Comparative Investigation of the Ultraviolet Stabilization of Polycarbonate/Poly(acrylonitrile–butadiene–styrene) with Different Ultraviolet Absorbers

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Received 2 June 2010; accepted 1 December 2010
DOI 10.1002/app.33878

ABSTRACT: When polycarbonate (PC)/poly(acrylonitrile–butadiene–styrene) (ABS) blends are exposed to outdoor conditions, they are mainly degraded by sunlight; this is known as *photodegradation*. It is the ultraviolet radiation in the sunlight that is responsible for the degradation of the blend. To stabilize the blend against the harmful ultraviolet radiation, ultraviolet absorbers (UVAs) are used. In this study, three different UVAs—Tinuvin 1577 (a hydroxyphenyl triazine type), Cyasorb 5411 (a benzotriazole type), and Uvinul 3030 (a cyanoacrylate type)—were compounded with a PC/ABS blend at 240°C with a twin-screw extruder. Accelerated aging of the compounded sample was done by an Atlas Suntest containing xenon lamp. The degradation studies were performed with ultraviolet–visible spectroscopy, attenuated total reflectance/Fourier transform infrared spectroscopy, and yellowing index measurements. The molecular weight of the compounded sample was determined by gel permeation chromatography. It was found that hydroxyphenyl triazine type UVA showed the best results for decreasing the degradation products, oxidation rate, and yellowing of the PC/ABS blend. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 3988–3995, 2012

Key words: compounding; infrared spectroscopy; UV-vis spectroscopy

INTRODUCTION

Because of its good physical and mechanical properties, polycarbonate (PC)/poly(acrylonitrile–butadiene–styrene) (ABS) blends are used in many fields of applications. However, one of the main disadvantages of these blends when they are used in outdoor applications is that they degrade with sunlight, humidity, and oxygen.[1] To increase the lifetime of PC blends, the undesired photodegradation reactions, photo-Fries rearrangement and photooxidation, need to be overcome.

The chemistry of the degradation process in PCs has been studied extensively over the past few decades[2–7] and has been ascribed to two different mechanisms: photo-Fries rearrangement and photooxidation. The relative importance of these mechanisms depends on the irradiation wavelengths used. Lemaire[5,6] illustrated that the photo-Fries rearrangement reaction is more likely to occur when light with wavelengths shorter than 300 nm is used, whereas photooxidation reactions are more important when wavelengths are longer than 340 nm. The major part of the natural sunlight spectrum contains wavelengths longer than 300 nm; therefore, photooxidation reactions are given preference in this article over photo-Fries rearrangement reactions. The polybutadiene component has been shown to be the prime reason for the fast degradation of the ABS phase.[8,9] It has been suggested that the photooxidation of ABS leads to a crosslinking of the rubber component and then to the destruction of the elastomeric properties of the rubber phase. This crosslinking is postulated to result from the reaction of alkoxy macroradicals with polybutadiene units.[10]

The protection of polymers against photodegradation is achieved with ultraviolet absorbers (UVAs). An effective UVA should strongly absorb the UV light, which is harmful to the polymers, and dissipate this energy as heat. Another requirement for a UVA, especially when colorless and transparent polymers are used, is that it should be a colorless compound and should not scatter light. UVAs are photostable because their excited states can dissipate the absorbed energy as heat by a rapid internal hydrogen transfer.[1,11] When photons are absorbed by the UVA, it is promoted to the first excited state. UVAs with an intramolecular hydrogen bridge can undergo an excited-state intramolecular proton transfer. The excited proton transferred product

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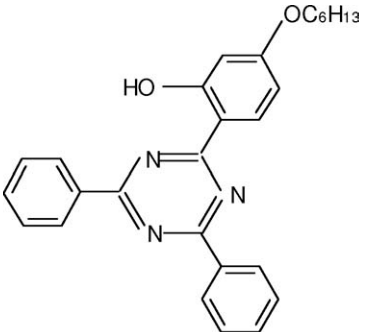
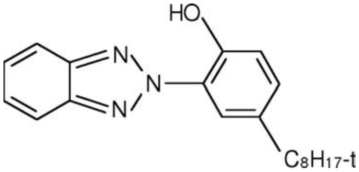
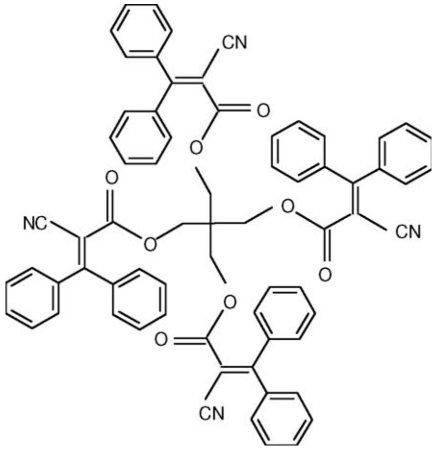
Journal of Applied Polymer Science, Vol. 124, 3988–3995 (2012)

