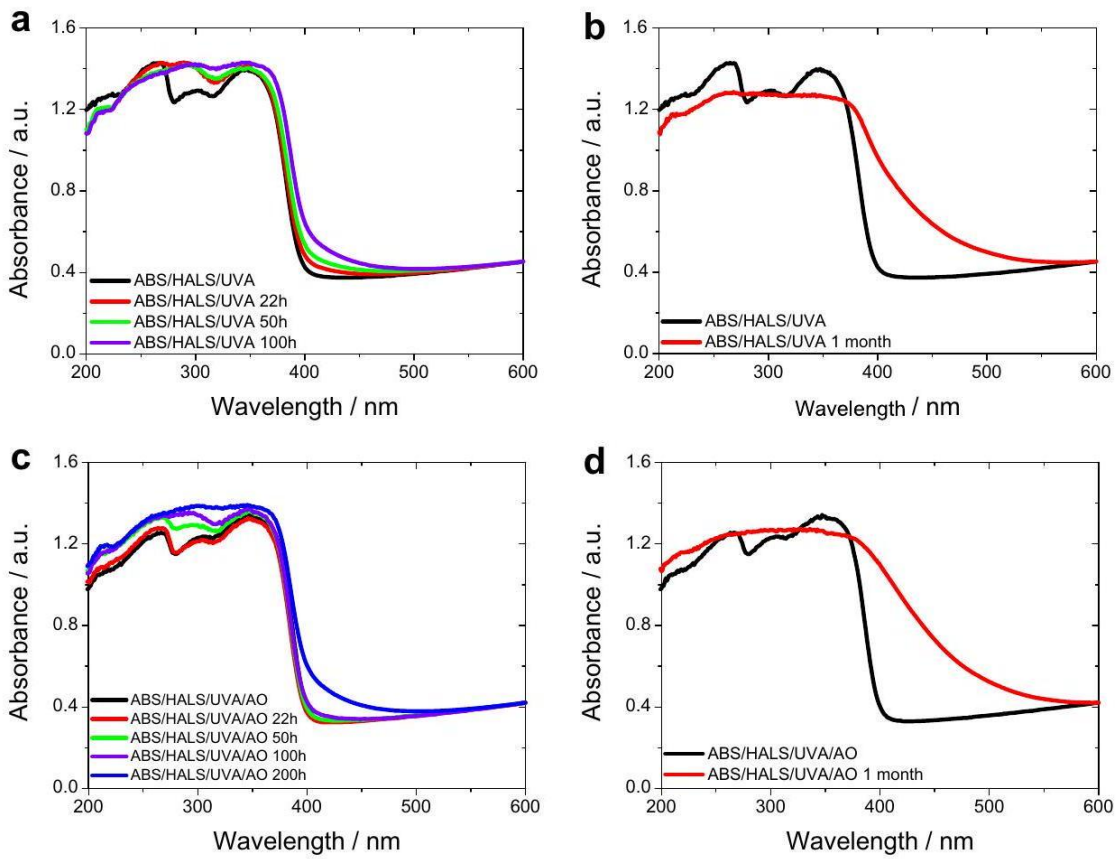

Fig. 3. UV/Vis spectra of UVA with HALS (a and b) and in combination with AO (c and d) submitted to accelerated and natural weathering conditions, respectively.
during the degradation process [11]. While in samples containing Tinuvin P® the initial amount of Chimassorb 119 FL(B) is reduced to 29% after 200 h of exposure, in samples containing a combination of light stabilizers and antioxidants the reduction was only about 41%. These results are in good agreement with data obtained by UV/Vis spectroscopy in solid-state ABS samples, showing that combinations of Chimassorb 119FL® and Tinuvin P® with Irganox 1076 ® and Irgafos 168 ® improved the ABS stability against photo-oxidative degradation.

