Enhancement of fluorescent stability of 2,5-bis-2-(5-tert-butyl)-benzoxazolyl-thiophene (BBOT) containing LDPE films

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Abstract

The photostability of an optical brightener 2,5-bis-2-(5-tert-butyl)-benzoxazolyl-thiophene (BBOT) was investigated in solution and in LDPE films, respectively. The films were either laminated with light-screening transparent films containing ultrafine titanium dioxide or taken into multilayer systems containing a cross-linked component. It could be demonstrated that in the 250 through 400 nm irradiation spectra of BBOT the range between 250 and 300 nm was responsible for the light sensitivity of the system, whereas that between 300 and 400 nm was responsible for the fluorescence of the system. The influence of systems prepared with lamination and the cross-linked layer on the intensity of fluorescence of BBOT was determined. The simple lamination with titanium-dioxide-containing films did not prove to be an effective way of protection as both the photostability and the fluorescence intensity decreased simultaneously in systems of this type. The drop in light stability could be attributed to the migration of BBOT into the TiO$_2$-containing film. A five-component system had to be produced for improving the light stability of the wanted product. LDPE film was linked to one side of a BBOT-containing film by means of a cross-linked adhesive. The other side of this film was linked to either another LDPE film or to TiO$_2$-particle-filled LDPE film by the same type of cross-linked adhesive. The initial intensity of fluorescence dropped simultaneously by 15 to 40%. The light stability could be increased up to 400% of the original value. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: BBOT; Optical brightener; High dispersity TiO$_2$; Photostability; Fluorescence stability; Cross-linked polymer; Multilayer films; Laminated films

1. Introduction

Optical brighteners transform UV light to the visible region. Besides the occurring fluorescence simultaneous UV-radiation-induced chemical decomposition of the optical brightener can also be observed. There is a wide range in photostability of the optical brighteners. The light stability of the optical brightener plays an important role in systems exposed to outdoor conditions. The types of optical brighteners applicable in various polymers are limited [1]. Optical brighteners containing a C=C double bond (ethylene bond) can lose their fluorescence properties under the influence of comparatively small light doses due to E–Z isomerization. The E–Z isomerization of the double bond is followed by an oxidative cleavage. No similar explanation can be adapted for the loss in fluorescence of 2,5-bis-2-(5-tert-butyl)-benzoxazolyl-thiophene (BBOT) because it does not contain

any olefinic double bond [2]. The optical application and photostability of BBOT in organic solvents and various polymer matrices had already been studied earlier [3–10]. The nature of the polymer matrix is decisive in the light stability of optical brightener particle filled films. Its value is rather high in HDPE and low in LDPE [1]. The shorter the wavelength of the light used for exposure the higher is the drop in light stability of the optical brightener [11]. Consequently the use of UV absorbers in the system may improve their light stability [12]. The rate-controlling step of the photodegradation of certain optical brighteners is their oxidation. This reaction is of a much higher speed at the air–film interface than in the internal region of the film. As the substrate migrates easily to that interface its protection can only be established by means of a multilayer system described above. As BBOT has been selected from the commercial optical brighteners for our experiments related data have been collected from the literature about its properties. UV absorbers applied so far caused a 1.5–2-fold increase in the photosta-

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Table 1
Materials used and their specific characteristics

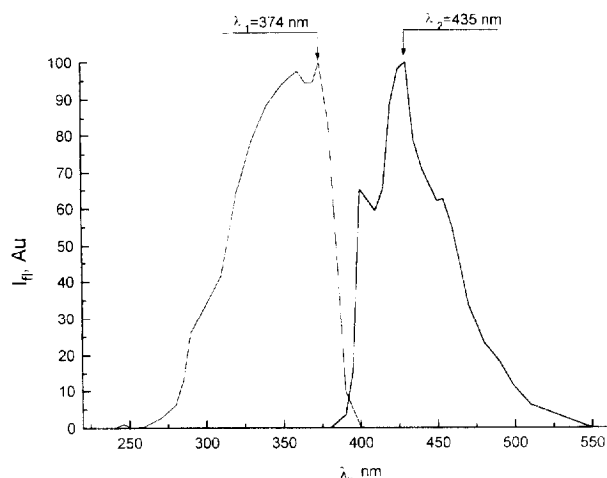| Code	Structure	Specific characteristics					
		M_w	ρ kgm^{-3}	η Pas	λ_A^{max} nm	λ_{ex}^{max} nm	λ_{em}^{max} nm
BBOT		918	–	–	374	374	435
TiO$_2$ Rutile		–	–	–	300	–	–
PHI		–	–	–	254 290	–	–
UO		1200	1.13	23	–	–	–
ER		980	–	0.16	–	–	–

