

Chemical Monitoring of Composite Matrices by Evanescent Wave Spectroscopy

P.B.S. Bailey, S.A. Hayes, R.J. Hand, B. Zhang

Department of Engineering Materials, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield, S1 3JD, UK.

KEYWORDS: Monitoring, Spectroscopy, Evanescent, Chalcogenide glasses, Fibre, Silane.

ABSTRACT

The results of an initial investigation into the monitoring of water absorption and chemical degradation in epoxy matrix composites using evanescent wave spectroscopy are presented. While conventional silica glasses have too low a refractive index and too short an IR transmission window to be useful as unclad sensing elements in most resin systems, chalcogenide glasses offer suitable refractive indices and infrared transmission windows. Arsenic selenide compositions with gallium or tellurium additions were initially investigated as they have been successfully demonstrated in other fibre sensing applications. However their glass transition point lies near or below the curing temperature for many commercial epoxy resins and thus germanium-antimony-lead sulphide glasses were also investigated as they display higher glass transition temperatures. The fibres were embedded in a representative matrix resin by casting samples of epoxy resin around sections of fibre. The end faces were prepared to allow an infrared beam to be passed along the fibre and the samples were subjected to hygrothermal aging. Changes in the transmitted spectra were observed, and photoelasticity was used to monitor the occurrence of fibre fragmentation. Both the arsenic selenide based compositions and the germanium-antimony-lead sulphide compositions displayed minimal bonding with the epoxy resin, so a simple silane treatment was used to improve adhesion.

INTRODUCTION

Polymer matrix composites are receiving ever increasing interest in the fields of aerospace and civil engineering for structural applications, but this raises a number of issues pertaining to the critical nature of some components with length of service life required. In particular unless a structure can be monitored and any impending failure of integrity predicted as readily as with the metallic equivalent, the engineer is potentially faced with safety factors so large as to waste the advantages of carefully designed composite components. In certain respects polymer matrix composite structures can be

more susceptible to performance degradation by both mechanical and environmental factors (*e.g.* impact or fluid contamination) than an equivalent metal or concrete structure, a situation made worse by the fact that they are arguably harder to inspect for the symptoms of such “damage”. A considerable number of researchers have ongoing work on systems to monitor and localise mechanical (impact) damage. However the focus of the current work is on sensing chemical degradation and thus the mechanical damage sensors will not be discussed further here.

Infrared spectroscopy can be an invaluable tool for determining the chemical structure of polymers, since different functional groups absorb light at characteristic wavelengths. While a simple, small, flat faced prism is now the standard in ATR sampling accessories, early work in this area was carried out using large cylindrical “light pipes” [1]. More recently unsheathed optical fibres have been demonstrated in a wide variety of applications examining liquid and gas phases [2,3,4], where it has come to be referred to as fibre evanescent wave spectroscopy (FEWS or EWS). Our current aim is to apply FEWS to examine the core of a structurally critical composite panel and thereby build in a system to check for absorption of contaminants or chemical degradation indicative of degradation in matrix properties.

Unfortunately the readily available silica based optical fibres are not suitable for this type of application for two reasons. Firstly the transmission window for pure silica ends at wavelengths a little above 2.5 μm ; while this allows some access to the near infrared region, one must look at least to the mid-infrared to isolate most organic functional groups with certainty. Secondly, most commercial epoxy resin systems have a refractive index of around 1.8 so any unsheathed fibre must have a higher refractive index than this. This is around the highest index of the more exotic silica based systems, which are incidentally very difficult to produce in a completely homogenous form. Chalcogenide glasses seem to offer the most likely solution since the heavier elemental components produce a transmission window that can extend to wavelengths beyond 10 μm . They also have high refractive indices, typically between 2 and 3.5, which should mean that a single type of fibre is suitable for any resin system.

