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Influence of catalyst in the synthesis of a cellulose-based sensor: Kinetic study of 3-glycidoxypropyltrimethoxysilane epoxy ring opening by Lewis acid

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ABSTRACT

Hybrid halochromic sensor coatings were realized immobilizing Nitrazine Yellow (NY) onto cotton fabrics via the epoxy group of 3-glycidoxypropyltrimethoxysilane (GPTMS) silica precursor in acidic condition. Boron trifluoride diethyl etherate (BF_3OEt_2) in a various percentage range (1–10%, w/w GPTMS) has been used to catalyze the epoxide ring opening. In order to optimize the system, an FTIR study has been developed and kinetic data were obtained for the epoxy ring opening process. A linear correlation between the obtained kinetic rates and BF_3 percentage was observed. By nuclear magnetic resonance (NMR) analysis in solution the real structure of NY, derived from an attack of diazonium salt to para hydroxyl position, was confirmed and the final product of the reaction between NY and GPTMS was characterized. Finally, the different amounts of catalyst were found to affect the coatings wash fastness and the halochromic response of the cellulose-based sensors.

1. Introduction

Since several years, smart textiles have attracted considerable attention due to their potential impact on human life. Recently, there have been many efforts to increase the textile "intelligence", i.e., capabilities to sense and react to the environment [1]. Wearable sensing systems represent a challenge, due to the coexistence of requirements like miniaturization, robustness, high accuracy, but also comfort and handiness for the user. The increasing sensibility of people on their health drives the need of real-time information on the physiological parameters and on the environment in which we live [2], that is the ability to monitor emotions, stress, but also pollution or the presence of toxic gases. Likewise the continuous increase of an elderly population, together with the decrease of the health budget and the awareness to the early detection of pathologies, are a strong input for patients remote monitoring [3]. Moreover, the potentiality of wearable sensors is also in good match with the fitness field, in which the athletes' parameters monitoring is mandatory for reaching optimal performances [4]. In situ measurements of athletes' physiological, biochemical, biomechanical parameters during training and competition are essential in revealing the underlining factors affecting training and competition strategies. As an intermediate interface, wearable sensors have the potential to monitor both the wearer and the environment parameters. Recently, different miniaturized wearable or implantable sensing devices have been developed to provide low cost, continuous, unobtrusive and real-time monitoring. Through the integration of novel technologies, flexible supports such as textile fabrics could be used as sensors with information transmission capabilities by wearable microsystems [5]. With this aim, the sol-gel textile finishing, which leads to the formation of self-assembled (nano) layers on the fiber surface, has remarkably proved its exceptional potential regarding the synthesis of new coatings with a high degree of homogeneity at molecular level and with outstanding physical–chemical properties [6]. Due to the low temperature of sol-gel processing and to the tuneable porosity of the formed 3D network, functional molecules can be immobilized into the inorganic matrix. The obtained organic–inorganic hybrid films are mostly used as coatings with a variety of purposes. In the textile field they are regularly used to induce self-cleaning [7],

