Outdoor and accelerated weathering of acrylonitrile-butadienestyrene: A correlation study

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Abstract

The influence of outdoor and accelerated weathering conditions on the photo-oxidative degradation of stabilized acrylonitrile-butadiene-styrene (ABS) was investigated, aiming to establish a correlation between both weathering types.

ABS samples containing combinations of light stabilizers (ultraviolet absorbers - UVA and hindered amine light stabilizers - HALS) and antioxidants were prepared by melt compounding, exposed to different weathering conditions and characterized by infrared spectroscopy and quasi-static measure ments.

The results obtained by infrared spectroscopy and quasi-static measurements are in good agreement, showing that the Q-Sun Xe-3-Hs resembles the outdoor weathering phenomena.

Applying a shift factor of $0.85 MJm^{-2}$ to the abscissa axis, it was found that the exposure of stabilized ABS samples to ca. 1260 h in Q-Sun Xe-3-Hs induces changes in its mechanical performance, which corresponds to one year of outdoor exposure at Lisbon.

Introduction

Over the past decades a lot of effort has been accomplished aiming to understand the photo-oxidative degradation and stabilization mechanisms of different polymeric materials using an appropriate combination of accelerated testing conditions [1-10].

However, a lack of scientific information is found on outdoor exposure, which is an important issue to predict polymer lifetime [11-16]. Problems involved in outdoor weathering experiments are more complex because the intensity of the solar radiation and spectral distribution varies with geographical localization, season and atmospheric pollutants.

Correlations between outdoor and accelerated weathering testing are an interesting but contradictory subject for over a century. While some authors state that it is possible to correlate findings obtained by different weathering conditions [8,17,18], others have an opposite opinion, or indeed impossible at all, for some polymers [19].

Several methodologies have been developed and applied to predict polymer lifetime, although many require extrapolation of

accelerated weathering results to outdoor conditions. One of the most common methods used is based on the following equation [17]:

$$k = \frac{t_{\text{outdoor}}}{t_{\text{accelerated}}} \tag{1}$$

where k is the acceleration factor, t_{outdoor} and $t_{\text{accelerated}}$ are the time to reach a property change under outdoor and accelerated conditions, respectively.

An important contribution to the subject comes from studies developed by Pickett et al. [1-3,20]. Correlations can be determined by the superposition method, plotting outdoor and accelerated data on the same graph and applying a shift factor to the abscissa axis (radiant exposure dosage), which corresponds to the relative rate. The comparison of light sources on yellowing of the polycarbonate samples showed that a perfect superposition of data obtained from Florida and CIRA/soda lime xenon arc was found by applying a shift factor of 2.7MJm^{-2} to the abscissa axis [2].

Gijsman et al. studied the influence of outdoor and accelerated weathering conditions on the degradation rate of bisphenol A polycarbonate [11]. Aiming to establish a correlation between experiments carried out at the Atlas Sanary sur Mer Test Service Site (France) and in a Suntest XXL $^{+}$weathering, a shift factor of 0.67 to the radiant dosage axis was applied for correlating the UV absorbance at 320 nm . A similar degradation rate was found by the following equation [20]:

$$\frac{k_2}{k_1} = \exp\left[\frac{E_{\text{a}}(T_2 - T_1)}{R(T_2 \times T_1)}\right] \tag{2}$$

where k_1 and k_2 are the relative degradation rate, E_{a} is the activation energy in cal mol $^{-1}$, R is the gas constant ($8.314\ \text{J mol}^{-1}\text{k}^{-1}$), T_1 and T_2 are the temperatures, in kelvin. It was established that one year of outdoor exposure (341MJm^{-2}) correspond to 980 h of irradiation in Suntest XXL^{+}(230MJm^{-2}).

