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Microstructure and properties of polyester/urethane acrylate thermosetting blends, and their use as composite matrices

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Thermosetting blends of a rigid polyester (PE) and a poly(urethane acrylate) elastomer (UA) have been investigated over a wide range of compositions in the cast condition, and in use as matrices of unidirectional glass-fibre composites. Transmission electron microscopy showed that blends in the composition range 20%–60% UA have a two-phase structure, probably with a phase inversion from PE-rich to UA-rich matrix between 40% and 50% UA. It was found that the observed variation in Young's modulus with blend composition could be represented by a simple geometrical model based on series/parallel combination of phases with a regular dispersion. This analysis provided supporting evidence for the proposed phase structures of the blends. Further evidence as to the phase structures was the rapid decline in indentation hardness and in temperature of distortion under load which occurred between 40% and 50% UA. Blends with up to 15% UA were found to have higher tensile strength, and slightly higher failure strain, than the unblended polyester. For composites with PE-rich matrices, the transverse Young's modulus exceeded that of the matrix in bulk, and it was found that the relationship could be expressed approximately by a version of the series/parallel model referred to above. Transverse tensile strengths of the composites were, in all cases, lower than the bulk matrix strength. To account for the observed relationship, a modified version of the Cooper and Kelly model for transverse strength is presented.

1. Introduction

Unidirectional fibre composites with matrices of thermosetting polymer have high specific strength and stiffness when loaded in the fibre direction, but off-axis stresses, which arise in all but the simplest loading regimes, render them liable to inter-fibre splitting because of the brittle nature of the matrix. Under fatigue loading also, initiation of failure frequently occurs in the matrix. There is, therefore, considerable interest in methods to improve these matrix-dominated properties of composites.

One approach has been to seek improved ductility, and/or fracture surface energy of the matrix material in bulk, while retaining as far as possible the original values of the associated properties: stiffness, glass transition temperature, and heat distortion temperature. The replacement of thermoset matrices with thermoplastics has met with some success in the aerospace composites field, but is at present of less interest for the general engineering market, because of material costs and the need to re-equip for a different technology.

The most widely employed technique of toughening composite matrices is to "modify" the thermoset by a dispersion of elastomer particles [1, 2]. For epoxy matrices, rubber modification is now virtually an industry standard, but for polyesters, where the kinetics of cure are different, it is sometimes less easy to obtain satisfactory dispersions of elastomer particles [3]. As an alternative, use has recently been made of polyester/poly(urethane acrylate) (PE/UA) blends to improve resistance to matrix cracking in critical locations such as joints in GRP structures [4]. Our research has involved a study of the properties and constitution of blends in one PE/UA system, with the object of determining the conditions which give rise to toughening or flexiblization. This paper presents observations on the properties and microstructure of the blends, and attempts to account for the observed variation in elastic modulus with composition by the use of a simple model [5]. It then compares the transverse strengths of unidirectional glass-fibre composites incorporating selected blends, with the yield strengths of the same blends in bulk. As is invariably found in such comparisons, the transverse strengths are much lower. A development of the well-known Cooper and Kelly model for transverse strength [6] is presented in an attempt to rationalize the observations.

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TABLE I Mechanical properties of polyester/urethane acrylate (UA) cast blends. Figures in brackets are 95% confidence limits.

Composition (% UA)	Modulus (GPa)	Yield stress (MPa)	Failure strain (%)	Hardness (Barcol)	HDT (°C)
0	3.46 (.24)	61.0 (3.9)	2.03 (.13)	38 (2.5)	75
5	3.55 (.54)	70.1 (6.3)	2.36 (.23)	35 (2.3)	
10	3.17 (.11)	70.1 (1.1)	3.16 (.16)	32 (2.0)	
15	3.08 (.13)	64.5 (5.0)	5.09 (1.4)	28 (2.0)	
20	2.88 (.06)	60.5 (.31)	9.60 (1.6)	25 (2.2)	70
25	2.85 (.29)	54.0 (.77)	15.2 (2.8)	23 (1.8)	
40	2.35 (.03)	46.8 (.62)	24.2 (1.6)	20 (2.0)	62
50	1.80 (.08)	41.2 (.20)	34.6 (.68)	3 (1.0)	49
60	1.65 (.10)	33.0 (.20)	47.4 (2.6)		
80	1.35 (.01)	21.5 (.96)	67.0 (9.8)		
100	0.99 (.02)	14.9 (2.2)	83.5 (5.5)		

2. Experimental procedure

2.1. Cast resins

The resin used as a basis for the experimental blends was an isophthalic polyester formulated for high-performance applications [7]. The second component was an unsaturated urethane acrylate [4] (both supplied by Scott Bader Co. Ltd, Wollaston, UK). The components were presented as solutions in styrene, compatible in all proportions, and were cured at room temperature using a combination of cobalt accelerator and amine catalyst in a constant proportion for all blend compositions. Plaques 3 mm thick were prepared by casting between glass plates, and allowing to cure for 24 h before demoulding.

Tensile testpieces, to ASTM specification D638, were machined from the plaques, and tested, with a minimum of five replications, in a screw-driven testing machine, with non-contact extensometer of gauge length 50 mm. Aluminium end-tabs were used. The crosshead speed was 1 mm min^{-1} for blends with less than 25 % – UA, and 5 mm min^{-1} for the remainder, so that all tests were completed within 1–2 min.

The temperature of distortion under load (HDT) was measured according to ASTM specification D648, on samples 130 mm × 12.8 mm × 6 mm, cut from cast plaques. Two samples of each blend were tested under a maximum bending stress of 1.8 MPa.

