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Nanoparticle Coatings for UV Protective Textiles

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ABSTRACT

As the intensity of ultraviolet (UV) radiation increases every year, effective methods to block UV rays to protect human skin, plastics, timber and other polymer materials are urgently sought. Textiles serve as important materials for UV protection in many applications. The utilisation of nanoparticles to textile materials has been the object of several studies aimed at producing finished fabrics with different performances. This article reviews the recent advancements in the field of UV blocking textiles and fibers that are functionalised with nanostructured surface coatings. Different types of UV blocking agents are discussed and various examples of UV blocking textiles that utilise zinc oxide (ZnO) and titanium dioxide (TiO_2) are presented. Future challenges, such as wash-fastness and photocatalysis, are also discussed.

Keywords: UV Blocking, Nanoparticles, UPF, Functional Coatings, ZnO, TiO_2

1. Introduction

The detrimental effects of ultraviolet (UV) radiation are having an increased impact on our society (Ramirez & Schneider, 2003).

UV light has wavelengths that range from 40 to 400 nm. Hence, its energy is sufficiently high enough to cause various damages to organic substances. The primary source of UV rays in nature is the sun. Since the stratospheric ozone layer shields most of the UV radiation from the sun, only the UV rays with relatively long wavelengths, i.e., UVB (290-320 nm) and UVA (320-400 nm) radiation, reach the Earth's surface. Yet, these UVA and UVB rays can still cause adverse effects onto our body and other organic materials around us. For example, UVA and UVB rays are responsible for the development of various pathologies, such as skin cancer, suppression of the immune system, cataracts, premature aging of the skin, Alzheimer's disease and inflammatory disorders (Ansel, 1985; Downes, 1993).

UV radiation can also cause severe damage in textiles, plastics, paints and timber products in the forms of discoloration, chalking and reduced mechanical properties. This situation is aggravated every year due to the recent ozone depletion caused by the increased generation of man-made free radical catalyst gas molecules, such as nitric oxide, nitrous oxide and organo-halogen compounds. Therefore, the development of effective UV-shielding materials is of great importance to our health, society and environment.

Textiles have been used in sun-shielding applications for centuries, owing to their unique characteristics, such as flexibility, good mechanical strength, soft feel, fashion appeal and so on. The World Health Organisation recommends that loose-fitting full-length clothing be used for outdoor activities to protect our skin from UV rays (World Health Organization, 2002).

The number of other UV-blocking applications of textiles, such as hats, awnings, and cover sheetings, has increased drastically in the last decades. Outdoor professionals and outdoor-sports practitioners have increased their awareness toward the importance of UV protection with textiles (Moehrle, 2000).

The UV blocking properties of textiles can be improved by changing the parameters, such as thickness, fabric opening, fiber types and colours (Dulęba-Majek, 2009).

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However, UV blocking provided by untreated textiles is generally insufficient to protect the skin (Hoffmann, 2001).

This is particularly true for light summer clothing that is worn in the season when UV light is stronger (Adam, 1998).

Moreover, textiles need to protect their own fibers and dyes from harsh UV radiation in addition to the skin and other materials that lie beneath the textiles (Katangur, 2006; Sun, 2008).

This "self-protection" is of particular importance when the exterior textiles require good mechanical properties, such as in applications as parachute, tent, awnings, etc. Self-protection of textiles cannot be achieved by altering the fabrication parameters, such as thickness, fabric opening, fiber types and colours. Hence, in order to protect both textiles themselves and the materials under the textiles, it is necessary to provide UV-blocking treatment to the textiles. This article reviews the recent advancements in the field of UV blocking textiles and fibers that are functionalised by using nanostructured surface coating technologies.

2. Ultraviolet Protection Factor (UPF)

For the assessment of UV blocking properties of textiles, "ultraviolet protection factor (UPF)" is normally used (AS/NZS 4399:1996; AATCC 183-2004; EN 13758-1:2002).