Two main families of chalcogenide glasses have been used in the current work, namely tellurium-arsenic selenide and germanium-antimony-lead sulphide (hereafter referred to by their common acronyms TAS and GSPS respectively). TAS and similar arsenic selenide based compositions have been widely examined for various infrared optical applications and experienced great success in other fibre applications. Unfortunately these materials typically have a glass transition temperature between 120°C and 150°C; which while convenient for processing, is near or below the cure temperature for many epoxy resin systems. Clearly therefore TAS fibres will not be universally applicable in epoxy resin matrices, but fibres of known quality, similar to those used in some published work on FEWS [2], were available to us. Since any commercially viable system would need to be suitable for hot cured resins, extant work on a wide variety of compositions was examined; the germanium-antimony-lead sulphide family examined by Xia et al [5] appears to have the most desirable combination of properties recorded. Nominally based on the stoichiometric sulphides GeS_2 , Sb_2S_3 and PbS , (hence the

acronym GSPS), the most stable glasses are formed with a moderately high germanium content and have been reported as having moderately high fracture toughness compared to other chalcogenide glasses [5].

EXPERIMENTAL

Glass fibres

TAS fibres of 170 μm in diameter were supplied by the University of Nottingham, UK. GSPS fibre preforms of nominal composition, $5\text{GeS}_2.4\text{Sb}_2\text{S}_3.\text{PbS}$, were produced in-house by reacting the elements in sealed fused silica tubes in a rocking furnace at 950°C . The samples were rapidly quenched in cold water, then annealed at 280°C . Fibres were drawn from the resulting preforms using a Heathway fibre tower equipped with an in-house convection based furnace. The fibre drawing temperature was 290°C and the resulting useable fibres were 200 μm to 250 μm in diameter. The native transmission loss of the GSPS fibres produced to date is very high; a major cause being the number of surface defects. Whilst work is ongoing to produce better fibres the fibres were of sufficient quality to enable their use in the current small scale test pieces.

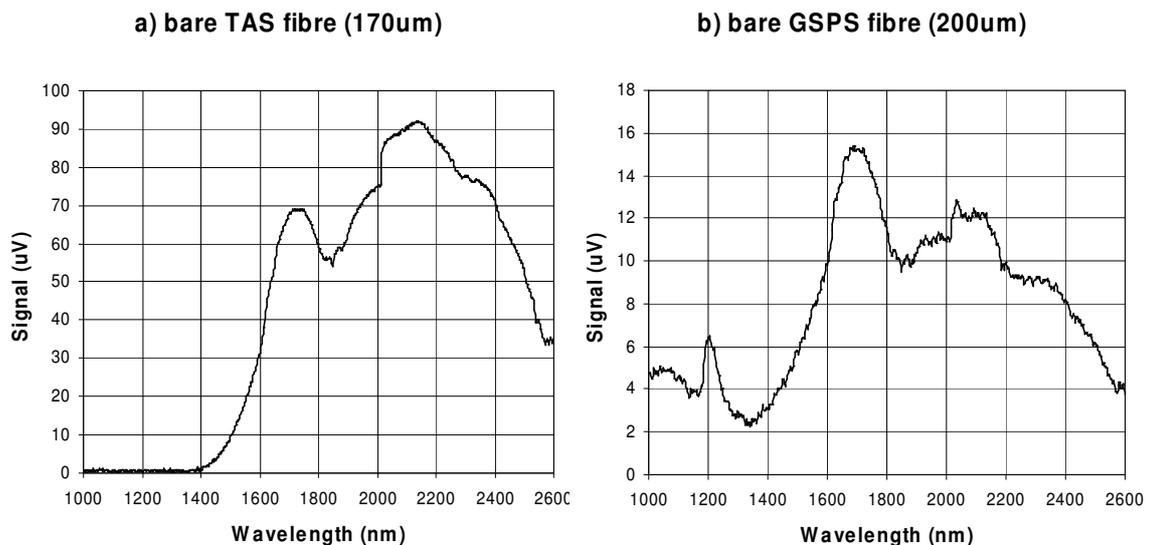


Figure 1: Bare fibre transmission for 13cm lengths of a) TAS and b)GSPS

Sample Preparation

Initial work has been limited to using single chalcogenide fibres embedded in resin without reinforcement or filler. Samples were prepared by placing cleaned fibres 60mm or 80mm in length (washed first with acetone, then propan-2-ol) into flat silicone moulds which were then filled with mixed, degassed resin until the fibre was just submerged and not perturbing the meniscus. To allow direct comparison between TAS and GSPS fibres, a low temperature cured, aerospace grade resin was used (Araldite 5052 system) since the TAS glass had a T_g of only 137°C . Prior to testing, samples were conditioned at 50°C under vacuum for 5 days.

