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LETTER

On the use of dynamic mechanical thermal analysis (DMTA) for measuring glass transition temperature of polymer matrix fibre reinforced composites

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The glass transition temperature (T_g) is one of the most important and representative parameters of the chemical and physical properties of polymer matrix composite materials. T_g can be correlated to the mechanical properties of a composite material, to the chemical structure of its matrix and to the materials performance under specific environmental conditions [1, 2]. The possibility of characterising the properties and performance of a composite material by measuring T_g is an extremely attractive possibility for the industry. For this reason in recent years much effort has been devoted in developing efficient test methods capable of measuring T_g in composite materials that could be used for both development and quality control purposes. The dynamic mechanical thermal analysis (DMTA) consists of measuring the dynamic response of a sample of material typically in terms of the loss modulus E'' as a function of temperature. The T_g can be defined as the temperature corresponding to the peak in the E'' (T) plot [3]. The DMTA is one of the most used techniques for measuring T_g, since it is relatively rapid and particularly suitable for quality control applications.

Previous studies conducted using DMTA to measure T_g in unidirectional fibre composite materials, indicated differences in the measured values of T_g with respect to the sample fibre orientation [4–7]. These differences, up to 20 °C, were observed for samples of the same batch. These observations were sometimes considered indications of the fact that T_g is a non-isotropic property of composite materials. This is clearly in contrast with the fact that T_g is essentially an intrinsic property of the polymer matrix and as such should not depend on the fibre orientation.

In this work, the influence on measured T_g of test parameters such as static and dynamic test loads and fibre orientation was observed and measured. It was found that the value of T_g determined using DMTA can be influenced by the applied test loads, this influence being observed only in the direction orthogonal to the fibres. Results obtained from two different commercially available DMTA test equipment were also compared, and significant differences in the measured values of T_g were found. The implications of these results are discussed in the light of the use of DMTA in industry and the problem of standardisation of the test method.

The tests were carried out on unidirectional carbon fibre cyanate-ester matrix composite material. Plates, from which samples were cut, were manufactured by the lay-up technique using cyanate-ester resin intermediate modulus (IM6) carbon fibre pre-pregs. Laminates were cured in autoclave using vacuum bags at 180 °C and 5.6 atm for 4 h. Figure 1 and 2 show microsections of the laminate material in the direction parallel and orthogonal to the fibres, respectively. The

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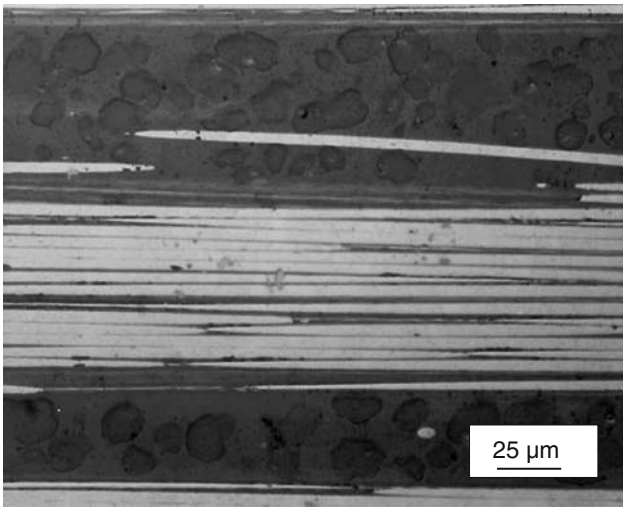

Fig. 1 Microsection parallel to the fibre direction showing the presence of thermoplastic resin particles, presumably Nylon, in the interlayer regions of the laminate

micrographs show a regular and compact structure with no visible voids within the resin-rich areas. Figure 1 shows in detail the fibre system and the resin-rich interlayer regions. The presence of round particles can be clearly observed. These thermoplastic resin particles, presumably nylon, were embedded in the matrix during the pre-preg production. The presence of these particles indicated that the matrix was a particle-toughened matrix system with softer resin particles introduced to increase the toughness of the material and its resistance to delamination [8].

