Development and integration of innovative glass fibre sensors into advanced composites for applications in hostile environments

B. Milsom[a*],M. Olivero[b], D. Milanese[a], M. Roseman[c], S. Giannis[c], R. Martin[c], A. Terenzi[d], M. Ferraris[a], M. Salvo[a]

a. DISAT, Politecnico Di Torino, 10129, Torino, ITALY
b. DET, Politecnico Di Torino, 10129, Torino, ITALY
c. Element Materials Technology Ltd., SG4 0TW, Hitchin, UK
d. M.D.P Materials Design & Processing S.r.l., 05100, Terni, ITALY
**ben.milsom@polito.it*

Keywords: Evanescent Field Sensor, Moisture Diffusion, Vinyl Ester, Chemical Sensor

Abstract

GRPs are increasingly used in the petrochemical industry, but there is a reluctance to use them in extreme conditions due to unknown long term stability. They are cheaper, lighter and easier to install than traditional steel pipes. However it must be possible to give accurate, non-invasive data on degradation rate during component lifetimes of up to 30 years. This research was focussed on the development and integration of innovative glass fibre sensors into glass reinforced polymers (GRP) composites for applications in hostile environments.
The diffusion and absorption of water into a vinyl ester resin in in simulated seawater, at 120°C in pressurised steel vessels, was measured using optical fibre sensors. Low cost evanescent field sensors were prepared from a standard multimode fibre and compared to commercially available Bragg fibre gratings. It was found that both sensors were capable of detecting the ingress of water into the resin through different mechanisms. The Bragg fibre gratings showed a 1.02±0.24nm peak shift due to the swelling of the resin after 48hrs, whilst the evanescent field sensors showed a progressive reduction in transmitted power due to a change in the environment surrounding the sensor starting from the very early stage of the water diffusion through the thickness of the GRP.

1. Introduction

There is an increasing demand for the use of vinyl esters in glass reinforced polymers (GRPs), particularly in the petrochemical industry for applications such as transport and storage of a wide range of corrosive materials under severe conditions. The use of GRP components can give a significant cost reduction due to lower material costs and cheaper manufacturing processes when compared to traditional steel components [1-3]. They are also easier to install due to a significant weight reduction, do not require welding and have the potential for greater corrosion resistance [1-3].

A major challenge which is stopping more widespread use of GRPs in hostile environments is the unknown long term stability and failure mechanisms compared to materials such as steel.

Damage such as cracking and delamination within the structure can be measured with techniques such as ultrasonic excitation but the initial damage to the composite which can lead to embrittlement and increase the probability of a catastrophic failure is more difficult to monitor [3]. This has led to work on corrosion resistant materials and accelerated ageing of GRPs [4-5].

In this work fibre low cost optic evanescent sensors and commercial Bragg fibre gratings (FBGs) were embedded in a vinyl ester to monitor ingress of chemicals through the thickness of GRPs. In particular, the diffusion of water was monitored as this is a very early step in the degradation of the resin, and in turn GRPs. The possibility to detect water (or other chemicals) diffusion is would be very useful to assist with the development of a more reliable accelerated ageing test to assess the performance of GRPs in hostile environments. Besides, the use of these innovative and sensitive sensors in the structural part of pipe, close to the interface with the liner, would allow the monitoring of the environment diffusion into the structural part, thus detecting that the liner has been compromised, that is, the failure of the pipe.

Evanescent field sensors are intrinsic fibre sensors that work on the principle of having a section of the core of an optical fibre exposed, the evanescent field is a portion of any transmitted radiation along the fibre which extends beyond the diameter of the core and interacts with the environment [6]. There has been extensive work on the use of evanescent sensors, and they have demonstrated the ability to detect a wide range of chemicals in various configurations [7-12]. FBGs are also intrinsic fibre sensors, however, they operate by selectively reflecting a certain wavelength [11-15]. They are produced in several ways but all consist of a periodically alternating refractive index, the spacing of which corresponds to the reflected light [14]. If the fibre is stretched or compressed, the reflected wavelength is also shifted to either a higher or lower wavelength respectively.

