Chemical Engineering Journal 147 (2009) 391–398

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Effects of undoped and manganese-doped zinc oxide nanoparticles on the colour fading of dyed polyester fabrics

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ARTICLE INFO

Article history:
Received 8 August 2008
Received in revised form 8 November 2008
Accepted 14 November 2008

Keywords:
Zinc oxide
Nanoparticles
UV protection
Colour fading
Polyester fabric
Photo activity

ABSTRACT

This paper describes the effects of applying coatings of an acrylic polymer containing nanoparticles of zinc oxide (ZnO) on the fading rate in artificial sunlight of polyester fabrics dyed with disperse dyes containing anthraquinone and benzopyran chromophores. Factors affecting the transparency and UV absorbance of the coatings are discussed. Removing the UV component of sunlight with ZnO nanoparticles markedly decreased the fading rate of the dyes, provided the polymer/ZnO film was not in direct contact with the fabric. When the treatment was applied directly to the fabrics, however, the protection against colour fading was different for the two dyes studied. Whereas the rate of colour fading of a benzopyran dye, of relatively low lightfastness, was decreased by the polymer-ZnO film, the treatment increased the fading rate of the dye of higher lightfastness, based on anthraquinone. This effect has been attributed to the generation of reactive oxygen species (ROS) when ZnO is exposed to UV. The effect of decreasing the photoactivity of ZnO by doping with manganese has been examined. For the benzopyran dye, the UV protection was greatly increased, whereas a much smaller improvement was found for the anthraquinone-based dye.

1. Introduction

Textile materials are degraded by exposure to sunlight, particularly from the ultra violet (UV) component (below 400 nm). Degradation produces a decrease in physical properties, such as tensile and tear strength. The useful life of many dyed textile products exposed to sunlight is often limited, however, by rapid colour fading. This is particularly important because it can lead to fabrics being discarded well before their physical properties have deteriorated significantly. In some cases, the rate of dye fading can be decreased with organic UV absorbers, which are often used in conjunction with antioxidants or free radical quenchers [1]. The protection afforded by organic UV absorbers is, however, limited as they are sacrificial and are ultimately destroyed by the radiation they absorb.

An alternative approach is to use an inorganic UV absorber, such as zinc oxide (ZnO), which is generally less toxic than organic UV absorbers. The use of ZnO is also attractive because it has a broad UV absorbance in both the UVA (315–400 nm) and UVB (280–315 nm) regions. Although typical organic UV absorbers have a high absorbance in the UVA range, their absorbance tends to decrease sharply in the UVB region, particularly below 300 nm [2]. Furthermore, as ZnO is inherently more stable than organic UV absorbers, it would be expected to provide a protective effect over a much longer period than these compounds. ZnO has been used as a UV absorber in sun block formulations [3], to increase the UV protection factor of wool and cotton apparel fabrics [4–6] and in a UV resistant coating to protect Kevlar fabric against UV degradation [7]. Little work has been published, however, on the effect of nano-sized ZnO particles on the colour fading of dyed fabrics [2].

Unlike dyestuffs, ZnO has no specific affinity for textile fibres. It cannot, therefore, be applied to fabrics by conventional dye exhaustion methods, which rely on polar and nonpolar interactions between dyes and fibres for the transfer of the dye molecules from a solvent (usually water) to the surface and into the interior of the fibres. An alternative approach is to apply a layer of ZnO nanoparticles to the surface of a pre-dyed fabric, where the particles can prevent UV radiation from reaching the dye molecules inside the fibres. An important requirement is that the ZnO particles must not be easily removed from the fabric, for example by laundering or exposure to the environment. One possibility is to bind ZnO nanoparticles to the fabric surface with an acrylic polymer. This approach was used by Katangur et al. for UV protection of a Kevlar fabric [7] and by Yadav et al. as a functional finish on cotton fabric [8]. In the present study, we have investigated the effect of a surface coating of acrylic polymer containing ZnO nanoparticles on the fading rate in artificial sunlight of two

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doi:10.1016/j.cej.2008.11.032

dyes containing different chromophores. An advantage of this approach is that it offers the possibility of improving the lightfastness of fabrics that have already been dyed. The incorporation of ZnO nanoparticles in a polymer film can decrease its transparency. The extent to which this occurs is strongly dependent on the ZnO particle size [9] and can result in an unacceptable change in fabric appearance [2]. The effect of treatment with polymer and ZnO on the shade of the fabric has been measured.

Although nano ZnO is an efficient UV absorber, it is also photoactive and can generate reactive radicals (ROS) when exposed to UV radiation. The influence of ROS arising from the ZnO in the surface coatings will be described. The photo activity of ZnO can be reduced by doping with a transition metal [10]. Results will be presented on the effect of doping ZnO with manganese ions in reducing the UV fading of the dyes.

2. Experimental

2.1. Materials

Aqueous dispersions of nanoparticles of ZnO and manganese doped ZnO were supplied by Micronisers Pty Ltd. The particle size distribution of the dispersions was measured on a Malvern Mastersizer 2000. Band gap energies were determined by the method described by Shinde et al. [11]. The band gap of the undoped ZnO (65 nm) was 3.29 eV and that of the 3% manganese-doped ZnO was 3.32 eV.