Acrylonitrile-butadiene-styrene (ABS) is an impact-modified styrenic polymer used in most of their technological applications with light stabilizers and antioxidants due to its susceptibility to ultraviolet (UV) radiation, in the presence of oxygen or other oxidizing media [21]. It is well known that the susceptibility of ABS to UV radiation is related to the abstraction of the hydrogen atom from the substituted tertiary carbon in the PB phase, which is

75 rpm . The ABS pellets were previously dried in an oven for 1 h at 80°C. Light stabilizers and antioxidants were pre-mixed, in powder form, with ABS pellets in a homemade rotary mixer and, then melt mixed. The extruded tapes, 0.5 mm thick, were cooled in water, dried with static air and cut according to suitable dimensions (100 × 25 mm).

Weathering

Accelerated weathering

Accelerated weathering experiments were performed in a Q-Sun Xe-3-Hs from Q-Panel containing xenon lamps filtered by daylight filters. The total UV irradiance, from 300 to 400 nm , used was 39 W m^{-2} corresponding to an hourly UV dosage of 0.14MJm^{-2}. ABS samples were collected after different exposure times. The relationship between exposure time and accumulated radiant exposure is depicted in Table 2 and was calculated by the following equation:

$$\text{Radiant exposure dosage} = \frac{\text{Exposure time} \times \text{irradiance} \times 3.6 \times 10^3}{1 \times 10^6} (\text{MJm}^{-2})$$

thermodynamically favorable, inducing structural modifications together with yellowing and drastic deterioration of the mechanical performance [22,23].

The prediction of ABS lifetime is very important for an appropriate selection of the material and should take into account both the processing and the expected end-use of the product, in order to reduce the risk of in-service failure. However, a literature overview reveals that there is a lack of published studies, which correlate the ABS lifetime in different weathering conditions.

The present work focuses on the study of the effects of outdoor and accelerated weathering conditions on the photo-oxidative degradation behavior of ABS containing combinations of light stabilizers and antioxidants, aiming to establish a correlation between both types of weathering.

Experimental

Materials and samples preparation

ABS Terluran High-Impact 10® commercially available at the BASF was used as raw material. Light stabilizers and antioxidants were used as received by BASF. The commercial name, code and amount of stabilizers used in preparation of ABS samples for weathering studies are shown in Table 1.

Stabilized ABS tapes were obtained by melt compounding in a single-screw extruder (L/D 30) Luigi Bandera using a temperature profile along the barrel from 170 to 220°C and a screw rotating at

The chamber air and black panel temperatures were 48 and 63°C, respectively and the relative humidity was 50%. The 102:18 cycle was used, which consists of a period of 18 min of rain every 2 h , with no black period.

Outdoor weathering

The outdoor weathering experiments were carried out at Arruda dos Vinhos - Lisbon according to ASTM-Method D1435. ABS samples were placed on a wood support, at an angle of 45° facing south and collected at different radiant exposure dosage for 6 months, from March to August.

According to Koppen-Geiger Climate Classification [24], Lisbon is inserted in Group C - Temperate/Mesothermal climates, sub-group dry-summer subtropical on Mediterranean climates (Csa). Details related to radiant exposure dosage, monthly average values of precipitation and temperature were supplied by a national meteorological and aerologic station in Lisbon/Gago Coutinho (latitude 38°43′N, longitude 09°, 09′W and altitude 77 m) and are displayed in Table 3.

Characterization techniques

Fourier transform infrared spectra were recorded using a Jasco 4100 spectrophotometer with an attenuated total reflectance accessory (ATR) accessory at a resolution of 8 cm^{-1} and an average of 128 scans.
10μ m thick sections were cut across the thickness of the ABS samples using a microtome Leitz, at room temperature. The surface

Table 1
Commercial and chemical name, code and amount of stabilizers used in the stabilized ABS samples.