TABLE I
Schematic Overview of the Stabilizers and Their Structures and Suppliers

Name	Supplier	Chemical structure
Tinuvin 1577 (425.53 g/mol)	Ciba (Basel, Switzerland)	
Cyasorb 5411 (323 g/mol)	Cytec (Brussels, Belgium)	
Uvinul 3030 (1060 g/mol)	BASF (Ludwigshafen, Germany)	

loses its energy by heat, fluorescence, or phosphorescence to form the ground-state proton-transferred product followed by a proton shift, which leads to the UVA in the ground state.[12,13]

There are different groups of UVAs.[1] The most important types that are commercially used are hydroxybenzophenones, hydroxyphenyl benotriazoles, cyanoacrylates, oxanilides, and more recently, commercialized hydroxylphenyl triazines. The UV absorption of these materials depends, besides on their type, on their chemical substitution.[14]

The objective of this study was to investigate the efficiency of three different UVAs—Tinuvin 1577 (a hydroxyphenyl triazine type), Cyasorb 5411 (a benzotriazole type), and Uvinul 3030 (a cyanoacrylate type)—in a PC/ABS polymeric blend. These were compounded in a twin-screw extruder at 240°C. The accelerated aging of the compounded samples was done by an Atlas Suntest containing xenon lamp. The degradation studies were performed with ultraviolet–visible (UV–vis) spectroscopy, attenuated total reflectance (ATR)/Fourier transform infrared (FTIR) spectroscopy, and yellowing index measurement. The molecular weight of the compounded sample was determined by gel permeation chromatography (GPC). Individual degradation studies of PC and ABS have been done by many researchers, and the mechanism of their degradation pattern is postulated, but here, the main aim was to study the efficiency of chemically different UVAs on the PC/ABS blend as a whole system and not the individual degradation mechanism of the polymer.

EXPERIMENTAL

Materials

The polymer used in the investigation was PC (Calibre 300-10, Dow Benelux, Terneazen, The Netherlands), and we also used ABS (Magnum F641, Dow Benelux, Terneazen, The Netherlands). A schematic overview of the stabilizers used is shown in Table I. The concentration of stabilizer used varied from 0 to 1 wt %. PC and ABS were blended at a weight ratio of 65/35.

Compounding experiments

A production-size corotating twin-screw extruder (ZSK-32 MEGA Compounder, Coperion Werner and Pfleiderer GmbH, Stuttgart, Germany) with 32-mm screws was equipped with gravimetric feeding units (DDW-MDI, Brabender, Duisburg, Germany). The barrel temperature was set to 240°C. A screw speed of 600 rpm and a throughput of 25 kg/h were chosen. A standard screw configuration was used for the compounding.

The film extrusion line (Chill roll type 136-350S, Dr. Collin GmbH, Ebersberg, Germany) had a roll face width of 350 mm preceding a slit die with a width of 250 mm and a lip that was adjustable between 0.3 and 2 mm. The roller conveyor following the chill roll had a length of 3300 mm and could be adjusted to throughput velocities between 0.5 and 5 m/min. The PC/ABS film extrusion was done at a velocity of 5 m/min, and the thickness of the film was 0.35 mm.

Testing procedure

The molar mass of unaged PC in the PC/ABS blend was determined by size exclusion chromatography/GPC in tetrahydrofuran with toluene as an internal flow marker. The GPC setup consisted of a Waters 515 isocratic high-performance liquid chromatography pump, a TSP AS 100 autosampler, a Waters UV 486 detector operated at 254 nm, and a Waters 410 differential refractometer (Milford, Massachusetts). Three SDV columns (Polymer Standard Service GmbH, Mainz, Germany) with nominal pore sizes of 10^6, 10^5, and 10^4 Å (30×0.8 cm^2 each) were used. Calibration was performed with narrowly distributed polystyrene standards. Data acquisition and processing was performed with WinGPC 6.2 (Polymer Standard Service).

The film samples were aged in an Atlas Suntest XLS+ (Chicago, Illinois) containing xenon lamps with daylight filters. The black standard temperature was set at 65°C. The irradiance level was 765 W/m^2 at a band width of 300–800 nm. The samples were aged for 672 h under dry conditions.

Yellowing index measurement of the PC/ABS films was done with a Hunterlab Colorquest colorimeter (Reston, Virginia). In samples, color can be measured in reflection and in transmission mode. However, in this case, as the samples were transparent, transmission mode was ere used for the assessment of color. As color data, the yellowness index YI D1925-70 was recorded.

