IOP Conf. Series: Materials Science and Engineering **254** (2017) 072027 doi:10.1088/1757-899X/254/7/072027

Synthesis and characterization of halochromic hybrid sol-gel for the development of a pH sensor fabric

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Abstract. A halochromic hybrid textile for pH-sensing applications was designed by employing a non-toxic dyestuff, *7*-Hydroxy-*3H*-phenoxazin-*3*-one (Resorufin), and an epoxy silane precursor, *3*-glycidoxypropyltrimethoxysilane (GPTMS) through sol-gel method. The reaction mechanism and the formation of a polyethylene oxide network of GPTMS containing Resorufin were established by NMR characterization. The pH response of the hybrid halochromic system was studied by UV/Vis spectroscopy and compared with the pure Resorufin in different buffered solutions. Morphology and washing fastness of treated textile fabrics were evaluated by SEM, AFM and FT-IR analyses.

1. Introduction

"Smart textiles" have attracted much interest in scientific research because of their capability to sense and react in presence of external stimuli. The integration of chemical sensor species into textiles involves many advantages to this field, by combining sensing properties with typical textile fabrics characteristics, such as toughness, strength and flexibility, thus obtaining useful "wearable sensors". In this regard a widely useful method for the realization of wearable sensors on fabrics is the sol-gel process [1,2]. Reactions of precursors like silicon alkoxides in mild reaction conditions, such as low temperature and acidic or basic catalytic conditions, involve the formation of a hybrid organic-inorganic 3D network with high degree of homogeneity and optical transparency, making it attractive for sensing optical applications [3]. Indeed, thanks to the incorporation into the sol-gel matrix of a halochromic indicator, bonded covalently or through weak interaction, it is possible to realize a functional fabrics coating that acts as wearable optical sensor device [4]. Optical sensors present some advantages (i.e. real-time measurements, high Signal to Noise Ratio, easiness of miniaturization), but also some disadvantages, such as interference by ambient light, poor selectivity due to the presence of other components of the sweat and poor stability due to halochromic dyestuff leaching or photobleaching [5].

In the last years, pH real-time measurements were fully studied and optimized because of their impact on daily life and in several fields such as medical, diagnostic and environmental. In particular, wearable pH sensors are able to detect acidic or alkaline values of the sweat, making them very interesting due to the wide range of information that they may provide about the wearer's health (i.e.

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body hydration level or potential pathogenesis of skin disease). As a matter of fact in earlier studies of some of us it has been shown the development of colorimetric pH sensors by the combination of pH-sensing dyestuff with textile fabrics and an optoelectronic circuit [1,2,6-8].

In this work, a halochromic hybrid system has been successful realized by the non-covalent immobilization of a non-toxic dyestuff, Resorufin, into a sol-gel GPTMS matrix and fully characterized in order to evaluate morphological, structural, durability, and pH-sensing properties.

2. Experimental part

In a one-pot reaction, the immobilization of *7*-Hydroxy-*3*H-phenoxazin-*3*-one (Resorufin), as halochromic sensing dyestuff, into an excess of *3*-glycidoxypropyltrimethoxysilane (GPTMS) was achieved in presence of *1*-methylimidazole, as catalyst for the epoxy ring opening of GPTMS, in acidic ethanol solution under reflux condition. After 3h, the obtained pink solution (R-GPTMS sol) was characterized by UV/Vis spectroscopy in McIlvaine Na_2HPO_4/citric acid buffers with different pH (2-8) and compared with pure Resorufin in order to study the functionalized Resorufin pH-sensitivity.

Scoured and bleached 100% plain-weave cotton fabric, previously washed in 2% non-ionic detergent (40°C and pH 7, 20 min) rinsed with de-ionized water and dried, was used as substrate for the realization of the wearable pH sensor. R-GPTMS sol was coated on textiles by pad-cure method (using a Werner Mathis padder, 75% wet pick up), dried (80°C, 5 min) and cured (170°C, 4 min) in a convention oven, obtaining CO_R-GPTMS. Treated textiles were washed according to EN ISO 6330:2000 (in a Werner Mathis AG) in order to evaluate the durability of the coating after 1 and 5 washing cycles.

