Photochromic Fabrics with Improved Optical Performance

By

Marzieh Parhizkar

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I am the author of the thesis entitled

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submitted for the degree of

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Signed .................................................. ........................................

Date .................................................. 12 June 2012.................................
Dedicated to my loving husband, Ehsan, for his support and encouragement throughout my PhD
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Publications list


Awards

- Acceptance of proposal by the Australian Synchrotron (AS) for beamtime at the SAXS beamline, 3 February 2011. Access to beamlines at the AS is limited and competitive, and the proposals undergo extensive review.
- Admission to and completion of the ANZAAS-Australian Synchrotron 2010 Winter School program, Melbourne, 12-15 July 2010. This program included highly specialised lectures on synchrotron science and practical sessions on beamlines. Only a limited number of attendants were admitted among many applicants.
- Deakin University International Research Scholarship (DUIRS), Australia, 2008.
Abstract

Photochromism has had many applications including sunglasses, optical devices such as memories and switches, and security printing. Photochromic textile is an exciting new application due to its implications for fashion and UV protection. The application of photochromic compounds to fibres and fabrics has recently been reported. However, in spite of their many advantages, the properties of the photochromic fabrics such as photostability and depth of colour require improvement. Moreover, while the pore microstructure of the silica matrix, in which the photochromic dye is encapsulated, greatly influences the properties of the photochromic fabric, little information is available on the pore structure of acid-catalysed silica coatings containing large non-hydrolysable groups. The aim of this PhD project is to improve the photostability and colour depth of photochromic fabrics prepared by a hybrid silica coating and study the relationship between the pore structure of the silica coatings and the photochromic properties of the coated fabrics.

In this study, three types of treatments have been applied to the photochromic fabric to improve photostability. These included incorporating different types of UV stabilisers in the silica coating, modifying the wettability of the coated fabrics, and sealing the matrix pores with silica to protect the encapsulated photochromic dye. The studied UV photo-stabilisers included a quencher UV stabiliser, two UV absorbers, and a free radical scavenger. All the studied treatments improved the photostability. Among them, incorporating a quencher UV stabiliser was the most effective. The next most effective treatment was sealing the matrix pores with a layer of (3-aminopropyl)triethoxysilane silica.
Modifying the wettability using fluoroalkylsilane was the least effective treatment.

Several techniques were employed to increase the depth of colour of photochromic fabrics. These included incorporating spirooxazine/cycloextrin complexes in silica coatings on fabric, changing the solvent, incorporating a surfactant, embedding spirooxazine in polymethylmethacrylate (PMMA) film, incorporating PMMA/silica copolymer in silica coatings on fabric, and embedding spirooxazine/PMMA particles in resin and silica coatings on fabric. Among the studied methods, embedding spirooxazine/PMMA particles in silica coatings on fabric led to the highest improvement in colour depth (102.4%).

The pore microstructure of the silica matrix was studied by small angle x-ray scattering (SAXS), nitrogen adsorption porosimetry, transmission electron microscopy (TEM), and atomic force microscopy (AFM). The SAXS study showed that the distance between pores was between 8.2 and 19.5 nm and increased with the size of the silica non-hydrolysable group. Nitrogen adsorption porosimetry led to 2.7 and 2.1 nm pore size measurements using the Barrett-Joyner-Halenda method, and 7.6 nm and 5.8 nm average pore diameters for phenyltriethoxysilane (PhTES) silica without and with dye, respectively. TEM revealed 0.43±0.14, 0.52±0.48, and 0.53±0.18 nm pore sizes for methyltriethoxysilane (MTES), vinyltriethoxysilane (VTMS), and PhTES silica, respectively. This suggested that pore diameter was linked to the size of silica non-hydrolysable group. AFM measurements showed an average pore diameter of 5.2±2.3 nm for PhTES silica. Maximum absorption was higher for silica containing a cyclic group or long alkyl chain or a combination
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CHAPTER ONE

1 Introduction

1.1 Significance and research question

Photochromism has found application in sunglasses and ophthalmic lenses, security printing, optical data storage, memories, optical switches, sensors, and displays. Developing photochromic textiles is an exciting prospect because of its implications for fashion and UV protection. There have been recent reports of applying photochromic compounds to fibres and fabrics. The methods involved in such applications have mainly included exhaust dyeing and screen printing, which often result in slow optical response or harsh fabric handle. Although silica coating through a sol-gel process has been previously employed to host photochromic compounds, the application of photochromic compounds to textiles by this method has not been reported until recently. Despite many advantages, the photochromic fabrics require improvement in photostability, depth of colour, and durability to abrasion and washing. Furthermore, the present knowledge of the microstructure of sol-gel coatings from silica precursors containing long alkyl chains is limited. Due to the strong dependence of the properties of silica-encapsulated photochromic compounds on the porous structure of silica, i.e. pore size and morphology, the study of pore microstructure is essential to improving the properties of photochromic silica coatings.

The research questions of this thesis are:
1. How can the photostability and depth of colour of photochromic fabrics prepared by a hybrid silica coating be improved?

2. How does the pore structure of the silica matrix affect the photochromic properties?

1.2 Specific aims

The lifetime of the photochromic effect in fabric with prolonged irradiation, or its photostability, is of great importance for practical applications. Free radicals have been identified as a major cause of degradation of photochromic compounds, as they readily react with the excited form of the chromophore [1]. Oxygen (in free or radical form) has also been linked to the photo-degradation of chromophores [2-4]. Different types of UV stabilizers can be used to protect photochromic compounds against photo-degradation [5, 6]. These compounds work via different mechanisms including quenching, free radical scavenging, and UV absorbing [4, 7-9]. The presence of moisture can also contribute to the deterioration of photochromic compounds [10]. Therefore, in this work three methods are employed for the purpose of improving photostability. These include incorporating UV stabilizers in the coating solution, modifying the coating’s wettability to reduce the exposure of the photochromic dye to moisture, and sealing the matrix pores by adding a protective layer in order to prevent harmful elements including oxygen radicals and moisture from accessing the encapsulated dye. Therefore, the first specific aim of this PhD project is:
Specific aim 1: improving photostability by incorporating UV stabilizers, modifying coating wettability, and sealing pores.

In order to achieve an obvious photochromic effect on textile, it needs to develop a deep colour when exposed to light. This means that the silica matrix needs to be doped with a large amount of photochromic dye. However, once a saturation point is reached in the matrix, further increase in dye concentration does not improve colour depth due to dye aggregation. Therefore, it is important to find ways of increasing dye loading while keeping the dye molecules separated from one another as much as possible. Creating host-guest inclusion complexes for dispersion in sol-gel can be a potential route for achieving this goal. Cyclodextrins with a large enough cavity, relatively hydrophobic interior and hydrophilic exterior are suitable candidates for hosting hydrophobic spirooxazine dye molecules. Furthermore, as different solvents have different abilities for dispersing the dye molecules, and the quality of dye dispersion greatly influences the depth of photochromic colour, the choice of solvent is also of importance. Surfactants due to their amphiphilic nature, i.e. hydrophilic heads and hydrophobic tails, can also potentially aid the dispersion of hydrophobic dye molecules and contribute to a higher colour depth. Due to the hydrophobic nature of spirooxazine dye, the incorporation of a hydrophobic polymer such as polymethylmethacrylate (PMMA) in the silica coating can help improve the dye’s affinity to the matrix and facilitate its dispersion [11]. Therefore, the second specific aim of this project is:

Specific aim 2: improving colour depth using a variety of techniques including host-guest complex formation between spirooxazine and cyclodextrin, examining the dispersing ability of different solvents, incorporating a
surfactant in the coating solution, embedding spiropihazine in PMMA film, incorporating photochromic dye in co-polymerised silica/PMMA sol-gel coating, and synthesizing spiropihazine-PMMA particles for dispersion in silica coating.

As the photochromic dye’s performance is greatly dependent on the amount of free space available to it, the shape and size of the hosting pores are key factors in determining the properties of the coated fabric. The microstructure of organically modified silica is greatly affected by the type of non-hydrolysable group. However, the studies in the field mostly concern silica modified with short-chain non-hydrolysable groups [12, 13]. Furthermore, the catalysis conditions of the studied sol-gel processes are mostly basic [14] or acidic-basic [15, 16]. In this work, the aim is to study the porous structure of acid-catalysed sol-gel silica from precursors containing different size organic non-hydrolysable groups. Small angle x-ray scattering, transmission electron microscopy, and gas adsorption porosimetry are important techniques for characterising micro- and meso-pores and are frequently employed together [17-22]. Wide angle x-ray scattering can be utilised for determining the crystallinity and crystal size of a material. Atomic force microscopy can be used to examine the surface morphology of a porous structure on the nanometre scale. Ellipsometric porosimetry is an optical technique which can also be employed for pore characterisation of thin films [23, 24]. Therefore, the third aim of this project is:

**Specific aim 3:** characterising pore structure using the abovementioned techniques and identifying the relationship between pore structure and photochromic properties
1.3 Outline of thesis

This thesis consists of seven chapters:

- Chapter 1 gives an introduction of the thesis including the research question and its significance in the context of the literature, and the specific aims of this study.

- Chapter 2 contains background information and a review of the literature on photochromism and its applications, properties of photochromic compounds, and sol-gel processing of silica.

- Chapter 3 gives information on the materials, sol-gel synthesis and coating, as well as characterisation methods used for silica coatings and photochromic fabric.

- Chapter 4 describes the treatments applied for improving the photostability of photochromic fabric and their effects on the photochromic, durability, and wettability properties as well as the stiffness of the photochromic fabric.

- In chapter 5, different methods employed for improving the depth of photochromic colour and their effects on the photochromic properties of the dye are described.

- Chapter 6 gives a description of the methods used for characterising the pore structure of sol-gel silica coatings, such as small angle x-ray scattering. The relationship between the pore structure of different photochromic silica coatings and their photochromic properties is also investigated in this chapter.
• In chapter 7, a summary of the main conclusions of this work and suggestions for future research are given.
2 Background and literature review

2.1 Introduction
In this chapter, photochromism, the applications of photochromic materials, the sol-gel process and method, and the pore structure of sol-gel derived silica matrixes are discussed.

2.2 Photochromism

2.2.1 Definition
Photochromism is defined in simple terms as a reversible light-induced colour change [25]. A more accurate definition would be: a reversible transformation between two forms of a chemical compound with different absorption spectra, caused in one or both directions by electromagnetic radiation. The reversibility of the reaction is stressed upon [25-27]. A typical photochromic reaction is given in Figure 2.1. Form A, which is the more thermodynamically stable state of the photochromic molecule, is transformed into form B by radiation. This reaction can be reversed thermally or photo-chemically [25]. If the back reaction occurs thermally, the process is referred to as T-type photochromism, and if driven only by irradiation with light (other wavelengths than UV), it is known as P-type photochromism [25, 28]. Photochromic reactions can also be categorized in another way. The most common photochromic processes are
known as *positive*, where form A is colourless and form B coloured. In some compounds however, *negative* photochromism is observed, where form A is coloured and form B colourless.

![Absorption spectra of A (colourless) and B (coloured) forms](image)

Figure 2.1 Absorption spectra of A (colourless) and B (coloured) forms [29] – Reproduced by permission of The Royal Society of Chemistry

The change in the molecular structure of the photochromic compound leads to changes in its physical properties, such as refractive index, electrical conductivity, and solubility [29, 30].

### 2.2.2 Historical outline

Photochromism was first reported in the literature by Fritsche in 1867, who observed a colour change in tetracene in the presence of light, and later by ter Meer in 1876, who observed this phenomenon in the potassium salt of dinitroethane. Later, Phipson reported that a gate post (covered with a zinc pigment) appeared black in daylight and white at night. Marckwald identified
the colour change behaviour of benzo-1-naphthyridine and tetrachloro-1,2-keto-
naphthalenone in the presence of light as a new phenomenon and named it
“phototropy”. Nowadays, this term is used to describe the behaviour of plants
towards light. The term “photochromism” was suggested by Hirshberg in 1950.
It consists of the Greek words “phos” meaning light, and “chroma” meaning
colour, and is a more accurate term for describing a reversible colour change.

Before 1921, most studies of photochromism were focused on synthesis and
properties of photochromic molecules (e.g. bleaching and fatigue). A decline in
the study of this phenomenon occurred in the 1930s. Photochromism came
back to attention in the 1940s. This time however, the focus had shifted
towards the mechanism of photochromic processes, the structure of
photochromic molecules, and the intermediate species formed in the
photochromic reactions. These studies benefited from technological advances,
as such characterisation tools as NMR and IR became available. The
introduction of photochromic sunglasses was a breakthrough in the 1960s. The
discovery of time-resolved spectroscopy made it possible to study transient
processes and excited states, and their lifetime and properties. More recently,
some typical photochromic compounds such as fulgides and spiropyrans were
thoroughly investigated, and novel photochromic compounds such as
spiroindolizines were discovered. In recent years, embedding photochromic
molecules in polymeric or other matrices has attracted great interest. Figure 2.2
shows the rapid growth of the research literature on photochromism since the
1990s. Most of the studies have been conducted in the chemistry area, followed
by physics and materials science (Figure 2.3). Other areas include
crystallography, optics, and polymer science. Photochromism is still an
inviting field of research, and further investigation could help develop exciting new applications [25].

Figure 2.2 The relationship between the number and year of publications concerning photochromism

Figure 2.3 Subject areas where photochromism is studied
2.2.3 Photochromic compounds and their photochromic processes

Photochromism is observed in both organic and inorganic materials, as well as in biological systems. Examples of inorganic materials exhibiting photochromic properties include metal oxides, metal halides, titanides, alkaline earth sulfides, transition metal compounds and natural minerals. Examples of organic photochromic materials include hydrazones, osazones, semicarbazones, anilines, disulfoxides, succinic anhydride, spiro compounds, and derivatives of stilbene, camphor, and o-nitrobenzyl. The photochromic processes on the abovementioned compounds mostly involve pericyclic reaction, cis-trans isomerization, intramolecular hydrogen or group transfer, dissociation processes, and electron transfer. Among the photochromic dyes developed, spiropyran, spirooxazines, naphthopyrans, diarylethene, fulgides, and azobenzenes are the most widely known classes. The typical structure of the abovementioned families of photochromic dyes and their photochromic reactions are given in Figure 2.4 [29].
Figure 2.4 Structures and reactions of some photochromic compounds; The different colours represent the different states of the photochromic dyes [29]. Reproduced by permission of The Royal Society of Chemistry

T-type photochromic compounds include spiropyrans, spirooxazines, naphthopyrans (or chromenes), and azobenzenes [28]. They are often used in industry, except azobenzenes which are not as commercially significant as the other three groups. P-type photochromic materials include diarylethenes (with heterocyclic aryl groups) and furylfulgides [31].

2.2.3.1 Spiropyrans

Spiropyrans (SP) are the most widely studied family of photochromic dyes. They are easy to synthesise, exhibit high colour depth, and bleach rapidly.
Their photochromic reaction involves opening the pyran ring upon UV exposure, leading to a coloured form called photomerocyanine (Figure 2.5).

![Chemical structure of spiropyran and photomerocyanine](image)

- Colourless spiropyran
  - R: alkyl
  - R', R": alkyl (usually both methyl)
  - X, Y: halogen, nitro, etc.

- Coloured photomerocyanine dye
  - (mixture of isomers - others not shown)

Figure 2.5 Mechanism of photochromism of spiropyrans – Recreated from [28]

The colourless and coloured forms of SP are both present at all times, and in equilibrium with each other. UV irradiation shifts the reaction in Figure 2.5 to the right, that is, towards generation of the merocyanine (MC) species, which appears as a deeper colour. In the absence of UV irradiation, the reaction is reversed to produce higher concentrations of the colourless species. This appears as colour bleaching. As heat can shift the equilibrium towards generation of the ring-closed, colourless pyran form, elevated temperatures can increase bleaching speeds, thus reducing the photochromic effect.

The shortcoming of the SP family of photochromic dyes is their relatively low resistance to fatigue. However, they are still used in applications that do not require high photostability, for instance, as probes or controls, in tensile stress sensors, and in photo-switchable magnetic devices [28].
2.2.3.2 Spirooxazines

This class of photochromic dyes is similar in its structure and photochromism mechanism to spiropyrans. However, it is superior to spiropyrans in terms of photostability. It is due to their relatively high fatigue-resistance that they were used in the first commercial plastic photochromic lenses. Simple spirooxazine compounds have a blue shade in their excited state, and bleach relatively quickly. Their shade in the excited state, as well as their photo-coloration/bleaching can be tailored by selecting suitable functional groups [28].

![Chemical structures of some commercial spirooxazines](image)

Figure 2.6 Chemical structures of some commercial spirooxazines—Recreated from [28]

2.2.3.3 Naphthopyrans

This class of photochromic compounds, also known as chromenes, has become the most important in commercial applications. This family of dyes also undergoes a ring opening transformation when irradiated by UV light (Figure 2.7). The chemical structure of naphthopyrans allows the economical incorporation of many types of substituents, thus permitting the tailoring of photochromic colour, kinetics, and stability (Figure 2.8). The photostability of commercially available naphthopyrans is comparable to other classes of photochromic dyes. Furthermore, they are less heat-sensitive compared to
spirooxazines. This is why it has been used in the formulation of all marketed plastic photochromic lenses [28, 32].

![Diagram of spirooxazine structure](image)

**Colourless [2,1-b]naphthopyran**
X, Y: H, alkoxy, amino, etc.
R: H, amino, etc.

**Coloured dye; typically yellow, orange or red (mixture of isomers; others not shown)**

Figure 2.7 The ring opening mechanism of photochromism of naphthopyrans – Recreated from [28]

![Diagram of photochromic effect](image)

**Major kinetic and colour effects**

**H3CO**

**OCH3**

**Major kinetic and minor colour effects**

Figure 2.8 Effects of the insertion of different functional groups on the properties of a naphthopyran – Recreated from [28]
2.2.3.4 Diarylethenes

Diarylethenes (with heterocyclic aryl group) belong to P-type photochromic dyes. In other words, their photochromism is thermally irreversible. Furthermore, diarylethenes exhibit high levels of fatigue resistance, meaning they can undergo coloration/bleaching more than \(10^4\) times. It is due to these properties that they are suitable for applications in optical devices such as memories and switches [31]. Diarylethenes undergo a ring-closing reaction when stimulated by UV light [33]. The open form is thermally stable, while the thermal stability of the closed form depends on the type of aryl group.

![Figure 2.9 The ring-closing photochromic process (or photocyclization) of a diarylethene – Recreated from [34]](image)

![Figure 2.10 The spectral changes of a diarylethene derivative during conversion between the open and closed forms [33] – Reprinted by permission of SPIE](image)
2.2.3.5 Fulgides

These photochromic compounds exhibit photochromism with the same mechanism as diarylethenes, i.e. photocyclization. In other words, UV light triggers a reaction which converts the open colourless form to the closed coloured form. Fulgides belong to the P-type category of photochromic dyes. They were initially thermally reversible, but gained thermal irreversibility later, in the 20th century [35]. This means that once activated, fulgides tend to remain in their closed-ring, coloured state, unless they are irradiated with visible light. This feature facilitates the application of fulgides in optical devices, such as memories and switches. Furthermore, unlike spiropyans and spirooxazines, fulgides are photochromic in their solid form [28].

![Fulgide Photochromic Process](image)

Figure 2.11 The photochromic process of a fulgide – Recreated from [34]

2.2.3.6 Azobenzenes

The mechanism of photochromism of azobenzenes is trans-cis isomerization (Figure 2.12). The trans form is commonly referred to as “E”, and the cis form as “Z”. Azobenzenes are thermally reversible, meaning the Z isomer can be transformed into the E isomer by means of heat (or visible light). Azobenzene compounds generally have a yellow to red colour [25].
2.3 Photostability of photochromic dyes

Pardo, et. al. [36] embedded two naphthopyran photochromic compounds in different organically modified silica (or ormosil) coatings prepared via the sol-gel method. The preparation of their coatings is illustrated in Figure 2.13. RTES and TAS represent the silica precursor and catalyst, respectively.

They measured the photostability of their samples by subjecting them to UV irradiation with an intensity of 8.9 mW/cm$^2$. They investigated the effect of the amount of organic substituent (i.e. phenyl) in the silica precursor on the photodegradation of photochromic ormosil coatings. The results indicated that by increasing the amount of organic substituent, photostability was improved (Figure 2.14). However, there was a limit to this improvement. Samples with a ratio of organic group to silica (R:Si) of 0.3 or higher exhibited similar levels of photostability. The authors attributed the higher degradation rate of the dye
in matrixes with lower than 0.3 R:Si ratios to the lower porosity of these matrixes which drove the photochromic dye molecules towards inhabiting OH-rich pores. The OH groups have higher polarity and therefore stabilize the open form of the naphthopyran dye, speeding up its photo-degradation. On the other hand, once the R:Si ratio is increased to 0.3 or higher, the majority of dye molecules are already residing in phenyl-rich pores, and thus the photostability does not improve any further.

![Graph showing the effect of different phenyl groups on photo-degradation](image)

**Figure 2.14** The effect of the amount of phenyl groups on the photo-degradation of ormosil coatings – Reprinted from [36], Copyright (2009), with permission from Elsevier

The authors also studied the effect of different types of organic groups on the photostability of the coatings (Figure 2.15). The results indicated that photostability was higher for silica coatings modified with larger organic substituents. 113 hours of UV irradiation was required for the loss of 30% of the photochromic effect in silica matrixes modified with phenyl groups, whereas this took 20 hours in the case of matrixes modified with ethyl groups. The authors attributed this to the lower polarity induced in the pores of
matrices modified with larger organic groups, which promotes the longevity of the photochromic dye.

Figure 2.15 The effect of different types of organic substituent on the photodegradation of ormosil coatings – Reprinted from [36], Copyright (2009), with permission from Elsevier

In another work, Pardo, et. al. [37] investigated the effect of dye loading on the photostability of phenyl-modified silica coatings containing naphthopyran dye, and reported an increase in photostability with dye content (Figure 2.16). They attributed this to the reduction of dye interaction with pore walls at high dye loadings. Furthermore, high dye contents have a screening effect which hinders photo-degradation.
Figure 2.16 Effect of dye loading on the photo-degradation of phenyl-modified silica coatings containing naphtopyran dye – Reprinted from [37], Copyright (2008), with permission from Elsevier

Misura, et. al. [5] reported that a photo-stabiliser system consisting of a mixture of organic anti-oxidant compound, UV light absorber, and hindered amine light stabiliser, helped to reduce the photo-degradation of naphtopyran photochromic dye from 43% to between 21%-27%. UV absorbers have also been reported elsewhere [6] to have improved the photostability of a spirooxazine photochromic compound in coatings consisting of an epoxy-silane as precursor, an organic spacer based on bis-epoxide, an amine-based thermal cross-linking agent, and SiO₂ nanoparticles as surface modifier.

