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Preparation and properties of mid-infrared glass fibres and poly (chlorotrifluoroethylene) composites

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Fluorophosphate-glass-fibre-reinforced poly(chlorotrifluoroethylene) (PCTFE) composites with a transmittance of 80% from 0.4 to 3.7 μm were prepared. The transparent PCTFE composites transmit light to longer wavelengths and have a better chemical resistance to organic solvents (60–70% transmittance after immersing in *p*-xylene for 24 h) than transparent poly(methyl methacrylate) composites do. The tensile strength of the PCTFE increased by about 20% when it contained 1.1 vol% of unidirectional fluorophosphate glass fibre. The method for preparing the glass fibres and the composites is also described.

1. Introduction

Glass-fibre-reinforced polymer composites will be transparent when the refractive index of the fibre closely matches that of the polymer matrix [1, 2]. Optically transparent composites using borosilicate glass fibres and poly(methyl methacrylate) (PMMA) as the polymer matrix have been successfully prepared [3–5]. The flexural strength of the PMMA composite increases by two to three times without a significant loss of the transparency of the PMMA [3]. However, owing to C–H and C=O functional groups in the PMMA, which have absorption peaks in the infrared (IR) region, the composite transmits light only to 1.6 μm. A polymer will transmit to longer wavelengths if the C–H is replaced by a C–F or C–Cl such as in the case for poly(tetrafluoroethylene) (PTFE) and poly(chlorotrifluoroethylene) (PCTFE).

PCTFE can transmit up to about 4 μm which makes it transparent to several windows in the IR region through the Earth's atmosphere, e.g., 1.6–1.82 μm, 2.0–2.3 μm and 3.5–3.9 μm [6]. PCTFE has a working temperature range from − 200 to 200 °C and a chemical resistance to mineral acid and organic solvents comparable with Teflon [7]. Like Teflon, PCTFE is normally opaque owing to its high crystallinity (about 58%) but it can be thermally quenched to a transparent film whose crystallinity is about 40% [8]. PCTFE has a refractive index ($n_D = 1.425$) which is considerably lower than the refractive index of the silicate glass fibres ($n_D = 1.46$–1.7) commonly used to reinforce polymers. Glass fibres used to strengthen a PCTFE matrix must have a refractive index that closely matches that of PCTFE ($n_D = 1.425$) to achieve high transparency. Two other qualities necessary for the glass are firstly it should be transparent at least to 4 μm and secondly it must be capable of being pulled into fibres of the desired size. There are two types of glass with a high fluorine content that have an acceptable refractive index: BeF_2-containing glass; fluorophosphate glasses with a high fluorine (or low oxygen) content. BeF_2 glasses were excluded owing to their high toxicity. A fluorophosphate glass fibre was selected and produced to make transparent PCTFE composites.

The purpose of the present study was to develop a continuous fibre-reinforced composite which is transparent from the visible to the mid-IR. The preparation method together with the optical and mechanical properties of the fibre and transparent composites are reported. Comparison is made between PCTFE and PMMA composites. Factors affecting the transmittance of the composites are discussed.

2. Experimental procedure

2.1. Glass fibres

A commercial fluorophosphate glasses whose refractive index ($n_D = 1.437$) was used to pull fibres from the melt (FK54; Schott Glass Technologies Inc.). Fluorophosphate fibres are difficult to pull because of their small working temperature range (where viscosity is suitable for fibre pulling) and a high crystallization tendency. Glass fibres were successfully pulled from the melt using an electrically heated one-hole platinum bushing. Glass blocks (0.75 cm × 1.0 cm × 3.0 cm) were cut from a large glass rod of FK54 glass and placed in the platinum bushing where it was remelted at 540 °C. A glass fibre pulled at 3.0 $m\,s^{-1}$ had an average diameter of 27 ± 4 μm and a tensile strength of 335 ± 55 MPa.

