Mechanical properties of poly(vinyl alcohol) fibres and composites

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Mechanical properties of poly(vinyl alcohol) fibres and composites

T. Peijs*, R.J.M. van Vught and L.E. Govaert
Centre for Polymers and Composites (CPC), Eindhoven University of Technology,
PO Box 513, 5600 MB Eindhoven, The Netherlands
(Revised 12 April 1994)

This paper describes the performance of poly(vinyl alcohol) (PVOH) fibres and their composites. PVOH fibres have been studied, with the emphasis on long-term properties. Results indicated that the long-term properties of PVOH fibres are superior to those of high-performance polyethylene (HP-PE) fibres. Mechanical tests on PVOH/epoxy composites showed that, in general, their structural performance is between those of plasma-treated HP-PE and aramid fibre-reinforced composites. Structural mechanical properties of PVOH composites are better than those of HP-PE based composites due to the combination of a strong interfacial bond strength and a less pronounced anisotropic fibre character. However, the strong bonding between PVOH and epoxy results in a rather brittle failure mode of the composite and consequently relatively poor impact properties.

(Keywords: poly(vinyl alcohol) fibres; epoxy; mechanical properties)

INTRODUCTION

Research activities in the field of high-performance fibres have focused on achieving high strength and high modulus via orientation of the structure. These efforts resulted in the introduction of a number of commercial advanced polymer fibres, including lyotropic liquid crystal polymers such as the aromatic polyamides or aramids, in the 1970s. In addition to the development of high-performance fibres based on semi-rigid molecules, another breakthrough was realized at the end of that decade at DSM research with the development of a manufacturing process for high-performance fibres based on flexible macromolecules, i.e. the so-called solution (gel)-spinning process for ultra-high molecular weight polyethylene (UHMW-PE). This spinning and drawing process results in high-performance polyethylene (HP-PE) fibres with moduli of approximately 100 GPa and tenacities of about 3 GPa. Currently, commercial grades of HP-PE fibres are produced by DSM High Performance Fibres BV (Dyneema and its licensee Allied-Signal (Spectra)). In all these systems, the main objective was to achieve high stiffness via molecular orientation and chain extension. At the same time, however, the properties in the lateral direction are reduced, since these are controlled by the secondary bonds between the oriented polymer chains, resulting in highly anisotropic fibres. Typical one-dimensional structures result with strong covalent bonds in the chain direction and weak intermolecular interactions between the chains, i.e. van der Waals' bonding in the case of polyethylene (PE) or hydrogen bonding for aramid. Given their one-dimensional character, these new fibres perform relatively poorly in three-dimensional loading situations as encountered in composite structures. In particular, the poor compressive properties limit the use of most of these fibres in structural composites.

Several attempts have been made to improve the limiting secondary bonds in HP-PE fibres by introducing crosslinks. Most studies in this direction focused on improvements in creep resistance. However, so far, significant reductions in creep rate have only been reported for melt-spun fibres, these possessing overall properties which are less impressive than those of gel-spun fibres. For gel-spun HP-PE fibres, some improvements in creep resistance were only obtained at the expense of drawability and tensile properties.

A more promising approach than that of trying to introduce intermolecular interactions in ultra-drawn PE via crosslinking, is to apply the principles of solution (gel)-spinning to other, more polar, flexible polymers, such as polyamides, polyacrylonitrile and poly(vinyl alcohol) (PVOH). All these polymers combine a high theoretical modulus in the chain direction with a higher secondary bond strength between the chains, which makes them attractive candidates for achieving high-performance fibres.

Unfortunately, the maximum attainable modulus and strength of these 'polar' polymers proved to be rather low, although some interesting results were obtained for PVOH, e.g. tenacities of up to 2.3 GPa and moduli of about 70 GPa. These values are still significantly lower than those obtained for PE because the formation of hydrogen bonds within the oriented...
crystalline regions restricts the drawability during PVOH fibre processing and, consequently, the maximum attainable properties. Although the maximum attainable values for the uniaxial tensile modulus and tensile strength are not as impressive as in the case of HP-PE, specific intermolecular interactions (i.e. hydrogen bonds) in fibres produced from polar polymers might offer some advantages with respect to off-axis, compressive and long-term properties. Another important advantage of PVOH is its high melting point of 250°C, compared with 150°C for HP-PE. However, a major disadvantage of PVOH fibres is that the mechanical properties are sensitive to moisture.