Matsushima, et. al. [38] reported that sealing fulgide-containing sol-gel silica films with an adhesive helped to improve the photochromic photostability owing to reduced exposure to oxygen (Figure 2.17).
Figure 2.17 The process of sealing films with adhesive - Reprinted from [38], Copyright (2001), with permission from Elsevier

Hou, et. al. [10, 39, 40] investigated the photostability of a spirooxazine compound embedded in a silica sol-gel matrix exposed to UV irradiation with an intensity of 60 mW/cm² and reported that while the incorporation of additives such as sodium fluoride (NaF) and sodium acetate (NaAc) did not markedly improve photostability, the addition of 1-methyl-imidazole (MI), fluoro-alkyl silane (FAS), and bis-phenol A (BPA) improved photostability significantly. They reported that half-lifetime (T_{50%}) continued to increase with increasing BPA content, whereas it began to decrease after reaching a maximum in the case of MI. The authors attributed the direct relationship between photostability and BPA content to the interaction of OH and aromatic groups in BPA with the open form of spirooxazine dye which leads to higher photochromic absorption maxima. This explanation however contradicts that of Pardo, et. al. [36] that stabilization of the open form of the chromophore accelerates the dye’s photo-degradation. Hou, et. al. [10, 39] suggested that the enhancement of photostability caused by the addition of FAS was due to the prevention of harmful elements accessing the photochromic dye.

Hou, et. al. [41] investigated the photostability of spirooxazine in solution as well as various matrixes and found that:
• Photostability of spirooxazine was lowest in solution (i.e. ethanol), higher in sol-gel matrix, and highest in polymethylmethacrylate (PMMA) coatings, when no additives were applied to the sol-gel coating.

• The incorporation of small amounts of additive helped improve the photostability of spirooxazine in sol-gel coatings to higher than PMMA coatings. The additive type was not specified.

• The increase of spirooxazine content in PMMA coatings enhanced photostability.

2.4 Photochromic absorption

Pardo, et. al. [36] incorporated two naphthopyran photochromic compounds in different organically modified silica coatings prepared via the sol-gel method. Photographs of the colour change of ormosil coatings containing two photochromic naphthopyrans with exposure to UV irradiation are shown in Figure 2.18. The absorption spectra associated with different concentrations of the red dye are shown in Figure 2.19.
Figure 2.18 Images of coatings containing two naphthopyran dyes before and during exposure to UV light – Reprinted from [36], Copyright (2009), with permission from Elsevier

Figure 2.19 Absorption spectra of ormosil coatings with different amounts of photochromic dye – Reprinted from [36], Copyright (2009), with permission from Elsevier

The absorption maxima increased (to approximately 0.21) with dye to silica molar ratio up to 0.02 and became a plateau after this point, although with a slight fluctuation. The observed trend is shown in Figure 2.20.
We postulate that the reason for this behaviour could be the tendency of dye molecules to aggregate due to their hydrophobic nature. This hinders their ability to switch between the closed and open forms, reducing their photochromic functionality. As such, other methods should be employed in order to increase dye loading while preventing dye aggregation as much as possible.

### 2.4.1 Photochromic dye encapsulations

#### 2.4.1.1 Grafting photochromic dye to polymer backbone

Krongauz [42] proposed a method wherein photochromic molecules would bond to the backbone of a polymeric matrix (i.e. polysiloxane or polyvinyl), thereby increasing dye loading while keeping the photochromic molecules separate from each other. As the author notes, if each polymer unit was attached to a photochromic molecule, a dye loading of 100% could be
achieved. This approach however limits the movement of the dye molecule, as its bondage to the polymer backbone creates steric hindrance. Furthermore, the photochromic dyes in their open or merocyanine form can crystallize as a result of heating or irradiation [42]. Kulikovska et al. [43] appended a photochromic azobenzene to the backbone of a polysiloxane polymer by ionic bonds, as depicted in Figure 2.21. They reported that they were able to increase dye loading from the usual 10%-30% in host-guest systems to more than 55%. We however perceive a limitation to this approach. Azobenzene photochromic dyes exhibit photochromism by cis-trans isomerisation. The charged group of the dye molecule is a side group in this case, which does not interfere with the structural transformation required for photochromism. This facility however is not available in the case of spirooxazine, because the oxygen anion appears as a result of heterolytic cleavage, and if it interacts with the polymer backbone, the molecule will be unable to show photochromism.

![Figure 2.21](image)

Figure 2.21 Schematic of (a) a sol-gel matrix with ionic bonds to azobenzene photochromic dye molecules, (b) formation of a complex between the silica polymer and azo dye – Reprinted with permission from [43], Copyright (2008) American Chemical Society
2.4.1.2 Complex formation between photochromic dye and cyclodextrin

Cyclodextrin is one of the most suitable hosts for encapsulation of dyes as it contains a cavity in its structure, large enough for an organic guest. With a hydrophilic outer surface and a hydrophobic inner surface, cyclodextrin is the perfect host for hydrophobic photochromic compounds. The chemical structure of β-cyclodextrin and the cavity sizes of the cyclodextrin family are given in Figure 2.22 and Table 2.1, respectively.

![Chemical structure and spatial shape of β-cyclodextrin](image)

Figure 2.22 (a) Chemical structure and (b) spatial shape of β-cyclodextrin [44]

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<table>
<thead>
<tr>
<th>Type of CD</th>
<th>Cavity Diameter (Å)</th>
<th>Molecular Weight</th>
<th>Solubility (g/100 ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-CD</td>
<td>4.7-5.3</td>
<td>972</td>
<td>14.5</td>
</tr>
<tr>
<td>β-CD</td>
<td>6.0-6.5</td>
<td>1135</td>
<td>1.85</td>
</tr>
<tr>
<td>γ-CD</td>
<td>7.5-8.3</td>
<td>1297</td>
<td>23.2</td>
</tr>
<tr>
<td>δ-CD</td>
<td>10.3-11.2</td>
<td>1459</td>
<td>8.19</td>
</tr>
</tbody>
</table>

Table 2.1 Cavity sizes and other attributes of the cyclodextrin family – Recreated from [44]

Zhang, et. al. [45] produced an inclusion complex of photochromic spirooxazine in γ-cyclodextrin and cast it into film. The UV-VIS absorption spectrum of the resultant film is shown in Figure 2.23.
Figure 2.23 UV-VIS spectrum of spirooxazine/cyclodextrin inclusion complex in the (a) absence and (b) presence of UV light – Reprinted with permission from [45], Copyright (2007) American Chemical Society

Son, et. al. [46] synthesised a “hetero-bi-functional dye” which responded to both UV and electrical stimulation and created an inclusion complex of the dye in β-cyclodextrin. The dye structure is shown in Figure 2.24.

Figure 2.24 Chemical structure of hetero-bi-functional dye – Reprinted from [46], Copyright (2006), with permission from Elsevier

The coloration and bleaching spectra of the dye in DMSO with UV irradiation and electrical stimulation are shown in Figure 2.25.
Figure 2.25 (a) Coloration, and (b) bleaching of dye in DMSO solution with UV irradiation and electric current – Reprinted from [46], Copyright (2006), with permission from Elsevier.

When the dye/cyclodextrin complex is formed, the photochromic section of the dye is positioned inside the cavity of cyclodextrin while the electrochromic section protrudes outwards. This is shown in Figure 2.26.

Figure 2.26 The positions of the photochromic and electrochromic parts of the dye in β-cyclodextrin – Reprinted from [46], Copyright (2006), with permission from Elsevier.

The photochromic part of the dye requires free space for its structural transformation. However, the β-cyclodextrin cavity was not large enough to facilitate an efficient transformation, which was reflected in the reduced absorption maxima of the dye/cyclodextrin complex, shown in Figure 2.27.
Hadjoudis, et. al. [47] produced an inclusion complex of N-(1-adamantyl)salicylaldimine (ASA) in β-cyclodextrin. ASA, which is thermochromic in its free form as a crystal, became photochromic when included in a complex with β-cyclodextrin.

In some works, the complex formed between the photochromic dye and the cyclodextrin host is not an inclusion complex. In the work of De Sousa, et. al. [48], the spiropyran attached in a complex to β-cyclodextrin was located outside of the β-cyclodextrin cavity. The complex was incorporated into PMMA polymer and electrospun into nanofibres.

In the work of Hamada [49], a spiro[2H-benzopyran-2,2'-indoline] photochromic dye was attached to β-cyclodextrin in order to develop a photochemical switch. The photochromic dye is hydrophobic in its closed form, whereas its hydrophobicity is reduced in the open form. This property was used by Hamada to change the hydrophobicity in the area surrounding the cyclodextrin cavity, and therefore its affinity towards a guest, by means of irradiation.
2.4.1.3 Photochromic micro- or nano-particles

Lee, et. al. [50] produced PMMA micro-particles containing photochromic spirooxazine by in situ suspension polymerisation (Figure 2.28). The bleaching process of the photochromic micro-particles after removal of UV irradiation is depicted in Figure 2.29.

Figure 2.28 SEM images of (a) PMMA micro-particles, (b) spirooxazine-containing PMMA micro-particles with a 1 wt% dye content [50]. – Reprinted by permission of Springer

Figure 2.29 Optical images showing the progress of bleaching in the photochromic particles in one-minute interims after removal of UV light [50] – Reprinted by permission of Springer

Chen, et. al. [51] developed 40-80 nm photochromic nanoparticles containing a nitrobenzoxadiazolyl (NBD) fluorescent compound and a spiropyran
embedded in PMMA polymer by means of one-step mini-emulsion polymerisation. A TEM image of the nanoparticles is shown in Figure 2.30. The absorption spectra of the nanoparticles are shown in Figure 2.31.

Figure 2.30 TEM image of the photochromic nanoparticles [51] – Reprinted by permission of John Wiley and Sons

![TEM image of nanoparticles](image)

Figure 2.31 Absorption spectra of a 0.2 wt% dispersion of photochromic nanoparticles in the absence and presence of UV light [51] – Reprinted by permission of John Wiley and Sons

![Absorption spectra](image)

### 2.4.1.4 Incorporating PMMA into silica coating

comparison between their photochromic PMMA/PHPS hybrid film and pure PHPS photochromic film is given in Figure 2.32. Xylene was used as solvent for the photochromic dye. The films were soaked in xylene and the leaching out of dye from the films was compared between PMMA/PHPS and PHPS films based on their absorption spectra, as shown in Figure 2.33. The results indicated that the incorporation of PMMA helped reduce the leaching out of spiropyran dye from the film. The authors attributed this to the increased hydrophobicity of the matrix with incorporation of PMMA, which has enhanced the affinity of the hydrophobic spiropyran to the matrix.

![Image](image.png)

Figure 2.32 Spiropyran-loaded (a) PMMA/PHPS hybrid film and (b) PHPS film [11] – Reprinted with permission from Springer
2.5 Applications of photochromism

Photochromism has been employed in a range of applications in science and industry. These include photochromic ophthalmic lenses, optical information storage devices, sensors, switches, shutters, holography, optical modulation, actuators, waveguides, displays, security printing, and textiles [34, 52, 53]. Some of these applications are discussed in detail below.

2.5.1.1 Photochromic glass and ophthalmic lenses

The first commercial photochromic ophthalmic glass was developed at Corning Glass Works [54]. Stookey [55] developed a photo-sensitive glass containing the oxides of cerium and gold, which when subjected to UV irradiation and subsequently to heat, produced red and blue images. By incorporating palladium in the glass as the colorant, a dark brown-grey colour was obtained, and the colour-changing glass was then commercialized. Cohen and Smith [56] produced photochromic glasses with rapid coloration and bleaching by
incorporating europium and cerium in silicate glass. However, their product exhibited low fatigue resistance. Armistead and Stookey [57, 58] later reported their development of photochromic silicate glasses based on silver halides crystals, and patented the first marketable photochromic lens. Bestlite™ and Photogray™ [54, 59-61] commercial photochromic lenses can be named as some of the early products where photochromic glass was used in ophthalmic applications. It is approximated that 10 million pairs of photochromic ophthalmic lenses, consisting of silver halide crystals dispersed in inorganic glass, were distributed across the USA in 1989. The US ophthalmic eyewear market was later overtaken by plastic prescription lenses, constituting over 70% of the products. The domination of plastic eyewear made it necessary to develop photochromic lenses made of plastic with satisfactory properties. The criteria for an acceptable product included its colour and transparency in the light and darkened states, coloration and bleaching rates, and its resistance to photo-degradation [62]. Photolite™, a product of American Optical, can be named as the first plastic photochromic lens to be marketed in 1982, consisting of a polycarbonate matrix and an indolino spironaphthoxazine chromophore [61].

2.5.1.2 Functional devices
Photochromic polymers based on diarylethene have been employed in such applications as optical switches, actuators, and memories. Lucas, et. al. [63] developed an optical molecular switch by functionalising dithienylethenes to form dithienylcyclopentene compounds. Their synthesised thienylperhydrocyclopentene derivatives were capable of reversible photochromism depending on whether the substituent group was able to
conjugate with the π system in thiophene. Gan, et. al. [64] proposed that the acidochromic and photochromic properties of the dyad and triads of dithienylethene-oxazolidine and their reduced derivatives could be employed in developing a molecular switch responsive to multiple stimuli. Kobatake, et. al. [65] reported that diarylethene-based molecular crystals, varying in size from 10 to 100 μm, showed fast and reversible macroscopic transformations in size and shape when stimulated by UV and visible irradiation. The said transformations are shown in Figure 2.34. The possibility of triggering the aforementioned size and shape transformations by means of irradiation, without a need for physical contact suggests the application of these materials as actuators.
Figure 2.34 Chemical structures and reversible shape changes of the single crystals of two diarylethenes by UV and visible irradiation [65] – Reprinted with permission from Nature Publishing Group.

Jeong, et. al. [66] reported the recording and erasing of data on diarylethene materials and their disulfonyl derivatives by switching between UV and visible irradiation. The resulting strong changes in fluorescence intensity enabled the development of a data readout system with superior efficiency, which suggested an application for these materials in erasable optical information storage media.
2.5.1.3 Security printing

The photochromic protein, bacteriorhodopsin (BR), by combining three valuable attributes at the molecular level, has great potential for application in security printing. It has a photo-induced colour change, photochemical information storage capability, and an ability to be traced based on its molecular marker sequence. Furthermore, the crystallinity of this protein makes it highly stable. BR has been used in inks applied in pad-, screen-, and ink jet-printing. Such prints exhibit photochromic colour change as a result of the BR-containing ink. This photochromic functionality cannot be duplicated in photocopies, which therefore prevents counterfeiting. Furthermore, the aforementioned prints allow photochemical storage and reading of information by laser, otherwise known as “digital write-once-read-many (WORM) data storage” [67, 68].

2.5.1.4 Photochromic textiles

In recent years, interest in developing fibres or textiles with photochromic functionality has been reported. Lee, et. al. [69, 70] incorporated two types of spirooxazine dye in polyamide fibres by means of exhaustion dyeing, and studied the effect of temperature on the dyes’ exhaustion. Their photochromic fibres exhibited photochromism with UV irradiation at a slow coloration rate of approximately 10 seconds. The conventional exhaustion dyeing technique was employed by Billah, et. al. [71, 72] to disperse two spirooxazine compounds into polyester, nylon, and acrylic fabrics. The fabric was reported to have a low photostability problem. Aldib and Christie [73] also applied 6 photochromic dyes of spironaphthooxazine and naphthopyran types to a polyester fabric by means of exhaustion. They measured the photostability in 20 cycles, and in
each cycle, the fabric sample was subjected to UV irradiation for 4 minutes and subsequently bleached in the dark for 2 hours. Furthermore, they measured the stability of the photochromic effect with storage by keeping the fabric in the dark for 170 days. The 6 studied dyes exhibited different photostability, regardless of their photochromic class, from lower than 50% retention of the photochromic effect to as high as 100%. The photochromic fabrics retained between 71% and 84% of their functionality after 170 days of storage. The order of the dye storability was not the same as that of their photostability. Little and Christie [74-76] used screen-printing technique to apply commercially available photochromic dyes on cotton fabric. The problem with this method is the relatively low photostability, despite the use of UV stabilisers, which was reported as high as 825 minutes for the loss of half of the photochromic effect with exposure to UV light [76].

Microencapsulation has also been used for incorporating photochromic compounds. Microencapsulation is a technique wherein a tiny particle of solid or drop of liquid is coated with a thin layer of polymer. Photochromic compounds are encapsulated by interfacial polymerisation. Due to the small size of the resultant microcapsules (approximately 3-5 μm), microencapsulated photochromic dyes can be screen-printed onto fabrics [77]. The advantage of this technique is that the encapsulating polymer layer offers a protection to the photochromic compounds. However, it reduces the fabric handle properties.

In our group, Cheng, et. al. [78-80] have encapsulated photochromic spirooxazine dye in a silica sol-gel coating on wool fabric. They reported the absorption maxima of 0.24 and 0.25, coloration rates of 14.75 and 9.30 seconds, and bleaching rates of 54.25 and 22.75 seconds for silica coatings
from phenyltriethoxysilane (PhTES) and octyltriethoxysilane (OTES), respectively. Furthermore, they reported values of 38.16% and 37.31% for the wash fastness of PhTES and OTES sol-gel-coated fabrics, respectively [78]. After comparing the properties of photochromic coatings from silica precursors bearing different organic non-hydrolysable groups, they concluded that precursors bearing long alkyl chains produced better photochromic and handle properties [80]. In another work [79], they compared the properties of coatings from combinations of short- and long-chain alkyl silica with 3-glycidoxypropyltrimethoxysilane (GPTMS), and concluded that the epoxy group of GPTMS improved abrasion and washing durability.

2.6 Sol-gel technology

2.6.1 Definition

The sol-gel technology is in general terms a method of producing inorganic materials by way of synthesising a sol, causing it to gel, and subsequently drying and possibly sintering the gel. This process offers the possibility of fabricating materials with tailored properties in a range of forms including powders, fibres, and films, by selecting suitable precursors and controlling the reaction conditions [81]. The sol-gel process enables the control of pore size and pore arrangement in the inorganic or hybrid matrix [82].

A sol is defined as “a colloidal suspension of solid particles in a liquid”. A colloid is defined as “a suspension in which the dispersed phase is so small (∼1-1000 nm) that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface
The sol-gel method is a process wherein the starting materials or precursors of a colloid contain a central metal or metalloid atom with different non-metal/metalloid ligands attached to it. Alkoxides are the most common sol-gel precursors. An alkoxide contains an alkoxy ligand, which is the product of proton removal from the hydroxyl group of an alcohol.

In the sol-gel process, the metal/metalloid alkoxide precursor undergoes hydrolysis in the presence of water:

\[ Si(OR)_4 + H_2O \rightarrow HO-Si(OR)_3 + ROH \]  

(2.1)

In the case of alkoxide precursors, R represents an alkyl group and OR an alkoxy ligand. If sufficient amounts of water and catalyst are available, hydroxyl groups may replace all four of the alkoxy groups, producing Si(OH)_4. Otherwise, the hydrolysis reaction will be incomplete, leading to Si(OR)_{k-n} (OH)_n.

The sol-gel process also includes condensation reactions, which occur when partially hydrolysed metals/metalloids interact. The by-product of the condensation reaction could be water or alcohol, as in Reaction 2.2 and 2.3, respectively.

\[ (OR)_3Si-OH + HO-Si(OR)_3 \rightarrow (OR)_2Si-O-Si(OR)_2 + H_2O \]  

(2.2)

\[ (OR)_2Si-OR + HO-Si(OR)_2 \rightarrow (OR)_2Si-O-Si(OR)_2 + ROH \]  

(2.3)
The condensation reaction can also be viewed as a polymerisation reaction during which the monomer grows into a larger structure or polymer, depending on its functionality, i.e. number of reactive groups. A monomer with 2 reactive groups ($f=2$) can form a dimer, chain, or ring, as shown in Figure 2.35, whereas a monomer with a functionality larger than 2 can produce a cross-linked fractal polymer, as seen in Figure 2.36.

(a)

(b)

(c)

Figure 2.35 The possible products of the polymerisation process of a monomer with a functionality of 2: (a) dimer, (b) chain, (c) ring [83]
Figure 2.36 Computer simulation of a fractal polymer produced from a monomer with a larger than 2 functionality [83, 84] – Reprinted by permission of Annual Reviews

A gel is formed when a monomer molecule grows into a macroscopic-size polymer covering a large area of the solution. The point when the formation of this large polymer is completed is referred to as the gel point. Therefore, a gel can be described as a continuous solid framework within a continuous liquid phase.

In the sol-gel process, a sol may be transformed into different products. It can be spun to form fibres or used to produce uniform particles for various applications by precipitation. It can be deposited onto a surface where it gels with exposure to the atmosphere to form a xerogel film, which can
subsequently be transformed into a dense film by heating. On the other hand, a sol can be transformed into a gel and subsequently into an aerogel by solvent extraction, or alternatively into a xerogel by solvent evaporation. A xerogel can then be heated to produce a dense ceramic. The process is shown in a schematic in Figure 2.37 [83].

![Schematic of different routes in sol-gel processing](image)

**Figure 2.37** Schematic of different routes in sol-gel processing – Recreated from [83]

### 2.6.2 Historical outline

Ebelmen was the first person to discover that metal alkoxides formed gels in 1846. However, this discovery did not attract attention beyond the field of chemistry. It was only a century later that the application of alkoxides in oxide
film production was patented by Geffcken [85] and adopted by the German glass company, Schott.

After many theoretical studies regarding the structure of silica gel, a general consensus on a network structure in sol-gel was reached in the 1930s. This came to a great extent from the efforts of Hurd, who described the silica gel as a silicic acid polymeric framework surrounding a continuous fluid phase.

During the 1930’s, sols and gels were finding applications in mineralogy, and later in ceramics, and nuclear fuel production. In the ceramic industry, alkoxides were reacted under controlled conditions for the production of multi-component glass, and metal-organic starting materials were employed for the development of ceramic fibres. However, the popularity that the sol-gel method enjoys today stems from the endeavours of Yoldas and Yamane who developed a method for producing monoliths from gels by meticulous drying, in the 1970s. As a process that can be conducted at room temperature and therefore allows the fabrication of hybrid materials by combining inorganic and organic constituents, sol-gel has attracted great attention and ongoing research [81, 83].

### 2.7 Microstructure of sol-gel-derived silica

Pores are categorized based on their diameter into three groups: micropores, with \( d < 2 \text{ nm} \), mesopores with \( 2 < d < 50 \text{ nm} \), and macropores with \( d > 50 \text{ nm} \). Due to their small size, silica micropores are generally difficult to characterise in randomly oriented porous gels. The characterisation techniques mainly include nitrogen adsorption porosimetry, transmission electron microscopy (TEM), and small angle x-ray scattering (SAXS).
The catalysis conditions of the sol-gel process can have a significant effect on the microstructure of the gel. Xiao, et al. [86] studied the effect of catalysis conditions on the micropore structure of sol-gel derived tetraethylorthosilicate (TEOS) films. They characterised films produced in base, acid, and base/acid two-step catalysed conditions. The latter condition was created by mixing base and acid catalysed sols together. TEM micrographs revealed that the network produced from two-step catalysis was denser and contained larger particles compared to that of basic catalysis, as shown in Figure 2.38.

