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Photochromic Coloration of Wool Fabric

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Abstract: A method has been developed for producing photochromic wool fabric by applying a layer of hybrid silica containing a photochromic dye onto wool fibres. A number of different hybrid silicas were prepared by the sol-gel technique involving co-hydrolysis and co-condensation of alkyltrialkoxydimethylamines together with 3-glycidoxypropyltrimethoxysilane. With the dye Photorome II, it was possible to obtain a photochromic coating which showed fast optical response. The coating had only a slight effect on the fabric handle. The durability of the coating appeared to be acceptable, at least for fashion wear.

Key words: Photochromic fabric; Photochromic dye; Silica sol-gel; Surface coating; Durability; Washing durability; Abrasion durability; Bending modulus; Wool fabrics

1 Introduction

Photochromic dyes have been used in many different applications in industry[1, 2], these include ophthalmic lenses[3, 4], rewritable recording media[5-12], data storage[13,23] and sensors[24,28]. The main characteristic of photochromic dyes is that they change colour in the presence of ultraviolet light and revert to their original colour when the UV illumination is removed. The change in colour usually accompanies a physical transformation that increases the degree of conjugation in the dye molecule. On textiles, unique fashion effects can be obtained using the photochromic effect. Since the colour changes are triggered by absorption of UV light, the dyes also can have a UV protective function.

Several methods have been reported for preparation of photochromic textiles. The dyes are generally not very soluble in water but potentially can be applied to suitable synthetic fibres by conventional dyeing techniques for disperse dyes. However, dyed photochromic fabrics tend to have slow colour-transformation speeds, because the dyes become incorporated in rigid polymer matrices that physically hinder the photochromic transformations[29]. An alternative approach is to coat microencapsulated photochromic dyes onto textile surfaces, together with a suitable polymeric binder[30]. While good photochromic effects are obtained, the surface coating consisting of photochromic microcapsules and binder can affect the fabric handle.

Organic-inorganic hybrid silicas prepared by sol-gel methods contain many very small nano-sized pores. These pores can accommodate dye molecules and provide sufficient space for photochromic transformations to take place[31-34]. We have already demonstrated that photochromic wool fabric can be made by coating fibres with a hybrid photochromic silica which contains a photochromic dye[35]. However, the durability of these coatings was relatively poor.

The durability of a surface coating is determined by the mechanical strength of the coating and adhesion between the coating layer and the substrate. It has been reported that silicas containing epoxy groups have showed improved adhesion to many different substrates[36], and enhanced resistance to scratching[37]. In principle, the improved durability is due to increased covalent bonding between silicas containing reactive epoxy groups and wool which has amino groups on the surface of the fibres. Also, epoxy groups can self-crosslink, and this also may improve the mechanical properties of the crosslinked layer[38-41].

In this study, silicas containing a photochromic dye were prepared by co-hydrolysis and co-condensation of 3-glycidoxypropyltrimethoxysilane (GPTMS) with alkyl silanes, and applied to fabric by padding and drying. Chlorine/Hercosett treated, machine washable, wool was used for these experiments to determine the feasibility of producing shrink resisted photochromic fabrics. The optical properties and durability of the coating to washing and abrasion were examined.

2 Experiments

2.1 Chemicals

3-glycidoxypropyltrimethoxysilane (GPTMS), tetracetoxysilane (TAS), and the photochromic dye Photorome II, 5-chloro-1,3-dihydro-1,3,3-trimethylspiro- [2H-indole-2,3'-(3H)naphth[2,1-b][1,4]oxazine], were obtained from Aldrich. Octyltriethoxysilane (OTES) and vinyltrimethoxysilane (VTES) were obtained from Degussa, and ethanol was purchased from Asia Pacific Chemicals. All chemicals were used as received.
2.2 Fabric

The fabric used was an undyed, double jersey knitted interlock, construction of 245 grams per square metre, obtained from AIM Sports Pty Ltd, Australia. It was made from 19.5 Australian merino wool which had been chlorine/Hercosett treated to machine washable (Machine Wash) standards, in top form, by Michell Pty Ltd, Australia.

2.3 Spectrophotometry

Photochromic effects were measured with equipment consisting of a DH-2000-BAL UV-VID-NIR fibre optic light source (Mikropack) with balanced deuterium and quartz halogen lamps providing illumination in the wavelength range of 200-1100 nm, an Ocean Optics RPH1 specular optical fibre reflectance module fitted with a R400-7-UV-VIS reflection probe, an optical fibre UV-VIS spectrometer (SUB4000 UV-VIS, Ocean Optics) and a personal computer running SpectraSuite software (Ocean Optics). Absorption values ($A_0$) at the wavelength $\lambda$ were calculated according to the following equation:

$$A_\lambda = \log_{10}\left(\frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda}\right)$$

where $S_\lambda$ =sample intensity, $D_\lambda$ =dark intensity (with sources off), and $R_\lambda$ =reference intensity.

