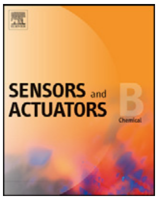
Sensors and Actuators B 162 (2012) 27–34

Contents lists available at SciVerse ScienceDirect

Sensors and Actuators B: Chemical

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



Novel cellulose and polyamide halochromic textile sensors based on the encapsulation of Methyl Red into a sol–gel matrix

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ARTICLE INFO

Article history:
Received 12 October 2011
Received in revised form
22 November 2011
Accepted 29 November 2011
Available online 7 December 2011

Keywords:
pH-sensor
Wide area textile sensor
Sol–gel
Methyl Red

ABSTRACT

pH-sensitive chromic textiles are promising materials that can be used as flexible sensor systems providing an easily visible signal. However to date, mainly conventional dyeing techniques have been applied for obtaining these textile sensors, which limits the possibilities in terms of pH-sensitive dyes and textile types. Therefore, the more versatile sol–gel technique was studied in this paper as an alternative dye loading method. The pH-indicator Methyl Red was applied on cellulosic and synthetic textile fabrics using both a conventional dyeing and a sol–gel technique. Textile fabrics treated with sol–gel were found to show a fast and clearly visible colour change with a pH-variation. In addition, the hydrophilicity of the polymeric material affected the distribution of the dye molecules inside the fibre and as a consequence the response of the resulting sensor. Moreover, due to interactions of Methyl Red with the sol–gel matrix the halochromic behaviour of the dye changed with respect to the dye in solution. In conclusion, sol–gel showed to be a highly effective technique for the development of flexible sensors which allow for monitoring pH-variations through a colour change.

1. Introduction

The application of pH-sensitive dyes to textile materials may lead to flexible, wireless and easy-to-handle sensors which are able to give a first, immediately visible signal. These sensors have potentials for many applications such as wound dressings able to follow-up the healing process [1], protective clothing, filtration, etc. The sensors would be complementary to both the glass electrodes and the optical pH-sensors as they offer the possibility of continuously and qualitatively monitoring the pH only by a visual colour observation [2,3]. Moreover, a pH-sensitive textile structure allows for a large area sensor with yet a local warning signal. Such halochromic textile sensors have already been realised using conventional dyeing processes [2,4,5]. However, the major drawback of this dyeing method is that different textile materials require different dyeing procedures. In addition, certain combinations of pH-indicator and textile are not compatible in conventional dyeing [2].

The sol–gel technique is a relatively simple method which gives a porous three-dimensional inorganic network. This network is formed by the hydrolysis and condensation in hydro-alcoholic solutions of a metal-organic precursor such as an alkoxide, $M(OR)_n$ [6,7]. Organic molecules can be incorporated in this solid matrix giving rise to sensors with a high chemical and mechanical stability [8–14]. Even though at present research is mainly focused towards sol–gel applications on rigid materials such as glass to obtain optical pH-sensors, the technique may also show potential for the development of textile pH-sensors.

Recently, sol–gel has indeed been applied on textiles for various other applications such as flame retardant [6,15], water and oil-repellent [16], antistatic [17] and antimicrobial textile materials [18]. Also an unchangeable colouration of textile fibres has been realised using sol–gel [19,20]. So far, colour changing textiles obtained by sol–gel have received only minor attention with little research on photochromic sol–gel textiles [21,22]. Nevertheless, the above mentioned studies indicate that sol–gel is a promising technique for applying new functional properties to a textile material while maintaining sufficient textile comfort [23]. With this, the influence of the surrounding matrix on the properties of the functionalising agent should be considered as they are possibly affected by the environment in which the agent is present.

The sol–gel technique may be beneficial for the development of textile pH-sensors as it provides the possibility of obtaining

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doi:10.1016/j.snb.2011.11.077

satisfactory colour depths on various textile materials using one single recipe [19]. Moreover, since sol–gel is regarded as a surface treatment, the dye molecules are expected to be mainly present at the surface of the fibres, especially for hydrophobic polymers [24]. This might lead to a fast response of the sensor because the dye molecules are easily accessible. In contrast, dyes in conventionally dyed fibres generally reach the centre of the fibre leading to a slower response [2,25]. Furthermore, leaching of the dye, which is a common phenomenon in traditional dyeing, might be minimised by applying a coupling agent giving a covalent bond between the silica sol and the pH-indicator molecule [26]. Despite these favourable characteristics, sol–gel has not yet been studied for the incorporation of pH-sensitive dyes in textiles.

Therefore in this paper the sol–gel technique was studied and compared to the conventionally dyeing method as to evaluate its performance. Methyl Red (MR), a widely used and well-known azo dye used as pH-indicator in the pH-region 4.4–6.0 [27,28] was selected as pH-sensitive dye. MR was applied on cellulosic cotton fibres and synthetic polyamide fibres as to also study the influence of the surrounding textile matrix on the halochromic properties of the sensor. The comparison between both the application method and the fibre type was based on spectroscopic measurements, for the colour assessment, as well as microscopic evaluation of the diffusion of the dye inside the fibre, for the determination of the dye location.

