2019 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
Florence, Italy, December 4-6, 2019

A novel fibre optic sensor of relative humidity for application in cultural heritage

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***Abstract* – In this work we present a novel relative humidity sensor of low invasiveness and visibility, well suited for applications in cultural heritage and in particular to monitor the moisture content in stone and wooden artworks. The sensor is based on fibre optic technology, produced by depositing a thin coating of a hygroscopic material on a thin and transparent, barely visible, fibre optic. The novelty of the projected sensor is in the proposed hygroscopic material, which is a mixture of Agar and Chitosan. This material overcomes the critical issues of sensors previously described, based on the same technology but produced with different polymers, typically pure Agar. We present results of the tests that proved the effectiveness of the proposed material and the results of long term measurements in the field.**

1. INTRODUCTION

Fibre Bragg Grating (FBG) are fibre optic sensors that have attracted an increasing interest among researchers in a number of applications. The relevance of FBGs is mostly due to their immunity to electromagnetic interferences, their small size and flexibility, as well as the possibility to design minimally invasive sensing systems [1].

Although FBGs are intrinsically sensitive to strain and temperature, FBG-based sensors have been developed for various parameters, as for instance pressure and displacement. Among the large number of applications, FBG-based sensing systems have already been used for relative humidity (RH) measurements [2]. Humidity measurements has become necessary in a number of areas, such as food process, pharmaceutical and chemical industries, structural health monitoring and so on [2]. The monitoring of temperature and moisture plays an important role also in building sector, in particular for the diagnosis of the stone and wood deterioration, even and above all in the cultural heritage conservation field. The FBG technology results to be particularly suitable for applications in cultural heritage due to its characteristics of low-visibility and tailoring to different surfaces [3].

The most popular and effective approach to develop FBG-RH sensors relies on the use of a hygroscopic material. The FBG is coated by this material that changes its volume with humidity (it swells when RH increases); if there is a good adhesion between this material and the FBG, the swelling strains the FBG itself, that can be used to indirectly measure RH [4].

Recently Agar and Agarose were used as hygroscopic materials for preparation of novel FBG-RH sensors. Agarose, the major component of Agar, is an algal polysaccharide, comprising alternating D-galactose and 3,6-anhydro-L-galactose repeating units. With its excellent ability to form thermo-reversible gels in hot water, Agar finds numerous applications, which include food industry, pharmaceutical formulations, electrophoresis, tissue engineering or as a matrix for soft-matter organic devices [5-7]. This fact could render FBG-RH sensors suitable for monitoring in the above cited applications, beyond cultural heritage.

The use of these polymers has advantages respect to other materials for the ease of preparation and coating stages, for the wide range of operation in terms of RH values and for the fast response [8, 9].

The swelling nature of hygroscopic materials causes also refractive index changes in accordance with the humidity and modulates the light propagating through the fibre. The latter phenomenon has been employed in the design and development of fibre optic humidity sensor in which the swelling polymers are chitosan and agarose [10].

In the same way as Agarose, Chitosan is a renewable and biocompatible biopolymer. Chitosan is a linearly linked polysaccharide derived from natural biopolymer chitin, and composed of randomly distributed (1–4)-linked D-glucosamine (deacetylated unit) and *N*-acetyl-D-glucosamine (acetylated unit). Because of its biocompatible, non-toxic, antimicrobial and metal-binding properties, it has been widely studied in chemical, biochemical and biomedical fields, and it is extensively used in pharmaceutical and biomedical fields [11]. However, the same characteristics may render it suitable for sustainable cultural heritage approaches [12]. Chitosan chemical nature renders its swelling properties highly dependent not only onto the starting material characteristics (*i.e.* molecular weight and deacetilation degree), but also on the device preparation process parameters (*i.e.* polymer concentration and acid content

of the starting gel, post-process drying treatments and so on) [13]. For example, being the polymer rich of amino groups, its swelling degree can be affected by the amino protonation degree. The above consideration make chitosan based FBG-RH sensors ideally tuneable as a function of the environmental condition and application "*in situ*".

The realization of blend composed of Agarose and Chitosan is receiving attention in various fields, mostly with the aim of a mutual enhancement in the mechanical and swelling performances of the blend-based devices [14]. In spite of this, the use of these biopolymers, both as single component both as a blend, is still only little researched in the FBG-RH sensors [10, 15, 16].