2.2. Preparation of composites

Prepregs were prepared by fastening a PCTFE film (Kel-F81, 3M; Alcar 22C, Allied Signal) to a drum and winding the glass fibres on the rotating drum. No coupling agent was applied to the glass fibre. Several

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layers (two to four) of prepreg were stacked together, with the fibre oriented unidirectionally, in a chrome-plated metal mould. The mould containing the sample was placed in a hot press without applying pressure and heated to 280 °C for 1 h. This heating raised the pressure to 2.1 MPa. The composite was then removed to cool to room temperature. During the slow cooling at about 0.25°C s^{-1}, the PCTFE partially crystallized and its transparency is decreased in both the visible and the IR region. The composite was reheated to 230 °C to melt the PCTFE crystals and then quenched at about 22 °C s^{-1} to minimize the crystallization of the PCTFE. The fibre content of the PCTFE composite was determined by heating the composite at 500 °C for 1 h to destroy the PCTFE, leaving only the glass fibre which was weighed. The density used to calculate the fibre volume fraction was 3.19 [9] and 2.13 g cm^{-3} [10] for FK54 glass fibre and PCTFE, respectively.

2.3. Property measurement

The refractive index of the glass was measured by a maximum transmission method similar to that [11] used to determine the dispersion curve of a glass. When measuring the dispersion of a glass by this method, glass fibres were put into a cell filled with an index liquid (Index liquid, Cargile Laboratories Inc.) [12] with a refractive index which is about 0.004 (n_D) higher than that of the glass at 25 °C. The transmittance was measured with a spectrophotometer equipped with a heating chamber so that the cell temperature could be changed as a function of wavelength at different temperatures to obtain transmittance versus wavelength curves. The wavelength where the transmission was a maximum (where the average refractive index of the glass fibres equals that of the liquid) was recorded at each temperature. The refractive index (RI) of the liquid at any wavelength and temperature can be calculated if the coefficients for the Cauchy equation ($\mathrm{RI}(\lambda) = A + B\lambda^{-2} + C\lambda^{-4}$) and the temperature coefficient for the refractive index are known [12]; this assumes that the shape of the dispersion curve of the index liquid does not change over a temperature range of less than 10 °C. Since the temperature coefficient for the refractive index of glass (about $10^{-6}\,°\mathrm{C}^{-1}$ is two orders of magnitude smaller than that of the index liquid (about $10^{-4}\,°\mathrm{C}^{-1}$), the relatively small change in the index of the glass can be ignored over the small temperature range used for these measurements.

The crystallinity of the PCTFE was determined by X-ray diffraction (Scintag model XDS-2000; Cu radiation). The diffraction curve is the convolution of four diffraction peaks, the integral intensities of three crystalline planes, $I_{(10.1)}$, $I_{(10.2)}$ and $I_{(10.3)}$, and the integral intensity of the amorphous phase, $I_{(\mathrm{amorp})}$. The crystallinity, cry(%), of the PCTFE was calculated from the following equation using the deconvoluted peak intensity:

$$\mathrm{cry}(\%) = [(I_{(10.1)} + I_{(10.2)}) + I_{(10.3)}] \times [I_{(10.1)} + I_{(10.2)} + I_{(10.3)} + I_{(\mathrm{amorp})}] \qquad (1)$$

The transmittance of the composites of 25 °C was measured with a photospectrometer (Beckman model 26) between 0.2 and 0.9 μm and by Fourier transform IR spectroscopy (Perkin–Elmer model 1760-X) from 1.5 to 22.5 μm. The solvent resistance for transparent composites was measured in terms of optical transmission. The effect of solvent on the optical transmission of the composite was studied by immersing a composite in solvents such as water,ethanol and *p*-xylene for 24 h at 25 °C and measuring the optical transmission between 200 and 900 nm at 25 °C. The tensile yield strength of the composites was measured at a cross-head speed of 0.5 mm min^{-1} in a direction parallel to the glass fibre. The specimen size was 10 mm × 0.9 mm × 50 mm.