Fig. 1. Uncorrected excitation and emission spectra of BBOT in cyclohexane solution; $c = 7.79 \times 10^{-4}$ mol l^{-1}, excitation maximum: $\lambda_1 = 374$ nm, emission maximum: $\lambda_2 = 435$ nm.

bility of BBOT while the initial fluorescent intensity decreased markedly [12]. On the other hand, it has been known that some inorganic UV-absorbers, e.g. TiO_2, act as quenchers on fluorescent materials [2]. The aim of this work was to increase the photostability of BBOT in an LDPE polymer matrix laminated with a TiO_2-containing LDPE film and in a multilayer structure containing a cross-linked adhesive layer between LDPE films.

2. Experimental

2.1. Materials

Polymers were made from LDPE granules Tipolen FB 243-54® by TVK, Hungary. BBOT used as a fluorescent material was supplied by Ciba-Geigy. As a UV absorber transparent ultrafine TiO_2 (UV-TITAN P160®, KEMIRA, Finnland) was employed. As a dispersant for TiO_2 Zn stearate (by E. Merck, Darmstadt, Germany) was used. The main components of the UV curable adhesive were a cationically polymerizable Bisphenol-A diglycidyl ether-based epoxy resin (Chemolepox 020®, Pevdi, Hungary) and a free radically polymerizable acrylated aliphatic urethane oligomer (Ebecryl 285®, UCB Chemicals, Radcure Specialties, Belgium). As a photoinitiator a mixture of hexafluoroantimonate salts

(Cyracure UVI-6974®, Union Carbide, Austria) was used. The main properties of the materials used are shown in Table 1. The excitation and emission spectra of BBOT are shown in Fig. 1.

2.2. Equipment

Brabender Plasti-Corder PL2000 (Brabender) with a 350E-type mixer and a 19/25D single-screw extruder was used for mixing and extrusion. The type of rotating disintegrator was RMA-1 (Rozmaring, Hungary). Laminates were prepared by means of a Meyer-type hot press made in our workshop. For curing of the adhesive layer a Fusion System 1500-W electrodeless UV lamp was used. The device used for light exposure of the solution with the light intensity of 6 mW cm^{-2} within the wavelength region 300–400 nm is presented in Fig. 2. Between the light source and the samples glass light screeners (GLS1, GLS2) were placed. Transmittancies (in %) were as follows: for GLS1: under $\lambda = 280$ nmm, $T = 0.5$; over $\lambda = 280$ nm, $T = 97.5$; for GLS2: under $\lambda = 300$ nm, $T = 0.6$; over $\lambda = 300$ nm, $T = 98.7$. Exposure lasted for up to 120 min.

Polymer samples were irradiated in a XENOTEST 450 (Original Hanau). A HP8482A (Hewlett Packard) diode array UV–Vis spectrophotometer and a Hitachi MPF 2A fluorescent spectrophotometer were used for spectroscopic studies of the BBOT solutions and the particle-filled film samples. For morphological studies a Hitachi S-570 model scanning electron microscope (SEM) was employed. The SEM was equipped with an energy disperse X-ray analyser (EDX) operated by a commercial Röntec software.

2.3. Methods

2.3.1. Master batch

For light-screening film: 10 g UV-TITAN® P160 previously mixed with 0.5 g Zn stearate was added to 100 g Tipolen® FB-243-54 (LDPE) and the mixture was homogenised to a master batch on the Brabender Plasti-Corder PL2000, 350E mixing system. For fluorescent film: 5 g BBOT was added to 100 g Tipolen® FB-243-54 (LDPE). Working parameters for both systems were as follows: $t = 10$ min, $n = 20$ min^{-1}, $T = 180°C$.

1. 250 W high pressure mercury vapour lamp. 2. Standard triangular optical bench. 3. Quartz blend 4. Filter cell, 5. Cuvette holder
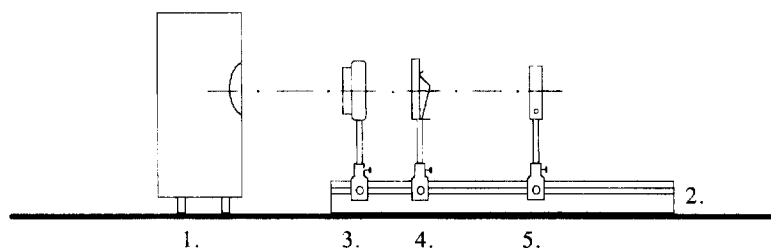
Fig. 2. Schematic representation of the device used for light exposure.