Samples exposed to natural weathering (Fig. 4b), show a slight synergistic effect at the initial degradation stage when all additives are present. However, for long exposure times the behavior of stabilized samples, with and without antioxidant, becomes similar. This can be the result of chain scission of the stabilizer molecules, with consequent volatilization and diffusion at the surface, in agreement with the results described by Scoponi et al. [28].

High performance liquid chromatography (HPLC)

The HPLC chromatograms of the prepared standard solutions indicated a retention time for Irganox 1076 ® of 10.02 and 11.7 min for Irgafos 168®, as it can be seen in Fig. 5.

Although good correlation was obtained for both antioxidants by HPLC analysis, the consumption of Irgafos 168 ® could not be evaluated during accelerated and natural

weathering experiments due to its low response factor ($f = 0.82$) when compared to Irganox 1076 ®(8) ($f = 2$), as shown in Fig. 6.

The amount of Irganox 1076 (8) decreases with exposure time (Fig. 7). This would be expected taking into account that Irganox 1076 (B) is a H -donor capable of reacting much faster than the polymer with peroxy radicals (ROO*) formed during exposure (competing with the propagation step) due to its labile hydrogen atom with low dissociation energy [30]. Moreover, Irgafos 168 (8) acts synergistically with Irganox 1076 (8) by increasing the H-donor AO effectiveness and decreasing the color development due to the formation of quinone species from phenolic antioxidants [30-33]. However, differences can be noted between the samples with different additives. While stabilized samples with antioxidants (ABS/AO) lose the Irganox 1076® after only 50 h of exposure, samples containing a combination of light stabilizers and antioxidants lose 50% of the initial amount after 100 h of accelerated exposure (Fig. 7a). Under natural weathering (Fig. 7b), the presence of light stabilizers enhances the performance of Irganox 1076 (8) against photo-oxidative degradation. Even although the amount of antioxidant became nil for both samples, when all additives were presented the stabilization time was four times longer. This can be related to phosphite antioxidants, which can hydrolyze during weathering experiments, especially in the presence of water. Chimassorb 119FL® is also responsible for inhibiting this process by deactivating acidic impurities, in agreement with Kikkawa [31].

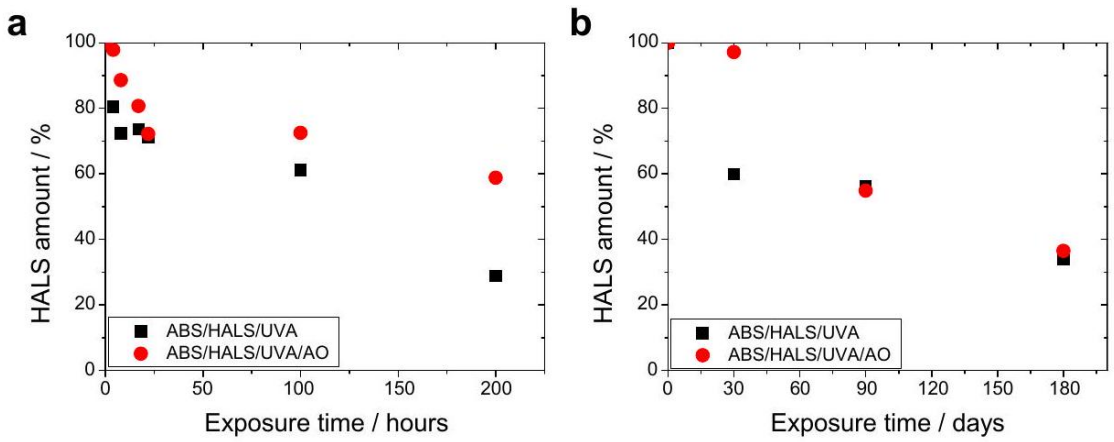

Fig. 4. Evaluation of Chimassorb 119FL(8) behavior by UV/Vis in ABS samples containing UVA and a combination of UVA and AO submitted to accelerated a) and natural b) weathering conditions, respectively.

