ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 86 (1995) 267-273

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

The effect of antioxidant/quenchers and a fluorescent whitening agent on the quantum yield of photoinduced degradation of tryptophan in a rigid, oxygen-permeable medium

P.D. Auer, M.T. Pailthorpe

Department of Textile Technology, University of New South Wales, Sydney, N.S.W. 2052, Australia

Received 28 March 1994; accepted 19 July 1994

Abstract

The quantum yield of photoinduced degradation of free tryptophan (TRP) encapsulated in oxygen-permeable methyl cellulose (MC) was studied with regard to the effect of the inclusion of a number of antioxidants and singlet oxygen quenchers. The effect of the inclusion of a fluorescent whitening agent (FWA) in the system was also evaluated. No beneficial effect was found for the direct photo-oxidation of TRP in the presence of antioxidant/quenchers. However, the degradation of TRP was sensitized in the presence of the FWA. The presence of oxygen was found to be essential for this sensitization to proceed. Several compounds, selected from the phosphite, sulphide and nickel chelate classes of antioxidant/quenchers, were found to reduce the degree of sensitization.

Keywords: Antioxidants; Quenchers; Degradation; Tryptophan

1. Introduction

The protein fibre, wool, is disadvantaged by its natural off-white colouration in markets where strong, bright, white textile substrates are required. The standard methods of bleaching and the application of fluorescent whitening agents (FWAs) to produce white substrates are effective [1], but make the wool susceptible to accelerated photoyellowing [2]. The photoyellowing of fluorescently whitened wool is approximately 12 times faster than that of unwhitened wool [3].

It is generally accepted that the major source of yellowness in natural and whitened wool exposed to UV radiation is the range of compounds formed by the photodegradation of the amino acid residue tryptophan (TRP) [4–9]. It has been proposed that the major pathway for the atmospheric photodegradation of TRP in wool is through its reaction with singlet excited oxygen ($^1O_2$) [10]. It is also thought that the presence of an FWA in whitened wool accelerates the degradation of TRP through photosensitization, i.e. by increasing the presence of $^1O_2$ in the system [11–14]. It has also been proposed that hydroperoxides are formed as intermediates in the dye-sensitized photo-oxidation of TRP [15], assuming that a type II mechanism predominates [16].

Various photoprotection options have been investigated for whitened wool, such as sensitizer/substrate separation [17] and FWA structure considerations [18], with limited success. This study investigates the photoprotection option of degradation pathway interference.

Various types of compounds have been used in the food and plastics industries as photostabilizers, including antioxidants and singlet oxygen quenchers. Generally, these compounds operate by interfering with the pathways involved in photodegradation [19].

The investigation, by quantum yield determination, of the effect of antioxidants and singlet oxygen quenchers on the photodegradation of TRP in wool is difficult because of wool's complex chemistry and morphology. Therefore these effects were investigated using the model system of a rigid, oxygen-permeable medium, methyl cellulose (MC) [20], to encapsulate the various compounds.

2. Materials and methods

The polymer grade used in these studies was Methocel MC (Fluka), USP; high viscosity. The polymer was used as received, without further purification. Solutions (3%)

1010-6030/95/$09.50
SSDI 1010-6030(94)03929-1

of MC were prepared, deaerated, and cast cold onto clean soda-glass plates (20 cm×20 cm) at a constant thickness. The cast solutions were then dried in a Heraeus fan-forced oven at 50 °C for 4 h; nine subsamples (4 cm×4 cm) were then cut from the centre of the dry films. The thickness of the dried cast films was of the order of 20 μm. Spectroscopic examination of the blank MC films revealed a small absorbance below 350 nm. This was taken into account in other spectroscopic measurements by using blank MC films as reference.

The FWA used was Uvitex NFW (Ciba-Geigy). Crystals of purified FWA were prepared from the supplied liquid preparation by salt precipitation, and subsequent recrystallization from water–ethanol.

