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Fibre-reinforced composites with tailored interphases using PPE/epoxy blends as a matrix system

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In this study poly(2,6-dimethyl-1,4-phenylene ether) (PPE) is introduced as a ductile thermoplastic matrix for high-performance carbon fibre-reinforced composites by using epoxy resin as a reactive solvent. An interesting feature of this reactive composite processing route is that the epoxy resin acts not only as an effective solvent, lowering the viscosity and processing temperature of the polymer matrix, but also provides an essential structural part of the final composite material. Upon curing and subsequent phase separation, a morphology of epoxy-coated fibres in a nearly pure PPE matrix results. This phenomenon is not only of great importance with respect to the possibility to drastically improve the adhesion between the fibres and the thermoplastic matrix, but also creates the challenge to tailor the mechanical properties of these *in situ* formed interlayers by changing the chemistry of the epoxy phase.

(Keywords: thermoplastic composites; reactive processing; tailored interphases; poly(phenylene ether); epoxy)

INTRODUCTION

It is well recognised that the optimal performance in terms of weight-saving efficiency of composite materials is often limited by their low damage tolerance¹, especially in the most commonly encountered case of brittle thermosetting matrices. A considerable increase in damage tolerance can be achieved by using tough, high-performance thermoplastics as matrix material^{2,3}.

Poly(2,6-dimethyl-1,4-phenylene ether)⁴ (PPE) is of interest for the production of tough thermoplastic composites, particularly in view of its high glass transition temperature ($T_g = 220^\circ\text{C}$), excellent mechanical properties and its relatively low cost. Since amorphous thermoplastics are processed at temperatures significantly higher ($\sim 100^\circ\text{C}$) than T_g , high-temperature polymers suffer from the occurrence of degradation. For this reason PPE cannot be melt-processed and is considered to be a classical example of an intractable polymer. In the case of PPE, solutions are sought in blending with more flexible polymers, e.g. in PPE/polystyrene blends (Noryl[®] from General Electric Plastics), thus compromising in T_g and subsequently lowering the processing temperature. More-

over, in the case of continuous fibre-reinforced composites, special impregnation techniques must be employed to wet-out the fibres with these highly viscous engineering plastics. Consequently, solution impregnation routes have to be considered to introduce polymers such as PPE in composites. Conventional solution impregnation techniques that use, for instance, methylene chloride as a solvent will, however, introduce additional problems related to complete elimination of residual solvent from the composite. Residual traces of solvent in the material result in a reduction in the mechanical properties, especially at elevated temperatures. Other problems may involve voids in the composite structure and a less satisfactory interface control, resulting in a reduction of the overall composite performance³.

A possible solution to these problems is the use of reactive solvents or monomers. Basically the idea is to sell the solvent with and within the product after applying a polymerization step. During processing, the solvent either allows a reduction in processing temperature (important for intractable high-temperature polymers) or decreases the viscosity of the polymer (important for composite processing). Reactive solvents with a large potential for such reactive processing route for thermoplastic resins are the epoxy resins. As described in the literature, epoxy resins are excellent solvents for an impressive range of engineering thermoplastics⁵⁻¹².

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Many of the investigations in the area of hybrids of thermosets and thermoplastics were triggered in the composites area and generally were focused on toughening of epoxy resins with engineering plastics such as poly(ether sulfone)⁶⁻⁹ or poly(ether imide)^{10,11}. However, it has also been reported in the literature that upon increasing the concentration of the thermoplastic additive, typically above 10–20 wt% thermoplastic, the morphology changes via a co-continuous structure into a phase-inverted morphology of dispersed epoxy particles in a thermoplastic matrix.

Both phenomena, i.e. epoxy resin as a reactive solvent and phase inversion at sufficiently high thermoplastic concentrations, are adopted in this study for the preparation of high-performance composites using PPE/epoxy blends^{13,14} as a matrix

system. First, the characteristics of the PPE/epoxy system are presented briefly. The influence of the presence of fibres on the blend morphology resulting from phase separation, is then reported. Next, some mechanical properties of carbon fibre-reinforced composites are discussed, focusing on transverse strength and interlaminar toughness. Finally, the influence of the properties of the *in situ* polymerized epoxy phase on composite performance is investigated by using different epoxy resin systems as a reactive solvent.