UV–vis spectra were taken on a PerkinElmer Lambda 40 spectrometer (Waltham, Massachusetts) from a wavelength of 1000 to 300 nm. The lower wavelength (<390 nm) for the UV–vis measurement was restricted by the large scattering occurring from the ABS phase. Infrared (IR) spectra were recorded with a Thermo Scientific Nicolet 8700 spectrometer (Waltham, Massachusetts) in an ATR mode at 100 scans and a resolution of 4 cm^{-1}.

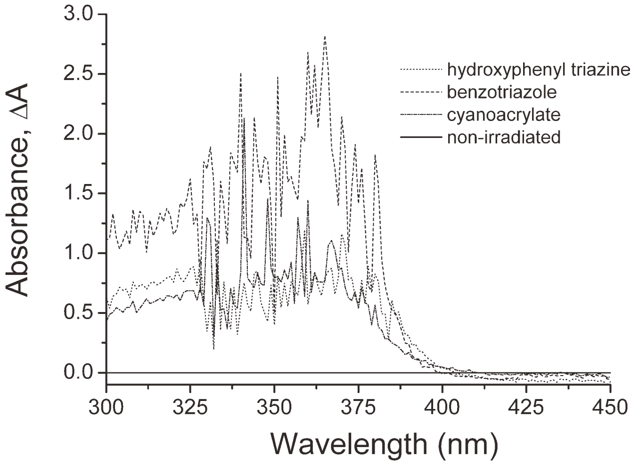


Figure 1 UV absorption spectra of the nonirradiated and stabilized PC/ABS films with different UVAs (ΔA = absorption spectrum of the irradiated sample − absorption spectrum of the corresponding nonirradiated sample).

RESULTS AND DISCUSSION

UV–vis spectroscopy analysis

The absorption of UV–vis radiation by polymers leads to transitions among the electronic energy levels, and an electronic absorption spectrum results. In Figure 1, the spectra of the nonirradiated samples of the unstabilized and stabilized PC/ABS films are depicted. The concentration of stabilizers used was 1 wt %. The spectrum of the unstabilized sample was taken as the reference spectrum for this graph. The absorption curves of the stabilizers show that the requirements for UVAs were met: there was a strong absorption in the UV range between 325 and 400 nm and a large reduction in absorption in the visible range, above 400 nm. Comparing the absorption spectra, we observed that benzotriazole had a higher absorption at wavelengths below 400 nm than the other two UVAs. Because the molecular weight of benzotriazole was the lowest of the three stabilizers used and all the three absorbers were compounded into the PC/ABS blend in weight percentage, benzotriazole had a relatively larger number of functional groups present than the other two stabilizers. This was attributed to the higher absorption level achieved by this UVA compared to the other two UVAs.

In Figure 2, the UV–vis absorption spectra of the PC/ABS blend compounded with hydroxyphenyl triazine at different concentrations are plotted against the wavelength. These samples were

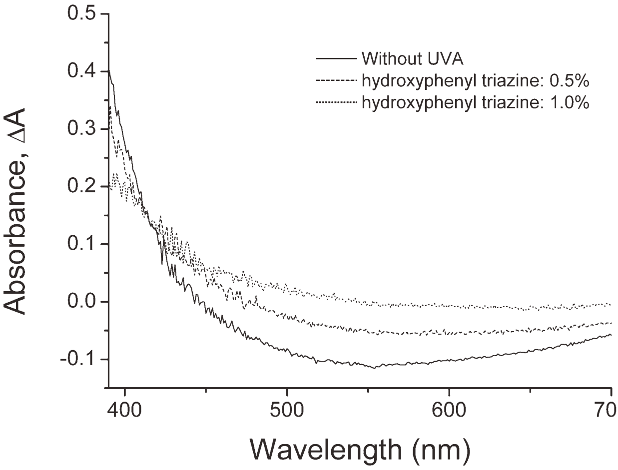


Figure 2 UV absorption spectra of the irradiated samples as a function of the concentration of hydroxyphenyl triazine at 600 rpm (ΔA = absorption spectrum of the irradiated sample-absorption spectrum of the corresponding nonirradiated sample).