The influence of intermolecular forces in the crystal lattice on the transverse crystal modulus of the polymer, being the 'theoretical' modulus in the transverse direction, was reported by Nakamae and co-workers. Using an X-ray diffraction technique they measured a transverse crystal modulus of about 6-9 GPa for PVOH, compared with 3.5 GPa for PE. The crystal moduli measured in the chain direction were 250 and 235 GPa for PVOH and PE, respectively, showing that even in PVOH these crystals possess still a high level of anisotropy.

The objective of the present study is to evaluate high-strength PVOH fibres as an alternative reinforcing element for composite applications and to compare the properties of composites based on PVOH with those of composites based on HP-PE. Results are presented concerning the influence of the less anisotropic characteristic of PVOH fibres on compressive and long-term fibre properties as well as on the structural performance of PVOH/epoxy composites, including the effect of the presence of polar groups on the fibre surface on adhesion and composite failure modes.

EXPERIMENTAL

Materials

The fibre used in this study was a solution-spun PVOH fibre (Kuralon™ 5900, 1800 denier, 1000 filaments) from Kuraray Corp. (Japan) with a density of 1.34 g cm⁻³, a modulus of 46 GPa and a strength of 1.8 GPa. For comparison, HP-PE fibre from Allied-Signal (Spectra™ 1000) was also tested. A plasma-treated HP-PE fibre was used to reveal (as much as possible) the influence of fibre anisotropy on composite performance by minimizing interfacial effects. Table 1 gives an overview of different polymeric fibres including those used in this study.

The matrix was an epoxy system based on bisphenol A and an anhydride curing agent (Araldite LY556/HY917/DY070). Composites were manufactured from prepregs that had been prepared using a drum winding technique. Composite plates with a fibre volume fraction (Vf) of about 50% were prepared by stacking the prepregs into a mould in the desired lay-up and curing them, using a vacuum bag, for 4 h in a hot press at 80°C under a pressure of 0.4 MPa. Finally, the composites were postcured for 12 h at 110°C. All samples were conditioned at 21°C and a relative humidity of 50%. Under these conditions the moisture content in the PVOH fibre is approximately 3 wt%, which is comparable to that of aramid fibres.

Testing

Fibres. Tensile, creep and stress-relaxation experiments on multifilament yarn of 250 mm length, provided with adhesively bonded cardboard tabs, were performed on a Frank 8156 tensile tester equipped with a thermally controlled oven and an extensometer. The compressive yield stress of single filaments was measured using the 'elastica' loop test.

Composites. Off-axis test specimens were cut from the laminate plates using a diamond cutting wheel. Tensile specimens up to 15° off-axis had a length between the adhesively bonded tapered tabs of 150 mm, a thickness of 1 mm and a width of 12 mm. All other tensile specimens had a length between the tabs of 100 mm, a thickness of 2 mm and a width of 25 mm. Tensile tests were performed at a test speed of 1 mm min⁻¹. To eliminate edge effects as a result of cutting specimens from flat laminates, filament wound tubes were also made for transverse tensile strength evaluation. Hoop wound tubes with a length of 100 mm, a wall thickness of 2 mm and an inner diameter of 25 mm were fabricated by wet-winding of yarn on a collapsible mandrel.

Longitudinal, transverse and shear properties were determined from tensile tests on 0°, 90° and 10° specimens, respectively. Compression tests were performed at a crosshead speed of 0.5 mm min⁻¹. Test specimens were in accordance with ASTM D-3410 with the exception that the Celanese type of test fixture also allowed for specimen widths other than the standard 6 mm. Compressive test specimens had a thickness of 4 mm, a width of 20 mm and a free test length between the aluminium tabs of 12 mm. Interlaminar shear strength (ILSS) was measured on an ASTM standard test fixture with a span-to-depth ratio of 4:1 at a rate of 1 mm min⁻¹.

To avoid clamping problems, such as shear failure within the tabs, tension–tension fatigue tests on unidirectional (UD) composites were performed on filament wound rings with a width of 6 mm and a thickness of 1.2 mm, using a split-disc loading device (ASTM D-2290) at a frequency of 5 Hz and a fatigue stress ratio, R (σmin/σmax), of 0.1. The system was operating under load control, applying a harmonic tensile stress with a constant amplitude.