Yellowness index

The yellowness index results of unstabilized and stabilized ABS samples, exposed to different testing conditions, are presented in Fig. 8. Yellowness index correlates very closely with the analytical findings, showing that although a similar trend was found, samples submitted to natural weathering exhibit more pronounced yellowing than samples exposed to accelerated conditions. Although the yellowing rate is different and depends on the effectiveness of each stabilizer system used and/or in its interactions, it can be noted that all stabilized samples exhibit less yellowing than the unstabilized ones.

While very similar behavior was found for stabilized samples with light stabilizers (ABS/HALS/UVA) and with antioxidants (ABS/AO), samples containing a combination of both (ABS/HALS/UVA/AO) show the least discoloration and the best results for stabilization against yellowing. This may be explained by the complementary role of light stabilizers and antioxidants, resulting in the restriction of the amount of Z and E isomers of benzalacetophenone groups formed during photo-oxidation of ABS, supporting

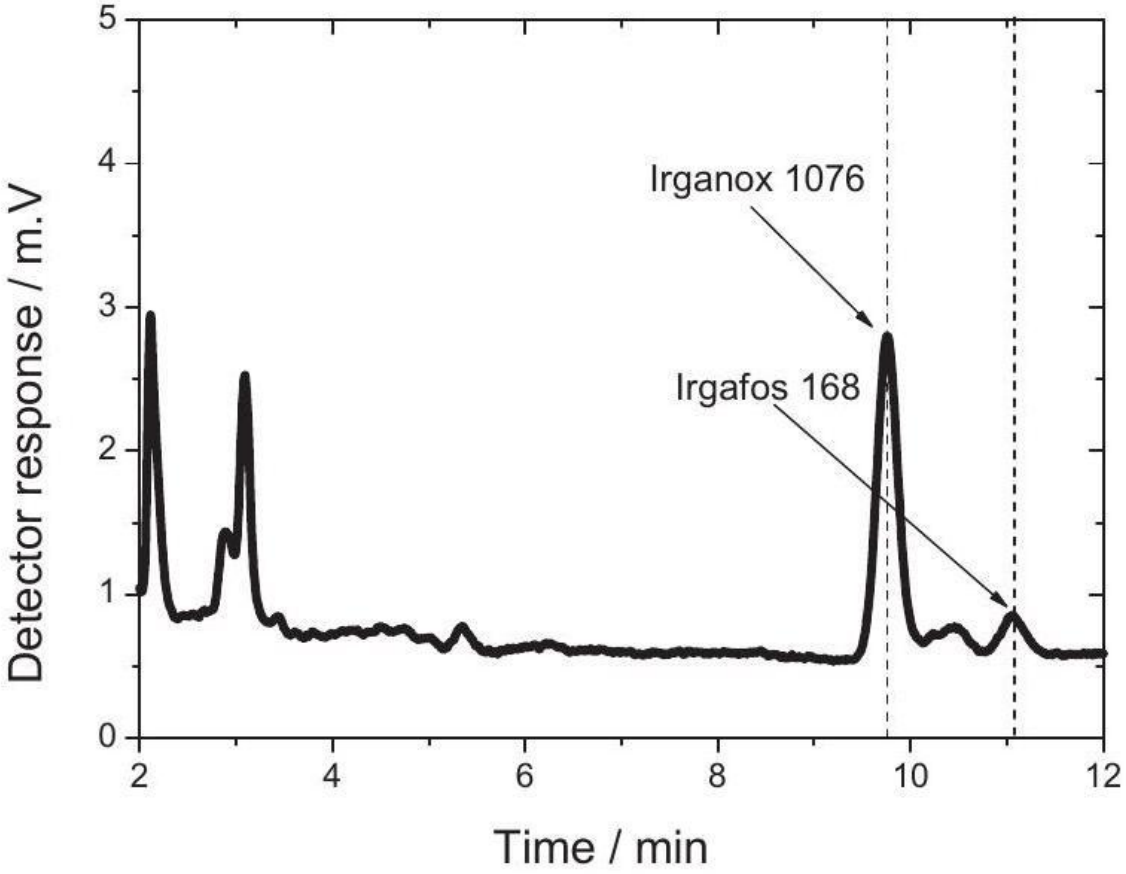

Fig. 5. HPLC chromatograms of Irganox 1076 [8] and Irgafos 168[8]. previous results which showed that a synergistic effect was achieved [19].

