Polymer optical fiber grating as water activity sensor

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ABSTRACT

Controlling the water content within a product has long been required in the chemical processing, agriculture, food storage, paper manufacturing, semiconductor, pharmaceutical and fuel industries. The limitations of water content measurement as an indicator of safety and quality are attributed to differences in the strength with which water associates with other components in the product. Water activity indicates how tightly water is "bound," structurally or chemically, in products. Water absorption introduces changes in the volume and refractive index of poly(methyl methacrylate) PMMA. Therefore for a grating made in PMMA based optical fiber, its wavelength is an indicator of water absorption and PMMA thus can be used as a water activity sensor. In this work we have investigated the performance of a PMMA based optical fiber grating as a water activity sensor in sugar solution, saline solution and Jet A-1 aviation fuel. Samples of sugar solution with sugar concentration from 0 to 8%, saline solution with concentration from 0 to 22%, and dried (10ppm), ambient (39ppm) and wet (68ppm) aviation fuels were used in experiments. The corresponding water activities are measured as 1.0 to 0.99 for sugar solution, 1.0 to 0.86 for saline solution, and 0.15, 0.57 and 1.0 for the aviation fuel samples. The water content in the measured samples ranges from 100% (pure water) to 10 ppm (dried aviation fuel). The PMMA based optical fiber grating exhibits good sensitivity and consistent response, and Bragg wavelength shifts as large as 3.4 nm when the sensor is transferred from dry fuel to wet fuel.

Keywords: Polymer optical fiber, PMMA, fiber Bragg grating, water activity, equilibrium relative humidity

1. INTRODUCTION

Recent technological advances have helped promote polymer optical fibers (POFs) as a lower cost alternative to silica optical fibers, though at a penalty of a much higher transmission loss. As sensors, POFs have additional advantages thanks to the physical and chemical properties of polymeric materials that are rather different to silica. Bragg gratings have been successfully inscribed into poly(methyl methacrylate) (PMMA) based polymer optical fiber in both step-index and microstructured geometries. The interesting features of polymer optical fiber Bragg grating (POFBG) include the negative refractive index change against temperature rise, and in the case of PMMA based fibers an affinity for water, which leads to a swelling of the fiber and an increase of refractive index. The former feature offers a well-conditioned performance for overcoming the cross sensitivity issues existing with silica fiber based FBGs[1] while the water affinity, which contributes to an increase in the Bragg wavelength of a FBG written in the fiber, is a potentially very useful property.

Water is recognized as being very important to the stability of many products in chemical processing, agriculture, food storage, paper manufacturing, as well as the semiconductor and pharmaceutical industries. Controlling the water within a product has long been used by man for preservation. Traditionally, discussions about water in products focus on moisture or water content, which is a quantitative or volumetric analysis that determines the total amount of water present. The water content of a product is a familiar concept to most people. In industries people measure the water content by using oven drying, infrared, NMR and Raman spectroscopy, or Karl Fisher titration [2]. However, water content alone is not a reliable predictor of microbial responses and chemical reactions in materials. The limitations of water content measurement as an indicator of safety and quality are attributed to differences in the intensity with which water associates with other components in the product. Water associated with a substance is classified as either free or bound. Bound water is directly or tightly associated with a material and is not readily available for chemical interaction with other species. Thus, the amount of free water rather than the amount of total water is critical to the chemical and physical stability of a drug substance that is moisture sensitive.