A Barcol spring-loaded impressor was used according to ASTM specification D2583 to test the hardness of the blends. Eight to ten readings of penetration depth were taken from each sample.

Ultra-thin sections of cast blends were examined by transmission electron microscopy (TEM). After considerable experimentation, satisfactory image contrast was achieved by the use of the following staining technique, performed on microtomed samples. Sections were immersed in a 2% aqueous solution of osmium tetroxide for 30 min, washed with distilled water, and immersed in Reynolds' lead citrate solution (1963) for 10 min. Both solutions were at room temperature.

2.2. Composites

For the preparation of composites, use was made of a unidirectional mat (Heinsco Ltd, Rochdale, UK) [8]. Instead of using rovings bound by transverse strands, this product contains parallel filaments closely packed in a flat crimp-free sheet, held in position by a fine "spider's web" of polymer fibrils. On wetting out, the binder dissolves, leaving a truly unidirectional reinforcement. The mats used were of E glass with a superficial weight of 300 g m^{-2}. Eight layers were incorporated in laminates 3 mm thick, the mats being individually wet out by hand, stacked, and finally pressed to size against stops. This produced a fairly consistent fibre volume fraction, although the more viscous UA-rich blends were more difficult to incorporate. As with the castings, curing was for 24 h at room temperature. Fibre volume fractions were determined by the burn-off method, using samples 25 mm × ~50 mm.

Testpieces for transverse (90°) and off-axis (15°) tensile tests were parallel-sided strips of 25 mm width, cut by diamond saw. The edges were carefully polished before testing, to remove any discontinuities. The crosshead speed was 1 mm min^{-1} in all cases. Aluminium end-tabs were used for the 15° samples. Interlaminar shear strength was determined by the short-beam bend test, using samples 30 mm × 10 mm × 3 mm with a loading span of 15 mm.

3. Characteristics of cast resins

3.1. Mechanical properties

Table I shows the compositions of all blends investigated, with mean values of initial tangent modulus, yield stress, failure strain, hardness and HDT. The figures in brackets are 95% confidence limits about the means.

For Young's modulus, the overall downward trend with increasing UA content is interrupted by a high value at 5% UA, but this observation was subject to greater scatter than others. This variation will be further discussed below, after consideration of the blend microstructures.

The tensile strengths of blends with up to 15% UA exceed that of the unmodified polyester. Only at 20% UA does the strength fall below that level. Thereafter, there is a progressive decrease in strength with increasing UA content.

Failure strain increases quite slowly with UA content over the range of compositions 0%–15%, where blend strength exceeds that of the unmodified poly-

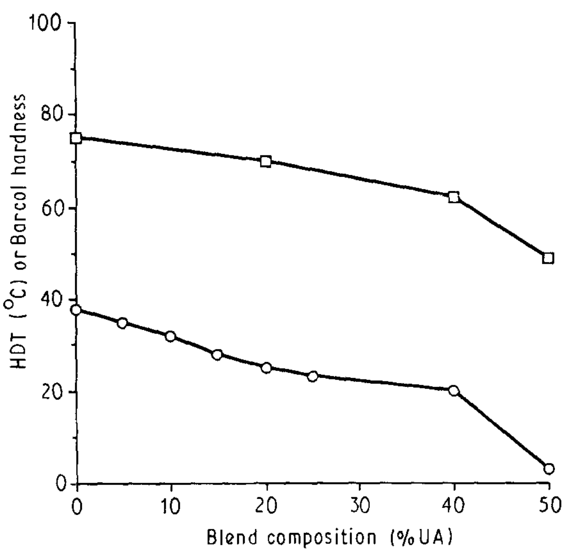


Figure 1 (○) Indentation (Barcol) hardness, H_b and (□) temperature of distortion under load (HDT) for cast PE/UA blends as a function of composition.

ester. At higher UA levels, a much faster rate of increase in failure strain is observed.

The variation of HDT and hardness with blend composition is shown in Fig. 1. It will be noted that neither of these tests could be applied to blends with more than 50% UA, because the samples deformed by creep under the applied loads. An interesting feature of these curves, in relation to the microstructural observations given below, is that the rate of decrease of both properties with increasing UA content is much greater in the range 40%–50% UA than at lower compositions.

3.2. Macro- and microstructural features of the blends

Within the composition range 20%–60% UA, cast blends turned opaque on curing, suggesting that a two-phase structure was present. Blends beyond this composition range were optically clear. It proved impossible to resolve the duplex structures by optical microscopy, and the accompanying micrographs (Fig. 2a–g) were taken by transmission electron microscopy at a magnification of ×5000, using samples stained in the manner described above.

An appropriately featureless image was obtained from the unmodified polyester (Fig. 2a). The unblended urethane acrylate, despite its optical clarity, had a mottled appearance in the TEM (Fig. 2g). This could not be resolved at higher magnification because of damage to the sample from the electron beam. Nor could the structure be satisfactorily explained, so it has been taken to be an etching effect characteristic of the UA, and of a UA-rich "solution" phase in PE/UA blends.

At 20% UA (Fig. 2b) the structure comprises a continuous dark majority phase, with islands of a lighter constituent. At 40% UA (Fig. 2c) the proportion of lighter phase is higher, and on the basis of these observations the dark phase is identified as PE-rich and the light as UA-rich. The micrographic appearance and mechanical characteristics of the 40% UA blend suggest that the two phases are co-continuous.

The blend with 50% UA (Fig. 2d) shows a higher proportion of UA-rich phase, which is here present in sufficient quantity to show the mottled texture previously identified with it. The PE-rich phase appears as islands, suggesting that a phase inversion has occurred, such that the UA-rich phase is now continuous.

