Investigation of the interphase of a silane-finished glass fibre/vinylester resin using a microscopic *FT*i.r. spectrometer

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The vinylester resin around a silane-finished glass fibre was measured using a microscopic *FT*i.r. spectrometer. It is argued that the silane affected the curing process of the vinylester resin at a great distance compared to the thickness of the silane interphase.

(Keywords: glass fibre; silane coupling agent; vinylester resin; *FT* i.r.; interphase)

It is well known that the mechanical properties of glass-fibre-reinforced composites are influenced by the adhesive property of the glass fibre/resin matrix interface. A silane coupling agent is widely used as an adhesive between the glass fibre and resin[1]. The authors reported previously that reduction in the fracture toughness of the composite was caused by an excessive amount of methacryl silane, which made the vinylester resin brittle[2]. The interlaminar fracture behaviour and toughness of the composite specimen were influenced by washing in methanol solvent. It was suggested that the resin region around the glass fibre/resin interface was affected by the silane adsorbed on the glass fibre and was defined as an interphase[3]. In order to investigate the resin region affected by the silane adsorbed on the glass fibre, the vicinity of the glass fibre of a glass fibre strand embedded in resin for a model of the glass-fibre-reinforced composite was measured using a microscopic Fourier transform infra-red (*FT*i.r.) spectrometer. The goal of this research was to understand the effect of the silane around the glass fibre on the vinylester resin curing process of the composite.

The glass fibre strand consisted of 400 glass fibres, each 9 μm in diameter. The size of the glass fibre strand was 90 μm × 650 μm. The coupling agent used was γ-methacryloxypropyltrimethoxysilane (methacryl silane). The methacryl silane has an organic functional group which can react with the double bond of the vinylester resin matrix. Aqueous solutions of the methacryl silane were acidified with acetic acid at pH 4.0. Glass fibre strands were dipped into the silane aqueous solutions of 1 wt% methacryl silane and then squeezed by squeeze rolls and dried at 110°C for 10 min. Vinylester resin with 43 wt% styrene monomer for a matrix was mixed with 0.7 wt% methylethylketoneperoxide. The chemical formula of the vinylester resin is shown in *Formula 1*.

The mixture was poured into a mould holding a glass fibre strand under tension, and was cured at 80°C for 2 h, then at 150°C for 3 h. The glass fibre strand/resin specimen was cut into pieces 5 μm in thickness using a microtome. A slice of the specimen was inserted between diamond cells and was set on a stage of a microscopic *FT*i.r. spectrometer with mercury cadmium telluride (MCT) detector (Perkin-Elmer PE-1600). A mask window (20 μm × 40 μm) was set across the i.r. path of the spectrometer through the diamond cells. The position of the mask window was shifted by 20 μm steps on a slice of specimen after every microscopic *FT*i.r. measurement. The transmission i.r. spectrum and the number of glass fibres were measured in each mask window. The spectra were recorded at a resolution of 4 cm^{-1} with a total of 128 scans.

The peak at 1606 cm^{-1} was used as a reference peak to obtain the difference spectra between the spectrum at every 20 μm and the spectrum at the furthest position from the glass fibre, because the methacryl silane did not show a peak at 1606 cm^{-1} due to the benzene ring of the resin. *Figure 1* shows a three-dimensional plot of the difference spectra on the basis of 1606 cm^{-1} in the region 1800–1300 cm^{-1} as a function of distance. The microscopic position range was divided into glass fibre field and resin matrix field as shown in *Figure 1*. The glass fibre field indicates that glass fibres and resin were observed by eye through the mask window when the specimen was measured using a microscopic *FT*i.r. spectrometer. The resin matrix field indicates that only resin was observed through the mask window.

The peak at 1450 cm^{-1} due to the methylene group, and at 1500 cm^{-1} due to the benzene ring of the resin which reacted with the methacryl silane, increases as a function of the distance from the resin matrix field. There was a gradual change of the peak height at 1450 and 1500 cm^{-1} in the difference spectra in *Figure 1*. The vinylester resin was cured in the process of crosslinking. It is supposed that the silane around the glass fibre influenced the curing process of the vinylester resin.

