Role of Ultraviolet Absorbers (UVA) and Hindered Amine Light Stabilizers (HALS) in ABS Stabilization

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Abstract

The present work evaluates the combination effect of hindered amine light stabilizers (HALS) and ultraviolet absorbers (UVA) on the ultraviolet (UV) stability of acrylonitrile-butadiene-styrene (ABS). Thus, two types of light stabilizers, Tinuvin P and Chimassorb 119 FL, were used to improve the ABS endurance against UV. Stabilized ABS samples were submitted to accelerated weathering in a Xenontest 150 S chamber, according to standard methods, in order to predict copolymer lifetime within a commercially acceptable time period. Infrared spectroscopy with attenuated total reflectance accessory (FTIR-ATR) was used to follow chemical modifications that occur on the material surface as a consequence of degradation process. While non-stabilized ABS samples loose the butadiene component in the first 22 h of exposure, in stabilized samples submitted to same accelerated conditions this component only disappears after 150 h of exposure. Non-stabilized and stabilized ABS samples present a similar yellowing behavior, a gradually increase with exposure time. Nevertheless, as expected, color modifications are less pronounced for stabilized ABS samples. The results obtained suggest that a better performance was achieved for stabilized ABS samples with Tinuvin P and Chimassorb 119 FL, which is very important to extend the copolymer lifetime.

Introduction

Atmospheric conditions such as ultraviolet radiation, oxygen, temperature, moisture, rain and pollutants have an important influence on photodegradation of many polymers, which are responsible for premature loss of material properties, restricting the long-term application of polymeric materials [1].

ABS is an amorphous copolymer with a high importance from a technological point of view due to its outstanding properties, namely attractive mechanical properties, gloss, easy processing, effortless self-coloring, high quality surface finish and low cost for an engineering polymer [2, 3]. This copolymer is broadly used in toys, refrigerators, vacuum cleaners, drilling machines and in vehicle interiors. Nevertheless, for outdoor applications, where good UV resistance is the key issue, this elastomeric copolymer presents a high weathering instability [4].

High mechanical performance of this material is due to the butadienic component, although it is the main responsible for ABS photodegradation. The higher susceptibility of ABS to degradation is related with the labile position of hydrogen on the carbon atom in α-position of the carbon-carbon double bonds that can be easily abstracted [5-8].

Along ABS photodegradation, several reactive species, such as free radicals (R^*, RO^* and ROO^*) and hydroperoxides (ROOH), are formed and is generally admitted that radicals recombination occurs leading to oxygenated compounds formation, which result in a drastic change in chemical structure, color and mechanical properties.

Actually, many additives are used in ABS formulations to protect the chemical structure and extend polymer lifetime [9]. However, ABS photostabilization continues to be a serious problem for plastics manufactures because the production is based in empirical knowledge. A wide range of light stabilizers, mostly hindered amines light stabilizers (HALS) and ultraviolet absorbers (UVA) are available to extend the polymer lifetime and some studies attempt to understand the degradation mechanism and the effectiveness of these additives against photodegradation. The stabilization mechanisms of light stabilizers are well documented in literature. While HALS are known to act as free radical scavengers, the UVA are known to absorb harmful UV radiation and to dissipate it as heat, without damaging the polymer [1]. The role and the performance of HALS as photostabilizers have been extensively investigated for polyolefins, such as polypropylene (PP) and polyethylene (PE) [10-12].

Nevertheless, there are not enough studies concerning ABS stabilization and the capability of light stabilizers to enhance UV stability is still not well understood [3, 13-15].

The purpose of this work is study the combination influences of light stabilizers, Tinuvin P (UVA) and Chimassorb 119FL (HALS), on ABS in order to increase copolymer lifetime. Stabilized ABS samples were submitted to accelerated weathering and removed periodically. Chemical modifications on ABS surface were monitored by FTIR-ATR and optical properties were also evaluated. Obtained results show a better performance for stabilized ABS samples.