The blends with 60% and 80% UA appear very similar (Fig. 2e, and f), showing predominantly the mottled UA-rich phase. Some small areas of PE-rich phase are discernible in Fig. 2e, but none is apparent in Fig. 2f, which is considered to be a single-phase structure.

3.3. Discussion of cast blend characteristics

The contention that a phase inversion, from PE-rich matrix to UA-rich matrix, occurs between 40% and 50% UA is supported by our observations of the mechanical properties of blends. HDT and hardness both show a sharp decline over this composition range, consistent with the change from thermoset-dominated to elastomer-dominated properties. Careful inspection of the variation of Young's modulus with blend composition gives further corroboration.

A simple "series/parallel" (SP) model for the elastic modulus of phase mixtures has recently been presented [5]. A phase mixture is considered as a regular array of particles of the discontinuous phase D (modulus E_d) in a matrix of the continuous phase C (modulus E_c). The phases are assumed to be perfectly bonded, and to have identical values of Poisson's ratio. Fig. 3 illustrates the model. It shows a view (a), in the plane of the load direction FF, of an array of cubical particles. The corresponding sectional view (b) shows that in the load direction, the composite comprises two sets of strips in parallel, one duplex and the other single-phase. Thus we have:

(i) duplex strips (pqrs), in proportion by volume: x^2, with modulus E_s (see below);

(ii) matrix-only strips (being the area surrounding pqrs, out to ABCD), in proportion by volume: $(1 - x^2)$, with modulus E_c.

Because the strips are in parallel, we have

$$E = E_s x^2 + E_c(1 - x^2) \qquad (1)$$

where E is the overall modulus of the composite. Within the duplex strips, the two phases are in series. Thus, by the Reuss model

$$E_s = E_c/[1 - x(1 - R')] \qquad (2)$$

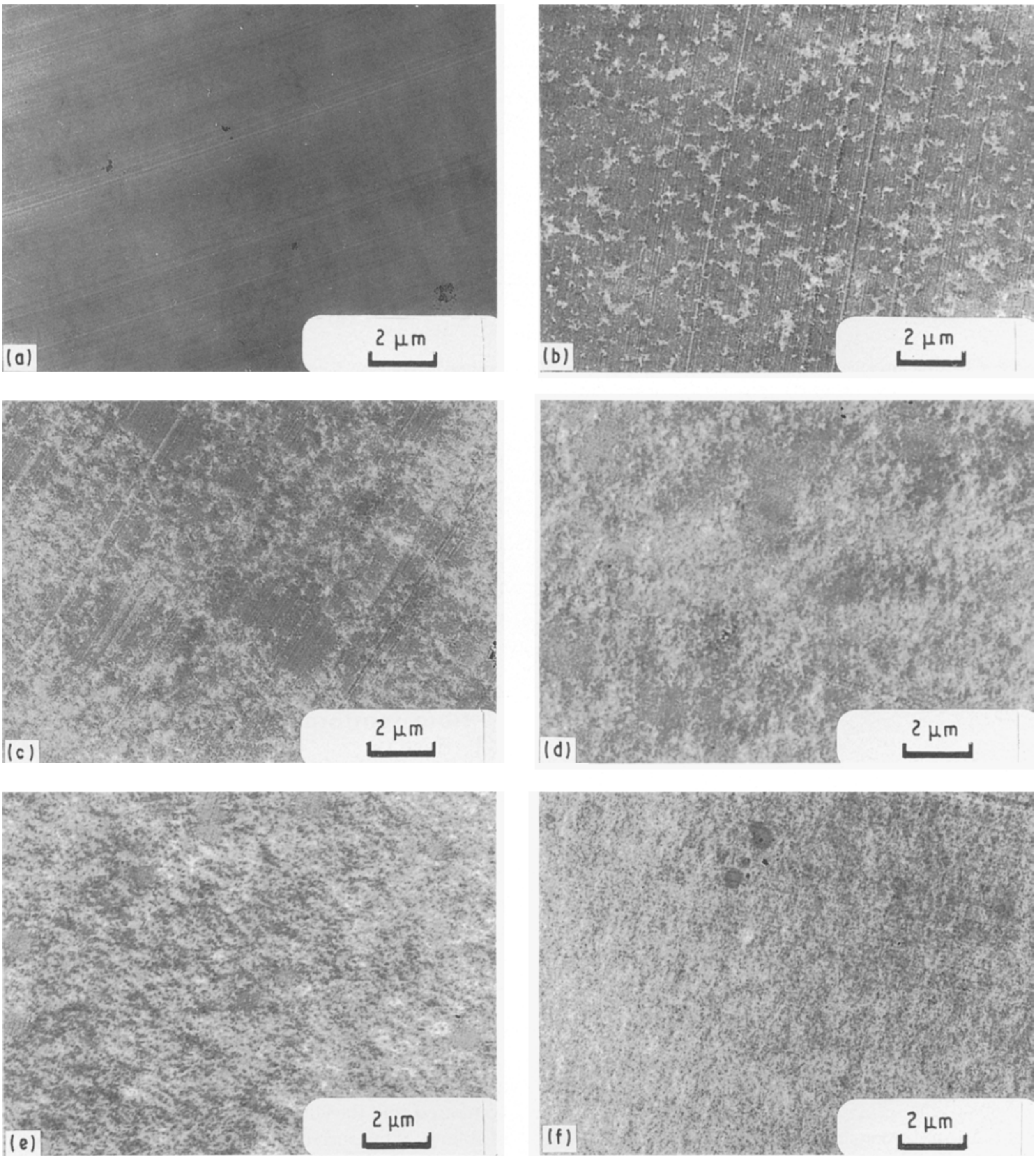
where $R' = E_c/E_d$. The ratio of composite modulus to modulus of the continuous phase is then given by