Commercial name	Chemical name	Code	Amount (w/w)
Tinuvin P®	2-(2'-Hydroxy-5'-methylphenyl)benzotriazole	UVA	0.10
Chimassorb 119 FL ®	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] imino]-3,1-propanediyl]] bis[N′, N′′-dibutyl- N′, N′′-bis (1,2,2,6,6-pentamethyl-4-piperidinyl)	HALS	0.30
Irganox 1076 ®	Octadecyl-3-(3,5-di-tert.butyl-4-hydroxyphenyl)-propionate)	AO_1	0.15
Irgafos 168 ®	Tris(2,4-di-ter-buthylphenyl)phosphite	AO_2	0.15

Table 2
Relationship between exposure time and accumulated radiant exposure.

Exposure time/hours	0	22	50	100	150	200
Accumulated radiant exposure dosage /MJm^{-2}	0.0	3.1	7.0	14.0	21.6	28.1

of stabilized specimens were analyzed by optical transmission microscopy using a Perkin Elmer Spotlight 300 attached to a microscope.

The mechanical properties of ABS samples were assessed by stress-strain experiments using a Miniature Materials Tester (MINIMAT) from Polymer Laboratories with a 200 N load cell. The tests were carried out at room temperature, using a deformation rate of 0.2 mm/min. For each sample submitted to a specific accumulated radiant exposure dosage, six specimens were tested and the sample thickness was measured with a pachymeter Mitutoyo with 0.025 mm of exactitude.

Results and discussion

Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of unexposed and exposed ABS samples containing a combination of light stabilizers and antioxidants are presented in Fig. 1. The absorption bands of the styrene (PS) component can be observed at 1494 and 1600 cm^{-1}, attributed to carbon double bonds from the aromatic group, and the absorption band corresponding to acrylonitrile (AN) at 2239 cm^{-1}. The $C-H$ deformation for hydrogen atoms linked to carbons of the 1,2 and 1,4 butadiene (PB) are shown at 911 cm^{-1} and at 965 cm^{-1}, respectively. As a consequence of the photo-oxidative degradation process new absorption bands appear in the region corresponding to carbonyl ($1600-1800\ cm^{-1}$) and hydroxyl ($3000-3400\ cm^{-1}$) stretching vibrations [12]. A decrease of the absorption bands related to butadienic phase was also observed with the increase of radiant exposure dosage.

The peaks intensity corresponding to carbonyl and butadiene absorptions were evaluated using the baseline method [25]. A baseline was drawn on the base of the selected absorption band and the peak height was calculated connecting two points between the draw baseline and the maximum peak height. Using the data of the spectra of stabilized samples, plot of Fig. 2 was made.

For all tested samples an increase of the carbonyl absorbance as a function of radiant exposure dosage can be observed. Moreover, Fig. 2 also shows that similar oxidation rates were achieved for stabilized ABS samples with combinations of light stabilizers with phenolic antioxidants and trivalent organo phosphorus compound exposed to accelerated and outdoor weathering conditions.

The influence of the weathering conditions on the 1,2 and 1,4 PB component of stabilized ABS samples is depicted in Fig. 3.

The PB amount decreases drastically as the radiant exposure dosage increases, although the decrease of the 1,4 PB(965 cm^{-1}) is higher than the 1,2 PB(911 cm^{-1}), in good agreement with the results previously reported [12]. This behavior is explained by the

Table 3
Parameters average values for outdoor exposure.

Accumulated radiant exposure / MJm^{-2}	Maximum ambient temperature / °C	Minimum ambient temperature / °C	Relative humidity / %	Rain / mm
137.6	23.6	14.6	65.7	3.1