3. Results and discussion

Fig. 1 shows the dispersion curves of the as-received FK54 bulk glass and FK54 glass fibres (27 μm in diameter). The refractive index of the glass fibre is slightly less than that of bulk glass ($\Delta n \approx 0.003$–0.004) because the density of the fibre is less owing to the rapid cooling. The difference in refractive index, n_D, between the glass fibre and the PCTFE is about 0.008.

The diameter of glass fibre pulled from a melt can be predicted [13] from

$$d = 2\left(\frac{m}{3.14 v \rho}\right)^{1/2} \qquad (2)$$

where m (g s^{-1}) is the mass flow rate, ρ (g cm^{-3}) is the density of the glass and v (cm s^{-1}) is the velocity at which the fibre is pulled. Fig. 2 shows that the glass fibre diameter was close to the calculated fibre diameter for a mass flow rate of 0.26 g min^{-1} (solid curve). Fig. 3 shows how the fibre strength increased with decreasing fibre diameter which has been observed for many types of glass fibre.

It is well known that PCTFE easily crystallizes and this reduces not only its transmittance at optical

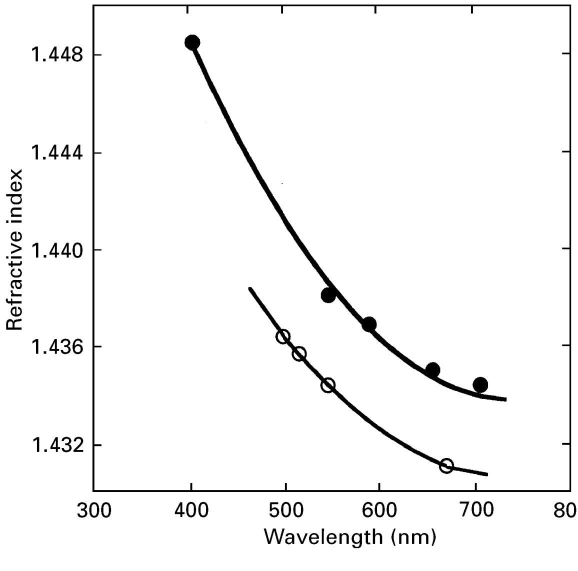

Figure 1 Dispersion curves for fluorophosphate glass (FK-54) in bulk (●) and fibre (○) form (27 μm).

wavelengths but also its transmittance at IR wavelengths as shown in Fig. 4. The transmittance at (589 nm) of a PCTFE 0.5 mm thick (type A) is 90% which has 40% crystallinity. The transmittance reduces to only 50% when it has 60% crystallinity (type B). The transmission of the type-A PCTFE is still about 20% higher than that of type-B PCTFE at a wavelength of 4.0 μm. The transmission of the type-B PCTFE increases with increasing wavelength between 1.38 and 3 μm while the transmission of type-A PCTFE is constant. In a partially crystallized polymer such as PCTFE, the transmission is inversely proportional to the scattering coefficient of the crystal in an exponential manner. The increased transmission with increasing wavelength arises because the scattering efficiency of the crystal size, d, becomes smaller when its size parameter, $x(=\pi d/\lambda)$, decreases with increasing wavelength, λ [14]. The X-ray diffraction pattern in Fig. 5 shows the development of (10.1), (10.2) and (10.3) crystalline planes with decreasing cooling rate. Faster cooling rates decreased the crystallinity of the PCTFE, which in turn increased the transparency (measured at 589 nm) as shown in Fig. 6. The crystallinity also decreased as the temperature at which quenching (cooling rate 22 °C s^{-1}) began was increased. The crystallinity increased when the quenching temperature was lower than 200 °C, as indicated in Fig. 7. This suggests that the minimum quenching temperature should be above 200 °C to achieve high transparency. However, higher quenching temperatures are not favoured because a higher quenching temperature is likely to induce larger thermal stresses

