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Temperature-dependent mechanical behaviour of PI and PES resins used as matrices for short-fibre reinforced laminates

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Composite materials have increasing success in engineering application. To extend their usage to higher temperatures, specially adapted polymer resins must be used. Polyimide (PI) and polyethersulphone (PES) are among the candidate materials for service at high temperatures. The mechanical behaviour of the PI and PES matrix systems under different temperatures, the resulting properties and the damage and failure, under static as well as fatigue loading, are investigated in the present study together with unidirectional laminates of aligned short fibres in the 0° or 90° direction. The room-temperature results are compared to a conventional epoxy resin.

1. Introduction

The application of advanced polymer matrix composites is at present mainly limited to temperature ranges up to about 120° C. This is because the epoxy matrix materials used at present have relatively high strength and stiffness, low creep and, in general, good chemical resistance up to intermediate temperatures. However, the desired high stiffness retention at high temperatures is inherently linked to poor fracture resistance and what is the main limitation, epoxy matrices are adversely affected by moisture absorption, which has a plasticizing effect and limits their long-term structural use to temperatures below about 100° C. Only dry epoxies can be used up to 180° C [1].

To extend the structural application of advanced composites to higher service temperatures, specially adapted polymer resins have to be used. Among the candidate material for service at high temperatures above 180° C when dry and 120° C when under humid conditions, are the polyimide (PI) resin systems. Polyimides appear as both thermosets and thermoplastics.

While the application of thermoplastic polyimides is only infrequently reported in technical reports, the bismaleimide-based thermoset polyimides became rather popular, because they are easy to process and comparatively low in cost. The bismaleimide-based resins have the lowest service temperature of the polyimides, but still a good high-temperature property retention is achievable [1–4]. Bismaleimides absorb moisture to a high degree, but because of their extremely high glass transition temperature, T_g, in the dry state, they still have a high T_g when saturated with water. Therefore, they are applicable even in the hot wet environment up to 250° C [2–4].

One other possible resin system for high temperature use in composites is the thermoplast polyethersulphone (PES). This material combines good processibility and a heat resistance up to 200° C. However, it is not chemically resistant against concentrated oxidic acids, some organic solvents and chlorhydrocarbons, and as the main drawback, its compatibility with carbon fibre seems to be questionable.

In recent publications the fatigue properties of aligned short carbon-fibre reinforced composites with epoxy resins [5], and polyimide and polyethersulphone matrix resins [6] were reported. Damage development and damage mechanisms were investigated for laminates with different stacking sequences in tests at room temperature only. It is the objective of the present paper, being a part of a more comprehensive study [7], to report on the investigations of the mechanical behaviour of neat PI and PES matrix systems under different temperatures, the resulting properties, and the damage and failure under static as well as fatigue loading. In addition, unidirectional laminates, with an alignment of fibres in the 0° or 90° direction only, were investigated. The room-temperature results of the PES and PI laminates and the neat resins are compared with data obtained from a conventional epoxy resin system.

2. Experimental procedure

Tests were carried out with two different resin systems which can tolerate, in service, higher temperatures up

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to 250° C, the first, a bismaleimide based polyimide (PI), type H795E (Technochemie Dossenheim, West Germany), and the second, the thermoplast polyethersulphone (PES) (ICI). The neat resin plates were produced by the manufacturers. The unidirectional laminates using Graphil XA-S fibres, with an average length 3 mm, were made by the Zentrallabor of MBB, Munich. The fibre alignment was achieved by the vacuum drum filter technique [8], reaching a fibre volume fraction between 50 and 55%. The unidirectional laminates were tested as $[0_8]$- and $[90_8]$-sheet specimens.

Tensile tests were carried out on the neat resins and the unidirectional laminates at three different temperatures: room temperature (RT); 100° C; and 180° C. Fatique tests were performed at room temperature only. For comparison, additional tests were made with the epoxy resin (EP) system (MY720/HT976, Ciba-Geigy). Only tensile tests at RT were performed.

Using sheet specimens (unidirectional laminates: 200 mm × 25 mm, thickness 1.6 mm; neat resins: 150 mm × 10 mm, thickness: 3.4 mm), fatigue experiments were carried out under tension–tension loading with a stress ratio of $R = \sigma_u/\sigma_0 = 0.1$ and a frequency of 10 Hz (σ_0 = upper stress level and σ_u = lower stress level per load cycle). The fracture strength, elongation (using grain gauges), elastic modulus and Poisson's ratio were determined from tensile tests performed with a crosshead speed of 1 mm min^{-1}.

The development of damage was characterized by intensive optical and scanning electron microscopy.

3. Results and discussion

3.1. Behaviour under static loading

The reinforcement of resins with aligned short carbon fibres by applying the vacuum drum filter technique results in a very high degree of fibre orientation, illustrated in Fig. 1a which shows the polished cross-section taken parallel to the fibre direction of a PI $[0_8]$ laminate, whereas locally individual fibres exhibit a high deviation from the main fibre direction. The high degree of alignment is also visible in Fig. 1b showing the polished cross-section perpendicular to the fibre direction. The additional information to be obtained from Figs 1a and b is that the fibre alignment takes place in the form of separated fibre bundles, which can be illustrated, if the matrix material is pyrolysed after curing (Fig. 1c). The alignment of the individual fibre bundles has a deviation of about 2 to 3° from the main fibre direction. The impregnation with a resin was good for the PI and epoxy laminates (compare Figs 1a and b); however, in the case of the PES laminate it was not always satisfactory. Here, some pores were always present in the laminate. An extreme case, not used for the experimental testing, is shown in Fig. 1d.

In Fig. 2a the stress–strain behaviour of the PI, PES and MY720 neat resin systems at RT is shown. The PI resin is at RT the most brittle system (ε_B = 0.71), while PES is comparatively ductile (ε_B = 3.7). In comparison the epoxy resin has a fracture strain of