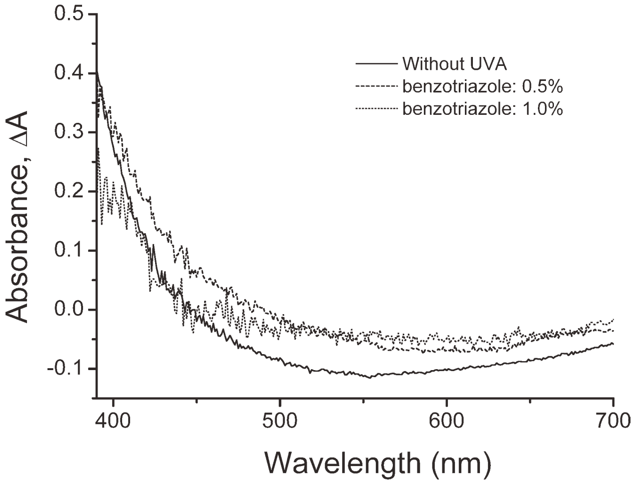


Figure 3 UV absorption spectra of the irradiated samples as a function of the concentration of benzotriazole at 600 rpm (ΔA = absorption spectrum of the irradiated sample-absorption spectrum of the corresponding nonirradiated sample)

irradiated in the Atlas Suntest XLS+ apparatus for 672 h. Throughout the article, the UV–vis curves are plotted as difference spectra, which were obtained by subtraction of the irradiated spectra of the blend extruded with additives at different conditions from the spectrum of the corresponding nonirradiated blend. It was observed that with increasing amount of UVA, the absorbance at shorter wavelength, at 390 nm, decreased linearly. The decrease in absorbance with increasing amount of UVA showed that they were effective in shielding the PC/ABS sample against the harmful UV light because the degradation products due to photodegradation absorbed mainly in the short wavelength. The decreasing absorbance in the short wavelength region corresponded to a decrease in the yellowing of the film. In Figure 2, it is shown that at longer wavelengths, above 450 nm, the absorbance increased with increasing concentration of UVAs. This was due to the increasing amount of UVA that was incorporated into the blend, which caused an increase in the absorption level at high wavelengths.

The UV–vis absorption spectra of the irradiated PC/ABS blends compounded with benzotriazole at different concentrations are plotted against the wavelength in Figure 3. At a lower concentration of benzotriazole, 0.5 wt %, there was no decrease in the absorbance level, whereas at 1.0 wt %, the absorbance decreased sharply; this shows that benzotriazole was effective at higher loadings, whereas at lower loading levels, it was not as effective as hydroxyphenyl triazine.

The UV–vis absorption spectra of the irradiated PC/ABS blends compounded with cyanoacrylate at different concentrations are plotted against the wavelength in Figure 4. It was found that at a lower concentration of cyanoacrylate, 0.5 wt %, the absorbance decreased sharply, but when the concentration was increased to 1.0 wt %, no further decrease in the absorbance was observed. This shows that cyanoacrylate was effective even at low concentration levels, whereas an increase in the concentration did not increase the shielding efficiency.

Figures 2–4 show that the curves had negative absorbance values between 450 and 700 nm. This was attributed to the bleaching or degradation of the polymer after the light irradiation.

IR spectroscopy analysis

FTIR spectroscopy is an important tool for investigating polymer degradation because of its ability to

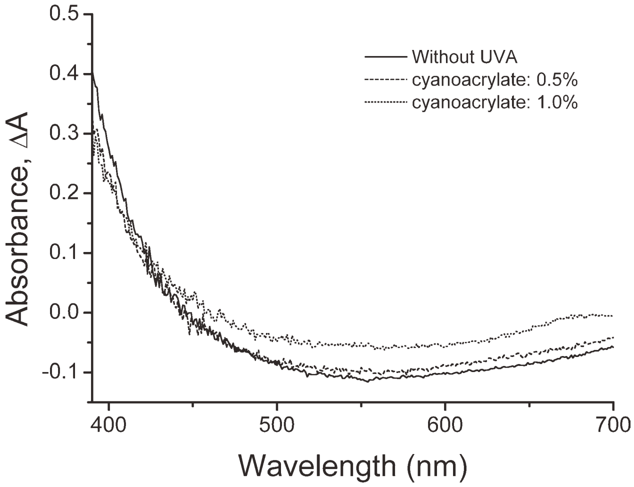


Figure 4 UV absorption spectra of the irradiated samples as a function of the concentration of cyanoacrylate at 600 rpm (ΔA = absorption spectrum of the irradiated sample-absorption spectrum of the corresponding nonirradiated sample).

