Letters

*Infra-red spectroscopic characterization of surface coatings on glass fibres**

A wide variety of coating formulations are applied during the production of glass fibres to facilitate processing and, in some cases, to modify the adhesion characteristics of the glass fibres in a polymer matrix. Analysis of these formulations, as required for quality control and research purposes, is a complex problem which requires the application of a range of analytical techniques [1]. The potential of Fourier Transform Infra-red (FTIR) spectroscopy for examining silane coupling agents on E-glass micro-fibres and fumed quartz has been clearly demonstrated by Ishida and Koenig [2, 3]. The purpose of this communication is to illustrate the usefulness and limitations of the FTIR technique as applied to the important practical problem of analysing complex coating formulations applied at low (< 1%) weight add-on to commerical E-glass fibres.

E-glass fibre roving ($2.4\,\mathrm{g\,m^{-1}}$, 9792 fibres per strand) was supplied by Fiberglas Canada Inc. The coating formulation used had epoxy compounds as the major component with lesser amounts of polyvinyl acetate and other proprietary components. The coating was applied at a weight add-on of 0.97% immediately after spinning.

The glass fibres were examined directly either by winding between two sodium chloride windows, as described by Tirpak and Sibilia [4], or by grinding them to a powder for pressing into a potassium bromide disc [2, 5]. Infra-red spectra were obtained using a Nicolet 7199 FTIR equipped with a mercury–cadmium–telluride detector. Analysis of the coating is obviously complicated by the intense i.r. absorption of glass, particularly around $1100\,\mathrm{cm^{-1}}$ (Fig. 1). The spectral subtraction ability of the FTIR was used to remove this absorption wherever possible but, in order for spectral subtraction to be reasonably successful, the absorbance of the glass must be kept below about 1.0 (10% transmission). To do this it is necessary to limit the glass content of the disc to less than about 2 mg of glass in 300 mg KBr, although this amount does vary slightly with the grinding procedure because of scattering effects. This amount of glass produces coating absorptions of only $\sim 10^{-2}$ absorbance units and even with the low-noise spectra accessible with an FTIR ($\sim 5 \times 10^{-4}$ absorbance units at $2000\,\mathrm{cm^{-1}}$) the usefulness of such a difference spectrum (Fig. 2a) is limited. To obtain measurable coating absorptions it is necessary therefore to increase the amount of glass in the i.r. beam either by increasing the glass content of the KBr disc or by direct examination of an array of glass fibres (Fig. 2b). This results in the spectral region 1400 to $800\,\mathrm{cm^{-1}}$ being sacrificed because of low energy transmission. Only a partial qualitative analysis is therefore possible by direct examination of the glass fibre, although this may provide useful information in

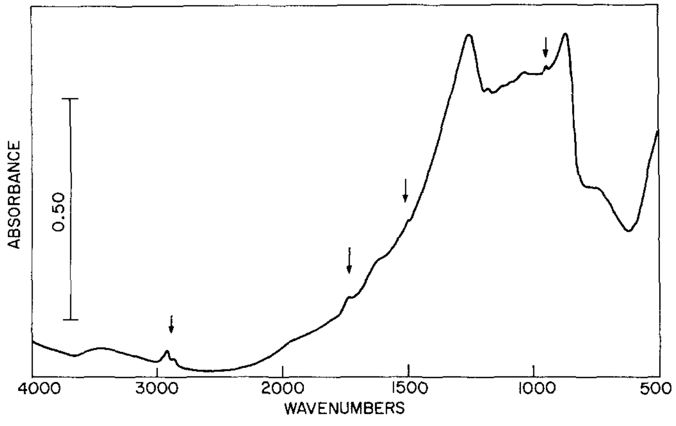

Figure 1 The i.r. absorbance spectrum of 2 mg of glass fibre in a KBr disc. Absorptions due to coating are marked with arrows.

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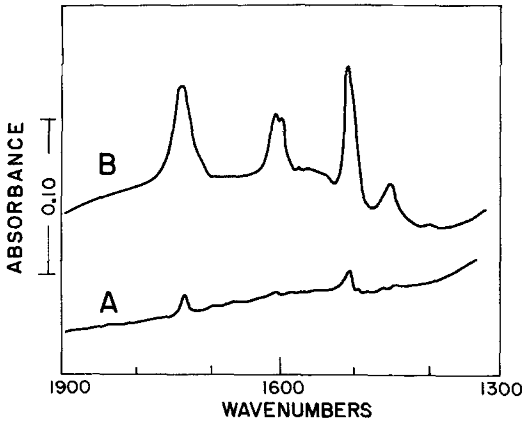

Figure 2 I.r. absorbance spectra of glass fibre after subtraction of spectra for uncoated glass fibre: (a) 2 mg of ground glass fibre in a KBr disc and (b) glass fibre array between NaCl windows.

some cases, such as when the proportions of two known components (e.g. polyvinyl acetate, 1730 cm^{-1} and epoxy, 1510 cm^{-1}, Fig. 2) are being compared.