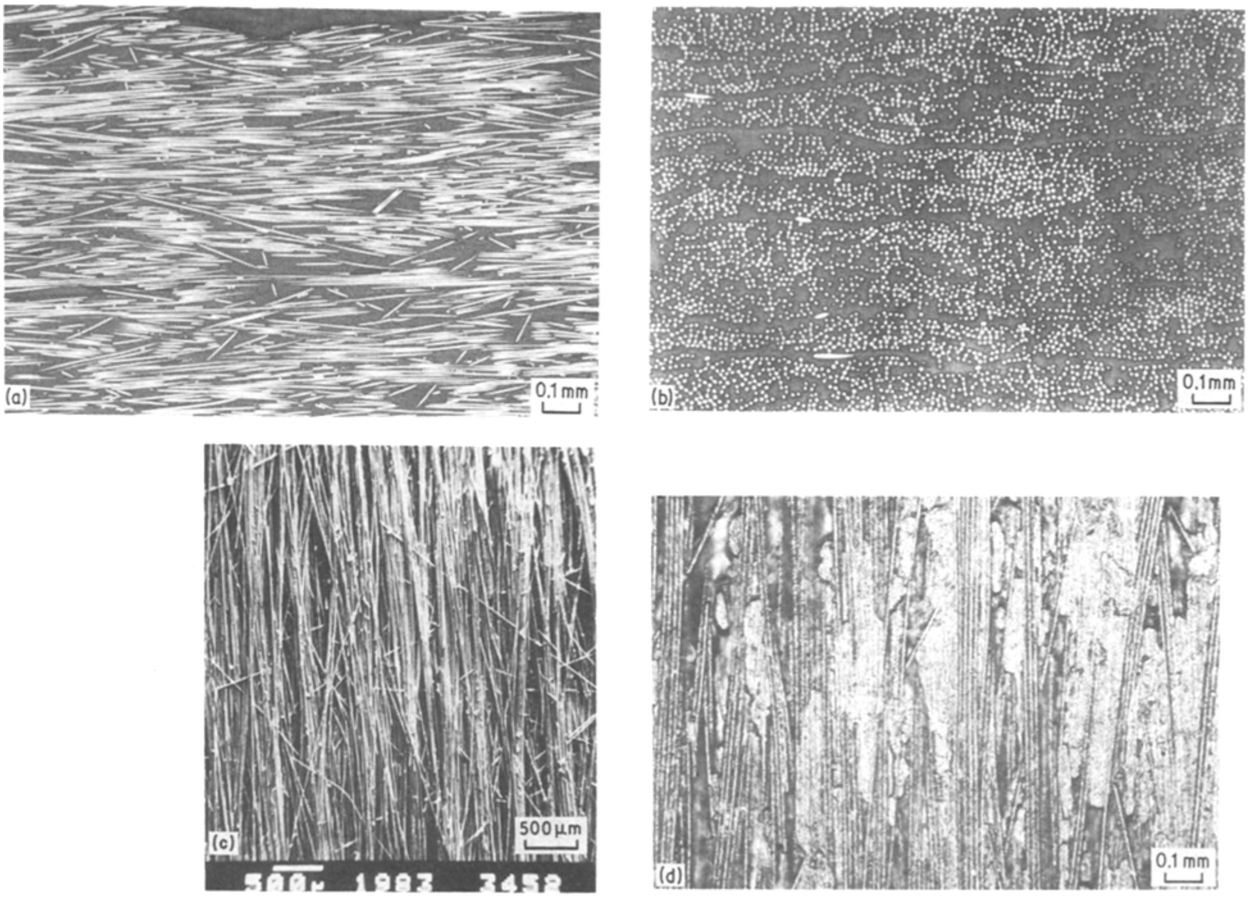


Figure 1 Micrographs of polished cross sections (a) parallel, and (b) perpendicular to the fibre direction, PI $[0_8]$ laminate. (c) Scanning electron micrograph of an unloaded pyrolysed PI $[0_8]$ laminate. (Pyrolysis conditions: 1 h at 680° C.) (d) Surface of a PES $[0_8]$ laminate. Example of bad impregnation with resin. Extreme case not used for experiments.

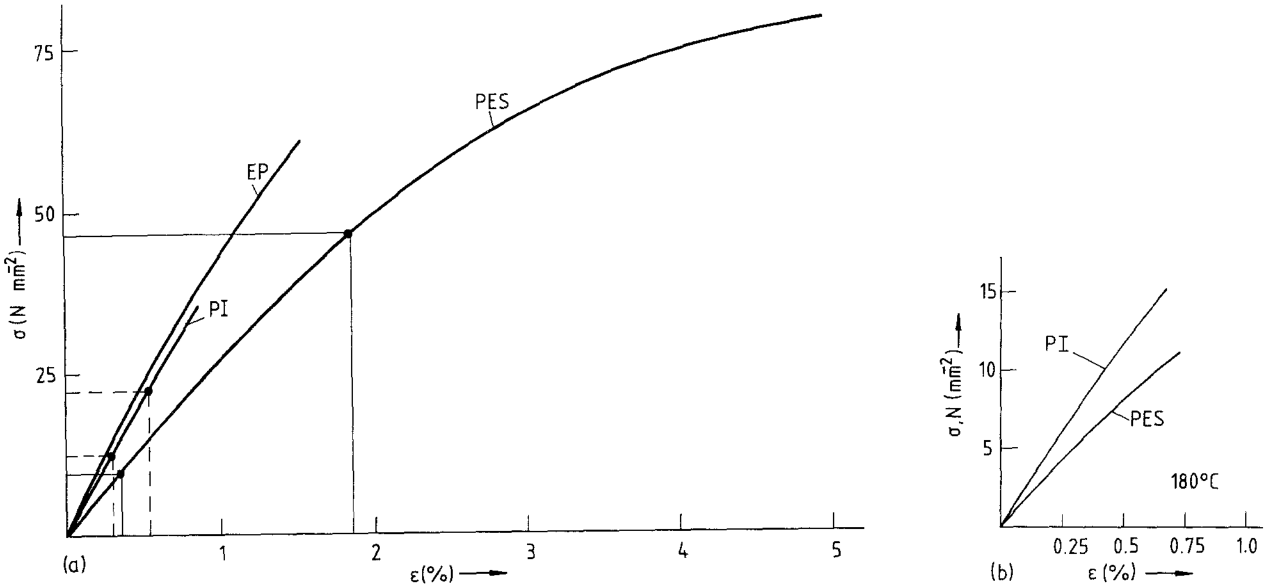
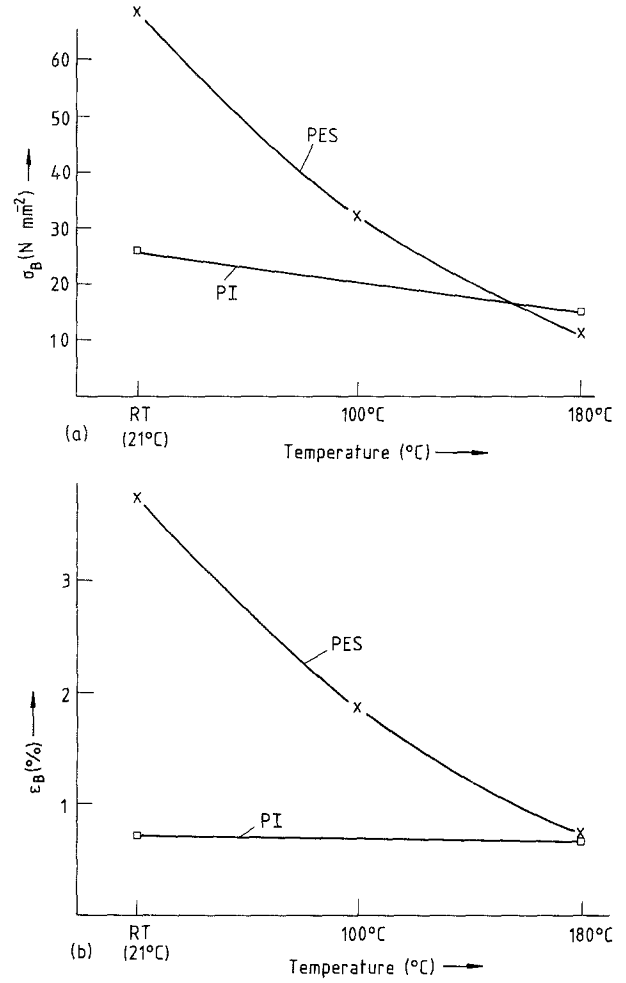