The DMTA tests were carried out on unidirectional samples having dimensions $1.7 \times 7.0 \times 50$ mm. For comparison purposes, samples having the same dimensions were also manufactured in epoxy resin 914/carbon fibre (intermediate modulus) unidirectional laminate. Samples, machined from the same cured unidirectional laminate, had the fibres parallel (longitudinal samples) or perpendicular (transverse samples) to the sample longitudinal axis. Tests were carried out using a GABO Eplexor 25N test machine in the three-point bending test configuration. The GABO Eplexor allows real time controlling, monitoring and recording of temperature, sample static load (preload), dynamic load, static and dynamic displacement. The samples were subjected to a temperature sweep of 2 °C/min. The test frequency was 1.0 Hz. Longitudinal samples were tested in displacement control mode both in the static and the dynamic component. Transverse samples were tested using a mixed control mode. For temperatures lower than T_g, the dynamic component was controlled in displacement control mode and the static component in load control mode. For temperatures equal or higher than T_g, both the dynamic and static components were controlled in displacement control mode. This was necessary to avoid sample collapse at temperatures higher than T_g. In all cases, for temperatures lower than T_g the samples were subjected to maximum stress levels within the linear elastic domain of the material. Comparative tests were carried out using a Polymer-Laboratories DMTA equipment, with samples loaded in double cantilever beam (DCB) configuration, test frequency and heating rate being the same as in the previous tests.

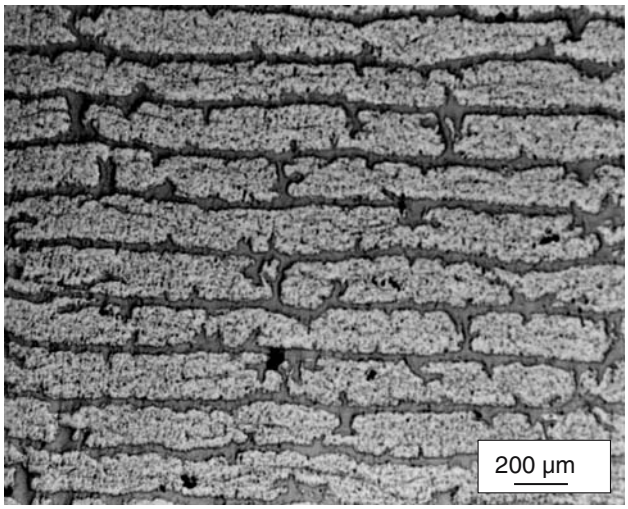

Fig. 2 Microsection orthogonal to the fibre direction showing a regular and compacted structure of the cyanate-ester carbon fibre laminate

Table 1 shows the static properties obtained for the cyanate-ester carbon fibre laminate in terms of the elastic moduli E_{11} and E_{22}, ultimate strength σ_{11} and σ_{22}, Poisson ratio v_{21} and the corresponding static flexural properties E_{f11}, E_{f22}, σ_{f11}, σ_{f22}. The shear modulus G_{12} of the unidirectional laminate was determined with plate twin test method [9]. Figures 3–6 show plots of the loss modulus E'', as a function of temperature, measured for the cyanate-ester carbon fibre composite samples.

T_g measured on samples with 90° fibres: Figure 3 shows that in the direction perpendicular to the fibres,

Table 1 Static properties obtained for the cyanate-ester carbon fibre laminate (average of six test results)

σ_{11}	2773 MPa	σ_{22}	55 MPa
E_{11}	150 GPa*	E_{22}	8.7 GPa*
σ_{f11}	2366 MPa	σ_{f22}	89 MPa
E_{f11}	147 GPa*	E_{f22}	9.5 GPa*
v_{21}	0.023	G_{12}	4.9 GPa

*Measured for $0.0005 \leq \epsilon \leq 0.0025$

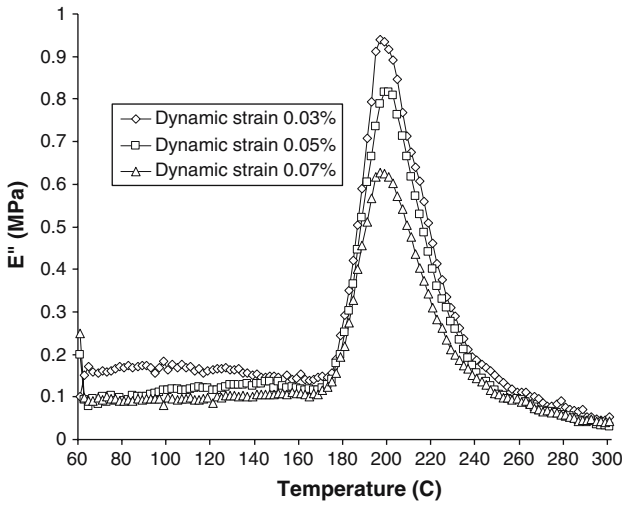

Fig. 3 $E''(T)$ plots obtained in the direction orthogonal to the fibres for different values of the specimen dynamic strain. Changing the dynamic strain did not produce any relevant shift in the loss peak temperature (T_g), this being between 198 °C and 200 °C

