Preliminary assessment on the detection of putrescine using long period fiber gratings coated with titanium dioxide and poly(ethylene-co-vinyl acetate)

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ABSTRACT

Biogenic amines, such as putrescine are potential indicators of food storage condition and deterioration. The real time measurement of their concentration in food may become an important method of food control. It was found that putrescine diffuses through a thin layer made from a solution of Poly(ethylene-co-vinyl acetate) (PEVA) and maleic anhydride. Poly(ethylene-co-vinyl acetate) is a common non-chlorinated vinyl capable to adsorb specific analytes as putrescine which upon diffusion, reversibly binds to the maleic anhydride causing the polymer swelling resulting in spectral changes from the optical point of view. Long Period Fiber Gratings coated with 30 nm titanium dioxide, a high refractive index material used to increase the intrinsic sensitivity to the external refractive index, were overcoated with a thin layer of maleic anhydride doped Poly(ethylene-co-vinyl acetate). When exposed to solutions containing small concentrations of putrescine the resonant band corresponding to the LP\textsubscript{1,6} cladding mode was found to move to shorter wavelengths. The observed blue shift corresponds to the increasing concentration of putrescine in the fiber sensor structure. Further work is being carried out to improve the sensitivity and the limit of detection of the sensing system as well as to increase range of operation, which is presently limited to 0.3 to 0.5 M.

Keywords: biogenic amines, putrescine detection optical fiber sensors, long period fiber gratings, Poly(ethylene-co-vinyl acetate), maleic anhydride

1. INTRODUCTION

Deterioration of fresh food is a multifaceted process characterized by changes in its quality, flavor, smell and appearance that makes it unacceptable to be consumed. The most common source of food deterioration is the microbial activity, which led to a visible growth of slime, colonies and texture changes, due to polymer degradation, and development of off-odors and off-flavors [1].

Because of microbial activity in fresh meat and fish products, cheeses and fermented vegetables, among others, high concentrations of biogenic amines develop, which are nitrogenous organic polar or semi-polar bases of low molecular weight. They can be classified as aliphatic (cadaverine, putrescine, spermine and spermidine), aromatic (phenylethylamine, tyramine), or heterocyclic (pyrrolidine, histamine) [2], and according to their number of amine

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groups they can be divided into monoamines (tyramine and phenylethylamine) and diamines (histamine, putrescine and cadaverine) [3].

Biogenic amines are formed mainly by microbial decarboxylation of amino acids and by amination and transamination of aldehydes and ketones. The presence of biogenic amines is an indication of food spoilage [4] and, therefore, the measurement of their concentration may become an important method of food control [5]. In this work Long period fiber gratings (LPFG) coated with titanium dioxide (TiO$_2$), and overcoated with a thin layer of Poly(ethylene-co-vinyl acetate) (PEVA) doped with maleic anhydride (MA) were used to monitor the concentration of putrescine by following the wavelength position of attenuation band corresponding to the LP$_{1,6}$ cladding mode.

2. MATERIALS AND METHODS

A solution of 59 wt% PEVA (Sigma-Aldrich, Germany) and 41 wt% of MA (Sigma-Aldrich, Germany) was prepared for a total of 0.75 g in 15 mL of chlorobenzene (Sigma-Aldrich, Germany). The solution was heated on an hot plate for 1 hour at 80ºC following a procedure identical to the reported in [6].

Long period fiber gratings fabricated in single mode fiber (SMF28e, Corning, Inc.), were produced using the induced electric arc technique as reported in [7, 8]. The period of the LPFG was 389 μm, a value chosen in order to obtain the asymmetric 6$^{th}$ order cladding mode resonance (LP$_{1,6}$) around 1475 nm. A visibility value of ~25 dB for the LP$_{1,6}$ attenuation band of the bare LPFG was reached with a sensor length of 40 ± 5 mm. Titanium oxide thin films 30 nm thick were produced around the grating region by thermal evaporation of pure Ti metal (Goodfellow, U.K.) using an electron beam evaporator (Auto 306 from Edwards Ltd, U. K.) in an oxygen atmosphere. The deposition chamber was fitted with a homemade rotary system in order to produce homogeneous coatings around the fibers [9].

In order to produce thin film of PEVA doped with MA around the LPFG, the Teflon holder illustrated in Fig. 1, was fill with the PEVA doped with MA solution and the fiber was kept submerged for 2 minutes, after which it was left to dry at room temperature.