Mechanical performance

Since in literature it is often accepted that the loss of 50% of elongation at break is taken as the failure criterion, indicating that the material is not suitable for application [34], the mechanical behavior of unstabilized and stabilized ABS samples as a function of degradation time was characterized and the results are shown in Fig. 9. Unstabilized samples exhibited a loss of more than 50% of ε_b in the first 22 h and 15 days of accelerated and natural weathering, respectively. Similar trends of mechanical properties of ABS exposed to accelerated weathering conditions were reported by other authors. Salari et al. [35] studied the effect of weathering on the flow, microstructure and physicalmechanical properties of ABS, and the results showed a significant decrease of impact strength and elongation at break in the first stages of UV exposure. Kelleher et al. [36] verified that the impact strength of stabilized ABS decreases approximately 70% of its original impact

strength after exposure.

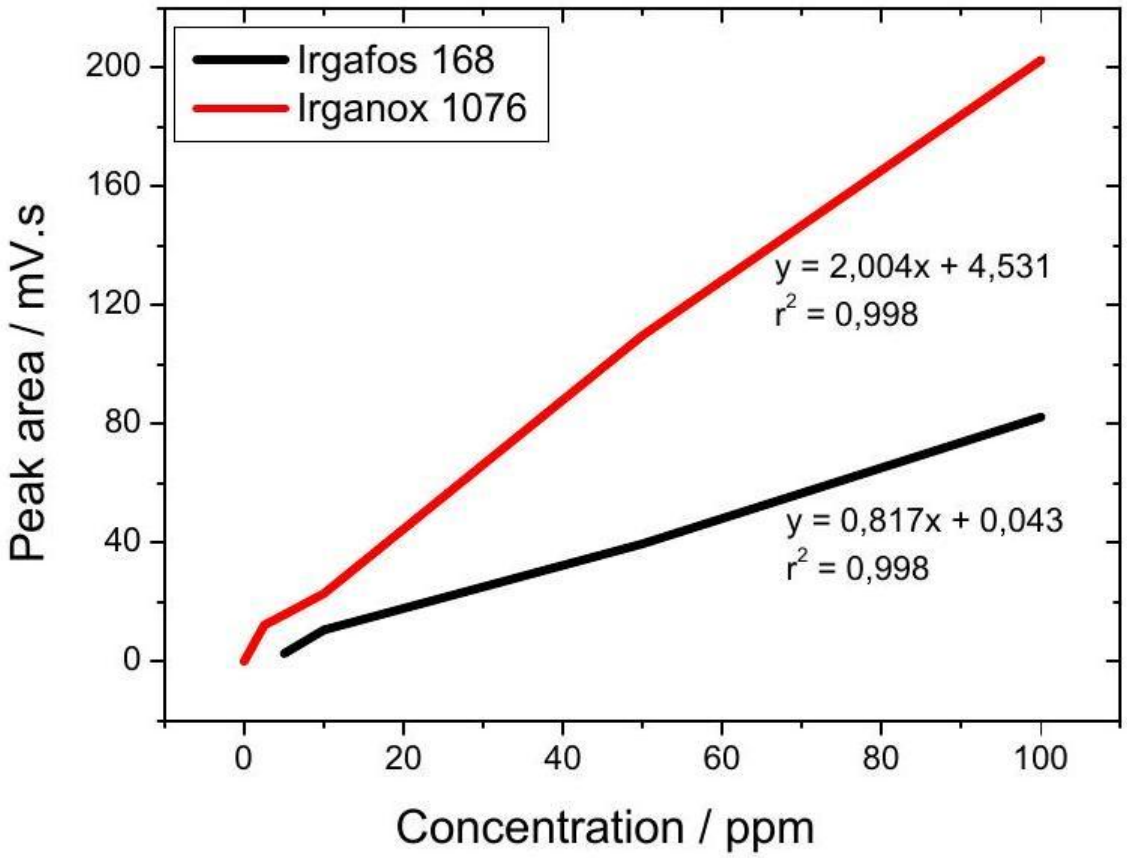

Fig. 6. Calibration curves of Irganox 1076 [8] and Irgafos 168[8].

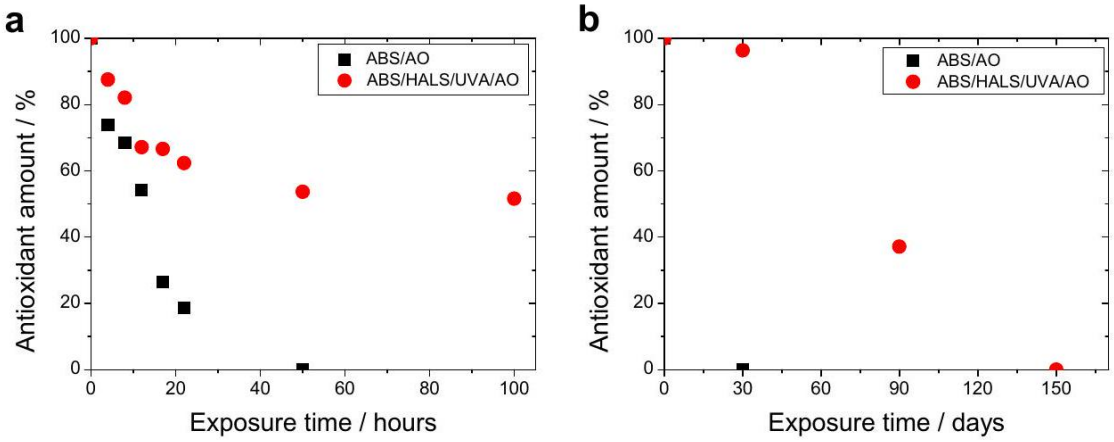

Fig. 7. Evaluation of Irganox 1076 [8] behavior by HPLC in ABS samples containing only AO (ABS/AO) and a combination of HALS, UVA and AO (ABS/HALS/UVA/AO) submitted to accelerated a) and natural b) weathering conditions.

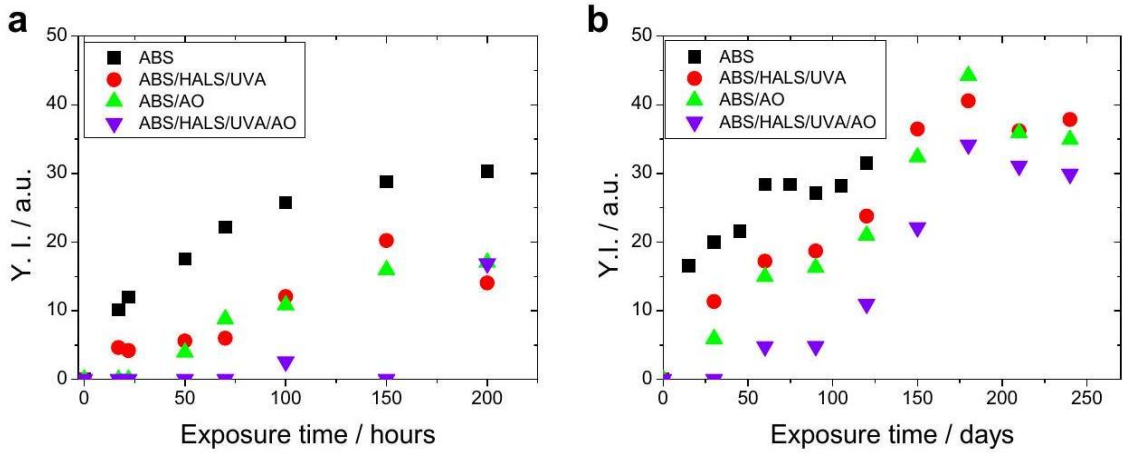

Fig. 8. Yellowness index of unstabilized and stabilized ABS samples submitted to accelerated a) and natural b) weathering conditions.