The codes referred to in the lists of water-soluble (Table 1) and water-insoluble (Table 2) reagents will be used throughout this paper. Water-insoluble reagents were incorporated into the polymer solution, at the concentrations listed in Table 3, as dispersions made up with the non-ionic surfactant Teric 16A22 (ICI), an ethoxylate of a long-chain aliphatic alcohol (hydrophile lipophile balance (HLB) = 15.8). Spectroscopic analysis of MC films containing Teric 16A22 showed that the surfactant exhibited zero absorbance in the spectral region of interest. However, the concentration level of the dispersing agent Teric 16A22 was found to have a significant effect on the photodegradation of the FWA [21] and hence the dispersant concentration in the films was kept constant. The dispersant concentration in all films employed in this study was 0.115 g per gram of dry polymer.

Table 1
Water-soluble reagents

Tradename (supplier)	Chemical name	MW	Code
Tryptophan (Fluka)	L-Tryptophan	204	TRP
Uvitex NFW (Ciba-Geigy)	*trans*-4,4′-Bis(2-sulphostyryl)-biphenyl (sodium salt)	562	FWA
DABCO (Aldrich)	Triethylene-diamine-1,4-diazabicyclo[2.2.2]octane	112	DABCO

MW, molecular weight.

The abbreviation TRP/ANTIOX refers to films containing antioxidant/quenchers and TRP, whilst TRP/FWA/ANTIOX refers to films containing antioxidant/quenchers, TRP and the FWA, Uvitex NFW.

Two different types of broad spectrum UV radiation were used in these studies. The radiation referred to as far-UV radiation was produced by Oliphant FL8E and Clemco 9008 fluorescent lamps. These lamps emit 70% of their radiation in the 280–360 nm spectral region, with an emission maximum at 310 nm. The measurable intensity is zero below 250 nm. TRP/ANTIOX films were exposed to this radiation. The radiation referred to as near-UV radiation in this work was produced by Oliphant FL8 T5 BL fluorescent lamps. These lamps emit 80% of their radiation in the 300–420 nm spectral region, with an emission maximum at 375 nm. The measurable intensity of these lamps is zero below 300 nm. TRP/FWA/ANTIOX films were exposed to this radiation. Exposure of TRP/ANTIOX films to UV radiation from these lamps resulted in negligible TRP degradation. Figs. 1 and 2 show the relative spectral intensities of these lamps.

The lamp output intensity was measured using the chemical actinometer, potassium ferrioxalate [22], to determine the number of quanta incident on the specimens. The procedure has been described elsewhere in detail [23].

Film samples were exposed to the two types of UV radiation in an Oliphant irradiation chamber (model PCR-128W) (Oliphant Bros., S.A.). The temperature inside the chamber was stabilized with a cooling fan to 47 °C. The whole surface of the film was exposed

Table 2
Water-insoluble reagents

Tradename (supplier)	Chemical name	MW	Code
Irganox 1425 (Ciba-Geigy)	Calcium bis[3,5-di-tert-butyl-4-hydroxybenzyl-monoethyl-phosphonate]	695	HP5
Irgafos 168 (Ciba-Geigy)	Tris(2,4-di-tert-butyl-phenyl)phosphite	647	P2
Cyasorb 1084 (Cyanamid Aust.)	[2,2′-Thiobis(4-tert-octylphenolato)]*n*-butylamine nickel (II)-	571	NC1
Tinuvin 770 (Ciba-Geigy)	Bis[2,2,6,6-tetramethyl-4-piperidyl]sebacinate	480	HAL1
Cyanox LTDP (Cyanamid Aust.)	Dilaurylthiodipropionate	514	S1

MW, molecular weight.

Table 3
Reagent concentrations

Reagent combination	[TRP] (μM g^{-1})	[FWA] (μM g^{-1})	[Antioxidant/ quencher] (μM g^{-1})
TRP/ANTIOX	20	–	60
TRP/FWA/ANTIOX	20	30	60

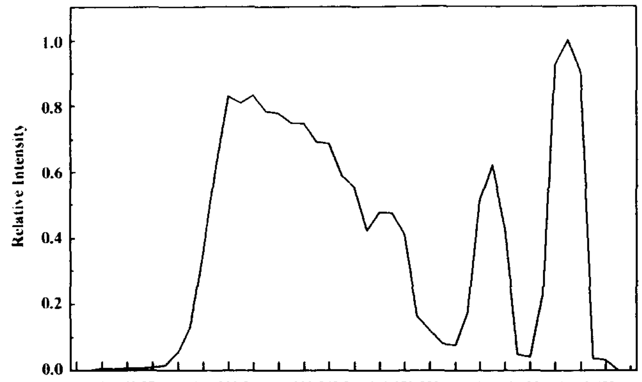

Fig. 1. Relative spectral intensity of Oliphant FL8E/Clemco 9008 lamps (far-UV radiation).

