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Combined Molecularly Imprinted Polymer and Surface Plasmon Resonance transduction in Plastic Optical Fiber for monitoring oil-filled power transformers

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Abstract

In this work the feasibility of an optical method for an early and high sensitivity detection of chemical agents in oil-filled power transformer is reported. It concerns the assessment of accelerated ageing of transformer insulating systems, primarily constituted of oil, paper and cellulose through an online detection of cellulose degradation by-products. The proposed optical device exploits the Surface Plasmon Resonance (SPR) excitation in a plastic optical fiber (POF) platform. High selectivity is obtained by a joint detection with a Molecularly Imprinted Polymer (MIP) layer, very specific for one of the most significant indicators of the transformer possible failure, furfural, in contact with the SPR active surface. Preliminary results of tests, carried out on calibrated furfural concentration diluted in transformer oil, confirm the feasibility of the proposed optical approach.

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Keywords: Surface Plasmon Resonance (SPR); Plastic Optical Fibers (POF); Oil Filled Power Transformer; Furfural

1. Introduction

The power transformer is a key component of the Transmission and Distribution (T&D) network; its failures are costly either in terms of maintenance costs and of outages involving the T&D network [1]. The availability of reliable and potentially low-cost sensors to be used as diagnostic tools for detecting aging and failures of this component is of significant interest to improve Asset management of the electric power system.

In the last few years, some low cost tools were made commercially available for on line Dissolved Gas Analysis (DGA) in transformers [1]; instead, no low cost devices or sensors are available yet for an on-line monitoring of

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accelerated aging process of the paper insulation, probably due to stringent on-line application requirements: high sensitivity and reliability in oil detection, high immunity to electromagnetic and environmental interferences.

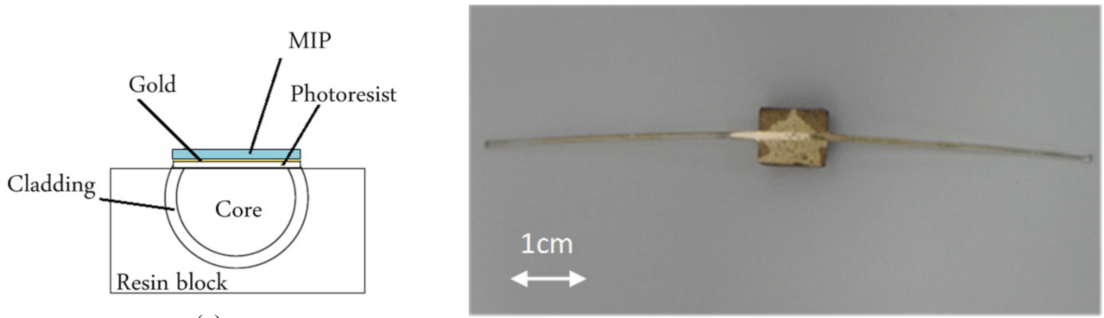
In this work a new optical approach is proposed for an early and high sensitivity detection of chemical agents correlated with paper aging in oil-filled power transformers, such as furfural (2-FAL) and its derivatives [2]. It is based on Surface Plasmon Resonance (SPR) excitation in a plastic optical fiber (POF) platform. The SPR excitation in optical fibers is widely used as a detection principle for many sensors operating in different application fields, such as bio and chemical sensing [3,4,5]. In general, the optical fiber employed is either a glass one or a plastic one. For low-cost SPR sensing systems, POFs are especially advantageous due to their excellent flexibility, easy manipulation, great numerical aperture, large diameter, and the fact that plastic is able to withstand smaller bend radii than glass. Furthermore, the advantage of using POFs is that the main features of POFs, that have increased their popularity and competitiveness for telecommunications, are exactly those that are important for optical sensors based on glass optical fibers, with the addition of simpler manufacturing and handling procedures [6,7].

The optical device reported herein exploits a Molecularly Imprinted Polymer, MIP, layer as an artificial receptor in connection with SPR transduction in POF for a selective detection of furfural in oil-filled power transformer.

1.1. Sensor and optical layout

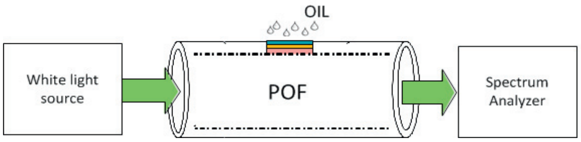
The SPR active surface of the POF platform was obtained by removal of the plastic cladding along half of the fibre circumference and by sputtering a thin gold film on a buffer of Microposit S1813 photoresist, previously spin coated on the exposed core of the plastic fibre [7]. The gold surface was washed with ethanol and then dried in a thermostatic oven at 60°C prior to deposition of the sensing layer: a Molecularly Imprinted Polymer (MIP) layer, very specific for one of the most significant indicators of the transformer possible failure, furfural (furan-2-carbaldehyde), put in contact with the SPR active surface. A schematic view of the active surface cross section is shown in Figure 1a. The prepolymeric mixture for MIP was prepared according to the procedure reported in [7,8,9] by dissolving in divinylbenzene (DVB) (the cross-linker) the functional monomer (that is, methacrylic acid, MAA), and the template, furfural (2-FAL). The reagents were at molar ratio 1 (2-FAL) : 4 (MAA) : 40 (DVB). For example, a typical prepolymer mixture for the MIP specific for furfural is composed of 1.4 ml of DVB, 80 μl of MAA and 20 μl of FUR. Notice that DVB is at the same time the cross linker and the solvent. The mixture was uniformly dispersed by sonication (visually homogeneous solution) and de-aerated with nitrogen for 10 min. Then the radicalic initiator AIBN (16 mg in the example described) was added to the mixture. Fifty microliters of the prepolymeric mixture were dropped over the sensing region of the optical fibre and spun for 2 minutes.