2.3.2. Disintegration of the composite

The master batch was disintegrated by an RMA-1 disintegrator at 1440 rpm to particles of 5-mm average size.

2.3.3. Extrusion

Films were extruded from mixtures on a Brabender Plasti-Corder single screw extruder. Working parameters: temperature of zones: 170, 180, and 190°C; temperature of die: 210°C; $n = 5$ rpm; speed of conveyor belt: in the case of 100-μm-thick film, 6 m min^{-1} and in the case of 20-μm-thick film, 7.3 m min^{-1}.

2.3.4. Preparation of laminated films

Polymer films were pressed in a Meyer hot press at $t = 120$°C applying $p = 160$ Pa pressure for $T = 10$ min.

2.3.5. Preparation of multilayer systems

An ~ 100-μm-thick adhesive layer was fixed between two films, one of which was a BBOT particle filled one. This ternary system was laminated with a cold press. The adhesive was cured through the transparent films by a Fusion System 1500-W electrodeless UV lamp (dose: 0.1 J cm^{-2}).

2.3.6. Exposure to light

The cyclohexane solution of BBOT was exposed to light on the optical bench (Fig. 1) in such a way that the applied glass light screener (GLS) and light screening polymer film were placed between the light source and the substrate. Polymer samples were irradiated in a XENOTEST 450 apparatus. Parameters: intensity of radiation $= 8.1$ mW cm^{-2} within the wavelength region of 300–400 nm, blackboard temperature $= 48$°C, inner temperature $= 33$°C, relative humidity $= 55\%$, duration of irradiation $= 0$–170 h.

2.3.7. Analytical methods

Photodegradation of BBOT was followed by UV photometrically in selected periods of time from 8 through 20 min. The photodegradation of BBOT particle filled films, however, could be followed by fluorescence spectrophotometrically. Scanning electronmicrographs were taken from the cross section of the multilayer systems and laminated films, respectively. The surface of the cross section was coated with
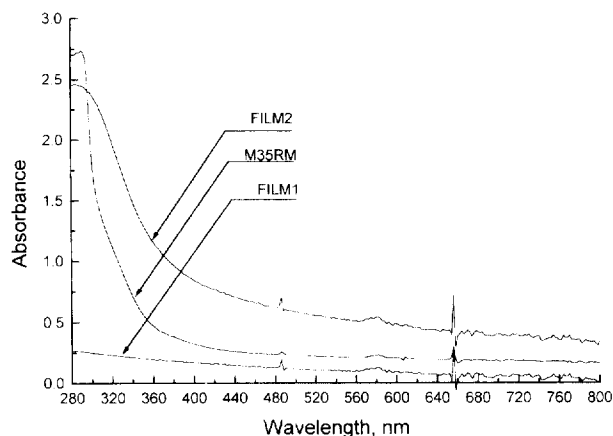

Fig. 3. UV–Vis spectra of FILM1, FILM2 and M35RM from 280 nm through 800 nm.

1 μm carbon for SEM. Energy disperse X-ray analysis (EDX) was performed after the appropriate cross-section surfaces were coated with 2 μm carbon. The distribution of BBOT in the laminated system was determined on the basis of change in the sulphur content (namely BBOT is the only S-containing compound in the system). The change in TiO$_2$ content was measured by means of Ti analysis.

3. Results and discussion

3.1. Characteristics of films, laminates and multilayer systems

Various light-screening layers and systems respectively were elaborated for the protection of BBOT against light-induced decomposition. The various systems are described in Table 2.

The composition of the adhesive (M35RM) cross-linkable after UV irradiation [13–15] is as follows: 49.5 w/w% ER, 49.5 w/w% UO, 1% PHI (for details see Table 1). The corresponding UV–Vis absorption spectra of FILM1, FILM2 and M35RM layer are presented in Fig. 3.

SEM micrographs taken at cross sections of FILM5 and FILM6 are shown in Fig. 4a and b, respectively.

