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Photochromic wool fabrics from a hybrid silica coating

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Abstract: In this work, a photochromic wool fabric has been prepared by applying a photochromic-dye hybrid silica sol-gel onto the surface of fabric. The photochromic fabric was found to have a very quick optical response. Two types of silica were used as the matrix material and the type of silica had a small effect only on the photochromic performance, the fabric washing fastness and water contact angle, but affected the fabric handle property considerably. The silica from a precursor containing a long alkyl chain showed very little influence on the fabric handle and better photochromic performance than that containing a phenyl group.

Key words: photochromic, wool fabrics, sol-gel technology, surface coating

0 Introduction

Photochromic dyes, undergoing a reversible colour change upon irradiation by UV light [1], have been used as smart colorants in a wide range of areas, such as ophthalmic lenses [2-4], printing materials [5-6], optical recording media [7], optical switches [8] and optical shutters [9]. Applying this functional dye to a textile will provide the textile with both a colour changing effect and a UV protective function. Such a textile may find applications in areas like fancy clothes and camouflage fabrics.

Several techniques have been used to apply a photochromic dye to textiles. For example, the photochromic dye can be inserted into the fibre matrix using a traditional dyeing technique [10]; or the photochromic dye can be first blended with a polymer and then extruded or wet spun into photochromic fibres [11]; also the photochromic dye can be mixed with a resin and surface coated onto fabric surface [5]. However, most of these techniques use an organic polymer as the matrix material. Because of its rigid nature, the polymer matrix restricts the configuration change of photochromic molecule [12]. As a result, the photochromic fabric usually has a poor optical response speed and a short cycling life time. In addition, the commercially available photochromic dyes are dispersible dyes. Applying these dyes to natural fibres, such as wool, cotton and silk, usually results in poor washing fastness.

Silica, a material containing a huge number of tiny pores, has been extensively used as a matrix material for hosting a variety of functional materials, such as TiO₂ nanofibrils [13] and enzyme [14]. Embedding the photochromic dyes into a silica matrix has been proven to improve the photochromic performance (e.g. optical response speed and cycling lifetime) [15], because these tiny pores provide free space for photochromic molecules to accomplish the configuration change. However, it has not yet been established if a photochromic dye containing silica can be used to create a thin layer of coating onto fibre surface such that the coated fabric shows improved photochromic effect.

In addition, little has been reported in the literature on the application of photochromic dyes to wool textiles.

In this paper, we report on using silica as matrix material for fixing photochromic dye onto the surface of wool fibres. We have found that when the photochromic dye is embedded into a silica sol gel and applied onto wool sur-
face, the hybrid silica sol gel is able to form a homogeneous coating that shows a very quick photochromic optical response and good fastness properties. The type of silica used affects both the photochromic performance and textile properties.

1 Experimental

1.1 Materials and instrument

Phenyltrioethoxysilane (PhTES), Tetracetoxyisilane (TAS), 5-chloro-1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-napth[2,1-b][1,4]oxazine] (photochromic dye) were obtained from Aldrich Co. Octyltrioethoxysilane (OctTES) was provided by Degussa. All chemicals were used as received.

1.2 Preparation of the dye hybrid silica sol solution and surface coating

The silica sol was prepared by mixing silane, tetracetoxyisilane (TAS), water and ethanol with the ratio of silane: TAS: ethanol: water at 1:1:10:7 (mol), and stirring intensively at room temperature for 24 hours. 0.5% of photochromic dye-ethanol solution was then added into the as-prepared silica sol solution (15ml) and stirred for 20 mins to give a homogeneous solution. A piece of wool fabric (20x20 cm²) was padded with this dye-silica sol solution and dried at the room temperature. The coated fabric was then cured at 110°C for 10 min.

1.3 Characterization

The optical absorption and optical response speed were recorded using an optical fibre UV-VIS spectrometer (SUB4000 UV-VIS, Ocean Optics). The washing fastness was tested according to Australian Standard (AS 2001.1.4). The flexural rigidity was measured by M003B Shirley Stiffness Tester, and the flexural rigidity $G$ (mg·cm) was calculated according to formula:

$$G = 0.10MC^2.$$

Where $M$ (g/m²) and $C$ (cm) are the mass per unit area of the fabric and the bending length, respectively.

2 Results and discussion

2.1 Photochromic effect

When the fabric was just irradiated by visible light, no new optical absorption was observed in the wavelength range of 450 - 800nm. However, once the fabric was irradiated by a UV light, a new absorption peak occurred with the absorption maximum at ~630nm. This absorption declined quickly when the UV irradiation was stopped. The visible absorption spectra of the photochromic fabrics before and after UV irradiation are shown in Figure 1 and the photochromic reaction is depicted in Scheme 1.

![Figure 1 Absorption spectra of photochromic fabrics](image_url)

When all operating conditions were kept the same, the silica materials used had little effect on the absorption maximum wavelength, but the optical absorption intensity in the range of 450 - 520nm and 670 - 800nm was a little different (Figure 1). The absorption maximum was listed in Table 1.
2.2 Optical response

At a given absorption wavelength (620nm), a real-time absorption intensity change during the UV irradiation is shown in Figure 2. The absorption is increased rapidly when the fabric is irradiated by UV light. Within 37 seconds, the absorption intensity reaches 90% of the saturated absorption. It takes another 115 seconds of UV irradiation for the fabric to reach its saturated absorption completely. When the UV irradiation is stopped, the absorption fades to its original colourless state within 2 minutes.