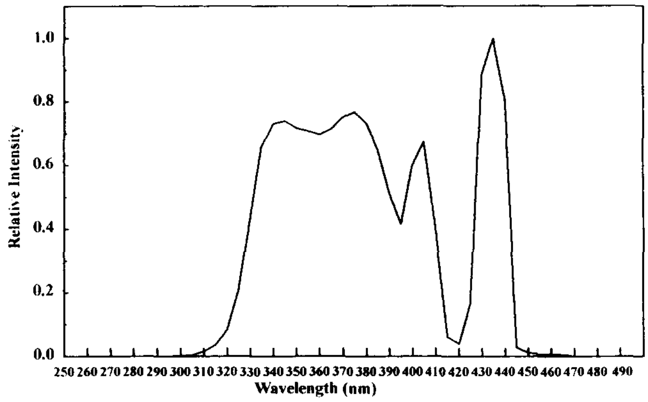

Fig. 2. Relative spectral intensity of Oliphant FL8 T5 BL lamps (near-UV radiation).

by placing it against the inside surface of a quartz cuvette.

The degradation of the FWA was monitored by absorbance readings taken on a Varian Cary 3 UV–visible double-beam spectrophotometer at 355 nm. The concentration of the FWA was found to be linearly proportional to the film absorbance at this wavelength after adjusting for film thickness variations and light scattering [21].

The degradation of TRP was determined using a modified Denckla–Dewey method (norharman test) [24] on solutions of dissolved films. This test determines the amount of free TRP in the solution by converting the TRP to the fluorescent product, norharman. The reaction is very specific to free TRP, since an unblocked α-amino acid is required. An incubation time of 1.5 h at 125 °C was used in this analysis. The fluorescence of solutions excited at 373 nm was measured on a Perkin–Elmer filter fluorometer at 460 nm. Allowances were made for the fluorescent emission of the FWA in this analysis.

The effect of the antioxidant/quenchers on the FWA absorbance readings and TRP concentration analysis was assessed and allowed for in the calculation of the degradation quantum yields.

The normalized absorption spectrum of the FWA incorporated in the 20 μm MC films is presented in Fig. 3. Fig. 4 shows the normalized absorption spectrum of TRP incorporated in the 20 μm MC film. A blank MC film containing a fixed concentration of Teric 16A22 was used as a reference in both cases. The spectra were measured on a Varian Cary 3 UV–visible double-beam spectrophotometer, modified with a film sample holder.

The quantum yield ϕ (molecules quanta^{-1}) was calculated by dividing the initial degradation rate (molecules min^{-1} (cm^2 film)$^{-1}$) by the rate at which quanta are absorbed by the system (quanta min^{-1} (cm^2 film)$^{-1}$). A total error of 15% (95% confidence level) was estimated for each quantum yield determination. The quantum yield determination applied to the whole region

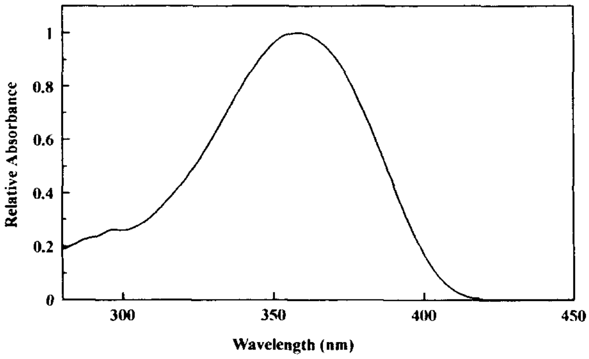

Fig. 3. Absorption spectrum (normalized) of Uvitex NFW (Ciba-Geigy) (reference, MC).