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hydrophobicity [8], flame retardant [9], bacteriostatic properties [10] or to immobilize dyestuffs on textile fabrics [11–14]. These findings are particularly challenging for the textile field as they allow designing innovative applications that exploit sol-gel methods also for controlled release of agents, optical and electrochemical biosensors [15]. Alternatively to the encapsulation, the organic groups can be linked by stable chemical bonds. The latter approach requires precursors in which the organic group is bonded to the oxide-forming element (i.e., silicon alkoxide) in a hydrolytically stable way. Doped silica gels seem to be ideal materials for construction of sensible surface for textile sensors, thanks to properties like visible transparency, porosity, thermal and chemical stability [16]. The list of molecules that can be incorporated into matrices, for optical or electro-optical applications, are almost unlimited and include halochromic dyes, biological or enzymatic functional molecules and liquid crystals [17–19]. Furthermore, leaching of the dye, which is a common phenomenon in traditional dyeing, might be minimized by applying a coupling agent giving a covalent bond between the silica sol and the pH-indicator molecule. In this way, the feasibility of introducing halochromic molecules into a sol-gel matrix by 3-glycidoxypropyltrimethoxysilane (GPTMS) and the durability of the color change, also after immobilization onto textile fabrics, have been recently demonstrated in our previous research [20,21]. GPTMS is a very versatile precursor to synthesize organic–inorganic hybrid materials. Its strong points are represented by the epoxy-ring at the end of an alkyl chain and the hydrolysable methoxy groups. So, by elimination of methanol Si—OH bonds are formed, while the epoxy-ring can be opened to bind moieties like —OH or —COOH. The sol-gel synthesis to produce epoxy-organic molecule hybrids and their properties are highly dependent on the catalyst employed and much more complicated by the presence of different possible side reactions in the first stage of epoxy-ring opening and by the presence of water or other solvents that can be in competition with the organic molecule. Hydrolysis and condensation reactions in sol-gel processing of GPTMS based materials can be realized using acid or base catalysts, although specific catalysts must be selected for epoxy ring-opening polymerization that can be achieved by cationic, anion or covalent nucleophilic mechanisms. Ring opening of GPTMS epoxides is usually achieved in sol-gel derived materials by Lewis acids such as zirconium [22], titanium [23], or aluminum alkoxides [24] whose use has, however, some disadvantages because of their high reactivity and the necessity of using a chelating agent to reduce their hydrolysis rate. Moreover, these catalysts could be incorporated into the obtained hybrid material influencing their final properties. A survey of up-to-date literature shows that BF_3OEt_2 is reported as an interesting catalyst for organic/inorganic polymerization in GPTMS based materials, due to the low temperature required, the preparation time, the yields and the highly homogeneous material carried out [25–27]. Innocenzi and co-workers have extensively studied the GPTMS epoxy-ring reaction catalyzed by BF_3OEt_2 [25–27]. As reported in their research papers, BF_3OEt_2 acts as a strong catalyst of inorganic Si—O—Si network formation and at the same time it catalyzes the organic polymerization from an epoxy ring opening. Large amounts of BF_3OEt_2 favor a fast and extensive polymerization of the inorganic side, hindering the formation of long organic polymers. On the other hand, low amounts of BF_3OEt_2 allow the formation of poly-(ethylene oxide) derivatives. The polymerization of organic and inorganic units in this class of hybrid materials results in a competitive process that is controlled by the amount of catalyst employed during the synthesis. From this observation, the ability of GPTMS to immobilize sensing molecules onto textile fabric was investigated in this paper. The aim is therefore to enable more precise conclusions about the parameters influencing the GPTMS epoxy ring opening during the immobilization of a pH sensitive organic molecule onto textile fabric. To verify both the reactivity of the epoxy ring opened by the catalyst and the sensing properties of a molecule immobilized onto a cotton sample, a halochromic dye was involved as reactive agent in the presence of the GPTMS precursor and the BF_3OEt_2 catalyst. As a test case for this approach, Nitrazine Yellow (NY), 1-((2,4-dinitrophenyl)diazenyl)-4-hydroxynaphthalene-2,7-disulfonic acid disodium salt, was selected. It is an example of an azo pH-indicator that changes color from yellow to blue in the neutral pH-range (pH 6.0–7.0) [28]. The kinetic model of the reaction and the possible mechanism involving GPTMS and NY has been investigated. The reaction of GPTMS with the halochromic dyestuff, using BF_3OEt_2 to catalyze epoxide ring opening at room temperature, has been reported for the first time aiming to realize a wash fastness wearable sensor on textile fabric. Moreover, these results describe the development of a new, generally applicable, synthetic approach that can be employed to prepare a related family of sensors using simple, readily available precursors.

2. Experimental

2.1. Materials and methods

Scoured and bleached 100% plain-weave cotton fabric (weight 237 g/m^2) was used in this research. The fabrics were washed in 2% non-ionic detergent (Berdet WF, wetting agent, kindly supplied by Europizzi, Urgnano, Italy) at pH 7 and 40 °C for 20 min, and then rinsed several times with de-ionized water, dried and stored under standard atmospheric pressure at 65 ± 4% relative humidity and 20 ± 2 °C for at least 24 h prior to all the experiments. Nitrazine yellow (NY), 3-glycidoxypropyltrimethoxysilane (GPTMS), BF_3OEt_2, Na_2HPO_4/Citric Acid buffers (A.R. grade) and other chemicals were purchased from Aldrich and used as received. The pH dependence of the measurements was first evaluated by using eight different pH values, obtained by McIlvaine Na_2HPO_4/Citric Acid buffers [29]. For the kinetic studies by FT-IR, the GPTMS precursor was added dropwise to a water solution containing BF_3OEt_2 as catalyst (in a percentage range from 1% to 10% w/w GPTMS) to obtain a final GPTMS concentration of 0.5 M, and stirred at room temperature. The kinetic starts when the GPTMS addition is completed. In order to monitor the reaction evolution, a known amount of each solution was taken at constant interval times, depending on the reaction speed, and deposited on a glass slide to remove the solvent and to obtain the xerogel by a curing process. At the same time, a known amount of reference (a 0.1 M water solution of $K_3Fe(CN)_6$) was added to the deposited GPTMS sol and then dried at 80 °C for 5 min and cured at 170 °C for 4 min. Finally, the obtained xerogel was analyzed by FT-IR as powder. For each time two withdrawals were carried out. The kinetic method was the same when the reaction was carried out in the presence of NY (1:20 molar ratio with respect to GPTMS). ^1H–^{13}C HSQC and HMBC correlation experiments were also performed to characterize the new hybrid compound, like GPTMS–NY, in solution, and were recorded in a gradient-selected phase-sensitive mode. DMSO-d_6 (D, 99.9%) and D_2O (D, 99.90%) for NMR measurements were purchased from Cambridge Isotope Laboratories, Inc. and used as received. To study the properties of the hybrid sols as a function of BF_3 percentage, three different sols (G-NY-B1%, G-NY-B5%, G-NY-B10%) were synthesized and applied on cotton textiles. All synthesis were carried out by adding GPTMS (0.3 M, 20:1 molar ratio with respect to NY) to a water solution of NY in the presence of a catalytic amount of BF_3OEt_2 (1%, 5% and 10% w/w GPTMS) and stirred for 2 h at room temperature. A scheme of the reaction is shown in Fig. 1. Before application on the cotton surface, the obtained hybrid sols were characterized by UV–vis spectroscopy in buffered solutions at different pH values. Moreover, an FT-IR study of the corresponding