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Novel optical chemical sensor based on Molecularly Imprinted Polymer inside a trench micro-machined in double Plastic Optical Fiber

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Abstract

For the detection of chemical agents in different environments, the combination of plastic optical fibers (POFs) and molecularly imprinted polymer (MIP) layers has been tested as a way to obtain a low cost, highly selective and sensitive surface plasmon resonance (SPR) chemical sensor. A novel type of optical chemical sensor based on POF-MIP has been designed and fabricated, and in this work it has been applied for the selective detection of dibenzyl disulfide (DBDS) in transformer oil. This analyte is important in the control of transformer oil, since it is responsible for the corrosive properties of the oil. The new optical sensor platform is based on two plastic optical fibers coupled through a polymer molecularly imprinted for DBDS. The new sensor has been found to be useful for the determination of DBDS in transformer oil.

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Keywords: Plastic optical fiber; Molecularly imprinted polymer; Dibenzyl disulfide (DBDS); Optical chemical sensors; Transformer oil

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1. Introduction

Biosensors and chemical sensors in optical fibers have been shown to be suitable for application in numerous important fields, when fast, portable, low cost and rugged devices are needed for detection and identification [1-4]. In general, the optical fiber is either a glass one or a plastic one (POF). Recently, the Authors reported surface plasmon resonance sensors, based on a D-shaped POF and on a molecularly imprinted polymer layer as an artificial receptor, for rapid and selective detection of different analytes [5-7]. The very interesting characteristics of the MIP sensors have been recently reviewed [8]. MIPs are synthetical receptors obtained by the molecular imprinting methods, presenting a number of favorable aspects for sensing in comparison to bio receptors such as, for example, antibodies, including a better stability out of the native environment, the reproducibility and the low cost. They are porous solids containing specific sites interacting with the molecule of interest according to a “key and lock” model. For this reason, a distinctive feature of MIPs, in comparison with other receptors, is the selectivity [8].

In this work, a novel optical sensor platform, with a specific MIP receptor for the selective detection of dibenzyl disulfide (DBDS) in transformer oil, is presented. Dibenzyl disulfide (DBDS) is an important analyte in the control of transformer oil since it is commonly added to the oil as an antioxidant. At the same time it is responsible for the corrosive properties of the oil, even at relatively low concentration. The determination of its level in transformer oils is of paramount importance for diagnostic purposes to monitor the “health status” of the transformer [9,10]. To this aim, analytical methods based on chemo-sensors appear to be very helpful for making in situ or even on line controls. The power transformer is a key component of the Electric Transmission and Distribution system. Its integrity assessment is very complex but essential to avoid irreversible damages with consequent heavy impacts on maintenance costs and on Transmission and Distribution (T&D) network services, due to outages. Among causes which can lead to a transformer failure (i.e., hot spots, partial discharges), the accelerated degradation of its solid insulating system, i.e., oil impregnated cellulosic insulation materials, strongly depends on the operating condition of the transformer. In this field, the use of optical chemical sensors for on-line measurements is very important, because they are not subject to noise and to electromagnetic interferences. Authors will present an optical chemical sensor simple to fabricate, uses a low cost experimental setup, and shows a resolution suitable for the chemical applications in this field. The sensor has been obtained with the following procedure: the two POFs without jacket were firstly embedded in a resin block, parallel each other and in contact. Successively, a trench was drilled between the two fibers by a PC controlled micro-milling machine. Finally, the prepolymeric MIP solution was deposited in the trench by drop coating, and the polymerization was carried out (see Fig. 1).

2. Materials and methods

2.1. Optical chemical sensor

The fabricated optical platform was realized in three steps: in the first one, two POFs were embedded in a resin block, parallel and in tight contact; in the second one, a trench was fabricated between the two fibers by a computer numerical control (CNC) micro-milling machine; finally, the trench has been filled with a MIP receptor. The proposed sensor relies on two "segmented waveguides" sensors coupled to each other [11-14].

The sample consisted in two plastic optical fibers with a PMMA core of 980 μm and a fluorinated polymer cladding of 20μm, without jacket, embedded in a resin block. The refractive index, in the visible range of interest, is about 1.49 for PMMA, 1.41 for fluorinated polymer. A trench about 6mm long, 1mm wide and 600μm deep was fabricated between the two fibers with a CNC machine by using 1mm diameter end-mill. A digital camera has been used to align the tip of the milling tool to the sample in order to engrave the trench parallel to the fibers axis and equally wide across the fibers. The engraving parameters were optimized to reduce the surface roughness of the trench walls. The fabricated trench results in a sensing region of about 6 mm in length. Then the trench has been filled with a prepolymeric MIP solution, by drop coating (30 μl), and the polymerization was carried out. The MIP's refractive index is about 1.42 in the visible range of interest. Figure 1 shows the optical sensor platform with the MIP receptor. The prepolymeric mixture for MIP was prepared according to a well-established procedure [5-8]. It is composed of DBDS as template (20 mg), MAA as functional monomer (30 μl), DVB as cross-linker (665 μl) and AIBN as the radicalic initiator (15 mg). The reagents were at molar ratio 1 (DBDS): 4 (MAA): 40 (DVB). The mixture was uniformly dispersed by sonication (visually homogeneous solution) and de-aerated with nitrogen for 10 min. It was polymerized at 70°C in an oven for about 16 h. The template molecule was extracted by washing with ethanol 10 times, leaving the imprinted sites free for successive template rebinding.