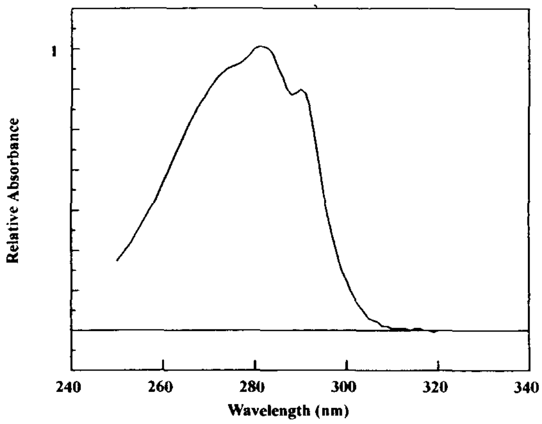

Fig. 4. Absorption spectrum (normalized) of TRP (reference, MC).

of wavelength overlap between the absorbing species and the incident radiation. The quantum yields referred to in this work are all degradation quantum yields; however, depending on which reagent is undergoing photodegradation and which species in the system is absorbing the radiation, different types of quantum yields were evaluated. These quantum yields are defined in Table 4.

3. Results and discussion

The discussion will include reference to a "positive antioxidant effect", i.e. the presence of the antioxidant results in a lowering of the quantum yield of TRP degradation compared with films containing no antioxidant, and a "negative antioxidant effect", i.e. the opposite effect.

Table 5 shows the quantum yield results for the direct photo-oxidation of TRP, i.e. TRP absorbing, TRP degrading. Results of 0.10 for ${}_{\mathrm{TRP}}\phi^{\mathrm{TRP}}$ in poly(vinyl alcohol) (PVA) film and 0.025 for ${}_{\mathrm{TRP}}\phi^{\mathrm{TRP}}$ in MC film have been obtained previously [9]. Taking into consideration the error estimated for the quantum yield determinations, the corresponding results in this work would appear to be in very good agreement with those obtained previously.

In terms of the effect of antioxidants on ${}_{\mathrm{TRP}}\phi^{\mathrm{TRP}}$ in the MC film, the results given in Table 5 indicate that none of the antioxidant/quenchers tested exhibited a positive antioxidant effect in this situation. Indeed, the antioxidant/quenchers P2 and NCl appeared to have a significant negative antioxidant effect in this situation.

Table 4
Quantum yield differentiation

Degradation quantum yield	Degraded species	Absorbing species
${}_{\mathrm{TRP}}\phi^{\mathrm{TRP}}$	TRP	TRP
${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}$	TRP	Uvitex NFW

The photosensitization of TRP degradation in the near-UV by the FWA can be seen in Table 6, where quantum yields of FWA and TRP degradation have been evaluated at various FWA concentrations. A ratio (${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}/{}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$) was obtained by dividing ${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}$ at each concentration by ${}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$ at that concentration. This ratio represents the number of TRP molecules degraded per FWA molecule degraded per quantum absorbed by the FWA. The data in Table 6 lead to a number of interesting conclusions. Firstly, it seems that the quantum yields of degradation of both FWA and TRP are independent of the concentration of FWA, at the 95% confidence level. In other words, for each increase in FWA concentration, there is a corresponding increase in FWA and TRP degradation in the films accompanied by an increase in the number of quanta absorbed by the system. This result indicates that the photodegradation of both FWA and TRP is unimolecular. Secondly, the values obtained for the ratio ${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}/{}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$ indicate that one TRP molecule is degraded per FWA molecule degraded during the initial stages of exposure. This ratio could be coincidental, since the degradation of one FWA molecule would not necessarily directly cause the degradation of one TRP molecule. However, since the absorption of UV radiation by TRP in the wavelength region studied is negligible, it must follow that the degradation of TRP is being sensitized by the energy absorbed by the FWA.