2. Materials and testing methods

2.1 Sample Preparation

The evanescent sensors used in this work were prepared from a GIF 625 silica multimode fibre, (Thorlabs, Germany). The radii of the core, cladding, and coating were 62.5, 125 and 250 µm respectively. Each fibre was cut to a length of 1m and had a 10cm sensing region. The sensor was prepared by mechanically stripping 10cm of the coating and then chemically etching the cladding using >40% HF (Sigma Aldrich,).

The Bragg fibre grating sensors were all commercially available gratings supplied by (Raysung photonics Inc., China). They are prepared from single mode fibres (Corning 28e) and the radii of the core, cladding, and coating were 8.2, 125 and 245 µm respectively. The FBGs were used as supplied.

Nine sensing fibres were embedded in a vinyl ester (ame6001,Ashland, Italy) using a silicone mould with dimensions of 110 x 90 x 6mm. The fibres were arranged in three stacks that were spaced 20mm apart: the three fibres in each stack had a vertical spacing of 1.5mm. The resin was cured at room temperature for 2 hours and then underwent a post curing heat treatment at 90°C for 2 hours.

The samples were then placed in a vessel that exposed a single face to simulated seawater at 120 °C in pressurised steel vessels, at a pressure of approximately 2 bar. to induce degradation of the resin. Degradation times up to 192hrs were used.

2.2 Sample Characterisation

The spectra of all fibres were measured on a HP 70951 optical spectrum analyser (OSA) with the spectra centred at 1550nm with a 100nm span. A Er doped broadband light source (Photonetics) was used for all samples and the power was kept constant at 437.4 µW. All the spectra were taken from freshly cut cross sections of the resin to limit any effect from surface contamination and give a true indication of absorption of water into the resin rather than the surface conditions of the sample. The fibres were connected to both the OSA and the light source using multimode pigtails with AT connectors. The pigtails and sensor fibre were cleaved (Fujikura CT07 high precision cleaver), and spliced using a fusion splicer (Fujikura FSM-40S arc fusion splicer). Both multi and single mode pigtails were used to generate different optical signatures for the sensor. The multimode pigtails were supplied by Thor labs and had dimensions of 62.5, 125 and 250 µm for the core, cladding, and coating, matching the dimensions of the optical sensors.

The ingress of water into the VE sample was measured using FTIR (Bruker Equinox 5 spectrometer operating at 2 cm^{-1} resolution, equipped with an ATR cell).

3. Results

The stability of the evanescent sensors was examined before being embedded in the resin. The results are shown in Figure 1. This was to ensure that the exposure of the core would not lead to severe changes in the optical signature in the time between etching the fibre and embedding it in the resin. It was found that over a period of 12 days there was very little deviation from the initial signal and with respect to both signal intensity and the obtained spectral pattern.

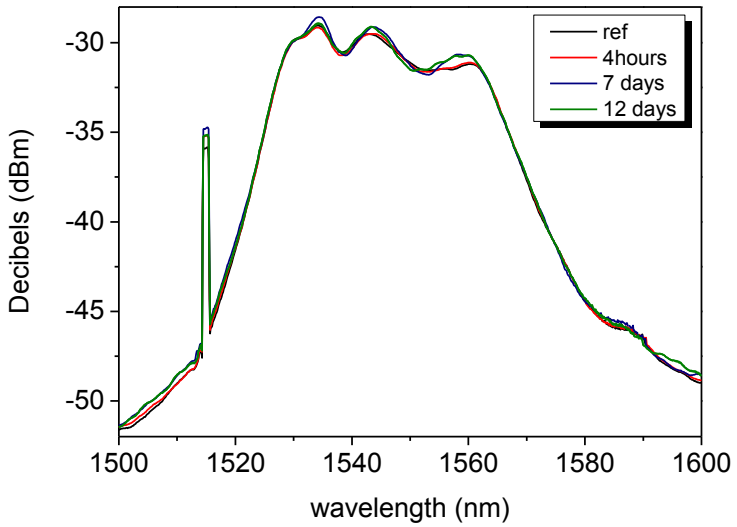

Figure 1: The spectra of an evanescent fibre from 0 – 12 days under atmospheric conditions.