![Figure 2.38 TEM images of (a) base-catalysed and (b) two-step catalysed silica sols – Reprinted from [86], Copyright 2007, with permission from Elsevier](image)

The reason for the larger particle size of the two-step catalysed sol was the presence of acid, which promotes cross linkage and branching of the chains. The average particle size of the base-catalysed sol remained at 11.5 nm after 60 days of storage, while that of the freshly-mixed base/acid catalysed sol was 52 nm, and slowly increased with storage time. According to Xiao, et al. [86], sols are suitable for coating when the average particle size is smaller than 100 nm.

In acidic synthesis conditions, hydrolysis is rapid, while condensation is slow, and therefore, the cluster growth follows the reaction limited cluster-cluster aggregation (RLCA) model. Consequently, dense films with small pores are
obtained. In basic conditions however, the hydrolysis reaction occurs more slowly compared to condensation, and the aggregation follows a diffusion limited cluster-cluster aggregation (DLCA) model. As a result, a loose film with larger pores and spherical particles is obtained.

The study also showed that acid-catalysed silica films have a higher refractive index than the base-catalysed. According to Wu, et al. [87], the refractive index of the silica films is inversely related to the square root of their porosity, which is why acid-catalysed films with smaller pores have a larger refractive index. In other words, light travels more slowly in films produced via acid-catalysed sol-gel synthesis, due to their more compact structure. Figure 2.39 shows an illustration of acid- and base-catalysed sol-gel networks.

![Schematic of sol-gel-produced networks](image)

Figure 2.39 Schematic of the sol-gel-produced networks with (a) acid and (b) base catalysis – Recreated from [86]

The studies on the microstructure of sol-gel silica have often employed the more common silica precursors bearing four alkoxy groups, such as tetraethoxysilane (TEOS) [88-90] and tetramethoxysilane (TMOS). Shimizu, et. al. [20] produced microporous silica from tetramethylorthosilicate (TMOS)
using a catalytic sol-gel method based on a non-ionic hydroxyacetone (HA) catalyst. They characterised the structural development of the silica, from polymer-like aggregates in the precursor solution to agglomerates after heat treatment and finally to microporous solid, via SAXS, nitrogen adsorption, and TEM. Figure 2.40 shows the TEM micrographs of silica powder made by heating the sol at 40°C, and hydrolysed silica powder heated at 200°C, respectively. The images indicated that the two forms of silica had similar morphologies and an estimated pore size of 0.5 nm. They concluded that the microporous structure of the final solid product is an outcome of the Gaussian polymer-like nature of the silica aggregates in the precursor, which have a microscopic-scale mesh size.
Krause, et. al. [22] investigated the effect of the synthesis conditions on the pore structure, absorption and luminescence properties of silica xerogels loaded with Rhodamin6G. They used SAXS and nitrogen adsorption techniques to characterise the pore structure of their xerogels. They found that loading dye into TEOS sol-gel during synthesis or after gelation did not affect its luminescence properties. However, post-loaded dyes were mainly located in micropores, while those loaded during sol-gel synthesis mostly occupied
mesopores. The effect of this behaviour was observed in the wavelength of maximum absorption.

Some studies involve silanes with three alkoxy groups, but the one non-hydrolysable group is often a short-chain alkyl, e.g. methyl [12, 13]. Furthermore, most works involving SAXS study of sol-gel-derived silica microstructure have employed base [14] or acid-base [15, 16] rather than acid catalysis, which is a crucial factor in determining the properties of the solid product.
3 Experimental procedure

3.1 Materials

3.1.1 Silica precursors and additives

Octyltriethoxysilane (OTES), phenyltriethoxysilane (PhTES), 3-glycidoxypropyltrimethoxysilane (GPTMS), 2-(cyclohexenyl)ethyl]triethoxysilane (CycTES), methyltriethoxysilane (MTES), (3-aminopropyl)triethoxysilane (APS), and (3-trimethoxysilyl)propylmethacrylate (MPS) were obtained from Sigma-Aldrich and used as received. Vinyltrimethoxysilane (VTMS) and tridecafluoroocetyltriethoxysilane (fluoroalkysilane or FAS) were kindly donated by Evonik Degussa.

3.1.2 Catalyst

Tetraacetoxy silane (TAS) or silicon tetraacetate was obtained from Aldrich and used as catalyst [91] for slow acid catalysis.
3.1.3 Photochromic dye

5-chloro-1,3-dyhydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]-naphth [2,1-b] [1,4] oxazine], a spirooxazine dye also known as Photorome II, was obtained from Sigma-Aldrich. The chemical structure of the dye is shown in Figure 3.2.

3.1.4 UV stabilisers

2,2'-thiobis(4-tert-octylphenolato)-Nbutylamine nickel (II) (UV-1084), 2-hydroxy-4-methoxy-benzophenone (HMBP), 2-(2Hbenzotriazol-2-yl)-4-(1,1,3,3-tetramethylbutyl) phenol (Tinuvin 329) and poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol-alt-1,4-butanedioic acid) (HALS-622) were obtained from Sigma-Aldrich.
3.1.5 Cyclodextrin

β-cyclodextrin was obtained from TCI company in China.

3.1.6 Solvents

Ethanol was obtained from Univar, acetone from Merck, tetrahydrofuran (THF) from Ajax Finechem Pty Ltd, and dimethylformamide (DMF) and dichloromethane from Chem Supply.

3.1.7 Surfactant

Dodecyl Trimethyl Ammonium Bromide (DTAB) surfactant was obtained from Sigma-Aldrich.

3.1.8 Precursors of photochromic particles

The precursors of photochromic nanoparticles were all obtained from Sigma-Aldrich. These included: methylmethacrylate (MMA), sodium dodecyl sulphate (SDS), tetradecline (TD), and potassium persulfate (KPS). Aluminium oxide (basic), used for removing the inhibitor from MMA, was also obtained from Sigma-Aldrich. The precursor of photochromic particles, i.e. polymethylmethacrylate (PMMA), was also a product of Sigma-Aldrich.

3.1.9 Polymerisation initiator

4,4'-azobis(4-cyanovaleric acid) (ACVA) was a product of Fluka Analytical, obtained from Sigma-Aldrich.
3.1.10 Fabric

An undyed, chlorine/Hercosett treated fabric from AIM Sports Pty Ltd (Australia) made of 19.5 µm Australian merino wool top was used in the photochromic studies. The fabric was a double jersey knitted interlock which weighed 245 g/m².

3.1.11 Coating substrates for microstructural study

Mica sheets obtained from SPI Supplies and quartz capillaries from Hampton Research were used as coating substrate in the SAXS studies.

3.2 Fabrication methods

3.2.1 Silica sol-gel synthesis and coating

Silica sols were prepared by mixing TAS, alkyltriethoxysilane (RSi), and ethanol, and stirring until the TAS crystals were dissolved. Water was subsequently added using an NE-4000 Adelab Scientific syringe pump at a 1 ml/h rate and the mixture was stirred for 24 hours at room temperature. The molar ratio of TAS: RSi: H₂O: ethanol was 1:32:100:320. TAS was selected as catalyst to slowly release acetic acid into the mixture, to avoid rapid hydrolysis. 10 ml of spirooxazine-ethanol solution (SO: RSi molar ratio of 1:100) was mixed with 10 ml of synthesised sol-gel, and stirred at about 70 °C until a clear solution was obtained. A 20cm×20cm piece of wool fabric was laid flat in the solution, air-dried horizontally to reduce coating non-uniformity, and cured at 110°C for 10 min. The coated fabric was left for 1-2 days before
measurement to ensure complete stabilization of the silica matrix while avoiding wool yellowing caused by excessive heat treatment.

To add UV stabilizer to sol, the stabilizer was dissolved in ethanol. After ultrasonication for 5 minutes, dye-containing sol was added, and stirred at about 70 °C to produce clear solutions. The molar ratio of photochromic dye: UV stabilizer was 1:1. To adjust the wettability of the coating, FAS was added to the silane at the beginning of synthesis (before adding water). To seal off the dye-containing pores, a second layer (20 ml) of sol (from the same or different precursor to the first layer) containing no dyes was applied after air drying the first for 24 hours, and was heat-treated 24 hours later.

3.2.2 Synthesis of spirooxazine-cyclodextrin inclusion complex

The spirooxazine-cyclodextrin inclusion complexes which were coated on fabric were prepared according to the method described in the work of Zhang, et. al. [45]. 1 mmol of β-cyclodextrin (β-CD) was dissolved in 50 ml of water and 5 ml of ethanol and stirred until a clear solution was obtained. 0.1 mmol of photochromic spirooxazine (SO) dye was dissolved in 10 ml of ethanol by stirring and heating at around 70° C. Subsequently, the dye solution was mixed with the β-CD solution under stirring. The transparency of the mixture started to reduce after a few minutes, indicating precipitation. The mixture was stirred for 12 hours at room temperature and refrigerated at 4°C for 20 hours. The mixture was then passed through a filter in order to separate the precipitates. The precipitates were then washed with 5 ml of 40 v/v% water-ethanol solution and dried in a vacuum oven at room temperature overnight. A greenish-yellow powder was obtained which was dispersed in ethanol and mixed with
OTES:PhTES 1:2 sol-gel and coated on fabric. The fabric was air-dried for 24 hours, cured at 110°C for 10 minutes and air-dried again for 24 hours.

The spirooxazine-β-CD complexes which were characterised by XRD, TGA, and DSC were prepared by mixing a solution of 0.01 g SO in 25 ml acetone with a solution of 0.03 g β-CD in 25 ml water under stirring. The mixture was passed through a filter and the obtained precipitates were washed with water and methanol and dried under vacuum overnight [92]. Furthermore, another mixture of SO and β-CD was prepared by simply adding β-CD to the solution of SO in acetone and allowing acetone to evaporate, leaving a powder mixture of SO and β-CD. This mixture was also studied by XRD, TGA, and DSC for comparison purposes.

3.2.3 Preparation of coatings for investigating the effect of solvent

Different amounts of photochromic spirooxazine dye were added to 1.75 ml of ethanol, acetone, DMF, or THF, depending on the dye’s solubility in the solvent. 0.0073 g of dye was added each time to a solvent, and once the dye was dissolved (i.e. a clear solution was obtained), the solution was left undisturbed for 24 hours. If no sediments had formed after this period, the same dose of dye was added again. Stirring and heating were required for dissolving the dye in ethanol, while generally only shaking was required for the other solvents. Each solution was then mixed with 1.75 ml of OTES:PhTES 1:2 sol-gel. It is noteworthy that the solvent used for the preparation of the sol was ethanol. The dye content was calculated based on the amount of dye (g) divided by the total amount of dye and silica (g). The solution was coated on a
5cm×10cm piece of fabric. The coated fabric was air-dried, cured at 110°C for 10 minutes and air-dried again for 24 hours.

3.2.4 Preparation of coatings for investigating the effect of surfactant

OTES:PhTES 1:2 sol-gel coatings were prepared (with ethanol for solvent), and different amounts of spirooxazine dye and dodecyl trimethyl ammonium bromide (DTAB) surfactant were incorporated into the coatings. Where an increase in solution uptake was required, additional sol containing corresponding amounts of dye and DTAB was applied to fabric.

3.2.5 Synthesis of spirooxazine-PMMA film

Spirooxazine dye and methylmethacrylate monomer were dissolved separately in dichloromethane and subsequently mixed together and cast into film. The studied dye contents were 1.2%, 2.4%, and 4.8% (dye (g)/[dye+PMMA] (g) ×100).

3.2.6 Synthesis of spirooxazine-PMMA nanoparticles

Spirooxazine-PMMA nanoparticles were synthesised based on a method described in the literature [51]. To an ice-cooled solution of 0.04 g sodium dodecyl sulphate (SDS) surfactant in 20 ml water was added 0.1 g spirooxazine (SO) dye, 0.12 g tetradecane (TD), and 2 g inhibitor-free MMA. The mixture was stirred for 20 minutes and ultrasonicated for 15 minutes while ice-cooled. The mixture was then stirred for 30 minutes under nitrogen atmosphere at 60°C before adding a solution of 0.0734 g potassium persulfate (KPS) in 2 ml water
to start polymerisation. The reaction was continued for approximately 4 hours until the spirooxazine-PMMA nanoparticles were formed. As some of the dye precipitated, only the top part of the mixture was collected and centrifuged at 50,000 rpm. The sediments were washed with water and dried at 70°C.

3.2.7 Synthesis of PMMA/silica sol-gel

Ploymethylmethacrylate (PMMA) was incorporated into silica sol-gel by modifying a method described elsewhere [93, 94]. The Inhibitor was separated from methylmethacrylate (MMA) monomer using basic aluminium oxide, and MMA was subsequently copolymerized with (3-Trimethoxysilyl)propyl methacrylate (MPS) in 5 ml of 99.9% pure THF by adding 4,4'-azobis(4-cyanovalecular acid) (ACVA) initiator. The high purity or low water content of THF was required to prevent premature hydrolysis of MPS. The solution was purged with nitrogen for 15 minutes and reacted at 85°C for 2 hours. The resulting MMA-MPS copolymer was used along with OTES and PhTES as precursor for the sol-gel reaction. A molar ratio of 1:0.5:1 was maintained between Silica:MPS:MMA, and a molar ratio of 1:10.7:21.3:50 was maintained between TAS:OTES:PhTES:H₂O. 12 ml of 99% pure THF was used in the sol and water was added drop wise to the solution. 1.75 ml of sol was mixed with an equal amount of spirooxazine/THF solution, coated on a 5cm×10cm piece of fabric, air-dried and cured. The dye concentration was calculated based on the amount of dye (g) divided by the total amount of solid present in the coating (i.e. MMA, MPS, ACVA, TAS, OTES, PhTES, and dye).
For comparison purposes, OTES:PhTES 1:2 sol-gel was also prepared, with THF used as solvent for both the sol and the dye. A molar ratio of 1:10.7:21.3:100:320 was maintained between TAS:OTES:PhTES:H₂O:THF. The earlier mentioned method for incorporating dye into the coating was also employed here, and the dye concentration was calculated based on the amount of dye (g) divided by the total amount of silica and dye (g) in the coating.

3.2.8 Synthesis of spirooxazine-PMMA particles in resin and in sol-gel

Spirooxazine-PMMA particles were synthesized by dissolving spirooxazine and PMMA in acetone separately, mixing the two solutions together, and adding the combined solution to water at a rate of 15 ml/h while stirring vigorously. The precipitates formed in water were separated by centrifugation and dried at room temperature under vacuum. The particles were coated on fabric by embedding in Hercosett resin and in OTES:PhTES 1:2 sol-gel. For incorporating the particles in resin, the resin was diluted in 2.5 ml of water and mixed with a dispersion of particles in 2.5 ml water, and the mixture was coated on a 5cm×10cm fabric. For embedding the particles in sol-gel, the particles were dispersed in 1.75 ml of ethanol and 1.75 ml of sol-gel, and heated at 80°C while stirring. A 5cm×10cm fabric was coated with the solution and cured at 110°C for 10 minutes. The dye contents were 1.74%, 6.63%, and 15.1%, which were calculated according to Equations 3.1 and 3.2 for the resin and sol-gel coatings, respectively. The studied dye to PMMA ratios were 1:1 and 1:2 (g/g). To allow comparison, the amount of resin and silica content were kept equal and constant in the three studied dye contents.
\[
dye \text{ content (\%)} = \frac{\text{dye} (g)}{[\text{dye} + \text{PMMA} + \text{resin}] (g)} \tag{3.1}
\]

\[
dye \text{ content (\%)} = \frac{\text{dye} (g)}{[\text{dye} + \text{PMMA} + \text{silica}] (g)} \tag{3.2}
\]

### 3.3 Characterisation methods

#### 3.3.1 Uptake of coating solution on fabric

The uptake of the coating solution, i.e. the amount of solution absorbed onto the fabric, is calculated according to Equation 3.3.

\[
\text{Uptake} \% = \frac{W_2 - W_1}{W_1} \times 100 \tag{3.3}
\]

where \( W_1 \) and \( W_2 \) are the weight of the fabric before and after coating, respectively.

#### 3.3.2 Measurement of photochromic properties

A SUB4000 optical fibre UV-VIS spectrometer and a DH2000-BAL UV-light source with a wavelength range of 230-2000 nm, both from Ocean Optics, and a personal computer were employed to measure the photochromic properties of the coatings (Figure 3.3). The colour changes are expressed using the differential absorption between the state of presence and absence of UV light, \( \Delta A = A_{\text{light}} - A_{\text{dark}} \), at the wavelength of maximum absorption.
The photochromic coloration and bleaching were recorded in real time as the ascent and descent of absorption when UV light was turned on and off, respectively. The coloration and bleaching rates were calculated from the time required for absorption to rise and subsequently fall to half of its maxima. These were expressed as coloration and bleaching half-life times, $t_{1/2}$ and $t'_{1/2}$, respectively, and were measured using the absorption versus time graph obtained from SpectraSuite software.

To measure photostability, samples were illuminated by strong UV light from an Hg metal halide lamp, type OH N30/50E from Heraeus Noblelight (UV-A: 350-400 nm, relative irradiance around 90-120, and an intensity of approximately 80 mW/cm² at 365 nm) and their photochromic absorption was recorded after each exposure period (approximately 3.2 hours). The required time for the coated fabric to lose its entire photochromic effect (i.e. for absorption to no longer rise with UV stimulation) was considered the lifetime
of the photochromic coating. For some samples, an ATLAS Suntest CPS was used which is a xenon arc instrument for artificial weathering. Samples were placed in the Suntest device for 5 hour cycles and the changes to their absorption maxima were monitored.

3.3.3 Abrasion Durability

The durability of the coated fabric was measured on a Martindale abrasion tester, as shown in Figure 3.4.

Figure 3.4 Martindale abrasion tester

The samples were abraded for 100, 300, 500, and 1000 cycles under a pressure of 9 kPa and the changes in their absorption maxima were monitored after each cycle. Durability was calculated according to Equation 3.4.

\[
\text{Durability} \% = \frac{\Delta A_2}{\Delta A_1} \times 100
\]  

(3.4)
where $\Delta A_1$ and $\Delta A_2$ are the differential absorption maxima before and after abrasion.

### 3.3.4 Wash Fastness

The wash fastness or durability of the coated fabrics to washing was tested according to the Australian Standard AS 2001.4.15.C. The samples were cut into 4 cm×10 cm strips and encased in fabric pockets which were sewn around each sample. The test was conducted in an Ahiba Nuance (Top Speed) dyeing machine using a solution of 5 g/l of ECE phosphate reference detergent B and 2 g/L of sodium carbonate in water at 60°C for 30 minutes. The washed fabrics were air dried and the changes in their maximum absorption were monitored before and after washing.

### 3.3.5 Water Contact Angle

The wettability of the coated fabrics was assessed based on their water contact angle which was measured using a KSV CAM101 contact angle meter (Figure 3.5).
Figure 3.5 KSV contact angle meter

The fabric samples were cut into 2 cm x 2 cm pieces and fixed onto microscope slides. The contact angle was measured immediately after placement of a water drop on the fabric surface (Figure 3.6). The software calculates the contact angle of the two sides of the droplet with the fabric and the average of the two values is reported in this work.

Figure 3.6 Image of a water droplet on fabric viewed in the KSV contact angle meter
3.3.6 Handle Properties

The handle or bending properties of the fabric was measured using an SDL ATLAS (Shirley) stiffness tester, shown in Figure 3.7, and according to the method explained in BS 3356 BS 9073 part 7 and ASTM D1388.

Figure 3.7 Stiffness tester

The fabric was cut into 2.5cm×20 cm strips along the warp and weft directions. A ruler was placed on the strips and slid horizontally along the designated platform of the stiffness tester until the suspended end of the strip met two parallel marks on the wall of the tester which were 41.5 degrees below the horizontal plane. The length that the ruler had travelled was recorded as the bending length (C) as illustrated in Figure 3.8. The bending length of both ends as well as the face and back of each strip were averaged.
The flexural rigidity and bending modulus were then calculated from Equations 3.5 and 3.6.

$$G = 0.1MC^3$$  \( (3.5) \)

where \( G \) is the flexural rigidity (mg·cm), \( M \) is the fabric’s mass per unit area (g/m\(^2\)) and \( C \) is the bending length (cm).

$$Q = \frac{12G \times 10^6}{g^3}$$  \( (3.6) \)

where \( Q \) is the bending modulus (kg/cm\(^2\)), \( G \) is the flexural rigidity, and \( g \) is the fabric thickness (cm). The thickness of the fabrics was measured using a MESDAN LAB thickness meter immediately after placing the fabric under 1 N of pressure.

3.3.7 Scanning Electron Microscopy (SEM)

SEM images of untreated and sol-gel coated fabrics were obtained using a Jeol Neoscope at 5kV and 2000 magnification. The samples were cut into 5mm×5
mm pieces and fixed onto specimen mounting stubs. The samples were gold-coated in a Bal-tec SCD50 sputter coater.

3.3.8 Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis was conducted on a Netzsch STA 409. The heating rate was 10°C/min, the start and end temperatures were 30°C and 700°C, respectively, and the experiment was conducted under an atmosphere of nitrogen. The sample preparation method of spirooxazine-cyclodextrin complex for TGA analysis is described in section 3.2.2.

3.3.9 Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry measurements were conducted on a Mettler Toledo DSC 821 with a heating rate of 10°C/min and start and end temperatures of 20°C and 300°C, respectively. The sample preparation method used for DSC analysis of spirooxazine-cyclodextrin complex is described in section 3.2.2.

3.3.10 X-Ray Diffraction (XRD)

XRD analysis was conducted on a PANalytical X’Pert PRO diffractometer using Cu Kα radiation with a wavelength of 1.54184 Å at 40kV and 30 mA. The sample was spun over a range of 5 to 140° (2θ) with a step size of 0.01. The crystal size calculations were performed using Xpert High Score Plus software. For determination of crystallinity and crystal size of silica, PhTES sol-gel was deposited onto a microscope slide. The coating solidified with
exposure to the atmosphere. The sample preparation method used for the XRD study of spirooxazine-cyclodextrin complex is described in section 3.2.2.

3.3.11 Small Angle X-ray Scattering (SAXS)

SAXS experiments were carried out on the SAXS/WAXS beamline at the Australian Synchrotron. The beam source was an in-vacuum undulator capable of producing a very high flux. An energy level of 12 KeV ($\lambda=1.0322$ Å) was utilised and the scattering curves, recorded by a 1 M Pilatus detector, were assessed at a $q$-range of 0.02-1.5 Å$^{-1}$. The samples were examined in the form of coatings on mica sheets, films, or dried powder inserted into quartz capillaries. To obtain the powders, sol-gel was deposited in a shallow container, air-dried, and cured at 110°C for 10 minutes. The resultant solid was ground into powder. The scattering of uncoated mica sheets and empty capillaries were measured for background correction, performed in the SAXS15ID program.