Experimental

Raw material, additives and sample preparation. Experiments were performed using ABS Terluran High Impact-10 (BASF) kindly supplied by Colorgal, Cores de Portugal, Lda. The additives used in this work to impart ABS photostability were Tinuvin P and Chimassorb 119 FL from CIBA - Specialty Chemicals.
ABS blends containing 0.2%(w/w) of light stabilizers were obtained by extrusion. Previously, copolymer granules were dried in an oven at 80°C during 1 hour and mixed with the light stabilizers in a rotary mixer. The tapes were extruded in a "Luigi Bandera" single-screw extruder (L/D 30) using a barrel set temperature from 170 to 220°C and a screw speed of 75 rpm (for more details see ref. 4).
Accelerated weathering and characterization techniques. Accelerated weathering experiments of stabilized ABS films were carried out in a Xenontest 150 S . The samples were submitted to UV radiation with a Xenon lamp with an intensity of $60 \mathrm{Wm}^{-2}$, filtered with six IR filter glasses combined with UV window. The samples ($100 \mathrm{~mm} \times 2.5 \mathrm{~mm} \times 0.5 \mathrm{~mm}$) were exposed to different periods of time and during 2 hours ageing cycle (18 min of rain period and remaining time is considered dry period) [16]. The samples were removed periodically to monitor changes in chemical modifications on the surface and optical properties.
A Datacolor $650 TM$ was used to measure total color difference, with a light source of D65 and viewing angle of 10°, in accordance with CieLAB Color System.
Infrared spectra of samples, after and before accelerated weathering, was obtained using a FTIR Perkin Elmer Spectrum Spotlight 300 between 4000 and $650 \mathrm{~cm}^{-1}$, 64 scans with $4 \mathrm{~cm}^{-1}$ resolution. A horizontal attenuated total reflectance accessory was used to obtain ATR spectra. The internal element accountable for the reflectance was a ZnSe crystal at an angle of 45°. The crystal was cleaned with acetone between the measurements. Infrared absorptions were calculated as the difference between the absorption peak maximum and the absorption at baseline, according to the baseline method [17]. For the absorption at $965 \mathrm{~cm}^{-1}$ (C-H stretch of 1.4 butadiene) the baseline was draw between 990 and $935 \mathrm{~cm}^{-1}$ and for the absorption at $911 \mathrm{~cm}^{-1}$ (C-H stretch of 1.2 butadiene) between 935 and $885 \mathrm{~cm}^{-1}$.

Results and discussion

Oxidation of butadiene component is the major process involved in ABS photodegradation leading to properties change, especially drastic loss of deformation capability and yellowing formation.

ABS yellowing during processing and lifetime is an important problem from a technological point of view that can restrict the copolymer applicability. Color modifications during weathering are due to photoproducts formation responsible for light absorption such as α, β unsatured ketones [5]. Figure 1 displays the yellowness index (Y.I.) as a function of exposure time. The results obtained show that a similar trend was found between non-stabilized and stabilized samples, an increase of yellowing along exposure time.