As well as the stability, it was also necessary to confirm that the evanescent field was interacting with the surrounding media. Figure 2 shows the change in optical response when an evanescent fibre sensor is immersed in isopropyl alcohol (IPA). The stability of the spectra is also demonstrated in IPA with a dwell time up to 84hrs. The reference spectrum is that obtained under atmospheric conditions. The change in signal after immersion is evident across the wavelength range; however, the change in profile is strongest around 1560nm where a strong peak can be observed for the reference sample which is almost lost entirely after

immersion in IPA. This provided clear evidence that the evanescent field of the fibre was interacting with the environment as intended.

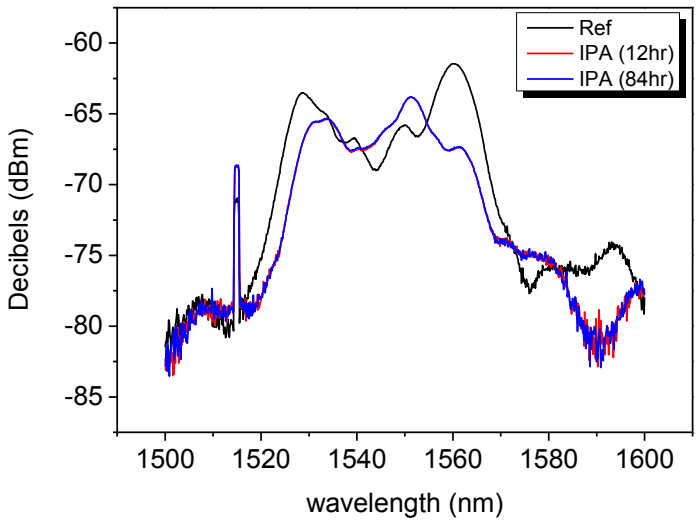

Figure 2: The optical spectra of an evanescent sensor immersed in IPA compared to atmospheric conditions.

The FTIR spectra were obtained for the vinyl ester samples after the exposure to pressurised seawater at 120°C for up to 192hrs. Figure 3a shows the spectra obtained around the OH stretching peak (3200-3600cm^{-1}). Figure 3b shows the region of the spectra associated with hydrocarbon bonding. These regions were investigated to determine the extent of water absorption and degradation within the sample. The increase in the intensity of the OH stretching peak with time confirms the absorption water into the resin. The absorption can be seen in all samples and is particularly strong for the samples with dwell times over 48hrs. There is no significant change in the spectra for the region associated with hydrocarbon bonding. This indicates that the structure of the resin has been unaffected by the salt water immersion with a dwell time up to 192hrs.

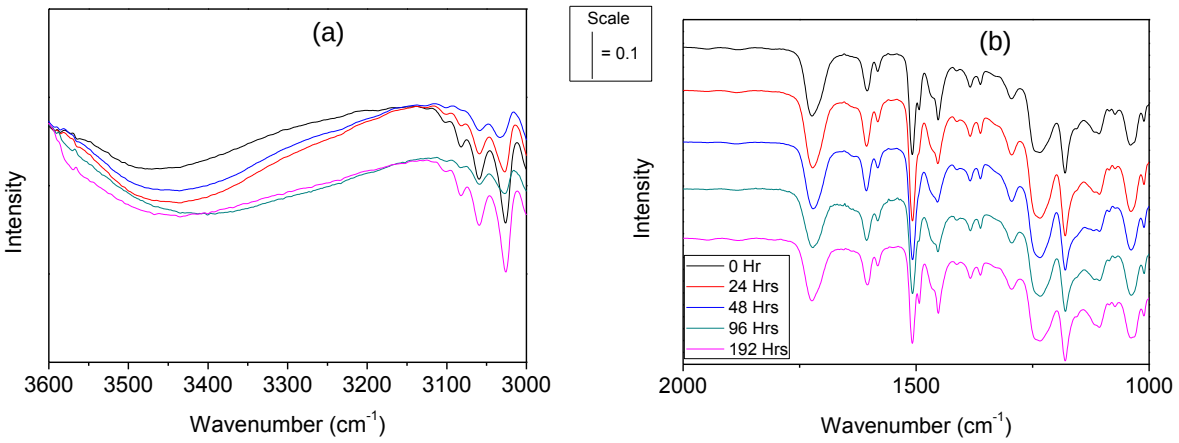

Figure 3: FTIR spectra of vinyl ester samples after degradation in simulated pressurised seawater at 120°C with dwell times from 0 to 192 hrs.