Figure 2 Stress–strain behaviour at (a) RT of the PI, PES and epoxy neat resins, and (b) 180° C of the PI and PES neat resins.

$\varepsilon = 1.8$. Also, the fracture stress, σ_B, is low in PI ($\sigma_B = 26\,\mathrm{N\,mm^{-2}}$) but more than twice that value in the PES system ($\sigma_B = 689\,\mathrm{N\,mm^{-2}}$). The epoxy resin reaches a fracture stress of $\sigma_B = 60\,\mathrm{N\,mm^{-2}}$.

At 180° C the stress–strain behaviour of PI and PES is significantly different. Relative to the RT situation, the fracture stress σ_B, strain to failure, ε_B, and the elastic modulus, decrease drastically (Fig. 2b). If the two different static tensile data are analysed separately, it turns out that the fracture stress in PES is strongly affected by the temperature; increasing test temperature leads to a rapid decrease in the fracture stress, while in PI the decrease in fracture stress is not as severe (Fig. 3a). The variation of the strain to failure is shown in Fig. 3b. The fracture strain of the PI neat resin is only slightly affected by the temperature; however, the PES resin also shows an essential decrease. The elastic modulus (Fig. 3c) in both resin systems also decreases with increasing temperature.

The behaviour mentioned above has an essential influence on the mechanical properties of fibre-reinforced composites. In Fig. 4, the matrix properties are shown for different temperatures in comparison to the tensile test properties of unidirectional composites, tested either in fibre direction [0_8] or perpendicular [90_8] to them. The neat resins have essentially higher fracture stresses than the [90_8] specimen (Fig. 4a). In addition the fracture strain is drastically reduced by reinforcing a resin perpendicular to the loading direction (Fig. 4b). If the RT results of the three different



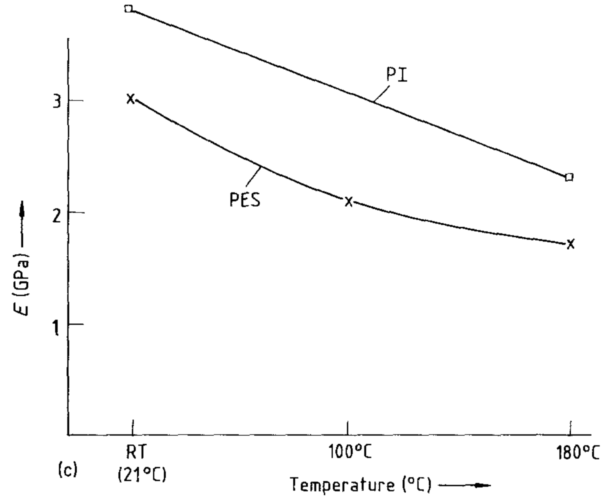


Figure 3 Tensile test results of the PI and PES neat resins obtained at different test temperatures. (a) Fracture stress, σ_B; (b) fracture strain, ε_B; (c) elastic modulus, E.