An acrylic polymer (Nanocryl S), described in a patent (WO 2005/061602 A1), was used. A 100% plain weave polyester fabric (fabric weight 100 g/m^2) was provided by Bruck Textiles Pty Ltd. Samples of commercial disperse dyes (Disperse Red 60: C.I. 60756 and Disperse Red 277) were obtained from Concept Chemicals Australasia Pty Ltd. These dyes were selected because they contain chromophores of relatively high and low lightfastness. The lightfastness of a dye is quantified on a scale of 1–8, according to ISO 105/BO2, a ranking of 1 being the lowest and 8 the highest. Each step is double the previous one. Samples are deemed to have failed when a visible change in shade has occurred. Disperse Red 60 is based on an anthraquinone chromophore and has a lightfastness of 6–7 on polyester [12]. Disperse Red 277 is based on a benzopyran chromophore and has a lightfastness on polyester of 4–5 [12]. All products were used as received.

2.2. Dyeing method

Fabrics were dyed with 1% dye on mass of fabric (omf) in sealed pots in a Mathis laboratory dyeing machine at a liquor: fabric ratio of 20:1. The initial dye bath pH was adjusted to pH 5.5–6 with acetic acid. The liquor was heated at 2 °C per minute from 40 to 130 °C, where it was maintained for 60 min. It was then cooled at 2 °C per minute to 60 °C. The fabric was removed and rinsed in running water.

2.3. Fabric treatment

Fabric samples were treated with the acrylic polymer containing various amounts of the dispersions of ZnO nanoparticles by a pad-dry-cure method. After padding to a wet pick-up of 80% on the mass of the dry fabric, the fabrics were dried for 2 min at 120 °C and then the polymer was cured by heating for 1 min at 150 °C. The total concentration of polymer solids plus ZnO solids applied to the fabrics was 5% omf. Concentrations of ZnO are stated as a percentage omf.

2.4. Preparation of polymer/ZnO films on quartz slides

Quartz slides were coated, by a dip-drain method, with mixtures of the zinc oxide dispersions and acrylic polymer. The films were dried in an oven for 5 min at 120 °C. Multiple coatings were applied until the UV absorbance of the film was in the required range.

The UV absorbance and transparency of the films on quartz slides coated with acrylic polymer containing ZnO dispersion were determined with a Varian Cary 3 UV–visible spectrophotomer. The absorbance at a particular wavelength (A_λ) of the coated slides is defined as:

$$A_\lambda = \log_{10}\left(\frac{I_0}{I}\right)$$

where λ is the wavelength of the UV radiation; I_0 and I are the intensities before and after passing through the sample. From this equation, a UV absorbance of 2.8–3.0 is equivalent to a UV absorption >99.8%.

2.5. Surface characterisation

The surface of the fabrics was examined before and after treatment with a scanning electron microscope (SEM) (model: LEO 1530 FEG-SEM, Gemini, Germany). Atomic zinc was detected on the fabric surface by energy dispersive X-ray spectroscopy (EDS) with an ISIS Link Analytical instrument (Oxford Instruments, UK). An accelerating voltage of 5 kV was used at a working distance of 15 mm and an EDS collection time of 120 s. Six randomly selected points in the central area of each sample were analysed.

2.6. Measurement of dye fading

Dyed fabric samples were exposed for various times in a MBTF light box (Australian Standard S 2001.4.21–2006). Air at 65% relative humidity was circulated through the box by means of a fan. The temperature inside the box was 40 °C. Principal wavelengths of the light source in the UV region were 364, 271, 246 and 249 nm. The change in shade (fading) of samples following exposure was determined by measuring Delta *E* values with a Datacolor SF 600 Plus-CT Spectraflash spectrophotometer. This parameter is used to quantify the difference between two coloured samples [13]. Delta *E* values include the difference in lightness (*L*) between two samples and also the difference in the red–green (a) and yellow–blue (b) colour components, according the following equation [13]:

$$\mathit{Delta}\,E = \{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2\}^{1/2}$$

In general, Delta *E* values of 1 and above are visible by eye.

3. Results and discussion

3.1. Effect of particle size of ZnO on colour change produced by treatment of dyed fabric

Two dispersions containing ZnO nanoparticles of mean particle sizes 65 nm (Dispersion 1) and 100 nm (Dispersion 2) were used. The particle size distributions of these are shown in Fig. 1.