Like "sun protection factor (SPF)" which is used to evaluate the UV blocking effects of sunscreens, UPF is based on the erythemal action spectrum, i.e., the spectral range which causes skin redness. The definition of UPF is pretty much the same as that for SPF as shown in Equation (1):

$$UPF = \frac{\int_{\lambda_1}^{\lambda_2} E(\lambda) \cdot S(\lambda) d\lambda}{\int_{\lambda_1}^{\lambda_2} E(\lambda) \cdot S(\lambda) \cdot T(\lambda) d\lambda} \tag{1}$$

where E(λ) is the relative erythemal action spectrum, S(λ) is the standard solar spectral irradiance, and T(λ) is the optical total transmittance of the textile specimen. E(λ) and S(λ) are defined by the CIE International Commission on Illumination (CIE Research Note, 1987). UPF ratings indicate how much the textile material reduces UV radiation that causes skin reddening. For example, UPF 50 indicates that the UV rays in the wavelength range of E(λ) is reduced by 50 times.

In the past, it was considered that UVB rays are more harmful than UVA rays, as UVB rays cause sunburns and suntans. For many years, sunscreen lotions blocked only UVB rays and science was not clear on the body's reaction to UVA. However, recent research shows that UVA is the primary cause of premature skin aging (photo-aging), and exacerbates UVB's carcinogenic effects (Gasparro, 2000). Such findings help increase the awareness of the importance of broad spectrum UV protection.

UPF tests are normally carried out across both the UVA and UVB regions. However, E(λ) has very small values in the UVA range and is significantly high in the UVB range, as shown in Figure 1. Hence, UPF rating mostly reflects UVB protection instead of a broad spectrum UVA-UVB protection.

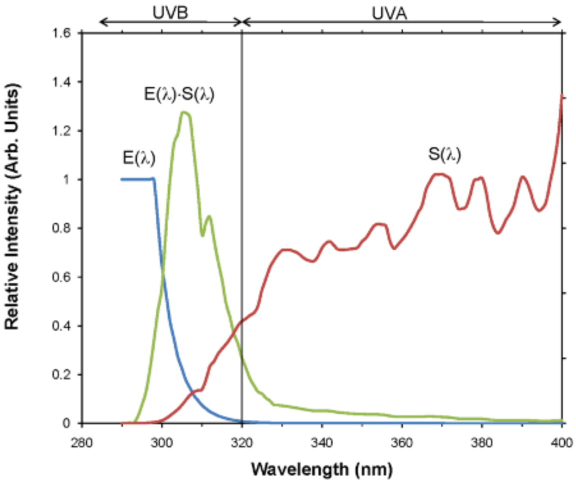

Fig. 1. Relative erythemal action spectrum, E(λ), standard solar spectral irradiance, S(λ), and E(λ)•S(λ) in the UV light region.

Currently, the textile industry does not use ratings for UVA protection. The personal care industry has started introducing new rating systems to assess broad spectrum UV absorption in the forms of "UVA/UVB ratio" and "critical wavelength" (Tadros, 2008).

It may be helpful to adopt similar parameters in the textile industry to assess the overall UV protection properties of fabrics.

The UPF values of a textile depends on the production conditions, such as fiber content and weave, fabric colour, finishing processes and the presence of additives. UPF values also vary depending on the post-production conditions, such as stretch, wear and moisture content. It is recommended that the minimum UPF values for UV-protective clothing should be 40 to 50+ (Adam, 1998).

However, an average weight cotton T-shirt that is often worn in the summer has an SPF value of only ~ 7, which offers a much weaker UV protection than any commercial sunscreen on the market (Adam, 1998).

As such, untreated textiles provide inadequate skin-protection (Palacin, 1997).

3. Nanoparticle UV Absorbers

3.1 UV Absorbers

The use of UV absorbers on textiles to improve UV protection of the skin, dyestuff and textile itself is a relatively new field of research (Hoffmann, 2001; Eckhardt & Rohwer, 2000; Palacin, 1997; Reinert, 1997; Hilfiker, 1996).

Nonetheless, many types of organic UV absorbers have been tested (Riva, 2006).

Organic UV absorbers are relatively cheap and generally transparent so that they can be used in many coloured fabrics and textiles (Ibrahim & El-Zairy, 2009; Scalia, 2006).

However, the majority of the organic absorbers are ultimately destroyed by the UV radiation they absorb and hence, the UV-absorption efficiency decreases over time. In addition, upon photo-decomposition of organic UV absorbers, free radicals are often generated, which contribute to the degradation of other organic molecules (Scalia, 2006).

Furthermore, organic UV absorbers are small sized molecules and can leach out from textiles, which may cause health problems once they contaminate food and drinks (Mahltig, 2005).