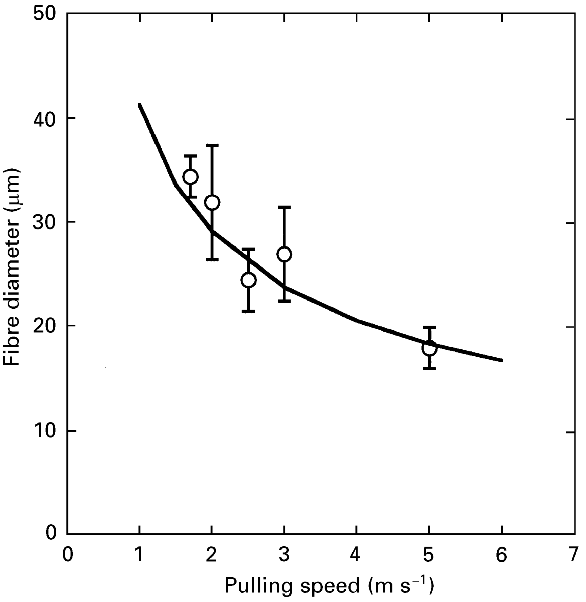

Figure 2 Diameter of fluorophosphate glass fibre as a function of pulling speed at 540 °C. (—), calculated curve; (○), measured data.

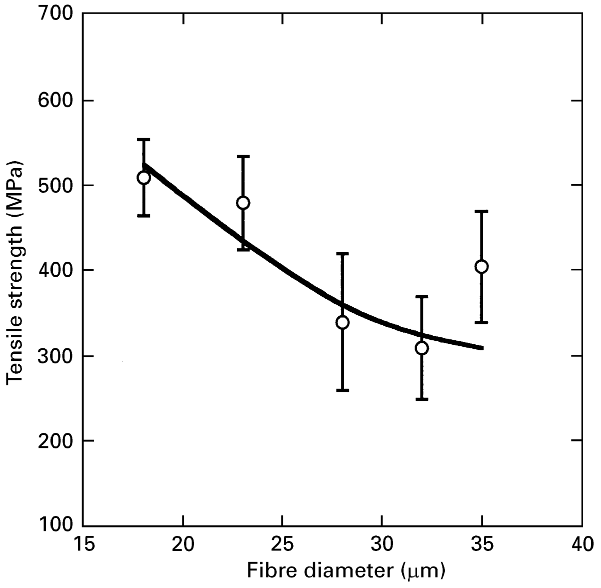

Figure 3 Tensile strength of fluorophosphate glass fibres (seven to ten fibres were tested for each data point).

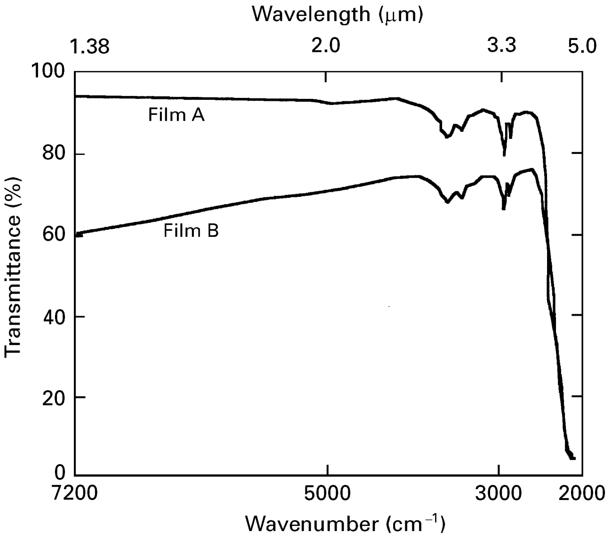

Figure 4 IR spectra of type A (cry% ≈ 40%) and type B (cry% ≈ 60%) PCTFE film (0.55 mm thick).