The effect of antioxidants on the photosensitized degradation of TRP is shown in Table 7. The reagent concentrations correspond to those shown in Table 3. Considering the ratio ${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}/{}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$ calculated in Table 7, it is clear that the antioxidant/quenchers P2, NCl and S1 have a significant positive antioxidant effect on the amount of TRP degraded in the presence of a whitener. The light stabilizer HAL1 has a significant antagonistic effect in this situation. The absence of an effect by DABCO indicates that this volatile reagent may have sublimed during the drying process, and therefore had no influence on either the TRP or FWA

Table 5
Quantum yields of degradation for TRP/ANTIOX exposures in MC films

Reagent combination	Degradation rate (R) (molecules min^{-1} cm^{-2}) ($\times 10^{14}$)	Rate quantum absorption (I_{abs}) (quanta min^{-1} cm^{-2}) ($\times 10^{16}$)	Quantum yield (${}_{\mathrm{TRP}}\phi^{\mathrm{TRP}}$) (molecules quantum^{-1})
TRP (PVA film)	15.1	1.9	0.08
TRP	2.3	1.0	0.023
HP5/TRP	2.1	0.9	0.024
NCl/TRP	3.9	1.0	0.039
P2/TRP	4.9	0.9	0.055

Exposure, far-UV; atmosphere, ambient air.

Table 6
Quantum yields of FWA and TRP degradation for various whitener concentrations in MC films

Uvitex NFW concentration [X] (μmol (g MC)$^{-1}$)	Whitener quantum yield (${}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$) (molecules quantum^{-1}) ($\times 10^{-4}$)	TRP quantum yield (${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}$) (molecules quantum^{-1}) ($\times 10^{-4}$)	Ratio (${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}/{}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$)
6	3.7	3.8	1.0
12	4.3	5.6	1.3
18	4.4	4.2	1.0
24	5.1	4.7	0.9
30	4.4	4.4	1.0

Exposure, near-UV; atmosphere, ambient air.

Table 7
Quantum yields of FWA and TRP degradation for TRP/FWA/ANTIOX exposures in MC films

Reagent combination ([FWA] 30 μM g^{-1})	Whitener quantum yield (${}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$) (molecules quantum^{-1}) ($\times 10^{-4}$)	TRP quantum yield (${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}$) (molecules quantum^{-1}) ($\times 10^{-4}$)	Ratio (${}_{\mathrm{FWA}}\phi^{\mathrm{TRP}}/{}_{\mathrm{FWA}}\phi^{\mathrm{FWA}}$)
FWA/TRP	4.4	4.4	1.0
P2/FWA/TRP	2.2	0.9	0.4
NC1/FWA/TRP	4.2	1.0	0.2
HAL1/FWA/TRP	3.1	6.8	2.2
S1/FWA/TRP	3.7	1.9	0.5
DABCO/FWA/TRP	3.8	3.7	1.0

Exposure, near-UV; atmosphere, ambient air.

photodegradation. However, the presence of DABCO was not analysed.

The effect of the exposure atmosphere on TRP degradation in the presence of a whitener was assessed by exposing MC films containing TRP (20 μM g^{-1}) and the FWA (30 μM g^{-1}) to near-UV radiation. The exposure atmosphere was altered by purging the sealed quartz cuvette. The percentages of TRP retained after various exposures in oxygen, nitrogen and air are presented in Table 8. The results indicate that oxygen has a significant effect on the degradation of TRP by near-UV radiation in the presence of a whitener. A comparison of the results for 32 and 64 min exposures in oxygen and air indicates that a greater proportion of TRP is degraded in the saturated oxygen environment, i.e. after the atmosphere has equilibrated with the film. In an atmosphere of nitrogen, the degradation of TRP proceeds to a certain level and then goes no further. This could be explained by the fact that a residual amount of "dissolved" oxygen is present in the films, causing a certain amount of TRP degradation. When a saturated nitrogen atmosphere is present, the degradation of TRP is minimal.

Table 8
Effect of exposure atmosphere on TRP photo-oxidation in the presence of a whitener in MC films

Exposure time (min)	Oxygen (%)	Nitrogen (%)	Air (%)
32	76	97	76
64	62	91	70
96	52	92	64

Exposure, near-UV; purge, 15 min; results given as percentage of TRP retained.