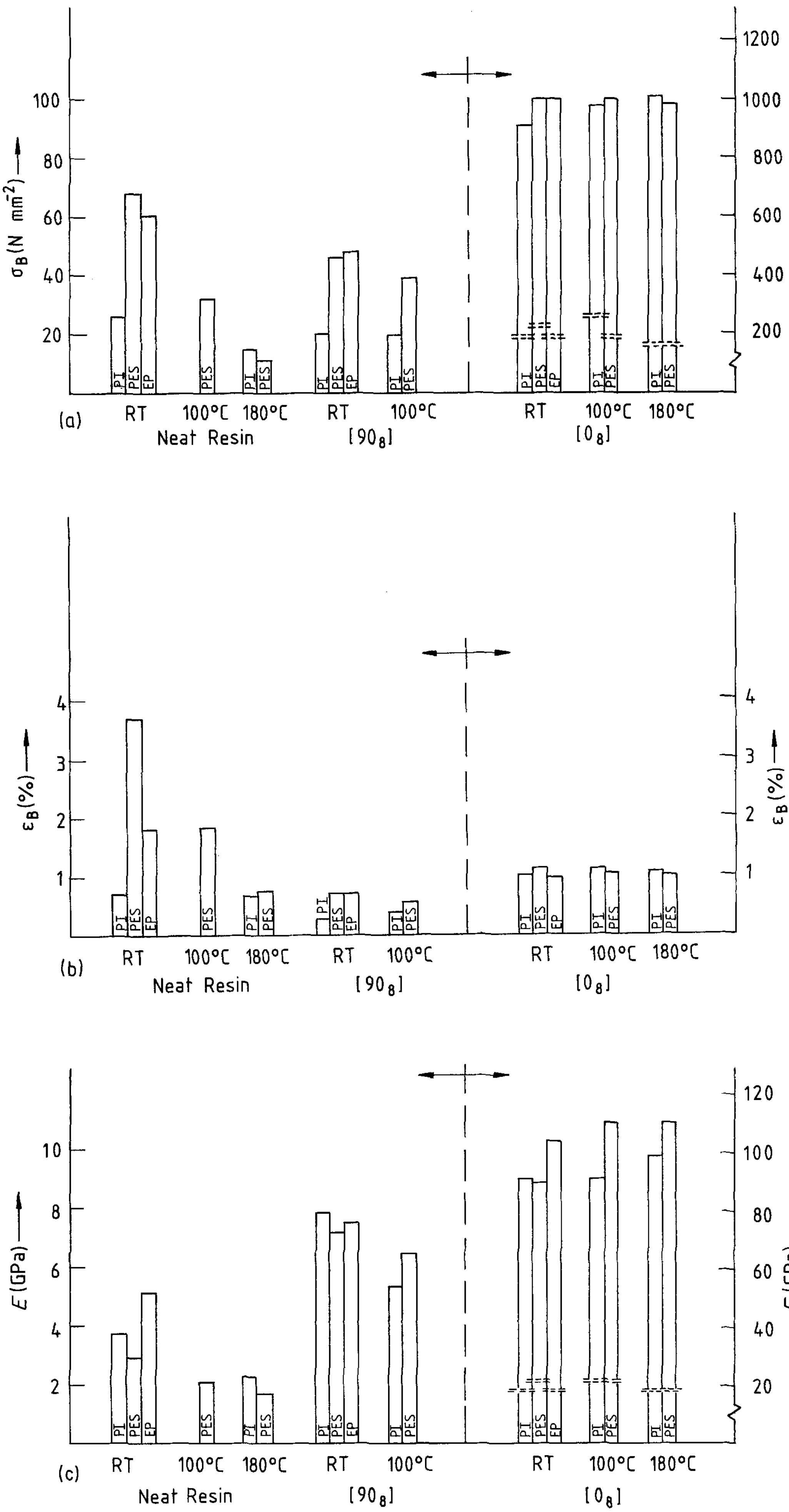


Figure 4 Matrix properties at different temperatures compared to the properties of unidirectional $[0_8]$ and $[90_8]$ laminated. (a) Fracture stress, σ_B; (b) fracture strain, ε_B; (c) elastic modulus, E.

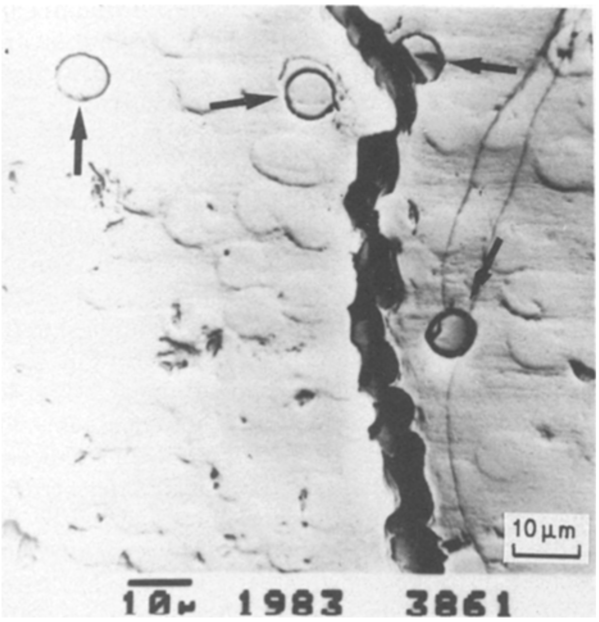


Figure 5 Scanning electron micrograph of a replica of a 90° ply from a PI laminate. Poor fibre–matrix bonding indicated by circumferential cracks (arrow) around a 90° fibre.

resins are compared, it turns out that the fracture strain is reduced by a factor of approximately 2.7 for the PI and EP, while in PES the reduction reaches a factor of 5.4, which gives rise to the poor compatibility of PES with carbon fibres. The elastic modulus for the three resin systems also increases in a transverse tensile test, when reinforced with aligned fibres (Fig. 4c), but higher test temperatures adversely decrease the elastic modulus. However, the longitudinal properties in the 0° direction remain apparently unaffected by the test temperature.

Increasing the test temperature leads mainly in PES, when tested in the 90° specimen, to a reduction in the mechanical properties, while the PI test specimens were rather unaffected. The better test results of the neat resins compared to the 90° composite can be expected, taking into consideration that the likelihood of failure at the fibre–matrix interface is due to a weak bonding between fibre and matrix, which makes a transverse tensile test an effective tool in determining bond quality. Fig. 5 is an example of poor bonding. A replica was taken from the edge of a specimen and examined in the scanning electron microscope. It shows that a transverse crack follows the fibre–matrix interface and that, in some cases, circumferential cracks are formed around 90° fibres as a result of tensile load.

The fracture energy (area under the transverse stress–strain curve) can be used as a transverse performance parameter to identify the strength of a bond [9]. The energy absorbed during a fracture process is a measure of the toughness of a material which is an important material characteristic, as it represents resistance to fracture. The fracture energy given by

$$E = \int_0^{\varepsilon_f} \sigma_{(\varepsilon)} \, d\varepsilon \qquad (1)$$

where E is the fracture energy, $\sigma_{(\varepsilon)}$ the stress as a function of strain and ε_f the fracture strain, reaches, in the neat PES, a value of $1.25\,\mathrm{MJ\,m^{-3}}$. The equivalent values for PI and EP are 0.092 and $0.54\,\mathrm{MJ\,m^{-3}}$, respectively. This makes PES superior over the other resins. For example, PES has a more than ten times higher fracture energy than the PI neat resin.

In a 90° composite the fracture energy for PES specimens is $0.16\,\mathrm{MJ\,m^{-3}}$, which means a reduction compared to the neat resin of about a factor of 7.8. The fracture energy for PI and EP is reduced in a 90° composite only by a factor of about 3.5, leading to a fracture energy of $0.025\,\mathrm{MJ\,m^{-3}}$ in PI and $0.16\,\mathrm{MJ\,m^{-3}}$ in the EP transverse tensile test specimen.

The reinforcement of the resins with carbon fibres reduces the toughness (fracture energy) of PES so much that in the composite it is now equivalent in its quality to EP, losing its superior behaviour, but it is