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On the other hand aviation fuel has the ability to hold a certain amount of dissolved water. The maximum amount of water that a given fuel can contain is referred to as its saturation point. This becomes critical when the water content nears the fuel's saturation point, creating a risk of actually exceeding the saturation point and forming free water – a destructive contaminant to almost all fuel applications. In an aviation fuel system (FS), water, in addition to not burning in an engine, will freeze at the low temperatures encountered in high altitude flights. The resulting ice may plug fuel filters and otherwise impede fuel flow. In addition to water already present in fuel, humid air in hazardous weather is also transformed to water in the fuel tanks by absorption leading to abnormal presence of water in the FS with in addition increased risk for lightning damage (due to the water conductivity). Water in the fuel also may facilitate the corrosion of some metals and the growth of microorganisms. The solids formed by microbial growth are very effective at plugging fuel filters. Some microorganisms also generate acidic by-products that can accelerate metal corrosion. [3] The best approach to microbial contamination is prevention and the most important preventive step is keeping the amount of free water in fuel storage tanks and aircraft fuel tanks as low as possible. A typical water-saturated fuel contains between 40 and 80 ppm dissolved water at 21°C (70°F). If the temperature of the fuel increases, it can dissolve more water. Conversely, if the temperature of water-saturated fuel decreases, some of the water dissolved in the fuel will separate as free water. Compared to the amount of fuel the saturated water content is very small either in volume or in mass. This makes the measurement task difficult. The traditional unit of measurement for quantifying water content in fuel has been ppm (parts per million). It is an absolute moisture parameter that describes the volume or mass ratio of water to fuel. By actively measuring ppm levels of water in fuel, the absolute amount of water can be determined. However, a ppm measurement has one major limitation – it does not account for any variation in a fuel's saturation point. In other words, in a dynamic fuel system with a fluctuating saturation point, a ppm measurement would provide no indication of how close the moisture level is to the fuel's saturation point.

Water absorption in PMMA is a function of the equilibrium relative humidity (ERH). Water absorption introduces changes in the volume and refractive index of PMMA. Therefore for a grating made in PMMA based optical fiber, its wavelength is an indicator of water absorption and PMMA thus can be used for water activity sensing as water activity is defined by ERH. In this work we have investigated the performance of a PMMA based optical fiber grating as a water activity senor in sugar solution, saline solution and Jet A-1 aviation fuel. Samples of sugar solution with sugar concentration from 0 to 8%, saline solution with concentration from 0 to 22%, and dried (10ppm), ambient (39ppm) and wet (68ppm) aviation fuels were used in experiments. The PMMA based optical fiber grating exhibits good sensitivity and consistent response. This particular feature of water activity measurement allows PMMA based optical fiber gratings to detect very tiny amounts of water in some solutions that have a low water saturation limit (such as aviation fuel).

2. PRINCIPLE OF MEASUREMENT OF WATER ACTIVITY

Water activity describes the energy status or escaping tendency of the water in a sample. It indicates how tightly water is "bound," structurally or chemically, in products. Pure water is taken as the reference or standard state from which the energy status of water in a material is measured. At equilibrium, the water activity of a material is equal to the relative humidity (RH) of the atmosphere in which it is stored. If the materials are moved to a higher or lower RH then the water content will increase or decrease, respectively, until equilibrium is reached.

Water activity is defined as [4]

$$a_W = P_S / P_O \tag{1}$$

where P_S is the vapor pressure of water above a sample and P_O that of pure water at the same temperature. Water activity values represent a scale that ranges from 0 (bone dry) to 1.0 (pure water). In a fuel system a_W=0 means dry fuel and a_W=1 water saturated fuel. From its definition water activity is equal to equilibrium relative humidity (ERH).

On the other hand PMMA can absorb a certain amount of water. Water absorption in PMMA, as derived from the multimolecular theory of absorption, can be expressed as [5],

$$s = \frac{s_1 cx}{1-x}\left[\frac{1-(n+1)x^n+nx^{n+1}}{1+(c-1)x-cx^{n+1}}\right] \tag{2}$$

where s is the weight of absorbate per gram of adsorbent, s_1 the weight of absorbate per gram of absorbent when each absorption site is covered by one mole of absorbent, c and n are constants; $x = P_S/P_O$ where P_S is the equilibrium

absorption pressure in the absorbate and P_O the saturation pressure over a free liquid surface of the absorbate. Here the absorbate is water and the absorbent PMMA. Therefore the ratio of these two parameters represents the equilibrium relative humidity. For PMMA (Perspex), w_1 is 6.25, c=1, n=5. According to (2) water absorption in PMMA is a function of ERH and can be calculated.

