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Microstructure–property relationships of GRP

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Fibre-reinforced composite materials are being used increasingly in critical applications, when the primary function of the material is to support loads, but very high safety margins are commonly used for such applications. Such large safety margins arise from the uncertainties regarding the mechanical behaviour of composite materials. The authors believe that the lack of microstructural definition of composite materials may make a substantial contribution to these uncertainties. In this initial study, relationships are sought between microstructure and properties of a model microstructure. The methods used are applicable to a very wide range of composite materials.

1. Introduction

Composite materials are being used increasingly in applications where a precise prediction of the mechanical behaviour of the material is essential. Glass-reinforced plastics have become well accepted for applications in which load-bearing ability is not particularly critical; examples of such applications include the hulls of small boats and yachts, the front nose section of the B.R. 125 high speed train and the body-work, including replacement components, of motor vehicles. The lack of precise knowledge regarding the mechanical behaviour of composite materials is, however, illustrated by the very high safety margins applied when the primary function of the material is to support loads; examples of such applications include the hull of the Royal Navy's experimental mine-hunter, H.M.S. Wilton, and the Central Electricity Generating Board's box for cooling water at power stations [1, 2]. A safety margin of around 20 is commonly used for such applications; the comparable safety margin for structural steel is often around 5. However, economic factors and required strength/weight ratios are increasingly making the use of such high safety margins for reinforced plastics unrealistic. Increasingly then, the mechanical behaviour of composite materials must be better specified.

The reasons for the uncertainties regarding the mechanical behaviour of composite materials may be divided into two broad areas. The first concerns the lack of knowledge regarding failure mechanisms in composite materials; an understanding of such mechanisms is particularly important for the prediction of the long term behaviour of composite materials including, for example, environmental degradation and fatigue behaviour. Considerable research effort is presently being applied to the elucidation of failure mechanisms. Non-destructive tests are being developed both for the monitoring of small test pieces and for the monitoring of large structures during proof tests. These non-destructive test methods include acoustic emission monitoring, and other methods for the detection of existing or growing flaws, such as ultrasonic testing and vibration testing (e.g. [3–5]). The second reason for the uncertainties regarding the mechanical behaviour of composite materials is the lack of consistency in mechanical test results from specimens which are considered identical in terms of the usual description of composite materials.

The usual description of fibre composite materials consists of a specification of the type of matrix and fibres, the volume fraction occupied by, and the orientation of, the fibres. No information regarding the fibre sizes or their distribution in the matrix is given normally. Thus, materials which are considered identical in terms of the

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usual description may have very different microstructures. It is postulated that the inconsistencies found in the mechanical behaviour of apparently identical test specimens may frequently be explicable in terms of different microstructures. A quantitative definition of the microstructure of composite materials is, therefore, essential to allow reliable use of these materials in critical applications.

In the present study, the aim has been to establish methods by which relationships between microstructure and properties may be established. Further, the extent to which these relationships may be quantified has been sought and in order to achieve this it has been necessary to confine this initial study to a model microstructure.

Methods have been developed and described for producing a quantitative description of such microstructures and for specifying its statistical homogeneity [6]. This method depends on acquiring large amounts of data using an image analysing computer (a Quantimet 720 in this case) from unidirectional glass-fibre reinforced polyester resin composites. The methods of microstructural definition are not, however, restricted to this particular composite material. The methods could be applied to any volume fraction at any scale; steel-reinforced concrete could, for example, be examined using reduced photographs. The methods could easily be extended to include the distribution of a further phase, for example gas bubbles or a different type of fibre as in hybrid composites. The shape classification available on the Quantimet means that the methods could be extended to the examination of multi-directional materials; the principal axes would be examined separately and the fibre orientation would simultaneously be measured. The gross inhomogeneities in commercial hand lay-up glass-reinforced polyester resin are probably too marked for direct application of the methods. However, it may be possible to modify the methods, for example by using a coarser measurement grid, to allow some quantitative description of the microstructures of these commerically produced materials.