Fig. 2A shows the UV–vis absorbance of polymer films containing 65 and 100 nm ZnO nanoparticles, cast onto quartz slides. Quartz slides were used because this material has very low absorbance in both the UV and visible regions. This ensured that the UV/visible absorbance properties of the coated slides were due only to the acrylate/ZnO coatings. Both film thickness and ZnO concentration influence UV absorbance. The purpose of this experiment was not, however, to relate either of these parameters to UV absorbance, but rather to compare the % Transmission in the visible

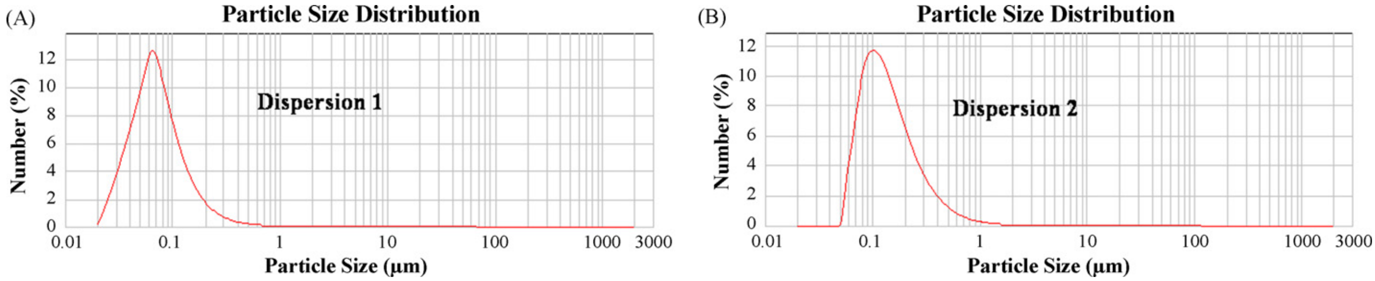

Fig. 1. Particle size distribution of zinc oxide dispersions.

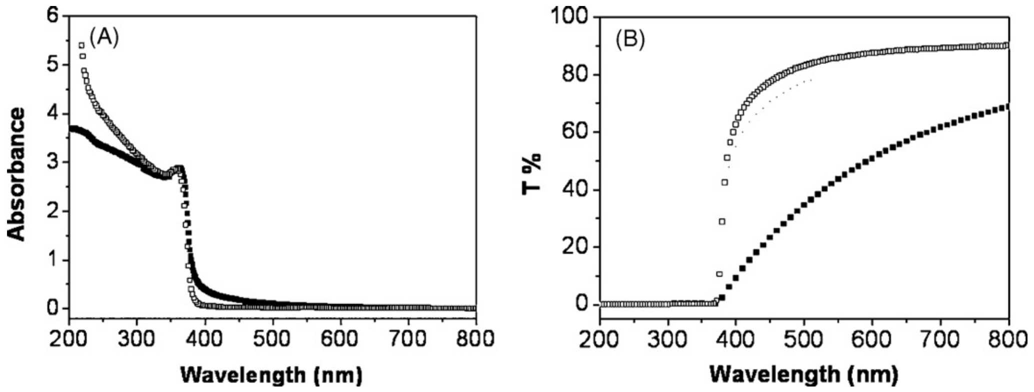

Fig. 2. UV–vis (A) and transmission (B) spectra of films of acrylic polymer containing. □ Dispersion 1 (65 nm) ■ Dispersion 2 (100 nm).

region (>400 nm) of films containing 65 and 100 nm nanoparticles that had high UV absorbance. Fig. 2A shows that the UV absorbance of the two coated slides was around 2.8, which was equivalent to a UV absorption of >99.8%. In both cases, the absorption edge was around 390 nm, which is just below the generally accepted threshold between the UV and visible region of 400 nm. Fig. 2B shows the corresponding transmission of the films, which is related to their visible transparency. Although Fig. 2A shows that both films had similar UV absorbances, Fig. 2B shows that the transparency in the visible region (>400 nm) of the film containing 65 nm ZnO particles was significantly greater than that containing 100 nm sized particles. This is reflected in the curves in Fig. 2A, which shows a slightly higher absorbance for the film containing 100 nm particles in the visible part of the spectrum up to around 500 nm. The difference in transparency of the two films was significant, as it was clearly visible. These results contrast with the conclusion of other workers that good UV shielding results in a reduction in the transparency of coatings [14].

One factor affecting the difference in transparency between the films containing different size particles relates to the scattering of visible light. Scattering increases with particle size. Therefore, for a given film thickness and ZnO concentration, the transparency of a film tends to decrease with increasing particle size.

A second factor relates to the inter-particle distance between the ZnO nanoparticles in the film. This distance increases with increasing particle size. For a similar mass of ZnO, the greater the spacing between particles the higher the amount of UV light transmitted through the film. Thus, in order to obtain films of similar UV absorbance, such as those used for the results in Fig. 2, films containing larger particles need to be thicker (and less transparent) than those containing the same concentration of ZnO of smaller particle size.

The transparency of coatings applied to dyed fabrics is important because the lower the transparency, the greater the effect on fabric appearance. Although some change in shade can be tolerated, a large change would be commercially unacceptable.

Application of transparent coatings to dyed fabrics will have some effect on shade, usually making them darker. Dyed polyester fabrics were treated with acrylic polymer or acrylic polymer containing 65 nm ZnO nanoparticles (1% omf). A total add-on of 5% solids omf was used as this was considered to be the upper limit for a fabric polymer treatment. Above this treatment level the handle of the fabric became unacceptable due to the stiffening effect of the surface polymer. Katangur et al. [15] have calculated that a film of 4 µm thickness containing 5% by weight of ZnO nanoparticles is required to completely block UV radiation. Although fabrics are not flat structures, we have used a similar approach to calculate that a treatment level of 5% polymer omf is expected to give a film thickness of around 2 µm. This is 50% of the thickness estimated to be required by Katangur et al. As we have, however, used films containing up to 20% ZnO by weight of ZnO nanoparticles (equivalent to 1% omf ZnO), this would be expected to more than compensate for the lower film thickness used in this study.

