

# The effect of the measurement frequency on the elastic anisotropy of fibre laminates

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Static tests and ultrasonic measurements (2.25 MHz) have been carried out on a series of composite laminates of glass fibres in a polypropylene matrix. A range of angle ply laminates were prepared for this study, with laminate angles  $\theta$  of  $\pm 0$ , 10, 20, 30 and 40°. The high frequency measurements were made using the ultrasonic immersion technique, which allows the determination of a complete set of the elastic constants of a material. The relationship between the ultrasonically determined elastic constants of the angle ply laminates was found to be in excellent agreement with theoretical predictions, as previously validated for carbon fibre/epoxy angle ply laminates.

A comparison between the ultrasonic and statically measured values was made for two of the angle ply laminates ( $\theta = 0$  and 20°). It was found that the static values were lower than those measured at ultrasonic frequency, particularly those constants that were more matrix dominated (for example the transverse moduli of the laminates). Measurements on a pure polypropylene sample at both testing frequencies confirmed that the change in matrix properties with frequency was the cause of this difference. The change in properties with test frequency is likely to be much larger in this system than in other composite materials because the glass transition temperature of polypropylene is close to ambient temperature. Dynamic mechanical tests (1 Hz) were carried out on a sample of pure polypropylene to assess this effect. We also give an appropriate method of estimating the dependence of glass transition temperature on frequency. The results for polypropylene are compared with those for other commonly used polymer matrix materials: epoxy resin, nylon and polyetheretherketone (PEEK): DMTA measurements were also made on these samples.

The effect of test frequency on matrix properties, for the glass/PP laminates, was further investigated by examining the relationship of the Poisson's ratios with laminate angle using a mixture of ultrasonic experiments and theoretical predictions. Previously we have shown that the degree of anisotropy between the reinforcing fibre and the matrix phase is paramount in determining whether the material will show a negative Poisson's ratio at a critical laminate angle. The ultrasonic measurements carried out in this study on the glass/PP laminates showed a minimum in one of the Poisson's ratio at a laminate angle of 32°, but the value did not become negative. However, theoretical predictions showed that for a static frequency measurement (1 Hz), where the matrix is softer and hence the anisotropy of each laminate ply is higher, the laminate will show a negative Poisson's ratio with a minimum at a laminate angle of around 28°.

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## 1. Introduction

The use of ultrasonic methods to measure the elastic properties of fibre composites is a very powerful tool and has been applied since the discovery of high stiffness fibres in the 1960s [1], the

method having been originally developed to measure the anisotropic properties of single crystals. In a practical case it is necessary to use a wavelength which is large compared with the fibre diameter but small compared with the dimensions of the specimen:

ultrasonic wavelengths of the order of 0.5 mm are normally used.

Classic papers, such as those by Smith [2] and by Read and Dean [3], showed that by using ultrasonic waves with frequencies in the range 1–10 MHz all nine elastic constants of an orthotropic array could be determined including the off axis stiffness constants  $C_{ij}$  (where  $i$  is not equal to  $j$ ), which are very difficult to measure by other means. These early papers had as their aim, amongst other things, the determination of the elastic properties of the fibre because in the case of fibres such as carbon or the aramids, where the mechanical properties are anisotropic, it is necessary to be able to obtain, for example, values for the transverse and longitudinal shear stiffnesses, both of which are very difficult to measure accurately by other means. If determination of the properties of a fibre in a composite is the aim of the experiment, then a rather simple shape of specimen is all that is required since only the properties of a unidirectional ply are to be measured. Recent methods include laser generated ultrasonics [4] to determine the five elastic constants of a transversely isotropic array and combining measurements of the three thermal expansion coefficients and two in-plane elastic constants [5].

Later workers with the ultrasonic technique have applied it to measurement of the properties of laminates. These studies had the aim of successfully validating the theoretical expressions used in relating the properties of a single ply to those of a laminate consisting of plies in a variety of orientations. In addition, some of the more unusual properties of anisotropic fibre laminates may be confirmed experimentally e.g. negative and/or very large values of Poisson's ratio. In such studies, the laminate must usually be cut into sections in order to ensure sonic wave propagation in the relevant directions. A comprehensive review by Aristegui and Baste [6] demonstrates that the stiffnesses of materials of any class of symmetry may be extracted from the ultrasonic measurements, if suitably cut sections are available.