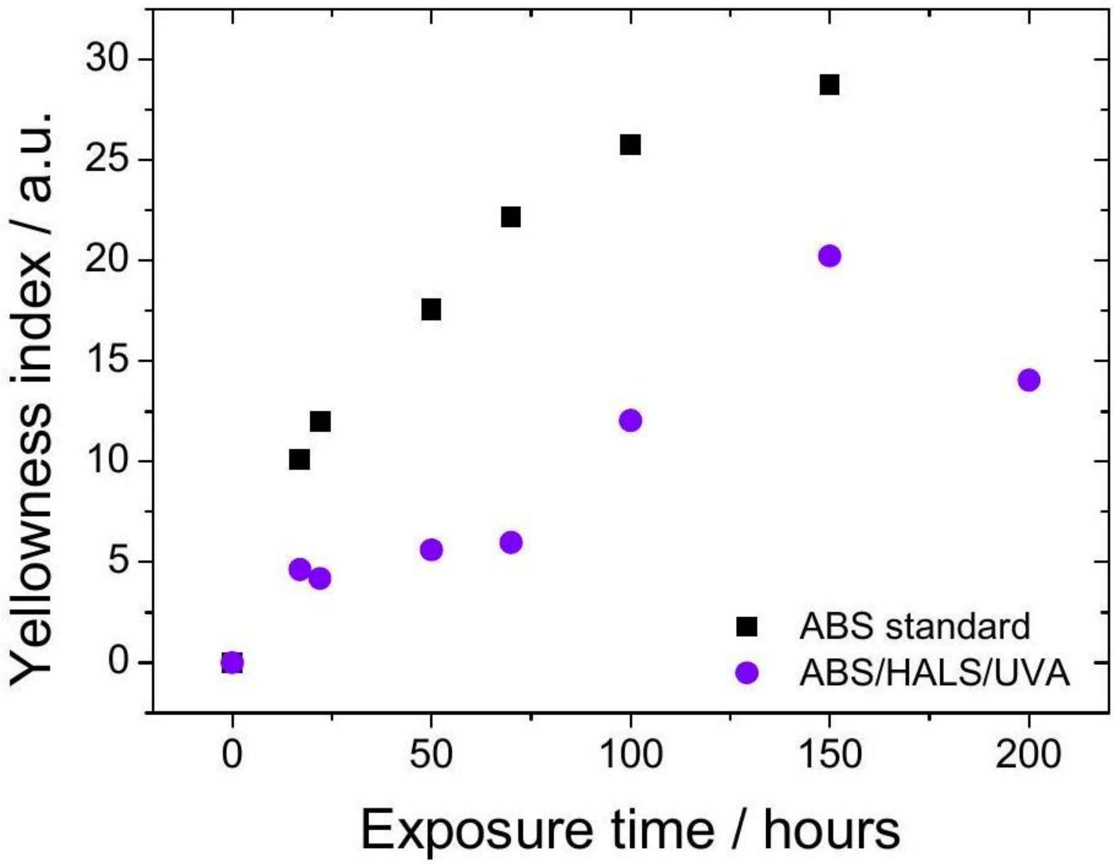


Fig. 1. Evolution of yellowness index for non-stabilized and stabilized samples submitted to accelerated weathering during 200 h .

Concerning to non-stabilized ABS samples, it is possible to observe a continuous yellowness index increase during exposure time achieving a maximum at approximately 30 of Y.I.

Stabilized ABS samples present 3 steps: the first characterized by a slight increase of yellowing during the first 70 h of exposure (roughly 6 of Y.I.) and the second present a gradual increase until 150 h of exposure reaching a maximum at 20 of Y.I. Finally, a small decrease of Y.I. was observed and, later, tends to stabilize around 15. The results indicate that stabilized samples are less susceptible to weathering and, consequently, color modifications are fewer pronounced.

The chemical modifications, which occur preferentially on the surface, are very important and have a considerable influence on mechanical, rheological, thermal and optical properties [4].

Infrared spectra of non-degraded samples show absorption bands characteristic of homopolymers: acrylonitrile ($2239 \mathrm{~cm}^{-1}$), butadiene (1.4 PB at $965 \mathrm{~cm}^{-1}$ and 1.2 PB at $911 \mathrm{~cm}^{-1}$) and styrene (1400 and 1600 cm^{-1}) [4].

Tinuvin P and Chimassorb 119 FL are amines characterized by presenting absorption bands in similar wavenumber region. The bands corresponding to aromatic and aliphatic C-H stretch are seen at $3200-3000 \mathrm{~cm}^{-1}$ and $3000-2800 \mathrm{~cm}^{-1}$, respectively. The 3454 and 1599 cm^{-1} bands are attributed to the N-H stretch and C=N, correspondingly. The hydroxyl group stretch present in the chemical structure of Tinuvin P is a broad band in the range of $3400 - 3200$ cm^{-1}. Although the absorption bands of light stabilizers are very intense in a pure compound, they are unperceivable in the ABS spectra because the amount added into the polymeric matrix is very small (0.2%(w/w)), as it can be seen in Figure 2. The general aspect of the spectra is quite similar: neither modes are totally suppressed nor new vibrational modes seem to appear due to the small incorporation of the light stabilizers.

The absorption of carbon-hydrogen deformation corresponding to PB was used as indicator of degradation degree. Figure 3 a) present the ATR-FTIR spectra, in butadiene region, of ABS samples submitted to accelerated weathering.