Table 1

Effect of treatment with acrylate and acrylate containing zinc oxide or manganese-doped zinc oxide on the shade change (Delta *E* value) of pre-dyed fabrics.

Dye	Delta *E* values between untreated and treated fabrics		
	Acrylate only	Acrylate containing undoped ZnO (1% omf)	Acrylate containing manganese-doped ZnO (1% omf)
Disperse Red 60	1.9	1.5	2.8
Disperse Red 277	3.9	1.8	2.7

The particle size of the undoped and manganese-doped zinc oxide nanoparticles was 65 nm.

Table 2
Delta *E* values of dyed fabrics after exposure to artificial sunlight for 300 h in MBTF light box.

Dye	Delta *E* after exposure	
	Fabric exposed directly	Fabric covered by a quartz slide coated with acrylate/ZnO
Disperse Red 60	5.7	1.2
Disperse Red 277	20.5	7.1

Table 1 shows that the change in shade (Delta *E*) of dyed fabrics produced by treatment with the acrylic polymer alone, or with polymer containing 65 nm ZnO nanoparticles, was small in both cases.

3.2. Effect on the colour fading of dyed polyester fabric of removing the UV component of artificial sunlight with a polymer/ZnO film

The effect of the UV component of artificial sunlight on the fading of the two dyes was determined by exposing dyed fabric beneath quartz sides coated with a mixture of polymer and 65 nm ZnO nanoparticles. This technique enabled the effect of the UV absorption property of the acrylate/zinc oxide films to be separated from other possible interactions with the dyed fabrics. As discussed above, the UV absorbance of uncoated quartz slides was negligible. Therefore, the UV absorbance of the coated slides (2.8 at 350 nm; equivalent to a UV absorption >99.8%) was due solely to the acrylate/zinc oxide coating. Similar fabric samples, not covered with coated slides, were exposed at the same time. Table 2 shows that although some fading occurred with both the covered and uncovered samples, the colour change was much smaller for the fabrics covered by the coated slides. These results show that, for both dyes, the UV component of the artificial sunlight was the major cause of fading. The results also show that transparent polymer films containing ZnO nanoparticles were very effective in protecting the dyed fabrics against sunlight fading. The small change in shade that occurred with samples exposed under the coated quartz slides can be attributed partly to the effect of the relatively low UV absorbance of ZnO in the region 390–400 nm, shown in Fig. 2A, and also to the effect of the visible component of sunlight (>400 nm). As exposure to the visible component cannot be attenuated without affecting the colour of a dyed fabric, the values in Table 2 are the best results that can be obtained with these dyes.

In order to establish whether the acrylic polymer gave any protection against UV fading, fabric samples were also exposed beneath slides coated with polymer, but without zinc oxide. Fig. 3 shows that the fabrics that were exposed under the coated slides and the fabrics that were exposed directly to the MBTF lamp faded at similar rates. It can be concluded, therefore, that in the absence of zinc oxide, the quartz slide and acrylic polymer had minimal effects on the results.

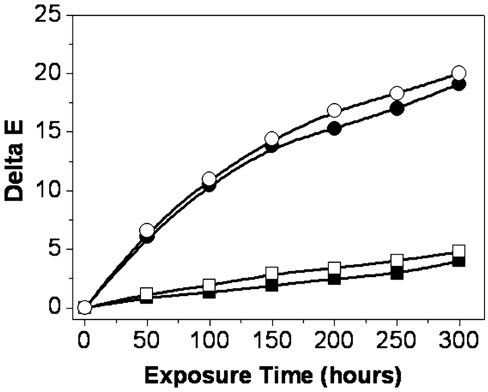

Fig. 3. Effect of acrylic polymer on the colour change after exposure in MBTF light box of untreated fabric dyed with Disperse Red 60 and Disperse Red 277.
☐ Fabric dyed with Disperse Red 60, exposed directly
■ Fabric dyed with Disperse Red 60, exposed under a quartz slide coated with acrylic polymer
○ Fabric dyed with Disperse Red 277.
● Fabric dyed with Disperse Red 277, exposed under a quartz slide coated with acrylic polymer.

Fig. 4 shows SEM images of a fabric sample dyed with Disperse Red 60, before and after treatment. It can be seen that the treatment produced a continuous film on the fabric surface. EDS curves confirm the presence of some zinc oxide nanoparticles on the fabric surface. The SEM images of the untreated fabric also show some large particles on the surfaces of the fibres, which are clearly not ZnO. Similar SEM images and EDS curves (not shown here) were obtained for the fabric dyed with Disperse Red 277.