3. Results

3.1. NMR characterization

R-GPTMS sol, Resorufin, and Resorufin sodium salt were analyzed in methanol-d_4 solution for ^{1}H NMR spectroscopy in order to establish the structural conformation of the obtained dyestuff sol-gel. This is important because, the epoxy ring opening of GPTMS can follow two different synthetic routes for the realization of the R-GPTMS sol: (i) epoxy ring opening of GPTMS due to the nucleophilic attack by –OH group of Resorufin, resulting in a covalent ether bond between GPTMS and Resorufin moieties; (ii) formation of a polyethylene oxide network (PEO), due to the polymerization of GPTMS, followed by immobilization of the dyestuff through hydrogen bonds or weak electrostatic interactions.

In particular, analyzing the aromatic region of the ^{1}H NMR it is possible to establish the quite stable encapsulation of the dyestuff, through weak interaction, into the PEO 3D network in the resulting R-GPTMS sol because of the coincident aromatic signals of the proton resonances of R-GPTMS with ones of anionic Resorufin itself (Resorufin sodium salt) as evidenced in figure 1.

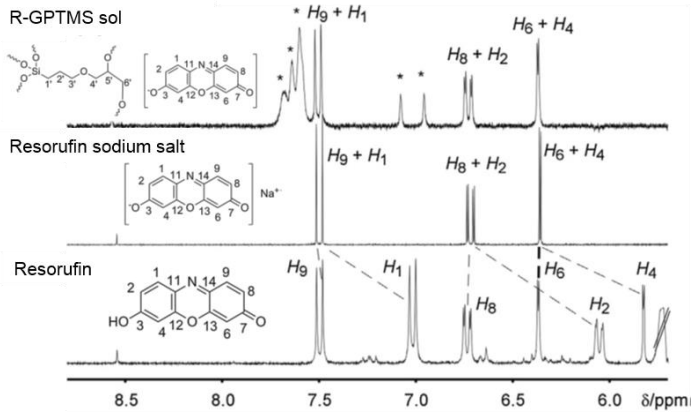


Figure 1. ^{1}H NMR spectra of Resorufin, Resorufin sodium salt and R-GPTMS sol in methanol-d_4 at 298 K (300 MHz) with proton assignment.

3.2. FT-IR analyses

FT-IR spectra of cotton fabrics treated with R-GPTMS sol were collected in order to evaluate the durability of the coating even after 1 and 5 washing cycles (CO_R-GPTMS_1W and CO_R-GPTMS_5W, respectively). Spectra of CO_R-GPTMS shows the presence of the silylated film due to the presence of Si-O-Si absorption bands at 852 cm^{-1} and 790 cm^{-1} (bending and stretching, respectively) that are still present in spectra of CO_R-GPTMS_5W thus confirming the durability of the R-GPTMS sol coating (figure 2a). Moreover after 1 washing cycle, the halochromic hybrid cotton fabric shows a small dye leaching, as evident in figure 2b, that still remain constant after 5 washing cycles; this data are also confirmed by the corresponding add-on%.

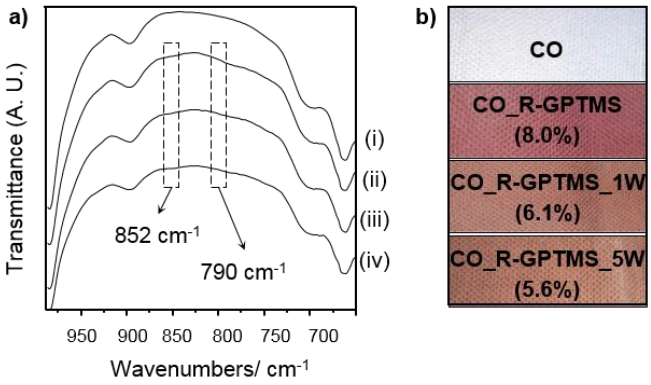


Figure 2. a) FT-IR spectra of untreated cotton (i), CO_R-GPTMS (ii), CO_R-GPTMS_1W (iii), CO_R-GPTMS_5W (iv), in the range 650-1000 cm^{-1}. b) Samples images with corresponding add-on (%).

3.3. pH response: UV/Vis spectroscopy

With the aim to realize a wearable halochromic pH-meter device on textiles, the pH response of the hybrid dyestuff-GPTMS system was evaluated by UV/Vis spectroscopy in buffered solutions at acidic and basic pH (2-8), in comparison with the pH response of the pure dyestuff. The Resorufin dyestuff leads to a dark-yellow protonated species and to a pink anionic form in acidic and alkaline media, respectively. In particular, at pH 2, R-GPTMS sol presents a red shift of the absorbance maximum peak from 450 nm to 481 nm maybe due to the formation of weak electrostatic bond between PEO and the dyestuff (Figure 3) which makes the nitrogen of Resorufin less available to protonation in an acid environment with respect to unfunctionalized Resorufin. These evidences, define the maintenance of the pH-sensitivity of Resorufin despite its encapsulation into the PEO-3D network.