Rather little attention has been paid, however, to relating the measured properties of a composite obtained by ultrasonic methods to the values found by other methods of measurement. In the current work we have examined the elastic properties of glass fibre reinforced polypropylene laminates. A paper on the expansivity of this system has already appeared [7]. The interest in this system arises from the possibility of obtaining a negative thermal expansion coefficient in a laminate through the use of cheap and readily available materials, which are also easily formed to shape.

In order to achieve a negative expansivity, Ito *et al.* point out [8] that the in-plane shear stiffness of a fibre composite must be very small in comparison with the longitudinal stiffness of the fibres. Since glass is not very stiff, this implies the use of a very compliant matrix such as polypropylene. With such a matrix, we have found a marked difference in the values of some of the elastic properties measured by ultrasonic methods and by static methods (e.g. a bend test or stress-strain curve), as well as between the sonic measures and those predicted from the properties of the material as given in

the literature. Such an effect had been noted a number of years ago in composites with an epoxy resin matrix [9, 10]. In the current work the effect is much larger and in addition we have made quantitative measurements of the effect on a pure sample of the same matrix as that used in the composites. It will be shown that these differences are of major importance in the choice of materials for the control of the elastic behaviour of fibre composites.

## 2. Experimental details

The material used for the laminates was a unidirectional prepreg tape with a thickness of  $0.26 \pm 0.02$  mm and a width of 72 mm provided by St Gobain Vetrotex (Chambéry, F). It was composed of 50 vol% of glass fibres and 50 vol% polypropylene, confirmed by density measurements. The properties of the fibre and matrix phases are given in Table I: the matrix properties shown here were measured under static conditions.

The laminates were composed of 12 plies, pressed at 6.2 bar for 4 min, cooled, and then cut with a diamond saw to  $25 \times 5 \times 3$  mm. This procedure was carried out accurately in order to obtain samples with a variation in length of only  $\pm 0.3$  mm and with faces as parallel as possible. After cutting, samples were dried for 15 min with hot air ( $60\text{--}70^\circ\text{C}$ ) and subsequently stored in sealed containers. Laminates were made at values of  $\pm\theta$  of 0, 10, 20, 30 and  $40^\circ$ : the laminates were balanced and symmetric.

For the ultrasonic measurements we have used the ultrasonic immersion technique, originally described by Smith [2] and Read and Dean [3] and further developed by Dyer [11]. In this technique, ultrasonic pulses (2.25 MHz) are propagated through the sample under investigation, at a series of angles, allowing the relationship between the longitudinal and shear wave velocities with angle in a particular plane to be determined. It can be shown [2, 3] that these two velocity/angle relationships are determined by the stiffness constants  $C_{ij}$ , in the plane of propagation; a simple fitting procedure therefore allows these constants to be determined. For example, if sound is propagated in the 23 plane, then the experiment will determine  $C_{22}$ ,  $C_{33}$ ,  $C_{23}$  and  $C_{44}$ . By propagating sound in the three principal planes of the material (i.e. along the three principal axes) we can then determine all nine of the independent elastic constants necessary to specify the anisotropy of orthotropic materials. The procedure is described in detail in [12] and [13]. The definition of axes is such that 3 is the longitudinal axis in the laminate plane, which is the  $0^\circ$  direction for the aligned composite (fibre direction) axis 1 is normal to this in the laminate plane and axis

TABLE I Elastic properties of the glass fibre and the polymer matrix

	Young's modulus $E$ (GPa)	Poisson's ratio $\nu$	Shear modulus $G$ (GPa)
<i>E</i> -glass Vtex	73	0.2	30.4
Shell PP (static measurement)	1.3	0.3	0.5

2 is in the through thickness direction. It is to be noted that our definition of the value of Poisson's ratio does not follow the normal convention. In our case, the direction of the primary stretch is indicated by the second subscript.