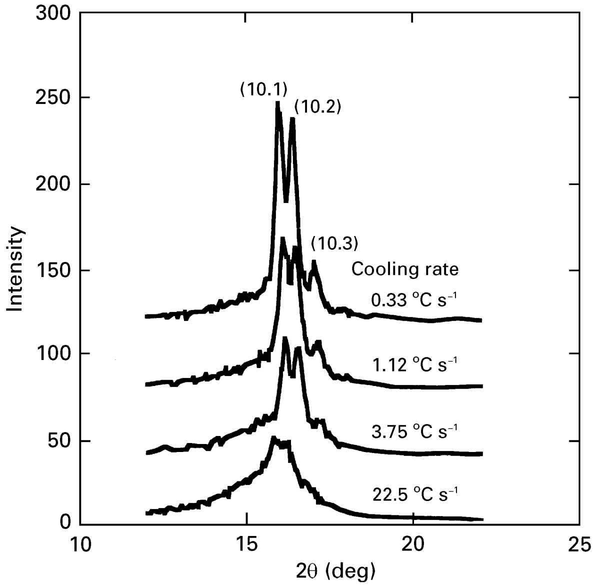

Figure 5 X-ray diffraction pattern for PCTFE quenched at different rates.

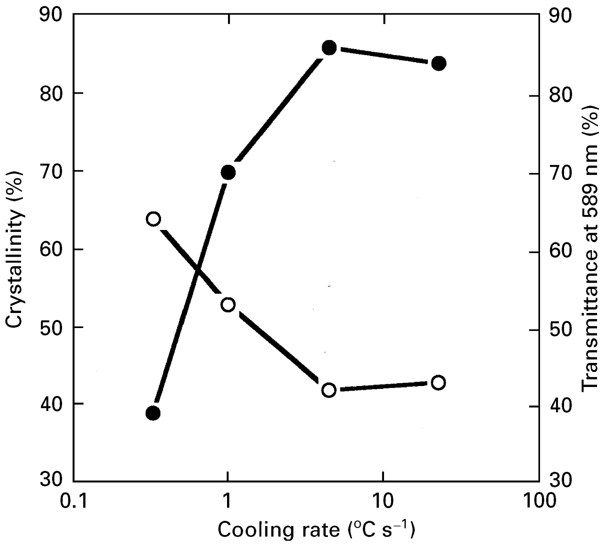

Figure 6 Percentages of crystallinity (○) and transmittance (●) at 589nm of PCTFE film (1 mm) as functions of cooling rate when cooled from 220 °C.

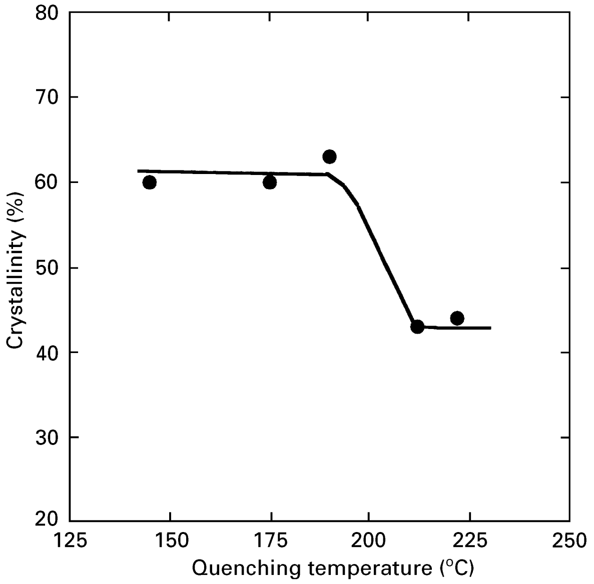

Figure 7 Percentage of crystallinity of PCTFE film quenched from different temperatures at a rate of 22.5 °C s^{-1}.

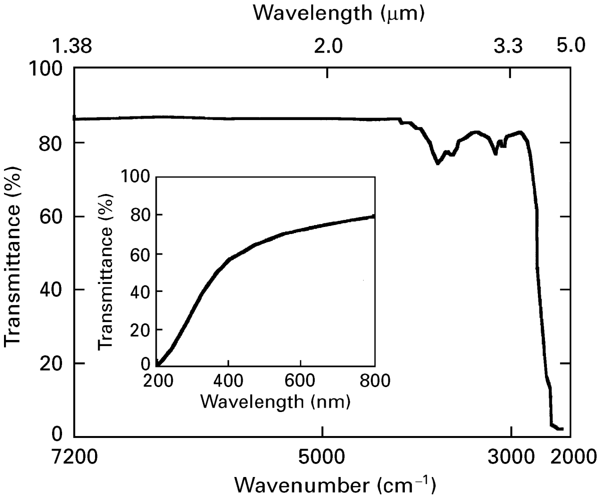

Figure 8 UV–visible and IR spectra for a fluorophosphate glass fibre–PCTFE composite (1.1 vol% fibre; 0.92 mm thick).