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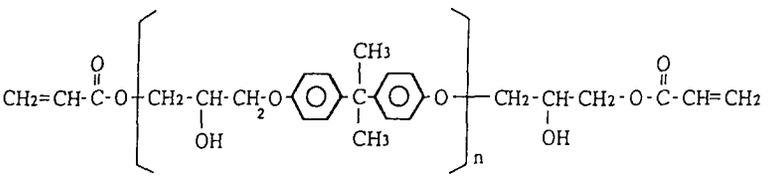

Formula 1

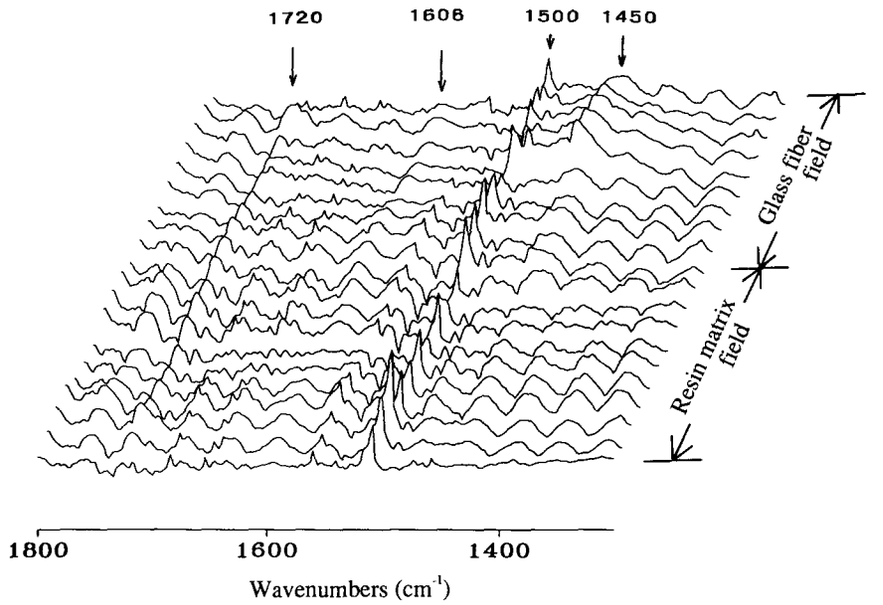

Figure 1 Three-dimensional plot of the difference spectra between the spectrum at every 20 μm and the spectrum at the furthest position from the glass fibre

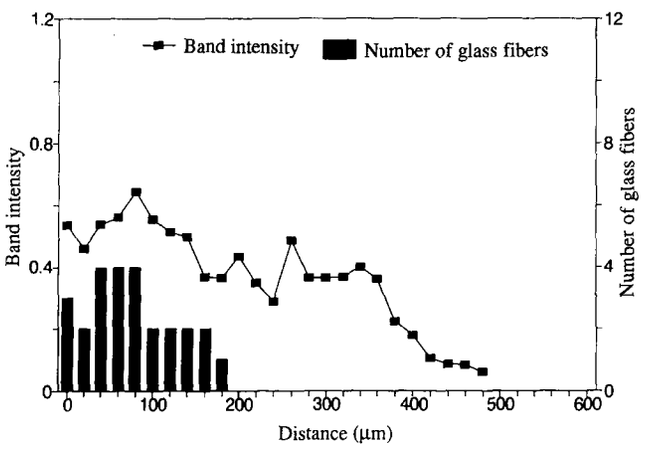

Figure 2 Band intensity and numbers of glass fibres observed in a mask window as a function of distance from the glass fibre to the matrix resin field

On the other hand, the peak at around 1720 cm^{-1} changed irregularly and was probably due to the carbonyl function of the methacryl silane, because all spectra in *Figure 1* were subtracted from the spectrum of the only vinylester resin.

The band intensity at 1430–1462 cm^{-1} due to the methylene group was chosen to avoid interference with the other band intensities in comparison with the peak at 1500 cm^{-1} due to the benzene ring of the resin. *Figure 2* shows the band intensity at 1430–1462 cm^{-1}, of the difference spectra and the number of glass fibres observed in a mask window as a function of distance from the glass fibre field to the matrix resin field, as shown in *Figure 1*. The band intensity showed a constant value at about 0.4 and drastically decreased over 200 μm from the glass fibre field. It was suggested that the reaction of the methacryl silane with the resin affected the curing process around the glass fibre in a range of 200 μm from the glass fibre field, according to *Figure 2*. It was possible that the property of the resin around the glass fibre strand as well as within the strand was changed.

The authors proved that glass fibres finished with 1 wt% methacryl silane had physisorbed silane which could be removed by washing in methanol solvent[3]. This physisorbed silane could migrate into vinylester resin with styrene monomer during fabrication of the glass fibre/resin specimen. The irregular peak intensity change at around 1720 cm^{-1}, as shown in *Figure 1*, indicates that the physisorbed silane migrated into the matrix resin from glass fibres. The distribution of the physisorbed silane in resin matrix around the glass fibre is not homogeneous.

We concluded that the change in chemical structure of the vinylester resin around silane-finished glass fibres was measured using a microscopic *FT*i.r. spectrometer and the methacryl silane affected the curing process of the vinylester resin at a great distance compared to the thickness of the silane interphase[3].

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