The ultimate aim of the application of quantitative microscopy to composite materials is the derivation of bounds of acceptable microstructures for the materials to be suitable for a particular application. The first step must, therefore, be the correlation of microstructural parameters with mechanical properties. The bounds of acceptable mechanical properties for a given application must be derived, both from theoretical considerations and experimental measurements. Such experimental measurements would include the non-destructive test methods developed for the elucidation of fracture mechanisms described above. The two steps could then be combined to allow the statement of acceptable bounds for microstructural parameters for the given application. The initial stage of this correlation, namely the correlation of microstructural parameters with mechanical properties, is discussed in this paper. The material considered is unidirectional glass fibre-reinforced polyester resin, but, as discussed above, the approach and analyses are not restricted to this particular composite material.

2. Experimental details

The experimental procedures adopted in this study are summarized here while a fuller description of them may be found in [7].

2.1. Material and section preparation

Unidirectional beams of glass fibre-reinforced polyester resin were prepared in the laboratory using a pre-impregnation technique. The fibres were all oriented parallel to the long axis of the beam. Glass fibres in tows, that is bundles containing around 10 000 fibres, were clamped in a frame and impregnated with polyester resin. The impregnated tows were laid up in successive layers in an open-ended mould. The mould was pressed, and some dispersion of the tows occurred and the excess resin was expelled from the open ends of the mould. The mould was left overnight for the resin to cure, and the finished beams were then removed. Typical beam dimensions were 250 mm × 12 mm × 10 mm; the volume fraction occupied by the fibres was about 20%.

Sections for microstructural examination were cut perpendicular to the long axis of the beam; that is perpendicular to the fibre direction. The sections were mounted in cold-setting mounting resin and pre-ground before they were diamond polished. On completion of polishing the glass fibres were barely distinguishable from the resin (Fig. 1a). However, contrast was enhanced markedly by the use of Nomarski interference indicating that the resin had been removed preferentially (Fig. 1b). It was found possible to preferentially etch the interface between the fibre