The photochromic colour effect was measured as the differential steady-state absorption, $\Delta A = A - A_0$ of the fabric, with (A) and without (A_0) UV irradiation (from the deuterium lamp), at the wavelength of maximum absorption in the visible wavelength range (620 nm for Photochrome II)

2.4 Optical response

The rates of appearance and disappearance of the photochromic effect were measured by recording the differential absorption at 620 nm, as a function of time, when the UV source was switched on and off. The optical response times for development and fading of the photochromic colour were characterized by the UV exposure periods to reach half of the saturated absorption ($t_{1/2}$) after the UV source had been switched on, and the time for the absorption to fall to half the saturated absorption value ($t'_{1/2}$) after the UV source had been switched off.

2.5 Durability of the photometric effect

The durability of the photochromic effect was measured:

- after the fabric had been washed in a washing machine, according to the method specified in Australian Standard AS 2001.4.15.C,
- after the fabric had undergone 1000 abrasion cycles in a Martindale test machine with a 9.0 kPa load on the fabric.

The durability of the photochromic effect was evaluated according to the following equation:

$$\text{Durability}(\%) = \frac{\Delta A_{2} - \Delta A_{1}}{\Delta A_{2}} \times 100$$

where, $\Delta A_1$ and $\Delta A_2$ were the differential absorption intensities of the photochromic fabric samples before and after the test, respectively.

2.6 Bending modulus

The bending modulus of the fabric samples was measured in the wale direction of the fabric by the cantilever method using a M003B Shirley Stiffness Tester, according to BS 3356 BS9073 part 7 and ASTM D1388.

2.7 Silica sol-gel preparation

Silica sol-gels were prepared by mixing a silane (OTES, VTES, GPTMS) or 1:1 mixtures of OTES or VTES with GPTMS, together with the acid catalyst, tetracetoxysilane (TAS), and ice cold water. The TAS/alkyl silane ratio was 1:32, the TAS/ethanol ratio was 1:10, and the TAS/water ratio was 1:100. The mixtures were stirred vigorously at room temperature for 24 hours. Then 10 ml of a 1% (w/w) solution of the photochromic dye in ethanol was added to 10 ml of each sol-gel solution and the mixture was stirred at ambient temperature for 20 minutes to give a homogeneous solution.

2.8 Fabric coating

Wool fabric (20 cm x 20 cm) was dip-coated with the dye-containing sol-gel solution and dried at room temperature. After heating at 110°C for 10 minutes, the fabric was kept at room temperature for 3 days.
3 Results and discussions

3.1 Optical properties

The optical differential absorption spectra of the photochromic wool fabric samples treated with silicas prepared from 1:1 mixtures of OTES/GPTMS and VTES/GPTMS are shown in Fig. 1.

![Differential absorption spectra of samples under UV irradiation](image)

**Fig. 1** Differential absorption spectra of samples under UV irradiation

The samples had no absorption in the visible region without UV irradiation but when the fabric was irradiated with UV light, a strong absorption spectrum appeared, with an absorption maximum at 620 nm\[35\].

As listed in Table 1, the differential absorption intensities varied slightly with the composition of the sol-gel, but all were in the range of 0.19-0.22. The mixed silanes gave treated fabric samples with the highest absorption values.

Typical plots of absorption with time, as the UV source was turned on and off, are shown in Fig.2 and the values of $t_{1/2}$ and $t'_{1/2}$ are given in Table 1.

![Colouring and decolouring curves of photochromic fabrics](image)

**Fig. 2** Colouring and decolouring curves of photochromic fabrics

<table>
<thead>
<tr>
<th>Silica type</th>
<th>$\Delta A$</th>
<th>$t_{1/2}$ (s)</th>
<th>$t'_{1/2}$ (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTES</td>
<td>0.19</td>
<td>5.1</td>
<td>8.0</td>
</tr>
<tr>
<td>VTES</td>
<td>0.19</td>
<td>6.9</td>
<td>9.9</td>
</tr>
<tr>
<td>GPTMS</td>
<td>0.19</td>
<td>6.4</td>
<td>3.2</td>
</tr>
<tr>
<td>OTES/GPTMS</td>
<td>0.21</td>
<td>1.4</td>
<td>1.9</td>
</tr>
<tr>
<td>VTES/GPTMS</td>
<td>0.21</td>
<td>3.1</td>
<td>4.9</td>
</tr>
</tbody>
</table>

The $t_{1/2}$ and $t'_{1/2}$ values of fabric treated with the sol-gel preparations containing OTES or VTES together with GPTMS were relatively small compared with those found with the single precursors. The smallest $t_{1/2}$ and $t'_{1/2}$ values were found with OTES/GPTMS silica coatings.