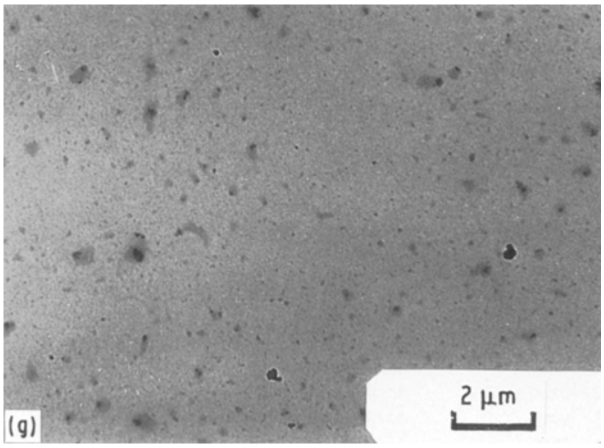
$$E/E_c = x^2/[1 - x(1 - R')] + (1 - x^2) \qquad (3)$$

The parameter x can be related to the volume fraction of discontinuous phase, V_d, by an expression of the form

$$x = (P'V_d)^{1/3} \qquad (4)$$

where P' is a disposable parameter which may be shown to be a "relative volume fraction", because it is





the ratio: (volume of equivalent cubical particles)/(volume of actual particles). P' may assume values in the range 0.37–1.91 [5].

Figure 2 Transmission electron micrographs of polyester/urethane acrylate (PE/UA) cast blends covering a range of compositions. (a) unmodified PE, (b) blend with 20% UA, (c) blend with 40% UA, (d) blend with 50% UA, (e) blend with 60% UA, (f) blend with 80% UA, (g) unmodified UA.

For particulate composites comprising two phases of different moduli, we may consider each in turn to be continuous. Equation 3 then gives two different curves for E as a function of volume fraction, with appropriate substitutions of E_c and R'.

The variation of modulus with composition for the blends is compared with predictions of the SP particulate model with $P' = 1$ in Fig. 4. The densities of the two components are almost equal, so that the use of weight fraction instead of volume fraction introduces little error. Evidence for the existence of a phase inversion in the system, from PE-continuous to UA-continuous, at about 40% UA, is provided by the shift

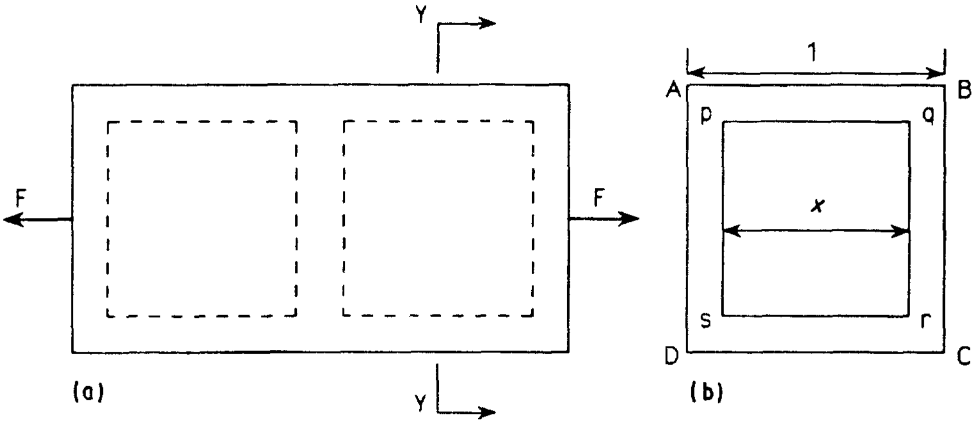


Figure 3 Illustration of the series/parallel (SP) model for modulus of particulate composites. (a) View in plane of load FF, showing cubic array of cubical particles. (b) Section YY perpendicular to load direction, showing unit area of the model. For explanation of notation, see text.

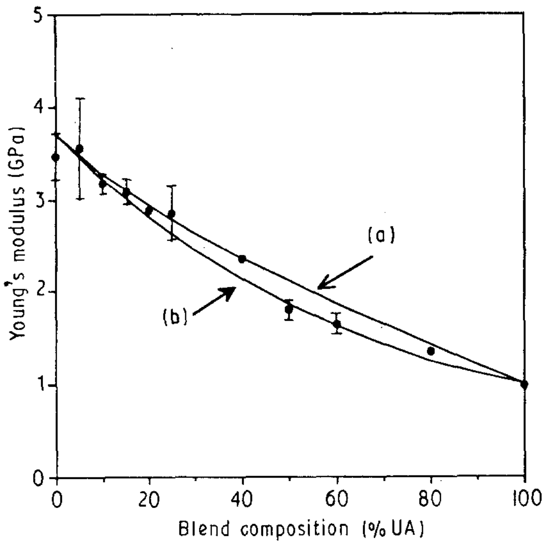


Figure 4 Modulus as a function of composition for a series of polyester/urethane acrylate blends. Error bars show 95% confidence limits. Curves represent SP particulate model with $P' = 1$. (a) polyester phase continuous, (b) urethane acrylate phase continuous.

of experimental points from the upper (PE-continuous) to the lower, UA-continuous curve, between 40% and 50% UA.