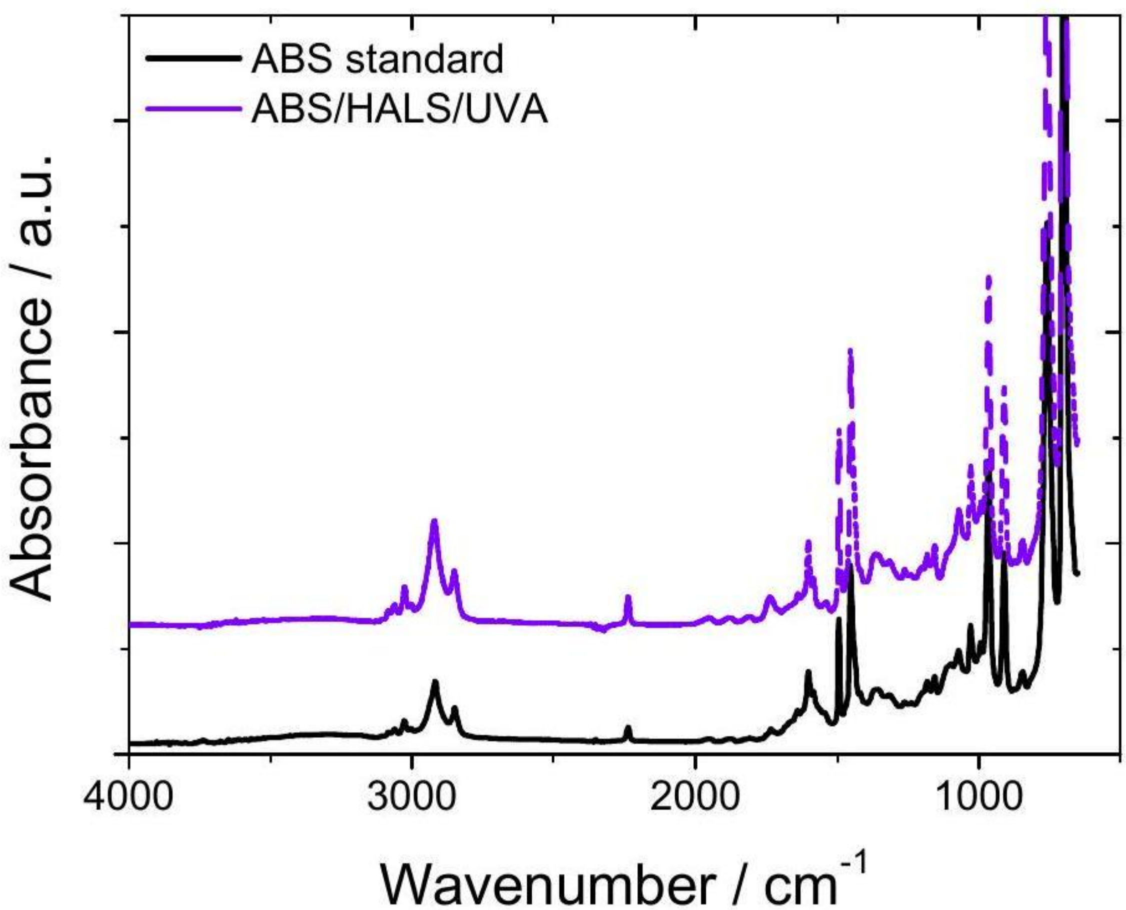
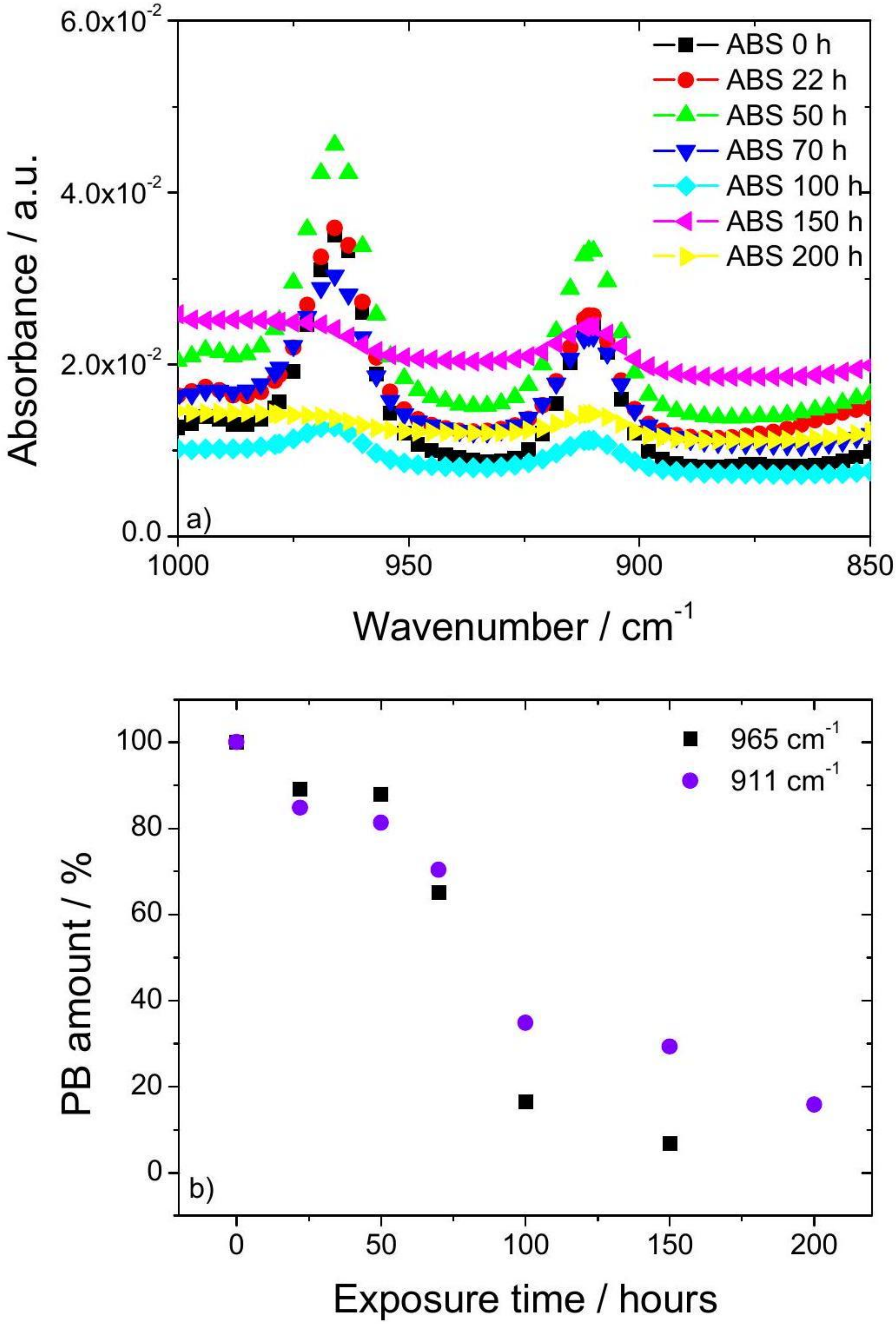