The preparation of composite biopolymer hydrogels offers the capability to produce biocompatible materials with cooperative properties. Particularly, Chitosan seems to have a stabilization effect onto Agarose both because of intermolecular hydrogen bonds between the –OH and $–NH_2$ groups in the Chitosan molecules and the –OH groups in Agarose and both because of a reciprocal entanglement between the macromolecular chains, *i.e.* a topological restriction of molecular motion of Agarose by Chitosan [17, 18].

In previous papers, the authors presented the use of Agar-coated FBG sensors (where Agar is mainly composed of Agarose) to monitor moisture in stones of cultural heritage buildings and monuments, considering a scenario, in which their use is intended to provide alarm for imbibition of stones due to various causes, as for instance water absorption from the ground by capillarity or rain water infiltration. In addition, in case of materials treated with hydrophobic layer, a monitoring procedure based on comparative analysis of "in tandem" sensors can provide early warning of layer deterioration [15, 16].

Tailoring the characteristics of the Agar-coated FBG sensors to the required features for "*in-the-field*" stonework monitoring is a critical issue: this involving an improvement of stability, reproducibility, and sensitivity to RH variation. In this paper we present a work aimed to solve that issue controlling the agar coating characteristics. Three different sensor prototypes were made and tested in laboratory and "*in-the-field*" environments: two of them were made both with Agar, but in different concentrations and thickness; the third was made with a mixing of Agar and Chitosan.

2. MATERIALS AND METHODS

A. FBG Working Principles

FBGs are produced by a controlled modification of the refraction index of the core of the fibre, along a short segment (10mm typical) of it. The controlled modification produces a diffraction grating that acts as a reflector that mirrors a specific wavelength (i.e. the Bragg wavelength, λB) of the broadband spectrum of light that flows along the fibre. If an FBG is exposed to strain or temperature variations: λ_B shifts to higher values when the FBG is stretched or heated: λ_B shifts to lower values when the FBG is compressed or cooled. The λ_B value can be expressed as a function of both grating pitch (Λ_B) and refractive index (η_{eff}) of the fibre core as follows:

$$\lambda_B = 2\eta_{eff} \cdot \Lambda_B \quad (1)$$

These parameters, in turn, depend on strain and temperature. When an FBG is coated with a hygroscopic material, the volumetric expansion of the coating causes the grating pitch changes ($\Delta\Lambda_B$) and, in turn, $\Delta\lambda_B$.

B. Fabrication of the sensors

Agar, used for the production of two sensor prototypes, was chosen because of its low tendency to evaporate, its stability and nontoxicity, good swelling properties and good adhesion to silica. Agar is made of Agarose, the component with the greatest gelling ability, and agaropectin, in different proportions, commonly 75% of agarose and 25% of agaropectin. Agar is soluble in hot water, and the solution forms a gel when cooling at about 35–45 °C, which melt above 85°C.

Chitosan, used for the production of the third sensor prototype coated with Chitosan/Agar solution, is a natural and abundant biopolymer. It is derived primarily from chitin, the second most abundant carbohydrate on earth (after cellulose), which plays a structural role in the exoskeletons of invertebrates. Chitosan is a semicrystalline polysaccharide that is insoluble in water at neutral pH, even if it can be dissolved in weakly acidic aqueous solutions and be made into hydrogels. The hydrogel form of Chitosan can absorb up to 2000% of its own weight in water. Chitosan is no toxic and presents excellent physiochemical properties such as biodegradability, film forming ability, antibacterial, good adhesion and elastic properties. More over Chitosan films undergoes very large swelling with increasing RH, which is easily observed by eye and by optical microscopy.

In this work all materials and solvent were reagent grade. Agar used for the synthesis was purchased from Sigma-Aldrich, Italy, while Chitosan (M.W.100000-500000) was purchased from Acron Organics.

The Agar solution was prepared in two different concentrations, 1% and 5% w/w, by dissolving the powder in distilled water at 100 °C. The Agar/Chitosan solution was prepared by dissolving Chitosan at 1% w/w in a 5% acetic acid solutions in distilled water and, when the solution was clear, an equal volume of hot Agar solution at 1% w/w was added. All the mixtures have to be deposited on the optical fibre when the solution is still hot, to avoid formation of gel.