Water absorption introduces changes in both the volume and refractive index of PMMA. The volumetric change in PMMA can be estimated. Considering a unit volume of an initially dry polymer, of density ρ_0, which takes up s wt% water, the density change of PMMA against water uptake rate can be calculated as [6],

$$\rho = \rho_0 \frac{1+s/100}{1+s\rho_w f/100} \tag{3}$$

where f is the fraction of the water contributing to an increase in the PMMA volume and ρ_w the density of water.
For a PMMA based polymer optical fiber Bragg grating (POFBG), its Bragg wavelength depends on the effective core refractive index n_{eff}, and the grating pitch Λ, both of which can be modulated by the water content in PMMA optical fiber. At a specified temperature the wavelength change of POFBG against relative humidity can be expressed as

$$\lambda_B = 2n_{eff}(a_W)\Lambda(a_W) \tag{4}$$

This indicates that the POFBG can detect the change of water activity when placed in any water solution.

3. EXPERIMENTS AND RESULTS

An experimental arrangement was set up to control the dissolved water content in fuel and investigate the performance of a POFBG for water detection in fuel, as shown in Fig. 1. A Bragg grating with a wavelength of ~1535 nm was fabricated into a 10 cm length of step index few mode POF. It then was attached to a single mode silica fiber down-lead using UV curable glue (Norland 78), as described in [7]. This was illuminated via a fiber optic circulator with light from a broadband light source (Thorlab ASE730) and observed in reflection using an IBSEN I-MON 400 wavelength interrogation system.

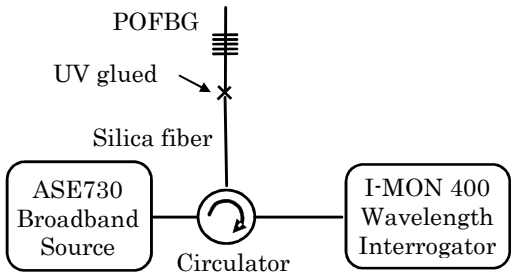

Fig. 1 Experimental arrangement

3.1 Measuring saline and sugar solutions

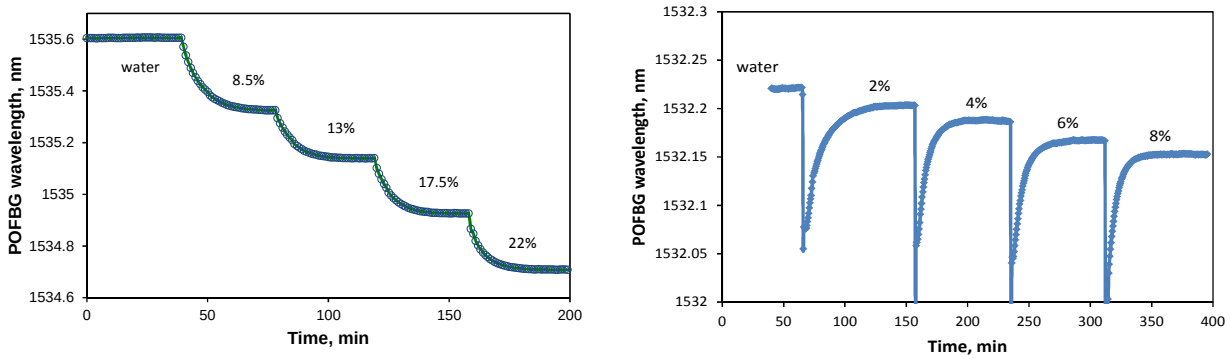

Fig. 2 POFBG wavelength response vs. different concentration. (a) salt solution, (b) sugar solution.

The POFBG was first inserted into a test tube of distilled water to get fully swelled by the water, then pulled out and inserted into the test tubes of saline solution and sugar solution. Four samples of saline solution (7.5%, 13%, 17.5% and 22%) and four samples of sugar solution (2%, 4%, 6% and 8%) were prepared and tested, respectively, in the order of ascending concentrations. The recorded POFBG wavelength variations are shown in Fig. 2.