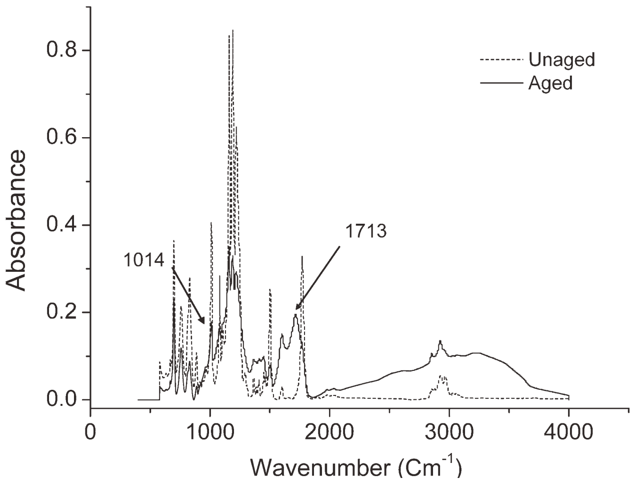


Figure 5 IR absorption spectra of the unaged and aged PC/ABS films without any stabilizers.

detect stable degradation products. The degradation of PC and ABS is a surface phenomenon, which extends about 25 μm into the exposed surface;[15,16] therefore, the PC/ABS films were analyzed with FTIR spectroscopy in ATR mode. This technique is used to investigate the influence of UVAs on the photooxidation rate at the surface of the PC/ABS film. Degradation produces oxygen-containing groups, such as esters, hydroxyls, acids, and carbonyls. Chemical processes can be followed by observation of the appearance of new peaks in the hydroxyl (3600–3200 cm^{-1}) and carbonyl regions (1800–1600 cm^{-1}).

The degradation of the ABS phase mainly gives peaks in the carbonyl and hydroxyl region, whereas PC gives peaks in the carbonyl region. It was previously reported that the absorption band at 1713 cm^{-1} is due to aliphatic acids, which are typical oxidation products for PC/ABS blends.[17] In this study, the peak at 1713 cm^{-1} was used as a measure of the

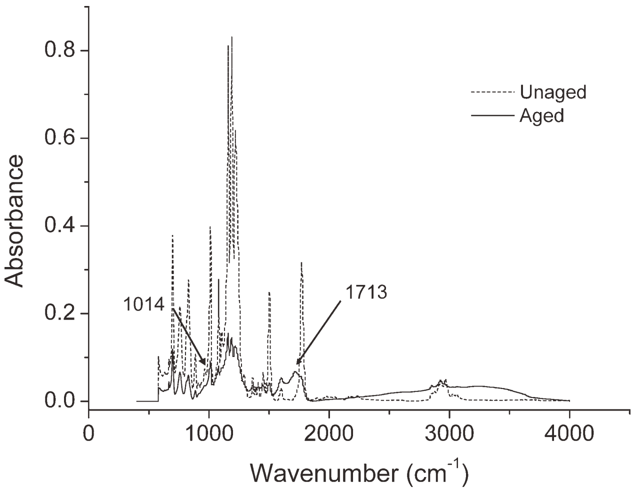


Figure 6 IR absorption spectra of the unaged and aged PC/ABS films containing hydroxyphenyl triazine.

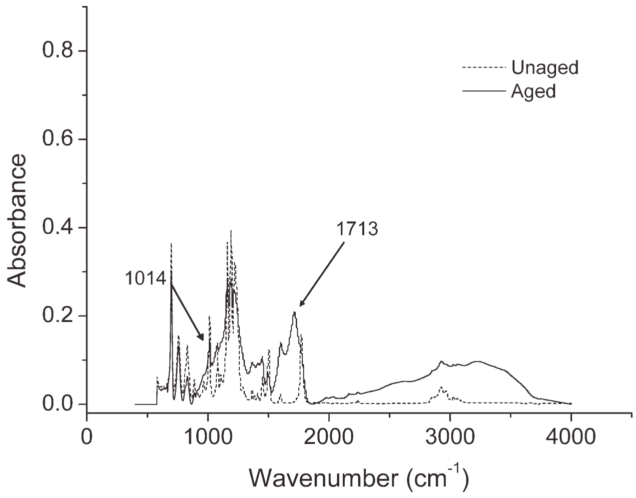


Figure 7 IR absorption spectra of the unaged and aged PC/ABS films containing benzotriazole.

photooxidation rate.[17–19] When the spectra are normalized with the peak located at 1014 cm^{-1}, the absorption as a function of the concentration of UVAs can be quantified. The other important peaks seen in the spectra are described next. The PC showed following peaks: 2970 cm^{-1}, methyl asymmetric C—H stretching; 1772 cm^{-1}, C═O stretching; 1505 cm^{-1}, ring C—C stretching; 1080 cm^{-1}, C—C—C deformation; 1015 cm^{-1}, symmetric O—C—O stretching; and 831 cm^{-1}, out of plane C—H deformation. The IR spectra of ABS showed distinctive —CH_2— rocking modes of two different polybutadiene structures, that is, one at 966 cm^{-1}, which was due to the trans-1,4 structure, and another at 913 cm^{-1}, which was attributed to the 1,2 structure. Bands also formed in the 3500–2500-cm^{-1} region and were due to the formation of hydroxyl, acid and per acid species.