Fig. 2. ATR-FTIR spectra of non-degraded ABS samples (non-stabilized and stabilized).



6.0x10-2
4.0x10-2
2.0x10-2
0.0
1000
950
900
850
Absorbance / a.u.
Wavenumber / cm-1
ABS 0 h
ABS 22 h
ABS 50 h
ABS 70 h
ABS 100 h
ABS 150 h
ABS 200 h
a)
100
80
60
40
20
0
0
50
100
150
200
PB amount / %
Exposure time / hours
965 cm-1
911 cm-1
b)

Fig. 3. ATR-FTIR spectra in the butadiene region a) and influence of exposure time in butadiene component b) of stabilized ABS samples submitted to accelerated weathering during 200 h .

For non-stabilized ABS samples, a drastic absorbance decrease of 1.2 PB and 1.4 PB components was observed; the two peaks disappear after 22 h of exposure. For stabilized samples submitted to the same accelerated conditions the loss of 1.2 PB only occurs after 200 h and the 1.4 PB disappears after 150 h of accelerated exposure. Thus, the capability of light stabilizers to reduce the degradation rate is clearly seen.

Using data presented in Figure 3 a) and applying the baseline method, the plot of Figure 3 b) was constructed. Concerning to stabilized ABS samples, the peaks of 911 (1.2 PB) and $966\ \mathrm{cm}^{-1}$(1.4 PB) present a similar behavior, a moderate absorbance decrease along degradation time.

In Figure 3 b) a major decrease of $965\ \mathrm{cm}^{-1}$ peak is observed in accordance of previously results obtained in a comparative study of artificial and natural weathering of ABS [4].

As a consequence of the photo-oxidative degradation process new absorption bands appears in carbonyl (1700-1800 cm-1) and hydroxyl ($3100-3600\ \mathrm{cm}^{-1}$) region. Chemical changes in hydroxyl and hydrocarbon ($3000-2800\ \mathrm{cm}^{-1}$) region are reported in Figure 4.