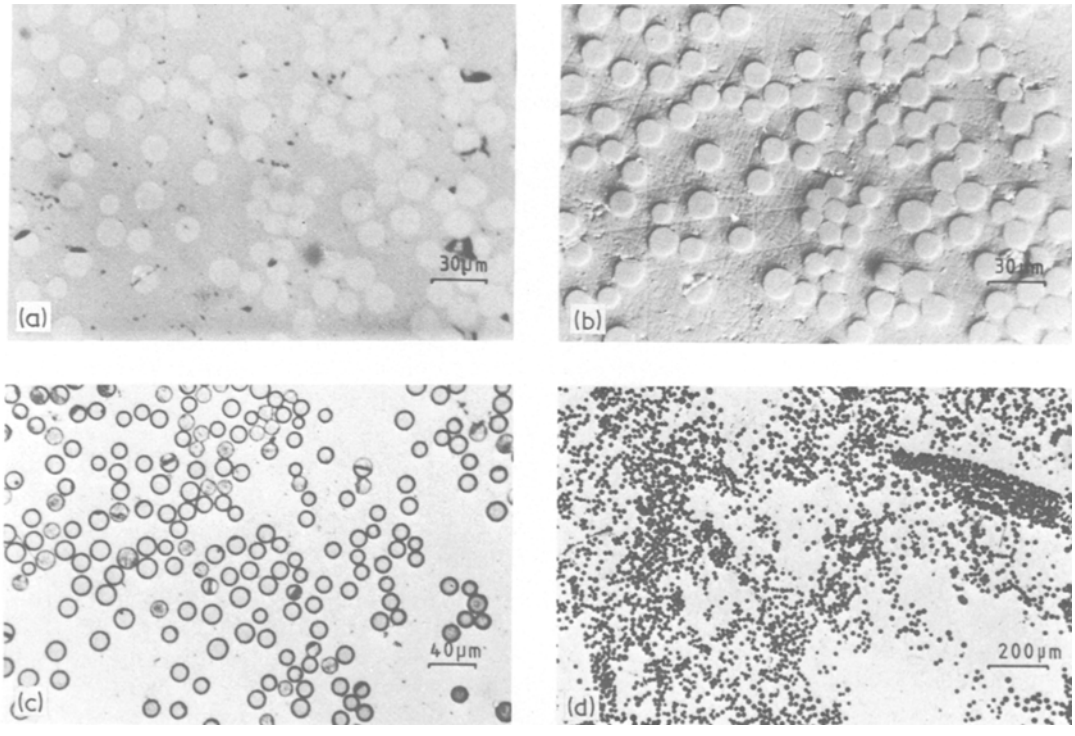

Figure 1 Micrographs of transverse sections of unidirectional glass fibre-reinforced polyester resin beams, perpendicular to the fibre direction. (a) Polished cross-section, examined with bright-field illumination. (b) Polished cross-section, examined with Nomarski interference. (c) Polished cross-section, etched in the vapour of 40% hydrofluoric acid for 5 to 10 sec, examined with bright-field illumination. (d) Polished cross-section, etched in 40% hydrofluoric acid for 5 to 10 sec, examined with bright-field illumination.

and resin by holding specimens in the vapour above hydrofluoric acid for 5 to 10 sec (Fig. 1c). Sections were fully etched by immersion in 40% hydrofluoric acid for 5 to 10 sec; the acid etches the glass such that each fibre appears as a black dot under low magnification (Fig. 1d). A number of sections along the length of each bar were taken and section-to-section comparisons made using quantitative microscopy. These comparisons established that the microstructure was relatively constant along the bars. Thus, the full quantitative analysis, which involved establishing the statistical distribution of fibres, was in each case only performed on one section in the middle of each bar.

The distribution of fibre cross-sectional areas was measured with a fully automated Quantimet 720 using sections etched such that fibre interfaces were outlined, as shown in Fig. 1. Unlike the fully etched cross-sections (Fig. 1d) these rings remain distinct at higher magnifications. The fully etched cross-sections, like that shown in Fig. 1d, were used for investigating the statistical distribution of fibres in the resin. The analytical methods are described later.

2.2. Characterization of mechanical properties

A series of property measurements have been made on these experimental beams. The non-destructive property measurements (dynamic modulus and specific damping capacity, Section 2.2.1) have been quantitatively related to the microstucture (Section 4.2). Section 2.2.2 considers the crack-growth characteristics of these beams which are here related only qualitatively to the microstructural elements (Section 5).

2.2.1 Dynamic modulus and specific damping capacity

Values of dynamic modulus and specific damping capacity were measured by exciting the beam to vibrate in free-free flexure. These measurements have been discussed in detail elsewhere [7], and

are only given in outline here. The critical factor about these results in interpreting the microstructural observations is that the internal energy absorption has been found to be accurately proportional to stress squared at all amplitudes, as expected [7]. This establishes that although the surface layers clearly carry the highest loading when beams are flexed, all the other elements of the microstructure cross-section (except those at the neutral axis) contribute similarly as far as dynamic modulus and specific damping capacity are concerned. The method of analysis of the vibration data, and the derivation of values of dynamic modulus and specific damping capacity are summarized later.

2.2.2. Fracture characteristics

Cracks were grown in four-point flexural loading while monitoring acoustic emission. Failure was found to occur by the growth of a tensile crack which initiated at a corner on the lower, tensile, face of the beam, between the central rollers. Cracks grew towards the neutral axis spreading across about one third of the face. Stable crack growth under increasing load was found to continue until the crack depth was around 1.5 mm, when failure occurred by splitting parallel to the neutral axis, along the fibre/matrix interface. The progress of crack growth was monitored by an acoustic emission circuit which recorded fibre failures [7].