In contrast to organic UV absorbers, inorganic UV absorbers, such as zinc oxide (ZnO), titanium dioxide (TiO_2) and cerium oxide (CeO_2), have excellent light-fastness. It is expected that the inherent stability of inorganic UV absorbers would provide a UV protective effect over a much longer period than organic UV absorbers. The mechanism of UV absorption in these semiconductor inorganic materials involves the use of photon energy to excite electrons from the valence band to the conduction band. For example, ZnO has a bandgap energy of ~3.3 eV that corresponds to the wavelengths of ~375 nm. Light below these wavelengths has sufficient energy to excite electrons, and hence, is absorbed by ZnO. On the other hand, light with a wavelength longer than the bandgap wavelength will not be absorbed. The absorbed light does not destroy the inorganic semiconductors, but is generally converted to heat which is negligible at room temperature. Therefore, such wide bandgap inorganic semiconductors absorb UV light, and if small enough, give good transparency to visible light (Dodd, 2008).

Inorganic UV absorbers have other superior properties over organic UV absorbers. For example, ZnO has a long history of safe topical use and is known as an anti-irritant, astringent and skin-healing agent (Baldwin, 2001).

In addition, ZnO has broad UV absorption spectra while typical organic UV absorbers have UV absorption peaks only at a specific wavelength range due to the typical absorption bands of molecular systems (Figure 2) (Scalia, 2006, Mahltig, 2005).

In fact, ZnO is said to have the broadest spectrum absorption range among many inorganic UV absorbers (Figure 2) (Innes, 2002).

However, ZnO suffers from poor chemical stability. It can dissolve under both high and low pH conditions. TiO_2 has excellent chemical stability, but the UV-absorption range is narrower than ZnO so that it often relies on light scattering effects in addition to light absorption effects to block UV light.

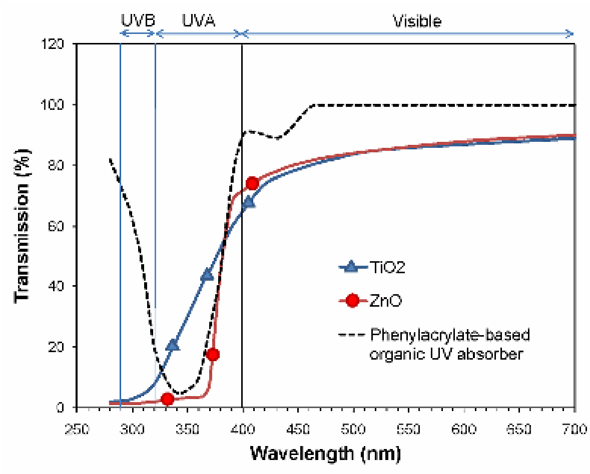

Fig. 2. Typical transmission spectrum of a TiO_2 nanoparticle suspension, ZnO nanoparticle suspension and phenylacrylate-based organic absorber solution. Note that the relative transmission values between the curves depend on the concentration of the UV blocking agents in the system.

3.2 Nanoparticles

Since inorganic UV absorbers are normally provided in particulate forms, it is difficult to obtain high UV-shielding properties while maintaining high visibility. Light scattering by small particles leads to an opaque whitening effect, much like the clouds in the sky that appear white due to light scattering by small water droplets, which may result in an unacceptable hazy appearance of textiles. This is of particular importance for applications on coloured fabrics. This problem can be overcome by reducing the particle size down below 50 nm, which is explained as follows.

The intensity of scattered light by a single particle is a function of the particle size as well as the refractive indices of the particles and the media. According to the Mie theory, when the particle size is small in comparison to the wavelength of light, the intensity of scattered light by a particle, *Is*, is given as (Kerker, 1969):

$$I_S \propto \frac{Nd^6}{\lambda^4}\left|\frac{m^2-1}{m^2+2}\right|^2 I_i \qquad (2)$$

where N is the number of particles, I_i is the intensity of incident light, d is the diameter of the particle, λ is the wavelength of incident light, and m is the relative refractive index defined as (refractive index of particles) /(refractive index of matrix). As shown in Equation 2, the intensity of scattered light is proportional to the sixth power of the particle diameter, and therefore, the particle size has a dominant effect on the strength of light scattering. Reducing the particle size will dramatically decrease the scattering. For a particle suspension with a constant weight percent of particles, Nd^3 is fixed in Equation 2 and the scattering intensity is proportional to the particle diameter to the power of 3.