Concerning hydroxyl groups formation, non-stabilized and stabilized samples exhibit a different behavior. While non-stabilized samples present a high absorption increase in hydroxyl region during exposure time, stabilized samples show a new broad absorption band with maximum at 3390 cm^{-1}. The evolution of hydroxyl groups during photo-oxidative degradation process present two stages: the first characterized by a fast formation of hydroxyl groups till 22 h of exposure and the second branded by a decrease of these oxygenated compounds until 100 h . This behavior can be explained by the photostabilizing effect of light stabilizers. Tinuvin P is a UVA with a benzotriazole structure capable to absorb UV radiation and to dissipate it as heat, via a mechanism known as ketoenol tautomerism [11]. Chimassorb 119 FL is a high molecular weight HALS recognized by presenting a fundamental stabilizing effect, which is associated with the nitroxile radical formation, during degradation, is capable of scavenging radicals through a reaction cyclic mechanism, called Denison cycle, where regeneration of nitroxile occurs [11,17].

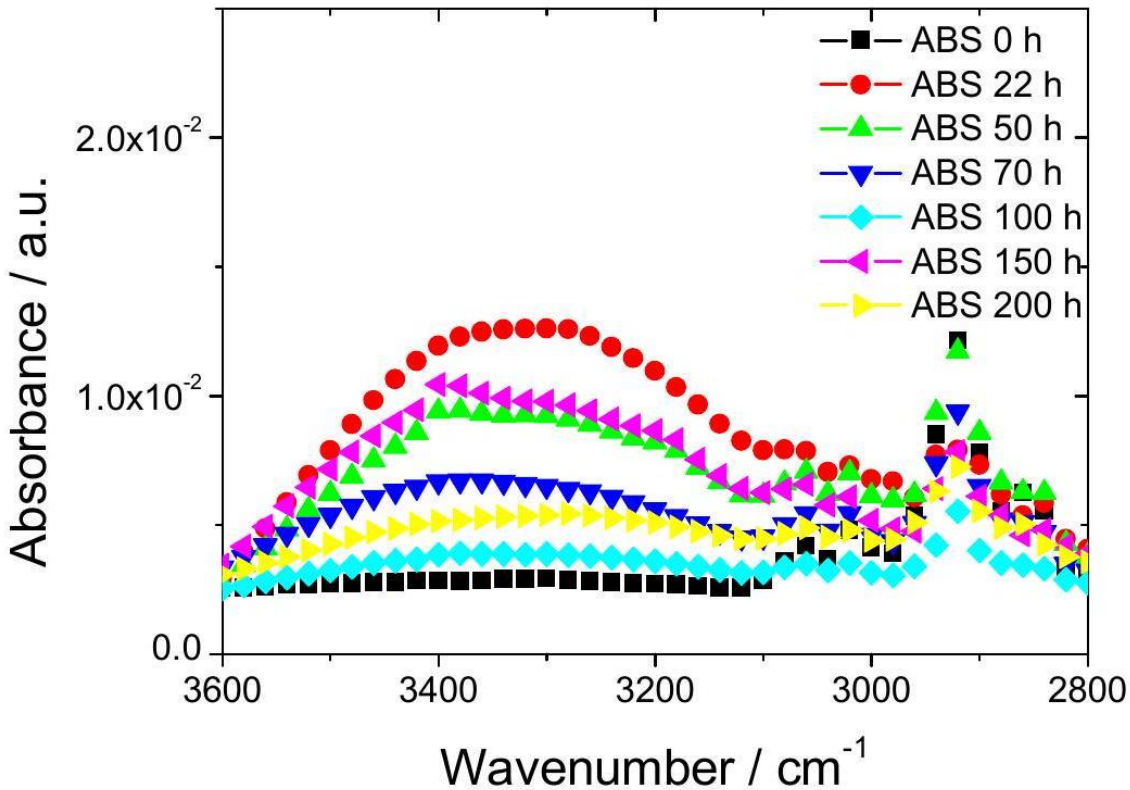


Fig. 4 ATR-FTIR spectra in the hydroxyl and hydrocarbon region of stabilized ABS samples submitted to accelerated weathering during 200 h .

Chemical changes in carbonyl ($1800 - 1500\ \text{cm}^{-1}$) region are reported in Figure 5. In nonstabilized ABS samples, the carbonyl absorbance with maxima at $1646\ \text{cm}^{-1}$ rapidly increased in the first hours of exposure. These groups result from α, β-unsatured hydroperoxides that can originate (by homolysis) different species, namely oxygenated compounds, such as, saturated carboxylic acids, aliphatic esters, α, β-unsatured aldehydes, satured ketones and γ-lactones [6].