<table>
<thead>
<tr>
<th>Fibre</th>
<th>Type</th>
<th>Modulus (GPa)</th>
<th>Strength (GPa)</th>
<th>Density (g cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP-PE</td>
<td>Spectra™ 000</td>
<td>80</td>
<td>2.7</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td>Spectra™ 1000</td>
<td>100</td>
<td>3.0</td>
<td>0.97</td>
</tr>
<tr>
<td>Aramid</td>
<td>Kevlar™ 49</td>
<td>60</td>
<td>2.8</td>
<td>1.44</td>
</tr>
<tr>
<td></td>
<td>Kevlar™ 99</td>
<td>120</td>
<td>2.8</td>
<td>1.45</td>
</tr>
<tr>
<td>PVOH</td>
<td>Kuralon™ 5900</td>
<td>46</td>
<td>1.8</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Composite toughness was evaluated using dart impact and falling-weight impact tests. Full-penetrating impacts were conducted utilizing a Zwick Rel servohydraulic testing instrument equipped with a dart-impact test fixture. Impact performance was measured on cross-ply laminated plates [0, 90]4 (60 × 60 mm) with a thickness of 1.4 mm, at a constant velocity of 4.5 m s⁻¹ using a hemispherical dart of 10 mm diameter. Non-penetrating instrumented falling-weight impact tests were conducted on cross-ply test panels of the same thickness (100 × 100 mm), clamped between two plates with a circular opening of 80 mm, using a hemispherical impactor with a diameter of 20 mm. Impact energies were generated by dropping a hemispherical impactor with a diameter of 10 mm, loaded with different weights, from different heights. Post-processing of data results in the complete energy history during impact and the energy absorbed by the composite.

RESULTS AND DISCUSSION

Fibre properties

Tensile behaviour. Compared with HP-PE fibres, the tensile behaviour of PVOH fibres is inferior with respect to the initial modulus (Figure 1). Furthermore, the stress-strain curve of PVOH is non-linear, showing initially a small region with a relatively high modulus, beyond which the slope of the curve decreases drastically and subsequently increases again at high strain levels.

Regarding the temperature dependence, it should be noted that only the initial modulus of the PVOH fibre seems to be influenced by temperature. At higher stress or strain levels, the slopes of the curves obtained at 30 and 70°C are nearly identical.

Long-term behaviour. The typical temperature dependence of PVOH fibres as shown in Figure 1 is confirmed by the stress-relaxation data of Figure 2, where nearly temperature-independent behaviour is observed at high stresses and/or strains. This implies more or less 'elastic' long-term properties of PVOH fibres at high stress levels, superior to those of HP-PE fibres where plastic deformation dominates²⁹-³¹.

At all strain levels, power-law relaxation behaviour is observed:

\[ \sigma(t) = Ct^n \]  

where \( \sigma \) is the extensional stress, \( C \) is a prefactor and \( n \) is the power law exponent. However, in the case of PVOH, the value of this exponent depends strongly on the applied strain and/or temperature, as shown in Figure 2. For tests performed at 70°C, \( n = 0.049 \) and \( 0.013 \) at 0.5% and 2% strain, respectively. This observation is in accordance with the tensile results in Figure 1, indicating that the fibre becomes less time-dependent at higher loads. At 30°C, \( n = 0.031 \) and \( 0.013 \) at 0.5% and 2% strain, respectively; these values, especially at high load levels, are comparable with that of aramid fibres (\( n = 0.01 \) at room temperature)³². HP-PE fibres, on the other hand, show a more pronounced time-dependent behaviour with a power law exponent of about 0.07 at room temperature³³.