Static bend tests were carried out on a small number of specimens and for only two laminate orientations ( $\theta = 0^\circ$  and  $\pm 20^\circ$ ). The load was monitored by the load cell of the testing machine (ESH 10 kN) and the strains were measured by two strain gauges fixed perpendicular to each other with adhesive in the centre of the lower surface of the sample. The gauge type was: Kyowa, KFG-5-120-C1-11, length 5 mm, resistance 120  $\Omega$ , gauge factor 2.11, adopt. CTE  $11.7 \cdot 10^{-6} \text{ K}^{-1}$ .

The strain gauges were connected with a strain gauge amplifier, which in turn was connected with a Maclab analog/digital converter. Analogous data from the load cell and the LVDT (displacement) was acquired. Testing was carried out meeting the ASTM D 790 M standard [14] requirements. However, the flexural Young's modulus ( $E_{33}$ ) was determined differently i.e. based on the slope of the stress-strain curve. Poisson's ratio ( $\nu_{13}$ ) was obtained by dividing the transverse strain by the longitudinal strain.

Dynamic tensile tests were carried out on a variety of unreinforced polymers using a dynamic mechanical test apparatus (Rheometrics RSAII). A sinusoidal frequency of 1 Hz and a strain of 0.05% were used, equivalent to a nominal strain rate of  $2 \times 10^{-3} \text{ s}^{-1}$ .

### 3. Results

#### 3.1. The effect of test frequency ( $0^\circ$ and $\pm 20^\circ$ specimens)

The ultrasonic method of measurement yields the complete matrix of the stiffness tensor  $C_{ij}$ , which can simply be inverted to determine the engineering constants. On the other hand, the static three point bend tests gave values for two of the elastic constants of the laminate, namely the longitudinal modulus,  $E_{33}$ , and the Poisson's ratio,  $\nu_{13}$ . In Table II we show a comparison of these constants measured both statically and ultrasonically for the  $0^\circ$  unidirectional sample and the  $\pm 20^\circ$  sample. The results, particularly those for  $\nu_{13}$  of the  $\pm 20^\circ$  sample, show a clear difference between the laminate elastic constants determined statically and ultrasonically.

We can determine a theoretical prediction of the laminate elastic constants using a suitable micromechanical

TABLE II Comparison of measured (both ultrasonically and determined at by a bend test) and theoretically predicted values of  $E_{33}$  and  $\nu_{13}$  for laminate angles of  $\theta = \pm 0^\circ$  and  $20^\circ$

$\theta$	$E_{33}$ (GPa)			$\nu_{13}$		
	Bend	Ult	Theory	Bend	Ult	Theory
$0^\circ$	41	40.5	37	0.36	0.32	0.24
$20^\circ$	24	29	25	0.99	0.53	1.04

Ult = ultrasonically determined; Bend = bending measurement; Theory (based on static matrix modulus measurement and fibre properties from Table I).

TABLE III A comparison of the ultrasonically measured and theoretically predicted values of the transverse modulus  $E_{11}$

$\theta$	$E_{11}$	
	Ult	Theory
$0^\circ$	12.0	3.60
$20^\circ$	10.4	3.51

model. To be consistent with our previous work we have used the NPL program LAMPROPS based on the work of McCartney [15]. The properties of the two phases as given by the manufacturers (matrix properties from a static test), are shown in Table I and the results of the calculations are shown in Table II. It is seen that the predicted laminate properties, based on a matrix modulus determined from a static test, agree much better with the statically determined laminate properties, rather than those determined ultrasonically. We can infer that the difference in the laminate properties measured statically and ultrasonically is due to the effect of the different test methods (specifically frequency but also temperature is a possibility) on the properties of the polypropylene matrix.

To make this point more strongly, we have compared the ultrasonically measured values of the transverse modulus,  $E_{11}$ , with those determined from a theoretical prediction, again based on the static modulus measurements from Table I: these are shown in Table III. It is seen that for this laminate elastic constant, which is a more matrix dominated property, that the difference between the ultrasonically measured property and that predicted based on a static matrix modulus measurement is much more pronounced.