Figure 5 shows that an increase of absorption bands, with maxima at 1738 and $1645\ \text{cm}^{-1}$, were observed for long exposure time. The increase of carbonyl absorbance is lower than for nonstabilized samples due to the stabilizing effect of HALS (light stabilizers).

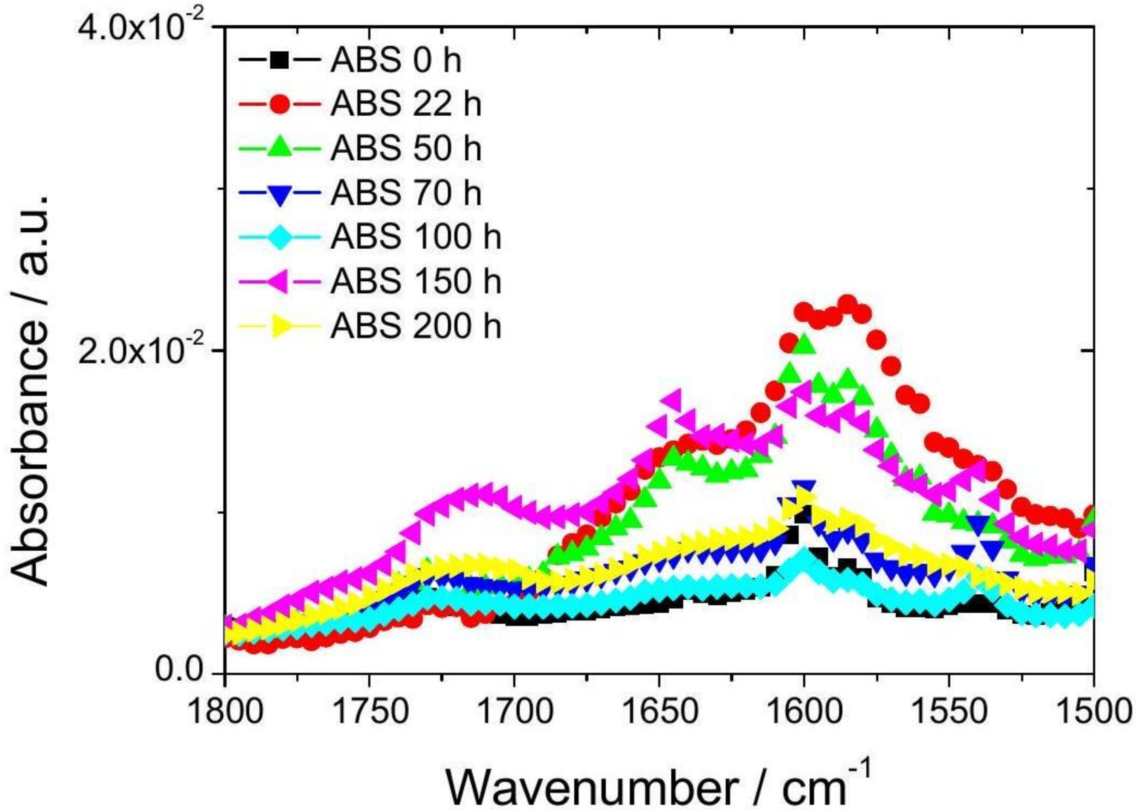


Fig. 5. ATR-FTIR spectra in the carbonyl region of stabilized ABS samples submitted to accelerated weathering during 200 h .

Conclusions

The purpose of this work was to study the capability of light stabilizers combination to protect ABS chemical structure and, consequently, to enhance the UV stability of this copolymer.

Oxidation of the butadiene component is the main process involved in ABS degradation. As expected, modifications in chemical structure of ABS are more abridged for stabilized ABS samples. While non-stabilized ABS samples loose the PB after 22 h of exposure, stabilized ABS samples loose the 1,4 PB after 150 h and 1,2 PB behind 200 h of exposure time.

The results indicate that the surface oxidation affects considerable the optical properties of ABS leading to an increase of yellowing. However, stabilized ABS samples with Chimassorb 119 FL and Tinuvin P are less susceptible to accelerated weathering and color modifications are fewer pronounced. This behavior is probably due to a reduced amount of photoproducts capable to absorb UV radiation.

The obtained results indicate that a better performance was achieved for stabilized ABS samples.

Acknowledgements

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