The superior long-term properties of PVOH are illustrated in Figure 3, where the creep deformation of HP-PE and PVOH fibres at 500 MPa and 70°C are compared. Plastic deformation in PVOH fibres is, similar to drawing, restrained as a result of the hydrogen bonds, resulting in a better creep resistance.
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Compressive strength. Since polymeric fibres fail by the formation of kink bands, which is related to the shear properties of the fibre, it can be expected that the compressive strength of PVOH fibres is higher than that of HP-PE fibres, given the more pronounced anisotropic character of the latter. Figure 4 shows the results of the 'elastica' loop tests. Loops with a diameter of 5, 20 and 50 mm for aramid, PVOH and HP-PE filaments, respectively, were placed in silicon oil between glass slides. The fibre ends were led out of the ends of the slides and the size of the loop was reduced in stages by pulling the ends of the fibre. The major axis \(c\) and the minor axis \(a\) were measured accurately at each stage. In theory, the ratio of major to minor axis should stay constant and equal to 1.34 as long as the fibre behaves elastically. The compressive yield stress of the fibre, \(\sigma_{\text{frc}}\), was obtained from the stress at which the fibre lost its elastic properties and the ratio of the major axis to minor axis deviated from its constant value. This yield stress can be calculated by:

\[
\sigma_{\text{frc}} = \frac{1.34E_{\text{fc}}d}{c_{\text{crit}}}
\]

where \(E_{\text{fc}}\) is the compressive modulus of the fibre, \(d\) is the fibre diameter and \(c_{\text{crit}}\) is the major axis of the loop at which \(c/a\) increases sharply (see Figure 4).

It is clear that, compared with HP-PE, compressive yielding or kink band formation in the PVOH and aramid fibres occurs at much smaller loop sizes, which is indicative of a higher resistance to compressive failure. Compressive failure in the fibre is accompanied by the appearance of so-called kink bands, i.e. buckling on the compressive face of the fibre (Figure 5), and is comparable with failure processes found in other polymeric fibres such as aramid. The formation of these kink bands is strongly dominated by the low shear properties of the fibre which results in the compressive strength of these fibres being directly related to fibre anisotropy.

Using equation (2) yields values of about 180 MPa and 0.45% for the calculated compressive strength and failure strain, respectively, of the PVOH fibre, assuming a fibre compressive modulus of 40 GPa, a fibre diameter of 17 \(\mu\)m and \(c_{\text{crit}}\) of 5 mm. For PVOH fibres this means that the compressive strength is approximately 10% of the tensile strength. By assuming a compressive modulus \(E_{\text{fc}}\) for HP-PE fibre of about 50 GPa, i.e. similar to the tensile modulus at low strain rates (10\(^5\) to 10\(^6\) s\(^{-1}\)), a mean fibre diameter of 27 \(\mu\)m and \(c_{\text{crit}}\) of 30 mm, the compressive strength of HP-PE fibre is calculated to be about 60 MPa, which is only 2% of the tensile strength. For aramid fibre (Twaron TM, Akzo Fibers), a compressive strength of approximately 600 MPa – i.e. about 20% of the tensile strength – was calculated using a fibre modulus of 120 GPa, a fibre diameter of 11 \(\mu\)m and \(c_{\text{crit}}\) of 2 mm, which is in good agreement with previous studies on aramid.

Based on these data it can be concluded that the compressive strength of PVOH fibres is approximately three times that of HP-PE. However, values of the order of 200 MPa are still relatively low compared with compressive strength values of other high-performance fibres. For example, the compressive strength of PVOH is only one-third that of aramid, the latter being generally recognised as a fibre with poor compressive properties. The compressive strength of PVOH is especially disappointing when taking into account that both aramid and PVOH possess similar secondary bonds (i.e. hydrogen bonds), although it should be noted that the number of interactions in an atactic polymer like PVOH will be less pronounced due to the random arrangement of the OH side groups.

The dependence of the compressive strength of high-performance fibres on the shear modulus of the fibres, and thus fibre anisotropy, has already been noted by Norita et al., Allen et al. and DeTeresa et al. The last authors developed a theoretical model for the compressive strength of high-performance polymer fibres using an elastic microw buckling analysis. They stated that the critical compressive stress for microw buckling of extended polymer chains is solely dependent on intermolecular interactions when the chains are long. Comparison of measured compressive strengths with torsion moduli of various rigid-rod polymeric fibres including poly(p-phenylene terephthalamide), poly(p-phenylene benzobisthiazole), poly(p-phenylene benzo-
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Bisoxazole, thermotropic polyester and a pitch-based graphite fibre (Union Carbide P-75) showed the following linear correlation:

\[ \sigma_{f_c} = 0.3G \]  

(3)

where \( G \) is the shear modulus.