Table 2
Light-screening systems applied for the protection of BBOT against light-induced decomposition

Code	Composition	Thickness (μm)
FILM1	LDPE without additive	100
FILM2	LDPE with 0.2 w/w% TiO$_2$*	$\cong$ 50
FILM3	LDPE with 0.1 w/w% BBOT	100
FILM4	LDPE with 2.5 w/w% BBOT	100
FILM5	Laminated film (FILM1 + FILM3)	(100 + $\cong$ 50)
FILM6	Multilayer film (FILM1 + M35RM + FILM3 + M35RM + FILM1) see Fig. 4a	(100 + $\cong$ 100 + 100 + $\cong$ 100 + 100)
FILM7	Multilayer film (FILM2 + M35RM + FILM3 + M35RM + FILM1)	(50 + $\cong$ 100 + 100 + $\cong$ 100 + 100)
FILM8	Laminated film (FILM4 + FILM2), see Fig. 4b	(100 + 50)

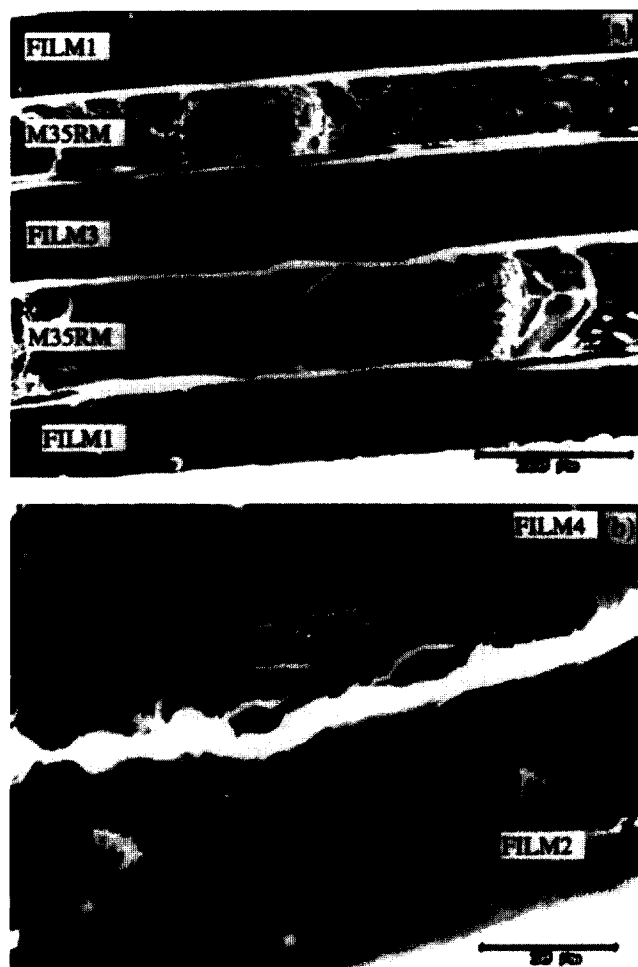*0.5 w/w% Zn stearate was used related to TiO$_2$ quantity.

Fig. 4. SEM photographs of the cross sections of the selected film samples. (a) FILM6: cut by microtome, (b) FILM8: broken in deep-frozen state.
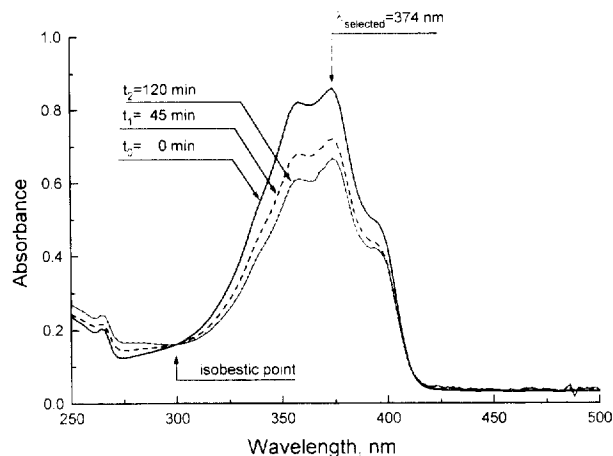