A set of refractive indices calibrated solutions were used in the characterization of the coated LPFG.

Sample solutions of putrescine (PUT), NH$_2$(CH$_2$)$_4$NH$_2$ (1,4-diaminobutane) with concentration from 0.3 to 4.0 M were prepared using pure water. The refractive index of the sample solutions was measured at 589.3 nm with an Abbe refractometer (Atago, DR-A1) using the sodium line.

![Figure 1. Set-up used to coat the Long period fiber grating with Poly(ethylene-co-vinyl acetate) doped with maleic anhydride.](image-url)
The wavelength sensitivity of the attenuation band of the LPFGs coated with TiO$_2$, with and without a layer of PEVA doped with MA, was measured using the set-up represented in Fig. 2. A microfluidic chamber was built in such a way that the liquid samples enter the channel and pass through the sensitive region of the LPFGs and leaves the chamber in the opposite side, while the sensor is kept at constant strain. A broad band light source (BBS) is coupled to one end of the LPFG and the other end is connected to an optical spectrum analyzer (OSA).

Figure 2. Illustration of the set-up used in the optical characterization of the coated long period fiber grating.

BBS – broad band source; OSA – optical spectrum analyzer.

3. EXPERIMENTAL RESULTS

A SEM picture of the LPFG coated with a layer of PEVA doped with MA is shown in Fig. 3 from which a value of 350±50 nm was estimated for the thickness of the polymer overlayer. A very smooth surface can be obtained using our methodology.

The wavelength shift of a TiO$_2$ coated LPFG was measured using both calibrated refractive index solutions and the PUT sample solutions. The corresponding normalized wavelength shift is presented in Fig. 4. As can be observed the PUT solution has no effect on the TiO$_2$ coating, other than the one caused by the variation of the refractive index. The refractive index of the PUT sample solutions was measured and the results presented in Table 1.

After coating the TiO$_2$ coated LPFGs with a 350 nm thick layer of PEVA doped with MA the wavelength sensitivity of the attenuation band was again measured with calibrated refractive index solutions and with 0.3, 0.4 and 0.5 M PUT sample solutions. A very different behavior can now be observed. Figure 5 (a) represents the normalized wavelength shift due to calibrated refractive index liquids and due to the PUT sample solutions. For the same refractive index of the surrounding medium (either refractive index liquid or PUT solution) there is a different wavelength shift behavior. It can be seen that the PUT solutions causes an augmented shift in the attenuation band. To separate the refractive index effect of the PUT solutions, the normalized wavelength shift due to the refractive index was subtracted and the results presented in Fig. 5 (b).
Figure 3. SEM picture of a long period fiber grating coated with Poly(ethylene-co-vinyl acetate) doped with maleic anhydride: (a) side fiber roughness; (b) top view of a cleaved fiber end and (c) close of the thin layer of Poly(ethylene-co-vinyl acetate) doped with maleic anhydride.

Figure 4. Normalized wavelength shift of a TiO$_2$ coated long period fiber grating for calibrated refractive index liquids and putrescine sample solutions.

Table 1. Refractive index of the putrescine sample solutions (M – molar)

<table>
<thead>
<tr>
<th>Putrescine concentration (M)</th>
<th>Refractive index</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (pure water)</td>
<td>1.3328</td>
</tr>
<tr>
<td>0.3</td>
<td>1.3370</td>
</tr>
<tr>
<td>0.4</td>
<td>1.3380</td>
</tr>
<tr>
<td>0.5</td>
<td>1.3396</td>
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<tr>
<td>1.0</td>
<td>1.3465</td>
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<tr>
<td>1.3</td>
<td>1.3507</td>
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<td>2.0</td>
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<td>3.2</td>
<td>1.3755</td>
</tr>
<tr>
<td>4.0</td>
<td>1.3863</td>
</tr>
</tbody>
</table>
It was demonstrated for the possibility of monitoring the concentration of putrescine using a long period fiber grating coated with titanium dioxide and overcoated with a subsequent layer of Poly(ethylene-co-vinyl acetate) doped with maleic anhydride. Further work is being carried out to improve the sensitivity and the limit of detection of the sensing system as well as to increase range of operation, which is presently limited to 0.3 to 0.5 M.

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