Fracture surfaces were examined using a scanning electron microscope operating in secondary electron mode; the microscope used was a Cambridge Stereoscan 2A. Surfaces were coated first with carbon and then with gold prior to examination in the microscope. Fibre pull-out lengths were measured from enlarged micrographs.

3. Data analysis

3.1. Microstructural parameters

The microstructural analyses and the statistical meaning of the resultant data have been described in detail elsewhere [6]. The basic method developed and used here consists of a comparison of measured parameters of the distribution of the fibres with the values of the parameters calculated from the null hypothesis; the null hypothesis used is that the fibres are randomly distributed in the matrix.

The distribution of fibre cross-sectional areas was first measured using sections etched as shown in Fig. 1c, and examined at relatively high magnification. This measured distribution was used in the analysis of all further measurements. Fully etched sections, as shown in Fig. 1d, from beams whose mechanical properties had been measured, were examined at lower magnification such that fibres appeared as black dots. The area of the black dots, that is the area covered by the fibres, inside a small test cell was measured. This test cell was moved around the cross-section of each specimen in a contiguous grid. The chosen size of the measurement test cell was 39.8 μm square, which was selected on the basis of microstructual observations to correspond to the smallest pattern element of the microstructure; in this case three fibres in mutal contact. The total area examined on each section was 180 x 100 test cells, that is 7.16 mm x 3.98 mm. It was found that this total area gave volume fraction and variance data applicable to the whole specimen cross-section with a confidence of better than 1%. It should perhaps be stressed that because of the very large quantities of data taken, the measurement errors were below 10^{-2}%. Since the measurement grid was contiguous, data additions could be made subsequently in order to determine values of the area covered by fibres in larger square and rectangular cells which are multiples of the test cell [6].

The resultant data was analysed in two ways. The variance analysis consisted of a determination of the values of the variance of fractional area covered for different cell sizes. These values of variance were then compared with values of variance calculated assuming the null hypothesis, and expressed as the ratio experimental variance/theoretical variance. The second method of analysis, the sparsity analysis, consisted of a determination of the proportion of cells containing no fibres or the equivalent of less than half a fibre; probabilities of the occurrence of a sparse cell were thus determined. These values of probability were compared with values of probability calculated assuming the null hypothesis, and expressed as the ratio experimental probability/theoretical probability.

3.2. Dynamic modulus and specific damping capacity

The method of analysis adopted in this study has been presented in detail elsewhere. The vibration characteristics were analysed by solving