2. Experimental

2.1. Materials

MR was purchased from Sigma–Aldrich and used as received. The sol–gel precursor glycidoxypropyltrimethoxysilane (GPTMS, purity grade 97%) was also supplied by Sigma–Aldrich. Scoured and bleached cotton fabric supplied by Mascioni Spa (Cuvio, Italy) and polyamide 6 (PA 6) and polyamide 6.6 (PA 6.6) fabrics obtained from Concordia Textiles (Waregem, Belgium) were used in this research. Acetic acid used for the dyeing of polyamides and hydrochloric acid and sodium hydroxide used for the preparation of the pH-baths were also supplied by Sigma–Aldrich. Perfixan was obtained from Chemotex (Kortrijk, Belgium).

2.2. Methods

All conventional dyeings were performed in a Mathis Labomat BFA-8 lab dyeing machine using a direct dyeing process for cotton (60 min at 100 °C at neutral pH) and an acid dyeing process for polyamide (60 min at 100 °C at pH 5). The dye concentration was 5% on mass of fibre (omf) for cotton and 0.5% omf for polyamides. After dyeing, all fabrics were dried in a conditioned room.

The sol–gel textile samples were prepared by modifying the procedure reported by Xing et al. [29]. Because the size of standard pH-indicators is too small for a permanent entrapment in a sol–gel matrix [30], the organosilicon precursor GPTMS was applied which is likely to result in a covalent bond formation. The precursor GPTMS firstly reacted with the pH-indicator MR in ethanol (EtOH) at 70 °C for 6 h in the presence of a catalytic amount of HCl at a GPTMS:HCl:EtOH molar ratio of 1:0.008:60 and a GPTMS:MR ratio of 20:1 (sol A), 10:1 (sol B) and 2:1 (sol C). In the second step water was added to the mixture (molar ratio GPTMS:HCl:EtOH:H_2O 1:0.008:60:55) and the reaction was left to react at 70 °C for 3 h. During this second step the hydrolysis and condensation reactions took place leading to the hybrid sol–gel material. The reactions are displayed in Fig. 1. Next, the cotton and polyamide samples were impregnated with these sols by passing them through a two-roll laboratory padder (Werner Mathis) four times at a nip pressure of 4 bar and twice at 2 bar [31]. After drying (80 °C for 30 min) the fabrics were cured (at 120 °C for 5 min) in an electric laboratory oven.

The washing fastness of the samples was determined according to the standard ISO 105-A01:2010 and evaluation was done using a greyscale going from 5 (best performing) to 1 (worst performing).

pH measurements were executed with a combined reference and glass electrode (SympHony Meters VMR). Potassium nitrate with a concentration of 10^{-2} mol l^{-1} was added to ensure a constant activity coefficient during measurements. Hydrochloric acid and sodium hydroxide were used to adjust the pH of the aqueous pH-baths.

The UV–vis spectra were recorded with a Perkin-Elmer Lambda 900 spectrophotometer. For the absorption spectra of solutions 1 cm matched quartz cells were used, for the reflection measurements on fabrics an integrated sphere (Spectralon Labsphere 150 mm) was used. The spectra were recorded from 380 nm to 780 nm with a data interval of 1 nm (absorption) and 4 nm (reflection). Out of these spectra, the absorbance (for solutions) or Kubelka–Munk value (for fabrics) as a function of pH at the acidic and alkaline peak maximum were depicted. In case of a textile fabric showing a relatively low washing fastness, a normalisation was performed as to eliminate the effect of dye release. The spectra were normalised to a value of one at the peak maximum. The resulting figures provide a qualitative image of the halochromism but not a quantitative due to the normalisation.

The pK_a value of the dye was calculated based on absorbance spectra using formula (1), with A_x the absorbance obtained at a defined pH and A_a and A_b the absorbance of the acid form and of the base form of MR, respectively.

$$\mathrm{p}K_\mathrm{a} = \mathrm{pH} - \log \frac{A_\mathrm{x} - A_\mathrm{a}}{A_\mathrm{b} - A_\mathrm{x}} \tag{1}$$

The colour differences were calculated out of the UV–vis spectra by CIE-Lab using a D65/10° illuminant. The magnitude of the colour difference was quantified by ΔE (formula (2)) with ΔL the lightness difference, Δa and Δb the differences in a and b values, wherein a is a measure of redness/greenness and b of yellowness/blueness [32]. A ΔE value higher than 1 indicates a visually detectable colour difference with higher values for greater colour changes.

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \tag{2}$$

In order to obtain images of the fibrous cross-sections, fibres of the dyed fabrics were first mounted in historesin blocks and trimmed to obtain one clear-cut surface perpendicular to the fibre axis. Next, confocal laser scanning microscopy (CLSM) experiments were performed using a Nikon A1R confocal microscopy (Nikon Instruments, France) mounted onto a Nikon Ti Eclipse body, equipped with a Plan Apo VC corrected 60× (1.4) oil lens. Dye excitation was achieved using a 405 nm diode laser and detection was done on a PMT using a 525/50 nm bandpass filter. The physical pixel size of the recorded images was 0.1036 μm.

3. Results and discussion

3.1. Methyl Red in aqueous solution

To accomplish the main aim of the current study, being an elaboration of the differences between sol–gel treated and conventionally dyed cellulose and polyamide, it is first essential to investigate the properties of the pH-indicator MR in aqueous solutions. Therefore, two MR solutions were prepared, one based on the dissolution of the as received MR powder (50,000 times diluted) and another one obtained by the sol–gel procedure (sol B, 1600 times diluted). Both solutions visually changed colour from yellow in alkaline or neutral solutions to red in acidic solutions. The