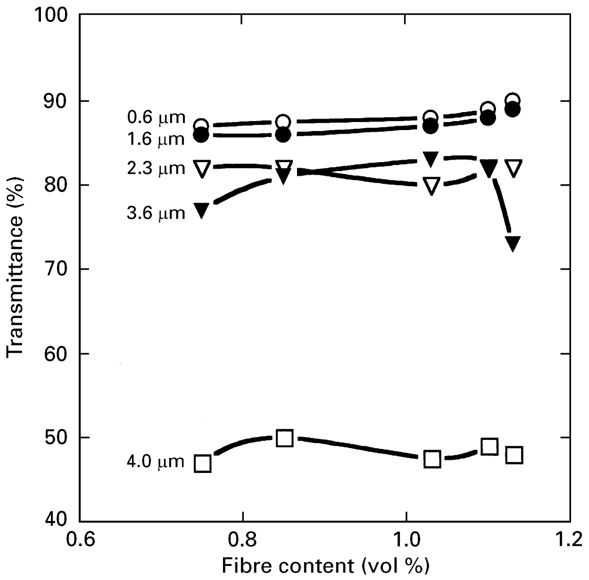

Figure 9 Percentage transmittance at selected wavelengths as a function of glass fibre content for a fluorophosphate glass fibre–PCTFE composite (1.1 vol% fibre; 0.92 mm thick).

which could weaken the mechanical strength of a composite.

A typical ultraviolet (UV)–visible–IR spectrum for a PCTFE composite containing about 1.1 vol% fibre and 0.92 mm thick is shown in Fig. 8. The cut-off is at 0.2 μm (200 nm). The transmittance for different windows in the atmosphere is 90% at 1.6 μm (6250 cm^{-1}), 90% at 2.3 μm at (4348 cm^{-1}) and 84% at 3.5–3.7 μm (2703–2857 cm^{-1}). The IR cut-off at about 4 μm (2500 cm^{-1}) is due to the absorption of the polymer matrix. The transmittance of the unidirectional composites did not change significantly from 3.5 μm to 3.9 μm (from 2564 to 2857 cm^{-1}) over the range of volume percentage of fibre used in the composite as shown in Fig. 9. High transmittance (85–88% transmittance) from 1.6 to 3.7 μm (from 6250 to 2703 cm^{-1}) was observed for composites (0.5 mm thick) containing 0–1.2 vol% glass fibre. The transmittance decreased to 45–50% at 4 μm (2500 cm^{-1}). The most important factor affecting the optical quality of a transparent composite is the extent to which the fibre is wetted by the polymer. For poor wetting, the refraction and reflection of a light ray hitting the fibre are large because of the mismatch in the refractive indices of the polymer ($n_D = 1.425$) or fibre ($n_D = 1.433$) and the air gaps ($n_D = 1.00$) formed where the polymer does not wet (completely contact) the glass fibre. The composite becomes opaque (loss of transparency) if the fibres are not completely wetted by the polymer matrix. Fig. 10 compares the transmittance for a composite where there is poor wetting and good wetting (0.7 vol%; 0.7 mm thick). The transmittance between