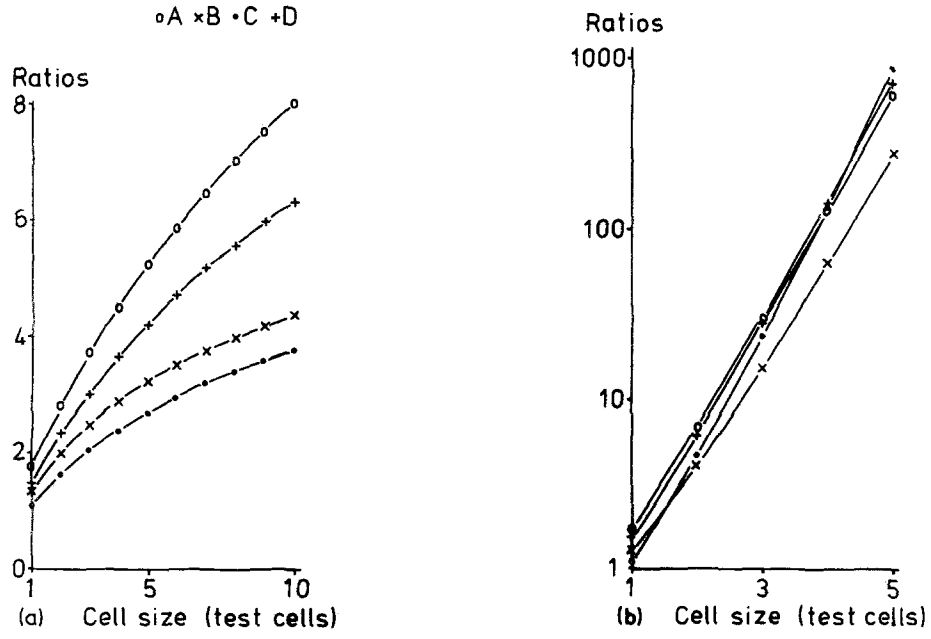

Figure 2 Microstructural parameters of four beams A to D, at different cell sizes, expressed as the ratio measured value: theoretical value calculated assuming the null hypothesis. The mechanical properties of these beams are given in Table I. The test cell unit size is 39.8 μm^2. (a) Experimental/theoretical variances in terms of fractional area covered by the fibres. (b) Experimental/theoretical probabilities that a cell contains no fibres.

the Bernoulli–Euler classical wave equation for the appropriate boundary conditions. Using this analysis, the dynamic modulus of the beam could be calculated from the observed resonant frequency. The specific damping capacity is defined as the ratio of the energy absorbed by the beam during one cycle to the total strain energy stored by the beam during that cycle. The energy input per cycle was calculated from the power input to the coils. The energy stored per cycle was taken to be approximately equal to the energy stored in bending, and was calculated from the measured maximum deflection and mode shape of the beam deduced in the analysis. Thus values of specific damping capacity could be calculated.

4. Results

4.1. Microstructural parameters

The results of the microstructural analyses are presented as the ratios experimental/theoretical values, where the theoretical values have been calculated assuming the null hypothesis. The results of the variance analysis are shown in Fig. 2a, where it may be seen that all values of the ratio are greater than unity, and that the ratio increases with increasing cell size, although the rate of increase decreases at the higher cell sizes. The graphs for the different beams do not cross, i.e. the ranking of the ratios for the different beams remains the same for all the cell sizes. The results of the sparsity analysis are shown in Fig. 2b, where the ratios are plotted logarithmically. It is seen that all values of the ratio are greater than unity, and that the ratio increases rapidly with increasing cell size, the rate of increase rising at the higher cell sizes. The graphs for the different beams cross several times, i.e. the ranking of the ratios changes several times in the range of cell sizes.

4.2. Mechanical properties

Values of dynamic modulus and specific damping capacity for the four beams are shown in Table I. The measured properties have been normalized for a fibre volume fraction of 20%. The values of dynamic modulus were normalized assuming the rule-of-mixture; the values of specific damping capacity were normalized using the relationship used by Adams and Bacon [8]. The ranking of the two measured propertes is identical; as the modulus increases the specific damping capacity decreases. This is the usual relationship between stiffness and specific damping capacity for a unidirectional composite material [8]. However, after normalization, the ranking of the two

TABLE I Mechanical properties

Beam identification	Volume fraction (%)	Measured properties		Normalized properties	
		S.D.C. (%)	E (GN m^{-2})	S.D.C. (%)	E (GN m^{-2})
A	17.7	3.9	16.0	3.5	18.1
B	18.2	4.5	14.9	4.1	16.4
C	23.2	3.6	18.5	4.2	16.0
D	19.9	3.8	16.2	3.8	16.3

The measured values of the specific damping capacity (S.D.C.) and dynamic Young's modulus (E) have been shown to be accurate to better than 1% and around 4%, respectively [7]. In the normalized values, the 1% confidence on the volume fraction measurements means that the properties have ± 1% limits on S.D.C. and ± 4% on E.

properties is not identical. The range of values of specific damping capacity is greater, and these values are thought to be the more accurate.