Therefore, for decreasing the whitening effect, it is important to use particles as small as possible. Figure 3 shows UV-Vis transmittance spectra of ZnO nanoparticles with different average particle sizes. It is evident that smaller particles give higher transparency in the visible light region while the UV blocking property remains the same.

As shown in Equation 2, the refractive index is another important parameter which governs the intensity of scattered light. Most of the organic materials have refractive indices of around 1.4-1.6. TiO_2 (rutile) has a refractive index of 2.7. ZnO, however, has a refractive index of only 2.0. As such, the scattering intensity of ZnO is significantly smaller than that of TiO_2, provided that the particle size is the same, and hence, gives higher transparency than TiO_2.

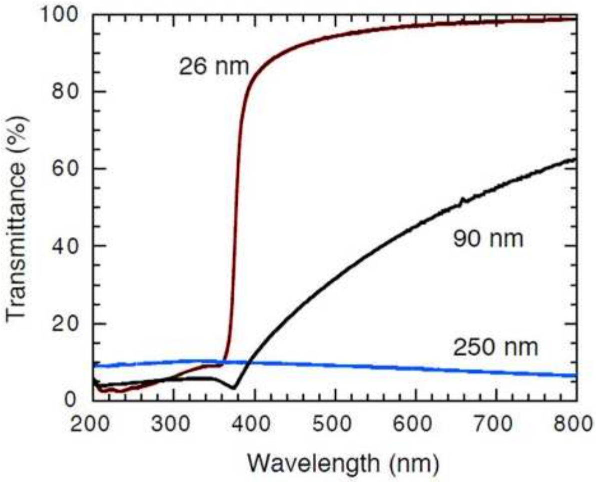

Fig. 3. Typical transmission spectrum of ZnO nanoparticle suspension in water at a particle loading level of 0.01 wt%.

By using nanoscale UV-blocking particles, it is possible to achieve high transparency while retaining good UV-absorption properties. The nanoscale diameters can also realize a uniform distribution of the particles in host matrices, which results in a significant increase in the effectiveness of blocking UV radiation (Dodd, 2008; Innes, 2002; Tsuzuki, 2002).

High surface area and high surface energy of nanoparticles are advantageous for better affinity to fabric surfaces which increases the durability of the coatings.

4. UV Blocking Treatment by Nanoparticles

Nanoparticles that contain functional coatings to achieve UV-blocking properties have been developed during the last decade. Such coatings have been applied in commercial products as sunscreens and paint systems (Spanhel, 2006).

In the textile industry, the last five years have seen the rapid development of UV-blocking treatment of textiles by means of nanotechnology. In most cases, TiO_2 or ZnO nanoparticles are used.

4.1 TiO_2 Nanoparticles

Xin et al. (2004) studied the improvements of UV blocking properties in cotton fabrics with TiO_2. The coating was prepared using a sol-gel method in ethanol. A thin layer of TiO_2 with a thickness of ~ 100 nm formed on the fiber surfaces. The films were not made of dispersed nanoparticulates, but were nanograined continuous films (Daoud & Xin, 2004).

Nonetheless, the UPF value of the cotton fabrics increased from 10 to 50+. The high UPF value was maintained even after 55 home launderings.

Direct synthesis of TiO_2 nanoparticles onto fabrics have been investigated by Fei et al. (2006) and Daoud et al. (2005). Fei et al. first synthesised nanosized TiO_2 particles which consisted of granular anatase and brookite, and rod-like rutile. Then, the peptized TiO_2 sols were adsorbed onto cellulose fabrics using a dip-pad-cure process. As a result, a homogeneous film of nanocrystallites that consisted of nanoparticles and nanorods of less than 100 nm, formed on the cotton fibers. The nanoparticles and nanorods covered the entire surface of the fibers, and there was evidently no agglomeration. A promising bactericidal photocatalytic activity and excellent protection against UV radiation were achieved (Fei, 2006).

Daoud et al. dipped knitted cotton substrates into a titanium tetraisopropoxide solution in absolute ethanol at a pH of 1–2 using a dip-pad-cure process. The process resulted in the formation of a uniform coating of TiO_2 nanoparticles with a near spherical grain morphology and 15–20 nm in diameter. The UPF value increased from 10 to 50+. Twenty repeated washings induced no deterioration in the UPF rating (Daoud, 2005).

The synthesis of TiO_2 nanoparticles often require solvent or expensive raw materials that leads to costly processes. Hence, the use of commercial TiO_2 nanoparticles has been explored.