Comparing the values of stabilized samples submitted to accelerated weathering conditions, the contribution of light stabilizers and antioxidants to minimize the reduction of ABS mechanical properties can easily be detected, as was observed by other authors with other polymers [37]. The efficiency of stabilization systems in protecting ABS against mechanical performance loss under accelerated weathering conditions follows the order: ABS/HALS/UVA/ AO >> ABS/HALS/UVA ≥ ABS/AO.

Concerning samples exposed to natural conditions, the faster consumption of stabilizers in the first 30 days of exposure leads to higher oxidation at the surface and, consequently, to a faster decrease in the elongation at break.

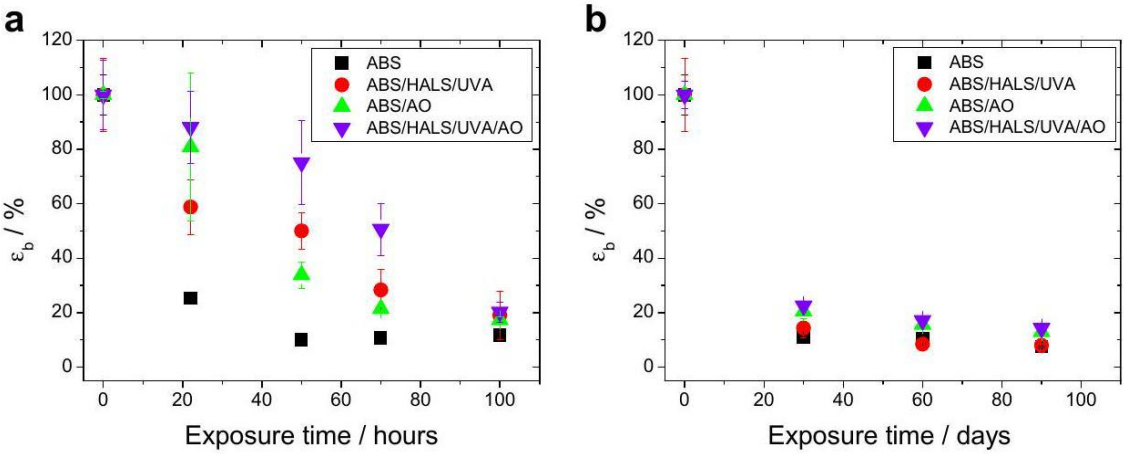

Fig. 9. Elongation at break of unstabilized and stabilized ABS samples during accelerated a) and natural b) weathering conditions.

Conclusions

Several ABS compositions with different stabilizers and antioxidants were prepared by extrusion and submitted to different weathering conditions to evaluate the influence of the testing conditions on the effectiveness of the stabilizers.

It was found that, under accelerated weathering conditions, the behavior of samples containing light stabilizers and antioxidants was very similar. Combinations of light stabilizers (HALS and UVA) with antioxidants (Irganox 1076 (8) and Irgafos 168(8)) showed a synergistic effect to protect ABS against photo-oxidative degradation under accelerated conditions.

The results obtained for ABS samples exposed to natural weathering showed that a combination of light stabilizers and antioxidants induces a decrease of oxidation rate in the initial stage of the degradation process, although the synergetic effect becomes less efficient for longer degradation times. The results of the analysis of stabilizers under natural weathering indicate that there are other atmospheric parameters that play an important role.