Exposure of PVA films (a polymer impermeable to oxygen [20]) containing TRP in the presence of a whitener to near-UV radiation also demonstrates the importance of oxygen. Minimal TRP and FWA degradation occurs in this situation, even after extended irradiation for 6 h.

Similar results were obtained for films containing the FWA only [21]. Therefore it seems that oxygen acts as an intermediate in the photodegradation of both TRP [10] and the FWA.

A list of the possible sensitized photodegradation mechanisms for TRP in the presence of an FWA is given below. The discussion assumes that the involvement of $^1\mathrm{O}_2$ is accepted.

$$\mathrm{FWA} + h\nu \longrightarrow {}^1\mathrm{FWA}^* \qquad (1)$$

$$^1\mathrm{FWA}^* \longrightarrow \mathrm{FWA} + h\nu' \qquad (2)$$

$$^1FWA^* \longrightarrow {}^3FWA^* \qquad (3)$$

$$^3FWA^* \longrightarrow FWA + h\nu'' \qquad (4)$$

$$^3FWA^* + {}^3O_2 \longrightarrow FWA + {}^1O_2 \qquad (5)$$

$$^1O_2 \longrightarrow {}^3O_2 + \text{heat} \qquad (6)$$

$$TRP + {}^1O_2 \longrightarrow TRP\text{–}O_2 \qquad (7)$$

$$TRP\text{–}O_2 \longrightarrow \text{Degradation} \qquad (8)$$

In terms of the positive effect of antioxidants on the photosensitized degradation of TRP, the nickel chelate NC1, which is thought to be both an excited state quencher and a $^1O_2$ quencher [25], would be expected to have most effect on the reactions represented in Eqs. (5) and (7). However, in the absence of luminescence and oxygen consumption results, it is difficult to distinguish which effect predominates.

The antioxidant S1, which has a secondary function as a $^1O_2$ quencher [26], could be expected to have an effect on the mechanism represented in Eq. (7).

If the antioxidants P2 and S1 act as hydroperoxide decomposers [19,27], or purely as reducing agents, they would affect the reaction represented in Eq. (8). Since the norharman test for the amount of TRP retained after exposure is very specific to free TRP, it seems unlikely that the positive antioxidant effect noted for these reagents is due to this mechanism, unless they regenerate TRP after oxidation.

Another possibility is that $^1O_2$ reacts with the MC substrate, since the sensitized photodegradation of cellulose and its derivatives is well documented [28]. This reaction seems likely, and may explain the 1 : 1 ratio for TRP to FWA destruction found in this simplified film system, as opposed to a ratio of 7 : 1 found with a wool substrate [14]. It is also possible that the type of FWA used may have a significant effect [14].

Another possible mechanism must also be considered. The presence of long-lived transient species has been observed during the laser flash photolysis of PVA films containing the FWA (Uvitex NFW). It has been proposed that the transients are radical cations formed following monophotonic photoionization. The transient species have been shown to be quenched in the presence of TRP, perhaps via direct electron transfer [29]. The presence of reducing agents has been shown to have a significant effect on the lifetime of the transient species [29]. It seems reasonable that the same transient species may exist in MC films, since they appear to be insensitive to the presence of oxygen [29]. In terms of the positive effect of antioxidants, P2 and S1, which possibly act as reducing agents, could be expected to have an effect if this mechanism is operating. The nickel chelate NC1 would not be expected to have an effect in this situation.

4. Conclusions

No antioxidant/quencher tested had a significant positive effect on the direct photo-oxidation of TRP in TRP/ANTIOX films.

The significant effect of oxygen on the photodegradation of TRP in the presence of a fluorescent whitener was demonstrated. In anaerobic conditions, neither TRP nor FWA was degraded. The action of oxygen as an intermediate in the photodegradation of both FWA and TRP was demonstrated.

It was shown that $_{FWA}\phi^{FWA}$ and $_{FWA}\phi^{TRP}$ for TRP/FWA/ANTIOX films were independent of the FWA concentration in the MC films. It appeared that one TRP molecule was degraded for each FWA molecule destroyed.