Yu et al. (2008) developed a method where UV-blocking treatment is applied onto cotton fabrics by dyeing and finishing in one bath and two steps. Commercial nano-TiO_2 of ~ 50 nm in diameter was used as an inorganic anti-UV agent and an adhesive; poly vinyl pyrrolidone (PVP) was used to improve the wet fastness. Nano-TiO_2 and PVP were added into the dyestuff solution and applied onto fabrics at 70°C followed by washing, soaping, washing and drying. It was found that when the TiO_2 content was increased from 0% to 1.5% in the treatment solution, the UPF values increase from 15 to 35. They found that the treatment of nano-TiO_2 in this approach has little effect on the wearability of the cotton fabric.

Sójka-Ledakowicz et al. (2009) applied commercial nano-TiO_2 and aminosilane-modified nano-TiO_2 onto polyester using common techniques, such as padding, spraying and sol–gel coating. The average particle sizes were as large as 300 – 460 nm. UPF values of 50+ were obtained. The treated fabrics also showed high efficiency in the degradation of red wine stains.

Many of the commercial TiO_2 nanoparticles are sold as dry powders that mostly consist of agglomerated nanoparticles. This poses practical challenges in making well-dispersed nanoparticles in the coating system to fully utilise the advantages of nanosized particles.

4.2 ZnO Nanoparticles

The preparation of ZnO in pH-neutral conditions is relatively easier and cheaper than the synthesis of TiO_2. In addition, the UV absorption spectrum of ZnO is broader than TiO_2 (Figure 2). ZnO has additional functionality, including antifungal (Sawaji, 2004) and antistatic (Zhang & Yang, 2009) properties that TiO_2 cannot offer. Hence, the use of ZnO nanoparticles for UV-blocking functionalization has been investigated more widely than TiO_2.

Wang at al. (2004, 2005) studied sol-gel derived ZnO crystallites for the UV protection of textiles. Transparent solutions of zinc acetate and triethenamine in 2-methoxyethanol, equivalent to 3 wt% ZnO, was applied onto cotton fabrics twice, using a dip-pad-cure process, and followed by curing at up to 400^{o}C. Dumbbell-shaped ZnO crystallites that were larger than 500 nm were grown on cotton fabrics. When a curing temperature of at least 150^{o}C was employed, a UPF of more than 400 was achieved. The UV-blocking range was 352-280 nm. This finishing process provided a constant wash-fastness after a washing process that is equivalent to 5 cycles of home laundering.

Yadav et al. (2006) studied the improvements of UV blocking properties in cotton fabrics using ZnO nanoparticles. In their research, a simple method was used to coat fabrics with ZnO nanoparticles. ZnO was prepared by a wet chemical method using zinc nitrate and sodium hydroxide as precursors and soluble starch as a stabilizing agent. These nanoparticles, which have an average size of 40 nm, were coated onto bleached cotton fabrics (plain weave, 30 s count) using an acrylic binder. The nano-ZnO (2%) coated cotton fabric blocked about 75% of the incident UV light.

Vigneshwaran et al. (2006) developed a method to impregnate ZnO–soluble starch nanocomposites. ZnO nanoparticles of ~ 38 nm in diameter were synthesized using water as a solvent and soluble starch as a stabilizer from zinc nitrate hexahydrate and sodium hydroxide in water. Nano-ZnO was impregnated into cotton fabrics using a pad-dry-cure method. The coated fabrics showed enhanced protection against UV radiation; the transmittance at 350 nm was reduced from ~ 80% to ~ 20%.

Lu et al. (2006) encapsulated commercial ZnO of 20–100 nm in diameter with polystyrene cells using an emulsion method. First, ZnO nanoparticles were dispersed in an oil monomer phase and then the oil phase was dispersed in water as nanoemulsion droplets. The monomers were subsequently polymerized using an oil-soluble initiator. The size of the prepared nanohybrids spheres was 50–200 nm in shell diameters and 20–100 nm in core diameters. In order to increase the affinity of nanospheres on cotton fibers via ester bonding, methacrylic acid was selected as the co-monomer. After the formation of nanoemulsion, cotton fabrics were dipped into the ZnO suspension for 12 h at 68^{o}C, followed by polymerisation, drying and curing at 120^{o}C for 5 min. It was found that almost all fibers are coated with a grainy layer. A UPF of more than 900 and a wide UV-blocking range (380–280 nm) was achieved. However, the UPF value decreased rapidly from 86.6 to 15.3 after only 10 home launderings.