The TAS fibres have such surface quality and native transmission loss that an acceptable signal can be introduced through a polished end face. However as mentioned above, the

GSPS fibres produced to date are not of particularly high quality making end preparation for transmission measurements difficult; it was found that the GSPS fibres needed to be cut to leave a reasonably flat fracture surface. For this reason it was necessary to allow a short section of the GSPS fibres to protrude from a slot in the mould which was then sealed with a soft non-hardening mould sealant.

Fibre transmission spectra were collected using a Bentham Optics spectroradiometric system comprising a chopped, monochromated light source, and a lead sulphide detector fed into a lock-in amplifier. For the configuration used, the instrument operates from 1 μm to 2.8 μm wavelength, over which the detector has been shown to give a signal directly proportional to intensity. Although an actual fibre chemical sensing system would be designed to operate further into the infra-red, at this stage the limited window of our current equipment is acceptable to provide proof of concept using chalcogenide fibres, especially as the waveband studied includes a strong absorption band associated with $-\text{OH}$ groups. All signal data show a step up at 2016nm wavelength due to a filter change in the monochromator at this point.

Tests on Untreated Fibres

As a proof of principle, the samples were immersed in distilled water at 50°C; water absorption is almost universally relevant to the use of epoxy matrix composites being probably the most malign yet common environmental influence on both resins and interfaces in fibre composites. Furthermore water gives rise to very strong, clear absorption bands in the infrared spectrum. The samples were weighed and fibre spectra collected; first when the samples were de-moulded after overnight cure, again after conditioning, then at intervals after immersion started.

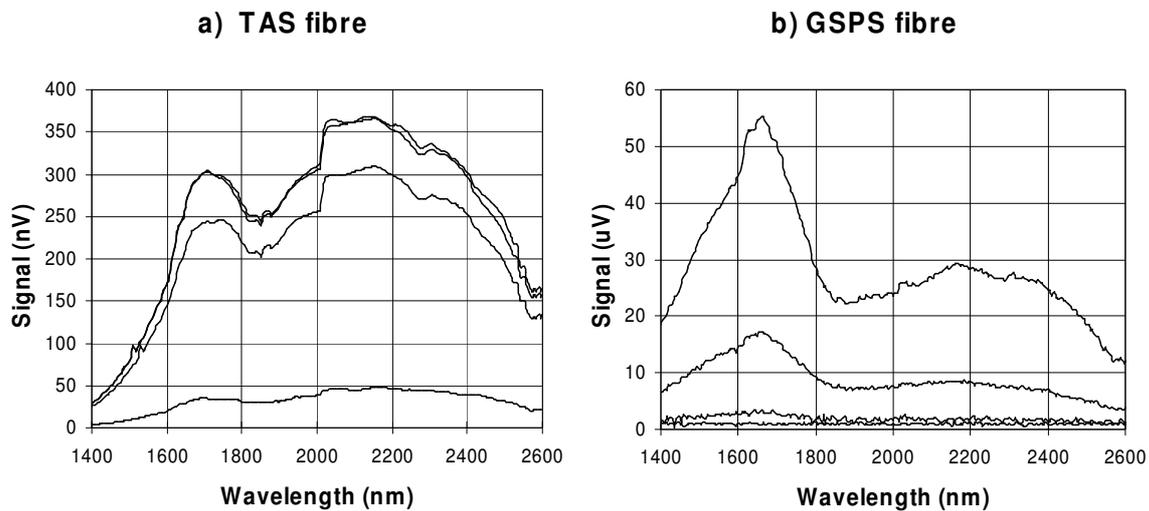


Figure 2: signal data after 0, 2, 20 and 45 hours' immersion for a) TAS fibre, b) GSPS fibre. For b) the signal strength decreases sequentially with length of immersion; for a) the third curve down is actually at 2 hours, probably due to poor alignment.