EXPERIMENTAL

Matrix materials

A commercial grade poly(2,6-dimethyl-1,4-phenylene

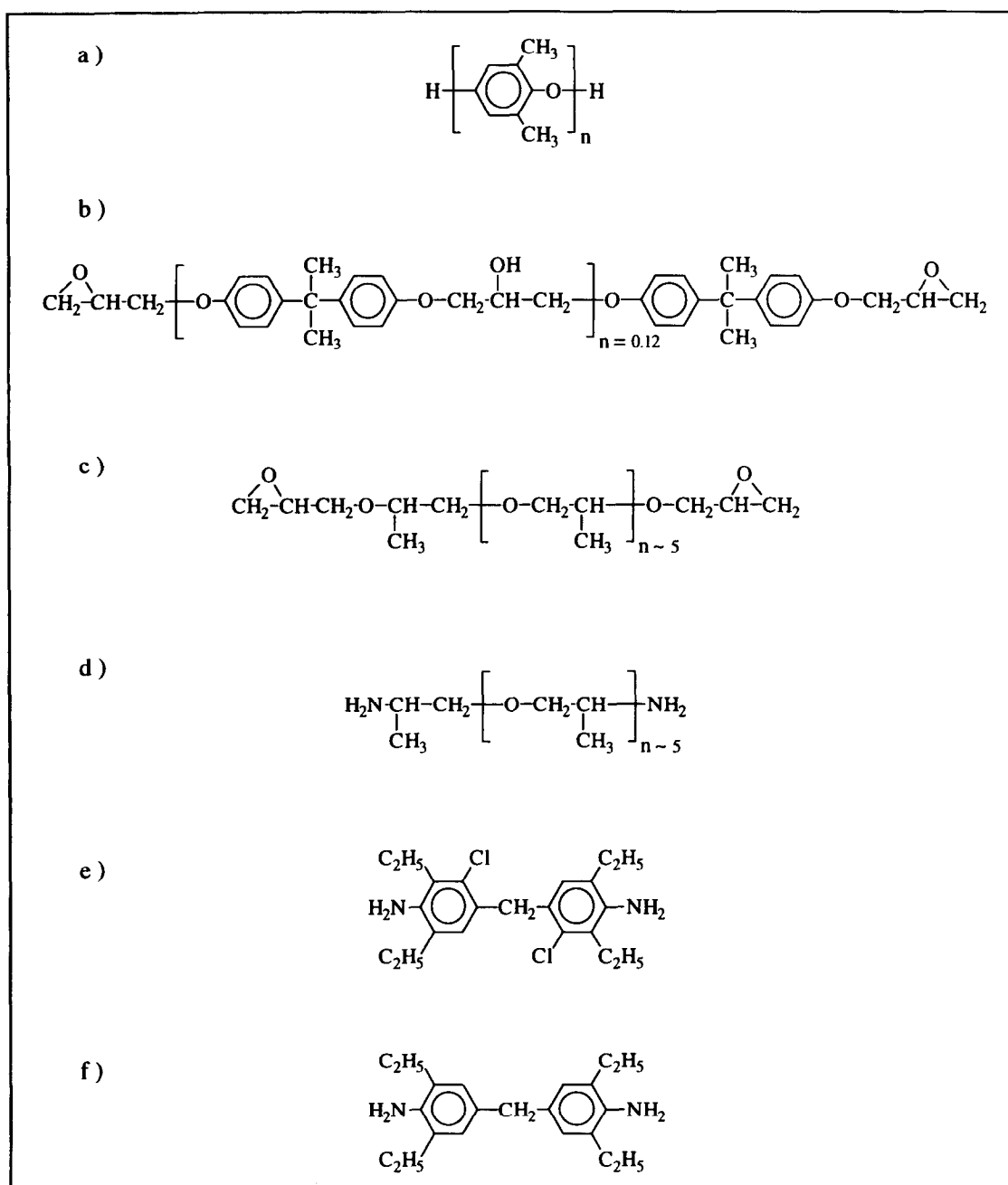


Figure 1 Structural formulae of the different components of the matrix system: (a) PPE, (b) DGEBA, (c) DGEPO, (d) M-CDEA, (e) M-DEA

ether) (PPE 803, $M_w = 32 \text{ kg mol}^{-1}$ was supplied by General Electric Plastics. Two types of epoxy resin were used throughout this investigation: a diglycidyl ether of bisphenol-A (DGEBA, Epikote 828EL) supplied by Shell and a diglycidyl ether of poly(propylene oxide) (DGEPO Epikote 877). Curing agents used were 4,4-methylene-bis(3-chloro-2,6-diethylaniline) (M-CDEA) and 4,4-methylene-bis-(2,6-diethylaniline) (M-DEA), both supplied by Lonza Ltd. The DGEBA resin was cured by using either 51 parts per hundred parts of resin by weight (phr) of M-CDEA or 42 phr of M-DEA, while the DGEPO resin was cured with either 31 phr M-CDEA or 27 phr M-DEA. Figure 1 shows the structural formulae of the different components used in this study.

Solutions of PPE in epoxy resin were prepared in Brabender Plasticorder kneader. At a kneading temperature of 175°C a kneading time of about 1 h was required to obtain transparent homogeneous solutions. From these compounds, thin films with a thickness of 0.2 mm (required for composite preparation) were compression-moulded in a hot-press (50 bar, 175°C , 5 min). After hot-pressing the films were quenched in a water-cooled press. Alternatively, plates required to determine the mechanical properties of the PPE/epoxy systems were moulded and cured. In general, a curing cycle of 2 h at 225°C was applied, followed by a post-cure of 4 h at 200°C in an inert atmosphere.

Composite manufacture

Composites with a fibre volume fraction of 50% were prepared using different PPE/epoxy systems. One group of composites was based on PPE/epoxy using DGEBA resin as a reactive solvent¹³, with composites based on pure epoxy resin and on pure PPE as reference material. A second group of composites was based on a PPE/epoxy composition of 40 wt% epoxy, using different epoxy resins as a reactive solvent. In this study epoxy resins with different DGEBA/DGEPO compositions¹⁴ were used to flexibilize the epoxy network and to enhance the ductility of the epoxy phase of the blend.

Carbon fabric-reinforced composites were prepared using plain weave fabrics (T300 fibre, CD168, 168 g m^{-2}) supplied by Ten Cate. Composites based on the PPE/epoxy systems were prepared by film stacking. The laminates were consolidated in a hot-press for 2 h at a temperature of 225°C and a relatively low pressure of 5 bar in a vacuum bag. A post-cure for 4 h at 200°C was applied. Besides the laminates based on the PPE/epoxy blends, reference materials were prepared based on pure epoxy resin and pure PPE. The PPE composites were based on prepregs prepared by solution impregnation using chloroform (CHCl_3) as a solvent. The neat PPE laminates were consolidated at a temperature of 300°C for <8 min at a pressure of 150 bar. The epoxy laminates were consolidated under the same conditions as applied for the PPE/epoxy laminates except for the temperature, which was 175°C . Specimens

were cut from the composite plates with a diamond cutting wheel.

Unidirectional carbon fibre-reinforced composites (Tenax HTA-5135, 12K, Tenax Fibres GmbH) were prepared from prepregs which were made by filament winding on a rectangular frame. In contrast to the general principle employed in this paper, the prepregs were manufactured by using trichloroethylene as a co-solvent. This was to exclude any influence of the composition of the matrix on composite quality or fibre volume fraction. The prepregs were stacked into an open-ended mould and were subsequently consolidated and cured in a hot-press, yielding a unidirectional composite panel ($120 \times 200 \text{ mm}$).

Mechanical testing

The Young's moduli and strengths of the neat matrix materials were determined from edge-polished specimens with dimensions according to ASTM D638 ($2 \times 13 \times 180 \text{ mm}$). The mode I fracture toughness of the matrix materials was determined using the three-point bend specimen geometry. The specimens ($4 \times 10 \times 50 \text{ mm}$) were tested using a span-to-depth ratio of 4 and a crosshead speed of 10 mm min^{-1} .

The transverse properties of the unidirectional composites were determined by three-point bending experiments. Three-point bending tests were conducted, with a span-to-depth ratio of 20, on transverse specimens with a geometry of $2 \times 18 \times 50 \text{ mm}$. All transverse specimens were intensively edge-polished.

The mode I and mode II interlaminar fracture toughnesses of the carbon fabric laminates were determined using the double-cantilever beam (DCB) geometry and the end-notched flexure (ENF) specimen geometry, respectively¹⁵. To initiate delamination an aluminium foil (35 mm long, 0.01 mm thick) coated with release agent was placed at the laminate mid-plane prior to moulding. The mode I DCB specimens (3.6 mm thick and 20 mm wide) with a $[0/90]_{20}$ lay-up (denoting 20 plies of fabric stacked in a 0/90 lay-up) were loaded at a crosshead speed of 0.5 mm min^{-1} . This test set-up facilitates the measurement of the critical strain energy release rate G_{Ic} as a function of crack length, yielding the so-called resistance or *R*-curve. The propagation value reported for G_{Ic} is the average value calculated in the range of ratios of displacements to crack lengths of 0.2–0.4. The data were analysed according to the corrected beam theory¹⁵.

$$G_{Ic} = \frac{3P\delta}{2B(a + \Delta_1)} \quad (1)$$

where P = load, δ = displacement, B = specimen width, a = crack length and $(a + \Delta_1)$ = corrected crack length.