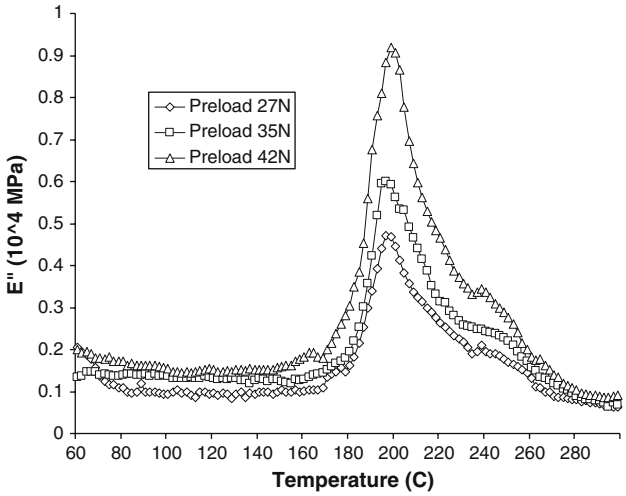

Fig. 5 E'' (T) plots obtained in the direction parallel to the fibres for different values of the specimen preload. Changing the preload did not produce any significant shift in the loss peak temperature (T_g)

for the same initial value of preload (8 N), changing the value of the applied dynamic strain did not produce any relevant shift in T_g, this being between 198 °C and 200 °C. With reference to Fig. 4, tests were run applying the same dynamic strain value of 0.05%, with a different initial preload for each test. Figure 4 shows the plots for 10 N, 8 N and 6 N of preload values. Maximum stress levels in the samples were estimated to be less than 34 MPa (worst case). It was observed that the temperature at the loss peak (i.e. the value of the measured T_g) monotonically decreased from 205 °C to 198 °C with increasing preload.

T_g measured on samples with 0° fibres: Figures 5 and 6 show the results obtained for the samples with fibres parallel to the sample longitudinal axis. In contrast with what was observed for the samples with fibres oriented at 90° (Fig. 4), no significant shift in the measured T_g was noticed for the different values of the selected static and dynamic component of the sample excitation. The T_g was 197 °C, obtained by averaging six test results, with a standard deviation of 1.5 °C.

Figure 7 shows a plot of the difference between the measured T_g in the direction orthogonal and parallel to the fibres, as a function of the sample preload. For the selected values of preload, the maximum difference

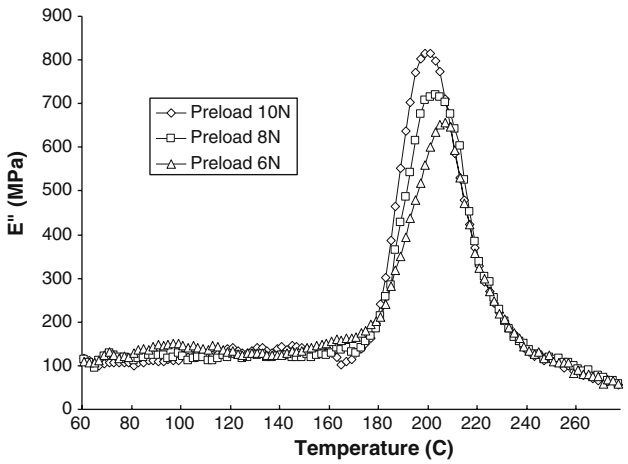

Fig. 4 E'' (T) plots obtained in the direction orthogonal to the fibres for different values of the specimen preload. The plots show that loss peak temperature (T_g) increases with decreasing preload

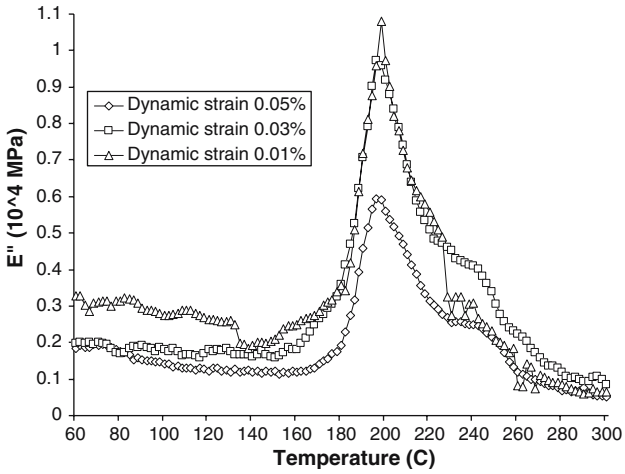

Fig. 6 E'' (T) plots obtained in the direction parallel to the fibres for different values of the dynamic strain. Changing the dynamic strain did not produce any relevant shift in the loss peak temperature (T_g)