Figure 2 shows typical intensity data for the two types of fibre after during immersion. While the potential for variation due to misalignment cannot be neglected, it is quite

clear that the overall signal level has been degraded after quite a short period of immersion. However despite the fact that after as little as 2 hours water absorption had reached 0.6 wt%, exceeding 2.5 wt% at the end of the test, there is also no indication of changing attenuation in specific spectral regions, even though a strong attenuation would be expected from the –OH water band near 1900nm wavelength. One notable contrast between the two types of fibre is that with the TAS fibres debonding of the fibres was clearly visible as reflective voids started to form around the fibre, in some cases before any appreciable loss of signal, whereas no such phenomenon was visible on the GSPS fibres. After the end of testing, the samples were left in water and the GSPS fibres did exhibit voiding after another few days.

Surface Treatment of Fibres

Due to the evident lack, or at least degradation, of bonding between the epoxy resin and these chalcogenide glasses, it was decided to apply a surface treatment to the fibres in an attempt to provide a durable bond which would at least survive until a significant and measurable degree of water absorption had occurred. To the best of our knowledge there is no published work pertinent to bonding organic chemicals to chalcogenide surfaces. In light of the extremely wide range of materials on which silanes are known to form a chemical bond, basic tests were conducted using readily available commercial formulations in a similar manner to that employed for work on E-glass reinforcing fibres [6].

Sections of clean fibre were immersed in 1 wt% aqueous glycidoxypropyltrimethoxysilane (Dow Corning Z-6040) solution for 1 hour, and then transferred to distilled water for a further hour. The fibres were then dried under partial vacuum for 1 hour at 80°C for TAS fibres or 30 minutes at 120°C for GSPS fibres; upon removal from the oven, the fibres were immediately moulded into samples as before.

The samples using treated fibres were tested in the same fashion as before, with much more favourable results. Figure 3 shows selected spectra during immersion. There is again a downward trend in intensity, but it is nowhere near as severe as that seen with the untreated fibres, and the TAS fibres did not visibly debond as before. The test was ended at 90 hours when all signal transmission through the GSPS fibres was suddenly lost; examination using a polarising strain viewer showed that this was due to at least three fibre fractures over the sensing length. In this case because the fibre-resin bond seems to have much improved it is thought that this has meant that swelling of the resin has led to sufficient tensile stress being placed on the fibre to cause fibre fracture; the high density of surface defects on the fibres used here means that the GSPS fibres will be relatively weak. The swelling of the matrix would be significantly constrained if reinforcing fibres were also present.

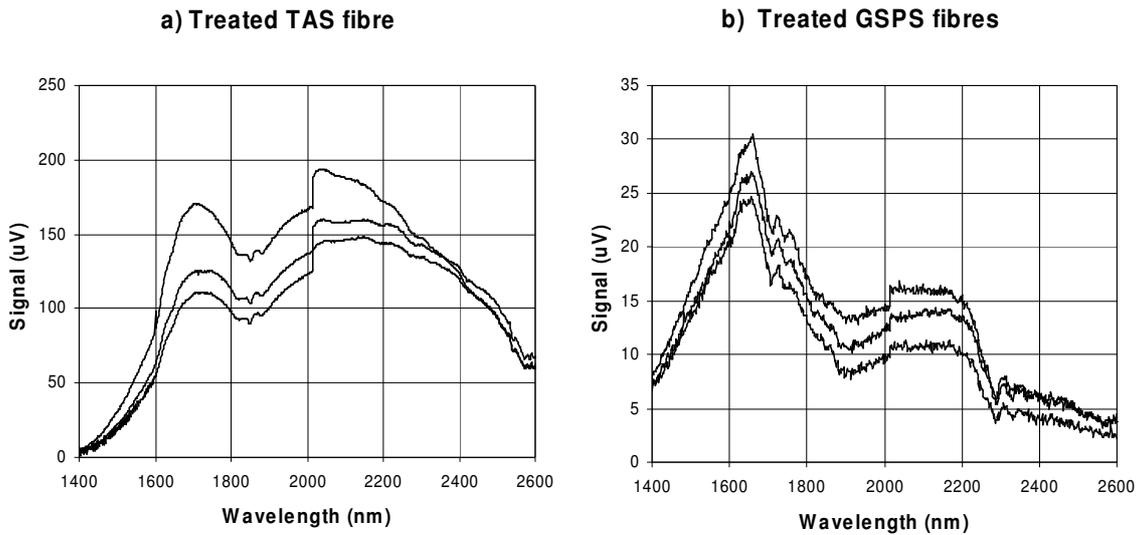


Figure 3: Signal data during immersion

a) treated TAS fibre after 3, 22, and 90 hours; b) treated GSPS fibre after 9, 22, and 50 hours.