Potentially, reflectance techniques are more sensitive than transmission techniques for detecting thin surface layers [6]. Practical limitations of the technique, however, restrict spectral quality to a level comparable to transmission techniques, e.g. Fig. 1. When using internal reflectance spectroscopy (IRS) it is necessary to have adequate optical contact between the glass fibre and the IRS element. This is usually accomplished by pressing the fibres against the IRS element, and when using KRS-5, which is a soft material, appreciable abrasion of the surface occurs, resulting in poor energy transmission and short element life. Germanium elements are harder, but the high refractive index of germanium (4.0) reduces the depth of penetration of the i.r. beam, compounding the optical contact problem. The spectral region 1400 to 800 cm^{-1} is also inaccessible to IRS because of the large refractive index fluctuations of glass in this region which cause marked spectral distortion [6, 7].

In several cases the coating was partially removed from the fibre by extraction with freshly distilled methanol. The extract was filtered and concentrated by evaporation before being dropped on to a zinc selenide IRS element. IRS was used in preference to conventional transmission measurements because of the greater sensitivity of the IRS technique (the i.r. beam "sees" the sample at each reflection, not just once as in the transmission technique) [5, 6]. This technique is illustrated in Fig. 3, where the methanol extract of the glass fibre is shown to consist largely of polyvinyl acetate and the epoxy component [8]. Methanol extraction resulted in the removal of ~45% of the coating, as determined by weight-loss measurements, and comparison with the spectrum of the unextracted fibre (Fig. 2) indicates that methanol extraction removed almost all the polyvinyl acetate and ~40% of the epoxy component.

The solvent extracts were also examined by liquid chromatography (LC, acetonitrile/water, reverse phase). If complete chromatographic separation can be achieved by a suitable choice of LC solvent, it is generally possible to isolate $>100\,\mu\text{g}$ of the minor coating components by

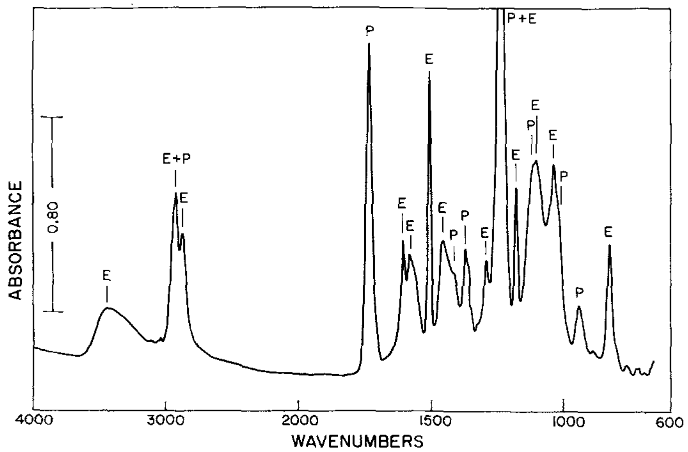

Figure 3 Methanol extract of glass fibre by IRS after evaporation of solvent. P denotes absorption due to polyvinylacetate and E denotes absorption due to the epoxy component.

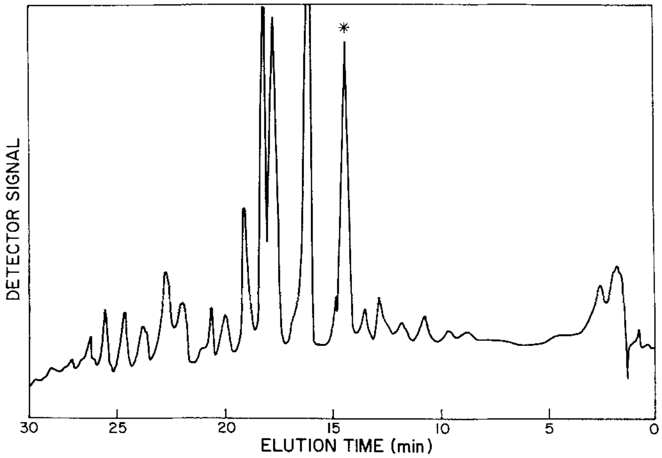

Figure 4 Liquid chromatogram of an iso-octane extract of the glass fibre. Peak marked with * collected for IRS analysis.

collecting that portion of the eluting solution. If the LC solvent is volatile, the solution may then simply be dropped on to the IRS element and the solvent evaporated. In the chromatogram shown in Fig. 4, the solvent was a water/acetonitrile mixture which is relatively non-volatile. The solvent was therefore removed from the fraction using a rotary evaporator and the solution redissolved in freshly distilled acetone. This more volatile solution was then dropped on to the IRS element. The resulting i.r. spectrum is shown in Fig. 5. Using this technique it is clear from Fig. 5 that the LC peak marked in Fig. 4 corresponds to an aromatic compound, which contains no Si–O bonds and has very weak carbonyl and hydroxyl absorptions (probably resulting from imperfect chromatographic separation). The compound is probably an impurity/degradation product in the epoxy component of the coating.