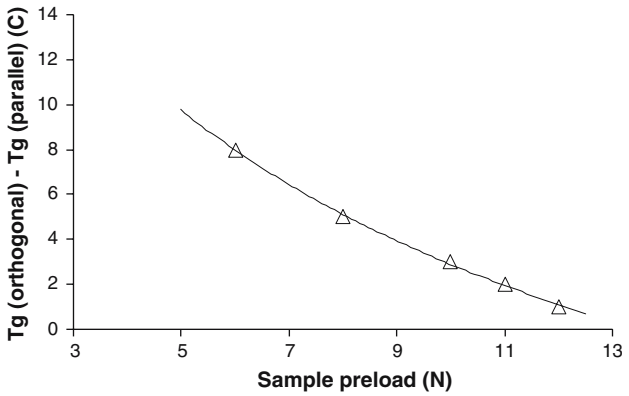

Fig. 7 Plot of the difference between the measured T_g in the direction orthogonal and parallel to the fibres as a function of the sample preload. The plot shows that the measured difference in T_g depends on the sample preload applied to the sample during the measurement

observed was 8 °C. The plot shows that the difference in the measured T_g depends on the sample preload values used during the test and decreases with increasing preload. A similar correlation was observed for the epoxy resin 914/carbon fibre unidirectional samples [10]. Table 2 gives the results of the DMTA carried out on this material in the direction parallel and orthogonal to the fibres. For samples with orthogonal fibres, increasing the sample preload produced a reduction of the measured value of T_g from 171 °C to 164 °C. No significant effects in the measured T_g were observed for the same material in the direction parallel to the fibres.

This behaviour was consistent with that observed for the cyanate-ester carbon fibre laminate. It shows that the measured value of T_g is influenced by the specific test conditions i.e. it depends on the values of preload applied to the sample during testing. The observed behaviour could be explained by the dependence of T_g on molecular mobility and free volume in polymers. In fact, the higher is the preload applied to the samples, the higher is the free volume and the molecular mobility, the lower is the T_g. This effect would be significant in samples with orthogonal fibres, where the mechanical properties are dominated by the matrix. In samples with longitudinal fibres, this effect would not be evident due to the higher elastic modulus of the fibres compared to that of the matrix. The experimental results also suggest that the difference in T_g between the parallel and orthogonal direction reported in previous works could have been caused by the different preload values applied during the measurements. In [11], the difference in measured T_g was explained by the presence of a secondary phase at the interface between fibres and matrix and by its effect on E'' peak when subjected to shear stress during testing. This mechanism would not account for the experimental evidence reported in the present work. In fact, any fibre-matrix interface is essentially subjected to shear in samples with fibres parallel to the sample longitudinal axis, whereas, for both of the tested materials, the dependence of the measured T_g from the applied preload was observed only for the samples with fibres orthogonal to the sample longitudinal axis, where shear stresses in the fibre-matrix interface are negligible.

Table 2 Test results obtained for the 914/carbon fibre unidirectional laminate. The results show a similar dependence of the measured T_g from the sample preload as that observed for the cyanate-ester carbon fibre laminate

Fibre direction	T_g (GABO DMTA)	T_g (PL DMTA)
Parallel	171 °C	169 °C
Orthogonal	from 171 °C to 164 °C*	160 °C

*Measured for increasing values of sample preload

The results also suggest that testing identical materials with different values of the applied preload produces different values of T_g. In the current industrial practice, this problem is difficult to appreciate since commercial DMTA test machines, used for materials development and quality control, do not often have the possibility of controlling and measuring the effective preload applied during testing. In these cases tests are generally carried out using predefined test conditions without specified preload values. In the light of the findings reported in this work, this practice is essentially incorrect. Test results obtained without specifying sample preload values are not directly comparable since differences in T_g up to 10 °C or higher are expected.

The observed dependence of the measured T_g from the preload is particularly relevant to the problem of standardisation of DMTA for measuring T_g in composite materials. In [12], an ISO standard currently in draft form, it is prescribed that the strain on the specimen shall be selected so that it is within the linear elastic range of the material being tested. However, no specific recommendations on preferred preload/prestress values and their effect on the measured T_g are given. Since in many of the commercial DMTA test equipment, applied preloads cannot be neither selected nor controlled, the problem of standardisation should, in the authors' opinion, be addressed by involving the test equipment manufacturers as well as the industrial users.

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