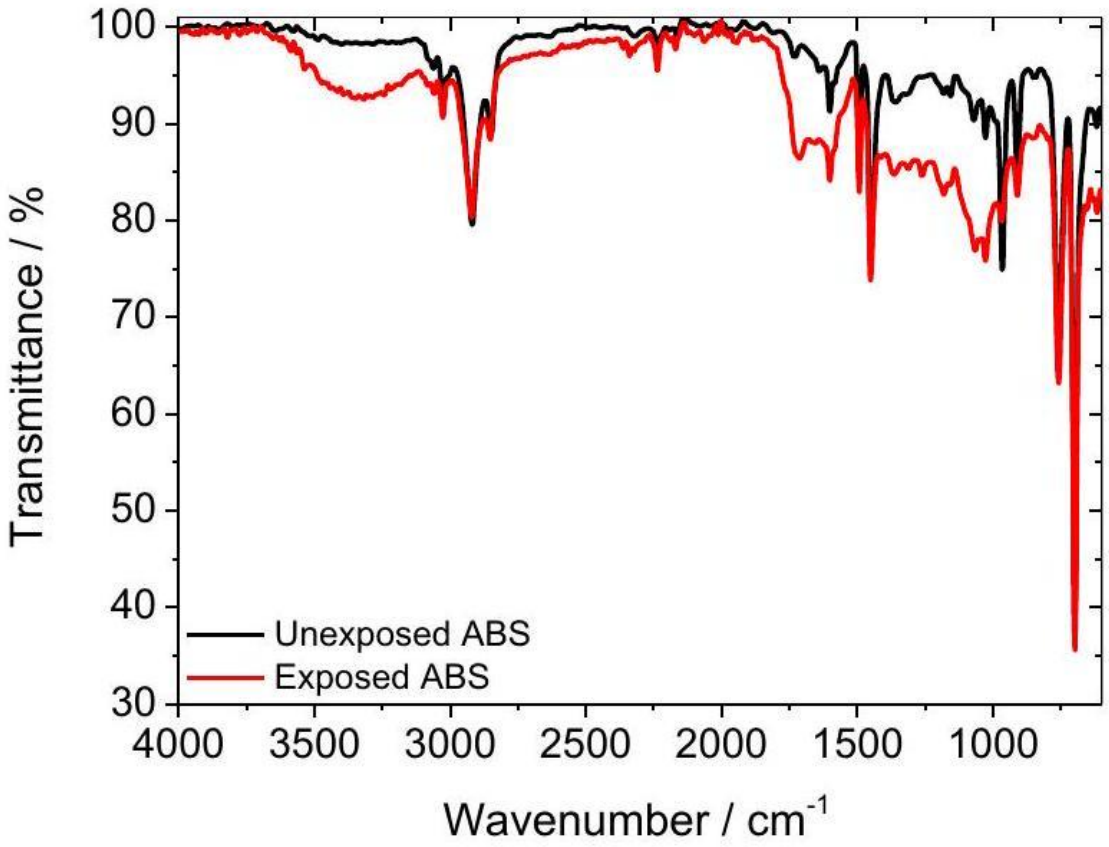

Fig. 1. FTIR spectra of unexposed and exposed ABS samples containing a combination of light stabilizers and antioxidants.

stability of the free radicals formed. While the 1,4 PB photo-oxidative degradation forms a secondary radical, the 1,2 PB give rise a more stable radical (tertiary), which can be further stabilized by resonance.

Moreover, it can be noted that similar oxidation rates were found for stabilized ABS samples submitted to accelerated and outdoor weathering conditions, as it would be expected taking into account the similar carbonyl formation rate.

The results obtained by FTIR showed that the Q-Sun Xe-3-Hs resembles the outdoor weathering phenomena taking into account that the photo-oxidative degradation mechanism of ABS is similar, remaining unchanged even at higher temperatures.

Quasi-static measurements

The influence of accelerated and outdoor weathering conditions on the mechanical performance of stabilized ABS samples was evaluated by stress-strain experiments and the results are shown in Fig. 4.

A similar behavior was found for irradiated samples under different weathering conditions, i.e. a decrease of the elongation at break with an increase of the radiant exposure dosage.