3.3.11.1 Calculations

According to Bragg’s Law, we have:

$$\lambda = 2d \sin \theta$$  
(3.7)

where $\lambda$ is the wavelength of the incident wave, $d$ is the lattice spacing, and $\theta$ is the angle between the incident rays and scattering planes. On the other hand, the scattering vector, $q$ is defined as:

$$q = \frac{4\pi}{\lambda} \sin \theta$$  
(3.8)
where $\theta$ is the scattering angle. From Equations 3.7 and 3.8, we have:

$$d = \frac{2\pi}{q}$$  \hspace{1cm} (3.9)

where $d$ corresponds to the distance between pores in the silica matrix [21]. $q_2/q_1$ was calculated as an indication of pore morphology [18], where $q_1$ and $q_2$ are the positions of the first and second broad intensity peaks on the $q$ axis ($\AA^{-1}$), respectively.

### 3.3.12 Nitrogen Adsorption Porosimetry

The nitrogen adsorption tests were performed using a Quantachrome Autosorb1 system at 77K. Silica coatings were grinded into powder and outgassed at 100°C overnight prior to analysis. For determination of surface area, multipoint Brunauer-Emmett-Teller (BET), performed in a P/Po range of 0.1-0.3, Langmuir surface area, Barrett-Joyner-Halenda (BJH) and Dollimore-Heal (DH) method cumulative desorption surface area, t-method external and micropore surface area, and Dubinin-Radushkevic (DR) method micro pore area were obtained. The total pore volume was measured at a P/Po of 0.99 for pores smaller than 3410.1 Å. Furthermore, BJH and DH method cumulative desorption pore volume, and Horvath-Kawazoe (HK) and Saito-Foley (SF) method cumulative pore volume were calculated for total pore volume. t-method and DR method micropore volumes were also obtained. The average pore diameter, BJH and DH method desorption pore diameter, DR method micro pore width, Dubinin-Astakhov (DA) method pore diameter, HK method pore width, and SF method pore diameter were also calculated.
3.3.13 Transmission Electron Microscopy (TEM)

TEM micrographs were obtained using a JEOL 2100 TEM at 200 kV and the HRTEM images were obtained using a JEOL 3000F at 300 kV. Pore diameters were measured using Image Pro Plus software.

3.3.14 Atomic force microscopy (AFM)

The samples were prepared by spin-coating\(^1\) sol-gel onto silicon wafer at two subsequent speeds, 1000 and 3000 rpm for durations of 18 and 50 seconds, respectively. The coated wafers were air-dried. The measurements were performed on an Asylum, Cypher AFM. The images were obtained in the tapping mode using a cantilever with a nominal spring constant of approximately 40 N/m (Budget Sensors). The Pore size measurements were performed on AFM phase images using Image Pro Plus software.

3.3.15 Spectroscopic ellipsometry

Ellipsometry measurements were conducted on SEMILAB PS-1100 and PS-2500 porosimeters. The samples were prepared according to the same method used for AFM measurements (section 3.3.14).

\(^1\) Spin coater from Institute of Microelectronics of Chinese Academy of Science
CHAPTER FOUR

4 Improvement of photostability

4.1 Introduction

In this chapter, the differential absorption maxima ($\Delta A_{\text{max}}$), photostability, and coloration/bleaching rates of photochromic fabrics and their changes with different treatments are discussed. For some photochromic fabrics, the effects of different treatments on abrasion and washing durability, rigidity, and wettability are examined.

4.2 Experimental details

The coatings have been prepared according to the method described in section 3.2.1 and characterised using the methods described in section 3.3.

The lifetime of the photochromic effect was measured by exposing the coated fabric to strong UV light and simulated sunlight for certain periods of time. The optical absorption was measured at the beginning of the experiment and after each exposure period. The test was continued until a photochromic peak was no longer distinguishable in the absorption spectrum. Photochromic coloration and bleaching rates were calculated from the strips in Figure 4.2b.
4.3 Results and discussion

4.3.1 Preliminary experiments on the effect of FAS, double-coating, and UV-1084 on the properties of silica sol-gel coatings on fabric

4.3.1.1 Photochromic properties of OTES systems

The photochromic reaction of the spirooxazine dye is shown in Figure 4.1. The visible absorption spectra of an organosilica coated fabric doped with spirooxazine (SO) photochromic dye in the presence and absence of UV irradiation is displayed in Figure 4.2 a. In the absence of UV light, the absorption spectrum was a flat line, whereas a photochromic peak around the wavelength of 627 nm was observed in the presence of UV light.

Figure 4.1 Photochromic reaction of the spirooxazine dye Photorome II
Figure 4.2 (a) Visible absorption spectrum, and (b) coloration-bleaching curve of a photochromic silica coating on fabric.

The maximum absorption value of the coating recorded in real time at 627 nm is shown in Figure 4.2b. The time required for the absorption to ascend and subsequently descend to half of the maxima were calculated using the strips depicted in this graph and denoted as coloration and bleaching (or fading) half-life times, $t_{1/2}$ and $t'_{1/2}$, respectively. Figure 4.3 shows the first 29 cycles of
coloration and bleaching for an octyltriethoxysilane (OTES) silica coating containing photochromic dye. The progressive decay of absorption also referred to as *fatigue* can be clearly seen during sequential cycles.

![Graph showing consecutive cycles of coloration and bleaching](image)

**Figure 4.3** Consecutive cycles of coloration and bleaching of an OTES silica coating on fabric

A coating solution uptake of around 16.9%±0.8 was typically observed for a 20cm×20cm piece of fabric, calculated as explained in section 3.3.1. The absorption maxima of silica coatings from OTES precursor with a 1:100 dye to silica molar ratio was typically around 0.3±0.1. Coloration and bleaching half-life times for OTES silica coatings were around 2.2±0.2 and 3.1±0.1 seconds. The observed speed of coloration and bleaching of photochromic dye in the silica matrix was notably faster compared with photochromic dye embedded in fibres by exhaust dyeing, with reported times of approximately 10 seconds [69, 70]. The photostability, or resistance of the photochromic effect to fatigue, was measured by UV irradiation in a UV light box as well as a Suntest, as
described in section 3.3.2. Figure 4.4 shows the progressive drop of the absorption maxima with irradiation cycles. The corresponding absorption vs. time graphs are shown in Figure 4.5. Photo-degradation under the intense light of the UV light box was most rapid in the first 5 hours of UV irradiation. In the case of experiments conducted under Suntest, the loss of photochromic functionality was fastest during the first 15 hours of UV exposure. The rate of photo-degradation reduced after an initial period of rapid loss of photochromism. This trend in the speed of photo-degradation can be attributed to a screening effect in which the photochromic dyes in the uppermost layers of the coating are the first to become degraded from UV irradiation, and their degraded products screen the inner layers of dye from UV exposure. This effect was also reported in the work of Pardo, et. al. [37], as mentioned in section 2.3 of this thesis.

Although the Suntest provides a closer simulation of the real-life application of photochromic fabrics, due to the length of experiments conducted in the Suntest, the UV light box was adopted as the main apparatus for photostability testing in this work to expedite measurements. All photostability measurements in this work therefore have been conducted in the UV light box, unless specified otherwise.
Figure 4.4 Progressive decay of absorption maxima with time of irradiation in (a) UV light box, (b) Suntest
Figure 4.5 Photo-degradation of an OTES photochromic coating in (a) UV light box, (b) Suntest

As discussed in section 2.3, photo-degradation of photochromic compounds is an issue faced in many works in this field. The preliminary experiments in the present work also indicated that the photostability of the coatings required improvement. This was achieved via three methods (Figure 4.6):
1. Modifying the wettability of coatings in order to limit the access of moisture and other harmful elements to the photochromic dye, thereby promoting its longevity. This was done by enriching the pores of the silica matrix with fluorine using a fluorinated silane (FAS).

2. Sealing the pores of the silica matrix, again to prevent degrading components from reaching the dye. This was achieved by adding a protective layer of silica on coatings. In the following section (4.3.1.2), this process is referred to as double-coating, which involves coating a second layer of silica the same as the first. The sealing silica layer can also have been produced from a different precursor. Such coatings will be introduced in section 4.3.1.7 and further investigated in this chapter.

3. Incorporating a UV stabiliser, UV-1084, to reduce the impact of UV irradiation on the photochromic dye and enhance its photostability.
Figure 4.6 Illustration of (a) porous silica matrix with embedded photochromic dyes, and the methods of enhancing photostability: (b) enriching pores with fluorine, (c) sealing pores with a protective layer of silica, (d) incorporating UV stabiliser
4.3.1.2 Photochromic properties of OTES systems with FAS and double-coating

The absorption maxima of photochromic OTES coating, OTES coating with FAS, and OTES coating with added protective silica layer are compared in Figure 4.7. The three coatings showed similar maximum absorptions. Incorporation of FAS and an additional silica layer only slightly increased $\Delta A_{\text{max}}$.

![Graph showing absorption maxima of different coatings](image)

Figure 4.7 Maximum absorption of photochromic OTES coating, OTES coating with FAS, and OTES coating with added protective silica layer

The photochromic coloration and bleaching rates of the three coatings are displayed in Figure 4.8. The coloration and bleaching rates of the three studied coating types were in the range of 1.7-2.8 and 2.8-4.2 seconds, respectively, which are considered rapid and therefore quite satisfactory for photochromic systems. Coloration and bleaching speeds were slightly reduced as a result of introduction of FAS and additional silica into the coating system.
Figure 4.8 Photochromic coloration and bleaching rates of photochromic OTES coating, OTES coating with FAS, and OTES coating with added protective silica layer

The half-lifetime ($T_{50\%}$) of the samples, i.e. the time required for absorption maxima to be halved by UV irradiation, is shown in Figure 4.9. It can be observed that the incorporation of FAS and additional silica layering enhanced the photochromic half-lifetime of the samples from 7 hours in OTES coating to 8.8 and 9.8 hours in OTES with FAS and double-coated OTES, respectively.
Figure 4.9 Photostability half-lifetime of photochromic pure OTES coating, OTES coating with FAS, and OTES coating with added protective silica layer.

The durability of the photochromic effect against fatigue was also measured by the cycling lifetime, i.e. the number of successive cycles of coloration and bleaching a photochromic compound is capable of undergoing before it no longer shows photochromic functionality. In this work, due to the length of time of the measurement, the experiment was stopped before the samples had lost all their photochromic effect. The results of this experiment, as shown in Figure 4.10, revealed that the samples were stable enough to undergo at least 800 cycles of coloration and bleaching. As the cycling lifetime test did not appear to reveal more information about photostability than the UV box test, and given its long duration, it was abandoned in later experiments.
Figure 4.10 The measured cycling lifetime of photochromic OTES coating, OTES coating with FAS, and OTES coating with added protective silica layer

4.3.1.3 Water contact angle

The wettability of a garment is a determining factor in its wearability. In order to assess the effect of OTES silica coating as well as incorporation of FAS and additional silica layer on the wettability of coated fabrics, a water contact angle test was performed. The results are reported in Figure 4.11. The water contact angle of the three coatings was generally in the same range as that of the untreated fabric, which shows that the coatings did not significantly increase the fabric’s hydrophobicity. Water contact angle was slightly increased by incorporation of FAS and additional silica layering compared to OTES silica coating.
4.3.1.4 Durability to abrasion

Another important factor in a fabric’s wearability is its durability to abrasion. Therefore, the ability of fabric to retain its photochromic functionality was measured with 100, 300, 500, and 1000 abrasion cycles, as explained in section 3.3.3. The results are presented in Figure 4.12. The final durability to abrasion of the coated fabrics was in the range of 58-67%, with the FAS-treated sample showing the highest durability. This could be attributed to the oiliness caused by fluorine and long aliphatic chain of FAS, which may have created a lubricating effect, thus reducing the loss of coating by abrasion.
Figure 4.12 Durability to abrasion with number of abrasion cycles for OTES, OTES with FAS, and double-coated OTES silica coated fabrics

4.3.1.5 Durability to washing

The durability of a coated fabric to washing is also of importance for practicality of use. The experiments were performed according to the method explained in section 3.3.4. The results are shown in Figure 4.13. The wash-fastness of the FAS-treated photochromic fabric was slightly lower but close to that of OTES silica coating. The wash-fastness of the double-coated fabric however was significantly higher than the other two coatings, indicating that the protective layer of silica has effectively reduced the leaching out of photochromic dyes by washing.
Figure 4.13 Wash fastness of OTES, OTES with FAS, and double-coated OTES silica coated fabrics

4.3.1.6 Handle properties

The handle or bending properties of a coated fabric are also of importance in practical use. Therefore, the effect of the silica coatings on flexural rigidity (G) and bending modulus (Q) were investigated. The calculation of values was performed according to the method explained in section 3.3.6. The results are shown in Figure 4.14. Flexural rigidity and bending modulus, which are measures of fabric stiffness, were both lower for all three coatings compared to the control, indicating a superior handle or drape induced by the coatings. This can be attributed to the long (octyl) aliphatic chain of OTES which softens the fabric.
Figure 4.14 (a) Flexural rigidity and (b) bending modulus of uncoated fabric (control), OTES, OTES with FAS, and double-coated OTES silica coated fabrics in warp and weft directions

4.3.1.7 Photochromic properties of OTES coatings with MPS and APS protective layers

In this section, experiments on sealing the pores of the silica matrix with an additional silica layer of (3-trimethoxysilyl)propyl methacrylate (MPS) or (3-
aminopropyl)triethoxysilane (APS) sol-gel are discussed. APS is used for chemical modification of silica and alumina surfaces in applications such as chromatography, or as coupling agent in treating glass fibres [96]. Similarly, MPS has applications in surface modification for promoting adhesion to particular surfaces and as a coupling agent [97].

Figure 4.15 Absorption spectra of double-coated fabric with the first layer containing OTES silica and photochromic dye and the second containing MPS or APS silica without dye

Figure 4.15 shows the absorption spectra of photochromic OTES silica coated fabrics with an additional layer of MPS or APS silica for sealing the pores. The sample containing MPS showed an enhanced absorption maximum, while that containing APS showed a significant reduction in absorption at peak. The absorption peak also became wider in the case of the APS sample. The photochromic properties of MPS and APS double-coated samples are shown in Table 4.1 along with those of OTES silica double-coating for comparison. The coloration and bleaching speeds of MPS and APS double-coatings were
slightly more rapid and their photostability especially that of APS was higher than OTES double-coating. The results indicated that sealing the matrix pores with a suitable silica type could have a significant effect on the resistance of the photochromic dye to photo-degradation. In the case of APS, it is thought that the amine group helps protect the chromophore from degradation with prolonged irradiation \[98\]. Furthermore, water contact angle test revealed that the presence of an amine group slightly affected the wettability of the APS coating. The contact angle of the OTES/APS sample was \[116^\circ\pm4.5\], which is lower than that of OTES/OTES \[132^\circ\], meaning the OTES/APS sample was slightly more hydrophilic as a result of the presence of an amine group.

Table 4.1 Photochromic properties of OTES silica coated fabrics containing photochromic dye with additional OTES, MPS, or APS silica coating as protective layer, and PhTES silica coated fabrics containing photochromic dye with additional PhTES, MPS, or APS silica coating as protective layer

<table>
<thead>
<tr>
<th>Coating</th>
<th>(\Delta A_{\text{max}})</th>
<th>(t_{1/2}) (s)</th>
<th>(t'_{1/2}) (s)</th>
<th>Photostability (h)</th>
<th>Uptake (%)</th>
<th>1st layer</th>
<th>2nd layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTES/OTES</td>
<td>0.43</td>
<td>2.5</td>
<td>4.2</td>
<td>31</td>
<td>34.7</td>
<td>23.6</td>
<td></td>
</tr>
<tr>
<td>OTES/MPS</td>
<td>0.56</td>
<td>1.2</td>
<td>2.4</td>
<td>50</td>
<td>42.3</td>
<td>33.9</td>
<td></td>
</tr>
<tr>
<td>OTES/APS</td>
<td>0.09</td>
<td>1</td>
<td>1.8</td>
<td>130</td>
<td>34.4</td>
<td>18.05</td>
<td></td>
</tr>
<tr>
<td>PhTES/PhTES</td>
<td>0.6</td>
<td>3</td>
<td>8.6</td>
<td>15</td>
<td>27.04</td>
<td>6.41</td>
<td></td>
</tr>
<tr>
<td>PhTES/MPS</td>
<td>0.5</td>
<td>1.3</td>
<td>2.4</td>
<td>50</td>
<td>26.6</td>
<td>33.1</td>
<td></td>
</tr>
<tr>
<td>PhTES/APS</td>
<td>0.15</td>
<td>6.1</td>
<td>41.5</td>
<td>40</td>
<td>28.6</td>
<td>24.03</td>
<td></td>
</tr>
</tbody>
</table>

\(^a^{\text{Fabric size: 15cm\times15cm}}\)

In order to further investigate the effect of MPS and APS silica protective layers as well as study the effect of the type of silica used in the underlying layer, double-coated samples were produced with phenyltriethoxysilane
(PhTES) rather than octyltriethoxysilane (OTES) as the precursor of the underlying layer. The photochromic properties of PhTES silica coated fabrics with PhTES, MPS, or APS silica coatings as secondary protective layer are reported in Table 4.1. Comparing the data of OTES-based double-coatings with PhTES-based double coatings, it can be observed that there was only a small difference between $\Delta A_{\text{max}}$ of OTES/MPS (0.56) and PhTES/MPS (0.5), and also between OTES/APS (0.09) and PhTES/APS (0.15). However, the $\Delta A_{\text{max}}$ of PhTES/PhTES (0.6) was noticeably higher than OTES/OTES (0.43). On the other hand, OTES/OTES was more photo-stable than PhTES/PhTES. Following the same trend, photostability of OTES/APS double-coating was significantly higher than PhTES/APS. Photostability of OTES/MPS double-coating however was very close to that of PhTES/MPS. While the coloration rate of PhTES/PhTES was similar to OTES/OTES, its bleaching rate was retarded by two-fold. This can be attributed to the interaction of the open merocyanine form of the photochromic dye with the phenyl ring of PhTES which has an increased presence in the PhTES/PhTES double-coating. This interaction hinders the off-reaction of the chromophore. Coloration and especially bleaching rates slowed down significantly in PhTES/APS double-coated fabric. This can be explained by ionic attractions occurring between the amine cation and oxygen anion which appears in the open form of spirooxazine as a result of cleavage of the spiro bond upon excitation with UV irradiation. The fact that such marked changes were not observed in the coloration and bleaching rates of MPS double-coatings supports the above theory.
4.3.1.8 Photochromic properties of OTES systems with UV-1084

In this section, the results of preliminary experiments concerning the effect of UV stabilisers on photostability are presented. The studied UV stabiliser in this part of the work was UV-1084, a quencher which seizes the energy received by the photochromic dye and dispels or “quenches” it, thereby prolonging the dye’s lifetime. The absorption spectrum of OTES silica coated fabric without and with different amounts of UV-1084 stabiliser is shown in Figure 4.16. It can be seen that the incorporation of 0.5% UV-1084 (mol/mol% of silica) caused a bathochromic shift, as a result of the green colour of the UV stabiliser.

![Absorption spectra of OTES silica coatings on fabric with different amounts of UV-1084 stabiliser](image)

Figure 4.16 Absorption spectra of OTES silica coatings on fabric with different amounts of UV-1084 stabiliser

The photochromic properties of OTES silica coated fabrics containing 0.1% and 0.5% UV-1084 are shown in Table 4.2. A comparison of the photostability half-lifetime ($T_{50\%}$) and total lifetime ($T_{100\%}$) of pure OTES silica coated fabrics with those containing UV-1084 shows that the incorporation of UV...
stabiliser improved photostability. The effect was less pronounced in half-lifetime than total lifetime. Half-lifetime ($T_{50\%}$) was initially adopted as a means of comparing the photostability of different coatings in a shorter length of time. However, as the absorbance maxima of the coated fabrics declined rapidly in the first few hours of UV irradiation, $T_{50\%}$ was deemed too small to enable an accurate comparison between coatings. Therefore, the total lifetime of a sample with UV irradiation was adopted as a measure of photostability in later experiments.

Table 4.2 Properties of OTES silica coatings on fabric with different amounts of UV-1084 stabiliser

<table>
<thead>
<tr>
<th></th>
<th>$\Delta A_{\max}$</th>
<th>$t^{1/2}$ (s)</th>
<th>$t^{1/2}$ (s)</th>
<th>$T_{50%}$ (h)</th>
<th>$T_{100%}$ (h)</th>
<th>CA (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTES</td>
<td>0.397</td>
<td>2.3</td>
<td>3</td>
<td>8</td>
<td>16</td>
<td>123</td>
</tr>
<tr>
<td>OTES with 0.1% UV1084</td>
<td>0.366</td>
<td>2.4</td>
<td>2.9</td>
<td>10</td>
<td>31.5</td>
<td>132</td>
</tr>
<tr>
<td>OTES with 0.5% UV1084</td>
<td>0.435</td>
<td>1.8</td>
<td>2.7</td>
<td>10</td>
<td>31.5</td>
<td>131</td>
</tr>
</tbody>
</table>

$T_{50\%}$: half-lifetime; $T_{100\%}$: total lifetime; CA: Contact Angle

The effect of UV stabiliser incorporation on absorption maximum was inconsistent between the 0.1% and 0.5% concentration samples. This also applied to coloration and bleaching rates. Overall, the effect of introduction of UV stabilisers on absorption maxima and coloration and bleaching rates was small.

The incorporation of UV stabiliser increased the water contact angle similarly to that observed for FAS and added silica.
4.3.1.9 SEM

The uncoated, OTES silica-coated, and OTES silica with UV stabiliser-coated fabrics were characterised by SEM. The results are shown in Figure 4.17. SEM was also employed to investigate whether any observable changes were caused on fibre surfaces as a result of prolonged UV irradiation, as shown in Figure 4.17 d. No significant effects were observed in this respect.

![SEM images](image)

Figure 4.17 SEM images of (a) uncoated fabric, (b) OTES silica coated fabric, (c) OTES silica coated fabric with UV-1084, (d) OTES silica coated fabric with UV-1084 after 16 hours of UV irradiation

4.3.2 Finding a combinatory silica system with optimal properties

The experimental results discussed in section 4.3.1.7 revealed the importance of the silica type of the underlying coating in a double-coated system. This
suggested the need for further investigation into the role of silica precursor in determining the properties of the final coating. This section deals with the following question: which silica precursor or combination of silica precursors leads to coatings with optimal photochromic, abrasion and wash durability, wettability, and handle properties? In order to answer this question, the properties of single and combinatory silica systems will be compared in this section.