The mode II ENF specimens ($[(0/90)]_{20}$ lay-up, 3.6 mm thick, 20 mm wide) were loaded at a crosshead speed of 1 mm min^{-1} in three-point bending using a ratio of crack length to half span (L) of 0.5. By using this test set-up an initiation value for G_{IIc} was determined. The specimens were precracked in shear in order to avoid effects of the aluminium starter defect. The data were analysed

according to the direct beam theory¹⁵:

$$G_{IIc} = \frac{9P\delta a^2}{2B(3a^3 + 2L^3)} \quad (2)$$

where L = half-span length.

COMPOSITES BASED ON PPE/EPOXY

The PPE/epoxy matrix system

At elevated temperatures ($>150^\circ\text{C}$) PPE can be dissolved in epoxy resin (including curing agent) to give medium-viscosity compounds (e.g. a zero shear viscosity of approximately 50 Pa s at 200°C for systems based on 60 wt% epoxy). Consequently, these materials can be processed relatively easily at temperatures between 175 and 225°C . Upon curing of the homogeneous solutions phase separation will inevitably occur, i.e. the increase in molecular weight of the epoxy resin and the resulting change in the polarity of the system due to conversion of the reactive groups yield a drastic decrease in miscibility of the system. After phase separation a phase-inverted morphology results of epoxy spheres dispersed in a continuous PPE matrix. Consequently, after curing, PPE is regained and the epoxy resin solvent is converted into a dispersed phase¹³.

The mechanical properties of the PPE/epoxy systems cured with M-CDEA and of both pure constituents are presented in Table 1. Since the properties are dominated by the continuous PPE matrix, materials are obtained that combine a high T_g with excellent toughness.

Interlayer formation and adhesion

Upon incorporating fibres into the PPE/epoxy system, a reinforcement is not only added but additionally a large amount of interface is introduced. It has been shown in the literature³ that the matrix characteristics can be influenced by the presence of such a fibre interface. For instance, in carbon fibre-reinforced semicrystalline thermoplastics the fibre surface may influence the nucleation and growth of spherulites within the matrix. Therefore, the influence of fibre incorporation on the final blend morphology after phase separation was studied first. This study was performed using model composites reinforced with short fibres (17 vol% fibres of 5 mm length).

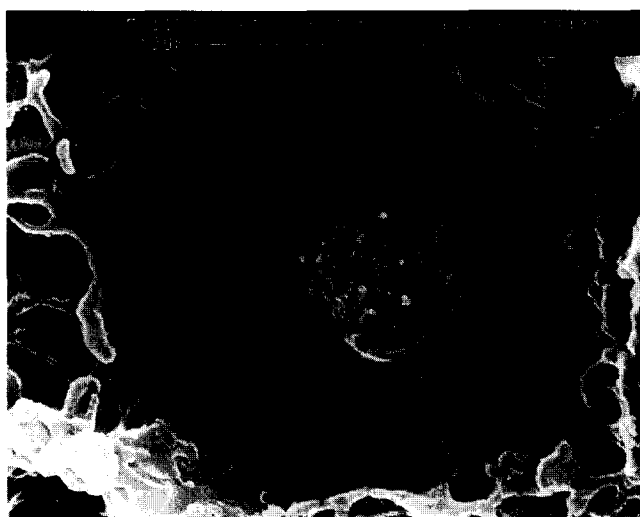
In Figure 2a the morphology of a PPE/epoxy blend

Table 1 Mechanical properties of the epoxy, PPE and PPE/epoxy systems (standard deviations are given in parentheses)

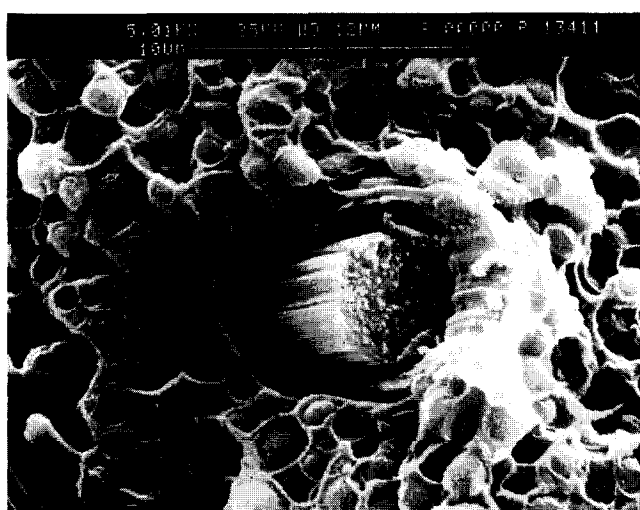
	Young's modulus (GPa)	Yield stress (MPa)	Fracture toughness G_{IIc} (kJ m^{-2})
Epoxy	2.4 (0.1)	67 (7) ^a	0.23 (0.04)
PPE/epoxy (60 wt% epoxy)	2.3 (0.1)	72 (1) ^b	3.7 (0.1)
PPE/epoxy (40 wt% epoxy)	2.3 (0.2)	75 (3) ^b	4.3 (0.2)
PPE	2.4 (0.1)	70 (1) ^b	5.9 (0.2)

^a Stress at break

^b Yield stress



(a)



(b)

Figure 2 SEM micrographs of fracture surfaces of short fibre-reinforced composites based on PPE/epoxy: (a) surface-treated carbon fibre; (b) untreated carbon fibre

(~60 wt% epoxy) in the vicinity of a surface-treated carbon fibre is shown. The scanning electron microscopy (SEM) micrograph of the fracture surface reveals a remarkable influence of the presence of the fibre on the final morphology of the blend. Epoxy resin accumulates preferentially at the fibre surface, resulting in an epoxy 'interphase' or better 'interlayer' around the fibre. It is likely that the polarity of the fibre surface plays an important role: as a consequence of the higher polarity of epoxy resin compared with PPE, the epoxy resin prefers to be located at the polar fibre surface. To investigate this hypothesis, model composites were prepared using untreated carbon fibres (Apollo IM-43-750, Courtaulds plc). In general, commercially produced carbon fibres are surface-treated in order to facilitate wetting and to improve adhesion^{16,17}. The oxidative surface modification increases the amount of chemically bound oxygen and consequently the fibre surface polarity. Whereas in Figure 2a, a bulky epoxy layer is present around the surface-treated carbon fibre, no such layer can be