The addition of antioxidants to films of this type showed that the antioxidant/quenchers P2, NC1 and S1 had a significant positive antioxidant effect on the sensitized TRP photodegradation.

Although a comparison is difficult, the contrast between the performance of P2 and NC1 in TRP/ANTIOX and TRP/FWA/ANTIOX films could be due to the fact that the mechanism of TRP degradation may change when the radiation wavelength is changed.

References

[1] R. Williamson, *Fluorescent Whitening Agents,* Elsevier Scientific, Amsterdam, New York, 1980.

[2] D.R. Graham and K.W. Statham, *J. Soc. Dyers Colour., 72* (1956) 434.

[3] I.H. Leaver and G.C. Ramsay, *Text. Res. J., 39* (1969) 730.

[4] F.G. Lennox and R.J. Rowlands, *Photochem. Photobiol., 9* (1969) 359.

[5] L.A. Holt and B. Milligan, *J. Text. Inst., 67* (1976) 269.

[6] L.A. Holt and B. Milligan, *Aust. J. Biol. Sci., 26* (1973) 871.

[7] L.A. Holt, B. Milligan, D.E. Rivett and F.H.C. Stewart, *Biochim. Biophys. Acta, II* (1977) 131.

[8] A.S. Inglis, I.H. Leaver and F.G. Lennox, *3rd Int. Wool Text. Res. Conf., Paris,* 1965, Section 2, p. 121.

[9] K.P. Ghiggino, *Ph.D. Thesis,* University of New South Wales, 1976.

[10] C.H. Nicholls and M.T. Pailthorpe, *J. Text. Inst., 67* (1976) 397.

[11] I.H. Leaver, *Text. Res. J., 38* (1968) 729.

[12] I.H. Leaver and G.C. Ramsay, *Photochem. Photobiol., 9* (1969) 531.

[13] L.A. Holt, B. Milligan and W.E. Savige, *J. Text. Inst., 68* (1977) 124.

[14] I.H. Leaver, *Photochem. Photobiol., 27* (1978) 451.

[15] I. Saito, T. Matsuura, M. Nakagawa and T. Hino, *Acc. Chem. Res., 10* (1977) 346.

[16] K. Gollnick, *Adv. Photochem., 6* (1968) 1.

[17] L.A. Holt, B. Milligan and L.J. Wolfram, *Text. Res. J., 45* (1975) 257.

[18] N.A. Evans, D.E. Rivett and P.J. Waters, *Text. Res. J., 46* (1976) 214.

[19] H.J. Heller, *Euro. Polym. J., Bratislava Suppl., 5* (1969) 105.

[20] F.E. Windover, in R.L. Davidson and M. Sittig (eds.), *Water Soluble Resins,* Reinhold, New York, 2nd edn., 1968, p. 52.

[21] P.D. Auer, *Ph.D. Thesis,* University of New South Wales, 1993.

[22] C.G. Hatchard and C.A. Parker, *Proc. R. Soc. London, Ser. A, 235* (1956) 518.

[23] J.G. Calvert and J.N. Pitts, *Photochemistry,* W.A. Benjamin, New York, 1966, p. 783.

[24] W.D. Denckla and H.K. Dewey, *J. Lab. Clin. Med., 69* (1967) 160.

[25] C.S. Foote, in B. Ranby and J.F. Rabek (eds.), *Singlet Oxygen Reactions with Organic Compounds and Polymers,* Wiley, Chichester, 1978, Chapter 11.

[26] D. Bellus, in B. Ranby and J.F. Rabek (eds.), *Singlet Oxygen Reactions with Organic Compounds and Polymers,* Wiley, Chichester, 1978, Chapter 9.

[27] J.C.W. Chien, *J. Polym. Sci. A1, 10* (1972) 1579.

[28] B. Ranby and J.F. Rabek, *Photodegradation, Photo-oxidation and Photostabilisation of Polymers,* Wiley, London, 1975.

[29] K.J. Smit and K.P. Ghiggino, *Dyes Pigments, 13* (1990) 45.