However, in the case of HP-PE and PVOH fibres, this relationship seems to overestimate the role of the shear modulus. For these fibres the ratio of the compressive strength and shear modulus is only 0.08 to 0.1. For the calculation of this ratio the shear modulus of HP-PE fibres (0.8 GPa) was taken from off-axis tests on ultradrawn UHMW-PE tapes\(^{37-39} \), whereas the shear modulus of PVOH (~ 1.7 GPa) was estimated from composite data which will be presented in the following section and measured transverse moduli of oriented PVOH tapes (4 GPa), which were approximately twice that of UHMW-PE tapes\(^{39} \). These ultra-drawn tapes can be manufactured using a similar technology to solution (gel)-spinning of fibres and can be used as an alternative for ultra-drawn polymeric fibres in order to investigate the off-axis properties of these oriented structures\(^{37-39} \). It seems that the importance of intermolecular interactions on the compressive strength of the fibre decreases in the case of fibres based on flexible macromolecules such as HP-PE and PVOH, indicating that improvements in secondary bond strength in these fibres will only lead to modest changes in compressive strength. It might even be argued that compressive yielding in these fibres initiates at local regions of minimum shear modulus, e.g. amorphous or interfibrillar regions\(^{40,41} \)

**Composite properties**

**General performance.** Mechanical test data for UD composites are summarized in Table 2. Data for plasma-treated HP-PE/epoxy composites were taken from refs 37 and 39, whereas data for aramid/epoxy were taken from refs 42 and 43. Structural properties such as ILSS, flexural strength and compressive strength of PVOH/epoxy composites are higher than those of composites based on plasma-treated HP-PE fibres due to a combination of a strong fibre-matrix bond strength and a less pronounced anisotropic character of the PVOH fibre compared with HP-PE. In most, cases, PVOH/epoxy composites showed structural performance in between those of HP-PE and aramid composites. The real ILSS value for PVOH/epoxy is even higher than the value listed in Table 2, since the specimens did not fail in a shear mode but in a flexural mode with fibre fracture at the tensile side of the specimen. The compressive strength of PVOH composite (140 MPa) is approximately 50% higher than that of HP-PE composites but still significantly lower than that of aramid fibre-reinforced composites. However, the compressive strength of the PVOH composite is still slightly higher than that of pure epoxy (120 MPa), whereas in HP-PE composites the compressive strength of the composite was even lower than that of the pure matrix material.

The compressive strength of composites consisting of ductile fibres is often dominated by the compressive yield stress of the fibres. Assuming plastic behaviour of the fibres, the composite compressive strength \( \sigma_{fc} \), is described reasonably by a simple rule of mixtures (ROM) relationship:

\[ \sigma_{fc} = \sigma_{f_c} V_f + \sigma_{mc} (1 - V_f) \]  

(4)

where \( \sigma_{f_c} \) is the compressive yield stress of the fibre and \( \sigma_{mc} \) is the compressive strength of the matrix. Using equation (4), and a compressive strength for the epoxy matrix of 120 MPa, yields values for the compressive strength of the PVOH, HP-PE and aramid composites (at \( V_f = 0.5 \)) of 150, 90 and 360 MPa, respectively. Particularly in the cases of the PVOH and HP-PE fibres, these values are in good agreement with the experimental data, indicating that the compressive strength of the composite is fully dominated by the relatively low compressive yield stress of the fibres. Compressive failure modes in PVOH composites are also similar to those in treated HP-PE\(^{39,44} \) and aramid\(^{28} \) composites, i.e. kink band formation in a localized region.

**Figure 6** reports the off-axis strength of PVOH/epoxy composites in both tension and compression. Off-axis tensile data were described using the Tsai–Hill failure