In conclusion, FTIR analysis of glass fibres can give important information about the coating formulation present even at a 1% add-on level, although a complete qualitative or quantitative analysis is not generally possible because the spectra are of inadequate quality in the 1400 to 800 cm^{-1} region. For example, FTIR analysis of glass fibres, either ground up in a KBr disc or wound between salt windows, can provide a screening technique for the presence or absence of certain major components through their characteristic absorptions. The technique also provides a means of determining the ratios of the proportions of two or more known components in a coating formulation. FTIR can also provide very precise analysis of sovent extracts of the fibres, since the interfering glass absorptions are then removed. Using IRS techniques, FTIR is also sufficiently sensitive to characterize individual peaks in a liquid chromatogram of the extract, making analysis of the minor components of the coating possible.

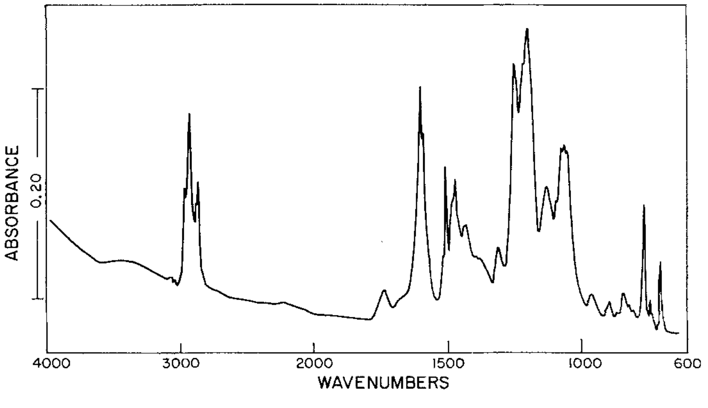

Figure 5 IRS spectrum of selected LC fraction after removal of solvent.

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Early work on rapidly solidified uranium

Rapid solidification is receiving considerable attention as a means of obtaining novel microstructures in metals and increasing the options available in alloy compositions [1]. Notably, rapid solidification can produce extremely fine grain structures and amorphous materials (glassy metals). The widely recognized value of rapid solidification prompts this summary of work carried out in the early 1960's on the application of this approach for the search for novel structures in uranium. The original report on this work [2] was classified and first became widely available in 1975.

This work was undertaken early in the development of the rotating electrode process (REP), which is now well established for the preparation of spherical powders of a wide range of metallic compositions [3, 4]. This method is based on the ejection of molten droplets from an electrode rotating rapidly while being arc-melted. Freezing of the droplets in flight yields spherical powder. From the outset, it was recognized that interception of a molten droplet by a solid surface effects more rapid dissipation of the heat of solidification. The flattened droplet can acquire a more refined structure as a result of the accelerated solidification. Applications of the process to other metals are cited in the annotated bibliography of Jones and Suryanarayana [5].

The effect of impingement of molten uranium droplets on solid copper was explored for its effect on the microstructure of the particulates collected and designated as "splat". The techniques developed were primarily concerned with (1) most effective cooling by the copper collector and (2) removal and recovery of individual splats from the collector so that succeeding droplets would impinge on a bare cold copper surface rather than build up on a preceding splat. Features incorporated to deal with these concerns included the following:

(1) The $\frac{1}{2}$-inch thick copper collector was cooled with helium pre-cooled by liquid nitrogen. This collector rotated at 1750 rpm in a direction to move the deposit away from the melting region of the rotating electrode.

(2) Hollow unalloyed uranium electrodes (2-inch o.d. by 1 5/8-inch i.d.) were rotated at 7000 rpm. The current was turned on for 5 to 10 sec bursts, between which the collector was given the opportunity to recover its cooling capability and bare surface.

Optical metallography of splat prepared in this way showed it to have a mixture of very fine grains (below 10 μm) and a structure that was more difficult to resolve. It was then described as "acicular" and approximated what would now be called "microcrystalline". No attempt was made to estimate the cooling rate. Test samples were heated

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