Fig. 5. Absorption spectrum from 250 nm through 500 nm of BBOT dissolved in cyclohexane before and after irradiation of different durations; $c = 7.79 \times 10^{-4}$ mol l^{-1}, $\lambda_{selected} = \lambda_1 = 374$ nm.
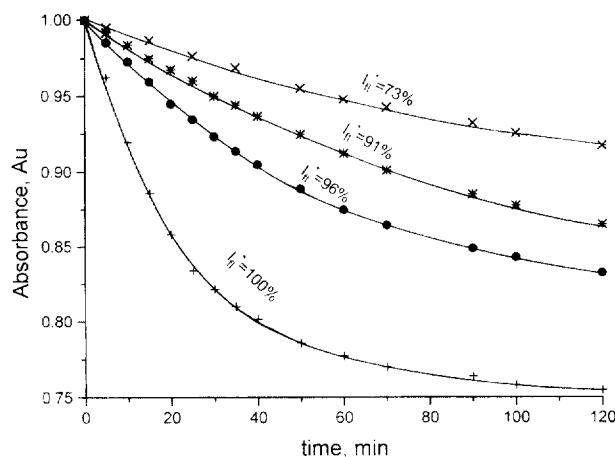

Fig. 6. Changes in kinetics of absorbance of BBOT solutions under irradiation behind glass light screeners (see Table 3) and FILM2 (see Table 2), respectively. (+) No screening, (•) GLS1, (*) GLS2, (×) FILM2. I_n^*: initial fluorescence intensities of BBOT.

3.2. Photostability of BBOT in solution

Changes in the absorption spectrum of the BBOT solution in cyclohexane in the course of irradiation are shown in Fig. 5.

There are two absorption peaks at 358 and 374 nm, respectively. The peak at 374 nm was chosen to monitor the photodegradation of BBOT. Since the solution of BBOT follows the Lambert–Beer's law at 374 nm, the drop in absorbance at that wavelength could be taken as the measure of photodegradation (Eq. (1)).

$$\Delta A = A_0 - A_t \qquad (1)$$

where: A_0 = the initial absorbance of BBOT; A_t = the absorbance of BBOT after exposure to light for t min.

Fig. 6 represents the kinetic changes of the photostability as well as the changes in the initial intensity of fluorescence of BBOT behind three different screeners and without each of them, respectively.

The initial intensity of fluorescence as well as the rate of photodegradation of the dissolved BBOT was influenced by the light screener. To evaluate the kinetic curves the change in absorbance (ΔA^{120}) after $t = 120$ minutes of exposure was

selected. This value, however, had to be corrected to eliminate differences in the distribution of light intensity in the different wavelength ranges. The correction factor ($f_{\lambda_i - \lambda_{max}}$) was the denominator under the nominator of ΔA^{120} (Eq. (2))

$$f_{\lambda_i - \lambda_{max}} = \frac{\int_{\lambda_i}^{\lambda_{max}} P(\lambda)d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} P(\lambda)d\lambda} \qquad (2)$$

where λ_i is the wavelength under which the transmittance of GLS is equal to zero; λ_{min} and λ_{max} are the shortest and the longest wavelength in the spectrum of the light source; $P(\lambda)$ = the light intensity at wavelength λ (mW cm^{-2}).

The measured and corrected values of ΔA^{120} are collected in Table 3.

As can be seen with GLS1 the initial fluorescence intensity of BBOT decreased by 4%, its photodegradation was lower

Table 3
List of the studied wavelength ranges, applied correction factors and measured and corrected values of the changes of absorbancies in the presence of light screeners

Code of the screener	I_0[*] ($\%$)[a]	λ_t[b] (nm)[b]	$f_{\lambda \, \lambda_{max}}$ ($\times 10^{-2}$)	ΔA^{120} after 120 min exposure to light ($\times 10^{-3}$)[c]	
				measured	corrected
No screening	100	–	1	25	25
GLS1	96	280	5.57	17	3.05
GLS2	91	300	8.10	14	1.73
FILM2	73	–	–	9	

[a]Initial fluorescence intensity of BBOT solution through the screener. Values related to nonscreened solution.
[b]Nominal cutting wavelength of the screener.
[c]$\lambda_{selected} = 374$ nm.

than that without screening. In the presence of FILM2 (see Table 2) the initial fluorescence intensity of BBOT decreased by 23% while its photostability was larger than with GLS1. In the presence of GLS2 the initial intensity of fluorescence decreased by 9%, with a similar drop in light stability as under the application of GLS1.