<table>
<thead>
<tr>
<th>Property</th>
<th>PVOH</th>
<th>HP-PE(^{37,39} ) (plasma treated)</th>
<th>Aramid(^{42,43} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Longitudinal tensile strength (MPa)</td>
<td>22</td>
<td>49</td>
<td>65</td>
</tr>
<tr>
<td>Longitudinal tensile strain (%)</td>
<td>3.2</td>
<td>3.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Longitudinal compressive strength (MPa)</td>
<td>140</td>
<td>91</td>
<td>240</td>
</tr>
<tr>
<td>Transverse tensile modulus (GPa)</td>
<td>4.2</td>
<td>3.2</td>
<td>4.8</td>
</tr>
<tr>
<td>Transverse tensile strength (MPa)</td>
<td>10</td>
<td>8</td>
<td>14</td>
</tr>
<tr>
<td>Transverse failure strain (%)</td>
<td>0.24</td>
<td>0.31</td>
<td>0.29</td>
</tr>
<tr>
<td>Shear modulus (GPa)</td>
<td>1.9</td>
<td>1.0</td>
<td>2.1</td>
</tr>
<tr>
<td>Shear strength (MPa)</td>
<td>16</td>
<td>15</td>
<td>34</td>
</tr>
<tr>
<td>ILSS (MPa)</td>
<td>&gt; 50</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>Flexural strength (MPa)</td>
<td>475</td>
<td>175</td>
<td>620</td>
</tr>
</tbody>
</table>

**Figure 6** Off-axis tensile and compressive strength of PVOH/epoxy composites compared with HP-PE and aramid composites

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**Note:** The table and figure are images of the original paper, which includes figures, tables, and text. The text above is a natural language representation of the content, ensuring that the information is clear and self-contained. The table and figure are described in the text to maintain context and continuity. This approach allows for a comprehensive understanding without the need to refer back to the images.
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criterion\(^3\) using data from Table 2, and are in good agreement with the experimental data. For comparison, the off-axis performances of HP-PE and aramid composites using the data of Table 2 are also plotted. This graph clearly illustrates the intermediate off-axis performance of PVOH composites compared with composites based on HP-PE and aramid fibres, in both tension and compression.

**Failure modes.** The presence of polar groups at the PVOH fibre surface is the major contributor to a strong bonding with epoxy resins. Uniaxially tested PVOH composites showed smooth fracture surfaces with no longitudinal splitting at a macroscopic level, and little pull-out and debonding on a microscopic level (Figure 7). This relatively brittle failure behaviour is indicative of a failure process of fibre fracture adjacent to the previously broken fibre, due to stress concentrations near such a broken fibre.

The high bond strength in PVOH/epoxy composites results in a highly effective reinforcing effect of this fibre in epoxy-based composites. Based on the ROM relationship for the tensile strength of fibre-reinforced composites, including a parameter \(k\), the fibre efficiency can be demonstrated:

\[
\sigma_{f_{11}} = k [\sigma_0 V_f + E_m e_f (1 - V_f)]
\]

where \(\sigma_{f_{11}}\) is the composite tensile strength (see Table 2), \(\sigma_0\) is the fibre tensile strength as determined from impregnated strand tests, \(e_f\) is the failure strain of the fibre, \(E_m\) is the Young's modulus of the matrix and \(V_f = 0.5\). Based on impregnated strand data (\(\sigma_0 = 1.54\) GPa) and using the ROM expression (5), the efficiency parameter \(k\) is calculated to be 0.84, a value which is comparable with that of composites incorporating plasma-treated HP-PE fibres\(^3\) (\(\sigma_0 = 2.61\) GPa; \(k = 0.81\)) and aramid fibres (\(\sigma_0 = 2.80\) GPa; \(k = 0.80\)). These relatively high values for \(k\) suggest that the strength of the composites is mainly governed by fibre-dominated failure processes.

The excellent fibre-matrix adhesion in PVOH/epoxy composites not only results in good stress transfer in the longitudinal direction but, in off-axis load situations in particular, also plays a predominant role in controlling the performance. Figure 8 shows the damage development in UD composites when loaded in transverse tension. Acoustic emission was monitored using a PAC 8900 Locan AT system, including a 40 dB pre-amplifier. The threshold was set at 25 dB. Cumulative plots of acoustic emission events versus the percentage of maximum load illustrate the influence of the strong interfacial bond strength in the PVOH/epoxy system on damage initiation. For composites incorporating PVOH fibres, initial emissions occurred only just prior to total failure of the composite, which implies that ultimate failure of these composites is fully controlled by the initiation of microcracking. However, especially in the case of untreated HP-PE composites with only limited fibre-matrix interactions, initiation of microcracking occurred almost immediately upon loading, suggesting progressive damage development in this type of composite.