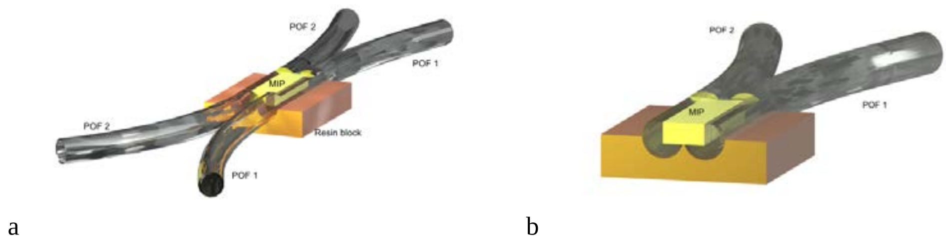

Fig. 1. (a) Chemical sensor based on two POFs and MIP receptor. (b) Cross section view of the sensing region

2.2. Experimental setup

Figure 2 shows the experimental setup. It is composed by an LED, whose wavelength is 730 nm, as light source, a splitter-POF-MIP sensor (previously described), two photodiodes and an oscilloscope for the signal (light intensity, I) acquisition connected to a PC.
The LED is connected at the input POF and the light intensity at the output (I_1) is normalized to the light intensity coming out from the other POF (I_2). The signal processing to obtain the normalized output (I_1 /I_2) has been carried out by Matlab software. When the refractive index of the MIP receptor increases (because the receptor is combined with the analyte) the light intensity at the output of the second POF (I_2) increases whereas in the other POF (I_1) it decreases. This approach permits to increase the sensitivity and to eliminate the error introduced by the intensity fluctuations of the light source itself and the possible instability of the source to fiber coupling.

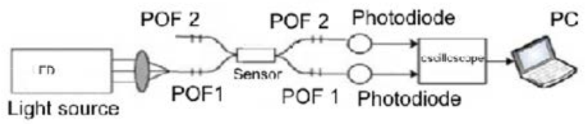

Fig. 2. Experimental setup

3. Experimental results

In Figure 3, the relative output (I_1 /I_2) is plotted versus the log of concentration of DBDS (ppm), together with the fitting of the data by Hill equation. It is clearly seen that the relative output is decreased when the DBDS concentration increases, indicating that DBDS effectively combines with MIP from the oil matrix here considered. The proposed sensor could be viewed as two segmented waveguides sensors coupled to each other, with the milled trench realizing the segmentation of both cores. The lower detection limit (LOD) is about 0.05 ppm ($5 \cdot 10^{-7}$ M) and the saturation is reached at a concentration of about 0.5 ppm ($5 \cdot 10^{-6}$ M). These parameters were calculated by Hill equation. It has been shown that this new sensor based on Splitter-POF-MIP sensor platform can be used to monitor the refractive index variation of an MIP receptor layer as a function of the amount of absorbed analyte. These experimental results are comparable to those obtained with an SPR-POF-MIP sensor [15].

4. Conclusions

The new optical chemical sensor has been found to be useful for the determination of DBDS in transformer oil (the LOD is about 0.05 ppm and the saturation is about 0.5 ppm). Experimental results are comparable to those obtained with an SPR-POF-MIP sensor, with some benefits in terms of easy fabrication process.

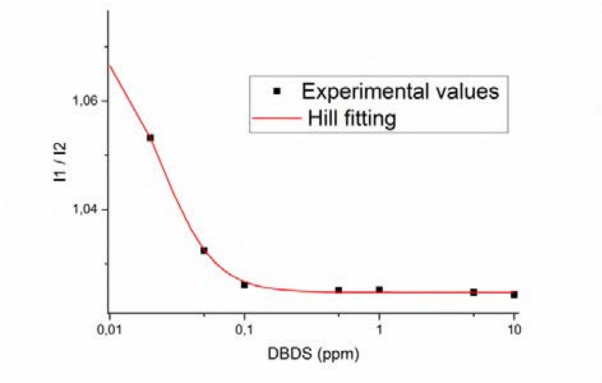

Fig. 3. Relative output versus log of concentration of DBDS [ppm] and the fitting of the data by Hill equation.

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