Sensor prototypes were made by locking and tensioning the FBG fibers (Commercial FBG, Broptics

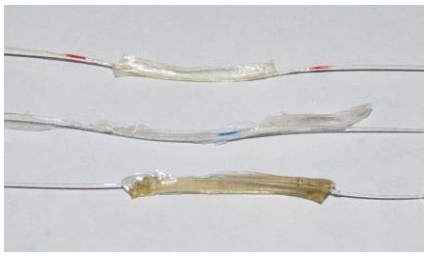

Fig. 1. Picture of the three sensor prototypes: on the top "Agar+Chitosan", in the middle "Agar thin", in the bottom "Agar thick".

Technology Inc., Taipei, Taiwan; 1 cm length of sensing length) inside PLLA molds, made by 3D printing, and depositing gel solutions inside the molds. The systems were slowly dried in air.

Three different sensor prototypes were prepared and tested: the one named "Agar+Chitosan" was made with the mixture Agar/Chitosan by using a mold with dimensions 1×1×20 mm; the one named "Agar thin" was made with Agar solution 1%w/w in a mold with same dimensions (1×1×20 mm); the one name "Agar thick" was made with Agar solution 5% w/w, but in a larger mold (5×5×20 mm). The obtained sensor prototypes are showed in Fig. 1. It worth be noted that the sensor thickness essentially depends on the dimensions of the mold. In fact "Agar+Chitosan" and "Agar thin", that were obtained by using the same mold, have the similar thickness, while "Agar thick" is larger.

C. Experimental set-up

Two experimental setup were used, to test the prototype sensors under two conditions: i) inside an RH controlled enclosure, to evaluate the relationship between the output of the FBG (λ_B) and RH; ii) installed on open air, to simulate expected "in-the-field" operating conditions.

In both conditions, an FBG for temperature compensation was used. That sensor is an FBG with acrylate coating, which is not hygroscopic; thus its $\Delta\lambda_B$ is due to the temperature variation ΔT only. In both setups, measurements from the sensor prototypes were done in temperature compensation mode as follows:

$$\Delta\lambda_B{}^{RH} = \Delta\lambda_B{}^{RH+T} - \Delta\lambda_B{}^{T} \quad (2)$$

$\Delta\lambda_B{}^{RH+T}$ being the total signal coming from the sensor prototype; $\Delta\lambda_B{}^{T}$ being the total signal coming from the FBG for temperature compensation. FBGs used to produce the sensor prototypes and the FBG used for temperature compensation come from the same production lot, so that assumption of equal intrinsic sensitivity to temperature is fully justified.

The output of the RH prototype sensors and the output of the reference FBG are collected by a fibre Bragg

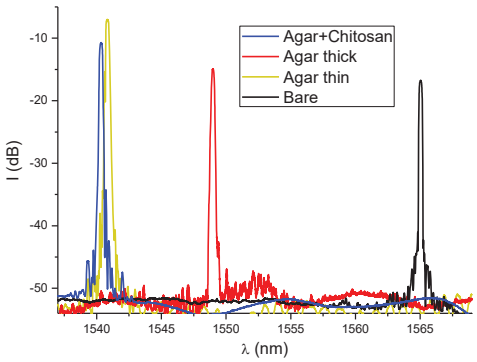

Fig. 2. Spectra of the three functionalised FBGs and one bare FBG, used for thermal compensation

grating interrogator system (FS22, HBM Fiber Sensing, Portugal; wavelength measurement range: from 1500 nm to 1600 nm, resolution= 1.0 pm) at a frequency of 1 Hz. A capacitive humidity sensor (EasyLog, EL-USB_2, USB interface, resolution 0.5%RH) is used to provide the RH reference value.