Figure 4 shows the optical spectra obtained for a series of evanescent field sensors with exposure times up to 72hrs. Figure 4a is plotted as decibels, whilst figure 4b is plotted in milliwatts to highlight the change in signal intensity on a linear scale. It can be seen in figure 4a that there is a reduction in signal intensity with dwell time across the observed spectrum.

There is, however, a reduction in the peak height at 1560nm, particularly after a 72hrs exposure, when this peak is lost entirely.

The total transmitted power between 1500 and 1600nm was calculated from figure 4b and is plotted in figure 5 against the dwell time in seawater. There is a rapid initial reduction in signal intensity from 0.230 – 0.085mW after 24 hours of exposure, followed by a further reduction to 0.017mW after 72hrs as the water content increased.

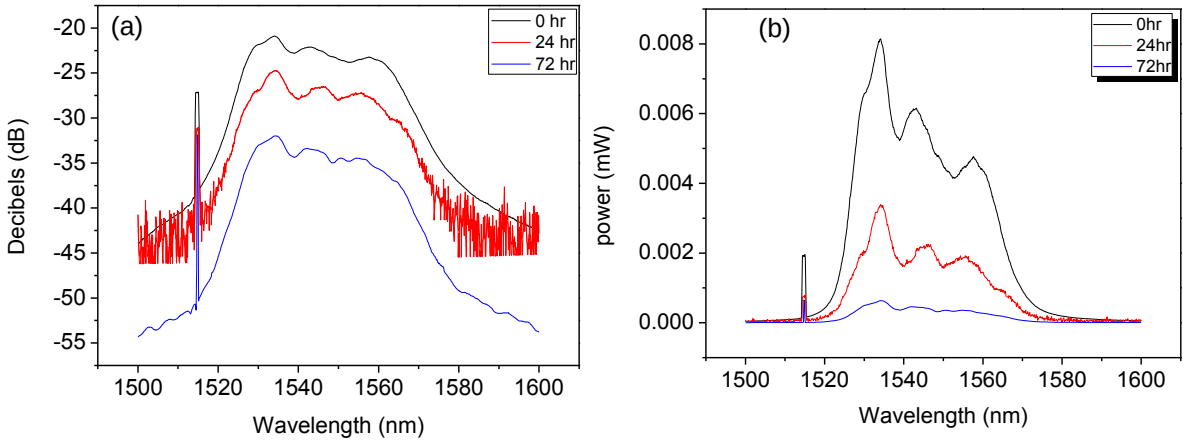

Figure 4: Optical spectra obtained for evanescent field sensors from 1500-1600nm with exposure to seawater at 120°C for up to 72hrs, plotted as: (a) decibels and (b) mill watts.

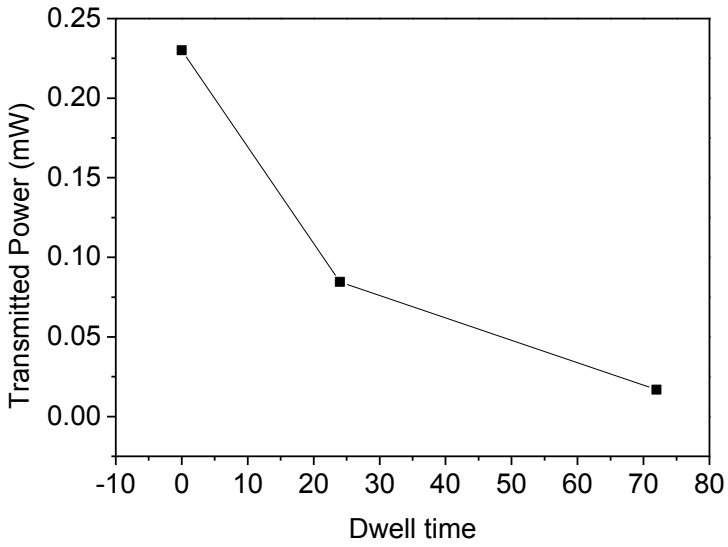

Figure 5: Shows the transmitted power from 1500-1600nm with a dwell time in seawater at 120°C of up to 72hrs.