Acknowledgments

The authors would like to thank the Portuguese Foundation for the Science and Technology (FCT) and Poliversal - Plásticos e Tecnologia, S.A. for the PhD grant SFRH/BDE/ 15657/2007. A. Pimenta is thankful to FCT for the attribution of grant UMINHO/BII/277/2009.

References

[1] A.P. Kumar, D. Depan, N. Singh Tomer, R.P. Singh, Nanoscale particles for polymer degradation and stabilization-trends and future perspectives, Progress in Polymer Science 34 (2009) 479-515.
[2] H. Zweifel, R.D. Maier, M. Schiller, Plastics Additives Handbook, second ed., Hanser Publications, 2009.
[3] G. Wypych, Handbook of Material Weathering, third ed., ChemTec Publishing, 2003.
[4] Billingham NC. Oxidative degradation of polymers: a tutorial on what we don't know. 233rd ACS National Meeting Chicago, United States 2007.
[5] R.L. Clough, N.C. Billingham, K.T. Gillen, Polymer Durability, American Chemical Society, 1996.
[6] A. Chrisochoou, D. Dufour, Styrenic Copolymers, Rapra Technology, Ltd, 2002.
[7] J.-L. Gardette, B. Mailhot, J. Lemaire, Photooxidation mechanisms of styrenic polymers, Polymer Degradation and Stability 48 (1995) 457-470.
[8] M. Piton, A. Rivaton, Photo-oxidation of ABS at long wavelengths ([lambda] > 300 nm), Polymer Degradation and Stability 55 (1997) 147-157.
[9] R. Ramani, C. Ranganathaiah, Degradation of acrylonitrile-butadiene-styrene and polycarbonate by UV irradiation, Polymer Degradation and Stability 69 (2000) 347-354.
[10] J.G. Bokria, S. Schlick, Spatial effects in the photodegradation of poly(acrylonitrile-butadiene-styrene): a study by ATR-FTIR, Polymer 43 (2002) 3239-3246.
[11] A. Davis, D. Gordon, Rapid assessment of weathering stability from exposure of polymer films. II. The effectiveness of different regions of the solar spectrum in degrading an ABS terpolymer, Journal of Applied Polymer Science 18 (1974) 1173-1179.
[12] P. Davis, B.E. Tiganis, L.S. Burn, The effect of photo-oxidative degradation on fracture in ABS pipe resins, Polymer Degradation and Stability 84 (2004) 233-242.