4.3.2.1 Photochromic properties

Table 4.3 shows the photochromic properties of photochromic fabrics coated with OTES, PhTES, and three combinations of OTES/PhTES silica. A comparison between the absorption maxima of the studied coatings showed that phenyl-modified silica (PhTES) produced the highest photochromic intensity. The coloration rates of all the coatings were around 2 seconds. The bleaching rates were approximately between 3 and 6 seconds, and PhTES silica produced the slowest bleaching rate among all coatings. Furthermore, OTES:PhTES 1:2 coating showed a slightly slower bleaching rate than the other two OTES/PhTES combinations, which can be attributed to the presence of a higher amount of PhTES. The hindering effect of PhTES on bleaching can be explained by the interaction of the merocyanine form with the phenyl ring, which was also mentioned in section 4.3.1.7. Photostability was highest in OTES:PhTES 2:1 silica coated fabric, followed by that of OTES coated fabric. Furthermore, the photostability of OTES/PhTES combinations increased in the order of their OTES content.
Table 4.3 Photochromic properties of single and combinatory silica coatings on fabric

<table>
<thead>
<tr>
<th>Coating</th>
<th>$\Delta A_{\text{max}}$</th>
<th>$t_{1/2}$ (s)</th>
<th>$t'_{1/2}$ (s)</th>
<th>Photo-stability (h)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OTES</td>
<td>0.25±0.03</td>
<td>2±0.2</td>
<td>3.2±0.3</td>
<td>20±1.4</td>
<td>31.9±0.6</td>
</tr>
<tr>
<td>PhTES</td>
<td>0.35±0.1</td>
<td>2.2±0.5</td>
<td>6.4±0.7</td>
<td>12.5±2.5</td>
<td>27.8±0.6</td>
</tr>
<tr>
<td>OTES:PhTES 2:1 $^a$</td>
<td>0.27±0.02</td>
<td>2.1±0.5</td>
<td>3.7±0.1</td>
<td>23.7±4.5</td>
<td>17.1±0.8</td>
</tr>
<tr>
<td>OTES:PhTES 1:1</td>
<td>0.26±0.02</td>
<td>2±0.1</td>
<td>3.6±0.3</td>
<td>16±1.7</td>
<td>13.2±1.1</td>
</tr>
<tr>
<td>OTES:PhTES 1:2</td>
<td>0.29±0.1</td>
<td>2±0.1</td>
<td>4.1±0.2</td>
<td>9.7±0.2</td>
<td>15.5±0.1</td>
</tr>
</tbody>
</table>

$^a$ molar ratio

4.3.2.2 Durability to abrasion

The durability of OTES, PhTES, and OTES/PhTES combinatory silica coated fabrics to abrasion is shown in Figure 4.18. PhTES coating exhibited the highest durability to abrasion. Furthermore, among the three OTES/PhTES combinations, durability to abrasion increased with PhTES content. Two deviations from the expected downward trend were observed, one in OTES:PhTES 1:2 and another in PhTES, between the 300th and 500th abrasion cycles. These could be due to slight non-uniformity in coating thickness across the sample which affects absorption and consequently the abrasion durability results. The decay of the photochromic absorption peak with abrasion in OTES/PhTES combinations is shown in Figure 4.19.
Figure 4.18 Durability to abrasion of single and combinatorial silica coatings on fabric
Figure 4.19 Decay of photochromic absorption maxima with abrasion in (a) OTES:PhTES 2:1, (b) OTES:PhTES 1:1, (c) OTES:PhTES 1:2

4.3.2.3 Durability to washing

The durability of OTES, PhTES, and OTES/PhTES combinatorial silica coated fabrics to washing is shown in Figure 4.20. Similar to the abrasion durability results, PhTES coated fabric displayed the highest durability to washing. Moreover, washing durability in OTES/PhTES combinations seemed to relate
to PhTES content, although OTES:PhTES 1:2 showed slightly lower (rather than higher) levels of wash-fastness compared to OTES:PhTES 1:1. The decay of the photochromic absorption peak with washing in OTES/PhTES combinations is shown in Figure 4.21.

Figure 4.20 Durability to washing of single and combinatory silica coatings on fabric

(a)
Figure 4.21 Decay of photochromic absorption maxima with washing in (a) OTES:PhTES 2:1, (b) OTES:PhTES 1:1, (c) OTES:PhTES 1:2 silica coated fabrics

4.3.2.4 Handle properties

The flexural rigidity and bending modulus of OTES, PhTES, and OTES/PhTES combinatory silica coated fabrics are shown in Figure 4.22 a and
b, respectively. PhTES coated fabric was the most rigid of the studied coated fabrics, with the highest flexural rigidity and bending modulus. OTES coated fabric showed the lowest flexural rigidity and bending modulus. OTES/PhTES combinations did not show the trend observed with abrasion and washing durability. In other words, no direct relationship was observed between the PhTES content of OTES/PhTES combinations and their rigidity. In general, all the studied coated fabrics except PhTES showed a level of rigidity in the same range as the uncoated control fabric.
Figure 4.22 (a) Flexural rigidity and (b) bending modulus of single and combinatorial silica coatings on fabric

4.3.2.5 Water contact angle

The water contact angle of OTES, PhTES, and OTES/PhTES combinatorial silica coated fabrics is shown in Figure 4.23. OTES coated fabric showed the lowest and PhTES coated fabric the highest contact angle. The contact angles of the studied OTES/PhTES combinations were quite similar to one another.
4.3.2.6 Conclusions

The comparative studies of photochromic, durability, handle, and wettability properties of OTES, PhTES, and OTES/PhTES combinatorial silica coated fabrics indicated that while OTES coated fabric showed higher photostability and faster coloration/bleaching, PhTES coated fabric exhibited higher absorption maximum and abrasion and washing durability. This is why a combinatorial silica system was considered in order to obtain a coating with optimal properties by combining the properties of individual precursors. For this reason, coatings with 3 molar ratios between OTES and PhTES precursors were studied. The three combinatorial coatings on fabric showed relatively similar photochromic, handle, and wettability properties. Among the three combinations, the OTES:PhTES 1:2 ratio resulted in the best abrasion durability and satisfactory wash fastness. Considering the aforementioned
reasons, the OTES:PhTES 1:2 precursor ratio was selected as the basic coating for the study of all treatments in the present work.

4.3.3 Effect of UV stabilisers, surface wettability modification, and additional silica layering on the properties of combinatorial silica coatings

In this section, the photochromic, handle, and wettability properties of OTES:PhTES 1:2 silica coated fabric with different treatments will be discussed. The first type of treatment involved adding three types of UV stabilisers to the sol, including a UV quencher (UV-1084), two UV absorbers (Tinuvin 329 and HMBP), and one free radical trapper (HALS 622). The second treatment involved modifying the wettability of silica coated fabric by adding FAS to the sol. The third type of treatments involved adding a secondary protective layer of silica for sealing the matrix pores. The protective layer was of a silica type the same as the first layer or from MPS or APS silica. The nomenclature for different coatings discussed in this section is given in Table 4.4. The chemical structures of the UV stabilisers, FAS, APS, and MPS are given in Figure 4.24.
Table 4.4 Coating conditions

<table>
<thead>
<tr>
<th>Method</th>
<th>Additives</th>
<th>Constituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>OP12 sol + dye</td>
<td></td>
</tr>
<tr>
<td>Adding UV stabiliser</td>
<td>UV1084</td>
<td>OP12 sol + UV-1084 + dye</td>
</tr>
<tr>
<td></td>
<td>HALS622</td>
<td>OP12 sol + HALS-622 + dye</td>
</tr>
<tr>
<td></td>
<td>Tinuvin329</td>
<td>OP12 sol + Tinuvin 329 + dye</td>
</tr>
<tr>
<td></td>
<td>HMBP</td>
<td>OP12 sol + HMBP + dye</td>
</tr>
<tr>
<td>Fluorinating</td>
<td>FAS</td>
<td>[OP12 + FAS] sol + dye</td>
</tr>
<tr>
<td>Dbl. coating with extra silica</td>
<td>APS</td>
<td>1st layer: OP12 sol + dye</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd layer: APS sol only</td>
</tr>
<tr>
<td></td>
<td>MPS</td>
<td>1st layer: OP12 sol + dye</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd layer: MPS sol only</td>
</tr>
<tr>
<td></td>
<td>Same silica</td>
<td>1st layer: OP12 sol + dye</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2nd layer: OP12 sol only</td>
</tr>
</tbody>
</table>

*a* OP12 stands for OTES:PhTES 1:2

Figure 4.24 The chemical structures of UV stabilisers: (a) UV-1084, (b) HALS-622, (c) Tinuvin-329, (d) HMBP, as well as (e) FAS, (f) APS, and (g) MPS
4.3.3.1 Photochromic properties

The photochromic absorption maxima of the studied coated fabrics are shown in Figure 4.25. The UV absorbers and extra APS silica coating reduced the maximum absorption while HALS-622 exhibited a smaller impact and UV-1084 displayed none. The observed reduction of absorption maxima by UV absorbers can be explained by the very nature of these stabilisers. In other words, this type of UV stabiliser competes with the dye in absorbing UV light and therefore reduces the photochromic dye’s exposure to irradiation, hence the decrease in $\Delta A_{\text{max}}$. The decline of maximum absorption caused by the inclusion of APS in the coating can be attributed to the ionic attraction between the amine group in APS and the open or merocyanine form of spirooxazine, as previously explained in section 4.3.1.7.

Figure 4.25 The differential absorption of the control silica coated fabric and fabric coatings with UV stabiliser, FAS, and added silica; (2xSS stands for double-coating with the same silica)
The photostability results of the studied coated fabrics are displayed in Figure 4.26. All the three studied types of treatment, namely UV stabiliser incorporation, surface wettability modification, and additional silica layering, improved photostability. The incorporation of UV-1084 was the most efficient treatment in terms of increasing photostability. UV-1084 is a nickel chelate which is believed to stabilize the photochromic dye by quenching the excited form of the dye or by quenching the oxygen radicals, which are the main cause of the dye’s oxidation, via an energy transfer mechanism [3, 4]. Superoxide anion oxygen is believed to be the cause of the photo-degradation of the dye [2].

The next most effective treatment was double-coating with APS silica. APS has not been previously used as a means of stabilizing spiropyrane dyes and therefore the mechanism by which APS increases the lifetime of spiropyrane molecules is unknown. Zhang, et. al. [99, 100] produced photochromic sol-gel films with molybdenum heteropolyoxometallate as the photochromic entity. APS was used as the precursor of the sol along with TEOS. They reported a higher absorption maximum and photostability observed for molybdenum heteropolyoxometallate compared with the other studied oxometallates, and concluded that this was the result of the higher reduction potential of the molybdenum compound. They proposed the existence of a charge transfer between the amine group of APS and the photochromic compound. The previously proposed idea in the present work concerning the existence of ionic attractions between the merocyanine form of spiropyrane and the amine group of APS is in line with the findings of Zhang, et. al. regarding the enhancement of photostability. However, their findings contradicted the observed reduction in maximum absorption in the present work for APS double coatings. This may
be due to the essentially different chemical structures of spirooxazine and oxometallate compounds which naturally affects the mechanism of their interaction with amine groups.

The incorporation of FAS slightly increased photostability. This can be attributed to the enrichment of pores with fluorine, which helps prevent access of degrading elements in the environment, such as moisture, to the dye [10]. However, the effectiveness of this treatment in terms of enhancing photostability was the lowest among the three studied types of treatment.

The UV absorbers (Tinuvin-329 and HMBP) and the free radical trapper (HALS-622) improved photostability. As implied by the name, UV absorbers capture the energy of UV rays, thus reducing the photochromic dye’s exposure to irradiation, therefore prolonging its lifetime. UV absorbers of the benzotriazol family, such as Tinuvin 329, undergo a transformation between enol and keto forms when excited by irradiation [8]. Benzophenones such as HMBP undergo proton transfer upon excitation [9]. Hindered amine light stabilisers (HALS) work as antioxidants and scavenge or trap peroxy radicals, which are detrimental to the photochromic dye [7]. It is difficult to judge the performance of the UV absorbers in comparison with the free radical trapper (HALS-622), as Tinuvin-329 performed better than HALS-622 in terms of improving photostability, while HMBP was slightly less effective.
Figure 4.26 Photostability of the control silica coated fabric and fabric coatings with UV stabiliser, FAS, and added silica
Figure 4.27 Change of photochromic absorption with UV irradiation time tested in (a) Hg metal halide lamp, and (b) Suntest

The changes of UV absorption with time for the two most photo-stable coated fabrics, measured in a UV light box, are shown in Figure 4.27 a. Absorption dropped with a rate of 0.01 and 0.03 for UV-1084 and APS, respectively, in the first cycle (3.2 hours). This was followed by a 0.04 and 0.01 drop in the following cycle for UV-1084 and APS, respectively. As also mentioned in section 4.3.1.1, photo-degradation was most rapid in the first few cycles of irradiation, but slowed down after approximately 10 hours of UV exposure, due to the screening effect of the degraded spirooxazine molecules in the upper layers of the coating. Figure 4.27 b shows the UV absorption change for the UV-1084 and APS coatings during irradiation with Suntest. The slope of the fall was 0.003 for UV-1084 and 0.009 for APS in the first exposure period (5 hours). This was followed by a 0.006 and 0.005 decline for UV-1084 and APS, respectively, in the second cycle of irradiation. The rate of photochromic loss in a Suntest was an order of magnitude slower compared to the UV light box.
The photostability of the control, UV-1084, APS, and FAS samples, measured using Suntest, were 45±0, 328.3±2.9, 113.3±5.8, and 36.7±2.9 h, respectively.

Figure 4.28 shows the coloration and bleaching half-life times for the control and treated samples. It was observed that the incorporation of UV stabilisers, FAS coating, and double-coating with the same silica as the underlying layer hindered coloration and bleaching, while extra layering with APS silica improved both these rates and MPS enhanced bleaching rates only. Overall, the impact of the treatments on coloration and bleaching rates was considered insignificant.

![Graph showing coloration and bleaching half-life times](image)

*Figure 4.28 Coloration and bleaching rates of the control silica coating and coatings with UV stabiliser, FAS, and added silica*

### 4.3.3.2 Durability to abrasion

The durability of the coated fabrics against abrasion after 1000 abrasion cycles is shown in Figure 4.29. The incorporation of Tinuvin-329 and HMBP UV absorbers reduced the durability by approximately 2%, while MPS and FAS
caused a 9% and 11% fall, respectively. Double coating with the same silica (2xSS) and APS treatments enhanced durability by 11% and 13%, respectively. In general, the treatments did not seem to lead to a significantly large change in abrasion durability and the overall level of abrasion fastness was satisfactory. The decline of absorption maximum with irradiation cycles is shown in Figure 4.30.

![Diagram showing abrasion durability](image)

Figure 4.29 Abrasion durability after 1000 abrasion cycles for the control silica coated fabric, and fabric coatings with UV stabiliser, FAS, and added silica
Figure 4.30 Decline of absorption maxima with number of abrasion cycles for (a) UV-1084, (b) HALS-622, (c) Tinuvin 329, (d) HMBP, (e) FAS, (f) APS, (g) MPS, (h) added silica (2xSS)
4.3.3.3 Durability to washing

The washing durability of the coated fabrics is reported in Figure 4.31. The incorporation of UV-1084 and Tinuvin 329 were found to improve the washing durability, while the other treatments showed reduced durability compared to the control. The washing durability of the MPS double coated fabric was the lowest among all of the treated fabrics.

![Graph showing wash durability](image)

Figure 4.31 Durability of the control silica coated fabric, and fabric coatings with UV stabiliser, FAS, and added silica to washing

4.3.3.4 Bending properties

The flexural rigidity (mg·cm) and bending modulus (kg/cm²) of the coated fabrics are shown in Figure 4.32. The results indicated an increase in stiffness caused by APS silica treatment. All the treated fabrics showed a higher flexural rigidity and bending modulus in the warp direction in comparison with the control, while this trend was not observed for all of the coated fabrics in the weft direction.
Figure 4.32 Flexural rigidity and bending modulus of the control silica coated fabric, and fabric coatings with UV stabiliser, FAS, and added silica

4.3.3.5 Water contact angle

The water contact angle of the coated fabrics is compared in Figure 4.33. All the treatments increased the contact angle compared to the control fabric. In other words, all of the coated fabrics were more hydrophobic compared to the control.
Figure 4.33 Water contact angle of the control silica coated fabric, and fabric coatings with UV stabiliser, FAS, and added silica

4.4 Summary

In this chapter, the effects of different treatments on the photochromic, durability, handle, and wettability properties of photochromic fabrics were investigated. The preliminary results indicated that the photostability of the coated fabrics required improvement. To this end, the effect of three types of treatment on photostability as well as other properties of the photochromic fabric was studied. The treatments included incorporating UV stabilisers, modifying surface wettability, and sealing dye-loaded pores with additional silica. A basic silica precursor ratio (OTES:PhTES 1:2) was selected for the underlying coatings in testing the effects of the three treatments. All the treatments improved photostability to different extents, but did not affect the other photochromic properties significantly. The highest photostability was obtained by incorporation of a quencher UV stabiliser. The addition of an extra
layer of APS silica was the next most effective treatment in terms of photostability, although it lowered maximum absorption and increased coating rigidity. All coatings exhibited high abrasion durability and acceptable wash fastness.
5 Improvement of colour depth

5.1 Introduction
For a photochromic fabric to be appealing in application, a deep colour is necessary to generate a strong visual impact. In other words, a high absorption maximum is required upon irradiation with UV light. To achieve this, a high dye loading is necessary in the silica coating. However, this can lead to dye aggregation, which leads to reduced absorption maxima. In this chapter, possible ways of achieving high absorption maxima in fabric coatings were explored. The studied methods include encapsulating spirooxazine in cyclodextrin, changing the solvent, incorporating a surfactant, embedding spirooxazine in polymethylmethacrylate (PMMA) film, synthesizing spirooxazine/PMMA particles, and incorporating polymethylmethacrylate (PMMA)/silica copolymer in silica coating.

5.2 Experimental details
The experimental details for improving photochromic colour depth are given in sections 3.2.2 to 3.2.8. To increase the loading of spirooxazine on fabric without aggregation, the dye was encapsulated in β-cyclodextrin and then dispersed in sol-gel before the coating treatment. To investigate the effect of solvent on dye dispersion and the resultant absorption maxima, ethanol, acetone, THF, and DMF were used as solvent for preparing the coating
solution. DTAB surfactant was also used to investigate the possibility of obtaining high dye loadings with good dispersion. To explore the effect of PMMA on photochromic colour depth, spirooxazine was embedded in PMMA film, PMMA particles, and PMMA/silica coating. The PMMA particles were dispersed in a hydrophilic resin or silica sol-gel for coating treatment.

5.3 Results and discussion

5.3.1 Spirooxazine-cyclodextrin inclusion complex

Spirooxazine was encapsulated in the cavity of cyclodextrin in the form of an inclusion complex. Cyclodextrin was used for its hydrophobic interior and hydrophilic exterior which makes it ideal for hosting hydrophobic spirooxazine molecules and keeping them separated from each other. This allows the incorporation of more photochromic dye in silica coatings while avoiding dye aggregation. The photochromic properties of sol-gel-coated fabrics with spirooxazine-β-cyclodextrin complexes are shown in Table 5.1. The $\Delta A_{\text{max}}$ results of the SO-β-CD complex showed 26.7% improvement compared to the control coated sample. A comparison of the coloration and bleaching rates of the control and the SO-β-CD complex indicated that the double encapsulation of spirooxazine, first in the β-cyclodextrin cavity and then in silica pores, decelerated coloration and bleaching. On the other hand, this double encapsulation helped with protection of the dye from degradation, therefore increasing its photostability.
Table 5.1 Photochromic properties of SO-β-CD complex embedded in silica coating on fabric

<table>
<thead>
<tr>
<th>Samples</th>
<th>ΔA_{max}</th>
<th>t_{1/2} (s)</th>
<th>t'_{1/2} (s)</th>
<th>Photostability (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control a</td>
<td>0.3</td>
<td>1.6</td>
<td>3.3</td>
<td>9.5</td>
</tr>
<tr>
<td>SO- β-CD</td>
<td>0.38±0.0005</td>
<td>2.2±0.1</td>
<td>4.7±0.1</td>
<td>11.1±1.6</td>
</tr>
</tbody>
</table>

a control: OTES:PhTES 1:2 silica with SO dye

In another experiment, the dye to silica ratio (SO:RSi) was increased from 1:100 to 1:50 and 1:25 (mol:mol), and the amount of β-CD was increased accordingly to ensure full encapsulation of spirooxazine. The results are shown in Table 5.2. When comparing the maximum absorption of SO:RSi 1:25 with that of SO:RSi 1:50, as well as with ΔA_{max} of the samples in Table 5.1, it was evident that the large increase in dye content led to a decrease in maximum absorption, presumably due to dye aggregation, which occurred as a result of the hydrophobic nature of the dye. This limited the structural transformation of the dye, reducing its absorption maxima. The coloration and bleaching rates of SO-β-CD coatings did not change significantly with increased dye content (Table 5.2). The photostability of the coatings however increased with increasing the dye content. This phenomenon was ascribed to a screening effect of photochromic dyes (see section 4.3.1).

Table 5.2 Photochromic properties of SO-β-CD complex containing excess spirooxazine, embedded in sol-gel and coated on fabric

<table>
<thead>
<tr>
<th>Sample</th>
<th>ΔA_{max}</th>
<th>t_{1/2} (s)</th>
<th>t'_{1/2} (s)</th>
<th>Photostability (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO:RSi 1:50</td>
<td>0.22±0.03</td>
<td>2.6±0.2</td>
<td>5.05±0.4</td>
<td>12.7</td>
</tr>
<tr>
<td>SO:RSi 1:25</td>
<td>0.15±0.01</td>
<td>3.01±0.4</td>
<td>3.9±0.1</td>
<td>15.8</td>
</tr>
</tbody>
</table>
Figure 5.1 TGA curves of spirooxazine (SO), β-cyclodextrin (CD), SO-β-CD complex, and SO-β-CD mixture

The TGA results, shown in Figure 5.1, revealed that the decomposition temperature of SO-β-CD complex was almost identical to that of SO (i.e., 260°C) and different to β-CD’s (300 °C). On the other hand, the decomposition temperature of the mixture of SO and β-CD was very close to that of β-CD, with the difference between the two being a higher weight loss in the SO-β-CD mixture. Seeing that this initial weight loss occurred at temperatures lower than 100 °C, it can be attributed to the presence of moisture in the samples which was removed at higher temperatures [45].

Figure 5.2 shows the XRD patterns of spirooxazine, β-cyclodextrin, SO-β-CD mixture, and SO-β-CD complex. Both SO-β-CD mixture and SO-β-CD complex showed elements of both spirooxazine and β-cyclodextrin. However, the prominent peaks observed in the SO-β-CD complex were mostly in the
same coordinates as those in spirooxazine. On the other hand, the SO-β-CD mixture showed more common peaks with β-cyclodextrin.

Figure 5.2 XRD patterns of spirooxazine (SO), β-cyclodextrin (CD), SO-β-CD mixture, and SO-β-CD complex

Figure 5.3 shows the results of DSC test for β-cyclodextrin (β-CD), spirooxazine (SO), SO-β-CD complex, and SO-β-CD mixture. The studied samples showed only first order transition. Endothermic peaks were observed in the DSC curves which were indicative of melting. No peaks indicating glass transition or crystallization were observed.