4.3. Fractography

A typical fracture surface is shown in Fig. 3. The fracture surface shows several characteristic features including fibre pull-out, steps in the fracture plane and "river-lines" in the resin. Fibre pull-out lengths from micrographs of two fracture surfaces were measured; the histogram of measured lengths is shown in Fig. 4. The mean pull-out length was found to be 30 μm. From the usual assumption that the critical length is four times the mean pull-out length, the critical length is found to be 120 μm. This value is about two orders of magnitude smaller than the value generally reported, 13 mm [9]. However, it is noted from the histogram that although the peak occurs at small pull-out lengths (near the mean value) there is a long tail approaching that appropriate to the generally accepted critical length (and see Section 5).

5. Discussion

The ratios of both microstructural parameters are seen to be greater than unity. Considering first the results of the variance analysis, the values of experimental variance are greater than the values of theoretical variance calculated assuming the null hypothesis (a random distribution of the fibres). This result indicates deviations in the distribution which is less dispersed than random; that is the distribution has been shown to contain clusters or groups. The occurrence of fibre clusters is in accord with microscopic observation (Fig. 1).

Clusters are seen to occur on two scales; there are small groups of a few fibres, and there are regions of empty space arising from improper dispersion of the tows. As discussed below, the

Figure 3 Scanning electron micrograph of fracture surface with crack growth perpendicular to the fibre direction, showing pulled-out fibres.

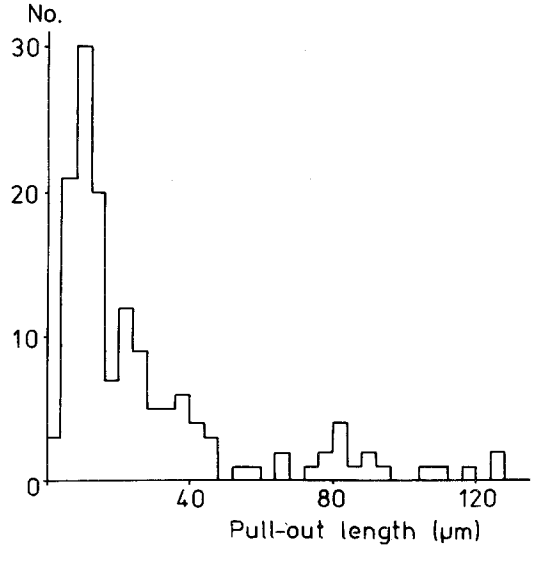

Figure 4 Histogram of measured lengths of fibre pull-out, measured from scanning electron micrographs such as Fig. 3.

variance analysis probably detects the small clusters. The results of the sparsity analysis also confirm the existence of the fibre clusters; more regions of empty space are found experimentally than predicted by the null hypothesis. If fibre clusters are present, empty space is more likely to be present.

A more detailed comparison of Fig. 2a and b reveals further correlation between the two methods of analysis. The ranking of the variance ratios is identical to the ranking of the probability ratios at cell size 1 (the measurement test cell size) which, as mentioned in Section 3.1, corresponds to the smallest pattern element observed in the microstructure, namely three contiguous fibres. The variance values describe only the second order structure, i.e. the position of a particle with respect to another particle; theoretical values of the variance may be expressed in terms of covariances. High values of the variance at small scales arise from small scale clustering of the fibres. This is caused by the lack of complete dispersion of the fibres; this lack of dispersion would also lead to empty space within the material and hence to high values of the probability of an empty space of given size [10].

Comparison of the ranking of the normalized values of specific damping capacity in Table I with the ranking of the variance ratios in Fig. 2a, or with the ranking of the probability ratios at cell size 1 in Fig. 2b, reveals that they are identical. The specific damping capacity is the least, so the modulus is anticipated to be the greatest, for the largest values of the ratios. A greater proportion of the load is carried by fibres in beams in which the fibres have the greatest tendency to cluster. These results show that the prediction of stiffness of beams from the measured microstructural parameters is a realistic proposition.