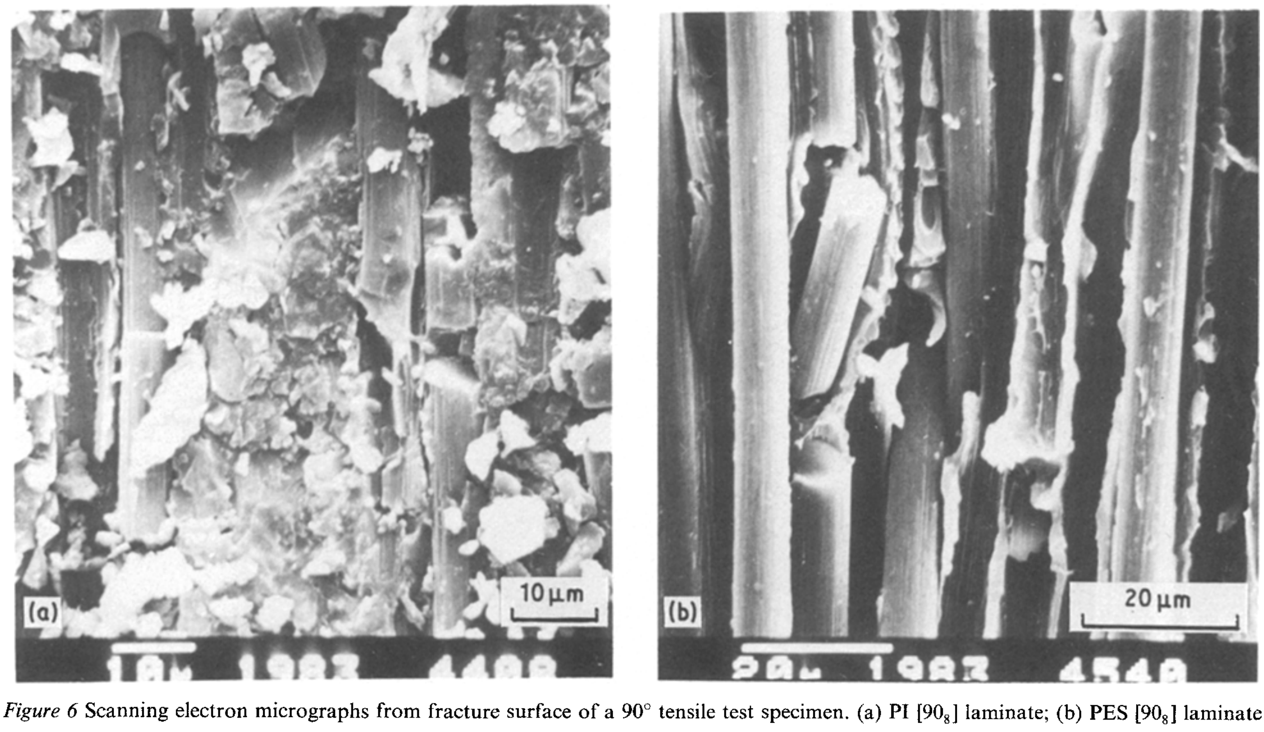


Figure 6 Scanning electron micrographs from fracture surface of a 90° tensile test specimen. (a) PI $[90_8]$ laminate; (b) PES $[90_8]$ laminate.

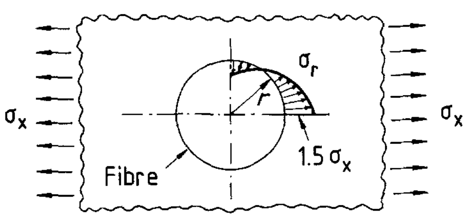


Figure 7 Radial stress distribution around a fibre at the fibre–matrix interface; loaded transverse to the fibre direction.

still better than the PI laminate. The decrease in fracture energy by a factor of 7.5 for the PES when used as the matrix in the $[90_8]$ specimen gives rise to the assumption that here a poor bond strength is dominant. This is illustrated in Fig. 6. While in the transverse tensile specimen with the PI matrix a relatively good bond quality leads to numerous fibre fractures and a substantial amount of interfibre fracture (Fig. 6a), in the specimen with the PES matrix the fracture path predominantly follows the fibre–matrix interfaces as a result of its very weak bond strength. Fig. 6b shows the relative clean fibre surfaces.

Not only does a weak bonding between fibre and matrix favour interfacial fracture in a transverse tensile specimen, but so also does the stress concentration caused by tension perpendicular to the fibre [9–11]. The maximum principal normal stresses can be expected in the fibre–matrix interface and exceed $1.5\sigma_x$ [10], where σ_x is the normal stress applied to the composite. This is shown schematically in Fig. 7.

The transverse composite stiffness (Fig. 4c) measured at room temperature is not remarkably different when varying the matrix resin. This indicates that the transverse stiffness is strongly influenced by the volume fraction of carbon fibres and less by the stiffness of the matrix material. However, the low increase in composite transverse stiffness has to be weighed against the corresponding increase in local stress concentration during loading which indicates the decrease in the composite strength when compared to the neat resin. Local yielding or viscoelastic behaviour of the matrix material will relieve the stress concentrations somewhat.

3.2. Microscopic analysis of the fracture surface

Because of the brittle fracture behaviour of the fibres the matrix is the only location in the composite at which microfractographic characteristics can be examined in order to differentiate between fatigue failure and tensile failure. For this reason the unreinforced resin was investigated so that microstructural characteristics obtained could, if appropriate, be transferred to the composite.

Fig. 8a shows the fracture pattern of a PI tensile test piece loaded at room temperature. The fractured surface, which represents the initiation of failure, appears in the lower part of the diagram as the smooth zone 1, also referred to as the mirror zone. Even at higher magnification (approximately 10,000), the surface of the mirror zone remains completely smooth without

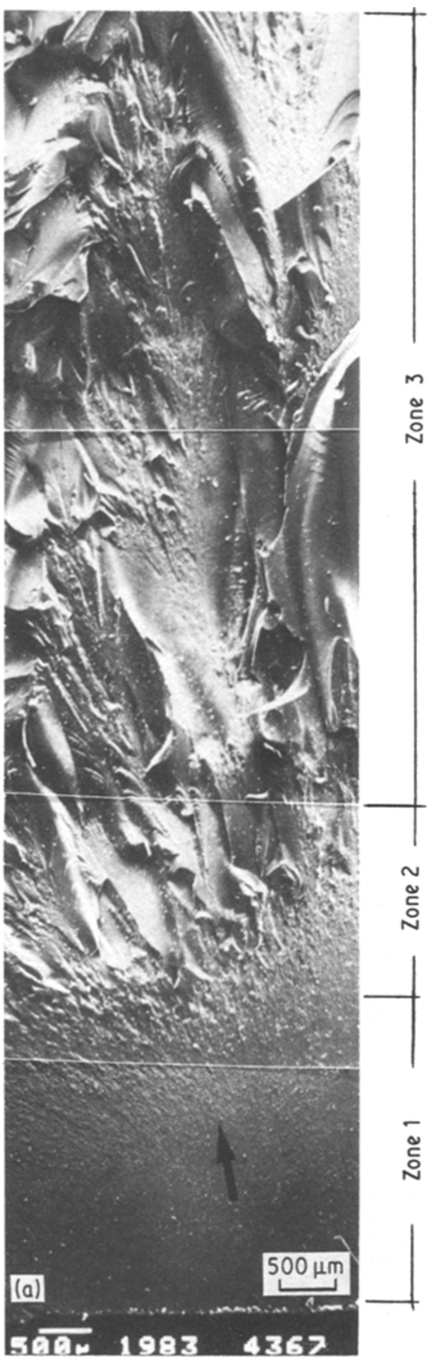
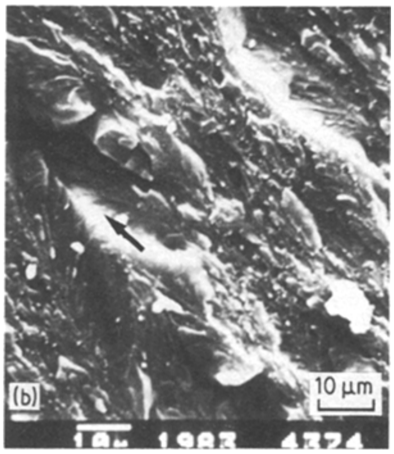
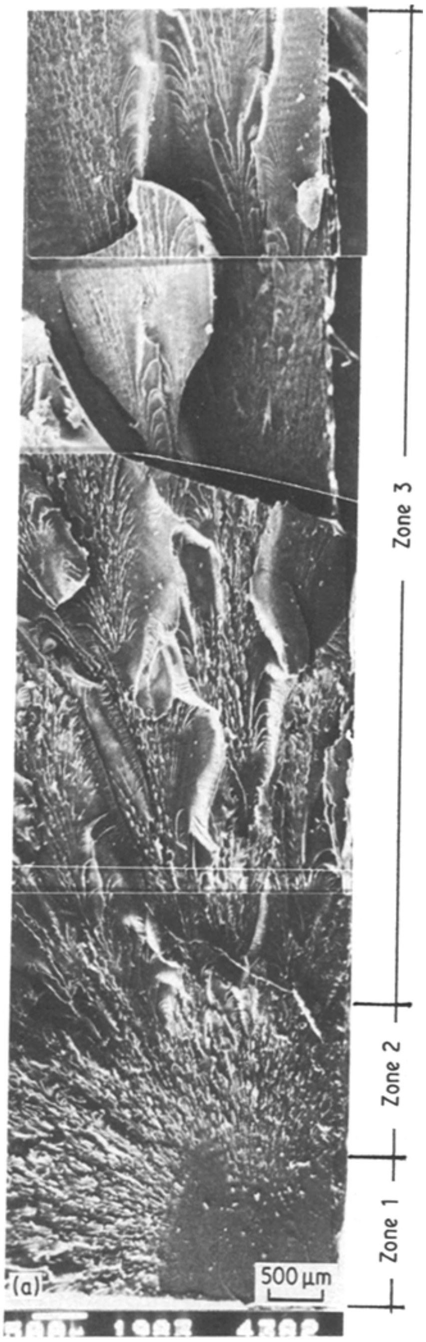