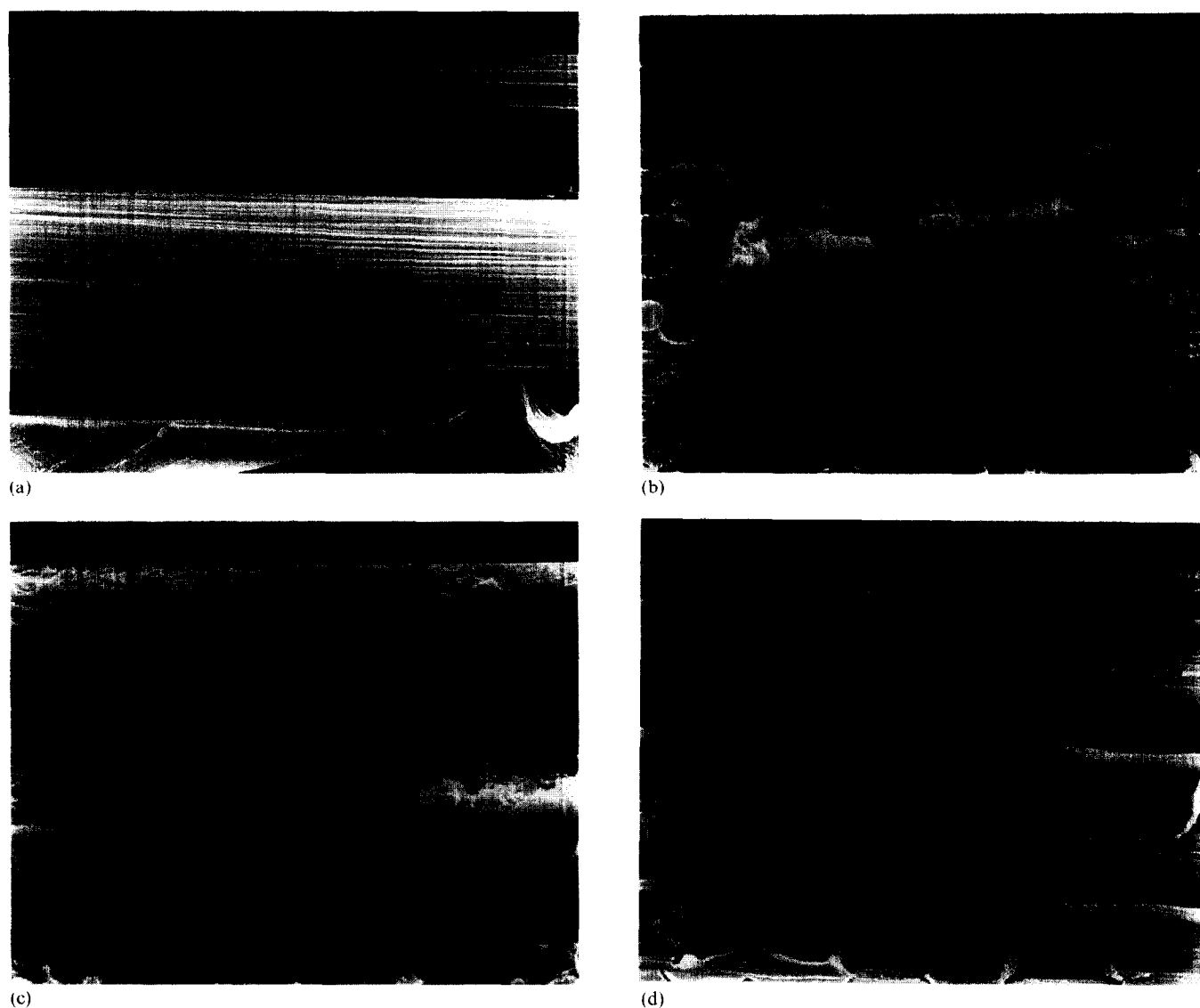


Figure 3 SEM micrographs of transverse fracture surfaces of unidirectional composites *versus* the epoxy (DGEBA) content of the PPE/epoxy matrix: (a) 0 wt%; (b) 20 wt%; (c) 30 wt%; (d) 40 wt%

distinguished around an untreated carbon fibre (*Figure 2b*), clearly illustrating that the polarity of the fibre surface is a major driving force for the accumulation of epoxy resin at the fibre–matrix interface. Moreover, this interfacial phase separation phenomenon is likely to occur at every polar interface, for instance also at metal substrates.

Other fractographic studies on carbon fabric laminates revealed a significant influence of the fibre volume fraction on the final composite morphology. In matrix-rich areas (low fibre volume fractions) the morphology corresponds to the one shown in *Figure 2a*, i.e. epoxy-coated fibres in a continuous PPE-rich matrix containing dispersed epoxy particles. In contrast, in fibre-rich areas (high fibre volume fractions) no dispersed epoxy particles could be distinguished in the PPE matrix. Consequently, the majority of the epoxy resin migrates to the fibre surface, resulting in a unique morphology of epoxy-coated fibres in a nearly pure thermoplastic matrix.

Besides fibre volume fraction (read: the amount of interface), another prerequisite for complete phase

separation to occur is that this diffusion-controlled process is given enough time. For the fixed reaction rate of the system employed in this study, the viscosity of the mixture plays a dominant role in this process. *Figure 3* shows the interlayer morphology in the case of 0, 20, 30, and 40 wt% of epoxy resin. This figure reveals that only when more than 30 wt% epoxy is present, i.e. when the viscosity is lowered, phase separation at the fibre surface is completed and a nearly pure PPE matrix, without inclusions of remaining epoxy spheres, results (see *Figure 3d*). In the case of an epoxy content of 20 wt%, the development of a continuous interphase is inhibited and regions with a droplet-like morphology at the fibre surface are observed (see *Figure 3b*). Interestingly, the droplet-like morphology at the fibre surface observed for low epoxy contents implies that the accumulation of epoxy resin at the fibre interface is to some extent the result of droplet break-up or coalescence phenomena at the fibre, and not the result of the fibre surface acting as a nucleus for phase separation. Unfortunately, this also implies that only rather bulky ‘interphases’ ($\sim 0.4 \mu\text{m}$ for

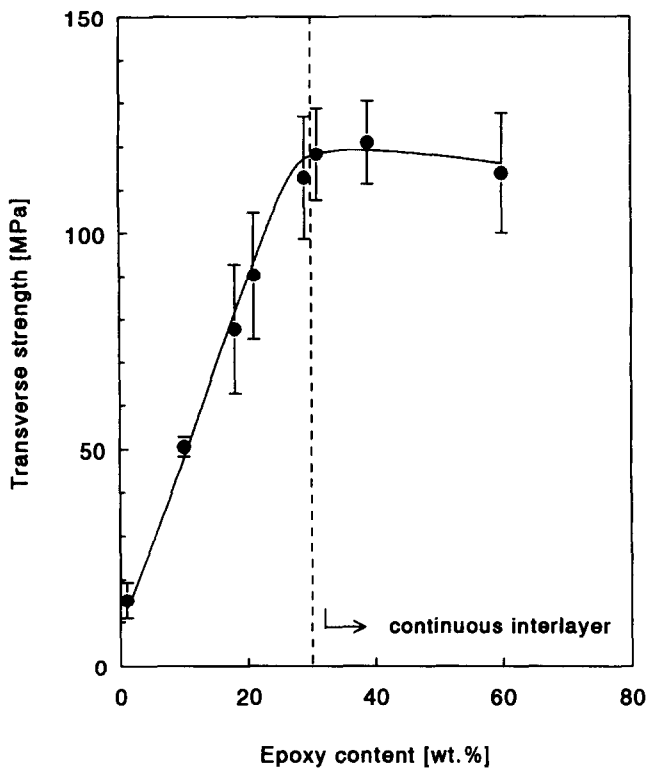


Figure 4 Transverse flexural strength of unidirectional composites versus the epoxy (DGEBA) content of the PPE/epoxy matrix

systems based on 40 wt% epoxy) are conceivable, since sufficient mobility in the system is required to obtain a completely segregated morphology.