If UA is to be considered as a modifying addition to PE for use as composite matrices, then the initial rise in strength and failure strain, together with slow decline of modulus, at UA levels up to 15%, suggest that appreciable improvements in composite properties may be attainable. Compositions beyond the phase inversion would not be of interest for this type of application. The remainder of this paper deals with the off-axis properties of unidirectional glass-fibre composites made with these blends.

4. Off-axis properties of unidirectional fibre-reinforced blends

4.1. Results

Table II brings together values of all the properties measured in this work. Column 1 gives the nominal compositions of the matrix blends, and column 2 the fibre volume fractions, with estimated errors of ± 2%. Mean values of the remaining parameters; transverse modulus, tensile strength and failure strain; short-beam shear strength and 15° off-axis shear strength, are accompanied by their respective 95%. confidence limits in parentheses.

Transverse modulus and tensile strength are discussed below. Transverse failure strain is seen to have consistently low values as UA content increases up to as much as 50%, where the value of 0.6% is to be compared with the failure strain of the cast blend: 35% (Table I). Thus, as is commonly found, additional ductility in the matrix does not improve transverse tensile ductility in the unidirectional composite.

TABLE II Matrix-dominated mechanical properties of unidirectional composites as a function of PE/UA matrix blend composition. Figures in brackets are 95% confidence limits

% UA	Fibre V_f	Transverse Modulus (GPa)	Tensile strength (MPa)	Failure strain (%)	Inter-laminar shear strength (MPa)	Intra-laminar shear strength (MPa)
0	0.35	9.47 (0.80)	17.30 (0.85)	0.19 (0.02)	39.51 (1.78)	20.85 (1.28)
5	0.35	7.43 (0.52)	17.96 (0.97)	0.19 (0.03)	42.56 (0.76)	24.79 (1.25)
10	0.34	6.24 (0.66)	17.75 (0.65)	0.29 (0.04)	43.88 (0.49)	26.70 (1.62)
15	0.32	5.99 (0.22)	16.94 (0.69)	0.23 (0.03)	44.20 (1.00)	28.48 (3.12)
20	0.30	5.43 (0.75)	18.38 (0.61)	0.34 (0.05)	47.09 (0.48)	29.41 (0.93)
25	0.30	4.97 (0.32)	16.56 (0.62)	0.34 (0.05)	44.67 (0.37)	30.63 (0.67)
50	0.31	3.44 (0.21)	16.97 (0.89)	0.62 (0.07)		21.88 (0.96)
80	0.31	1.38 (0.12)	14.25 (0.66)	4.02 (0.92)		
100	0.30	0.81 (0.10)	07.91 (0.22)	12.22 (0.96)		

There are, however, measureable improvements in the shear properties of the composites, both intralaminar and interlaminar, as the UA content of the matrix is increased. The higher reported values from the short-beam test as compared with the 15° off-axis tensile test are taken to be artefacts of the measuring techniques, because it is not clear why interlaminar shear strength should exceed the intralaminar shear strength of the same composite. Intuitively, the reverse might be expected. However, the simultaneous increase in both measures suggests that improvement of shear strenth with increasing UA content is a genuine effect.

4.2. Discussion of transverse modulus

Fig. 5 shows the variation with composition of the matrix modulus, from Table I, and the composite transverse modulus (open squares) from Table II. It will be seen that in the highly flexible UA-rich compositions (80% and 100% UA) the stiffening effect of transverse fibres is negligible within the limits of experimental error. As UA content decreases, matrix and composite become stiffer, as expected, but the rate of increase of transverse modulus greatly exceeds that of matrix modulus. The point of interest here is to determine whether the two quantities can be related in any systematic way.

The transverse modulus of a fibre composite is frequently represented by the Reuss, or series model. This has been applied to systems where the moduli of fibre and matrix are constant, and the only variable is fibre volume fraction. Agreement is generally not good, and the model is unsatisfying because its assumptions are clearly not even approximately valid for a fibre composite.

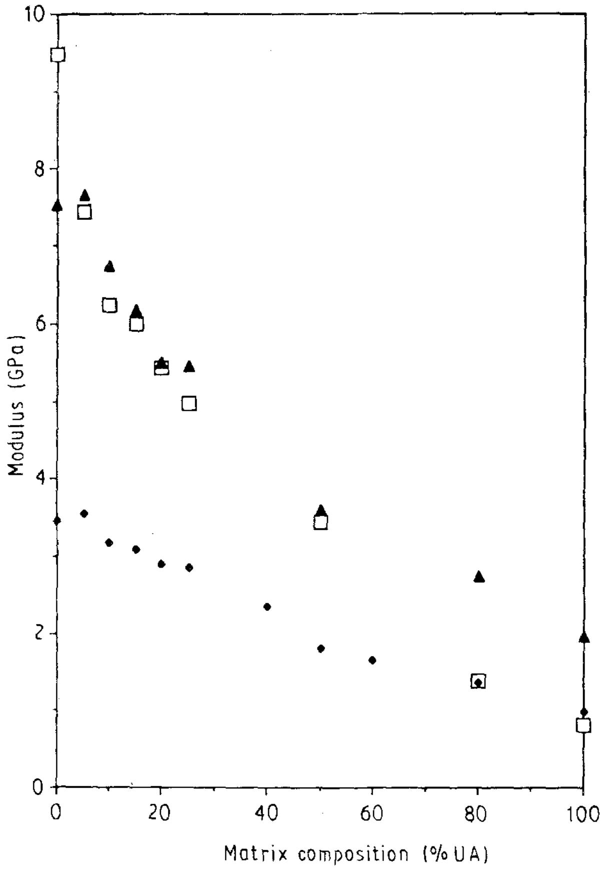


Figure 5 (◆) Matrix blend moduli, and (□) corresponding composite transverse moduli found by measurement, and (▲) by calculation from SP fibre model with $P = 1.27$.