Figure 6 shows the peak shift obtained for the FBGs compared to the suppliers indicated value. The initial value of +0.4nm had an error of less than 0.1nm and was assumed to be a calibration error in the testing equipment. There was no significant peak shift when the FBGs were embedded in the resin, the values for the as received sensor and the embedded sensor are within the margins of error. After degradation however there was a -1.02±0.24nm peak shift, indicating a compressive force on the sensor.

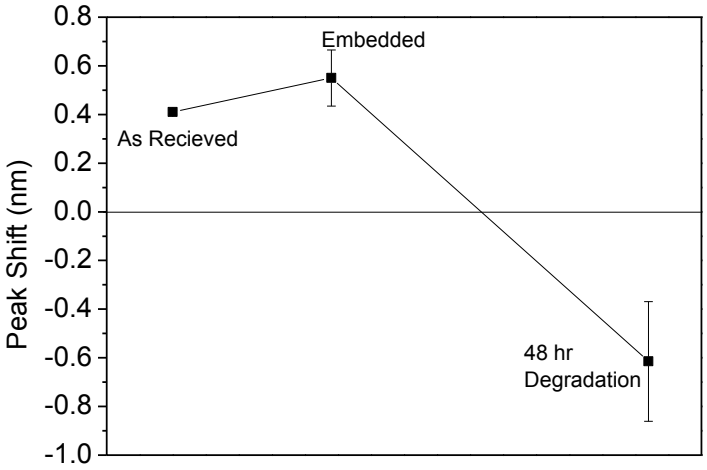

Figure 6: Shows the peak shift of the FBGs compared to the value given by the manufacturer.

4. Discussion

The stability of the signal received from the evanescent senor demonstrated in figure 1 is a crucial aspect of the sensor. If significant deviations in the response were observed over time the reliability of the sensor would be severely impaired, it would very difficult to know whether changes in the signal were due to the environment or not. The response of the sensor is to the presence of IPA, demonstrated in figure 2, confirmed that the evanescent field was able to respond to changes in the surrounding environment due to a change in the refractive index of the material surrounding the sensor.

To monitor the initial stages of ageing within the resin it was important to determine the optimum exposure conditions for the samples. If the samples were overexposed the vinyl ester would begin to break down and would exhibit a change in optical properties. The FTIR results shown in figure 3 confirm that ageing of the polymer has been initiated but is only in the early stages. There is water absorbed from 24hrs, however, no change in the hydrocarbon bonding is observed with dwell times of up to 192hrs. This means that any changes in the optical signal received from the sensors are a result of the diffusion of water into the GRP and not the degradation of the vinyl ester itself.

The evanescent field sensors were capable of measuring the diffusion of water into the resin, as shown in figure 4. The reduction in signal intensity is due to greater losses to the surroundings as the water content increases. There was an initial loss of 73% after 24hrs exposure, which increased to 92% after 72hrs, shown in figure 5. The initial loss of signal after 24 hrs is due to rapid diffusion of water into the resin which causes a change in the refractive index and in turn more of the radiation is lost due to the interaction of the evanescent field. The rate of signal loss is reduced after the initial rapid diffusion and was expected to reach a plateau as the resin becomes saturated and can be linked with increase in the strength of the OH peak observed in the FTIR results in figure 3a.

The commercially available FBGs also detected the diffusion of water into the vinyl ester, although based on a different principle. As the sample absorbed water the resin expanded, this compressed the embedded FBG which led to the observed peak shift of -1.02±0.24nm.

A major advantage of the FBG over the evanescent sensor is that it is more mechanically robust, which simplifies the embedding process. The evanescent field sensors, however, can

be modified through sensitive coating materials that can increase sensitivity to various chemicals such as H_2S and CO_2, two key chemicals involved in the degradation of GRPs in the petrochemical industry. This fact, coupled with the significant cost reduction of using standard multimode fibres means they are a viable option for the detection of diffused chemicals into polymeric materials. There is also the possibility to couple both types of sensors, as they could be calibrated to link the swelling of the resin, and in turn the peak shift of the FBG, with the signal reduction exhibited by the evanescent field sensors.