The presence of an epoxy phase offers the possibility to drastically improve the adhesion between fibre and PPE matrix by applying local chemistry. This is illustrated in Figure 4, in which the transverse flexural strength of unidirectional carbon fibre-reinforced composites is plotted against the epoxy content in the matrix. Clearly, the epoxy phase introduces adhesion to the poorly adhering PPE matrix (see also Figure 3a), resulting in maximum performance as soon as a continuous epoxy interlayer is formed at an epoxy content of approximately 30 wt%.

Based on the morphological observations, it is concluded that epoxy resin is not only effective as a solvent during processing, reducing viscosity and processing temperature and thus enabling the incorporation of amorphous high T_g polymers such as PPE into composite structures, but provides additionally an *in situ* formed structural part (the 'interphase' or 'interlayer') of the final composite material after curing. Figure 5 shows schematically this reactive processing route, resulting in essentially thermoplastic composites with epoxy interlayers. Interestingly, these materials may also be regarded as carbon fibre-reinforced epoxy with ductile layers of PPE positioned between the fibres, i.e. a morphology similar to that of interleaved composites¹⁸; however, in this case on a fibre scale instead of a lamina scale.

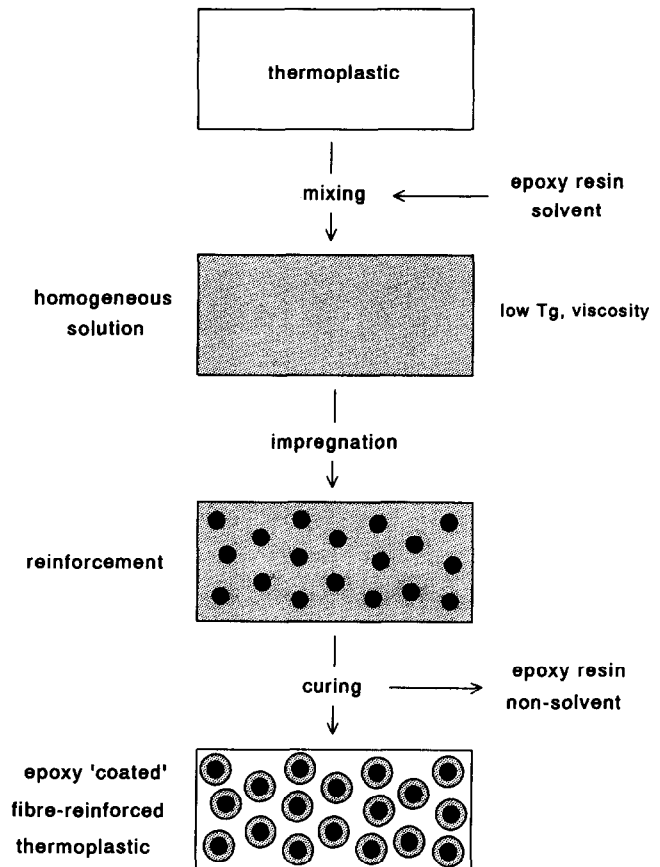


Figure 5 Schematic representation of the concept of processing of thermoplastic composites using reactive solvents

Interlaminar toughness

The main reason for introducing PPE in composite materials is its high ductility or toughness. For this reason, the mode I and mode II interlaminar fracture toughnesses of the fabric-reinforced laminates were studied.

In Figure 6 the critical strain energy release rates values (G_{Ic} and G_{IIc}) obtained for the composites based on the neat constituents and the blends are presented. As can be derived from Figure 6, the application of PPE/epoxy as matrix materials results in composites with relatively high G_{Ic} values. The correlation between composite mode I fracture toughness and PPE content (or matrix ductility; see Table 1) agrees well with results reported in the literature. As shown by Bradley¹⁹, no linear correlation exists between matrix and composite mode I fracture toughness. Generally, for brittle matrix materials (e.g. epoxy resin) a delamination fracture toughness is observed which is higher than the fracture toughness of the pure resin. This is explained by the increase in fracture surface as a result of the curved crack path imposed by the presence of fibres. For ductile matrix materials, on the other hand, the neat resin fracture toughness is only partly translated into the composite fracture toughness and an 'upper limit' for G_{Ic} is found of approximately 2 kJ m^{-2} . The rather disappointingly low G_{Ic} values are related to the high volume fraction of stiff fibres which prevent

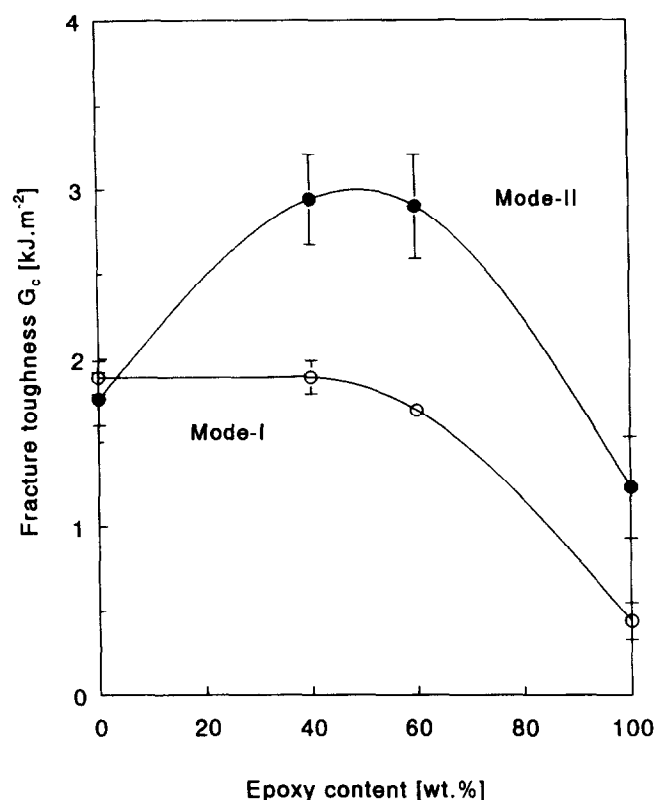


Figure 6 Interlaminar fracture toughness G_c of carbon fabric-reinforced composites versus the epoxy (DGEBA) content of the PPE/epoxy matrix ○, mode I; ●, mode II