3.2 Measuring aviation fuel

Aviation fuel has the ability to hold a certain amount of dissolved water. The amount of dissolved water depends on the relative humidity of the air above the fuel, assuming that the fuel is in equilibrium with its environment. Fuel close to a fuel-water or fuel-air interface will reach water equilibrium in a matter of minutes. Therefore the water content in a fuel sample can be varied by exposing fuel to humid air. Different amounts of water in fuel can be conditioned by changing the surrounding relative humidity. In the experiment Jet-A1 aviation fuel was held in a beaker placed in the environmental chamber to be in contact with air that can be set to a chosen temperature and humidity. A POFBG was inserted into the fuel and monitored under different relative humidities.

It takes time for fuel to reach water equilibrium. This equilibrium time closely depends on the volume and the geometry of the container of the fuel. If the volume of fuel is large and the area of the interface between fuel and air is limited it will take a lot longer to reach water equilibrium. In order to accelerate the water equilibration process in the fuel, a magnetic stirrer was used to stir the fuel in the beaker. The wavelength response of POFBG in fuel was monitored while the relative humidity of the chamber was set to different values. Fig. 3 shows a typical response of the POFBG sensor recorded while the humidity was changed in a step of 10% from 40% to 90% and the chamber temperature was kept at 24.5°C.

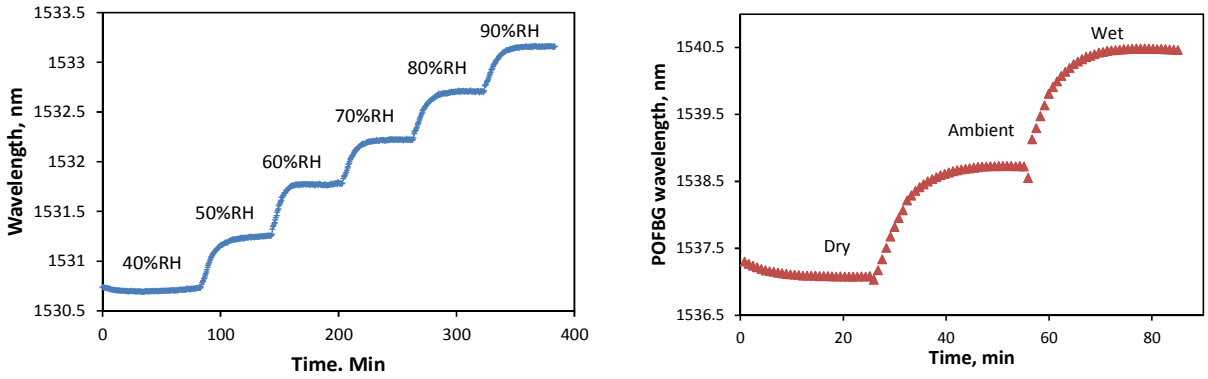

Fig. 3 POFBG wavelength response vs. varying ERH. (a) conditioned in chamber, (b) calibrated by coulometer.

Three samples of fuel were further used to test the POFBG sensor performance. The fuel was dispensed into three small glass vials, each of which contained about 20ml of Jet A-1. Sample 1 was dried, as far as possible, by placing the vial in a desiccator which contained a bed of silica gel. Sample 2 was left open and exposed to ambient air. Sample 3 was exposed to a 100% RH atmosphere by placing the vial in a desiccator that contained a small amount of distilled water, rather than dessicant. On conclusion of the conditioning period, the water content of each sample of fuel was measured using a Karl Fischer (KF) coulometer. The following measurements were recorded: 10 ppm dissolved water in sample 1 (by mass); 39 ppm dissolved water in sample 2; 68 ppm dissolved water in sample 3. These samples were actually processed in the same way as had previously been done in the environmental chamber, but with known water content measured by using the Karl Fischer (KF) coulometer. The POFBG response was recorded and is shown in Fig. 3.

4. DISCUSSIONS

The wavelength changes of the POFBG induced by different solution concentrations are plotted in Fig. 4a. When salt/sugar concentration increases the water concentration decreases. Due to the Osmosis effect the partial water vapor pressure inside the PMMA optical fiber varies with the external water vapor pressure [8]. Therefore the rising salt/sugar concentration (the falling water concentration) gives rise to lowering water pressure inside the PMMA fiber, *i.e.*, to a reduced POFBG wavelength.