[13] J.B. Adeniyi, Clarification and discussion of chemical transformations involved in thermal and photo-oxidative degradation of ABS, European Polymer Journal 20 (1984) 291-299.
[14] S.W. Beavan, D. Phillips, Mechanistic studies on the photo-oxidation of commercial poly(butadiene), European Polymer Journal 10 (1974) 593-603.
[15] J. Shimada, K. Kabuki, The mechanism of oxidative degradation of ABS resin. Part I. The mechanism of thermooxidative degradation, Journal of Applied Polymer Science 12 (1968) 655-669.
[16] G. Scott, M. Tahan, Comparison of the photo-oxidative behaviour of some polybutadiene-based polyblends, European Polymer Journal 13 (1977) 981-987.
[17] J.B. Adeniyi, E.G. Kolawole, Thermal and photo-degradation of unstabilized ABS, European Polymer Journal 20 (1984) 43-47.
[18] P. Delprat, J.-L. Gardette, Analysis of photooxidation of polymer materials by photoacoustic Fourier transform infra-red spectroscopy, Polymer 34 (1993) 933-937.
[19] X. Jouan, J.L. Gardette, Photo-oxidation of ABS: Part 2-Origin of the photodiscoloration on irradiation at long wavelengths, Polymer Degradation and Stability 36 (1992) 91-96.
[20] M. Piton, A. Rivaton, Photooxidation of polybutadiene at long wavelengths ([lambda] > 300 nm), Polymer Degradation and Stability 53 (1996) 343-359.
[21] Z. Khalil, S. Michaille, J. Lemaire, Photo-oxydation du polystyrène à grandes longueurs d'onde ($\lambda > 300$ nm) et à 60°C, Die Makromolekulare Chemie 188 (1987) 1743-1756.
[22] G. Li, X. Guo, W. Na, D. Hao, M. Zhang, H. Zhang, et al., Performance and synergistic effect of phenolic and thio antioxidants in ABS graft copolymers, Frontiers of Chemical Science and Engineering 5 (2011) 26-34.
[23] D.P. John Scheirs, Modern Styrenic Polymers: Polystyrenes and Styrenic Copolymers (2003).
[24] T. Kurumada, H. Ohsawa, T. Yamazaki, Synergism of hindered amine light stabilizers and UV-absorbers, Polymer Degradation and Stability 19 (1987) 263-272.
[25] E.G. Kolawole, J.B. Adeniyi, The effect of 3,5-ditert.butyl-4hydroxybenzylthioglycollate and tinuvin P on the thermal, photo and natural degradation of ABS, European Polymer Journal 18 (1982) 469-476.
[26] Materials ASfTa, ASTM D2244-Standard Practice for Calculation of Color Tolerances and Color Differences from Instrumentally Measured Color Coordinates (2009).
[27] H. Jia, H. Wang, W. Chen, The combination effect of hindered amine light stabilizers with UV absorbers on the radiation resistance of polypropylene, Radiation Physics and Chemistry 76 (2007) 1179-1188.
[28] M. Scoponi, S. Cimmino, M. Kaci, Photo-stabilisation mechanism under natural weathering and accelerated photo-oxidative conditions of LDPE films for agricultural applications, Polymer 41 (2000) 7969-7980.
[29] Y. Azuma, H. Takeda, S. Watanabe, H. Nakatani, Outdoor and accelerated weathering tests for polypropylene and polypropylene/ talc composites: a comparative study of their weathering behavior, Polymer Degradation and Stability 94 (2009) 2267-2274.
[30] R. Navarro, L. Audouin, J. Verdu, Reactions of antioxidants with molecular oxygen. Part III: influence of phenolic stabiliser structures on their oxidation in an inert matrix, Polymer Degradation and Stability 96 (2011) 1389-1396.
[31] K. Kikkawa, New developments in polymer photostabilization, Polymer Degradation and Stability 49 (1995) 135-143.
[32] A.J. Chirinos-Padrón, P.H. Hernández, N.S. Allen, C. Vasilion, G.P. Marshall, M. de Poortere, Synergism of antioxidants in high density polyethylene, Polymer Degradation and Stability 19 (1987) 177-189.

[33] I. Bauer, W.D. Habicher, S. Korner, S. Al-Malaika, Antioxidant interaction between organic phosphites and hindered amine light stabilizers: effects during photoxidation of polypropylene-II, Polymer Degradation and Stability 55 (1997) 217-224.
[34] F.A. Bottino, A.R. Cinquegrani, G. Di Pasquale, L. Leonardi, A. Pollicino, Chemical modifications, mechanical properties and surface photo-oxidation of films of polystyrene (PS), Polymer Testing 23 (2004) 405-411.
[35] D. Salari, A. Olad, A. Niaei, H. Ranjbar, The effect of weathering on the flow, microstructure and physico-mechanical properties of ABS, Iranian Polymer Journal 18 (2009) 713-722.
[36] P.G. Kelleher, D.J. Boyle, B.D. Gesner, Environmental stability of ABS plastics, Journal of Applied Polymer Science 11 (1967) 1731-1735.
[37] F.A. Bottino, A.R. Cinquegrani, G. Di Pasquale, L. Leonardi, A. Orestano, A. Pollicino, A study on chemical modifications, mechanical properties and surface photo-oxidation of films of polystyrene (PS) stabilised by hindered amines (HAS), Polymer Testing 23 (2004) 779-789.