An optimised length of 10 mm of the combined MIP and SPR active region for the POF sensor was typically used, as shown in Figure 1b.

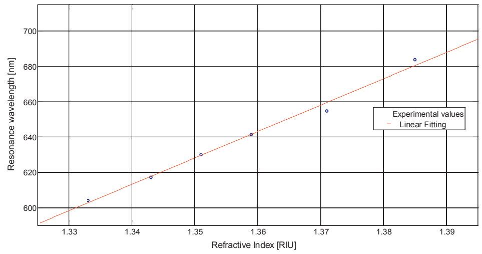


(a) (b)

Fig. 1. (a) cross section and (b) length of the active surface of the POF sensor



(a)



(b)

Fig. 2. (a) Optical layout;(b) linearity of the SPR sensor without MIP layer as a function of the refractive index change

The optical layout adopted for the interrogation of the sensing region is shown in Figure 2a; it is based on the use of a halogen lamp, whose emission range is from 360 nm to 1700 nm, and of a compact spectrometer directly interfaced to the PC trough USB connection. The transmitted spectra were recorded for wavelengths ranging from 200 nm to 850 nm.

3. Results

The behavior of the SPR active surface was previously tested without the MIP sensing layer. Figure 2b shows the linear response of the SPR active surface, before spin coating the MIP layer; the SPR resonance wavelength was recorded for solutions with different refractive indexes (from 1.333 up to 1.385) in contact with the sensing layer. It evidences a sensitivity equal to $1.5 \cdot 10^3$ [nm/RIU], adequate for biochemical applications.

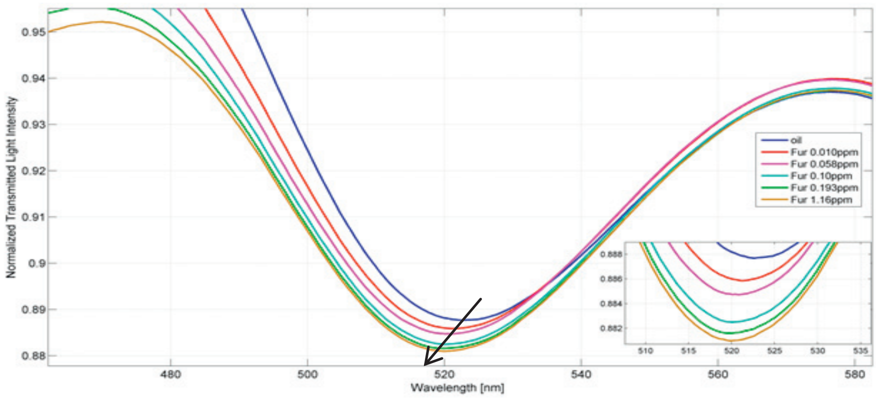


Fig. 3. Results; Normalized SPR spectra acquired by the combined MIP- POF sensors for different FUR concentrations C [ppm].

Furthermore, the feasibility of the optical detection of furfural in oil through the combination of this POF platform with the MIP layer was experimentally verified. A small amount of oil, about 50 µl, was dropped over the sensing zone, and the spectrum recorded after only a few minutes. Figure 3 reports some SPR transmission spectra, obtained at different calibrated concentrations of furfural (2-FAL) in transformer oil samples. The acquired spectra were normalized to the reference spectrum, recorded in air before spin coating the MIP layer, where no resonance takes place. It is clearly seen, from the inset in the above figure, that the resonance wavelength is blue shifted at increasing concentration of furfural in the oil phase, indicating that furfural effectively combines with MIP even from oil.

A linear behavior up to 0.1 ppm emerges from the experimental results. At higher concentrations the sensitivity decreases, probably due to the saturation of the specific imprinted sites in MIP.

4. Conclusions

In this work an optical device based on an SPR excitation in a POF platform has been described for the on-line monitoring of furfural (2-FAL) in power transformers; the regular detection of this chemical agent in oil allows an evaluation of the aging rate of transformer insulating paper. A combined Molecularly Imprinted Polymer (MIP) layer, specific for this analyte, and SPR transduction has been proposed to overcome the problem of a direct SPR detection of 2-FAL in oil as surrounding medium. Evidence of the feasibility of this approach emerged from the preliminary results of tests carried out on samples of insulating oil samples with different 2-FAL concentrations. Both the sensitivity and the detection limit (0.01ppm) of the sensor are suitable for the detection of 2-FAL in transformer oil, confirming the potential industrial applications of SPR detection based POF sensors.

Acknowledgements

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