Examination of fracture surfaces as shown in Fig. 3 indicates a further possible important effect of the distribution of the fibres. The histogram of the fibre pull-out lengths is shown in Fig. 4. As described above, the critical length calculated from the mean pull-out length is about two orders of magnitude smaller than the generally accepted critical length. The relationship between fibre pull-out length and critical length arises from the transfer of stress to the fibre which occurs when the crack has by-passed the fibre leaving the fibre as a "bridge"; this process is expected to occur when the failure strain of the resin is smaller than that of the fibre. However, even when the crack in the resin has crossed the fibre and extensive debonding has occurred, fibres in model composites have often been shown to fracture at the crack plane [9]. In the present case, the failure strain of the resin is 2.1% and that of the fibres is 2.6%. The discrepancy between the measured pull-out length and generally reported critical length may, therefore, arise from the process of crack growth being continuous, without the occurrence of fibre "bridges", or from failures occurring in the crack plane despite the occurrence of "bridges".

The contribution of the various processes to the overall fracture energies have been studied for model composites [9, 11]. The main contribution to the fracture energy has been previously considered to be the process of debonding. However, it has been concluded that this contribution may be small with respect to the contribution arising from the work done against friction between fibres and matrix after the debonding, including the work done in fibre pull-out. The work of fibre pull-out is dependent on the pull-out length, which, as discussed above, is not necessarily that calculated from the critical length.

The factors affecting the pull-out length have not been established, but it is postulated from observation of fracture surfaces, such as Fig. 3, that these factors may include the fibre arrangement. Longer pull-out lengths seem to occur more frequently in fibre clusters. This effect could perhaps arise from the crack speed being decreased as a cluster is approached. There is considerable discussion in the literature regarding values of fracture energy and the applicability of linear elastic fracture mechanics to composite materials (e.g. [12, 13]). Measurement of fibre pull-out lengths and comparison of fracture parameters with microstructural parameters could prove very valuable in future fracture studies.

6. Concluding remarks

The importance of the microstructural parameters in relation to mechanical and fracture properties has been shown for this material. The methods of microstructural definition adopted here are general and not restricted to a specific composite material. The use of a quantitative definition of the microstructure of composite materials would be an important step in increasing the confidence in the prediction of the mechanical properties of composite materials. This, in turn, would lead to

increased economic use of these materials in critical applications.

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References

1. C. S. SMITH, Paper 2, Proceedings of the Symposium on GRP Ship Construction, Royal Institution of Naval Architects, October (1972).
2. M. H. BRYAN-BROWN and D. M. WALKER, Paper 14, Proceedings of the British Plastics Federation Reinforced Plastics Congress, November (1978).
3. M. FUWA, A. R. BUNSELL and B. HARRIS, *J. Phys. D. Appl. Phys.* 9 (1976) 353.
4. G. D. SIMS, G. D. DEAN, B. E. READ and B. C. WESTERN, *J. Mater. Sci.* **12** (1977) 2329.
5. R. D. ADAMS, D. WALTON, J. E. FLITCROFT and D. SHORT, Composite Reliability ASTM STP 580, American Society for Testing and Materials (1975) p. 159.
6. F. J. GUILD and B. W. SILVERMAN, *J. Microsc.* **114** (1978) 131.
7. F. J. GUILD, Ph.D. thesis, Plymouth Polytechnic (1978).
8. R. D. ADAMS and D. G. C. BACON, *J. Comp. Mater.* 7 (1973) 53.
9. B. HARRIS, J. MORLEY and D. C. PHILLIPS, *J. Mater. Sci.* **10** (1975) 2050.
10. B. W. SILVERMAN, private communication (1978).
11. B. HARRIS and A. O. ANKARA, *Proc. Roy. Soc. London* **A359** (1978) 229.
12. P. W. R. BEAUMONT and D. C. PHILLIPS *J. Comp. Mater.* **6** (1972) 32.
13. C. D. ELLIS and B. HARRIS, *ibid.* 7 (1973) 76.

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