To confirm the basis for this difference in laminate behaviour, we measured the modulus of pure polypropylene at a frequency of 2.25 MHz, that is under ultrasonic conditions tested in the same manner as for the composites described above. As the material was isotropic, sound waves only needed to be propagated in one plane to obtain the necessary two independent stiffness constants. As expected, compared to the static measurements (Table I) this experiment gave a significantly increased Young's modulus for the PP material measured at 2.25 MHz of 4.46 GPa: the Poisson's ratio was slightly higher when measured at the higher frequency (Table IV).

We can now use these ultrasonically determined matrix properties to explain the previous results shown in Table II. Table V compares the experimentally measured ultrasonic values of a unidirectional ply with theoretical predictions using the values of the PP matrix determined ultrasonically at 2.25 MHz and statically.

TABLE IV Values of the Young's modulus and Poisson's ratio of polypropylene measured ultrasonically (2.25 MHz) at  $25^\circ\text{C}$

	Young's modulus (GPa) 2.25 MHz strain $\sim 10^{-6}$	Poisson's Ratio 2.25 MHz strain $\sim 10^{-3}$
PP	4.46	0.34

TABLE V Comparison of ultrasonic values for the unidirectional ply with theoretical predictions based on matrix properties measured ultrasonically and statically

	Experimentally measured values at 2.25 MHz	Theoretical predictions based on matrix properties measured at:	
		2.25 MHz	statically
$E_{33}$	40.8	38.7	37.3
$E_{11}$	$11 \pm 1$	11.3	4.36
$\nu_{13}/\nu_{23}$	$0.31 \pm 0.2$	0.242	0.242
$\nu_{12}$	0.345	0.342	0.356
$G_{13}/G_{23}$	$4.45 \pm 0.75$	4.47	1.72

It can be seen that the theoretical predictions of the composite properties, based on the matrix properties measured at the same frequency as the laminate, are in much better agreement than those based on the matrix properties measured at statically or at low frequency. These results confirm that the difference in the measured properties shown in Table II is due to the frequency dependent properties of the polypropylene matrix phase.

A similar effect might be expected in all composites with polymeric matrices. It is, however, likely to be much greater in the case of polypropylene than with other commonly used matrices in composites because polypropylene has a glass transition temperature,  $T_g$ , which is very close to room temperature (quoted values are around  $-10$  to  $0^\circ\text{C}$  e.g. Cowie [16]). It is well known that the mechanical properties of polymers, especially in the region of a molecular relaxation process such as a glass transition, are viscoelastic and the change in properties are correctly dealt with in terms of the time temperature equivalence (or superposition) principle. A comprehensive discussion of this is given by Van Krevelen [17] in his classic text book (p 402 et seq). Van Krevelen specifically describes polypropylene and quotes Ogorkiewicz [18] as the source of the required information for isotactic polypropylene.

For semi-crystalline polymers, Van Krevelen follows Seitz and Balazs [19] to relate the modulus,  $E_R$ , at time  $t_R$  and temperature  $T_R$  to the modulus,  $E$ , at time  $t$  and temperature  $T$  as follows

$$\log_e \left( \frac{E_R}{E} \right) = A \log_e \left( \frac{t}{t_R} \right) + B \left( \frac{1}{T_R} - \frac{1}{T} \right)$$

For polypropylene,  $A = -0.08$  and  $B = 800$  (K).

If we equate the two terms on the right hand side of the equation, i.e.

$$-A \log_e \left( \frac{t}{t_R} \right) = B \left( \frac{1}{T_R} - \frac{1}{T} \right)$$

then from this relationship we can determine the appropriate temperature, compared to room temperature (273 K), which would give the same change in modulus for two different test frequencies. From this we find that a test frequency of 1 Hz at a testing temperature of  $20^\circ\text{C}$  (293 K) is equivalent to a temperature of  $-88^\circ\text{C}$  (205 K) at a test frequency of 2.25 MHz.