The DSC results of spirooxazine and SO-β-CD complex were quite similar, as also seen in the TGA data. Spirooxazine and SO-β-CD complex showed almost identical sharp melting peaks at 181°C and 180°C, respectively. A broad asymmetrical peak was observed at 107°C in the β-CD curve which was also seen in the SO-β-CD mixture at 111°C, close to that of β-CD. This peak was
not observed in the curve of the SO-β-CD complex, confirming the formation of a complex. The SO-β-CD mixture also showed a sharp endothermic peak at 180°C, indicating the melting of the spirooxazine constituent of the mixture.

![DSC results](image)

**Figure 5.3 DSC results for β-cyclodextrin (β-CD), spirooxazine (SO), SO-β-CD complex, and SO-β-CD mixture**

### 5.3.2 Solvent effect

To increase the concentration of photochromic dye in the silica coating, the solubility of the dye in different solvents was investigated. The solubility of photochromic dye in ethanol, which was the main solvent in this work, was compared to that in acetone, dimethylformamide (DMF), and tetrahydrofuran (THF). The results are shown in Table 5.3. The dye showed 3, 6, and 7 times more solubility in acetone, DMF, and THF, respectively, than in ethanol.

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However, when these solutions were mixed with silica sol-gel and then coated on fabric, despite having larger dye content, they produced lower absorption maxima compared to that using ethanol. There was an optimum concentration of dye which had been exceeded in these coatings.

The coloration and bleaching rates were not significantly affected by the solvent type. Photostability was strongly dependent on dye content, as also seen previously.

Table 5.3 Photochromic properties of OTES:PhTES 1:2 silica coatings on fabric with different solvents for coating treatment

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dye content (%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>$\Delta A_{\text{max}}$</th>
<th>$t_{1/2}$ (s)</th>
<th>$t'_{1/2}$ (s)</th>
<th>Photostability (h)</th>
<th>Pick-up (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>1.7</td>
<td>0.34±0.02</td>
<td>2.05±0.3</td>
<td>4.1±0.5</td>
<td>9.2±0.8</td>
<td>15.8±0.4</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.2</td>
<td>0.25±0.06</td>
<td>3.2±0.1</td>
<td>5.4±0.4</td>
<td>29.6±4.8</td>
<td>17.71</td>
</tr>
<tr>
<td>DMF</td>
<td>10.4</td>
<td>0.23±0.04</td>
<td>2.5±0.4</td>
<td>4.6±0.2</td>
<td>35.4±5.4</td>
<td>19.42</td>
</tr>
<tr>
<td>THF</td>
<td>12</td>
<td>0.21±0.04</td>
<td>2.4±0.4</td>
<td>4.4±0.2</td>
<td>34.2±6.5</td>
<td>20.94</td>
</tr>
</tbody>
</table>

<sup>a</sup> dye (g)/[dye+silica] (g) × 100

Among the studied solvents, THF was capable of dissolving the highest amount of photochromic dye. The photochromic properties of silica coatings with 1.7% dye content and with ethanol and THF as solvent are shown in Table 5.4. The absorption maximum of the THF system was 17.6% higher than that of ethanol.
Table 5.4 Photochromic properties of OTES:PhTES 1:2 silica coatings on fabric with different solvents when the spirooxazine content (dye (g)/[dye+silica] (g) × 100) was 1.7%

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Delta A_{\text{max}}$</th>
<th>$t_{1/2}$ (s)</th>
<th>$t'_{1/2}$ (s)</th>
<th>Photostability (h)</th>
<th>Pick-up (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH</td>
<td>0.34±0.02</td>
<td>2.05±0.3</td>
<td>4.1±0.5</td>
<td>9.2±0.8</td>
<td>15.8±0.4</td>
</tr>
<tr>
<td>THF</td>
<td>0.4±0.02</td>
<td>2.7±0.3</td>
<td>5.2±0.4</td>
<td>12.7</td>
<td>17.6</td>
</tr>
</tbody>
</table>

5.3.3 Surfactant effect

DTAB surfactant was added to the dye solution to investigate the effect of the dye loading. The photochromic properties of the coated fabrics are shown in Table 5.5. In Table 5.5, row 1 contains information on a coating that contained no DTAB surfactant (as previously shown in Table 5.4). Row 2 reflects the effect of DTAB incorporation. It is noteworthy that the difference between the coating solution uptake in row 2 with the control is negligible. Row 3 represents the effect of solution loading on fabric on the photochromic performance. In row 4, both DTAB content and solution uptake were increased. Row 5 reflects the effect of dye and DTAB contents as well as solution uptake on photochromic performance.

Comparing row 2 with 1, it was evident that the incorporation of DTAB affected $\Delta A_{\text{max}}$ negatively and photostability positively, while not changing coloration/bleaching rates significantly. The observed negative impact of DTAB on $\Delta A_{\text{max}}$ can be attributed to the low solubility of DTAB in the sol-gel system which in turn reduced the solubility of spirooxazine. The photochromic absorption maximum is influenced by the quality of dye dispersion in the sol. Ineffective dispersion can hinder the dye’s performance, which influences
$\Delta A_{\text{max}}$. The positive impact observed on photostability may be due to the shielding effect of DTAB against UV irradiation. In other words, the presence of DTAB may have reduced the exposure of the dye to UV light. Such a function in DTAB could also explain the observed reduction in $\Delta A_{\text{max}}$.

Comparing row 3 with 2, it appeared that increasing the loading of coating solution onto fabric improved photostability, while leaving other photochromic attributes relatively unaffected. Although the dye and DTAB concentrations in rows 2 and 3 were the same, the higher loading in row 3 meant that a higher number of spirooxazine molecules were present. Therefore, a longer irradiation time was required for degradation of all spirooxazine molecules, hence higher photostability.

Comparing row 4 with 3, it can be seen that the combined effect of increasing DTAB content and solution uptake led to further increase in photostability without significantly affecting other photochromic properties.

Comparing row 5 with 3, it appeared that increasing dye and DTAB contents while leaving coating uptake relatively unchanged also led to a significant enhancement in photostability, matching the level observed in row 4.
Table 5.5 Photochromic properties of OTES:PhTES 1:2 silica coatings on fabric without DTAB surfactant (No. 1) and with different DTAB and dye concentrations (No. 2 to 5)

<table>
<thead>
<tr>
<th>No.</th>
<th>Dye content (%)</th>
<th>DTAB content (%)</th>
<th>Uptake (%)</th>
<th>ΔA&lt;sub&gt;max&lt;/sub&gt;</th>
<th>t&lt;sub&gt;1/2&lt;/sub&gt; (s)</th>
<th>t&lt;sup&gt;1/2&lt;/sup&gt; (s)</th>
<th>Photostability (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.74</td>
<td>0</td>
<td>15.8</td>
<td>0.34±0.02</td>
<td>2.05±0.3</td>
<td>4.1±0.5</td>
<td>9.2±0.8</td>
</tr>
<tr>
<td>2</td>
<td>1.72</td>
<td>1.5</td>
<td>21.61</td>
<td>0.13±0.004</td>
<td>1.4±0.3</td>
<td>2.4±0.4</td>
<td>34.8±0</td>
</tr>
<tr>
<td>3</td>
<td>1.72</td>
<td>1.5</td>
<td>44.43</td>
<td>0.15±0.01</td>
<td>1.6±0.3</td>
<td>2.03±0.5</td>
<td>48.5±0</td>
</tr>
<tr>
<td>4</td>
<td>1.71</td>
<td>1.94</td>
<td>67.95</td>
<td>0.17±0.01</td>
<td>1.4±0.3</td>
<td>1.7±0.2</td>
<td>64.3±0</td>
</tr>
<tr>
<td>5</td>
<td>3.31</td>
<td>3.51</td>
<td>46.23</td>
<td>0.1±0.003</td>
<td>1.3±0.2</td>
<td>1.7±0.4</td>
<td>63.2±1.04</td>
</tr>
</tbody>
</table>

5.3.4 Spirooxazine-PMMA film

When spirooxazine was embedded in polymethylmethacrylate (PMMA) film, it showed a deep blue colour upon UV irradiation. The maximum absorption data with dye content is shown in Figure 5.6 and images of the films after UV irradiation are shown in Figure 5.4. The highest absorption maximum of approximately 0.9 was achieved with a dye concentration of 2.4% (dye(g)/[dye+PMMA](g)×100). The ΔA<sub>max</sub> of the PMMA films at 1.7 wt% dye content was interpolated from Figure 5.6 as 0.77. This indicated an increase of 92.5% in absorption maxima as compared with the average ΔA<sub>max</sub> observed for silica coated fabrics with THF used as solvent (0.4). This suggested that incorporating PMMA in the silica matrix could be a way of increasing the photochromic color depth.
Figure 5.4 Images of PMMA films containing spirooxazine before UV irradiation in light box (top) and immediately after irradiation (bottom). Dye concentrations from left to right: 1.2%, 2.4%, and 4.8%

Figure 5.5 Maximum absorption versus wavelength of PMMA films containing different amounts of spirooxazine
Figure 5.6 Maximum absorption of PMMA films containing different amounts of spirooxazine, measured at 600.11 nm

The coloration and bleaching half-times of spirooxazine-PMMA films are given in Table 5.6. Although the coloration rates were in the same range as those of silica, the bleaching rates were markedly slower in PMMA films.

Table 5.6 Coloration and bleaching rates of PMMA films with embedded spirooxazine dye

<table>
<thead>
<tr>
<th>Dye Content (%)</th>
<th>( t_{1/2} ) (s)</th>
<th>( t'_{1/2} ) (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>4.3±0.5</td>
<td>22.9±9.1</td>
</tr>
<tr>
<td>2.4</td>
<td>4.5±1.2</td>
<td>18.6±4.2</td>
</tr>
<tr>
<td>4.8</td>
<td>4.3±0.7</td>
<td>51.5±38.2</td>
</tr>
</tbody>
</table>
5.3.5 Spirooxazine-PMMA nanoparticles

Spirooxazine photochromic dye was incorporated in PMMA nanoparticles according to the method explained in section 3.2.5. In brief, a mixture of spiropyran, methylmethacrylate (MMA), sodium dodecyl sulphate (SDS) surfactant, and tetradecane (TD) was added to a solution of potassium persulfate (KPS) in water, and the resultant spiropyran-PMMA nanoparticles were separated from the solution by centrifuging. Pictures of the nanoparticles in solution and after centrifugation are shown in Figure 5.7 a and b, respectively. As indicated in the pictures, some of the photochromic dye precipitated with centrifugation, and the nanoparticles formed above it. The nanoparticles were irradiated in the UV light box, but showed very limited colour change. After curing at 110°C for 10 minutes, the nanoparticles showed no colour change with UV irradiation. The photochromic dye does not show photochromic activity out of solution or if not encapsulated in a suitable matrix. The fact that the removal of traces of solvent from the particles by curing resulted in their irresponsiveness to UV indicated that the dye was not properly encapsulated in PMMA. Therefore, spiropyran-PMMA particles synthesized by this route are not suitable for preparing coating solutions.
5.3.6 PMMA/silica sol-gel coating

PMMA was incorporated into silica by co-polymerisation of (3-trimethoxysilyl)propyl methacrylate (MPS) and methylmethacrylate (MMA) and subsequent co-hydrolysis of the copolymer with OTES:PhTES 1:2 (mol:mol) combination. Spirooxazine dye was added to the resultant sol-gel solution and coated on fabric. The absorption spectra of PMMA/silica coating is compared with that of pure silica coating in Figure 5.8. The incorporation of PMMA caused a hypsochromic shift in the spectral band of silica coatings, moving the absorption maxima from approximately 627 nm to 600 nm.
The photochromic properties of the PMMA/silica sol-gel coatings are given in Table 5.7. $\Delta A_{\text{max}}$ increased with increasing the dye content up to 6.5% and then reduced.

The coloration rates of the PMMA/silica sol-gel coatings were only slightly higher than those of silica sol-gel coatings. On the other hand, the incorporation of PMMA increased the bleaching time significantly. This effect was also observed, although more markedly, in spirooxazine-PMMA films (section 5.3.4). No obvious relationship was observed between dye concentration and coloration/bleaching rates of PMMA/silica coatings.

The photochromic photostability increased with increasing the dye content from 1.15% to 4.44%, and then slightly reduced at the dye content of 6.51%. The photostability of coatings with 8.5% and 10.4% spirooxazine was not measured.
Table 5.7 Photochromic properties of PMMA-incorporated OTES:PhTES 1:2 silica with different dye concentrations on fabric

<table>
<thead>
<tr>
<th>Dye content (%)</th>
<th>( \Delta A_{\text{max}} )</th>
<th>( t_{1/2} ) (s)</th>
<th>( t'_{1/2} ) (s)</th>
<th>Photostability (h)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.58</td>
<td>0.18±0.01</td>
<td>5.6±0.6</td>
<td>10.7±2</td>
<td>39.5±0</td>
<td>19.3</td>
</tr>
<tr>
<td>1.15</td>
<td>0.22±0.01</td>
<td>4.9±0.8</td>
<td>9.3±0.7</td>
<td>39.5±0</td>
<td>21.0</td>
</tr>
<tr>
<td>2.27</td>
<td>0.31±0.03</td>
<td>5.2±0.4</td>
<td>14.7±0.7</td>
<td>42.8±2.9</td>
<td>21.6</td>
</tr>
<tr>
<td>4.44</td>
<td>0.4±0.02</td>
<td>5.9±0.2</td>
<td>15.7±1.8</td>
<td>66.2±2.9</td>
<td>23.4</td>
</tr>
<tr>
<td>6.51</td>
<td>0.5±0.02</td>
<td>5.05±0.6</td>
<td>17.0±1.8</td>
<td>62.8±2.9</td>
<td>24.9</td>
</tr>
<tr>
<td>8.5</td>
<td>0.37±0.01</td>
<td>4.7±0.3</td>
<td>14.4±2.2</td>
<td>( a )</td>
<td>25.7</td>
</tr>
<tr>
<td>10.4</td>
<td>0.3±0.01</td>
<td>4.06±0.3</td>
<td>11.2±0.8</td>
<td>( a )</td>
<td>26.4</td>
</tr>
</tbody>
</table>

*Not measured

For comparison, the photochromic properties of OTES:PhTES 1:2 silica coatings with different dye concentrations were also measured, as reported in Table 5.8. Images of the dye-containing OTES:PhTES 1:2 silica solutions and coated fabrics are given in Figure 5.9 and Figure 5.10, respectively.

Table 5.8 Photochromic properties of OTES:PhTES 1:2 silica with different dye concentrations on fabric

<table>
<thead>
<tr>
<th>Dye content (%)</th>
<th>( \Delta A_{\text{max}} )</th>
<th>( t_{1/2} ) (s)</th>
<th>( t'_{1/2} ) (s)</th>
<th>Photostability (h)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.88</td>
<td>0.30±0.01</td>
<td>2.6±0.3</td>
<td>4.4±0.7</td>
<td>10.5±3.7</td>
<td>20.46</td>
</tr>
<tr>
<td>1.74</td>
<td>0.34±0.02</td>
<td>2.03±0.3</td>
<td>3.8±0.2</td>
<td>12.7±0</td>
<td>20.5</td>
</tr>
<tr>
<td>3.43</td>
<td>0.42±0.02</td>
<td>1.9±0.2</td>
<td>4.3±0.2</td>
<td>25.3±0</td>
<td>21.4</td>
</tr>
<tr>
<td>6.63</td>
<td>0.42±0.01</td>
<td>1.6±0.2</td>
<td>4.2±0.5</td>
<td>40.1±3.7</td>
<td>22.7</td>
</tr>
<tr>
<td>9.63</td>
<td>0.42±0.02</td>
<td>1.7±0.1</td>
<td>3.7±0.01</td>
<td>43.3±1.8</td>
<td>24.2</td>
</tr>
<tr>
<td>12.44</td>
<td>0.34±0.06</td>
<td>1.6±0.2</td>
<td>3.01±0.2</td>
<td>42.2±1.8</td>
<td>25.4</td>
</tr>
<tr>
<td>15.1</td>
<td>0.30±0.02</td>
<td>1.9±0.04</td>
<td>3.9±0.09</td>
<td>50.7±0</td>
<td>25.6</td>
</tr>
</tbody>
</table>
Figure 5.9 Image of OTES:PhTES 1:2 silica with increasing dye concentration from right to left: 0.88%, 1.74%, 3.43%, 6.63%, 9.63%, 12.44%, and 15.1%

Figure 5.10 Image of OTES:PhTES 1:2 silica coated fabrics with increasing dye concentration from left to right and top to bottom

The relationship between dye content and $\Delta A_{\text{max}}$ was slightly different to that of PMMA/silica coatings in that $\Delta A_{\text{max}}$ increased from dye content of 0.88% to 1.74%, became a plateau between dye contents of 3.43% and 9.63%, and dropped after this point. The trends of $\Delta A_{\text{max}}$ with dye content for silica and PMMA/silica coatings are shown in Figure 5.11. $\Delta A_{\text{max}}$ of PMMA/silica coatings were lower than that of silica coatings at equal dye concentrations, except for the maximum $\Delta A_{\text{max}}$ which was higher in PMMA/silica coatings (0.5) than silica coatings (0.42). This suggested that incorporating PMMA in silica coatings led to approximately 19% increase in maximum absorption, compared to a control silica coating with approximately equal dye content wherein THF was used as solvent.
5.3.7 Spirooxazine-PMMA particles in resin and in silica

Spirooxazine-PMMA particles were prepared by another route different to the direct polymerisation (in section 5.3.5). In brief, the particles were prepared by mixing spirooxazine and PMMA in acetone, dispersing the mixture drop wise in water, and separating the resultant spirooxazine-PMMA particles by centrifuging. The experimental details are given in section 3.2.8. In this case, the particles showed photochromic effect. To find the optimum dye concentration and dye to PMMA ratio, the synthesized particles were first embedded into a water-borne Hercosett resin and then applied to fabric. The water-based resin was selected to prevent the dye from leaching out into the solution. The absorption spectra and photochromic properties of the resultant coatings are shown in Figure 5.12 and Table 5.9, respectively. As also observed in the absorption spectra of PMMA/silica coating, the presence of
PMMA shifted the absorption maxima to shorter wavelengths compared with silica coating.

![Absorption spectra of SO-PMMA particles in resin on fabric](image)

**Figure 5.12** Absorption spectra of SO-PMMA particles in resin on fabric (dye content (%) = dye (g)/[dye+PMMA+resin] (g) × 100)

<table>
<thead>
<tr>
<th>Dye content (%)</th>
<th>SO:PMMA (g/g)</th>
<th>ΔA_{max}</th>
<th>t_{1/2} (s)</th>
<th>t'_{1/2} (s)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.74</td>
<td>1:1</td>
<td>0.04±0.01</td>
<td>18.1±4</td>
<td>48.7±5.4</td>
<td>9.6</td>
</tr>
<tr>
<td>1.74</td>
<td>1:2</td>
<td>0.09±0.02</td>
<td>23.6±6.1</td>
<td>121.5±23.1</td>
<td>9.9</td>
</tr>
<tr>
<td>6.63</td>
<td>1:1</td>
<td>0.26±0.07</td>
<td>20±2.8</td>
<td>123.7±59.1</td>
<td>11.3</td>
</tr>
<tr>
<td>6.63</td>
<td>1:2</td>
<td>0.67±0.05</td>
<td>21.9±2.5</td>
<td>245.6±25.1</td>
<td>11.7</td>
</tr>
<tr>
<td>15.1</td>
<td>1:1</td>
<td>0.46±0.07</td>
<td>27±3.3</td>
<td>183.8±28.1</td>
<td>13.9</td>
</tr>
<tr>
<td>15.1</td>
<td>1:2</td>
<td>0.45±0.05</td>
<td>23.3±2.7</td>
<td>169.5±28.2</td>
<td>20.1</td>
</tr>
</tbody>
</table>

**Table 5.9** Photochromic properties of spirooxazine-PMMA particles dispersed in Hercosett resin and coated on fabric, measured at 604 nm

The results indicated that in the case of SO:PMMA 1:1, maximum absorption increased with increasing the dye concentration, while for SO:PMMA 1:2, absorption increased with dye content up to 6.63% and subsequently declined.
In other words, 6.63% was the optimal dye concentration in the case of SO:PMMA 1:2 and the matrix became saturated with particles beyond this point. The highest maximum absorption of 0.67 was achieved with a dye content of 6.63% and SO:PMMA ratio of 1:2. Compared with the maximum absorption of silica coating at 6.63% dye content (i.e. 0.42), an increase of 59.5% was achieved.

Colouration and especially bleaching rates were significantly slower compared to silica coatings (Table 5.8). This is due to the small free volume available in the pores of PMMA polymer which limits the structural transformation of spirooxazine.

Based on the results of Table 5.9, the dye content of 6.63% was selected for incorporating SO-PMMA particles in silica, and an ethanol-based sol-gel was used. The absorption spectra and photochromic properties of the particles at two SO:PMMA ratios are shown in Figure 5.13 and Table 5.10, respectively. The absorption spectra showed a shift to longer wavelength as a result of incorporation of the particles in sol-gel. Despite the similar solid content used in both methods, the sol-gel solution was absorbed better than the resin on fabric.
Figure 5.13 Absorption spectra of SO-PMMA particles in sol-gel on fabric (dye content (%) = dye (g)/[dye+PMMA+silica] (g) × 100)

Table 5.10 Photochromic properties of spirooxazine-PMMA particles dispersed in sol-gel and coated on fabric, measured at 624 nm

<table>
<thead>
<tr>
<th>Dye concentration (%)</th>
<th>SO:PMMA (g/g)</th>
<th>$\Delta A_{\text{max}}$</th>
<th>$t_{1/2}$ (s)</th>
<th>$t'_{1/2}$ (s)</th>
<th>Uptake (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.63</td>
<td>1:1</td>
<td>0.62±0.02</td>
<td>2.7±0.2</td>
<td>7.2±0.3</td>
<td>30</td>
</tr>
<tr>
<td>6.63</td>
<td>1:2</td>
<td>0.85±0.1</td>
<td>3.3±0.3</td>
<td>9.1±1.6</td>
<td>30.9</td>
</tr>
</tbody>
</table>

A comparison between the absorption maxima of SO-PMMA particles in resin and silica is provided in Figure 5.14. It can be seen that a dye:PMMA ratio of 1:2 at a dye concentration of 6.63% produced the highest absorption peak in both Hercosett resin and silica, and at this dye concentration, maximum absorption was higher for particles in sol-gel than in resin at comparable SO:PMMA ratios.
Figure 5.14 Absorption maxima of SO-PMMA particles in resin and silica at two SO:PMMA ratios

Compared to the maximum absorption of a photochromic silica coated fabric (i.e. 0.42), at 6.63% dye content, 47.6% and 102.4% improvement was achieved by embedding SO-PMMA particles in silica at 1:1 and 1:2 ratios, respectively.