Pore size in the silica coating may have been a major factor that influenced retention and structural changes of dyes within the silica matrix\[42\]. Large pores lined with flexible residues (such as octyl and
glycidoxypropyl residues in the OTES/GPTMS silica) would be expected to provide space for the photochromic dyes to undergo relatively quick structural transformations and rapid colour changes. Too large a pore size might be expected to adversely affect the durability of the dye within the photochromic coating, because the dyes could more easily diffuse out of the silica during washing of the fabric.

2.2 Abrasion and washing tests

The abrasion and washing durability data are listed in Table 2.

<table>
<thead>
<tr>
<th>Silica type</th>
<th>Abrasion durability (%)</th>
<th>Washing durability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTES</td>
<td>59</td>
<td>37</td>
</tr>
<tr>
<td>VTES</td>
<td>55</td>
<td>43</td>
</tr>
<tr>
<td>GPTMS</td>
<td>73</td>
<td>48</td>
</tr>
<tr>
<td>OTES/GPTMS</td>
<td>73</td>
<td>61</td>
</tr>
<tr>
<td>VTES/GPTMS</td>
<td>85</td>
<td>84</td>
</tr>
</tbody>
</table>

The durability to abrasion of the photochromic silica coatings prepared from the single precursors, OTES and VTES, was relatively low. The durability increased when GPTMS was included in the silica preparations. The coating made from the VTES/GPTMS mixture showed better durability to abrasion than that made with OTES/GPTMS. This may have been due to crosslinking between vinyl groups of the VTES and epoxy groups of GPTMS, which produced coatings with improved mechanical strength but with smaller pores as indicated by the increased response times. It is also worth noting that the silica prepared from pure GPTMS did not show better abrasion durability than the coatings made from the alkyl silane and GPTMS combinations. Thus, increasing the content of epoxy groups in the silica did not always result in higher durability to abrasion.

The durability to washing of the photochromic silicas prepared from the pure silanes, OTES, VTES and GPTMS all had relatively low values. However, the silicas made from the mixtures of OTES/GPTMS and VTES/GPTMS both showed improved washing durability values. The improved durability to abrasion and washing in the samples containing GPTMS was probably due to:

- increased mechanical strength of the silica coating,
- improved adhesion between the coating and the surfaces of the fibres.

Fig. 3 SEM images of fibres on the surfaces of fabric samples (a) untreated, (b) after sol-gel (OTES/GPTMS) treatment, (c) treated fibres after 1000 abrasion cycles, and (d) treated fibres after washing.

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The appearance of wool fibres extracted from the fabric samples is shown in Fig.3. The surfaces of the fibres before the sol-gel treatment (Fig.3(a)) are relatively smooth and the scales are clearly visible but the scale edges are indistinct because of the treatment which the wool had received to make it shrinkresistant. In fact, each fibre was covered with a continuous layer of crosslinked polyamide epichlorohydrin resin, Hercosett 128\textsuperscript{[43]}. There should have been amino groups available at the surface for reaction with vinyl or epoxide groups on the silica. After the wool surface had been treated with sol-gel silica it became rougher and appeared to be covered with a layer containing some small particles, generally $\approx 1\mu m$ in diameter. After the abrasion and washing tests, parts of some fibres appeared to have become smoother, suggesting that at least part of the surface coating had been removed during the tests. Removal of the silica by abrasion under dry conditions in the Martindale machine is easy to understand in terms of mechanical attrition of the layer. However, it appeared that in the washing test abrasion may have occurred under wet conditions when the fabric samples were tumbled together while suspended in the wash liquor and this caused at least partial removal of the silica coating from some of the fibres. This could have been aided by the swelling and softening of the Hercosett polymer layer under wet conditions\textsuperscript{[43]}.

2.3 Fabric stiffness

Stiffness is a property associated with the comfort characteristics of a fabric. In this study, we used bending modulus to evaluate the fabric stiffness. A smaller bending modulus suggests a fabric should be softer and have a better handle. As can be seen in Fig.4, the bending modulus of the treated samples was higher than the untreated but the fabric treated with the OTES silica gave the lowest bending modulus. When GPTMS was added to OTES in the sol-gel preparation, the stiffness of the treated samples was only slightly less than with GPTMS alone.

![Fig.4 Bending modulus values of the sol-gel treated fabric samples](image)

4 Conclusions

It has been established that photochromic wool fabric can be successfully produced by sol-gel technology by dispersing a photochromic dye in sol-gel solutions made from suitable alkyl trialkoxysilane precursors, and applying these to fabric by padding and drying. An effective way to improve the durability of such a coating was found to be by adding 3-glycidoxypropyltrimethoxysilane (GPTMS) to the synthesis of the sol-gel. A silica made from a mixture of octyltriethoxysilane and GPTMS showed the best improvements in both the washing and abrasion durability. These improvements appeared to have been due to increased crosslinking within the silica and between the silica and the fibre surface. Faster photochromic optical response speeds were probably a result of larger pore sizes in the mixed hybrid silica. However, these improvements were accompanied by a slight increase in fabric stiffness.

Acknowledgements

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References