Becheri et al. (2008) produced peptised ZnO nanoparticles from zinc chloride and sodium hydroxide solutions and applied them onto cotton and wool fabrics. The wool and cotton samples were soaked for 10 min in a 2-propanol dispersion of ZnO nanoparticles (5% w/w), under gentle magnetic stirring. The clothes were then squeezed to remove the excess dispersion, and dried in an oven at 130^{o}C for 15 min at atmospheric pressure. The UV transmittance of the fabrics was reduced from ~ 90% to ~ 20% at ~ 350 nm. After 5 launderings, the large agglomerates were removed from the textile surface and more than 50% of their initial amount remained on the fabric, despite the fact that the nanoparticles were not covalently grafted to the fabric materials.

Mao et al. (2009) reported direct growth of ZnO nanoparticles on silicon dioxide (SiO_2) coated cotton fabrics. After hydrothermal processing, the cotton fabric was covered with needle-shaped ZnO nanorods that were ~ 24 nm in diameter. The coated fabrics had an excellent UV-blocking property with a UPF value over 50. However, the UPF was reduced to 50% of the original value after laundering 5 times.

4.3 Other Nanoparticles

Grancarić et al. (2009) applied natural zeolite nanoparticles of ~ 200 nm in diameter onto white cotton and polyester fabrics. Zeolites are porous aluminosilicate hydrates. They do not possess UV absorption properties, but can scatter or diffuse UV light as other white mineral particles. The textiles coated with zeolilte nanoparticles showed increased UPF values up to ~160. Although natural zeolites are yellowish, the coatings did not significantly affect the fabric whiteness.

4.4 Ash-Fastness and Adhesion

Wash-fastness is a particular requirement for textiles and strongly correlated with nanoparticle adhesion to the fibers (Becheri, 2008).

High wash-fastness is achieved by forming continuous coating layers of TiO_2 and ZnO (Yu & Shen, 2008).

For the use of nanoparticles, increased wash-fastness can be achieved by mixing nanoparticles with binders (Yadav, 2006; Vigneshwaran, 2006), or by forming covalent bonding between nanoparticles and fibers (Lu, 2006).

Otherwise, the UV protection properties decrease rapidly through laundering (Mao, 2009; Becheri, 2008).

Improvement of wash-fastness still remains as a great challenge for achieving practical UV blocking textiles by using nanocoatings.

4.5 Additional Functionality

Applications of TiO_2 and ZnO nanoparticles onto textiles provide additional functions apart from UV blocking abilities. TiO_2 and ZnO show antibacterial properties under UV irradiation. Vigneshwaran et al. reported that UV blocking textiles made of coatings that contain ZnO nanoparticles show excellent antibacterial activity against two representative bacteria, *Staphylococcus aureus* (Gram positive) and *Klebsiella pneumoniae* (Gram negative) (Vigneshwaran, 2006).

Yadav et al. found that the air permeability of nano-ZnO coated UV-blocking fabrics is significantly higher than the control sample, and hence, increased breathability (Yadav, 2006).

They also found that friction is significantly lower for nano-ZnO coated fabrics than bulk-ZnO coated fabrics.

ZnO has higher electric conductivity than TiO_2 and hence, gives antistatic properties (Zhang & Yang, 2009) and electromagnetic-filed-shielding properties (Li, 2007) to textiles.

In addition, self-cleaning properties can be achieved with TiO_2 nanoparticle coatings on fibers as widely documented. By combining different types of nanoparticles and nanotreatments on the surface of fabrics, multifunctional textiles will be realised. Recently, Beringer and Hofer demonstrated that by combining the nanoparticles of hydroxyapatite, TiO_2, ZnO and Fe_2O_3 with other organic and inorganic substances, the surfaces of the textile fabrics can be appreciably modified to achieve considerably greater abrasion resistance, water repellency, UV resistance, and electromagnetic- and infrared-protection properties (Beringer, 2004).

5. UV Protection of Fibers and Dyes in Textiles

Most of the above examples concern only UPF values where the protection of underlying materials, such as human skin, plastics and timber products, are considered. However, as mentioned earlier, textiles also have to protect fibers and dyes in themselves from harsh UV radiation. Colour-fading and deterioration of mechanical strength are serious problems in exterior textile applications. It is expected that coatings that contain inorganic semiconductor nanoparticles would significantly prolong the lifetime of outdoor textile products by effectively blocking UV rays on the fiber surfaces.