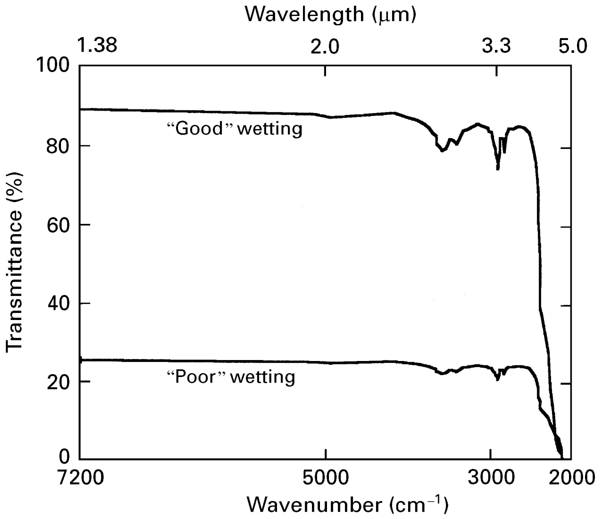

Figure 10 IR spectra for a fluorophosphate glass fibre–PCTFE composite (0.7 vol% fibre; 0.7 mm thick) taken in the poorly wetted (fibre-matrix) region and well-wetted region.

1.5 and 3.5 μm (6667 and 2857 cm^{-1}) decreased from 87 to 27% transmittance as a result of poor wetting.

Fig. 11 shows that the visible transmittance (350–900 nm) did not change more than 8% for the PCTFE composite after immersion in water, ethanol and *p*-xylene for 24 h at 25 °C. However, a 20% reduction in transmittance occurred in the UV (200–350 nm) after the composite was immersed in *p*-xylene for 24 h at 25 °C. The transmittance decreased from 90% to 70% for a PMMA composite after immersion in water and ethanol for 24 h at 25 °C and the transmittance was completely lost after its immersion in the *p*-xylene for 24 h at 25 °C, as shown in Fig. 11. The solvent attack for the PMMA composite caused a deterioration of the surface smoothness and debonding at the fibre–matrix interface because of solvent penetration along this interface. This debonding leads to light scattering which is responsible for the reduction in transmittance. The effect is especially noticeable for *p*-xylene.

The composite did not break during tensile testing but yield occurred as the fibres failed. The tensile yield strength of the composites decreased initially and then increased with increasing fibre content in a manner similar to that predicted from the simple rule of mixtures (see the solid line in Fig. 12. The initial decrease in the strength of the low-fibre-content (i.e. low-V_f) region is observed in a composite system when the failure strain of the matrix is higher than that of the reinforcing fibres. When fibre fracture occurs in low-V_f laminae, the extra load on the matrix is not sufficient to fracture the matrix. However, since the effective cross-section of the matrix is reduced by the presence of the "holes" at the fibre ends the load-carrying capacity is less than the strength of matrix [15]. All specimens tested in the comparison contained 40% crystalline PCTFE as the matrix. The composite containing 4.9 vol% glass fibre had a tensile yield strength of 39 MPa, which was 1.44 times that of pure PCTFE (27 MPa).

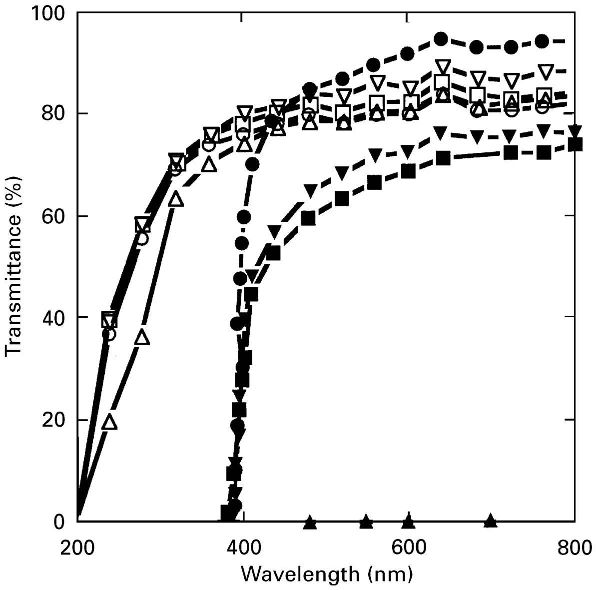

Figure 11 Comparison of the optical transmittance of PCTFE (1.1 vol% fibre; 0.92 mm thick) (○, ▽, □, △) and PMMA (5.2 vol% fibre; 0.6 mm thick) (●, ▼, ■, ▲) composites after immersion in different solvents at 25 °C for 24 h. (○), (●), control; (▽), (▼), water; (□), (■), ethanol; (△), (▲), *p*-xylene.