Figure 8 Scanning electron micrographs from the fracture surface of a tensile test specimen of PI neat resin: (a) fracture surface (general view); (b) detail from zone 2.





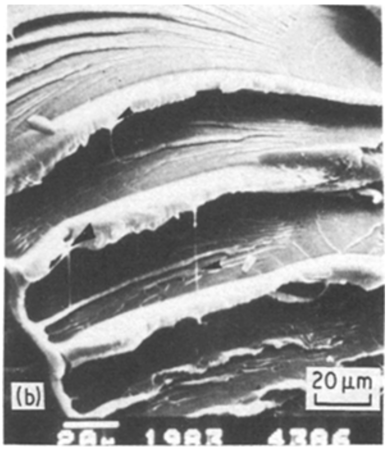


Figure 9 Scanning electron micrographs from the fracture surface of a tensile test specimen of the PES neat resin: (a) fracture surface (general view); (b) detail from zone 3.

any topographical variations. The small zone 2 which continues from it has a uniformly rough fractured morphology with facets pointing in the propagation direction of the crack (Fig. 8b, arrow). The subsequent zone 3 exhibits a very irregular fracture morphology; in addition to smooth regions there are strongly fissured fracture surfaces. A similar classification into three zones has previously been made by Skibo *et al.* [12] for the fatigue fracture surface of glassy polymers and for different epoxy resins for static fracture by other authors [13].

Just as in the PI, the fracture in the PES neat resin test pieces can be sub-divided into three zones (Fig. 9a). At the beginning of crack propagation (zone 1), a mirror zone can again be observed. In zone 2, the crack propagates radially starting from the mirror zone, the facets being repeated periodically at longer intervals with increasing distance from the zone 1/2 boundary. Zone 3 again shows a very irregular fracture pattern, but the matrix appears to be locally more stretched than in the case of the PI neat resin. Fig. 9b shows detail from this zone which indicates the high plastic deformations in the micro-range. These plastic deformations can be recognized at the overlap points of the facets and at the individual threads of matrix, which extend from the overhangs of the facets to the fracture surfaces under them. Towards the end of zone 3, the fracture pattern has an underlying structure which repeats periodically and is independent of the general topography. In contrast to the PI neat resin in the PES tensile test, strongly plastic deformations appear during the crack initiation stage in the mirror zone, documented in Fig. 10. However, in this case the crack initiated near the side surface of the specimen.

It was not possible to examine the PI neat resin test pieces from fatigue tests, because these test pieces had multiple failures during dynamic testing and an unambiguous allocation of the fracture surfaces as "fatigue fractures" was not possible. Fatigue tests of the PES neat resins allowed us to identify clear fatigue fracture surfaces, but no definite characteristics indicating

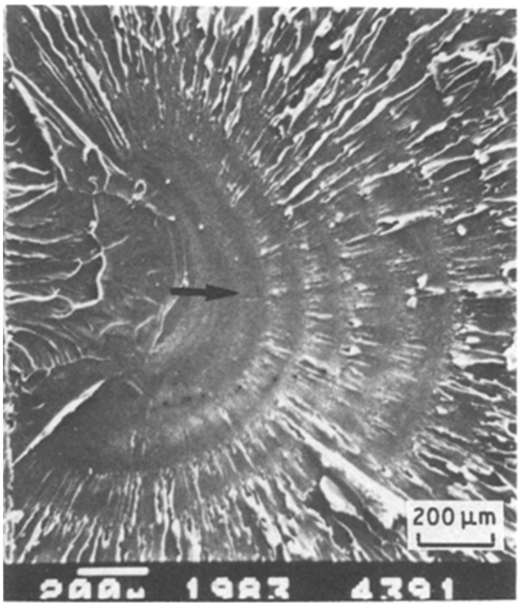


Figure 10 Scanning electron micrograph from the fracture surface of a tensile test specimen of the PES neat resin. Crack initiation at the side surface zone 1 and 2. Plastic deformation in zone 1.