In Figures 5–8, the IR spectra of the unaged and aged samples of PC/ABS blends that were unstabilized and

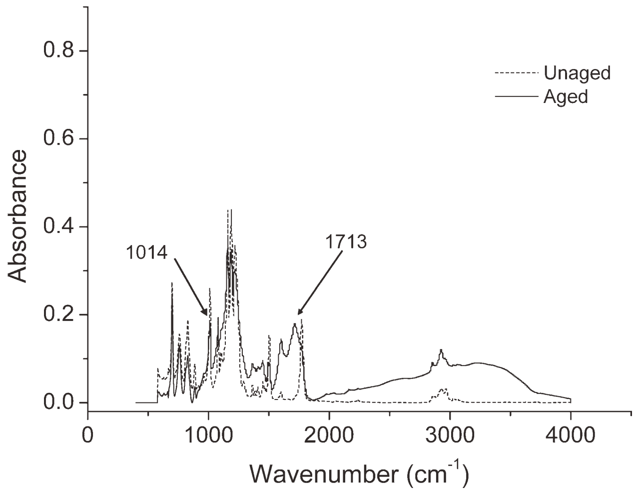


Figure 8 IR absorption spectra of the unaged and aged PC/ABS films containing cyanoacrylate.

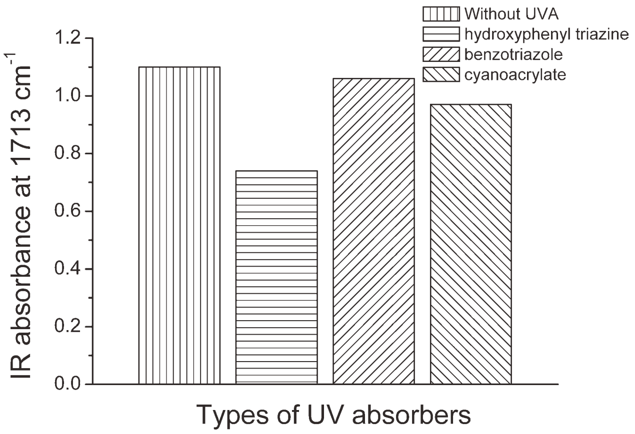


Figure 9 IR absorbance of the irradiated PC/ABS samples at 1713 cm^{-1} as a function of the different types of UVAs.

stabilized with hydroxyphenyl triazine, benzotriazole, and cyanoacrylate, respectively, are shown. It was seen that with aging, new absorption peaks were formed at different wavelengths. There was no absorption band at 1713 cm^{-1} (carbonyl) or at 3450 cm^{-1} (hydroxyl) for the unaged sample, whereas increased absorbance at the same wave numbers was observed for the aged PC/ABS films. The hydroxyl peak appeared as a broad signal with maximum at ≈3450 cm^{-1}, typical of OH stretching. The tail of this band extended beyond 3000 cm^{-1}; this suggested the presence of OH groups from carboxylic acids. Because both phases, PC and ABS, degraded to give carboxylic acids as the final product, the peaks obtained in the carbonyl and hydroxyl regions were taken as a cumulative peaks obtained from these two polymers. Because the study of the photodegradation of PC/ABS blends with different UVAs and the efficiency of different UVA were considered as a single system for this research, it was not necessary to separate the degradation products obtained from each phase. Therefore, these bands could be used as a measure of the oxidation of the stabilized PC/ABS films.

From Figures 5–8, a comparative study of the hydroxyl region of the PC/ABS blends, which was obtained directly from the FTIR spectra with different UVAs, was made. The study showed that the absorbance was minimum when hydroxyphenyl triazine was used as a UVA. For all of the other UVAs, the absorbance obtained was comparable to that of the unstabilized PC/ABS film.

The absolute values of IR absorbance at 1713 cm^{-1} for the unstabilized and stabilized samples aged for 672 h in the Suntest XLS+ apparatus are shown in Figure 9. The peak at 1713 cm^{-1} was normalized with the peak located at 1014 cm^{-1}. In this study, the peak at 1713 cm^{-1} was used as a measure of the photooxidation rate. The concentration of UVA in all cases was 1 wt %. The maximum IR absorbance at 1713 cm^{-1} was observed for the unstabilized sample. When the PC/ABS films were stabilized with UVAs, a reduced oxidation rate was observed. Hydroxyphenyl triazine showed the best result for the stabilization against surface oxidation for the PC/ABS sample with the lowest peak value. Benzotriazole had the lowest stabilization, whereas cyanoacrylate had a stabilization efficiency between those of the other two UVAs.