3.3. Effect on colour fading of treatment of pre-dyed fabric with polymer and ZnO

Figs. 5 and 6 show the change in the shade, after exposure for various times to the MBTF lamp, of pre-dyed polyester fabrics, treated with polymer containing a range of concentrations of 65 nm ZnO nanoparticles (5% omf total add-on). Control experiments were conducted by exposing dyed, untreated samples covered with quartz slides that were coated with acrylic polymer and ZnO. The slides had UV absorbances and % Transmissions similar to those shown

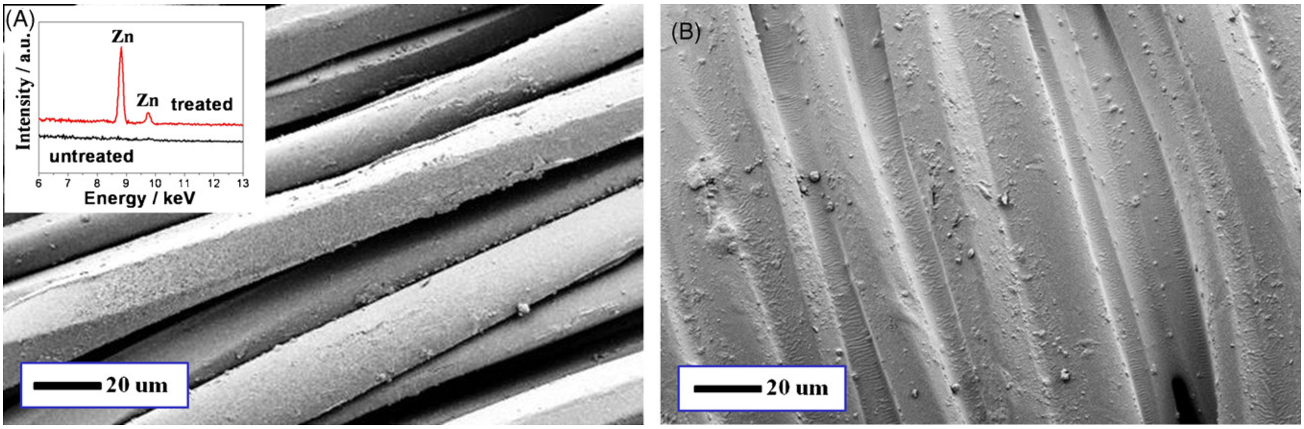

Fig. 4. SEM images of fabric dyed with Disperse Red 60 before and after treatment with acrylic polymer containing 65 nm zinc oxide nanoparticles (1% ZnO omf). The insert is the EDS plot of the fabric before and after treatment.

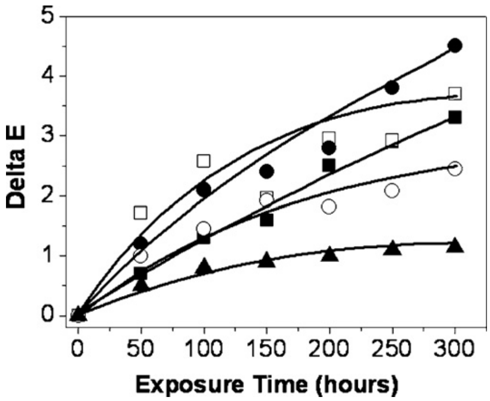

Fig. 5. Colour change after exposure of fabric dyed with Disperse Red 60 and treated with acrylic polymer containing various concentrations of zinc oxide.
■ Untreated; □ 0.5% ZnO omf; ● 0.75% ZnO omf; ○ 1% ZnO omf;
▲ Untreated fabric exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the coated slide was 2.8).

for 65 nm ZnO in Fig. 2. By exposing samples in this way we were able to investigate the effect of removing the UV component without any possible effects of direct interaction between the ZnO and dyed fabric. Fig. 5 shows that the untreated fabric, dyed with the anthraquinone dye (Disperse Red 60), faded at a lower rate when exposed under a coated slide than did the untreated fabric exposed without any covering. In general, however, no protection from colour fading was found for fabrics treated with polymer and ZnO and exposed directly to the MBTF lamp. Thus, for Disperse Red 60, the results for the treated fabrics exposed directly were in marked contrast with the findings for the untreated fabrics exposed beneath the coated slides. It can be concluded that for the polymer-ZnO coating to provide protection against the UV fading of Disperse Red 60, the coating must be separated from the fabric, in this case by a quartz slide. The data in Fig. 6 for the fabrics dyed with the benzopyran dyestuff (Disperse Red 277) also show that untreated fabrics covered with a coated quartz slide faded at a much lower rate than the treated samples that were exposed directly to the MBTF lamp. In contrast to the results for the anthraquinone dye, however, direct treatment with polymer and ZnO also decreased the fading rate of the dye based on a benzopyran chromophore.