Katangur et al. (2006) used commercial ZnO and TiO_2 nanoparticles of 15 - 70 nm in diameter to protect Kevlar fabrics from sun-induced degradation. Kevlar fabrics were coated with 5 wt% nanoparticle-embedded acrylic coatings that were 20 μm in thickness. After a week of UV exposure, the coated fabrics retained 95% of their tear and tensile strengths, whereas unprotected fabrics retained only 67% of their original strengths.

Sun et al. (2008) investigated the use of ZnO nanoparticles dispersed in an acrylic polymer to reduce the colour fading of dyed polyester fabrics under simulated sunlight. Highly transparent films of polymer and ZnO mixture were produced and applied onto dyed polyester fabrics. The results showed strong dependence on the type of dyes. The coating treatment reduced the fading rate of a dyestuff that contains a benzopyran chromophore. However, it did not provide protection to dyes that contain anthraquinone or azo chromophores. Furthermore, the fabric treatment increases the rate of colour fading of anthraquinone based dyes.

Sun et al. made a finding which indicated that the inherent photocatalytic activities of TiO_2 and ZnO can be detrimental to the fabrics and dyes that TiO_2 and ZnO are supposed to protect (Dodd, 2008). When ZnO absorbs UV radiation, its band gap energy of around 3.2-3.3 eV allows electrons to be excited from the valence to the conducting band. The consequence of this is the generation of positive charged holes in the valence band. The excited electrons in the conduction band can either recombine with the holes in the valence band, or both can react with water or oxygen on the surface of the ZnO particle to produce reactive superoxide and hydroxyl free radicals. Due to their photocatalytic properties, TiO_2 and ZnO are used to decompose dyes in effluent or organic contaminants in water using natural sunlight. Direct treatment of fabrics with TiO_2 and ZnO nanoparticles may allow the free radicals to migrate from the coating film into the fibers, which would result in the degradation of dyes and fibers. So far, the degradation of fibers by the photocatalytic activities of TiO_2 and ZnO has not been fully investigated.

Currently, our research group is investigating the methods to reduce photocatalytic activities of TiO_2 and ZnO to fully utilise the superior properties of these inorganic nanoparticles as effective UV blocking agents. In general, two different approaches have been taken. One approach is to coat nanoparticles with inorganic materials, such as SiO_2 or aluminium oxide (Al_2O_3) (Wang, 2009).

This is based on the assumption that if the coating layer is thicker than the diffusion length of photo-exited electrons and holes, photo-generated excitons would be trapped within the coating layer so that free radical generation would be inhibited.

Recently, we successfully produced ZnO@SiO_2 core-shell structures using the Stöber method (Wang, 2009) and a microemulsion technique. The SiO_2-coated ZnO showed significantly reduced photoactivity in comparison to uncoated ZnO while maintaining high transparency and strong UV blocking properties (Figure 4a). It was also shown that the yellowing of wool fabrics is drastically reduced by the coating of SiO_2-coated ZnO nanoparticles.

Hence, the novel ZnO-core@SiO_2-shell hybrid nanoparticles offer promising nanocoatings for the UV-blocking treatment of textiles without colour-fading of dye-stuff on the textiles. A silica-layer also helps to overcome the poor chemical stability of ZnO.

Another approach is to dope nanoparticles with impurity ions. It is generally considered that dopant ions create chemical, and in some cases, physical defects in the crystal lattice that act as trapping sites of the photo-generated electrons and holes, which promote the recombination of the charged particles, and result in reduced photocatalytic activity.

Recently, the authors and collaborators investigated the photoactivity of manganese and cobalt doped ZnO nanoparticles synthesised by using various techniques. The photocatalytic activity of powders produced by mechano-chemical processing was evaluated using the spin-trapping technique with electron paramagnetic resonance spectroscopy (Dodd, 2009). It was found that the photocatalytic activity of $Co_xZn_{1-x}O$ nanoparticles progressively decreases with the doping level. In contrast, the activity of $Mn_xZn_{1-x}O$ nanoparticles initially increases.