The relationship between water content and water activity can only be determined by experiment. The relations of water activity and salt/sugar concentration are plotted in Fig. 4b, which are retrieved from [9][10].By comparing Fig. 4a and 4b one can notice that POFBG wavelength change almost mirrors the water activity of the solution. In fact POFBG wavelength increases with the increment of water activity, but in a slightly nonlinear fashion, which is due to the nonlinear relation between PMMA swelling and water content inside PMMA optical fiber [11].

Traditionally people control the water within a product by some method of drying or by chemically/structurally binding (salting or sugaring) for preservation. Obviously salting has a larger a_w lowering factor than sugaring does and therefore is more efficient for food preservation. This can also be seen from the results that POFBG shows a much larger wavelength change over salt concentration than sugar concentration.

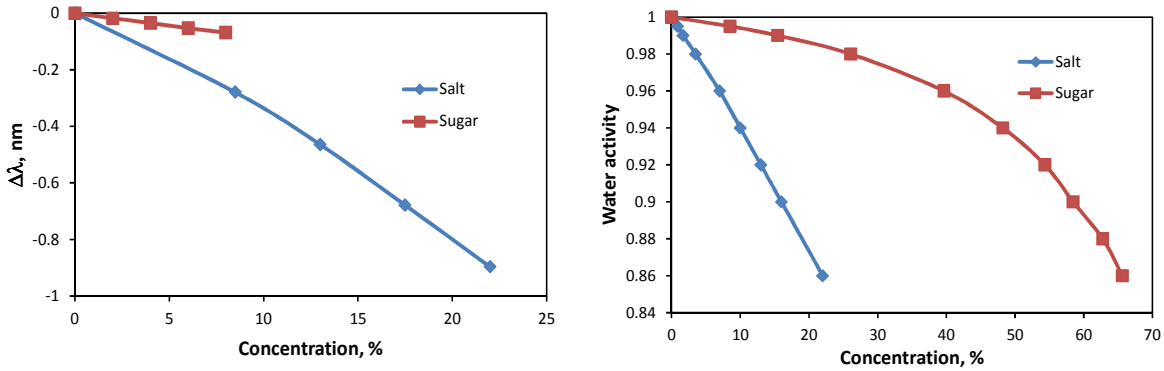

Fig. 4 (a) POFBF wavelength change vs. solution concentration, (b) water activity at different concentration.

One can readily obtain the relation of POFBG wavelength change and salt/sugar activity. The wavelength change of the POFBG is plotted against the water activity of salt/sugar solution, and fuel in Fig. 5. The results for the fuel conditioned in the environmental chamber and the calibrated fuel samples (conditioned in the desiccator) show very good agreement and consistent sensitivity (Fig. 5b).

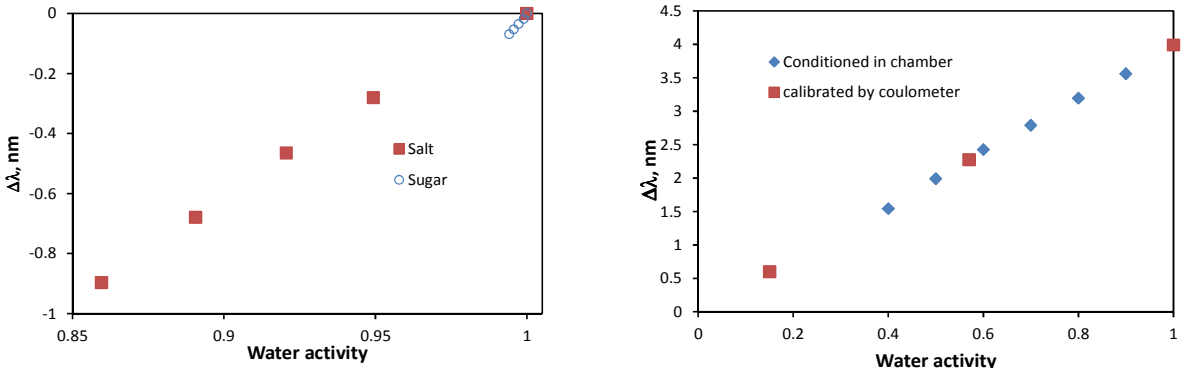

Fig. 5 POFBF wavelength change vs. water activity. (a) salt and sugar solutions (b) Jet A-1 fuel.