The colouration rates of the particles in silica were similar to normal photochromic silica coatings, and the bleaching rates were only slightly higher as a result of the presence of PMMA.

5.4 Summary

In this chapter, several methods were explored for enhancing the colour depth of photochromic coating on fabric. Encapsulating spirooxazine molecules in the cavity of β-cyclodextrin, thus creating spirooxazine-β-cyclodextrin
complexes led to 26.7% increase in the absorption maxima. However, increasing the concentration of spirooxazine-\(\beta\)-cyclodextrin complexes in sol-gel coating led to a decrease in the absorption peak, implying that the technique was not effective in preventing aggregation.

Investigating the effect of solvent type on colour depth revealed that using THF instead of ethanol raised the absorption maxima by 17.6%. This can be attributed to the higher solubility of the photochromic dye in THF.

Incorporating surfactant in the silica coating resulted in a decrease in the absorption maxima. However, it affected photostability positively, while not changing coloration/bleaching rates considerably.

Embedding spirooxazine in PMMA resulted in a 61.5% increase in colour depth. However, bleaching rates were considerably slower in PMMA than in silica coating.

Spirooxazine-PMMA nanoparticles were successfully synthesised for the purpose of dispersion in silica sol-gel to increase dye loading. However, the photochromic performance of the nanoparticles was unsatisfactory.

Silica coating containing PMMA copolymer increased maximum absorption by 19% compared to the control silica sample with the same dye content.

When spirooxazine was dispersed physically in PMMA and then shaped into particles, the particles showed similar photochromic performance to the film counterpart. When such particles were embedded in hydrophilic resin, an enhancement of 59.5% was achieved in maximum absorption. When the photochromic PMMA particles were dispersed in silica sol-gel, compared to
pure silica coating with the same dye content, the absorption maximum was increased by 102.4%. Compared to the coloration and bleaching rates of spirooxazine in silica coated fabric, the speed of colour change of spirooxazine-PMMA particles were significantly slower in hydrophilic resin, whereas the speeds remained almost unchanged when the particles were dispersed in silica coating.
6 Microstructure of silica pores

6.1 Introduction

In this chapter, the following subjects are discussed:

a) The pore structure of silica coatings from an acid-catalysed sol-gel process and its relationship with the type of non-hydrolysable group in the silica precursor;

b) The relationship between the microstructure of silica and the photochromic performance of spirooxazine-doped silica coatings.

In order to gain an understanding of the above, synchrotron SAXS, nitrogen adsorption porosimetry, TEM, and AFM are employed to characterise the pore size and morphology, as well as the distance between pores. XRD and spectroscopic ellipsometry are used as complementary methods of obtaining structural information on the silica coatings. The photochromic properties of different silica coatings embedded with photochromic dye are also investigated.

6.2 Experimental details

The sample preparation methods and other experimental details regarding the characterisation techniques used in this chapter are given in Chapter 3. For the study of photochromic properties, the samples were prepared by mixing 1.75
ml of OTES:PhTES 1:2 (mol:mol) sol-gel with 1.75 ml of a 0.004 g/ml solution of spirooxazine dye in ethanol. The mixture was stirred at room temperature for approximately 30 min, and subsequently heated at around 70°C while stirring until a transparent light green solution was obtained. The solution was poured onto a 5×10 cm² fabric, and the fabric was turned to ensure that all the coating solution was absorbed. The coated fabric was air-dried for 24 hours, cured at 110°C for 10 minutes, and remained at room temperature for a further 24 hours before testing. The fabric was weighed before and after coating to measure the pick-up.

6.3 Results and discussion

6.3.1 XRD

The XRD results for PhTES sol-gel are given in Figure 6.1. Two sharp peaks and a small broad peak were observed at 7°, 19.5°, and 76.5° positions, respectively. Crystallinity calculated according to the Segal method [101] (Equation 6.1) was 66.5% for PhTES silica coating, and crystal size obtained according to the Scherrer method [102] was 2.4 nm.
Figure 6.1 XRD pattern for PhTES silica coating

\[ \text{Crystallinity \%} = \frac{I_{20} - I_{am}}{I_{20}} \]  

(6.1)

6.3.2 SAXS

The chemical structures of the silica precursors used in this study are shown in Figure 6.2. The main difference between these chemicals is that they bear different non-hydrolysable groups. All silica types were measured in the form of coating on mica sheet. MTES, VTMS, and GPTMS sol-gel with and without SO dye were also tested in the form of free-standing film. PhTES sol-gel with and without SO was also tested in powder form in quartz capillary. The number of samples tested for each silica type is shown in Table 6.1.
Figure 6.2 Chemical structure of (a) MTES, (b) VTMS, (c) PhTES, (d) GPTMS, (e) 2-CycTES, (f) OTES

Table 6.1 Number of samples tested for each silica type

<table>
<thead>
<tr>
<th>Type</th>
<th>Coating Dye</th>
<th>Coating Film Dye</th>
<th>Coating Powder Dye</th>
<th>Total Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTES</td>
<td>4</td>
<td>3</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>VTMS</td>
<td>7</td>
<td>10</td>
<td>8</td>
<td>15</td>
</tr>
<tr>
<td>PhTES</td>
<td>12</td>
<td>14</td>
<td>-</td>
<td>14</td>
</tr>
<tr>
<td>GPTMS</td>
<td>10</td>
<td>5</td>
<td>6</td>
<td>16</td>
</tr>
<tr>
<td>OP 12</td>
<td>6</td>
<td>4</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>CycTES</td>
<td>12</td>
<td>12</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>OTES</td>
<td>16</td>
<td>14</td>
<td>-</td>
<td>16</td>
</tr>
</tbody>
</table>

Total: 89 74 163
Mica and quartz were used as substrate for SAXS characterisation because of the low x-ray scattering property. Figure 6.3 shows SAXS images and the corresponding scattering curves of uncoated mica and empty quartz capillaries used for background correction.

![Figure 6.3 SAXS images and curves of (a, c) uncoated mica, and (b, d) empty quartz capillary, respectively](image)

The scattering curves of hydrolysed MTES silica coating and film are shown in Figure 6.4 e and f, respectively. A comparison between the scattering curve of MTES silica coating before (Figure 6.4 c) and after (Figure 6.4 e) subtraction of the scattering of mica confirms that the peak positions remained unaffected by background correction.
The distance between pores \((d)\) was calculated according to the method described in section 3.3.11.1. It was revealed that \(d\) for MTES silica was approximately 8.2 Å. The SAXS image of the film (Figure 6.4 b) shows a ring with slightly better defined edges than that of the coating on mica (Figure 6.4 a), which can be attributed to the absence of the small angle scattering from mica.
Figure 6.4 SAXS images and curves of MTES silica coating: (a, c) before and (e) after background correction, and (b, d, f) MTES silica film²

Figure 6.5 shows the scattering patterns of MTES silica containing SO dye. The effect of the presence of the dye in the silica matrix can be clearly seen in Figure 6.5. Narrow rings were observed in the SAXS images (Figure 6.5 a and

² Background correction does not apply to films as no substrate was used, and therefore Figure 6.4 d and f are the same.
b) which were converted into sharp peaks with different intensities in the SAXS curves (Figure 6.5 c and). This can be attributed to the aggregated spirooxazine dye in the silica matrix. Comparing Figure 6.5 to Figure 6.4, the angular positions of MTES silica embedded with SO dye were very similar to that without dye (8.2 Å), suggesting that the inclusion of dye did not significantly affect the distance between pores.

Figure 6.5 SAXS images and curves of MTES silica with SO (a, c) coating, and (b, d) film, respectively

In the case of VTMS silica, the calculated $d$ value was 9.5 Å, which showed a slightly increased pore distance compared to that of MTES, suggesting the effect of the non-hydrolysable group in the silica precursor on the distance
between pores. The pore distance increased with the increase in the chain length of the non-hydrolysable group.

![SAXS images](image)

Figure 6.6 SAXS images and curves of VTMS silica (a, c) coating, and (b, d) film, respectively

Similar to the case of MTES silica with SO, VTMS silica embedded with SO showed sharp peaks as a result of dye inclusion (Figure 6.7 c and d). The presence of SO in the silica matrix resulted in a slightly increased $d$ value of 9.7 Å.
While MTES and VTMS silica both showed only one broad peak in the measured $q$ range, a second broad peak appeared for PhTES silica (Figure 6.8 c and d). The first peak corresponded to a $d$ value of 13.4 Å, which again showed an increase as compared to that of MTES and VTMS silica. The ratio between the position of the second peak to that of the first or $q_2/q_1$ (described in section 3.3.11.1) was 2.9 for PhTES silica. The $q_2/q_1$ value was used by other researchers to derive the morphology of ordered mesopores in an organically modified aluminosilicate [18]. However, the $q_2/q_1$ value obtained in this work was not comparable to the literature due to differences in materials and
preparation methods, which limited the understanding of pore morphology based on SAXS measurements.

Figure 6.8 SAXS images and curves of PhTES silica (a, c) coating, and (b, d) powder (in capillary), respectively.

SAXS scattering curves of PhTES silica containing dye (Figure 6.9 c and d) exhibited a decreased pore distance (12.5 Å). It was interesting to note that PhTES silica coating containing SO showed no sharp peaks in the SAXS curve. This indicates that no dye aggregation took place in the silica matrix. Also, $q_2/q_1$ (2.8) was found to be slightly lower than that of PhTES silica without dye.
Figure 6.9 SAXS images and curves of PhTES silica with SO (a, c) coating, and (b, d) powder (in capillary), respectively.

The SAXS curves of GPTMS silica, shown in Figure 6.10 c and d, revealed a $d$ value of 14.5 Å. GPTMS brings a longer alkyl chain in the molecule compared to methyl, vinyl, and phenyl groups. This could be the reason for the increased pore distance. The $q_2/q_1$ value was 3.5, which was higher than that of PhTES silica.
Figure 6.10 SAXS images and curves of GPTMS silica (a, c) coating, and (b, d) film, respectively.

Figure 6.11 c and d show the scattering curves of GPTMS silica with encapsulated spirooxazine. The sharp peaks resulting from the presence of dye can be observed, although with a lower intensity. The calculated $d$ and $q_2/q_1$ values were both similar to that of GPTMS silica without SO.
The SAXS images and curves of CycTES silica are shown in Figure 6.12. Bearing a cyclohexenyl-ethyl group, CycTES silica formed pores with larger pore distances compared with the previous silica systems. A $d$ value of 15.6 Å and $q_2/q_1$ value of 3.2 were obtained. The inclusion of SO dye in the silica matrix led to slight increase in $d$ spacing and $q_2/q_1$ to 15.9 Å and 3.3, respectively.
SAXS images and curves of OTES silica coatings are shown in Figure 6.13. OTES silica had the farthest pore distance of 19.5 Å among all the studied silica types and a $q_2/q_1$ value of 4.4. Similarly to PhTES with SO, a decrease in $d$ and $q_2/q_1$ values was observed for OTES silica when SO dye was added. The calculated $d$ and $q_2/q_1$ values for OTES with SO were 19.1 Å and 4.3, respectively.
All of the studied silica types were tested in the form of coatings on mica. Due to the good film forming property, MTES, VTMS, and GPTMS silica were also prepared in the form of free-standing films. The brittleness of the solid PhTES silica enabled its measurement in quartz capillary. However, due to the low scattering of quartz and mica, no notable difference was observed between the results of the different sample forms. In the case of silica hydrolysed from a combination of OTES and PhTES (1:2 mol:mol), the presence of the long octyl chain in the silica softened the coating, allowing the measurement only on mica (Figure 6.14). A $d$ value of 15.01 Å and $q_2/q_1$ value of 3.4 were obtained. The calculated $d$ and $q_2/q_1$ values for OTES:PhTES 1:2 silica containing SO were
15.7 Å and 3.6, respectively, which showed a small increase as a result of the presence of dye.

![SAXS images and curves of OTES:PhTES 1:2 silica coatings](a, c) without, and (b, d) with SO, respectively.

The SAXS curves of silica from different precursors, with and without embedded SO, are shown in Figure 6.15. The previously described relationship between the silica precursor type and the position of the peaks on the q axis can be clearly observed.
Figure 6.15 SAXS curves of silica coatings from different precursors, with and without SO

The calculated $d$ and $q_2/q_1$ values are listed in Table 6.2. The pore distance of OTES:PhTES 1:2 silica, which was a combination of OTES and PhTES precursors, was in the middle of the distances obtained for OTES and PhTES silica. It is noteworthy that in the case of coatings from GPTMS silica, $q_2$ was at the end of the measured $q$ range for all samples, which explains the zero standard deviation.
Table 6.2 Lattice spacing ($d$) and angular position ratios $q_2/q_1$

<table>
<thead>
<tr>
<th>Type</th>
<th>$d = 2\pi/q_1$ (Å)</th>
<th>$q_2/q_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTES</td>
<td>8.2±0.05</td>
<td>-</td>
</tr>
<tr>
<td>MTES+SO</td>
<td>8.2±0.08</td>
<td>-</td>
</tr>
<tr>
<td>VTMS</td>
<td>9.5±0.2</td>
<td>-</td>
</tr>
<tr>
<td>VTMS+SO</td>
<td>9.7±0.2</td>
<td>-</td>
</tr>
<tr>
<td>PhTES</td>
<td>13.4±0.2</td>
<td>2.9±0.01</td>
</tr>
<tr>
<td>PhTES+SO</td>
<td>12.5±0.2</td>
<td>2.8±0.04</td>
</tr>
<tr>
<td>GPTMS</td>
<td>14.5±0.06</td>
<td>3.5±0.06</td>
</tr>
<tr>
<td>GPTMS+SO</td>
<td>14.5±0.3</td>
<td>3.5±0.08</td>
</tr>
<tr>
<td>OP12*</td>
<td>15.0±0.4</td>
<td>3.4±0.1</td>
</tr>
<tr>
<td>OP12+SO</td>
<td>15.7±0.3</td>
<td>3.6±0.1</td>
</tr>
<tr>
<td>CycTES</td>
<td>15.6±0.2</td>
<td>3.2±0.04</td>
</tr>
<tr>
<td>CycTES+SO</td>
<td>15.9±0.1</td>
<td>3.3±0.02</td>
</tr>
<tr>
<td>OTES</td>
<td>19.5±0.4</td>
<td>4.4±0.1</td>
</tr>
<tr>
<td>OTES+SO</td>
<td>19.1±0.6</td>
<td>4.3±0.1</td>
</tr>
</tbody>
</table>

* OP12 stands for OTES:PhTES 1:2 mol/mol

The overall changes caused in $d$-spacing and $q_2/q_1$ from embedding photochromic dye in the pores were negligible. This indicated that the presence of dye in the pores led to small changes in the porous structure [22].

6.3.3 Nitrogen adsorption

Nitrogen adsorption-desorption porosimetry was performed to characterise the pore size of PhTES silica matrix. Considering the test requirements, PhTES was deemed most suitable for nitrogen adsorption porosimetry, as the best results were obtained with specimens in powder form. The silica powder samples were prepared according to the method explained in section 3.3.11. Several nitrogen adsorption techniques were employed for measurement of pore characteristics including surface area, pore volume, and pore diameter, which are mentioned in section 3.3.12. The results are summarised in Table 6.3.
Table 6.3 Nitrogen adsorption porosimetry results for PhTES silica with and without dye

<table>
<thead>
<tr>
<th></th>
<th>PhTES</th>
<th>PhTES+SO</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface Area (m²/g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(S_{BET})</td>
<td>1.076E+00</td>
<td>1.146E+00</td>
</tr>
<tr>
<td>(S_{Langmuir})</td>
<td>1.186E+00</td>
<td>7.929E-01</td>
</tr>
<tr>
<td>(S_{BH})</td>
<td>2.164E+00</td>
<td>2.142E+00</td>
</tr>
<tr>
<td>(S_{DH})</td>
<td>2.309E+00</td>
<td>2.279E+00</td>
</tr>
<tr>
<td>(S_{external}^{a})</td>
<td>1.076E+00</td>
<td>7.377E-01</td>
</tr>
<tr>
<td>(S_{micropore}^{b})</td>
<td>0.000E+00</td>
<td>4.084E-01</td>
</tr>
<tr>
<td>(S_{DR})</td>
<td>6.305E-02</td>
<td>5.381E-02</td>
</tr>
<tr>
<td><strong>Pore Volume (cc/g)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(V_{total}^{c})</td>
<td>2.039E-03</td>
<td>1.657E-03</td>
</tr>
<tr>
<td>(V_{total,BH})</td>
<td>2.446E-03</td>
<td>2.166E-03</td>
</tr>
<tr>
<td>(V_{total,DH})</td>
<td>2.447E-03</td>
<td>2.176E-03</td>
</tr>
<tr>
<td>(V_{total,HK})</td>
<td>2.268E-04</td>
<td>1.480E-04</td>
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<td>(V_{total,SF})</td>
<td>2.400E-04</td>
<td>1.654E-04</td>
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<tr>
<td>(V_{micro}^{i})</td>
<td>0.000E+00</td>
<td>-1.632E-04</td>
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<tr>
<td>(V_{micro,DR})</td>
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<td>1.912E-05</td>
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<tr>
<td><strong>Pore Size (Å)</strong></td>
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<tr>
<td>D_{average}</td>
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<td>5.784E+01</td>
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<td>2.132E+01</td>
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<tr>
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<td>7.181E+01</td>
<td>6.568E+01</td>
</tr>
<tr>
<td>D_{DA}</td>
<td>1.920E+01</td>
<td>1.920E+01</td>
</tr>
<tr>
<td>D_{HK}</td>
<td>1.538E+01</td>
<td>1.623E+01</td>
</tr>
<tr>
<td>D_{SF}</td>
<td>2.916E+01</td>
<td>3.073E+01</td>
</tr>
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</table>

*a-t-method external surface area; ^b-t-method micro pore surface area; ^c total pore volume for pores with diameter less than 3410.1 Å at P/P₀ = 0.99435

A slightly larger Brunauer-Emmett-Teller (BET) surface area (m²/g) was observed for PhTES silica when SO dye was embedded in the matrix. However, the surface area of PhTES silica with dye obtained by all other nitrogen adsorption methods was smaller than that of PHTES without dye. As the dye occupies the pores and leaves smaller accessible space for nitrogen adsorption, it would be more reasonable for the dye-containing silica to have a smaller surface area. Considering that the difference between the two values
obtained with BET was trivial, the different trend observed in the findings of the BET method compared to the other nitrogen adsorption methods could be attributed to test error. In the same way, the pore volume of PhTES silica with dye measured by all methods was smaller than that of PhTES alone.

The pore diameter measurements did not completely follow the abovementioned trend. The average, Barrett-Joyner-Halenda (BJH), Dollimore-Heal (DH), and Dubinin-Radushkevic (DR) pore diameters of PhTES silica with SO were smaller than those of PhTES silica, whereas those obtained with the Dubinin-Astakhov (DA) method were equal. On the other hand, Horvath-Kawazoe (HK) and Saito-Foley (SF) methods led to slightly larger pore size values for PhTES with dye compared with the control. The variation observed in the results between different methods of calculation stem from the different assumptions of pore geometry. For instance, the Horvath-Kawazoe (HK) method is based on an assumption of slit-shaped pores, whereas the Saito-Foley (SF) method is based on cylindrical pores. On the other hand, the calculation methods of Barrett-Joyner-Halenda (BJH) and Dollimore-Heal (DH) are very similar and lead to very similar results. Overall, the BJH pore diameter of approximately 2.7 nm for PhTES was within the expected range.
Figure 6.16 BJH pore size distributions for PhTES silica (a) without and (b) with SO

The pore size distribution graph, shown in Figure 6.16, revealed two main pore size ranges, one around 2.7 nm and the other around 5.4 nm for PhTES silica, and one around 2.1 nm and another around 5.5 nm for PhTES silica with SO. The two pore sizes observed for each silica matrix could be corresponding to the two prominent peaks which were observed in the SAXS study.

6.3.4 TEM

For TEM measurements, MTES and VTMS silica were cast into film, embedded in epoxy resin, ultra-cut using an ultra-microtome, and placed on a copper grid for examination. PhTES sol-gel was air-dried and the resultant solid was ground into powder, dispersed in ethanol, and deposited on a TEM grid. OTES:PhTES 1:2 sol-gel was diluted with ethanol and deposited on a
TEM grid. Pore diameters were measured for at least 100 pores in each TEM image. Figure 6.17 shows images of MTES silica under high resolution transmission electron microscopy (HRTEM). The images show randomly-oriented pores with an average diameter of $0.43 \pm 0.14$ nm.

Figure 6.17 (a) and (b) TEM Bright field images, and (c) and (d) HRTEM images of MTES silica film
Scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDX) were used to analyse the elemental composition of the material. The results are shown in Figure 6.18. The line scan confirmed the presence of silicon and oxygen, but failed to reveal that of carbon.

![STEM EDX line scan for MTES silica film](image)

Figure 6.18 STEM EDX line scan for MTES silica film

Figure 6.19 c and d show a channel-like structure in VTMS silica film at resolutions of 200 and 100 nm, respectively. HRTEM images of the VTMS
silica pores, shown in Figure 6.19 g and h, reveal a slightly different appearance to those of MTES film, with an average size of 0.34±0.11 nm. An image of a pore size measurement conducted based on an HRTEM micrograph of VTMS silica is shown in Figure 6.20.
Figure 6.19 (a) and (b) bright field TEM images, (c) and (d) TEM micrographs at 200 and 100 nm resolution, and (e) to (h) HRTEM images of VTMS silica film

Figure 6.20 Pore size measurement of an HRTEM image of VTMS film
To distinguish the silica sample from the underlying film of the TEM grid, HRTEM micrographs were taken of a VTMS film sample which was positioned at a distance from the background. The resulting images are shown in Figure 6.21. These images clearly reveal a porous structure with an average pore size measured at 0.52±0.48 nm, larger than the previous measurement for VTMS. Given the lower interference of the background film in Figure 6.21 compared with Figure 6.19, the pore diameter measurement of 0.52±0.48 nm can be considered more accurate than the previous measurement of 0.34±0.11 nm for VTMS silica film.
Figure 6.21 HRTEM micrographs of VTMS silica film

The results of the STEM EDX line scan for VTMS film are shown in Figure 6.22. The line scan confirmed the presence of silicon, oxygen, and carbon in the film.
Figure 6.22 STEM EDX line scan for VTMS silica film

Figure 6.23 shows images of a particle of PhTES silica powder. In the HRTEM images (Figure 6.23 c and d), the edges of the aforementioned particle have been examined. The results confirmed a porous structure with an average pore diameter of 0.53±0.18 nm. This is a smaller pore diameter compared to the BJH (2.7 nm) and average (7.6 nm) pore diameters obtained with nitrogen adsorption.
The HRTEM micrographs of MTES, VTMS, and PhTES revealed porous structures with similar appearance to that of tetramethyloxysilicate (TMOS) in other studies [20].