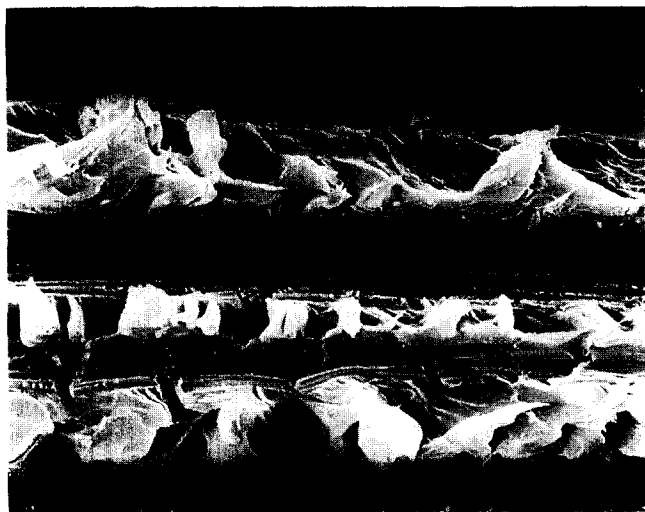


Figure 7 SEM micrograph of mode II fracture surface of carbon fabric-reinforced composite based on PPE/epoxy (40 wt% epoxy)

the development of a large plastic zone at the crack tip. For the PPE/epoxy-based composites this upper limit is reached for both epoxy contents. A positive consequence is that the penalty in matrix toughness due to the use of epoxy resin as a reactive solvent is negligible and will not affect the composite performance.

The results obtained in mode II loading conditions clearly differ from those found in mode I, and a

remarkably strong synergy in G_{IIc} is observed for the PPE/epoxy-based laminates. In order to explain the results found for the mode II fracture toughness tests, the fracture surfaces were examined. SEM micrographs revealed clean fibre surfaces in the case of neat PPE composites, similar to the one shown in *Figure 3a*, clearly demonstrating the lack of adhesion in these systems. The brittle epoxy resin composite showed S-shaped microcracks, referred to in the literature as 'hackling'^{2,19}. This multiple microcracking phenomenon results in relatively high G_{IIc} values, compared with G_{Ic} values, for composites based on the intrinsically brittle epoxy resin. Microcracking ahead of the crack tip redistributes the load, analogous to plastic deformation, and effectively increases the amount of energy absorbed. In contrast, for composites based on ductile matrices like PPE, mode II loading conditions result in localized yielding at the crack tip and debonding due to the poor interfacial adhesion. As a result, the gain in composite toughness achieved by exchanging brittle thermosets for ductile thermoplastics is generally in mode II conditions even more disappointing than under mode I conditions. While mode I testing revealed a fourfold increase in toughness on exchanging epoxy resin for pure PPE, in mode II loading conditions only a 1.5-fold increase in toughness was found.

For the composites based on the PPE/epoxy system, SEM micrographs of the mode II specimen reveal a more extensively deformed fracture surface and a combination of yielding of the PPE and brittle fracture or 'hackling' of the epoxy phase is distinguished *Figure 7*. The unique composite morphology may explain the observed synergy. Provided that microcracks in the epoxy interlayer can initiate yielding in the PPE-rich phase, multiple brittle fracture of the epoxy interlayer during mode II loading can effectively delocalize yielding of the PPE-rich phase ahead of the crack tip and subsequently increase the deformation volume and G_{IIc} . A schematic representation of the influence of brittle interphases on the mode II deformation mechanism in ductile thermoplastic composites is shown in *Figure 8*. Since mode II rather than mode I interlaminar fracture toughness correlates with the impact performance of composite materials²⁰, these results indicate that a brittle fibre coating in an intrinsically tough thermoplastic composite could act as an effective impact modifier. This observation is of particular interest, since in the existing literature attention is mainly directed towards the introduction of ductile or rubbery fibre coatings²¹⁻²⁴.

COMPOSITES WITH TAILORED INTERPHASES

Controlling the interlayer properties

An interesting feature inherent to the processing route presented in this paper is that the mechanical properties of the *in situ* generated epoxy interlayer can be tuned from, for example, glassy to rubbery through variations

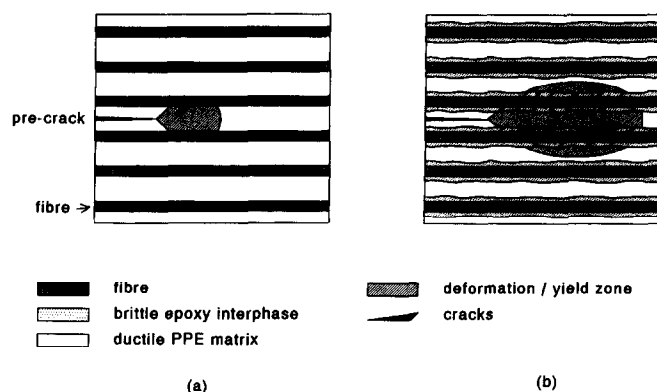


Figure 8 Schematic representation of the mode II deformation mechanism in ductile thermoplastic composites (a) without and (b) including brittle epoxy resin interlayers

in the type of epoxy resin solvent used¹⁴. This provides a powerful technique to study the correlation between interlayer characteristics and the macroscopic composite performance. For instance, increasing the ductility of the epoxy interlayer could be an elegant way of evaluating the toughening mechanism, as proposed in *Figure 8*. In order to systematically vary the mechanical properties of the epoxy phase, basically two routes are available: (1) varying the crosslink density and (2) varying the flexibility of the epoxy network. The first can be realized by using resins with a higher starting molecular weight; however, this will strongly reduce the solubility of the PPE. Alternatively, an excess in curing agent or the use of bifunctional curing agents could be considered, since both methods yield a more linear polymerization. These techniques show, however, a high sensitivity towards the stoichiometry and problems with the reproducibility are to be expected. Therefore, only the second route is explored here and flexibility was introduced by applying different combinations of aromatic (DGEBA) and aliphatic (DGEPP0) epoxies.

Incorporation of flexible monomers such as DGEPP0

reduced the T_g of the cured epoxy network gradually from 200°C to -25°C. Since all DGEBA/DGEPP0 resin mixtures are homogeneous over the entire composition range, the T_g -composition relationship could be described by a simple rule-of-mixtures relationship such as Fox equation¹⁴. *Figure 9* gives the Young's modulus of the cured epoxy materials and reveals the flexibility in tailoring the properties of the epoxy phase, from glassy (~2.5 GPa) to rubbery (~2.5 MPa), depending on the position of the T_g relative to room temperature. *Table 2* summarizes the mechanical properties of the constituents of the systems investigated. The first three compositions of 100/0, 80/20 and 60/40 yield glassy interlayers, however with a considerable increase in ductility. The latter two compositions with a DGEBA/DGEPP0 ratio of 20/80 and 0/100 are completely rubbery materials. The intermediate system with a ratio of 40/60 is of particular interest, since it exhibits a T_g close to room temperature. Since polymeric materials exhibit the highest ductility around T_g , this system reveals the highest strain at break of the whole series.