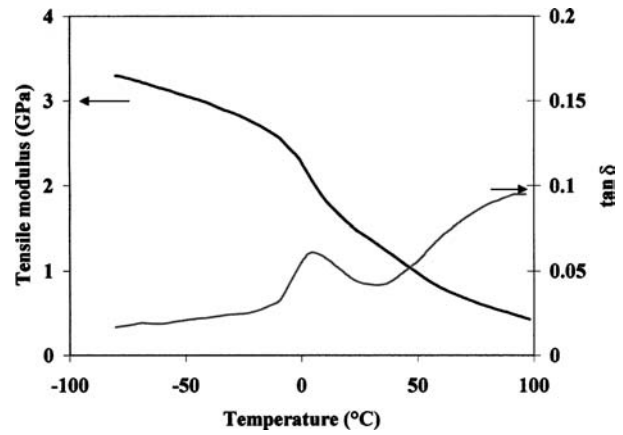


Figure 1 DMTA measurement of the elastic modulus and  $\tan \delta$  over a temperature range of  $-80$  to  $100^\circ\text{C}$  using an oscillating frequency of 1 Hz.

To corroborate this we carried out a DMTA temperature scan ( $-80$  to  $+100^\circ\text{C}$ ) at a frequency of 1 Hz on a very similar grade of PP to that used in the laminates: the results of this experiment are shown in Fig. 1. These results show a similar modulus ratio as that described in the literature [20] and also a similar range for  $T_g$ . While we do not have results quite as low as  $-88^\circ\text{C}$ , extrapolating the DMTA results gives a value for the modulus at this temperature of 3.35 GPa. This is still not as high as the ultrasonically measured value for pure PP of 4.46 (Table IV). A likely candidate for this further difference is the level of strain experienced by the material in the two test techniques, which is  $\sim 10^{-3}$  for the DMTA measurement and  $\sim 10^{-6}$  for the ultrasonic test: further experiments would be needed to confirm this supposition.

The obvious conclusion is that, with a polymer such as polypropylene, measurements at ultrasonic frequencies reflect the static properties of the polymer at a greatly reduced temperature.

Polypropylene is not the only polymer which is employed as the matrix of a composite laminate: other popular choices include Nylon, PEEK and epoxy resin. The effect of frequency, while important for other polymers, is less than that found with polypropylene. The results presented in Tables VI and VII explore the effect of test frequency on these four polymers.

Table VI shows the Young's modulus and Poisson's ratio of the four polymers measured ultrasonically and from a dynamic mechanical test at a temperature of  $25^\circ\text{C}$  at a frequency of 1 Hz [21–24]. In all cases, the

TABLE VI Values of the Young's modulus and Poisson's ratio of several polymers measured at room temperature and different frequencies

	Young's modulus 2.25 MHz strain $\sim 10^{-6}$	Young's modulus 1–10 Hz strain $\sim 10^{-3}$	Poisson's ratio 2.25 MHz	Poisson's ratio 1 Hz
PP	4.46	1.57	0.34	0.3
Epoxy*	5.04 [20]	3.8 [21]	0.36	0.37 [22]
Nylon 6	3.82	2.9	0.39	0.35 [22]
PEEK	4.27	4.03	0.394	0.4 [23]

\*Ciba Geigy 913.

TABLE VII Values of the stiffness ratio and glass transition temperature for several polymers

Polymer	Stiffness ratio	$T_m$ (K)	$T_g$ (K)	$T_g$ (°C)
PP	2.84	438	270	-3
Nylon 6	1.31	488-498	313	40
PEEK	1.06	607	420	147
Epoxy	1.32	-	-	-

high frequency/low strain modulus is higher than the 1 Hz DMTA modulus: PP shows the greatest difference between the two modulus measurements, PEEK shows the least difference between the two modulus measurements.

As described earlier, it is well known that the rate of change of stiffness with temperature or frequency is much greater when well above  $T_g$  as opposed to well below  $T_g$ . Table VII shows the stiffness ratio for the four polymers (defined as the ratio of the measured values for the two testing frequencies): this table also shows literature values for their glass transition temperatures,  $T_g$ . PEEK has the highest  $T_g$ , and is also highly crystalline, and so it will therefore be less frequency and temperature dependent when investigating room temperature properties. While epoxy resin is a thermoset, it is glassy and it can often show a glass transition temperature, the strength of which depends on the crosslinked density. Hence the stiffness ratio is similar for epoxy and Nylon, highest for PP and lowest for PEEK. A relatively large value for epoxy is also found by the measurements of Bodner and Lifschitz [25] whose measured results extrapolated over the frequency range given in Table VI yield a ratio of 1.7 for a Shell Epicote 815 resin. One expects there to be a dependence on the type of the epoxy resin and on the conditions of cure, crosslinked density etc.