From Figure 3 it can be seen that the spectra for GSPS fibre have minima around 1900nm, which appear to be getting deeper with length of immersion. The negative logarithm of the intensity was taken and the spectra normalised at 1800nm where functional group specific infrared absorption should be minimal [7]. Observing the resulting spectra shown in Figure 4, there is clearly an increasing peak in absorbance around 1900nm for the GSPS fibre. The TAS fibre continues to show no variation in wavelength specific features. This may be because the TAS fibres have a higher refractive index than the GSPS fibres which will lead to less penetration of the evanescent field into the matrix with TAS fibres. Thus TAS fibres could be expected to be less sensitive to changes in the matrix than the GSPS fibres.

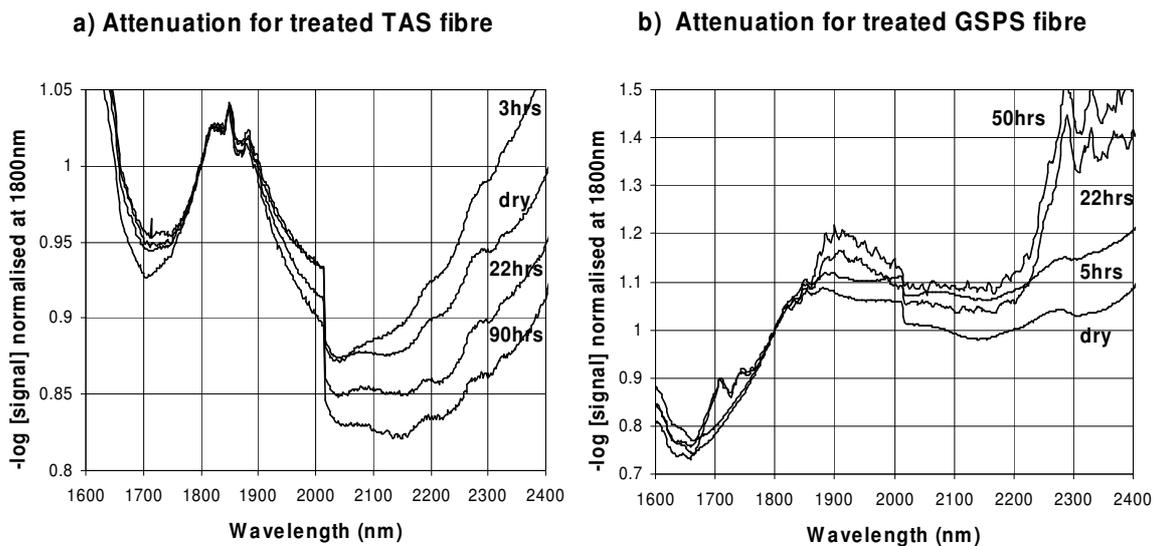


Figure 4: Relative absorbance spectra for treated fibres during immersion.

Figure 5 shows the peak height near 1900nm plotted against the measured water uptake of the sample for all measurements. There is a clear linear trend as would be expected from Beer's Law. The open mark indicates the height for the cured sample prior to drying.