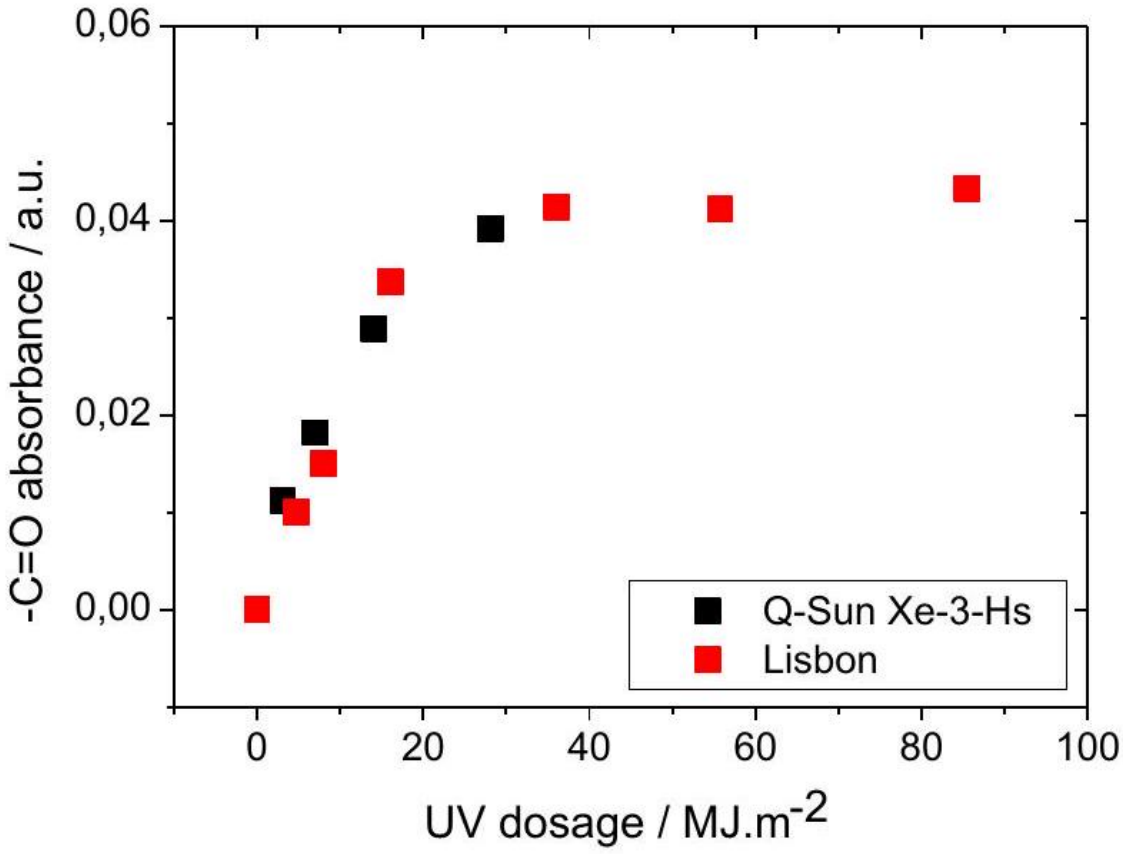

Fig. 2. Carbonyl absorbance of stabilized ABS samples exposed to different weathering conditions.