Appreciably better agreement with experiment can be obtained by applying a modified version of the SP model described above. For a reinforcement in the form of prismatic square fibres, the respective volume fractions of duplex and matrix-only strips (see Section 3.2, above) are x and $(1 - x)$. Thus, Equation 1 becomes

$$E_t = E_s x + E_m(1 - x) \qquad (5)$$

where E_t is the transverse modulus, and E_m the matrix modulus. The Reuss equation is applicable with a simple change in terminology

$$E_s = E_m/[1 - x(1 - R)] \qquad (6)$$

where $R = E_m/E_f$, and E_f is the transverse modulus of the fibre. Equation 3 thus becomes

$$E_t/E_m = x/[1 - x(1 - R)] + (1 - x) \qquad (7)$$

The relationship between x and the fibre volume fraction, V_f, is

$$x = (PV_f)^{1/2} \qquad (8)$$

where P is the empirical "relative volume fraction", i.e. the ratio: (volume of equivalent square fibres)/(volume of actual fibres). In Fig. 5, the values of transverse modulus for the composites were calculated from the corresponding observed matrix moduli using Equations 7 and 8.

The value of P used in Equation 8 is $P = 4/\pi$ (where $\pi = 3.142$). This is the upper bound value [5], which in physical terms indicates that (cylindrical) fibres of diameter x are contributing the same stiffening effect as would square-section fibres of thickness x.

The model grossly overestimates the composite transverse modulus where the matrix is highly flexible (80% and 100% UA). Here, the disparity in Poisson's ratio between the phases would alone be sufficient to invalidate the model. However, for a wide range of blends more representative of modified polyester resins, the SP model gives an acceptable measure of agreement with experiment.

4.3. Discussion of transverse tensile strength

The transverse strength of unidirectional composites is commonly observed to be much lower than the strength of the corresponding matrix material in bulk. Mean strength values for blends (Table I) and composites (Table II) are plotted as a function of composition in Fig. 6. The transverse strengths of the composites show a quite remarkable consistency across a wide range of compositions, with appreciable decrease only at 80% and 100% UA. Evidently, the reduction in strength caused by the introduction of transverse fibres is much less severe in matrices of lower initial strength and stiffness. This observation prompted a critical examination of some models which have been proposed to quantify the effect.

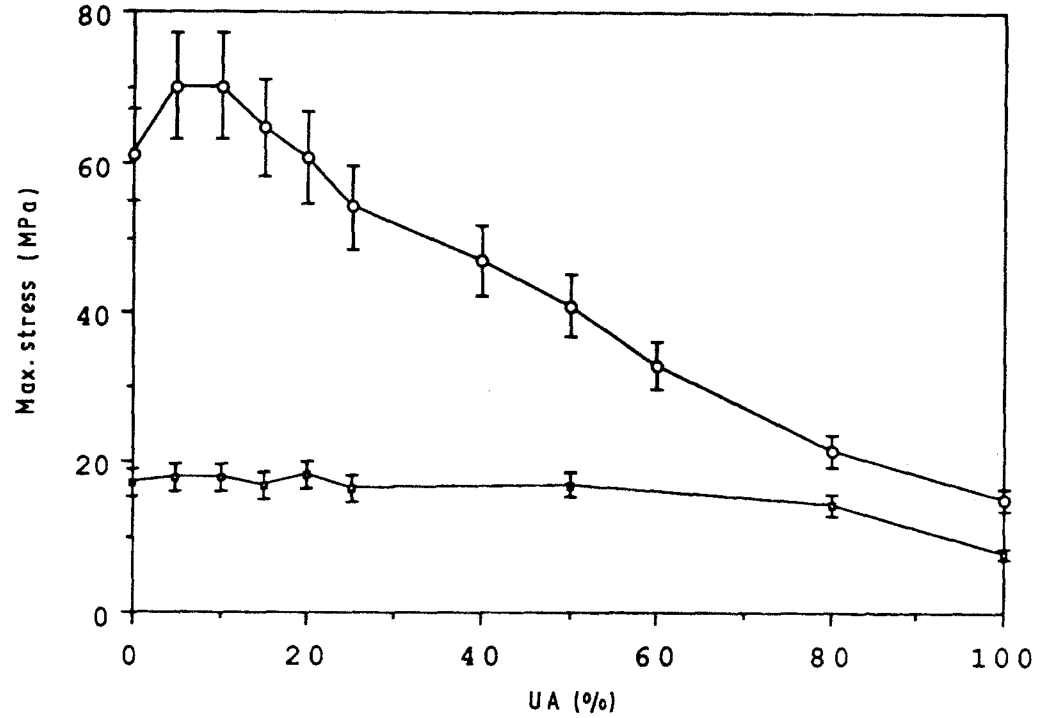


Figure 6 Effect of composition on (○) yield strength of PE/UA blends, and on (□) transverse tensile strength of unidirectional fibre composites made from them. Error bars show 95% confidence limits.

Published models [6, 9, 10] have concentrated on the influence of fibre volume fraction, V_f, in composite systems with a common matrix, such that the matrix stiffness, E_m, and strength, T_m, remain constant. The transverse strength, T_t is then related to T_m via a stress concentration factor, defined as

$$S = T_m/T_t \qquad (9)$$

We have previously found it to be convenient to invert the relevant equations, making the subject a "strength reduction factor", T_t/T_m, for which we have used the notation $1/S$ to facilitate comparison with the work of others. In an earlier publication [11] we demonstrated that the models of Kies [9] and Gresczcuk [10] were unable to predict the strength reduction factor for composites with similar values of V_f, but with matrices of widely differing moduli and strengths. We present here a development from the model of Cooper and Kelly [6] which enables the observations in Fig. 6 to be rationalized.