3.3. Photostability of BBOT in polymer composites

3.3.1. The effect of the composition on the initial fluorescent intensity of film samples

In films the absorbancies of BBOT were too high to measure, therefore the changes in concentration could be followed directly by monitoring the fluorescence intensity of the films. It has to be taken into consideration that the application of light screeners in such systems have to give different effects to the measured fluorescence intensity. The first effect is a decrease in the fluorescence intensity before any light-induced photochemical change (decrease of the initial fluorescence intensity). The second effect is, however, a slowing

down of the drop in fluorescence intensity during the light exposure. The initial fluorescence intensity of FILM5 is less by 29% than that of FIM3 because of the presence of the light-screening component FILM2 in the former system. Unfortunately FILM2 exhibits its light-screening effect also on the emission spectrum of the excited BBOT. At FILM6 multilayer system the decrease of initial fluorescent intensity was of smaller extent (15%) since the cross-linked layer has only UV absorbancy (at 374 nm, $A = 0.5$) in the excitation region of BBOT. A significant decrease (60%) occurred in the initial fluorescent intensity of FILM6 as compared with that of FILM3, since the synergistic action of FILM2 and M35RM takes place here. Decrease in the initial fluorescence intensity of the studied samples is shown in Fig. 7.

3.3.2. Light-induced decomposition and protection against it of BBOT in polymer composites

The fluorescent intensity of FILM3, i.e., unprotected film containing only BBOT, exponentially decreased under the influence of irradiation in XENOTEST 450. After 90 h the intensity of fluorescence sank to the level of 5% (Fig. 8).

If, however, FILM3 was covered with FILM2 (0.2% TiO_2 containing LDPE film) in the XENOTEST equipment the drop in fluorescence intensity markedly less (32%) than the initial value was retained. Applying a prolonged exposure of 170 h for both samples (FILM3 with and without covering by FILM2) the final value of fluorescence intensity remained only 5% of the initial one. In case of a multilayer film (FILM6) the fluorescence intensity decreased after 170 h of exposure only to 55% of the initial value of the unexposed sample due to good UV absorbing properties of the cross-linked layer and due to the fact that the migration of BBOT to the film–air interface was hindered. In the case of FILM7 80% of the initial fluorescence intensity was retained after 170 h of exposure. This improvement can be assigned to the UV-absorbing effect of the titanium-dioxide-containing FILM2. In the case of the laminated FILM5 the rate of the
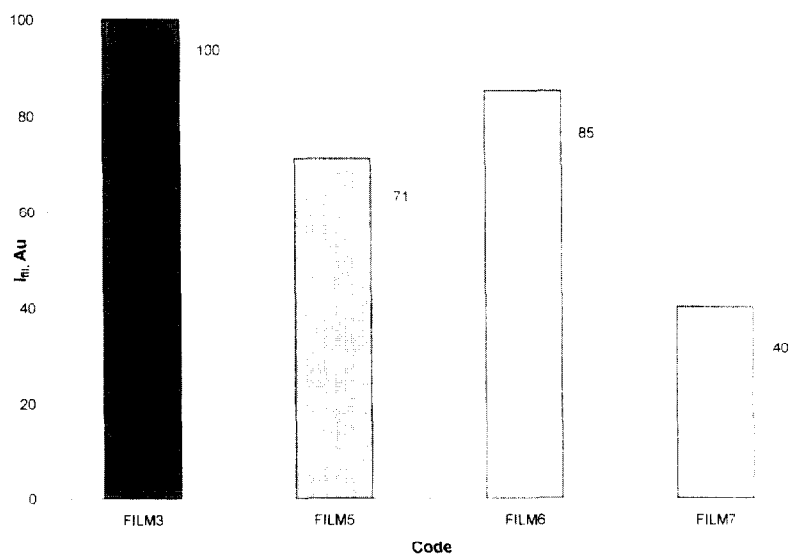

Fig. 7. Comparison among fluorescent intensities of nonirradiated film samples measured at their emission maxima ($\lambda_e = 435$ nm).
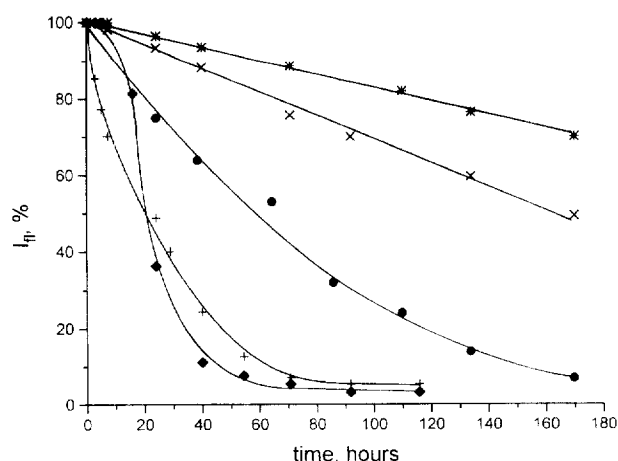
Fig. 8. Change of fluorescent intensities of the films exposed to light in Xenotest equipment vs. time. (◆) FILM4, (+) FILM3, (●) FILM3 covered FILM2 (irradiated behind FILM2, measured without FILM2), (×) FILM6, (*) FILM7.