For both dyes, concentrations of ZnO above 1% omf were also investigated (data not shown). This amount of ZnO was equivalent to a concentration in the polymer coating of 20% by mass. The results were similar to those obtained for the 1% omf level. It appears, therefore, that the inferior results obtained by direct fabric treatment compared with the protection obtained under coated slides were due to an interaction between ZnO and the dyes. Furthermore, the effect of the interaction on fading depended on the structure of the chromophore in the dyestuff molecule. A direct chemical reaction between the ZnO and dyestuff is unlikely because the dye is contained within the polyester fibres and the ZnO is in the acrylate film on the fibre surface. However, in order to eliminate this possibility, the following experiment was carried out. Quartz slides were coated with films of acrylic polymer containing the disperse dyes plus ZnO. Control slides were prepared without ZnO. The slides were air-dried and then heated under the conditions used to dry and cure the fabrics after pad treatment with acrylate and ZnO. The absorbance spectrum of the slides was measured after the air-drying and heating stages. It was found that the spectra, including the wavelengths of maximum absorption of the peaks, were identical in all cases. This shows that there was no direct interaction between zinc and the dyes, because if this had occurred a shift in wavelength of the absorbance spectra would have been obtained.

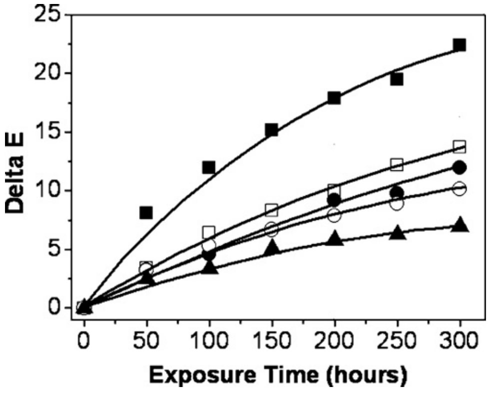

Fig. 6. Colour change after exposure of fabric dyed with Disperse Red 277 and treated with acrylic polymer containing various concentrations zinc oxide.
■ Untreated; □ 0.5% ZnO omf; ● 0.75% omf; ○ 1% ZnO omf.
▲ Untreated fabric exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the coated slide was 2.8).

Although the interaction between sunlight and dyes is very complicated, in most cases oxidative mechanisms are believed to be involved in reactions leading to dye degradation [16]. ZnO is known to be a photoactive material with a band gap energy of 3.2–3.3 eV [9,17]. When ZnO absorbs UV radiation, electrons are excited from the valence to the conducting band, with the generation of a positive hole in the valence band. The excited electrons and positive holes can recombine, with the generation of heat, or they can migrate to the surface of the ZnO particles, where they are able to react with water or oxygen to produce highly reactive superoxide and hydroxyl radicals (collectively called ROS), according to the equations below.

$$\mathbf{O_2 + e^- \rightarrow O_2^\bullet}$$

$$\mathbf{H_2O + h^+ \rightarrow HO^\bullet + H^+}$$

The results in this paper suggest that when polymer-ZnO coatings were applied directly to fabrics, the ROS migrated from the coating film on the fabric surface into the fibre, where they were able to interact with the dye molecules. This conclusion is supported by the results for exposure beneath slides coated with acrylate/ZnO films. In these cases, the slide prevented migration of ROS from the films into the dyed fabrics. It appears that dye chromophores vary in their sensitivity to ROS and, furthermore, that this may not be related to the inherent lightfastness of the dye, because Disperse Red 60 (lightfastness 6–7) was found to be more sensitive than Disperse Red 277 (lightfastness 4–5). This difference can be attributed to a difference in sensitivity of the two dye chromophores to oxidation. The chromophore in Disperse Red 277 may be more resistant to oxidation because its structure is based on benzopyran, which is similar in structure to coumarin. Compounds with coumarin-like structures are known to be effective antioxidants in some systems [18].

To confirm further whether the photo activity of the ZnO was related only to the UV component of artificial sunlight, dyed samples treated with a polymer-ZnO coating (1% omf ZnO), were exposed to the MBTF lamp beneath quartz slides coated with polymer containing 65 nm ZnO nanoparticles (UV absorbance 2.8). Slides with a ZnO coating were used to ensure a similar UV absorption spectrum to that of the coating applied directly to the fabrics. Samples of dyed, untreated fabric were also exposed beneath coated slides, and dyed and treated fabrics were exposed directly. The results for the two dyes are shown in Fig. 7. Both the treated and untreated fabrics that were covered with the UV absorbing slides faded at similar rates, whereas the treated fabrics that were exposed directly faded at a much faster rate. Thus, it can be concluded that

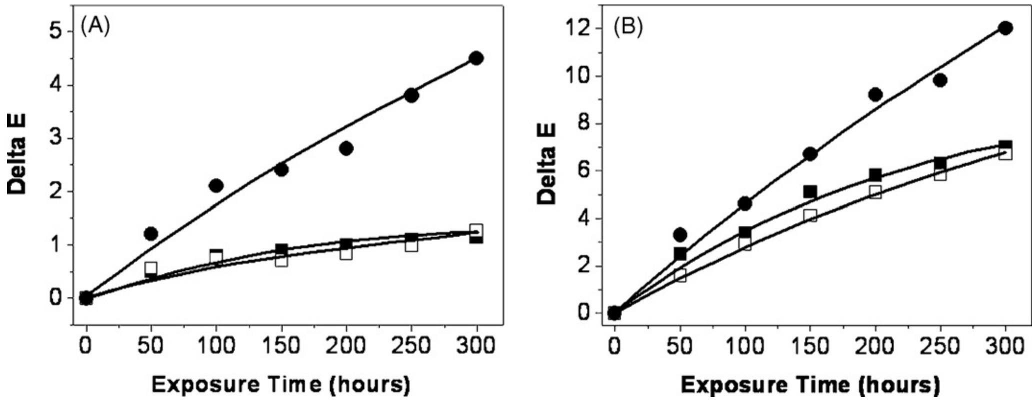

Fig. 7. Colour change after exposure of fabrics dyed with Disperse Red 60 (A) and Disperse Red 277 (B).
● Treated with acrylic polymer containing 1% ZnO omf – exposed directly. ■ Untreated fabric – exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the coated slide was 2.8) □ Treated with acrylic polymer containing 1% ZnO omf – exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the coated slide was 2.8).