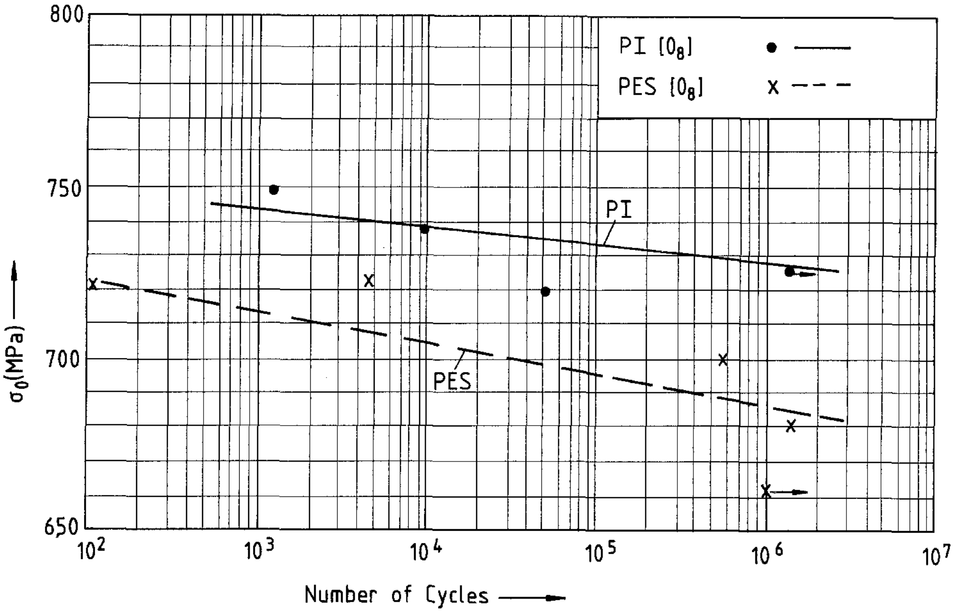


Figure 11 Fatigue behaviour of the unidirectional PI and PES [0_8] laminates.

fatigue failure could be observed on them. However, the appearance of three different zones formed during crack propagation could again be identified [7].

Although the mechanical properties of PI and PES are markedly different, the fracture behaviour is similar. The initiation of the crack is at the edges of the test pieces for both resins and features a mirror zone which is distinctly different from the brittle residual fracture area. Microscopic differences between the resins can be recognized in the transition area from the mirror zone to the residual fracture. Whereas, here again, the PI resin features microscopic brittle fracture, extremely large deformations (recognizable from the formation of threads between the facets) can be observed in the case of PES.

3.3. Fatigue behaviour

The fatigue behaviour of the unidirectional PI and PES laminates [0_8] is shown in Fig. 11. Both laminates exhibit a practically linear range up to 10^6 load cycles with only a slight drop in the upper stress level. However, this level ascertained under fatigue loading is considerably lower than the static tensile test value, and the absolute values are lower for the PES relative to the PI composites (opposite to the static tensile test data). The internal defects already present in the PES test pieces, when still in the unloaded condition (such as pores due to poor impregnation of the laminate) adversely affect the fatigue strength [6]. It is not possible to ascertain unambiguously whether this drop in fatigue strength is due to the material itself or to the defects in the composite.

Fig. 12 shows the fatigue behaviour (cyclic stress against fatigue life) of the neat PI and PES resins and of the appropriate [90_8] transverse test pieces. Both the PI matrix and the [90_8] pieces exhibit in their short term fatigue life a very low fatigue strength when compared to the PES material, reflecting the poor static values already mentioned in the previous sections. However, in the range of the endurance limit of

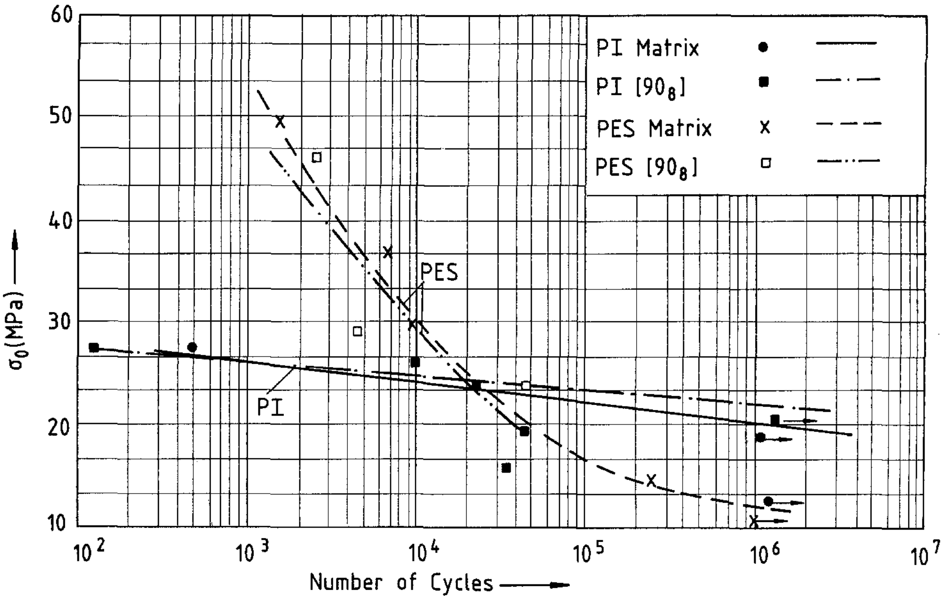


Figure 12 Fatigue behaviour of the PI and PES neat resins and of the corresponding [90_8] laminates.

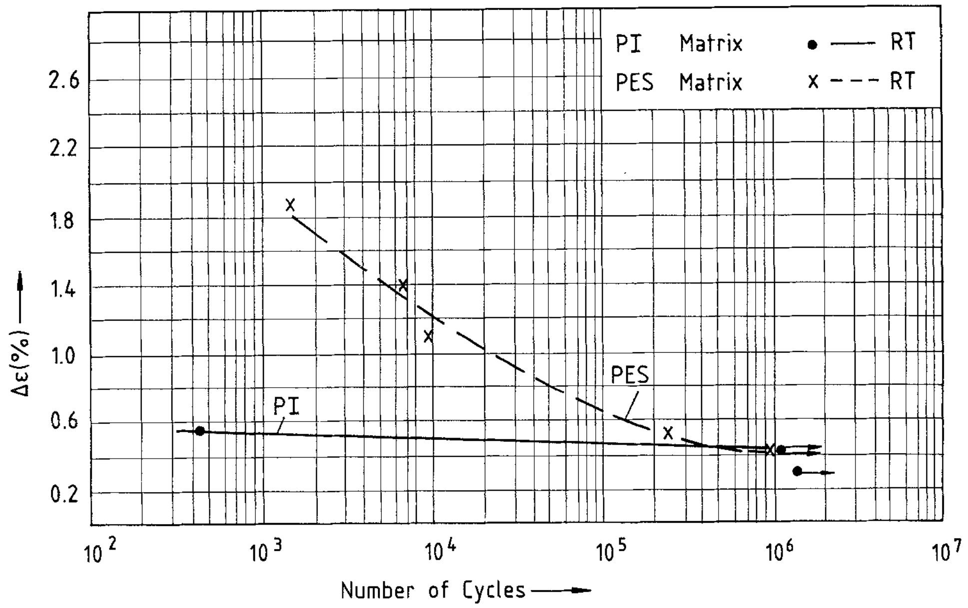


Figure 13 Total strain amplitude plotted against fatigue life for the PI and PES neat resins.

both of the materials, PI is now considerably better than PES. This is especially the case when only the results of the neat resins are compared. The ductile PES resin can withstand more high load cycles than the PI resin, but at low load levels the PI resin is less sensitive to fatigue loading.