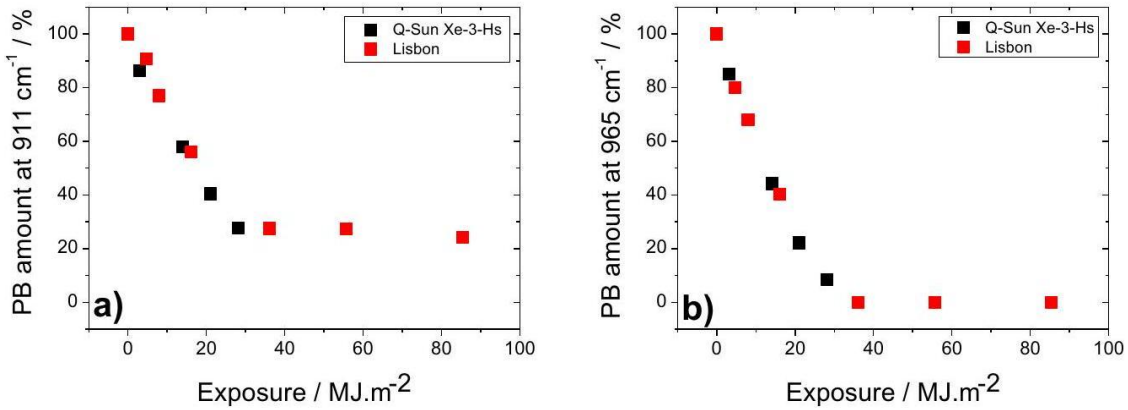

Fig. 3. Influence of different weathering conditions on the PB phase of stabilized ABS samples.

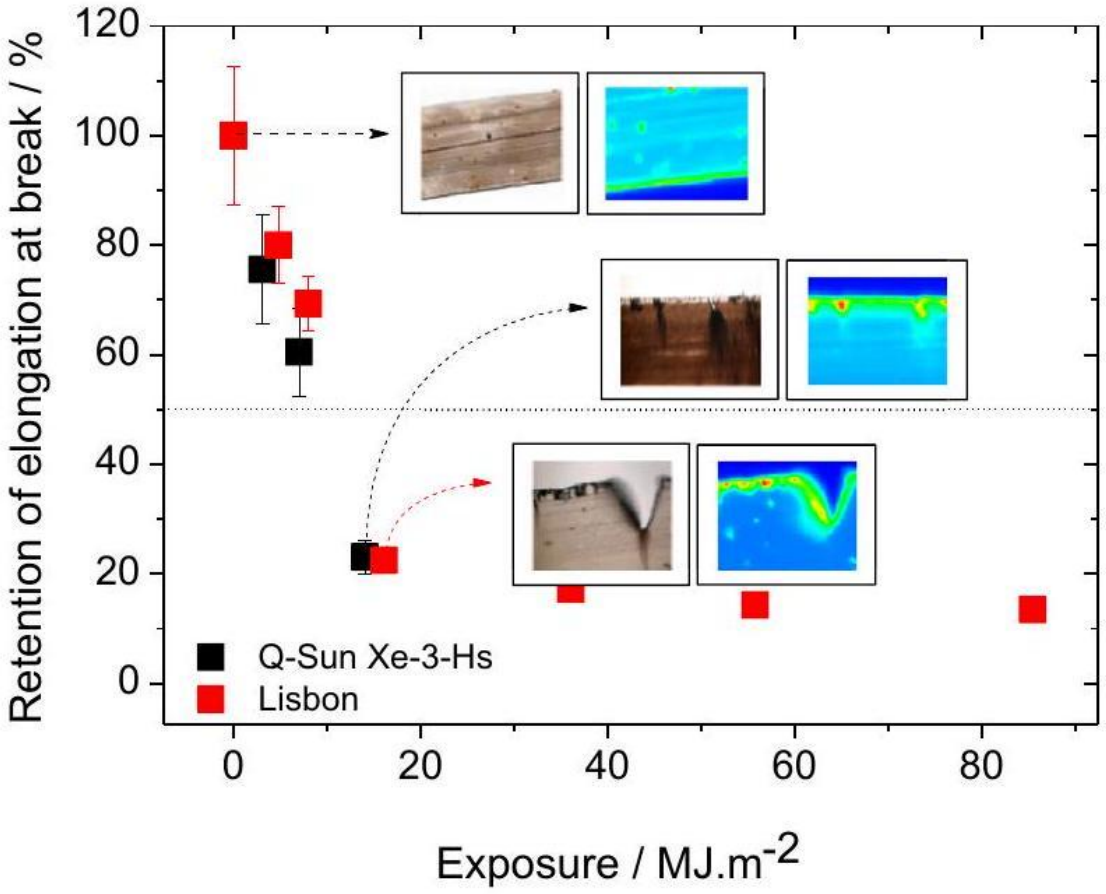

Fig. 4. Retention of elongation at break of stabilized ABS samples exposed to different weathering conditions.