### 3.2. The effect of ply anisotropy on angle ply laminate properties

While the result presented in the previous section suggest caution in extrapolating measurements made at ultrasonic frequencies to low frequencies, particularly for polypropylene, there is some merit in the technique as it allows a full set of elastic constants to be determined. This, in turn, allows the effects of the anisotropy of the individual lamina in determining the laminate properties to be investigated. In two previous published papers [12, 13] we demonstrated that angle ply laminates, comprising alternating unidirectional layers  $[\pm\theta]_s$  of high modulus carbon fibres in an epoxy resin matrix, could show interesting and unusual elastic properties, most pertinently a negative Poisson's ratio in a particular axis. The implication of a negative Poisson's ratio, for instance for  $\nu_{13}$ , is that if the material is stretched along the 3 axis, the material will expand in the 1 direction. This negative Poisson's ratio is often accompanied by a large Poisson's ratio in an associated direction (i.e.  $\nu_{23} > 1$ ). In these previous studies we showed that the level of anisotropy in the unidirectional layers is a key driving force for this unusual elastic behaviour. In the

TABLE VIII Experimentally determined stiffness constants ( $C_{ij}$ ) for the glass/PP angle ply laminates. Values in GPa

Laminate angle (°)	0	10	20	30	40
$C_{33}$	44.5	44.1	37	32.8	24.5
$C_{22}$	12.3	12.3	12.6	12.1	12
$C_{11}$	15	14.7	14.6	15.7	17.9
$C_{13}$	6.55	7.41	8.89	11.5	12.7
$C_{12}$	5.65	5.39	5.45	5.29	4.75
$C_{23}$	5.48	5.45	5.49	5.64	5.11
$C_{44}$	3.9	3.87	4.11	4.01	3.95
$C_{55}$	5	5.1	6.93	8.71	10.9
$C_{66}$	3.11	3.33	3.6	3.14	3.35

first study [12], an HTA carbon fibre was used (longitudinal modulus = 240 GPa) and at a laminate angle of  $\pm 28^\circ$  the composites showed values close to, but not less than zero. In a following study, using an HM370 carbon fibre (longitudinal modulus = 370 GPa) [13], a laminate angle of  $\pm 23^\circ$  gave a measured value for one Poisson's ratio of -0.5.

In the current study we have continued this research with a similar set of measurements on the glass/PP angle ply laminates. Table VIII shows the ultrasonically determined stiffness constants for the various angle ply laminates. For the  $0^\circ$  ply the through thickness stiffness  $C_{22}$  is lower than the in-plane transverse stiffness  $C_{11}$ . The material is therefore orthotropic implying that nine independent constants are required for a full description of the anisotropy. It was not the intention to produce such anisotropy. When the specimens were made, planar isotropy normal to axis 3 was aimed for. The reason for this discrepancy is not far to seek. A polished section taken through the  $0^\circ$  laminate (Fig. 2) shows that the reason for it is the presence of a resin rich layer between each lamina layer. In the 2 direction, this resin layer is in series with the individual laminae while in the 1 direction it is in parallel, leading to the lower stiffness value in the 2 direction.

That the ultrasonic measurements are very consistent among themselves is demonstrated in Fig. 3, which shows that the experimentally measured results from the angle ply specimens of all five orientations (solid symbols) fit the expectations of small strain elasticity theory and the approximations of laminate theory (shown by the solid lines) very precisely.

The various Poisson's ratios of the angle ply laminates are of special interest to us for two reasons. The

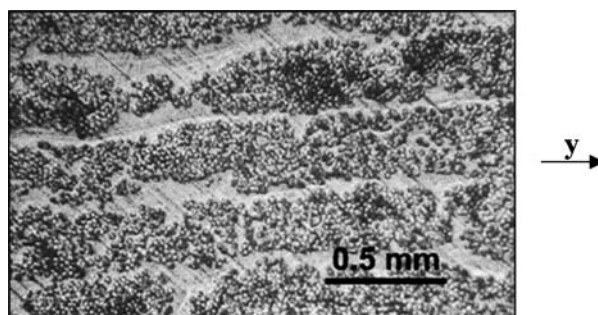


Figure 2 Section through an angle ply laminate.