drop in fluorescence intensity under light exposure is higher than that of FILM3 except that during the first 10 h inhibiting effect prevented any changes in its initial fluorescence intensity. The latter effect can be attributed to the UV-screening effect of TiO₂-containing film component of the system. The rapid drop in fluorescence intensity after the exposure for 10 h can be explained by the adsorption of the migrating BBOT

on the TiO₂ particles in the irradiated component of the laminate. In order to establish chemical analytical methods for the detection of the migration a new laminate (FILM8) had to be prepared. In this FILM3 was replaced by FILM4 to increase the concentration of BBOT and through this detectable amount sulphur in this layer. The sulphur content of the two layers of the laminate was analysed before and after exposure for 90 h. From the spectra in Fig. 9 it can be concluded that after 90 h of exposure a detectable part of BBOT migrated from FILM4 to FILM2 in the laminate whereas no migration of TiO₂ could be detected in the reverse direction from FILM2 to FILM4.

BBOT migrated onto the layer containing TiO₂ exhibits a diminished fluorescence as a consequence of the interaction with TiO₂ particles either by quenching or by increased rate photodecomposition.

4. Conclusion

The screening of the irradiating light has a higher effect on the rate of photodegradation of BBOT than on the fluorescence intensity. The chemical decomposition induced by that part of the spectrum which is below the wavelength of 280 nm is significantly stronger and faster than that which was induced by the range of spectrum over the wavelength of 280
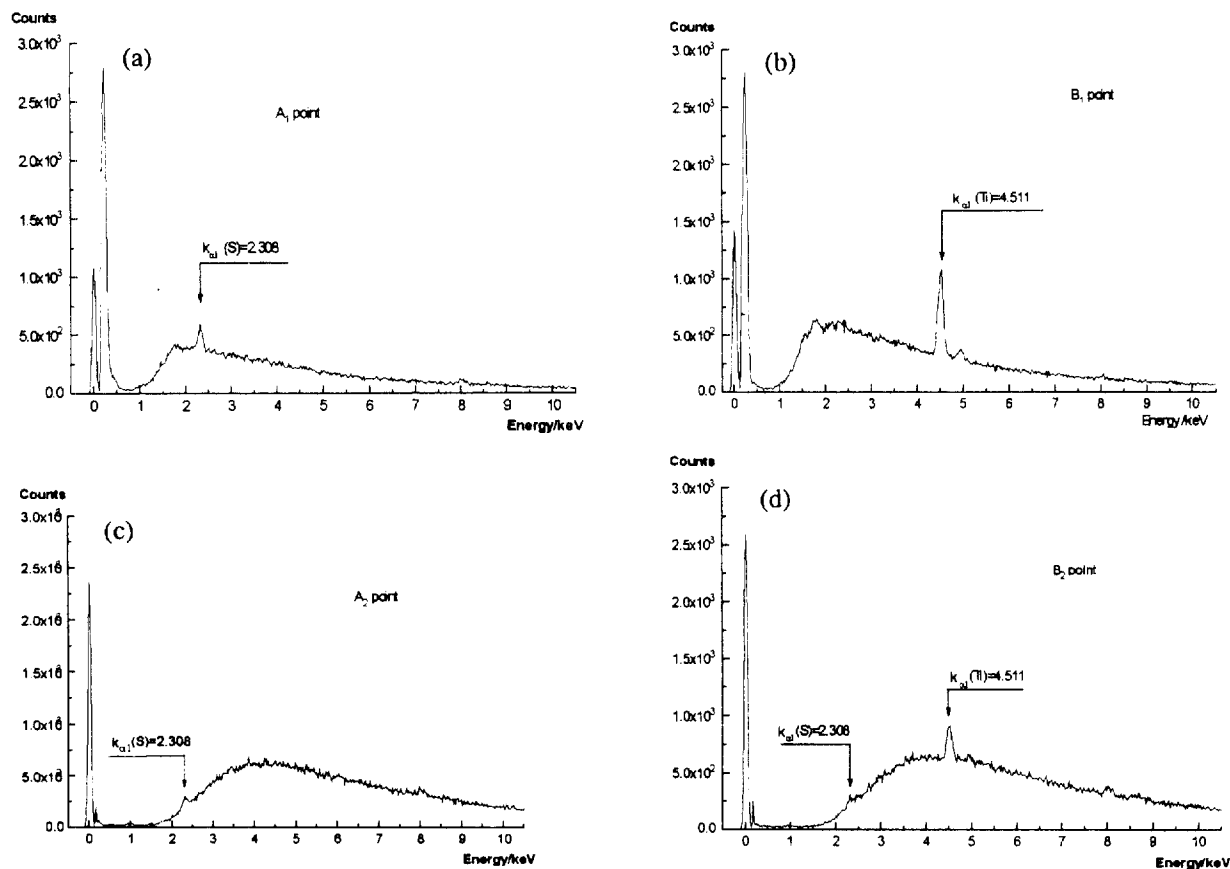