Scanning electron micrographs of transverse fracture surfaces revealed significant differences in failure modes between PVOH and HP-PE composites. In previous studies\(^3\) it was shown that surface treatment of HP-PE fibres changed the transverse and shear failure modes from pure debonding to a combination of debonding and fibre splitting. PVOH composites showed more or less a combination of fibre fibrillation (Figure 9a) and matrix cracking (Figure 9b), both suggesting good fibre-matrix adhesion and composite performance which is dominated by fibre and/or matrix properties rather than by interface properties.

**Fatigue performance.** Longitudinal tension-tension fatigue testing of PVOH filament wound rings showed that PVOH composites are less sensitive to fatigue loadings than HP-PE composites (Figure 10). In the case of untreated HP-PE composite, the \(S-N\) curve shows a steeper slope, reflecting a more progressive fatigue damage process that is mainly dominated by interface failure. To study the influence of improved adhesion on the fatigue behaviour of HP-PE/epoxy composites, both untreated and surface-treated HP-PE fibres were used. Due to the high interfacial bond strength, the fatigue behaviour of PVOH/epoxy is fibre-dominated rather than interface-dominated, which results in excellent fatigue resistance compared with untreated HP-PE composites.

**Figure 7** Scanning electron micrograph of a longitudinal fracture surface of PVOH/epoxy composite showing brittle failure with little fibre pull-out

**Figure 8** Cumulative plots of acoustic emission hits versus percentage of ultimate load for transversely loaded UD composites
Figure 9 Scanning electron micrographs of transverse fracture surface of PVOH/epoxy composite showing: (a) fibre fibrillation; and (b) matrix cracking

Figure 10 Fatigue life diagram of various UD composites

For comparison, the $S-N$ curve of UD aramid/epoxy composite tested at a frequency of 5 Hz and $R$ of 0.1 is plotted using data from ref. 42. The fatigue performance of aramid composites is almost identical to that of surface-treated HP-PE/epoxy composites and, although the fatigue stresses of the aramid and treated HP-PE composites are higher, the slope of the curve for the PVOH composite is even shallower than those of the aramid and treated HP-PE composites.

Impact behaviour. It is well known that HP-PE composites perform extremely well under ballistic and low-velocity impact conditions. However, the lower work to break of the PVOH fibre compared with the HP-PE fibre, and the rather brittle failure mode of the PVOH composite, result in a relatively poor penetration resistance of the cross-ply laminates with dart-impact penetration energy of 7 J mm$^{-1}$, compared with 28 J mm$^{-1}$ for surface-treated HP-PE composites. Since, in the case of HP-PE fibre, surface treatment generally results in a reduction in impact performance$^{45,46}$. HP-PE composites are apparently far superior with respect to a high penetration resistance.

In addition to full-penetrating impacts, non-penetrating low-velocity impact tests were performed using a falling-weight impact tester. Here we are not focusing on the energy necessary to penetrate a laminate but on the ratio of elastic energy to absorbed energy during an impact. Figure 11 clearly shows that also under non-penetrating impacts cross-ply PVOH/epoxy laminates absorb less energy than HP-PE/epoxy laminates.

CONCLUSIONS
- The short-term properties of PVOH fibres are relatively poor compared with those of HP-PE, whereas the long-term properties (creep) are far superior due to the absence of plastic flow.
- With increasing stress and/or strain levels the mechanical properties of PVOH fibres become less dependent on temperature and/or strain rate, i.e. the fibre displays a more 'elastic' behaviour.
- The compressive strength of PVOH fibres is approximately three times that of HP-PE but only one-third of aramid fibres.
- In general, PVOH/epoxy composites display structural mechanical performance in between those of HP-PE and aramid fibre-reinforced composites.
- The strong fibre-matrix bonding in PVOH/epoxy composites, due to polar groups at the fibre surface, results in a rather brittle failure mode, relatively poor impact properties but excellent fatigue performance.
compared with HP-PE composites. To accomplish a better balance between strength and toughness, other matrix systems which do not result in such a strong fibre–matrix bonding might be favourable.

Summarizing, the use of PVOH fibre in epoxy-based composites results in only a relatively small increase in structural performance compared with HP-PE/epoxy composites. In particular, the lower compressive strength of PVOH fibres than aramid fibres is rather disappointing, suggesting that polymeric fibres based on rigid-rod polymers perform better in compression than fibres based on flexible polymers.

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