3. RESULTS AND DISCUSSION

Before testing the prototype sensors in the two experimental setup, the spectral content of their signals were acquired and compared before and after the coating deposition. The FBG signal is a narrow-peaked bell-shaped signal whose peak determines λ_B given in equation 1. It was intended to check that no appreciable distortion of the spectral content had occurred, mainly with respect to its peaked shape that allows measurements with automatic detection of λ_B (Fig. 2). In fact, coatings can introduce anisotropic radial compression that could result in spectral broadening with top flattening. The evaluation of the Full Width at Half Maximum (FWHM) for each functionalized-FBG showed FWHM of about 0.3-0.4 nm before the polymer deposition, while all FWHM increase up to about 0.5-0.6 nm for all coatings after deposition. Moreover, a blue shift of the functionalised FBG spectra was observed, that is caused by an axial strain of the FBG during the drying process of the polymer.

A. Test in controlled RH enclosure

The test was intended to determine the sensitivity of the prototype sensors. This involved determining $\Delta\lambda_B{}^{RH}$ with ΔRH. The test was undertaken using the saturated salt solution technique (which can provide a known and constant RH value), with the sensor prototypes being placed in a sealed enclosure, in which three different saturated salt solutions were sequentially introduced, to provide a series of known relative humidity levels. In particular the salt solutions are: $CaCl_2 \cdot 6H_2O$, RH = 29%; $Ca(NO_3)_2 \cdot 6H_2O$, RH = 51%; KCl, RH = 84%.

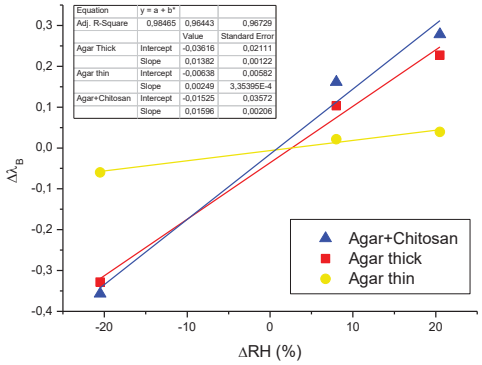

Fig. 3. Plot of $\Delta\lambda_B^{RH}$ value for the three sensors vs the ΔRH value. In the top legend the results of linear fit.

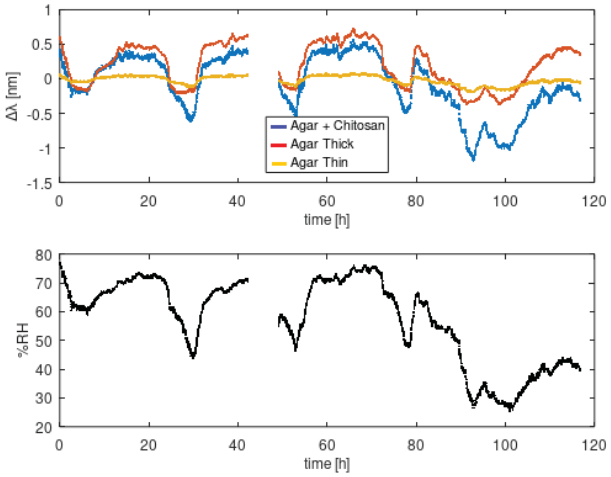

Fig. 4. Five days time trend of the $\Delta\lambda_B^{RH}$ value for the three sensors (top) and of RH value measured by the reference sensor (bottom).

The RH inside the enclosure was monitored by using a reference capacitive humidity sensor.

In Fig. 3 the $\Delta\lambda_B^{RH}$ value measured from the sensor prototypes are plotted *vs* the ΔRH value measured by the reference capacitive humidity sensor.

Results show that the sensor with the Agar+Chitosan coating shows the highest sensitivity, while for the sensors with pure Agar coating, sensitivity greatly increases with thickness of the coating.

A linear fit of the results was done with the following results: 0.01382 sensitivity (0.00122 rms) for "Agar thick"; 0.00249 sensitivity (0.00033 rms) for "Agar thin"; 0.01596 sensitivity (0.00206 rms) for "Agar+Chitosan". Despite a linear fit was done to have a merit figure for comparing sensitivities, a true linear relationship seems no to hold, since all sensor prototypes show a similar slope variation tendency in the plot, which suggests a lowering of sensitivity at higher RH values, which can be due to -somehow expected- saturation mechanism.

B. Test in open air

Since the prototype sensors were produced aiming at developing a reliable RH sensor, they were tested in representative condition on stone walls in open air. For reference, the environment RH was monitored by using a capacitive humidity sensor. The test lasted 13 days, with some short interruptions. Data were recorded at the frequency of 1/60Hz.