The period to reach the half value of the saturated absorption during UV irradiation, \( t_{1/2} \), can be used to express the optical response speed, and the period to reduce the optical absorption to its half value after stopping the UV irradiation, \( t'_{1/2} \), can be used to express the fading speed. The optical response speed and fading speed of the photochromic fabrics from two different silica materials are listed in Table 1. The silica from OctTES has faster responding and fading speeds than that from PhTES sol.

![Figure 2 Optical response curve of the photochromic fabric (PhTES sol).](image)

Table 1  Photochromic behaviour and fabric properties of the photochromic fabric

<table>
<thead>
<tr>
<th>Name</th>
<th>Silica precursor</th>
<th>Absorption (mg·cm)</th>
<th>Optical response ( t_{1/2} ) (s)</th>
<th>Fading speed ( t'_{1/2} ) (s)</th>
<th>Washing fastness (%)</th>
<th>Flexural rigidity (mg·cm)</th>
<th>Contact angle (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhTES</td>
<td>( \text{PhTES} )</td>
<td>0.24</td>
<td>14.75</td>
<td>54.25</td>
<td>38.16</td>
<td>192.89</td>
<td>1143.82</td>
</tr>
<tr>
<td>OctTES</td>
<td>( \text{OctTES} )</td>
<td>0.25</td>
<td>9.30</td>
<td>22.75</td>
<td>37.31</td>
<td>9.93</td>
<td>39.06</td>
</tr>
</tbody>
</table>

* The flexural rigidity of the control fabric is 9.22/28.52 mg·cm; ** The water contact angle of the control fabric was 126.54°.

2.3 Washing fastness of the photochromic fabrics

Washing fastness is a very important factor for evaluating the washing durability of the photochromic fabric. As shown in Figure 3, the optical absorption of the photochromic fabric is reduced after a standard repeat washing. The decrease in the absorption intensity can be used to express the washing fastness of the photochromic effect.

\[
\text{fastness} (\%) = \left( \frac{I_2}{I_1} \right) \times 100\%
\]

Here, \( I_1 \) and \( I_2 \) are the optical absorption intensities of the photochromic fabric before and after standard repeat washing, respectively.

The washing fastness of the photochromic fabrics using different silica matrix materials is also listed in Table 1. It indicates that the two silica materials lead to a similar photochromic washing fastness.

2.4 Flexural rigidity of photochromic fabric

![Figure 3 Optical absorption of the photochromic fabric before and after repeat washing (OctTES).](image)
The fabric flexural rigidity is an important factor that affects fabric handle. The flexural rigidity of the photochromic fabrics from different silica matrix materials is listed in Table 1. By comparison with the untreated fabric, the OctTES-treated fabric resulted in a slight increase only in the flexural rigidity value. This suggests that the OctTES coating treatment has little effect on the fabric handle property. However, the PhTES-treated fabric has much higher flexural rigidity value than both the untreated fabric and the OctTES-treated fabric, indicating an increase in fabric stiffness after the PhTES treatment.

2.5 Water contact angle

As shown in Figure 4, the water contact angle is increased when the fabric is treated by photochromic silica coating. The increase in the contact angle value suggests an increase in the fabric surface hydrophobicity. Also the type of silica used affected the contact angle value (Table 1). The silica containing a long chain alkyl such as OctTES led to a great increase in the contact angle value, while silica containing phenyl groups led to a smaller increase in the contact angle.

![Figure 4 Contact angles of (a) photochromic fabric (OctTES) and (b) untreated control fabric.](image)

2.6 The influence of the structure of sol

The effect of silica material on the optical response speed and flexural rigidity could derive from the silica network, the morphology of which is determined by the structure of its precursor. As illustrated in Scheme 2, the organic group affects the formation of pores and the pore size. The OctTES containing a long alkyl chain results in pores surrounded by flexible octyl chains, while phenyl groups in PhTES leads to a more rigid pore shell due to the rigid nature of phenyl groups. Within a pore with flexible shell, the photochromic molecule can easily undergo a photochromic reaction. Also the flexible chain of OctTES could lead to a flexible silica coating layer that has little effect on the fabric handle.

![Scheme 2 Dye hybrid organic silica sol networks.](image)

3 Conclusions

Photochromic wool fabrics can be prepared by a surface coating process using a photochromic dye-containing silica sol as the material. The highly porous structure of the silica matrix provides the photochromic dyes with free space to accomplish the photochromic reaction, thus leading to a very fast optical response to UV light. It has been found that the silica material used has an influence on the optical response speed, washing fastness, flexural rigidity
and water contact angle of the photochromic fabric. When the silica matrix is prepared from a precursor containing a long alkyl chain, the photochromic fabric shows excellent photochromic performance, and the coating treatment has little effect on the fabric handle, but leads to an increase in fabric surface hydrophobicity.

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References:

应用有机硅杂化涂层技术
开发光致变色羊毛产品

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(澳大利亚迪肯大学,材料与纤维创新中心)

摘要: 应用溶胶-凝胶(Sol-gel)工艺制备纳米多孔的光致变色有机硅杂化凝胶薄膜,涂抹于羊毛织物的表面,成功地研制了光致变色的羊毛织物。所得羊毛织物具有较快的光响应速度。两种有机硅材料被选为基质材料,实验表明,有机硅的种类对织物的光化学性质、耐水洗牢度和水接触角等性质的影响很小,但是对织物的手感有很大的影响。研究得出, 含有长碳链的有机硅材料对纺织品的手感几乎没有影响,并且比较耐用的有机硅原料表现出更好的光致变色效应。

关键词: 光致变色, 羊毛织物, 溶胶-凝胶工艺, 表面涂层