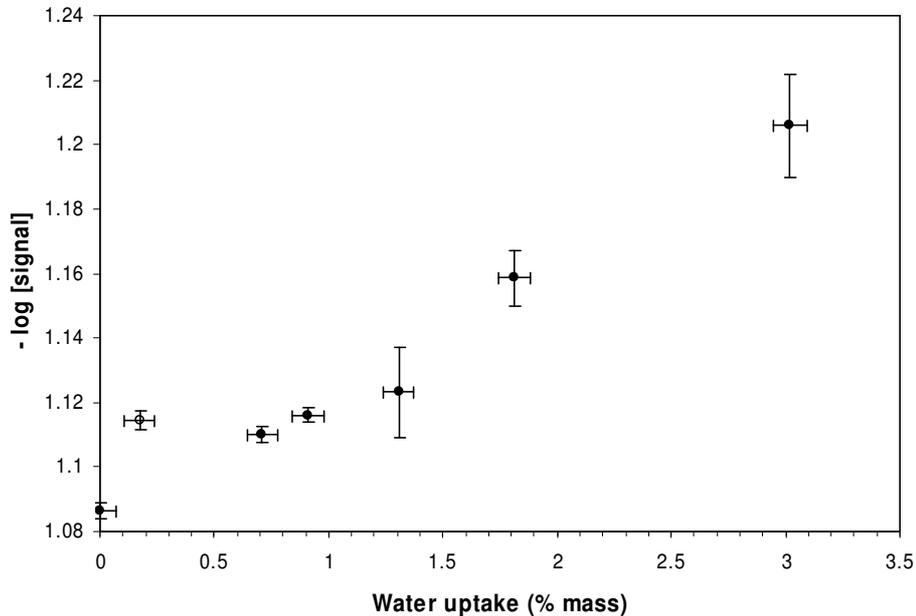


Figure 5: Relative absorbance at OH water peak versus water uptake, error bars indicate noise level.

CONCLUSIONS

It has been established that fibre evanescent wave spectroscopy is possible in an epoxy resin matrix. Using GSPS chalcogenide glass fibre, evolution of an infrared absorption band characteristic of $-OH$ has been observed clearly correlated with uptake of water in the surrounding resin.

Surface treatment of the fibre is necessary to produce and maintain sufficiently bonding with the resin; a silane solution treatment has been shown to be effective in promoting the required degree of adhesion. It seems that a side effect of this is that the swelling of the resin eventually transfers sufficient stress to fracture the fibre. It is proposed that this effect will be greatly reduced when surrounded with reinforcing fibres; work using both reinforcing and GSPS fibres is ongoing to investigate this.

Although the surface treatment also appears to be effective in promoting adhesion with TAS glass fibres, no changes spectral features were discernable using these fibres. It is hypothesised that this is largely due to the higher refractive index of TAS compared to GSPS; while the higher RI would permit slightly more modes to propagate along the fibre, it also considerably reduces the penetration depth of the evanescent field giving a smaller equivalent path length in the resin therefore making the TAS fibre system intrinsically less sensitive.

ACKNOWLEDGEMENTS

We thank the UK Engineering and Physical Sciences Research Council for funding parts of this work. We also thank Dr David Furniss of the School of Mechanical, Materials & Manufacturing Engineering University of Nottingham for providing the arsenic selenide based optical fibres.

REFERENCES

- [1] Harrick NJ, "Internal Reflectance Spectroscopy", *Wiley Interscience Publishers*, 1967.
- [2] Michel K, Bureau B, Boussard-Pledel C, Jouan T, Adam JL, Staubmann K, Baumann T, "Monitoring of pollutant in waste water by infrared spectroscopy using chalcogenide glass optical fibers", *Sensors And Actuators B – Chemical*, 2004; 101 [2] 252-259
- [3] Willer, U., Saraji, M., Khorsandi, A., Geiser, P., Schade, W., "Near- and mid-infrared laser monitoring of industrial processes, environment and security applications", *Optics and Lasers in Engineering*, 2006; 44 [7] 699-710
- [4] Hammody, Z., Huleihel, M., Salman, A., Argov, S., Moreh, R., Katzir, A., Mordechai, S., "Potential of 'flat' fibre evanescent wave spectroscopy to discriminate between normal and malignant cells in vitro", *Journal of Microscopy*, 2007; 228 [2] 200-210
- [5] Xia F, Zhang X, Ren J, Chen G, Ma H, Adam JL, "Glass Formation and Crystallization Behavior of a Novel GeS₂-Sb₂S₃-PbS Chalcogenide Glass System", *J. Am. Ceram. Soc.*, 2006; 89 [7] 2154-2157
- [6] Cheng T-H, Jones FR, Wang D, "Effect of Fibre Conditioning on the Interfacial Shear Strength of Glass-Fibre Composites", *Composites Science and Technology*, 1993; 48 [1-4] 89-96
- [7] Colthup NB, Daly LH, Wilerbey SE, "Introduction to infrared and Raman spectroscopy (3rd Edition)", *London Academic Press*, 1990, ISBN: 012182554x