Yellowing index measurement

To compare the effect of the added stabilizers in the PC/ABS films, the yellowing index was measured. The yellowing index is a number calculated from spectrophotometric data that describes the changes in color of a test sample from white toward yellow. The test is most commonly used to evaluate color changes in a material caused by a real or simulated outdoor exposure that causes photodegradation. In Figure 10, the delta yellowing indices are shown for the irradiated unstabilized and stabilized PC/ABS samples. The concentration of UVAs used was 1 wt %. The yellowing index is plotted as the delta yellowing index, which was obtained by subtraction of the yellowing index of the unirradiated PC/ABS from that of the respective irradiated samples. From this figure, it can be observed that the PC/ABS films stabilized with UVAs showed less yellowing than the unstabilized samples. Similar to the spectroscopic results, hydroxyphenyl triazine showed the lowest yellowing index after an irradiation of 672 h in the Suntest XLS+ apparatus. This was followed by cyanoacrylate, whereas benzotriazole had the highest discoloration among the UVAs used.

Molecular weight determination

The molecular weights of the unaged PC/ABS samples compounded with hydroxyphenyl triazine,

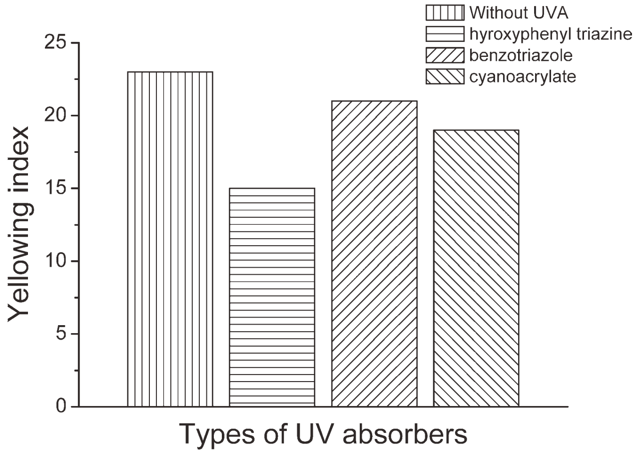


Figure 10 Yellowing index of the irradiated PC/ABS samples as a function of the different types of UVAs.

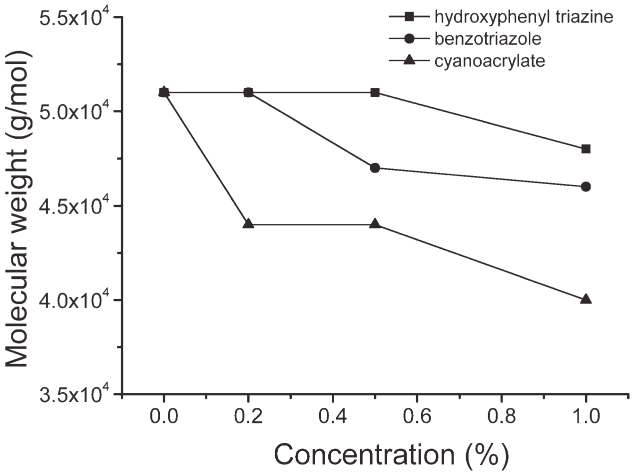


Figure 11 Molecular weights of the unaged samples as a function of the concentration of UVAs.

benzotriazole, and cyanoacrylate were measured at different concentrations and are depicted in Figure 11. From the figure, it is clear that hydroxyphenyl triazine accounted for the lowest decrease in the molecular weight with increasing concentration, whereas cyanoacrylate showed the largest decrease. The decrease in the molecular weight of the PC/ABS with benzotriazole was intermediate between those with the other two UVAs. With hydroxyphenyl triazine, the decrease in molecular weight was observed after a concentration level of 0.5 wt %, whereas with benzotriazole, it was found after 0.2 wt %, and for cyanoacrylate, a substantial decrease was observed when a small amount, 0.2 wt %, was added. The decrease in the molecular weight of PC with cyanoacrylate accounted for a value of 20%, whereas with benzotriazole, it was 10%, and for hydroxyphenyl triazine, a marginal decrease of only 6% was observed. Apart from the stabilization obtained from the UVAs, molecular weight reduction is another parameter that is to be monitored along with the other measurements. As the mechanical properties are a function of the molecular weight, UVAs with a good stabilization effect should also have no deterioration effect on the molecular weight. Even though cyanoacrylate had a relatively good stabilization effect against UV light, it also attacked the polymer backbone during compounding. Therefore, it could be stated that the hydroxyphenyl triazine type UVA had the best results in terms of molecular weight reduction during compounding of the polymer and was followed by the benzotriazole and cyanoacrylate type UVAs, respectively.