Cooper and Kelly give an expression for the transverse strength of a composite which takes into account, on the one hand, weakening by the reduction in effective area of matrix as V_f increases, and on the other, the contribution of the fibre/matrix bond, which increases with V_f. In the terms employed here, this may be written

$$T_t = T_m(1 - x) + T'x \qquad (10)$$

where T' is the mean stress required to separate fibres from the matrix. The parameter x is the same as in Equation 5. It may be interpreted as the projected width of fibre per unit width of composite in the transverse direction, and it therefore represents the area fraction of fibre in a longitudinal section.

The relationship between x and the fibre volume fraction is, for cyclindrical fibres, $V_f = \pi x^2/4$. The limiting V_f for round fibres in a square array is represented by $x = 1$.

Dividing Equation 10 by T_m, we obtain the Cooper/Kelly strength reduction factor, $1/S(C)$

$$1/S(C) = 1 - x + fx = 1 - (1 - f)x \qquad (11)$$

where $f = T'/T_m$.

Fig. 7 shows the variation of $1/S(C)$ as a function of the volume fraction parameter x, (Equation 11). Evidently this is a straight line of slope $(1 - f)$. The two curves corresponding to extreme values of f are shown by the bold lines in Fig. 7. The condition $f = 0$ corresponds to zero bond strength between fibre and matrix, such that the strength reduction factor is simply equal

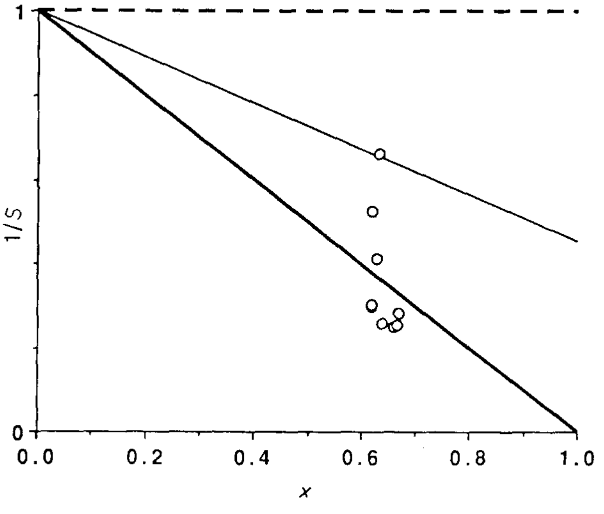


Figure 7 Transverse strength reduction factor for unidirectional composite, as a function of the fibre volume fraction parameter, x. Lines represent the model of Cooper and Kelly, with three values of the ratio $f = T'/T_m$ (- - -) $f = 1$, (—) $f = 0.46$, (—) $f = 0$, see text. (○) Experimental values for a range of PE/UA blend matrices.

to the proportion by area of resin in the composite cross-section, i.e. to $(1 - x)$. The condition $f = 1$ implies no reduction in strength by the introduction of glass fibres, so that this line is horizontal. Evidently, the Cooper/Kelly model is capable of accommodating wide variations in strength reduction factor at a given V_f.

Of the two terms involved in f, T_m can be directly measured, but T' is unknown. Thus, it seems reasonable to treat f as a disposable parameter, and obtain values of T' by fitting to experimental results. Measured strength reduction factors T_t/T_m for selected blends, taken from the curves in Fig. 6, are plotted in Fig. 7 as functions of x. It is seen that the scatter in V_f for the experimental laminates was very small.

Inspection of Equation 11 shows that where $x = 1$, then $f = 1/S$, so that it is easy to determine the value of f to match an experimental point in Fig. 7 by extrapolating the line from (0, 1) through the point, and reading off its intersection with the line $x = 1$. This process is illustrated by the middle line in Fig. 7, where the indicated value is $f = 0.46$.

In applying the Cooper/Kelly model to determine the experimental values of f, and hence of T', as functions of matrix composition, it was found [11] that negative values of T' resulted, because many of the experimental points in Fig. 7 fall below the line $f = 0$. Because T' clearly cannot be negative, some additional weakening factor must be operating to reduce the contribution of the matrix to the composite transverse strength. Residual shrinkage stress in the matrix is an obvious possibility.

4.4. Modification of the Cooper/Kelly model

To illustrate the principles of the revised model, we have assumed a constant shrinkage strain, e_s, across all blend compositions. If we further assume that the fibres are rigid, it follows that the matrix between fibres is subject to a tensile strain, e_s, and hence to a stress, T_s, before external load is applied. The contribution of the matrix to the recorded tensile strength will thus be reduced from $T_m(1 - x)$ (Equation 10) to $(T_m - T_s)(1 - x)$, and the modified Cooper/Kelly equation becomes

$$T_t = (T_m - T_s)(1 - x) + T'x \qquad (12)$$

T' and the other terms retain their original definitions, given above. Because matrix modulus, E_m, is known in every case, T_s may be set equal to $E_m e_s$. On dividing Equation 12 by T_m to obtain the strength reduction factor, we obtain:

$$1/S = (1 - E_m e_s/T_m) + [(T'/T_m - (1 - E_m e_s/T_m)]x \qquad (13a)$$

If we plot this quantity as a function of x, then for a particular matrix (i.e. constant values of E_m and T_m), and a particular shrinkage strain (constant e_s), we can define, as before, the envelope within which $1/S$ must fall. Again writing $f = T'/T_m$, the lower bound is defined by $f = 0$

$$1/S = (1 - E_m e_s/T_m) - (1 - E_m e_s/T_m)x \qquad (13b)$$

The upper bound corresponds to $f = 1$

$$1/S = (1 - E_m e_s/T_m) + (E_m e_s/T_m)x \qquad (13c)$$

Where E_m, T_m and $1/S$ have been measured, and a value of e_s assumed, an inferred value of T' may be obtained by the same construction as in Fig. 7. This is equivalent to substituting $x = 1$ in Equation 13a.