for the benzopyran and anthraquinone dyestuffs, the photoactivity of the ZnO present on the fabric was due solely to the UV component of the artificial sunlight. This is consistent with the band gap energy of ZnO of 3.29 eV, measured for the 65 nm ZnO nanoparticles used in this work. From the equation, $E = hc/\lambda$ (where E is the band gap energy; h is Plancks constant; c the velocity of light; λ the irradiating wavelength), it would be expected that irradiation with wavelengths below 375 nm is required to induce photo activity. This is well within the UV region.

3.4. *Effect of manganese-doped zinc oxide on colour fading of dyed fabric*

Although nano-sized ZnO is a very good inorganic UV absorber, its photoactivity limits its application for improving the lightfastness of dyed textiles. The photoactivity of both titanium dioxide [19,20] and zinc oxide [10] has been decreased by doping with manganese. Dyed polyester fabrics were treated with acrylic polymer containing ZnO doped with 3 atomic % of manganese ions. As the photoactivity of ZnO varies with particle size [21], the particle size distribution and the mean particle size of the doped ZnO were measured. These were found to be identical to the values for 65 nm dispersion of undoped ZnO, shown in Fig. 1. Unlike unmodified ZnO, however, the manganese-doped product was brown in colour. This affected the optical properties of an acrylic film containing the doped material in the visible region. Fig. 8 shows that the UV absorbance was very similar to that of a film containing undoped ZnO, in Fig. 2. The transmission in the visible region of films of similar UV absorbance was, however, different from that of the film containing the doped material having a slightly higher absorbance in the range 400–500 nm.

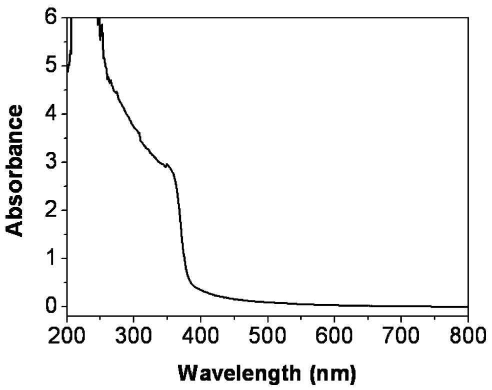

Fig. 8. UV/visible absorbance spectra of a film of acrylic polymer containing 65 nm nanoparticles of manganese-doped zinc oxide (3 atomic % manganese ions).

In view of the colour of the doped material, it was considered that its application to the surface of a dyed fabric might produce a significant change in shade. Table 1 shows that treatment with polymer containing 1% omf manganese-doped zinc oxide produced a larger colour change than did a similar treatment with undoped material. The colour change would be acceptable, however, for most applications. Figs. 9 and 10 give results for the fading of dyed fabrics treated with acrylic polymer containing various concentrations of Mn-doped ZnO. Fig. 9 shows that for the fabrics dyed with Disperse Red 277, the Mn-doped ZnO coating reduced the fading rate of the dyed fabrics significantly. For this dye, the level of protection obtained was as high as that of the dyed fabrics covered with a quartz slide coated with polymer and ZnO. For Disperse Red 60, Fig. 10 indicates that the doped product gave some protection at the highest ZnO concentration, which contrasts with the results for undoped ZnO in Fig. 6. In a separate experiment, it was found that dyed samples exposed beneath quartz slides coated with polymer containing either ZnO or manganese ZnO, of similar UV absorbance, gave the same level of protection against fading after 300 h of exposure. This showed that the small increase in the absorbance in the visible region of the manganese-doped material, compared with unmodified ZnO, was not responsible for its higher level of protection against dye fading.

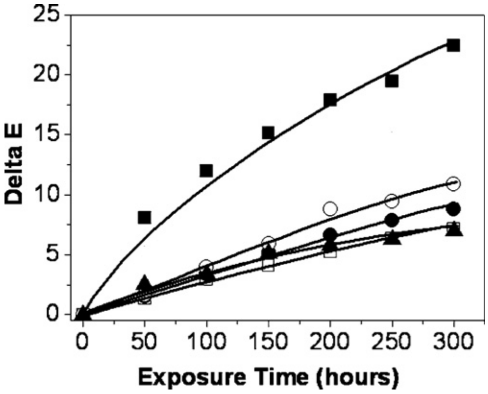

Fig. 9. Colour change after exposure of fabric dyed with Disperse Red 277 and treated with acrylic polymer containing various concentrations of manganese doped zinc oxide.
■ Untreated; □ 0.5% ZnO omf; ● 0.75% omf; ○ 1% ZnO omf. ▲ Untreated fabric exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the coated slide was 2.8).