TEM images of OTES:PhTES 1:2 silica (Figure 6.24) showed a different structure compared to MTES, VTMS, and PhTES. The reason for this could be
the presence of OTES with a long alkyl chain, which greatly changes the pore morphology. Nevertheless, a porous structure can be observed in Figure 6.24 b.

![Figure 6.24 TEM images of OTES:PhTES 1:2 silica](image)

Figure 6.24 TEM images of OTES:PhTES 1:2 silica

Considering pore sizes of 0.43±0.14, 0.52±0.48, and 0.53±0.18 nm for MTES, VTMS, and PhTES silica, respectively, a relationship between the size of the silica non-hydrolysable group and pore diameter can be deduced. In other words, it seems that the pore diameter increased with the size of the non-hydrolysable group.
6.3.5 AFM

AFM phase and height images of PhTES sol-gel coating are given in Figure 6.25. A porous structure is clearly visible in the images. The diameter of 142 pores was measured for PhTES sol-gel coatings, giving an average pore size of 5.2±2.3 nm. This result is close to the average pore size measured for PhTES silica using nitrogen adsorption (7.6 nm). It is noteworthy that the BJH pore diameter (2.7 nm) measured by N\textsubscript{2} adsorption reflects the size of the micropores present in the material, while the average pore diameter reflects both micro- and meso-pores, and is therefore more appropriate for comparison with the AFM results. The AFM pore diameter was larger than those measured with HRTEM (0.53±0.18 nm). This size difference can be explained by a variety of influencing factors. One factor is the different sample preparation techniques used for the two characterisation methods: spin-coating for AFM, and film-casting and grinding into powder for TEM. Spin-coating had to be adopted for AFM measurements in order to attain the required uniformity of coating thickness across the substrate. The inertia arising from spinning draws the pores, producing larger ones than those of PhTES sol-gel powder characterised by HRTEM. This effect is also evident in the shape of the pores in HRTEM images of PhTES silica (Figure 6.23) compared with AFM images (Figure 6.25). The pores in the HRTEM images are mostly circular, while many slit-shaped pores are present in the AFM image as a result of the spinning force. Another factor of influence was the size of the AFM tip, which was too large to detect smaller pores with diameters comparable to those measured with HRTEM, thus contributing to a larger average pore size. A combination of these factors can explain the larger average pore diameter obtained with AFM compared to HRTEM. Furthermore, due to the difference
in sample preparation methods used for HRTEM and AFM measurements, the pores of the HRTEM sample were more uniform in size, as reflected in the smaller standard deviation of the HRTEM pore size measurement (0.18 nm) compared to that of AFM (2.3 nm).

Examples of pore diameter measurements of an AFM phase image of PhTES coating are shown in Figure 6.26. The adjoined pore area indicated by a yellow circle was excluded from the measurements because of difficulty in identifying individual pores in this area.
Figure 6.25 AFM phase (left) and height (right) images of PhTES silica coating

Figure 6.26 Pore diameter measurement using AFM phase image of PhTES silica coating; the yellow circle indicates an area of adjoined pores.

6.3.6 Spectroscopic ellipsometry

Spectroscopic ellipsometry (SE) is an optical characterisation technique for measuring optical properties such as refractive index, and it enables the
measurement of film thickness. SE measures the change in the polarization of light after reflection from the specimen surface. It is a non-destructive optical method since the measurement does not require contact with the specimen. The concept is illustrated in Figure 6.27. Ellipsometry measures \( \rho \), which is the complex reflectance ratio calculated from Equation 6.2.

\[
\rho = \frac{r_2}{r_3} = \tan(\psi) e^{i\Delta} = f(n_i, k_i, T_i)
\]

(6.2)

where:

- \( \rho \): complex reflectance ratio
- \( \Psi \): amplitude ratio
• $\Delta$: phase shift

• $r_p$: complex reflection coefficient for the $p$ component of polarization

• $r_s$: complex reflection coefficient for the $s$ component of polarization

$\tan(\psi)$ and $\cos(\Delta)$ parameters are directly measured in spectroscopic ellipsometry. The polarization of light on the sample can be separated into $s$ and $p$ constituents, where $s$ is the constituent of light which oscillates parallel to the sample plane and perpendicular to the plane of incident light, and $p$ is the constituent parallel to the plane of incident light.

A regression procedure is employed in ellipsometry for verifying the thickness and optical properties of a film. The procedure includes experimental measurement as well as theoretical estimation of $\tan(\psi)$ and $\cos(\Delta)$. If the results of experimental measurements agree with the model, the film properties are verified. Otherwise, new values for film parameters are proposed and the calculation of $\tan(\psi)$ and $\cos(\Delta)$ is continued until an acceptable fit is achieved for the experimental data.

Ellipsometric porosimetry involves the monitoring of changes in film thickness and optical properties during the adsorption and desorption of a solvent in the sample pores in a vacuum chamber. The relative pressure of solvent in the chamber ($P/P_0$) is monitored with time, and the results are used for calculating $\tan(\psi)$ and $\cos(\Delta)$. Furthermore, the changes in refractive index ($n$) and thickness ($k$) with relative pressure during the adsorption and desorption process are also obtained. The Lorentz-Lorenz equation is used to calculate the solvent volume adsorbed isotherm from the refractive index isotherm. The
volume adsorbed isotherm is then used to calculate the mesopore size distribution [24].

The results of ellipsometry measurements for PhTES silica coating on glass substrate are shown in Figure 6.28. The spectroscopic ellipsometry regression was conducted between 1.25 and 3 eV. A layer thickness of 1809 nm and a refractive index of 1.556 at 632.8 nm were obtained. A goodness of fit (R^2) of 0.954 was reported.
Figure 6.28 Spectroscopic ellipsometry measurement and regression results
The changes of refractive index with relative pressure are shown in Figure 2.19. The changes of refractive index between saturated pressure vapour and vacuum condition were low (~0.01). Refractive index isotherm did not show a shape indicating capillary condensation. Therefore, no further evaluation of the isotherm was possible for this sample.

Vertical camera images of two sol-gel coatings with different thicknesses on silicon wafer substrate as well as the substrate alone are shown in Figure 6.30.
Figure 6.30 (a) Thick and (b) thin silica layers on (c) silicon wafer substrate

The ellipsometry spectrum of the sol-gel layers is shown in Figure 6.31. The spectrum of sample 2 overlayed that of the substrate due to discontinuity in the silica layer. A possible depolarization effect was observed in sample 1, which may be due to the inhomogeneity in the sample layer. This effect prevented the deduction of porosity information from the results of this test.
Figure 6.31 Ellipsometry spectrum comparison of thick (sample 1) and thin (sample 2) silica layers, as well as the silicon substrate (sample 3)

6.3.7 Summary of pore characterisation data

The pore size data obtained from different methods and the distance between pores obtained via SAXS are summarised in Table 6.4. A comparison between the pore sizes of PhTES silica measured with different methods indicates that HRTEM gave the smallest pore size results. This could be due to the different sample preparation techniques used for TEM compared with N$_2$ adsorption and AFM, as explained in section 6.3.5. Different methods of pore measurement
using nitrogen adsorption resulted in different pore diameter results. From these, only the BJH and average pore diameters of PhTES silica are reported in Table 6.4. The HRTEM and SAXS data both indicated that the diameter and distance between pores increased with the size and chain length of the non-hydrolysable group of the silica precursor. The smallest and largest pore diameter and distance between pores belonged to MTES and OTES, respectively.

Table 6.4 Summary of pores size and pore distance data obtained using different methods

<table>
<thead>
<tr>
<th>Silica type</th>
<th>N$_2$ adsorption</th>
<th>HRTEM</th>
<th>AFM</th>
<th>SAXS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTES</td>
<td>-</td>
<td>0.43±0.14</td>
<td>-</td>
<td>0.82±0.05</td>
</tr>
<tr>
<td>VTMS</td>
<td>-</td>
<td>0.52±0.48</td>
<td>-</td>
<td>0.95±0.2</td>
</tr>
<tr>
<td>PhTES</td>
<td>2.67 7.58</td>
<td>0.53±0.18</td>
<td>5.2±2.3</td>
<td>1.34±0.2</td>
</tr>
<tr>
<td>GPTMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.45±0.06</td>
</tr>
<tr>
<td>OP12</td>
<td>-</td>
<td>*</td>
<td>-</td>
<td>1.50±0.4</td>
</tr>
<tr>
<td>CycTES</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.56±0.2</td>
</tr>
<tr>
<td>OTES</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.95±0.4</td>
</tr>
</tbody>
</table>

* Could not be determined from the images.

6.3.8 Photochromic properties

The maximum absorption data (ΔA$_{max}$) of different silica coatings containing SO dye with UV irradiation, measured at 627 nm, is shown in Figure 6.32.
Figure 6.32 Maximum absorption of different silica coatings embedded with SO dye at 627 nm

$\Delta A_{\text{max}}$ was highest for coatings from silica precursors bearing a cyclic group (e.g. PhTES) or long aliphatic chain (e.g. OTES) or both (e.g. CycTES), and lowest for those with short aliphatic chains, e.g. MTES and VTMS. Expectedly, $\Delta A_{\text{max}}$ of OTES:PhTES 1:2 silica was in between those of its silica components, i.e. OTES and PhTES. The maximum absorbance of GPTMS was higher than MTES and VTMS, owing to the presence of a longer aliphatic chain in the matrix, but lower than CycTES and PhTES, despite their shorter-chain non-hydrolysable groups.

The absorbance of the dye is dependent on how well it is dispersed in the silica matrix. Whether the dye is present in the pore in aggregated or single molecule form is a determining factor in its functionality. Dye aggregation in pores inhibits the structural transformation of the photochromic dye. Therefore, the ability to disperse the dye greatly influences the final optical absorbance. Due
to the hydrophobic nature of spirooxazine, silica types bearing non-
hydrolysable groups which induce hydrophobicity in the silica have a better
ability to disperse the dye, and therefore lead to higher $\Delta A_{\text{max}}$. This explains
the abovementioned behaviour where silica precursors bearing longer aliphatic
chains or cyclic groups produced higher $\Delta A_{\text{max}}$. In the case of GPTMS,
although it bore a longer-chain non-hydrolysable group than CycTES and
PhTES, the determining factor was the more hydrophobic nature of the cyclic
groups in the latter silanes. In other words, the higher polarity of the epoxy
group in GPTMS led to its lower dye dispersing ability, and consequently
lower $\Delta A_{\text{max}}$. It is also interesting to note that between MTES, VTMS, and
PhTES silica, the absorption maxima increased in the same order as the pore
diameter, suggesting that larger pores facilitate the dispersion of the dye in
single molecular form in the matrix, leading to increased absorption. However,
because pore diameter information could not be obtained for the other silica
types, this explanation could not be extended to all the studied silica types.
Coloration ($t_{1/2}$) and bleaching ($t'_{1/2}$) half-life times are shown in Figure 6.33 a and b, respectively. The obtained trend in the $t_{1/2}$ results was quite similar to $\Delta A_{\text{max}}$, except that GPTMS exhibited a shorter coloration half-life time compared to MTES and VTMS. The faster coloration rates of MTES and VTMS compared to the other silica types (except GPTMS) can be explained by the smaller non-hydrolysable groups of these silica precursors (i.e. methyl and vinyl), which cause smaller steric hindrance. On the other hand, the large non-hydrolysable groups of PhTES, OTES, and CycTES, namely phenyl, octyl, and cyclohexenyl-ethyl, create large steric effects, inhibiting the dye’s transformation, and leading to slower coloration. Conversely, the polarity of GPTMS, resulting from the presence of an epoxy group, leads to the incompatibility of the dye and silica matrix in which it is embedded. In other
words, there are fewer interactions between the dye and pore wall of the GPTMS matrix, which leads to faster coloration upon UV irradiation.

The bleaching half-life time results showed that the $t'_{1/2}$ of VTMS was lower than MTES, which is the opposite of the $t_{1/2}$ results for these two silica types. This can be explained by the interaction of the $\pi-\pi$ bonds in the open form of spirooxazine with the double bond in the vinyl group of VTMS. PhTES showed the slowest bleaching rate among all of the studied silica types, with a relatively large difference to those of OP12, CycTES, and OTES. This can be explained similarly to the behaviour observed in the case of VTMS silica. In other words, it can be attributed to the interaction between the $\pi-\pi$ bonds in the open form of the spirooxazine molecule with the phenyl rings covering the pore walls of the PhTES matrix. The general trend observed for $t'_{1/2}$ of the other silica types can be explained in the same way as $t_{1/2}$.

A comparison between the observed trend in the HRTEM pore diameters of MTES, VTMS, and PhTES silica (Figure 6.33 c) and the colouration and fading rates of these types of silica embedded with dye (Figure 6.33 a and b) shows that pore size was not the predominant factor in determining colouration and fading rates. For instance, although PhTES silica had the largest pore size among the three, it had the slowest rate of colouration and fading. This suggests that the interaction between the pore walls and the embedded dye molecules was more influential in this respect. In other words, the chemical nature of the silica precursor in terms of the type of non-hydrolysable group and the steric effects induced by it affected the speed of structural transformation of the dye more than the size of the encapsulating pore.
Figure 6.34 (a) Photostability and (b) coating solution uptake of different silica coatings embedded with SO dye

The photostability results, shown in Figure 6.34 a, indicated a significantly higher photostability for GPTMS, while those of the other coatings were approximately on the same level. With the exception of OTES, the photostability result seemed to be influenced by the trend observed in the uptake of coating solutions on fabric (Figure 6.34 b). In other words, for most
of the studied silica types, wherever higher amounts of dye were present on the fabric, higher photostability was obtained. The availability of more dye on the fabric means that longer UV irradiation times are required to degrade all of the dye molecules. However, it is not clear why OTES silica did not follow this trend. Although the same coating conditions and liquid to goods ratio were maintained for all coatings, GPTMS and OTES coating solutions were absorbed better by the fabric, as indicated by their higher uptake.

6.4 Summary

In this chapter, the pore structure of acid-catalysed sol-gel silica, embedded with spirooxazine was studied by means of synchrotron SAXS, nitrogen adsorption porosimetry, TEM, AFM, and ellipsometric porosimetry. XRD was used for calculating the crystallinity and crystal size of a silica coating. Furthermore, the effects of the non-hydrolysable groups of silica precursors on the structural and photochromic properties of photochromic silica were investigated. The main results are summarised below:

- A crystal size of 2.4 nm and crystallinity of 66.5% were calculated for PhTES coating by XRD analysis.

- SAXS characterization of silica containing non-hydrolysable groups of different sizes revealed that the distance between pores \(d\), which ranged between 8.2 and 19.5 nm, increased with the size of the non-hydrolysable group in the silica precursor. The effect of the inclusion of spirooxazine dye in the pores on \(d\) and \(q_s/q_l\) was small.
• Nitrogen adsorption porosimetry using the BJH method gave pore diameters of 2.7 and 2.1 nm for PhTES silica without and with dye, respectively. The average pore diameters measured using nitrogen adsorption were 7.6 nm and 5.8 nm for PhTES silica without and with dye, respectively. The reason for the smaller pore diameter obtained for the dye-inclusive pores is that the filling of pores with dye molecules limits the available sites for nitrogen adsorption. The two peaks observed in the BJH pore size distribution results of PhTES silica corroborated with those of the SAXS curves.

• TEM images of MTES, VTMS, and PhTES silica revealed pore sizes of 0.43±0.14, 0.52±0.48, and 0.53±0.18 nm, respectively. This suggests a relationship between pore diameter and the size of the silica non-hydrolysable group.

• AFM measurements of PhTES silica showed a 5.2±2.3 nm average pore diameter. This was a larger figure compared to that obtained with HRTEM. This was attributed to factors including the effect of spin-coating and the size of the AFM tip used for measurement.

• Ellipsometric porosimetry did not provide structural information on PhTES coatings, due to layer inhomogeneity and discontinuity.

• The study of the photochromic properties of the silica coatings embedded with spirooxazine dye showed that the absorption maxima was higher when the silica precursor bore a cyclic group or long alkyl chain or a combination of these as non-hydrolysable group, and lower for silica types bearing short alkyl chains. The coloration/bleaching
times generally related to the steric effects induced by the non-hydrolysable groups in the silica precursors and the chemical interaction of these groups with the spirooxazine molecules. Where steric hindrance or the interaction of pore wall with dye was higher, coloration/bleaching rates were slower, with the exception of GPTMS, where the polarity induced by the epoxy group affected the compatibility of the matrix with the dye. The order of the colouration and bleaching rates of MTES, VTMS, and PhTES silica embedded with dye did not seem to be affected by the pore diameter of these silica matrixes. The photostability results did not show a relationship with the size of the non-hydrolysable groups and, with the exception of OTES, were influenced by the uptake of coating solution on fabric.
7 Conclusions and future work

7.1 Main conclusions of this thesis

In this work, photochromic fabrics were produced by incorporating photochromic dye in silica coatings prepared using the sol-gel technique and applying the coatings on fabric. Different treatments were applied to fabric to improve the photostability and depth of colour of photochromic fabrics. Furthermore, the microstructure of different silica matrices and the relationship between silica pore structure and photochromic properties of silica coated fabrics were investigated. The main results of this study are summarised below.

To enhance the photostability of photochromic fabrics, three types of treatment including incorporating UV stabilisers, modifying surface wettability, and sealing dye-loaded pores with additional silica were applied. The studied UV photo-stabilisers included a quencher UV stabiliser, two UV absorbers, and a free radical scavenger. All three types of treatment improved photostability without significantly affecting maximum absorption and speed of colour change. Incorporating a quencher UV stabiliser was the most effective treatment. The next most effective treatment was the addition of an extra layer of APS silica, although it reduced maximum absorption and increased the rigidity of the coated fabric. The photochromic fabrics showed high abrasion durability and acceptable wash fastness.
Different techniques were utilised to improve the depth of colour of photochromic fabrics. These included encapsulating spirooxazine in cyclodextrin, changing the solvent, incorporating a surfactant, embedding spirooxazine in polymethylmethacrylate (PMMA) film, incorporating PMMA/silica copolymer in silica coating on fabric, and synthesizing spirooxazine/PMMA particles for dispersion in resin and silica coatings on fabric. Photochromic fabric coated with silica containing spirooxazine-β-cyclodextrin (SO-β-CD) complexes showed 26.7% higher absorption maxima compared to the control photochromic fabric coated with silica containing photochromic dye. However, increasing the concentration of SO-β-CD in the coated fabrics led to reduced colour depth. The solubility of the photochromic dye in four solvents including ethanol, acetone, dimethylformamide (DMF), and tetrahydrofuran (THF) was investigated, and a 17.6% improvement in colour depth was achieved by using THF in the coating solution instead of ethanol. Incorporating surfactant in the silica coating reduced the absorption maxima. Incorporating spirooxazine in PMMA film led to 92.5% improvement in colour depth while considerably decelerating bleaching rates compared to silica coated fabrics. Silica coatings containing PMMA/silica copolymer enhanced maximum absorption by 19% compared to the control silica sample at equal dye content. While spirooxazine-PMMA nanoparticles synthesized by direct polymerisation did not display satisfactory photochromic performance, spirooxazine dispersed physically in PMMA and shaped into particles exhibited excellent photochromic performance. When the aforementioned particles were incorporated in hydrophilic resin, an improvement of 59.5% was achieved in absorption maxima. When the spirooxazine-PMMA particles were embedded in silica coated fabric, compared to silica coated fabric containing
an equal concentration of spirooxazine, the absorption maxima was enhanced by 102.4%. Compared to the coloration and bleaching rates of spirooxazine in silica coated fabric, the colour changing rates of spirooxazine-PMMA particles were significantly retarded in hydrophilic resin, whereas the rates remained almost unchanged when the same particles were dispersed in silica coating.

The pore structure of silica containing different types of non-hydrolysable groups was studied by small angle x-ray scattering (SAXS), nitrogen adsorption porosimetry, transmission electron microscopy (TEM), atomic force microscopy (AFM), and ellipsometric porosimetry. X-ray diffraction (XRD) was used for measuring the crystallinity and crystal size. The effects of the type of non-hydrolysable group on the structural and photochromic properties of photochromic silica were also studied. The XRD analysis revealed a crystallinity of 66.5% and crystal size of 2.4 nm for PhTES silica coating. The SAXS study of silica containing different non-hydrolysable groups showed that the distance between pores ranged between 8.2 and 19.5 nm and increased with the size of the non-hydrolysable group. Furthermore, inclusion of dye in the pores had little effect on the pore characteristics. Nitrogen adsorption porosimetry using the Barrett-Joyner-Halenda (BJH) method revealed pore diameters of 2.7 and 2.1 nm for PhTES silica without and with dye, respectively. The average pore diameters measured by nitrogen adsorption were 7.6 nm and 5.8 nm for PhTES silica without and with dye, respectively. The smaller pore diameters obtained for pores containing dye were attributed to the filling of pores by the dye molecules which reduced the number of available sites for nitrogen adsorption. TEM images of MTES, VTMS, and PhTES silica showed 0.43±0.14, 0.52±0.48, and 0.53±0.18 nm pore sizes, respectively, suggesting a relationship between pore diameter and the size of
silica non-hydrolysable group. AFM measurements of PhTES silica revealed an average pore diameter of 5.2±2.3 nm, which was larger compared to the HRTEM results. This was attributed to differences in sample preparation between the two methods as well as the size of the AFM tip. Ellipsometric porosimetry did not reveal structural information about PhTES silica due to inhomogeneity in the studied coating. The study of the photochromic properties of silica coated fabrics embedded with spirooxazine dye showed that maximum absorption was higher for silica containing a cyclic group or long alkyl chain or a combination of these as non-hydrolysable group, and lower for silica types with short alkyl chains. The colour changing rates were mostly affected by the steric effects induced by silica non-hydrolysable groups and the groups’ chemical interaction with spirooxazine molecules. The rates of coloration and bleaching were slower when steric hindrance or the interaction between the dye and pore wall was higher. Photochromic fabric coated with GPTMS silica however did not display this behaviour. This was explained by the higher polarity of the matrix which reduced its compatibility with the dye. The colouration and bleaching rates of photochromic fabrics coated with MTES, VTMS, and PhTES silica did not appear to be linked to the pore diameters of these matrices. The photostability results did not indicate a relationship with the size of non-hydrolysable group and, with the exception of OTES, were affected by the coating solution uptake on fabric.

### 7.2 Suggestions for future work

Based on the findings of this thesis, the following ideas are suggested for further research in this field:
- To improve the properties of photochromic fabrics, other porous matrices can be used instead of silica for encapsulating photochromic dyes and the effects of this on the photochromic properties can be investigated. For instance, a porous crystal matrix with highly ordered micropores could create interesting effects in a photochromic fabric.

- The possibility of enhancing the photochromic properties by chemically modifying the photochromic dye to increase its affinity to the matrix can also be studied. Furthermore, the dye can be modified to chemically bond to the matrix in a way that does not reduce its colour change rate by compromising its structural transformation.

- Using thermochromic, electrochromic, or halochromic compounds, colour-changing textiles can be produced which respond to thermal, electrical, or chemical stimulus. This can create novel applications in fashion and industry.
References