From Fig. 5a and Fig. 5b one can find some interesting facts. Looking into the wavelength change as a function of water activity for salt solution, sugar solution and Jet A-1 fuel, we can obtain a sensitivity of 6.4 nm, 13.8 nm, and 4 nm over 100%ERH or a_w, = 1, respectively. The POFBGs used in this work have a humidity sensitivity of 40 to 50 pm/%RH. The measured sensitivity for fuel is in good agreement with POFBG's humidity sensitivity. The sensitivities for salt and sugar solution are larger in the measured range due to the nonlinear relation between water activity and solution concentration. However, one can get an entirely different conclusion by looking into the wavelength change over water content change in a sample. A wavelength change of ~0.9 nm is measured for salt solution with water content varying from 78% to 100%; a wavelength change of ~3.4 nm measured for Jet A-1 with water content varying from 10 ppm to 68 ppm. It implies a very large sensitivity of water content in fuel and a small sensitivity for water content in salt/sugar solution. In fact the POFBG sensitivities of wavelength change as a function of water activity (ERH) for different samples are not very different, regardless of any nonlinear relation between water activity and water content for different

samples. The truth is that POFBG responds to the water content inside the PMMA optical fiber rather than external water content; the former is only determined by equilibrium relative humidity, as defined by (2). Therefore POFBGs always provide good water activity sensing no matter how much the water content is. This is a very useful property for quality and safety control in chemical processing, agriculture, food storage, paper manufacturing, semiconductor, pharmaceutical and fuel industries wherever the moisture/water content is of concern.

5. CONCLUSION

In this work we have investigated POFBGs for measuring water activity of salt solution, sugar solution and aviation fuel. The PMMA based optical fiber grating exhibits good sensitivity and consistent response. This particular feature of measurement allows a PMMA based optical fiber grating to provide an effective measure for quality and safety control in many industries where water content is critical.

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REFERENCES

[1] Zhang, C., Zhang, W., Webb, D. J., Peng, G.-D., "Optical fiber temperature and humidity sensor", Electron. Lett., vol.46 p. 643, (2010).
[2] "Fundamentals of Water Activity," (2006). http://www.aqualab.com/assets/Newsletters/Fundamentals-of-Water-Activity.pdf
[3] UNIFIL Lebanon Spanish Unit Helicopters, "Fuel Quality Control in the Field," Aviation Safety. Awareness Information, 4(7) (2010).
[4] Barbosa-Cánovas, G. V., Fontana, Jr., A. J., Schmidt, S. J., Labuza, T. P., [Water Activity in Foods-Fundamentals and Applications], Blackwell Publishing, (2007).
[5] Thomas, A. M., "Moisture Permeability, Diffusion and Sorption in Organic Film-Forming Materials," Journal of Applied Chemistry, vol.1, p141, (1951).
[6] Turner, D. T., "Polymethyl methacrylate plus water: sorption kinetics and volumetric changes," Polymer, 23, 197-202 (1982).
[7] Zhang, W., Webb, D. J., and Peng, G. D., "Investigation into time response of polymer fiber Bragg grating based humidity sensors," J. Lightwave Technol., 30, 1090-1096 (2012).
[8] Zhang, W., Webb, D. J., Peng, G.–D., "Polymer optical fibre Bragg grating acting as an intrinsic biochemical concentration sensor", Opt. Lett. Vol. 37, no. 8, (2012).
[9] Food and Drug Administration , [Bad Bug Book], 2nd ed., (2012). http://www.fda.gov/_downloads/Food/FoodborneIllnessContaminants/UCM297627.pdf
[10] Ward, Janet D., [Principles of Food Science] , 2nd Ed., Goodheart-Willcox Publisher, (2007)
[11] Zhang, W., Webb, D. J., Peng, G.–D., "Nonlinear response in polymer optical fibre Bragg grating based sensors", Proceedings of SPIE 8421, 354-357, (2012)