Table 2 Mechanical properties of the PPE/epoxy systems and the neat constituents (standard deviations are given in parentheses)

	Epoxy formulation		Young's modulus (MPa)	Yield stress (MPa)	Tensile strength (MPa)	Elongation at break (%)	Fracture toughness G_{Ic} (kJ m ⁻²)
	DGEBA/DGEPP0 ratio	Curing agent					
Epoxy	100/0	M-CDEA	2390 (65)	95 ^a	67 (7)	5 (0.9)	0.23 (0.04)
	80/20	M-CDEA	2560 (30)		68 (0.6)	6 (0.5)	
	60/40	M-CDEA	2410 (120)	54 (0.6)	48	18 (3) ^c	
	40/60	M-DEA	440 (10)	0.6 ^b	8.7 (0.8)	68 (5)	
	20/80	M-DEA	4 (0.1)		1.0 (0.1)	29 (5)	
	0/100	M-DEA	2 (0.1)		0.5 (0.1)	24 (4)	
PPE			2400 (75)	70 (0.6)		90 (17)	5.9 (0.2)
PPE/epoxy	100/0	M-CDEA	2310 (210)	75 (3.0)		48 (4) ^c	4.3 (0.2)
40 wt% epoxy	60/40	M-CDEA	2550 (80)	61 (0.4)		53 (3) ^c	3.5 (0.4)
	20/80	M-DEA	1120 (110)	36 (1.3)		> 90	7.5 (0.5)
	0/100	M-DEA	1160 (45)	33 (0.2)		> 90	10.4 (0.2)

^a Estimated from uniaxial tensile test by using a pressure-dependent von Mises yield criterion

^b Yield stress at strain rate of 0.2 s⁻¹ is 13.7 MPa

^c Estimated from neck geometry, assuming incompressible flow

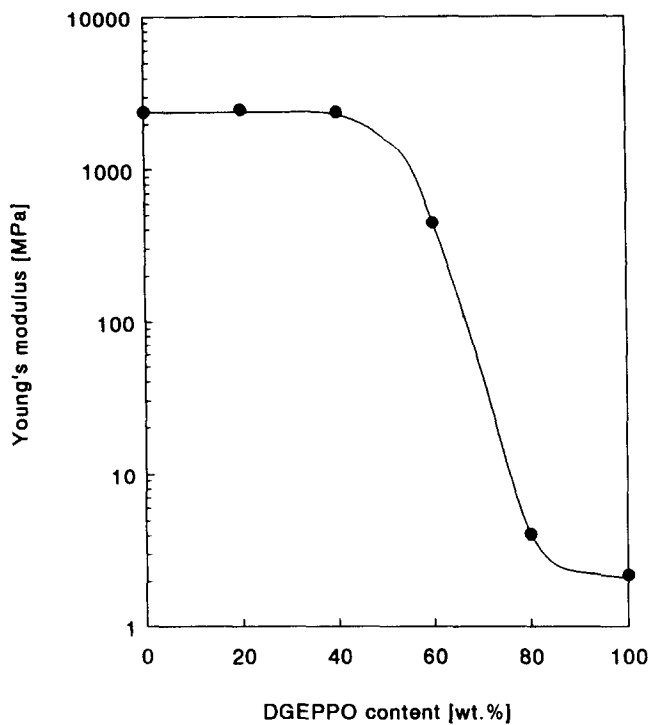


Figure 9 Young's modulus of epoxy resin system versus DGEPP0 content

Interlayer ductility and transverse properties

Table 3 summarizes the transverse properties of the unidirectional carbon fibre-reinforced PPE/epoxy composites. As expected, a significant influence of the interlayer properties on the transverse composite properties is found. Obviously, reducing the stiffness of the

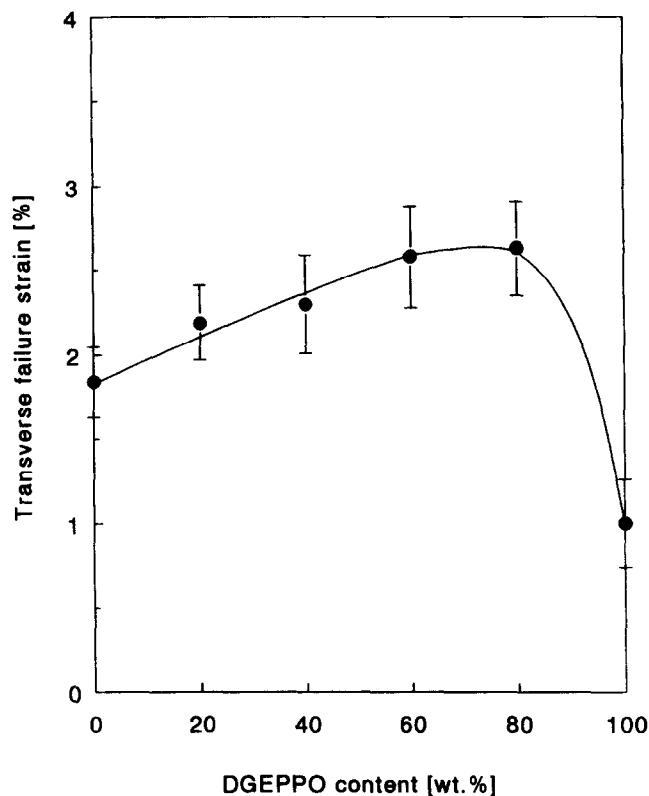


Figure 10 Transverse failure strain of unidirectional carbon fibre-reinforced composites versus DGEPP0 content of the epoxy phase

epoxy phase results in a reduction in transverse composite modulus. In fact, the transverse stiffness follows a similar trend to that shown in Figure 9 for the neat epoxy system, i.e. an upper plateau (~ 6 GPa) for the systems based on a DGEBA/DGEPP0 ratio of 100/0, 80/20 and 60/40 and a lower plateau (~ 2 GPa) for the 20/80 and 0/100 systems.

Of all the transverse properties of unidirectional composites, the transverse failure strain is of particular interest since it is often used as a design criterion for composite structures and as such limits the optimal use of composite laminates. Generally, upon loading, the high modulus fibres cause pronounced stress concentrations. Additionally, the stress situation inside the matrix is to a large extent triaxial, which restrains its plastic deformation. As a result, the deformation of the polymer matrix is strongly localized, yielding macroscopically very low strains to failure in transverse loading. As a possible solution to this problem the application of thin elastomeric fibre coatings is reported. For instance, Marom and Arridge²⁵, Jao and McGarry²³ and de Kok *et al.*²⁶ have shown that these coatings drastically change the stress situation in the matrix. By changing the properties of the epoxy interlayer in our system, the stress situation in the matrix may be altered, thus promoting plastic deformation in the adjacent PPE matrix²⁶.