Fig. 9. EDX spectra of the two layers of FILM8 sample before and after exposure to light of Xenotest equipment (A₁ point FILM4 layer and B₁ point FILM2 layer before exposure to light, A₂ point of FILM4 layer and B₂ point FILM2 layer after exposure to light).

nm. No remarkable difference (less than 5%) could be observed in the initial fluorescence intensity between the samples excited in either of the two selected wavelength ranges. These observations are equally valid for BBOT both in solution and in LDPE matrix. The photostability of BBOT containing LDPE films against the XENOTEST light can be improved twofold by screening with 0.2% TiO_2-containing film, while the initial fluorescence intensity dropped by 29%. In the multilayer system FILM6 and FILM7, the important light stability was 2-fold and 3-fold higher, respectively as compared with that of FILM3. The initial fluorescence intensity was found to be markedly lower in combined systems (laminates, multilayers) in which the light-screening sheet contains distributed TiO_2 particles (FILM5, FILM7). Moreover in the laminated FILM5 system the decrease of the fluorescence intensity by irradiation was even faster than the decrease in nonprotected FILM3. This statement is corroborated by the observation that the photostability of BBOT in this system shorted above that of the nonprotected film and it broke down after 10–20 h. The good protecting effect of the first hours could be stabilized by composing an isolated multilayer structure from the same elements (FILM6 or FILM7, respectively).

Acknowledgements

References

[1] R. Gächter, H. Müller (Eds.), Taschenbuch der Kunststoffe-Additive, Carl Hauser Verlag, München, 1989, pp. 552–564.

[2] H. Zollinger (Ed.), Color Chemistry, 2nd edn., VHC, New York, 1991, pp. 259–320.

[3] E. Kowalski, R. Anliker, K. Schmid, Int. J. Appl. Rad. Isotopes 18 (1967) 307–323.

[4] E. Schmidt, H. Loeliger, R. Zürcher, Helv. Chim. Acta 61 (39) (1978) 488–499.

[5] H. Hoegl, G. Barchietto, D. Tar, J. Photochem. Photobiol. A: Chem. 16 (1972) 335–372.

[6] H.W. Furumoto, H.L. Ceccon, J. Quantum Electron 6 (1970) 262–267.

[7] E. Kowalski, R. Anliker, K. Schmidt, Mol. Cryst. 4 (1968) 403–413.

[8] D.M. Rayner, A.E. McKinnon, A.G. Szabó, Can. J. Chem. 54 (1976) 3246–3258.

[9] I.B. Berlman, J. Phys. Chem. 77 (4) (1973) 562–567.

[10] Z. Seha, C.D. Weis, Helv. Chim. Acta 63 (41) (1980) 413–419.

[11] G.E. Kricsevszkij, Fotohimicseszkie prevrasenyia kraszityelej i szvetosztabilizacija okrasenyih materialov, Himija, Moszkva, 1986, p. 66.

[12] I. Kása, G. Túry, A. Víg, O. Kelemen, in: N. Marek, K. Szabó (Eds.), Investigation of fluorescent films XIX. National Congress on Luminescence Spectroscopy Pécs (Hungary) 1–3 Oct., 1996, Proceedings A LUMINESZCENCIA KUTATA'SOK AKTUA'LIS KÉRDÉSEI Vol. XIX (in press).

[13] J.V. Crivello, J.H.W. Lam, J. Polym. Sci., Polym. Chem. Ed. 17 (1979) 977.

[14] J.V. Crivello, J.L. Lee, D.A. Coulin, J. Rad. Curing 10 (1) (1983).

[15] J.V. Crivello, US Patent 4,058,401, 1977.