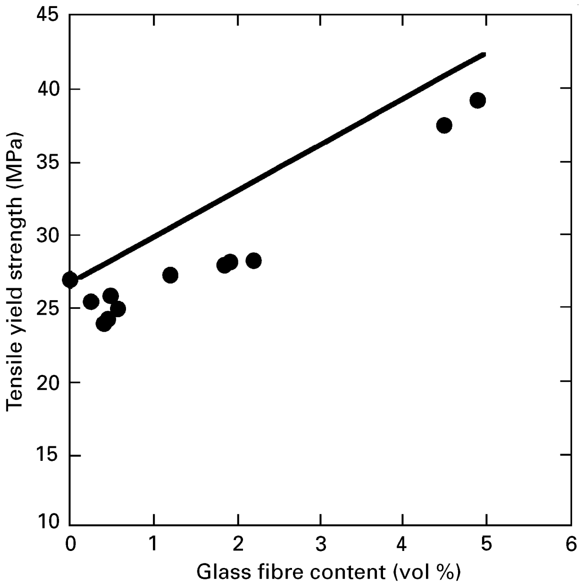

Figure 12 Calculated (—) and measured (●) tensile yield strength of unidirectional fluorophosphate glass fibre–PCTFE composites.

Because of the transparency of the composite, it was possible to measure the critical length of the broken fibres after the tensile testing. Fibre breakage followed by gap formation and debonding which extended a constant distance along the fibre axis made the fibre visible within this region. The fibre became invisible again where the gap disappeared. Fig. 13 shows that the fibres broke into segments of nearly equal length, L_C. The interfacial bond strength, τ, was estimated from [16]

$$\tau = \frac{\sigma R}{L_C} \qquad (3)$$

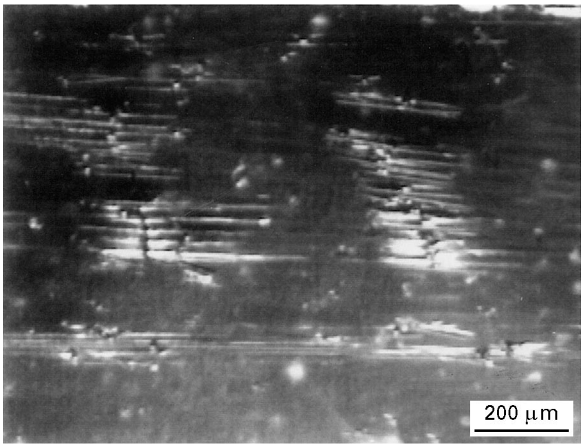

Figure 13 Fibre breakage and debonding within a PCTFE composite after tensile failure.

where σ is the tensile strength of the glass fibre and R is the fibre radius. The mean interfacial bond strength was calculated as 12.6 ± 2.9 MPa using the measured mean critical length of 313 µm.

4. Conclusion

Fluorophosphate glass fibres with a diameter of 27 µm and a tensile strength of 335 MPa were successfully pulled directly from the melt and used to reinforce a PCTFE matrix. A visible–IR–transparent composite containing 1.1 vol% fluorophosphate glass fibres has a tensile yield strength of 32 MPa and a transmittance of 85% between 0.4 and 3.7 µm and 45% at 4.0 µm. The solvent resistance of the PCTFE composites was superior to that for PMMA composites especially for solvents such as *p*-xylene. After being immersed in the *p*-xylene for 24 h at 25 °C, the PMMA composite suffered a complete loss of transparency while the PCTFE composite had a transmittance from 60 to 70% throughout the visible.

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