Fig. 4 shows the time trend of $\Delta\lambda_B^{RH}$ value measured from the sensor prototypes together with the RH value measured by the reference capacitive humidity sensor. It was reported the time history from five days, which is fully representative of the data from the 13 days long test. The variation of RH according to the circadian cycle is evident in the time history. As expected from the results shown in Fig. 3, the prototype sensors "Agar thick" and "Agar+chitosan" have similar sensitivity, whereas the prototype sensor "Agar thin" has much a lower sensitivity. As a merit figure to compare the three prototype sensors, correlation of their signal with measurement from the RH capacitive humidity sensor was calculated with the following results: 0.93 for "Agar+chitosan"; 0.70 for "Agar thick"; 0.89 for "Agar thin". Fig. 5 shows an expanded view of a short time history that can provide some understanding about the different results for correlation. At the large RH variations occurring from time 0h to 6h, the sensor "Agar+chitosan" nicely follows the variations, while "Agar thick" does not properly follow the negative variation, which could be due to either some saturation effect of to a slow time response. Similar behaviour is showed by the sensor "Agar+chitosan" at the large RH variation occurring from time 22h to 28h, while the deep negative variation of RH occurring at time 22h is nicely followed by the sensor "Agar thick", but it then shows to be either late or with some saturation effect. In both cases, the amplitude of the response for "Agar thin" is actually too low for such comments.

As a general result, it can be inferred that the better features of the coating made with the Chitosan/Agar mixture comes from a mixing of the specific feature of the two products. Chitosan has not only a large swelling capability but also structural capability that regulates the moisture adsorption preventing the swelling to occur too violently and easily saturate; on the other hand, it has strong filming attitude that prevent it to form a regular coating around the fibre. Agar has good swelling capability but its absorption occurs so easily that it soon saturates; on the other hand, it has a good adherence to the fibre (silica) and easily forms a regular coating around the fibre. Since Chitosan is a good interacting polymer having amine groups, it can combine or interact with the hydroxyl group of the Agarose in the Agar material forming a blend material with combined advantages

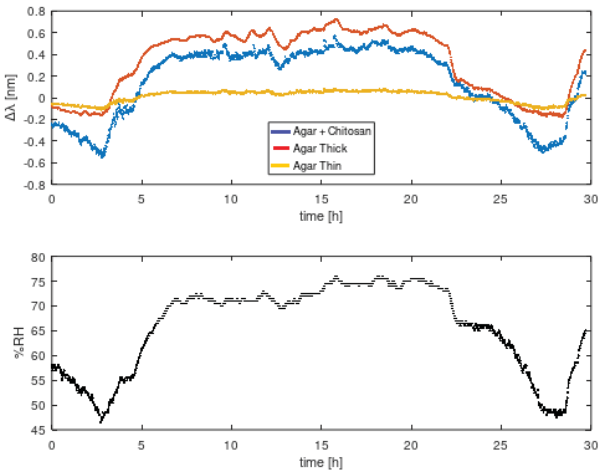

Fig. 5. Top: $\Delta\lambda_B^{RH}$ value for the three sensors for a period of 30 hours, bottom: RH value measured by the reference sensor for the same period.

suitable for different applications. In the Agar/Chitosan mixture the features of the two products evidently find a correct mixing thus becoming a good candidate for FBG-based RH sensors.

D. CONCLUSIONS

In this work, use of Agar/Chitosan mixture resulted as the right choice for the production of RH FBG-based sensors of very low visibility and invasiveness. The small dimension of the sensing part (1x1x20 mm) and cable (transparent un-jacketted optical fibre, 0.25mm in diameter) makes that sensor well suited to monitor the RH content on the surface of artworks displayed to the public, thus providing protection against deterioration due to moisture adsorption. The prototype sensor was tested in the long term in open air, providing good resolution and repeatability, thus allowing proposing it for outdoor applications too, as for instance imbibition monitoring of stone statues, wooden structures and wall stone. Future extensive work for testing mixtures with different percentage of agar and chitosan is planned, mostly with the aim to improve the monitoring features of the sensor with respect to long term stability and measurement error.

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