However, in our previous work [12], it was stated that the retention of the elongation at break of 50% occurs approximately at 2MJmm^{-2} for unstabilized, while for stabilized

samples this occurs at $10\mathrm{MJm}^{-2}$, showing the contribution of the stabilization system to minimize the changes in the mechanical performance of ABS .

Micrographs images obtained by optical transmission microscopy were acquired to observe cracks formation at the surface. For similar radiant exposure dosage, it can be seen that stabilized ABS submitted to outdoor conditions ($16\mathrm{MJm}^{-2}$) exhibits deeper cracks and missing parts, while samples exposed to accelerated weathering ($14\mathrm{MJm}^{-2}$) show few pronounced cracks. As predictable, these differences also explain and are responsible for the mechanical failure of the samples.

Fig. 5 shows the correlation between the mechanical performance, measured as a decrease of the elongation at break, and the degradation rate of stabilized ABS samples exposed to different weathering conditions.

The mechanical performance of stabilized ABS samples decreases as the amount of carbonyl increases and butadiene decreases. Although the higher oxidation rate and higher loss of butadiene component at the surface are mainly responsible for the faster decrease in the elongation at break of ABS samples, the results obtained by microscopy show that cracks formation on the surface can also play an important role on mechanical failure of the ABS .

Fig. 6 relates the mechanical performance of stabilized ABS samples, where a shift factor of $0.85\mathrm{MJm}^{-2}$ was applied to the abscissa axis. It was found that the exposure of stabilized ABS for about 1260 h in the accelerated camera Q-Sun Xe-3-Hs corresponds to approximately one year of exposure under outdoor conditions at Lisbon ($207\mathrm{MJm}^{-2}$).

Even though correlations between outdoor and accelerated findings of polymeric materials are not trivial, the results obtained in this study show that Q-Sun Xe-3-Hs successfully resembles outdoor weathering phenomenon.

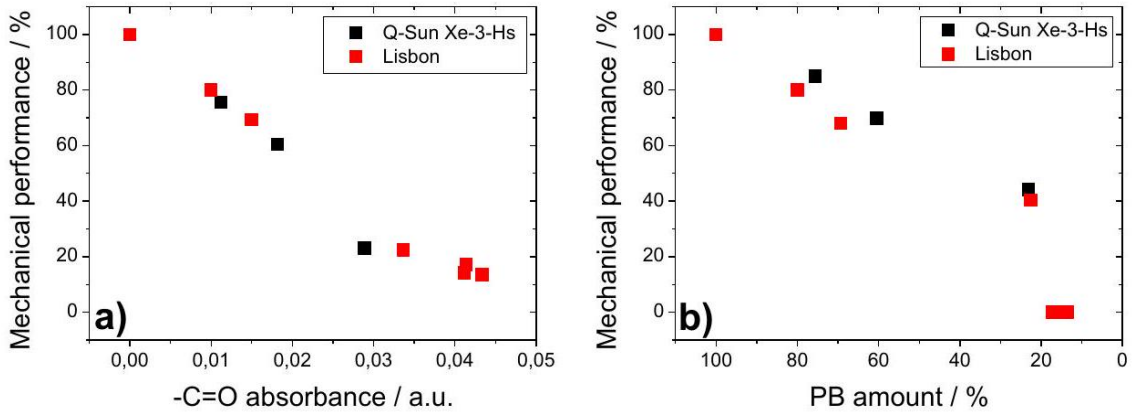

Fig. 5. Mechanical performance vs $-C=O$ absorbance a) and PB amount b) of stabilized ABS samples exposed to different weathering conditions.