In Fig. 8, experimental points from Fig. 7 have been replotted, and the bounds of the revised Cooper/Kelly model for one specific matrix constructed, using modulus and strength values for the 50% UA blend, with an assumed value of 1% for e_s. The construction for T'/T_m is illustrated for the same blend, giving a value 0.32. The inferred "bond strength" for this composite is therefore $T' = 13.2$ MPa, approximately.

Values of T' have been determined for all the composites tested, using a range of assumed strains, e_s.

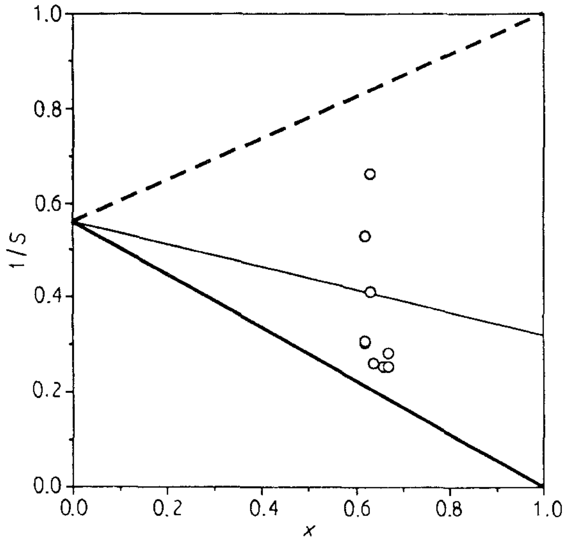


Figure 8 Transverse strength reduction factor for unidirectional composite, as a function of the fibre volume fraction parameter, x. Lines represent a modified version of the Cooper and Kelly model, with three values of the ratio $f = T'/T_m$: (- - -) $f = 1$, (—) $f = 0$, (—) $f = 0.32$, see text. (○) Experimental values for a range of PE/UA blend matrices.

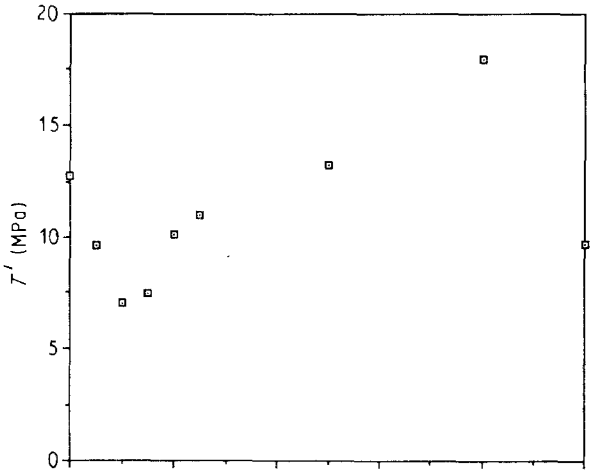


Figure 9 Inferred values of fibre/matrix bond strength, T', as a function of PE/UA matrix blend composition. Values calculated using the modified Cooper and Kelly model, with an assumed shrinkage strain of 1% at all compositions.

It was found that the minimum assumed strain to give non-negative values for T' at all compositions was 0.6%. Values of T' for $e_s = 1\%$ are plotted in Fig. 9 as a function of matrix blend composition.

The variation is erratic, which for at least two reasons is not surprising. First, there is no reason to suppose that the cure shrinkage would be the same for all of the blends, nor even that it would vary in a systematic manner with composition. Second, although each strength reduction factor reported is the mean of several determinations, that single experimental point has been used to locate each graph in Fig. 8. Evidently, there is a need for measurements of strength reduction factor over a range of fibre volume fractions for each matrix blend, if credible bond strength calculations are to be made. This paper has presented a means whereby the required data may conveniently be processed.

5. Conclusions

1. Thermosetting blends of a urethane acrylate elastomer and a polyester resin have been shown to exhibit duplex microstructures over a wide range of compositions.

2. A phase inversion near the middle of the composition range has been identified by TEM and by physical property measurements.

3. The variation in blend modulus with composition has been shown to be well represented by a simple geometrical model based on series/parallel combination of phases with a regular dispersion.

4. Blends with up to 15% UA are stronger than the unblended polyester, while their stiffness is comparable.

5. Unidirectional glass-fibre composites incorporating the above blends have been evaluated for their matrix-dominated properties. Shear strength, both inter- and intra-laminar, is progressively improved as the urethane acrylate content of the matrix increases up to 25%.

6. Transverse tensile modulus of a composite can be related to the modulus of its matrix (and the fibre volume fraction) by an extension of the above series/parallel model, provided that the matrix contains a continuous polyester-rich phase.

7. Transverse tensile strength of composites is neither increased nor decreased by additions of urethane acrylate to the polyester matrix, over a wide range of compositions.

8. As expected, transverse tensile strength of a composite is well below the yield strength of the matrix. A modified form of the Cooper and Kelly strength-reduction model [6] is presented as a tool for further investigation of this phenomenon.

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