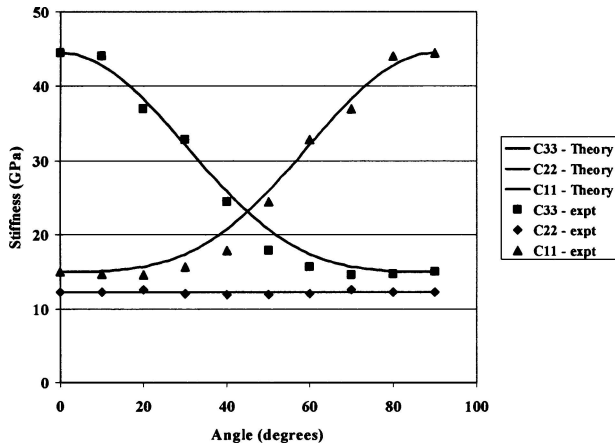


Figure 3 Relationship between the stiffness constants  $C_{33}$ ,  $C_{22}$  and  $C_{11}$  and the laminate angle  $\pm\theta$ : the solid symbols are experimental results, the solid lines are predictions based on the  $0^\circ$  ply measurements and standard laminate theory.

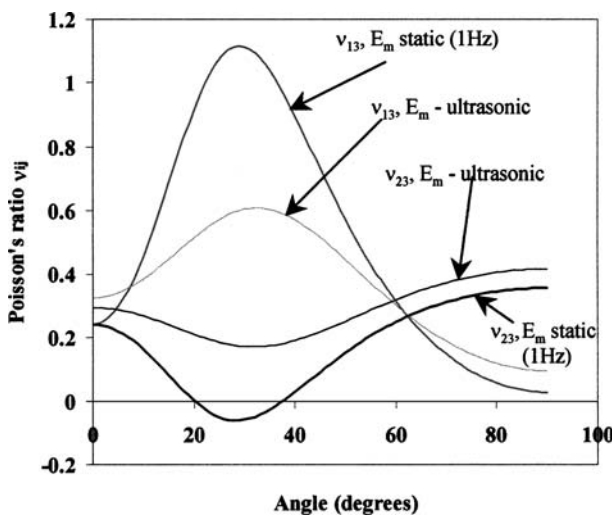


Figure 4 Effect of the matrix modulus ( $E_m$ ) on the Poisson's ratios  $\nu_{13}$  and  $\nu_{23}$ .

first is the necessary connection between the value of Poisson's ratio of a laminate and its in-plane thermal expansivity [7] and the second is the use of Poisson's ratio to control thermal expansion in practical devices [26].

The values of Poisson's ratio can be calculated directly from the measured stiffness constants and three of these, viz.  $\nu_{13}$ ,  $\nu_{23}$  and  $\nu_{12}$ , are shown in Fig. 4. Again, the solid symbols are the experimentally measured values and the solid lines are theoretical predictions based on laminate theory and the measured  $0^\circ$  ply values. As expected, the measured and predicted Poisson's ratios are in good agreement except for  $\nu_{13}$ . The reason for this measured value being less accurate is that the equations that relate wave velocity to the stiffness constants are rather insensitive to the value  $C_{13}$ —a 15% error is often given for this constant [12].

It is seen that at a laminate angle around  $32^\circ$ , there is a peak in the in-plane Poisson's ratio  $\nu_{13}$  and a minimum in the through thickness Poisson's ratio  $\nu_{23}$ , but that at the level of anisotropy in this material the through thickness Poisson's ratio does not become negative. From the previous studies we can understand that this is due to