Figure 10 shows the transverse failure strain of unidirectional PPE/epoxy with a fibre volume fraction of 50% and different compositions of the epoxy phase. With the exception of the composites with a DGEBA/DGEPP0 ratio of 0/100, rubbery interlayers reveal a significant gain in transverse failure strain up to values of approximately 2.6% for the 40/60 and 20/80 systems. These observations cannot be solely attributed to an enhanced failure strain of the epoxy interlayer, since results on neat epoxy revealed significantly lower failure strains for the 20/80 system compared with that of the 40/60 system (see Table 2). For this reason the high transverse strains in the case of the rubbery interlayers have to be attributed to an altered stress situation in the PPE matrix. As shown by numerical calculations by de Kok *et al.*²⁶, by incorporating rubbery interlayers a stress situation in the matrix is obtained similar to that in the case of holes or rubbery fibres. Basically, this effectively relieves the restrained (plastic) deformation of the matrix caused by the presence of the high-stiffness fibres.

Table 3 Transverse flexural properties of unidirectional PPE/epoxy composites with different compositions of the epoxy phase (standard deviations are given in parentheses)

DGEBA/DGEPP0 ratio	Modulus (GPa)	Strength (MPa)	Failure strain (%)
100/0	5.9 (0.1)	112 (14)	1.84 (0.21)
80/20	6.0 (0.3)	106 (12)	2.19 (0.22)
60/40	6.0 (0.2)	114 (8)	2.20 (0.29)
40/60	4.1 (0.2)	72 (9)	2.58 (0.30)
20/80	2.3 (0.1)	42 (5)	2.63 (0.28)
0/100	2.1 (0.1)	19 (3)	1.00 (0.26)

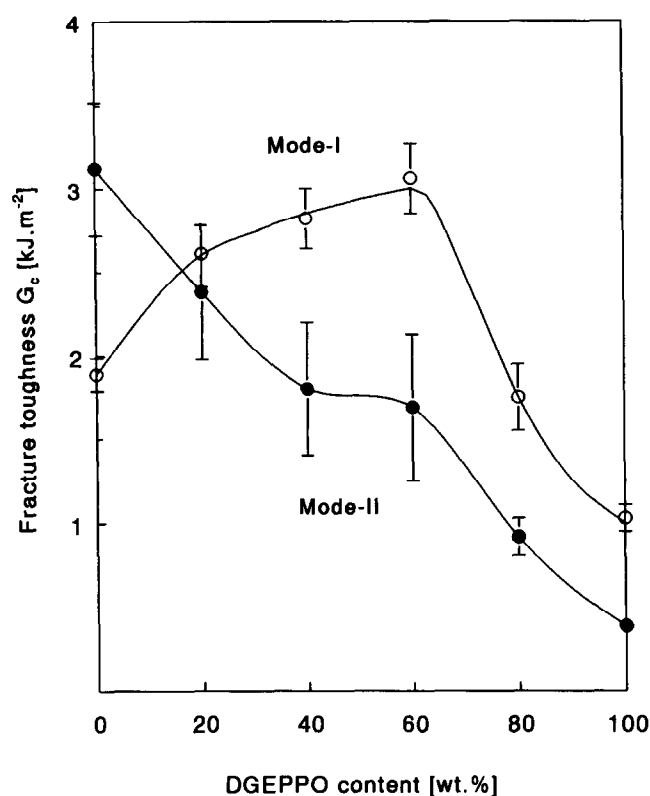


Figure 11 Interlaminar fracture toughness G_c of carbon fabric-reinforced composites versus DGEPP0 content of the epoxy phase: ○, mode I; ●, mode II

The low transverse failure strain of the composites with a DGEBA/DGEPP0 ratio of 0/100 is the result of poor adhesion of this epoxy formulation towards the PPE matrix and/or the carbon fibres. This effect is caused by the significantly lower reactivity of the DGEPP0 resin compared with the DGEBA resin and prevails mainly in the pure DGEPP0 epoxy system.

Interlayer ductility and interlaminar toughness

The mode I and mode II interlaminar fracture toughnesses were evaluated on carbon fabric-reinforced specimens, this time also including the rubbery epoxy interlayers systems. In order to minimize energy dissipation in the bulk of the composite as a result of plastic matrix deformation, in these composites the matrix composition was varied only in the composite mid-plane, i.e. the region of crack propagation. Unfortunately, however, no plateau values for G_{IIc} could be determined, due to a poorly defined crack propagation. Consequently, in the case of mode II, only a meaningful value for initiation can be given.

The mode I and mode II fracture toughness values of fabric-reinforced composites are presented in Figure 11. Upon flexibilizing the interphase, initially an increase in mode I fracture toughness is observed. A further increase in the DGEPP0 content, until a fully flexibilized interphase is obtained, yields a drop in mode I fracture

toughness. Again, the low values for toughness observed for the rubbery systems with a DGEBA/DGEPP0 ratio of 0/100 can be attributed to the low level of adhesion.

While the increase in mode I fracture toughness can be understood in terms of the intrinsic matrix and interphase properties, the reduction in mode II fracture toughness is more difficult to interpret. These results have to be related to secondary phenomena, such as the toughening mechanism as proposed in Figure 8. The results demonstrate indeed that when multiple fracture or 'hackling' of the interlayer is suppressed by flexibilization, the composites reveal a considerable reduction in toughness. This argument is supported by fractographic studies of the mode II fracture surfaces, where already in the case of a DGEBA/DGEPP0 ratio of 80/20 only plastic deformation in the matrix system is observed.

CONCLUSIONS

The use of epoxy resin as a reactive solvent enabled us to introduce PPE into high-performance composite structures using a simple film-stacking technique. Upon curing, phase separation was initiated and the epoxy resin was converted into a third phase. As a result of the polarity of the fibres, the epoxy resin accumulated preferentially at the fibre surface, resulting in the *in situ* formation of an epoxy interlayer at the fibre surface. Consequently, the epoxy resin was not only effective as a solvent, but also formed a structural part of the final composite material. Moreover, this epoxy interlayer provided a high level of interfacial adhesion which was not attainable in the pure PPE system. In the case of high fibre volume fractions, a morphology of epoxy-coated fibres in a virtually pure PPE matrix was obtained. As a result of this unique morphology, the composite materials revealed outstanding properties in terms of interlaminar toughness. A variation in interlayer properties strongly influenced the macroscopic composite behaviour. By increasing the ductility of the epoxy phase, the transverse strain at break could be improved significantly. Moreover, fracture toughness experiments revealed that ductile glassy interlayers were in favour of mode I fracture toughness, whereas brittle glassy interlayers were in favour of mode II fracture toughness. These results point out once more that the quest for the optimal 'interphase' or 'fibre coating' will always require a compromise and depends strongly on the type of application and the properties needed.

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