From the literature,[14] it is seen that the important step in the UV protection by a UVA is the excited-state intramolecular proton transfer followed by radiationless deactivation processes. The structural element that is responsible for the electronic deactivation is the internal hydrogen bond. Therefore, a prerequisite for an efficient UVA is its intact intramolecular hydrogen bonds, and this depends on the chemical structure of the molecule.[12,13] From X-ray crystal studies,[20] it was found that the geometry of the hydrogen-bond bridge in hydroxyphenyl triazine is more stable than in the other UVAs used in this research. A more stable intramolecular hydrogen bond is less likely to be broken, and therefore, hydroxyphenyl triazine acted as a better UVA than benzotriazole and cyanoacrylate.[21]

CONCLUSIONS

PC/ABS blends were compounded with three different UVAs to study the shielding efficiency of these absorbers against photodegradation. The UVAs used were hydroxyphenyl triazine, benzotriazole, and cyanoacrylate. Accelerated aging of compounded PC/ABS samples were done in an Atlas suntest apparatus for 672 h. After aging, the degradation was studied with spectroscopic and chromatographic techniques. UV–vis and ATR–FTIR spectroscopic studies showed that hydroxyphenyl triazine was able to protect the blend against the harmful UV light better than benzotriazole and cyanoacrylate. The blend surface studies done with ATR–FTIR showed that photooxidation was minimal with hydroxyphenyl triazine. The results from the spectroscopic studies were confirmed by the yellow index measurement. The same order of efficiency for UVAs obtained with the spectroscopic studies was found with the yellow index values. The molecular weight of the PC phase of the blend was measured with GPC. It was found that cyanoacrylate-based UVA caused the maximum reduction in molecular weight for the PC phase, whereas hydroxyphenyl triazine caused a marginal reduction.

This study is part of the research program of the Dutch Polymer Institute (project 613). The authors thank Jan Torfs (Dow, Benelux) for his valuable discussion.

References

1. Zweifel, H. Stabilization of Polymeric Materials; Springer-Verlag: Berlin, 1998.
2. Hrdlovic, P. Polym News 2004, 29, 187.
3. Pankasem, S.; Kuczynski, J.; Thomas, J. K. Macromolecules 1994, 27, 3773.
4. Rivaton, A. Polym Degrad Stab 1995, 49, 163.
5. Rivaton, A.; Sallet, D.; Lemaire, J. Polym Photochem 1983, 3, 463.
6. Lemaire, J.; Gardette, J. L.; Rivaton, A.; Roger, A. Polym Degrad Stab 1986, 15, 1.
7. Torikai, A.; Mitsuoka, T.; Fueki, K. J Polym Sci Part A: Polym Chem 1993, 31, 2785.
8. Shimada, J.; Kabuki, K. J Appl Polym Sci 1988, 12, 671.
9. Beavan, S. W.; Phillips, D. Eur Polym J 1974, 10, 593.

10. Scott, G.; Tahan, M. Eur Polym J 1977, 13, 981.
11. Pickett, J. Polym Prepr 2001, 42, 344.
12. Pickett, J. E.; Moore, J. E. Polym Degrad Stab 1993, 42, 231.
13. Gerlock, T. L.; Tang, W.; Dearth, M. A.; Korniskj, T. J. Polym Degrad Stab 1995, 48, 121.
14. Rieker, J.; Lemmert-Schmitt, E.; Goeller, M.; Roessler, G.; Stueber, G.; Schettler, H.; Kramer, H.; Stezowski, J.; Hoier, H.; Henkel, S.; Schmidt, A.; Port, H.; Wiechmann, M.; Rody, J.; Rytz, G.; Slongo, M.; Birbaum, J. L. J Phys Chem 1992, 96, 10225.
15. Factor, A.; Chu, M. L. Polym Degrad Stab 1980, 2, 203.
16. Nagai, N.; Okumura, H.; Imai, T.; Nishiyama, I. Polym Degrad Stab 2003, 81, 491.
17. Diepens, M.; Gijsman, P. Polym Degrad Stab 2007, 92, 397.
18. Diepens, M.; Gijsman, P. Polym Degrad Stab 2008, 93, 1383.
19. Diepens, M.; Gijsman, P. Polym Degrad Stab 2009, 94, 34.
20. Stueber, G. J.; Kieninger, M.; Schettler, H.; Busch, W.; Goeller, B.; Frauke, J.; Kramer, H. E. A.; Hoier, H.; Henkel, S.; Fischer, P.; Port, H.; Hirsch, T.; Rytz, G.; Birbaum, J. L. J Phys Chem 1995, 99, 10097.
21. Woessner, G.; Goeller, G.; Rieker, J.; Hoier, H.; Stezowski, J. J.; Daltrozzo, E.; Neureiter, M.; Kramer, H. E. A. J Phys Chem 1985, 89, 3629.