5. Conclusion

The viability of both evanescent field sensors and FBGs for the detection water diffusion into a vinyl ester has been demonstrated in this work. The evanescent sensor showed a change in signal profile at 1560nm and a reduction in signal intensity of 73% after only a 24hr immersion across the range 1500-1600nm. The commercially available FBG gave a peak shift of 1.02±0.24nm after 48hr. There is significant potential for the use of both sensors for the detection of the onset of degradation of vinyl esters in commercial applications. The evanescent sensor is a very low cost device that has the possibility to be modified to increase selectivity to a wide range of chemicals if necessary.
The availability of new and low cost photonic sensors for the hostile environments found in the petrochemical industry and for the evaluation of the status of GRP equipment and the related analysis procedure, as well as opening new commercial opportunities in this specific market segment (a niche, albeit strategic), would also provide the background for developing similar approaches in other applications requiring the continuous monitoring of the changes of a chemical quantity.

Acknowledgements

The research leading to these results has received funding from the European Union's Seventh Framework Programme managed by REA-Research Executive Agency http://ec.europa.eu/research/rea and it participates in a Marie Curie Action (GlaCERCo GA 264526).

The authors would also like to thank Dr S.L. Fiorelli at the Politecnico di Torino for assisting with the FTIR, and Dr R. Petrucci at the Univeritá Degli Studi di Perugia for his assistance embedding the sensor fibres.

References

[1] Martin R. A technology gap review of composites in the UK oil and gas industry. *Review for the National Composites Network,* **Merl C1889-1 rev B**, pp. 1-26 (2007).
[2] Hossain M.E. The current and future trends of composite materials: an experimental study. *Journal of Composite Materials,* **45 (**20), pp. 2133-2144 (2011).
[3] Nali K. Avoiding internal corrosion with glass reinforced plastic. *Pipeline and Gas Journal,* **239** (3), pp.1-3 (2012).
[4] Broughton W.R. *Towards accelerated ageing protocols for service in hostile conditions* in proceedings of the *16th International Conference on Composite Materials*, Japan, (2007).
[5] Li H., Gu P., Watson J., Meng J. Acid corrosion resistance and mechanism of E-glass fibres: boron factor. *Journal of Materials Science,* **48**, pp. 3075-3087 (2013).
[6] Yu F.T.S., Yin S. Fiber optic sensors. Marcel Dekker inc, New York (2002)

[7] Matias I.R., Bravo J., Corres J.M., Arregui F.J. *Evanescent field sensors based on fibre optic structures* in proceedings of the *1st International Conference on Sensing Technology*, New Zealand, (2005).
[8] Armin A., Soltanolkotabi M., Feizollah P. On the pH and concentration response of an evanescent absorption sensor using a coiled-shape plastic optical fiber. *Sensors and Actuators A: Physical*, **165**, pp. 181-184 (2011).
[9] Khijwania S.K., Gupta B.D. Fiber optic evanescent field absorption sensor: Effect of fiber parameters and geometry of the probe. *Optical and Quantum Electronics*, **31**, pp. 625-636 (1999).
[10] Linslal C.L., Mohan P.M.S., Halder A., Gangopadhyay T.K. Analysis and modelling of an optical fiber loop resonator and an evanescent field absorption sensor for the application of chemical detection. *Sensors and Actuators A: Physical*, **194**, pp. 160-168 (2013).
[11] McDonagh C., Burke C.S., MacCraith B.D. Optical chemical sensors. *Chemical Reviews*, **108**, pp.400-422 (2008).
[12] Lee B. Review of the present state of optical fibre sensors. *Optical Fiber Technology, **9**,* pp.57-79 (2003).
[13] Thakral S., Manhas P., Fiber optic sensors technology and their applications. *International Journal on Electronics and Communication Technology*, **2** (2) pp. 126-128 (2011).
[14] Thomas G., Bucaro J.A., Dandridge A. Sigel G.H., Cole J.H., Rashleigh S.C., Priest R.G. Optical fibre sensing technology. *Journal of Quantum Electronics*, **18** (4), pp. 626-665 (1982).
[15] Culshaw B. Fiber-optic sensing: A historical perspective. *Journal of Lightwave Technology*, **26** (9), pp.1064-1078 (2008).