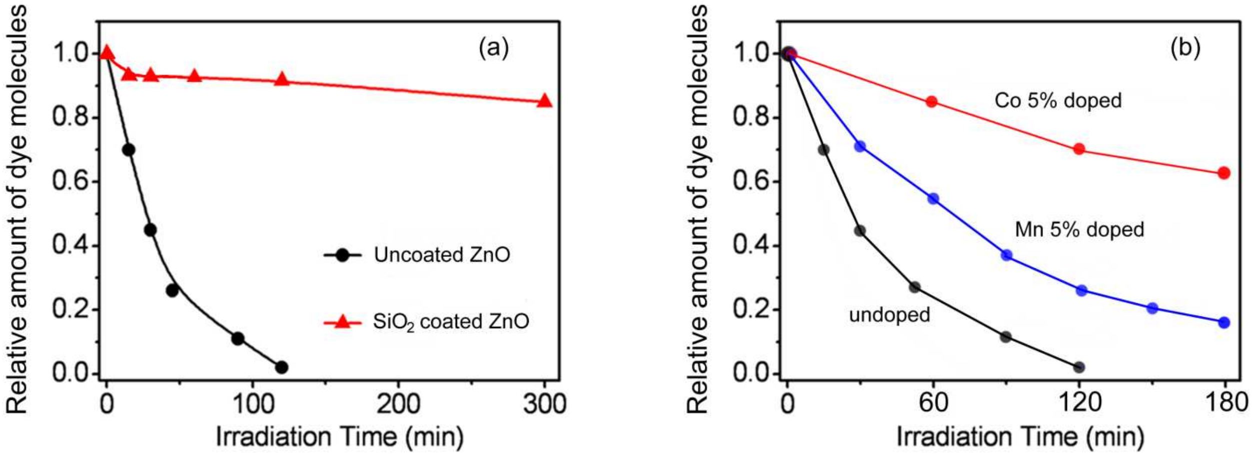

Fig. 4. Photo-degradation of Rhodamine-B dye molecules under simulated sunlight in the presence of
(a) uncoated and SiO_2-coated ZnO nanoparticles and
(b) undoped, Mn 5wt% doped and Co 5wt% doped ZnO nanoparticles.

with doping, up to a level of 2 mol% and thereafter declined. The effect of dopants on the photocatalysis of ZnO was found to be dependent on the synthesis methods. When $Mn_xZn_{1-x}O$ and $Co_xZn_{1-x}O$ nanoparticles were synthesised by co-precipitation methods, the nanoparticles show reduced photoactivity (Figure 4b).

We also studied the colour-fading of dyed polystyrene fabrics coated with undoped and manganese-doped ZnO nanoparticles (Sun, 2009).

It was shown that manganese doped ZnO, which were produced using a co-precipitation method, provide improved UV protection against colour-fading as compared to undoped ZnO. However, the level of improvement is different for the two different types of dyes. For a benzopyran dye, the colour fading is greatly reduced, whereas much less improvement is found for an anthraquinone based dye. Further research on the control of photocatalysis in ZnO is on-going at Deakin University for application in UV blocking textiles.

6. Summary

Textiles are important materials for protecting human skin and other materials from harsh UV radiation. However, untreated textiles have limited abilities to block UV light. Moreover, textiles lack the inherent ability to protect themselves against UV rays to avoid colour-fading and fiber-deterioration. Hence, it is important for textiles to be treated with UV absorbing agents. Organic UV absorbing agents have attractive features, such as low cost, high transparency and ease of application. However, they suffer from critical drawbacks, such as poor light fastness and toxicity. Inorganic UV absorbing agents have advantages over organic agents in terms of photostability and safety. High transparency can be obtained by reducing the size of particles to nanoscale. Nanosize particles offer additional advantages, such as enhanced UV shielding effect and higher affinity towards fiber surfaces.

In the past, UV blocking treatment of textiles by nanocoatings have been investigated mostly using TiO_2 and ZnO. Various techniques were studied to synthesise and apply nanoparticle coatings on cotton, polystyrene and Kelver fabrics. It was found that nanocoatings of ZnO and TiO_2 significantly increase the UV blocking properties. However, improvement of wash-fastness and control of the photoactivity of nanoparticles still remain as great challenges in achieving practical UV blocking textiles. We have made some progress in the development of the methods to reduce the photoactivity of ZnO nanoparticles using impurity doping and particle-surface coatings.

As the development of nanotechnology innovation progresses, more choices in commercial nanoparticles will be available on the market. By combining different types of nanoparticles and nanotreatments on the surface of fabrics, UV blocking textiles with multifunctionality may be realised.

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