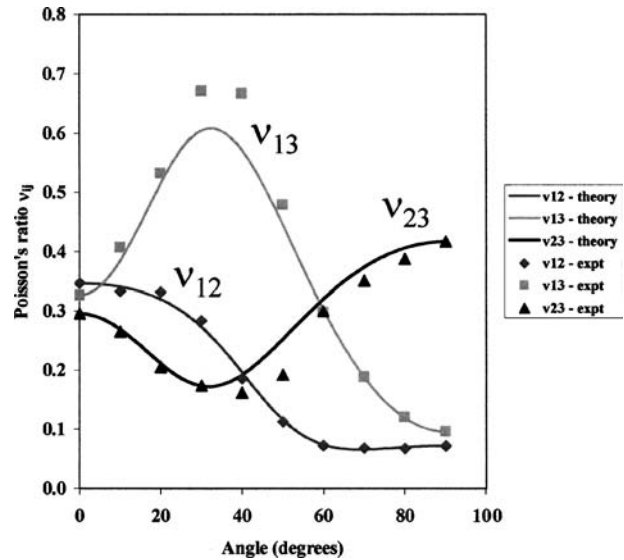


Figure 5 Relationship between Poisson's ratio and the laminate angle: the solid symbols are experimental results, the solid lines are predictions based on the  $0^\circ$  ply measurements.

the lower anisotropy of the individual glass fibre reinforced laminates, compared to using a stiffer reinforcement such as carbon fibres.

Rather than increase the fibre modulus, an alternative strategy for increasing anisotropy would be to decrease the matrix modulus. Unfortunately the ultrasonic immersion test can only be used over a small frequency range in the MHz region, and also over a limited temperature range, so it is not possible to measure experimentally the effect of a softer matrix on the composite properties (i.e. either at a much lower frequency or a much higher temperature). However, the excellent agreement between the measured stiffness constants, and those based on the  $0^\circ$  ply and laminate theory, as shown in Figs 3 and 4, suggest that we can assess this important issue using a theoretical approach, with the appropriate properties of the polypropylene matrix and a suitable micromechanical model.

We have already carried out this calculation in the previous section, when we used the micromechanical model of McCartney [15] to determine the lamina properties based on the matrix elastic constants measured at 1 Hz. Using these predictions, and laminate theory, we can predict the Poisson's ratios of a range of glass/PP angle ply laminates when tested at room temperature and a frequency of 1 Hz. As Fig. 5 shows, the softer matrix results in greater anisotropy of the individual lamina, leading to a much larger maximum value of  $\nu_{13}$  and a deeper minimum in the through thickness Poisson's ratio  $\nu_{23}$ , (a negative value  $\sim -0.15$ ) at a laminate angle of  $28^\circ$ . The coupling of Poisson's ratio with thermal expansion explained in [7] enables us to be sure that Fig. 5 shows what would be found from static measurements if these Poisson's ratios were measured experimentally.

#### 4. General comments and conclusions

It is to be remarked that static measurements of an elastic constant will always be less than that determined by

a high frequency method because constants determined under adiabatic conditions are always larger than those found under isothermal conditions by the ratio of the specific heat at constant pressure to that at constant volume. For solids the effect is very small at the frequencies we have been using.

Although an effect would not be expected in composites with a metallic matrix we have examined the literature known to us where elastic constants have been measured both ultrasonically and statically. The agreement between the values found by the two methods is within the experimental uncertainties. However, in the case of silicon carbide particulate reinforced aluminium [27], although the fact is not remarked upon by the authors, nonetheless the static values are always 5% or more lower than the values found with 5 MHz ultrasonic pulses.

The ultrasonic immersion test using frequencies in the 1–10 MHz range delivers a complete, consistent set of elastic constants for a composite laminate. It is a powerful method for investigating the anisotropy of materials, for instance for determining whether the material is transversely isotropic or orthotropic. When used with polymer matrix composites, where the polymer can be highly frequency dependent, then the behaviour at high frequency could be different to that measured by static methods. It follows that matrix dominated properties of a composite could then be higher at high frequencies and hence the degree of anisotropy of a composite will be underestimated compared with that found by static methods.

When both types of measurement are carried out at ambient temperature the effective difference will be more apparent with polymers whose glass transition temperature is close to that of room temperature, for example polypropylene. Polymers which are highly crystalline and have a higher  $T_g$  (e.g. PEEK) will show this effect less.

The choice of the most appropriate polymer to use for the matrix of the composite will depend on the properties that are required. Polypropylene would be a good choice if a high degree of ply anisotropy is required, for instance if a negative Poisson's ratio or low thermal expansion was required. If high temperature performance was a requirement then PEEK would be a better choice.

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