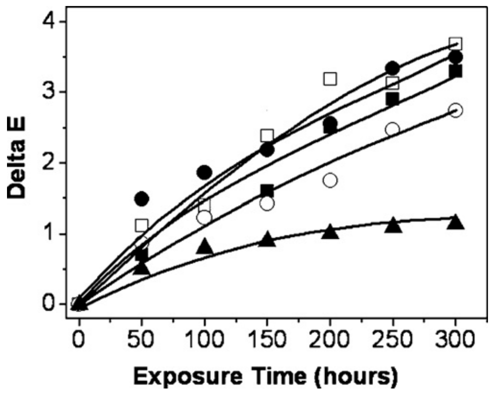

Fig. 10. Colour change after exposure of fabric dyed with Disperse Red 60 and treated with acrylic polymer containing various concentrations of manganese doped zinc oxide in MBTF light box.
■ Untreated; □ 0.5% ZnO omf; ● 0.75% ZnO omf; ○ 1% ZnO omf; ▲ Untreated fabric exposed under a quartz slide coated with acrylic polymer containing zinc oxide (UV absorbance of the film was 2.8).

When a photoactive material, such as titanium dioxide or zinc oxide nanoparticles, is doped with a transition metal, the dopant ions can be located in the metal oxide lattice [20]. These ions are believed to reduce the photoactivity of nanoparticles by acting as trap centre sites for recombination of the electrons and positive holes produced by UV radiation, before they can migrate onto the particle surface and generate ROS. For manganese-doped ZnO, however, studies involving channelling-enhanced microanalysis have shown that all the manganese ions are not fully incorporated on the zinc sublattice in ZnO nanoparticles [10]. In this case, some of the manganese ions may be located at or near to the surface. This situation would be less favourable for the manganese ions to act as trap centres, but would enable them to reduce photoactivity by other mechanisms. In the case of manganese-doped titanium dioxide, it has been shown that manganese ions close to the surface can act as scavengers for free radicals, such as ROS [20]. Manganese ions close to the surface of ZnO nanoparticles would be expected to have a similar scavenging effect.

Manganese can exist in a wide range of oxidation states and readily takes part in redox reactions. Reactions that could result in the scavenging of superoxide and hydroxyl radicals are shown below:

$$\mathbf{Mn^{2+} + HO^{\bullet} \rightarrow Mn^{3+} + OH^{-}}$$

$$\mathbf{Mn^{3+} + O_2{}^{\bullet} \rightarrow Mn^{2+} + O_2}$$

The effect of adding manganese ions directly to the polymer/ZnO treatment liquor was also examined. Similar fading rates were obtained, however, for fabrics treated with undoped ZnO, both with and without the addition of divalent manganese in the form of the acetate (3 atomic % Mn). This shows that, in this system, the manganese ions must be associated with the ZnO, either in the sublattice or on the surface.

Thus, there may be two mechanisms by which manganese doping improves the UV protection of ZnO nanoparticles in a polymer film applied to the surface of dyed fabrics. The first is by initiating the recombination of electrons and positive holes before they can reach the surface of the ZnO particles, and the second is by scavenging ROS that are generated at the surface.

It appears, however, that even a high doping level of 3 atomic % did not completely eliminate the photoactivity of ZnO and that some ROS were able to diffuse to dye molecules within the polyester fibres. Furthermore, the results show that some dye chromophores are sensitive to oxidative degradation at lower ROS concentrations than are others.

4. Conclusions

Transparent films of acrylic polymer containing zinc oxide nanoparticles can be produced with very high UV absorbance. The fading rate in artificial sunlight of two dyes, based on anthraquinone and benzopyran chromophores, on polyester fabric was significantly decreased when the UV component was removed by means of the polymer/ZnO films. The optimum reduction in fading rate was obtained only when the films were separated from the fabrics by a physical barrier, such as a quartz slide. When the polymer/ZnO coating was applied directly to the dyed fabrics, the level of UV protection depended on the dye. The sensitivity of a particular chromophore to oxidative degradation does not appear to be related to its overall lighfastness. Although the fading rate of the anthraquinone-based dye was not decreased by coating, the fading rate of the benzopyran dye was significantly lowered. These results have been interpreted in terms of the photoactivity of ZnO and the effect on different chromophores of reactive oxygen species generated by UV radiation. When the fabrics were coated directly with polymer and ZnO, the reactive species were able to migrate into the fibres and interact with dyes, whereas a barrier between the film and the fabric prevented this from occurring.

Doping ZnO with manganese (3 atomic %) has been found to improve the UV protection of the polymer/ZnO coatings on the dyed fabrics. The level of improvement was different for the two dyes studied, which shows that doping did not completely eliminate the photoactivity of ZnO nanoparticles.

These results show that conclusions on changes to the photoactivity of ZnO produced by various treatments, based on tests with a single dye, should be interpreted carefully.

Acknowledgments

We are grateful to the Australian Research Council and Micronisers Pty Ltd. for providing fund for this work.

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