In a plot showing the cyclic strain–fatigue life data (Fig. 13) it turned out that the endurance limit for both resin systems is reached at about the same cyclic strain level. Only a slight increase in the strain (load) level leads for the PI resin to a dramatic decrease in fatigue life, while the PES resin can withstand higher strain (load) levels for some thousand load cycles. This very different behaviour of the two materials investigated is understandable, if the static stress-strain behaviour is taken into consideration (compare

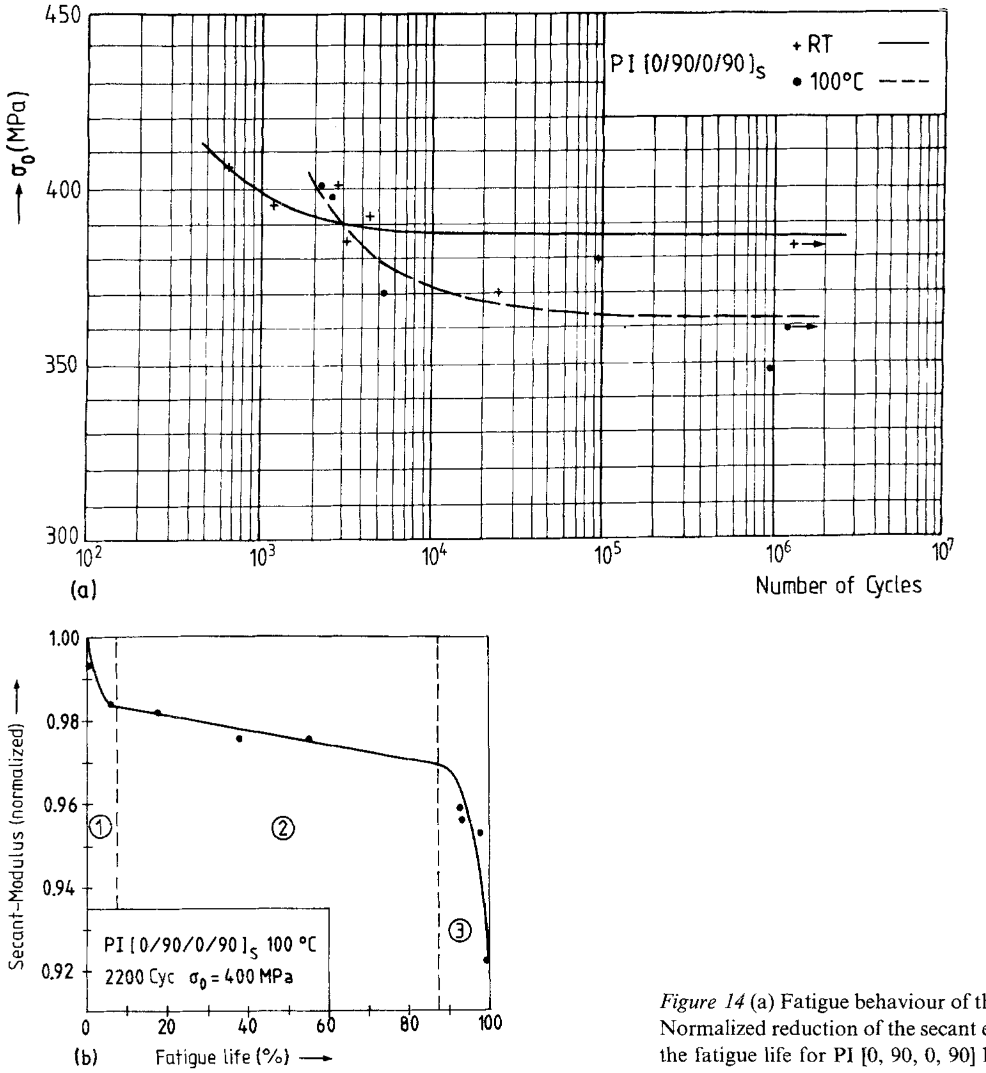


Figure 14 (a) Fatigue behaviour of the PI [0, 90, 0, 90]$_s$ laminate. (b) Normalized reduction of the secant elastic modulus as a function of the fatigue life for PI [0, 90, 0, 90] laminate at 100° C.

Fig. 2a). Loading the neat resin test pieces so that 0.3% strain is reached during each load cycle means that both resins survive more than 10^6 load cycles, but the stress in the PI resin is higher than in the PES due to its higher elastic modulus, explaining the behaviour illustrated in Fig. 12. Up to 0.3% strain, both resins behave in a totally elastic manner. At higher strain levels the onset of plastic deformation during cycling begins. The brittle PI resins react very sensitively to any plastic deformation, leading then to early failure during fatigue loading. However, the ductile PES resin can resist higher strain levels during short-term fatigue cycling.

Another explanation for the investigated behaviour that should be taken into consideration for the long-term fatigue behaviour is the reported sensitivity of PES to the environment. Under low-load long-term fatigue loading even laboratory air might deteriorate the material properties which then leads to the observed behaviour.

The influence of the test temperature due to the fatigue life of a composite laminate is given in Fig. 14 for the example of a PI $[0, 90, 0, 90]_s$ cross-ply laminate. At a test temperature of 100° C, the fatigue life is strongly affected, leading to a reduced fatigue life at comparable cyclic stress amplitudes. Only during short-term fatigue does the temperature influence remain small (Fig. 14a). During fatigue loading of laminated test coupons, a drop in stiffness (reduction of the secant modulus of elasticity) could be observed. At the start of a dynamic loading (Stage 1), the secant modulus of elasticity drops sharply, whereas in Stage 2, which covers the major proportion of the life, the modulus only changes slightly. Just prior to failure, a drastic reduction in the secant modulus of elasticity takes place (Stage 3). This behaviour has been described and discussed in detail [6] for room temperature tests. The same behaviour can also be expected for fatigue tests performed at 100° C. This is shown in Fig. 14b for a PI $[0, 90, 0, 90]_s$ test piece.

4. Conclusion

The mechanical tensile properties of PI and PES neat resins used as matrix material in fibre-reinforced plastics were investigated at different temperatures together with a conventional EP resin. These results were compared to the composite properties of unidirectional $[0_8]$ and $[90_8]$ laminates. Superior resin properties do not automatically lead to sufficient laminate properties, if an appropriate fibre matrix bond strength cannot be reached. The PES neat resins showed the best mechanical properties at all test temperatures; however, this superior behaviour disappeared in the laminate because of voids and poor bond strength. The fatigue strength of the PES laminates is slightly less than that of the PI laminates, because its quality is worse.

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