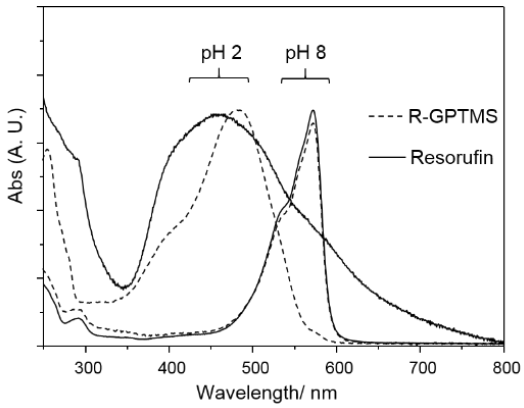


Figure 3. UV/vis spectra of pure Resorufin (black line) and R-GPTMS sol (dashed line).

3.4. Morphological characterizations

SEM and AFM microscopy were employed in order to evaluate the structural morphology, the homogeneity and the durability of the halochromic coating even after washing cycles. SEM images (figure 4a) showed a high degree of homogeneity of the CO_R-GPTMS and of CO_GPTMS (the latter synthesized according the same procedure with only GPTMS for the comparison with CO_R-GPTMS) samples even after washing cycles meaning that the Si distribution, and indirectly of the Resorufin, is homogeneously distributed onto the cotton fabrics. Microscope analysis, at different levels of magnification, clearly shows dissimilar surface morphology of the untreated (i) and treated (ii) cotton samples:(i) a typical interwoven in which the fibers result separated between them; (ii) fibers pasted between them. These observations result more evident in AFM images (figure 4b) according which it is possible to distinguish singular fibers into cotton fabrics and fibers with different feature among them, in the CO_R-GPTMS one. These morphological characterizations allow to confirming the established durability of the coating to the washing cycles and its homogeneity.

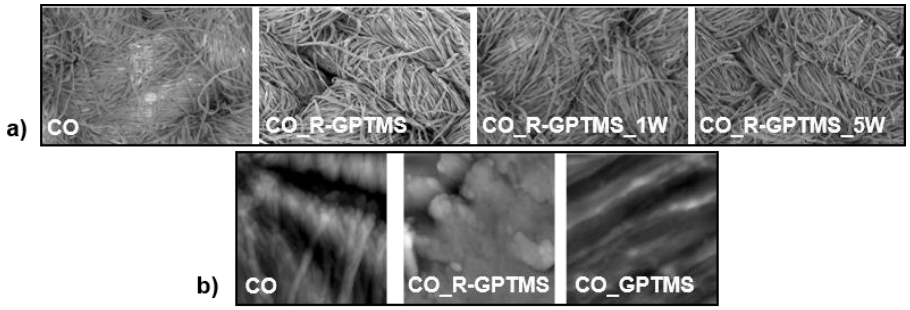


Figure 4. a) SEM images of untreated and treated samples and after washing cycles (magnification: 500 μm). b) AFM morphology of untreated cotton and comparison between cotton fabrics treated with R-GPTMS sol and GPTMS sol.

Conclusions

In this work, a simple synthetic strategy was employed for the realization of a hybrid halochromic system by sol-gel method using a non-toxic dyestuff (Resorufin) and an epoxy-silane precursor as cross-linker (GPTMS). According NMR characterizations, the structural conformation of the resulting halochromic sol was established through weak interactions between the dye and the polyethylene oxide 3D network formed through catalyzed epoxy ring opening of GPTMS. Morphological analyses evidenced the homogeneity of the coating on cotton fabrics which represents an important feature in sensoristic field due to its impact on optical transparency. All experimental findings confirm the durability and the effectiveness of the obtained functional hybrid coating and also the maintenance of pH-sensitivity of the encapsulated dyestuff. This halochromic system represents a good starting point for the development of pH sensor fabrics for technical and smart textiles.

Acknowledgments

Authors wish to thank: MIUR and CNR for financial support, Prof. C. Milone and Dr. E. Piperopoulos (Dept. of engineering UniME, Italy) for SEM characterizations, Dr. M. Brucale (CNR-ISMN Rome, Italy) for AFM characterizations and Dr. E. Guido (Dept. Engineering and Applied Sciences UniBG, Italy) for technical support.

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