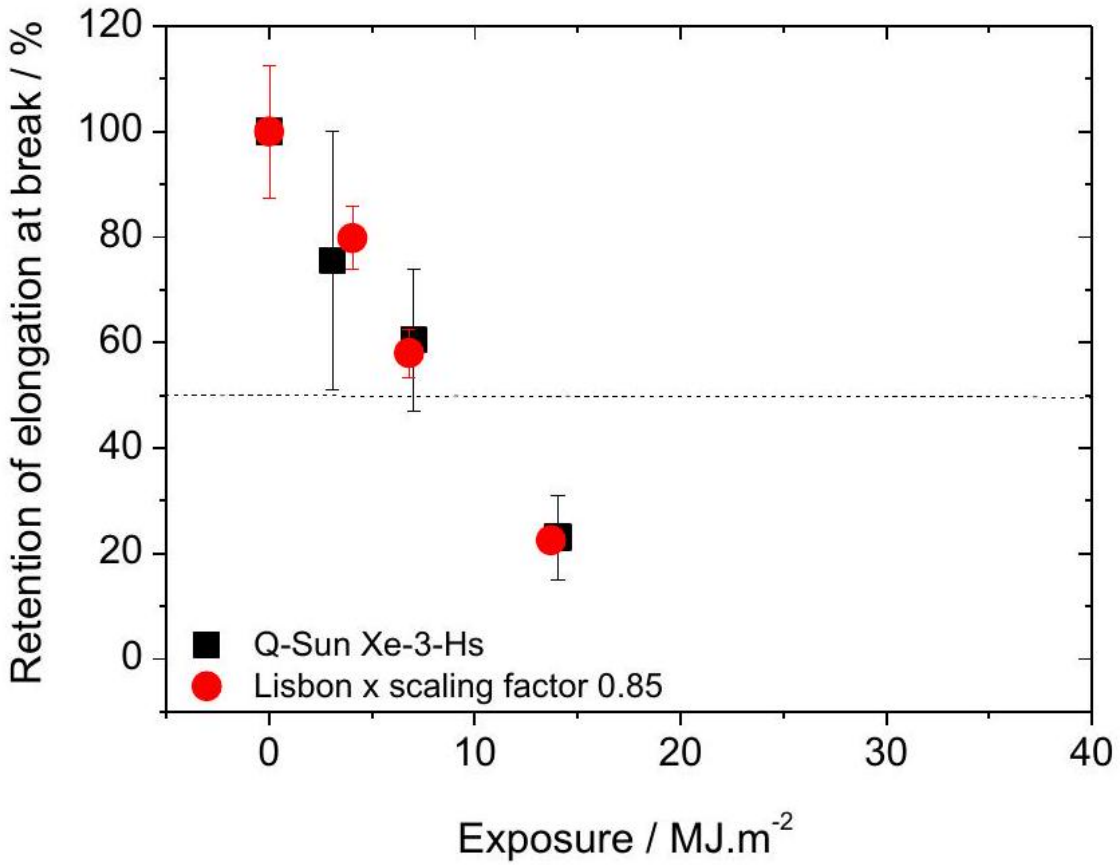

Fig. 6. Retention of elongation at break of stabilized ABS samples exposed to outdoor weathering conditions replotted using a scaling factor of 0.85 to overlay the data of *Q* Sun Xe-3-Hs.

Conclusions

The behavior of stabilized ABS samples with light stabilizers and antioxidants exposed to Q-Sun Xe-3-Hs and outdoor conditions was evaluated aiming to establish a correlation between both weathering conditions and predict copolymer lifetime.

Similar oxidation rates as a function of radiant exposure dosage were found for ABS samples exposed to accelerated and outdoor conditions. These findings are supported by stress-strain experiments, showing that the mechanical properties of ABS are affected by the carbonyl groups formation and degradation of the butadienic component at the surface. Cracks formation and its propagation within the copolymer also play an important role on the mechanical failure of ABS exposed to different weathering conditions.

Aiming to establish a correlation between both weathering types, a shift factor of 0.85 was applied to the radiant exposure dosage axis. For stabilized ABS samples it was found that the exposure of approximately 1260 h of irradiation in Q-Sun Xe-3-Hs induces mechanical modifications correspondent to one year exposure at Lisbon ($207 MJm^{-2}$).

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