JOURNAL OF MATERIALS SCIENCE 28 (1993) 5495–5499

Dynamic mechanical analysis of a two-dimensional carbon–carbon composite

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A two-dimensional carbon–carbon composite material consisting of stacked carbon cloths densified with a carbon matrix has been characterized with respect to its dynamic mechanical properties. Unprotected specimens and some protected against oxidizing conditions were investigated over the temperature range of subambient (− 100 °C) to 500 °C. The reproducibility of the calculated storage modulus as well as the loss factor was within 5% at any one temperature over the entire temperature range. Results concerning protected and unprotected specimens were compared analytically and the difference of the relative plots above 400 °C reflects the bad corrosion resistance of the unprotected samples under oxidizing conditions, where the carbon matrix material is more sensitive to oxidation than the fibre. The transition regions which appeared on the loss factor plots are strongly connected with the relevant secondary transition regions of the antioxidation protected material used. This technique, which has been demonstrated to be non-destructive for the sample analysed, proved that no differences exist in the dynamic mechanical properties of the specimens with respect to fibre orientation (warp or weft direction). Details of the experimental technique and assumptions made are also presented.

1. Introduction

Dynamic mechanical analysis (DMA) is a useful, well-established method for measuring, among others things, the dynamic characteristics (storage modulus and loss factor) at the resonant frequency of a wide range of materials such as metals, composites, elastomers, films, biomaterials and ceramics [1, 2]. In the present work, the dynamic mechanical properties of a two-dimensional carbon–carbon composite material [3] were investigated under an oscillatory load as a function of temperature.

The method is based upon the following principle: if a material is subjected to a deforming load, the potential energy associated with the deformation will be manifested as oscillation upon removal of the deforming load. In the case of purely elastic materials, the stored potential energy will be equal to the oscillation energy. In reality, most of the materials exhibit a viscoelastic rather than a purely elastic behaviour, and this type of material normally dissipates the deformation energy to heat [4]. In both cases, the storage modulus of the material under investigation is a function of the square of the oscillation frequency, while concerning the viscoelastic materials the dissipation energy is a direct measurement of the internal damping. If the dissipated energy is continuously renewed by an in-phase driven force, as a means of keeping the amplitude constant, then the energy lost by the vibrating sample on each cycle is known.

The values of frequency and the dissipated energy are continuously recorded at discrete time intervals as well as the reference temperature of the above data, and an analysis can be performed to provide the storage modulus and damping coefficient as a function of time or temperature. In an experiment the test specimen is oscillated at the resonant frequency of the sample–arms–pivot system and an amount of energy equal to that lost by the sample is added at each cycle to keep the sample in oscillation at the resonant frequency recognized, under constant amplitude. As the temperature is changed the above procedure is repeated. Commercial instruments are available to perform the experiment and acquire the experimental data.

A short presentation of the equipment and the used conditions, as well as a description of the two-dimensional carbon–carbon material are presented in Section 2. In Section 3 the obtained results are presented, both for protected and unprotected carbon–carbon specimens and a comparison is given analytically. Finally, Section 4 contains conclusions and evaluation of the used technique.

2. Experimental procedure

The DMA presented here was carried out in a DuPont Model 983 Module (with DuPont 2000 software for analysis) which is schematically represented in Fig 1.

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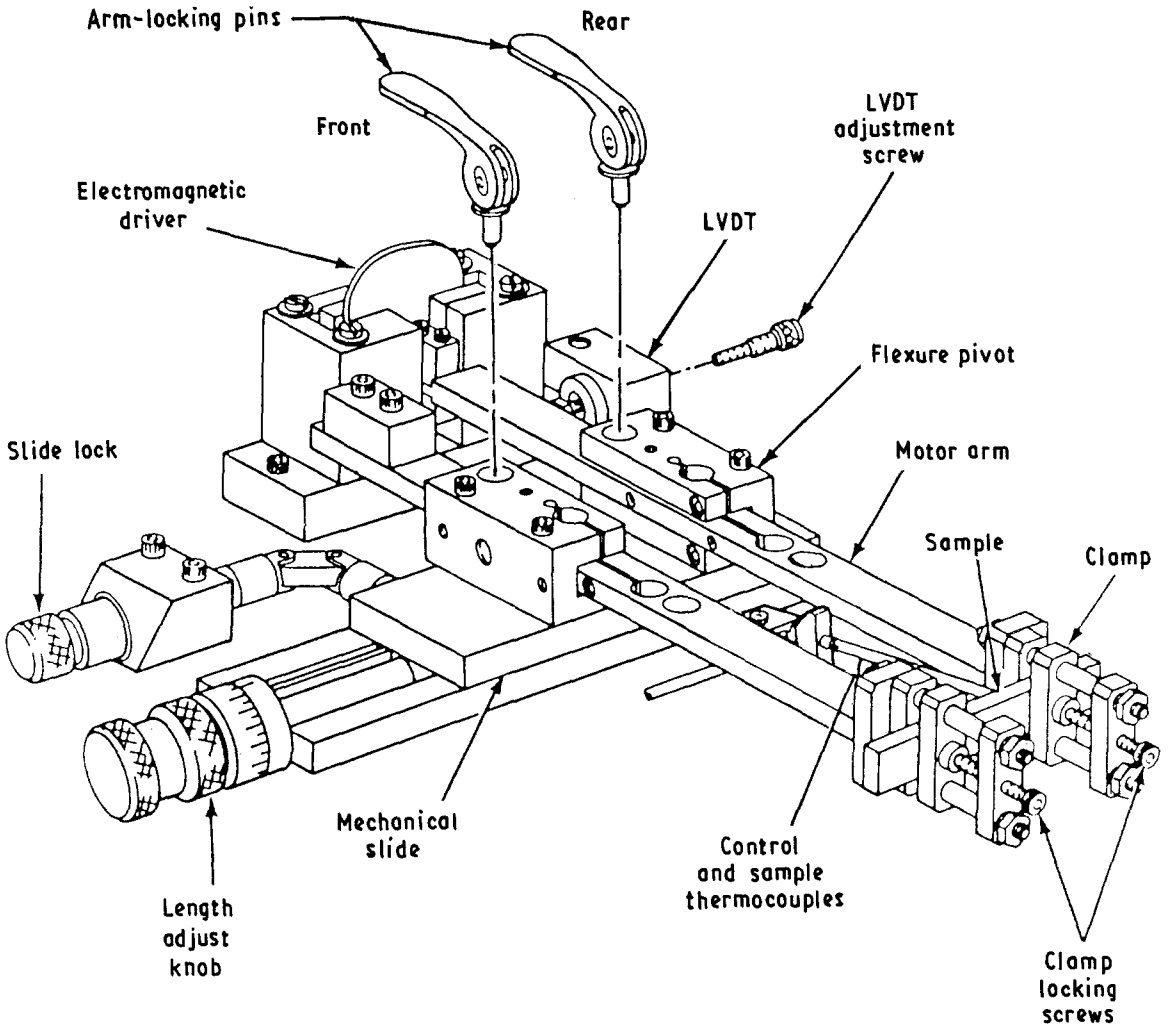

Figure 1 Representation of DuPont dynamic mechanical analyser.

Two parallel, balanced sample support arms, free to oscillate around flexure pivots, are the heart of this system. Both arms, the active and the passive, are locked in place during sample clamping and alignment. The arm locking pins are removed just prior to final balance of the mechanical system and the start of the heating programme. A furnace covers the sample area to provide a programmed temperature environment during the experiment and the system is supported by an LNCA liquid nitrogen unit for working at subambient temperatures.

To make a measurement, a material of known dimensions is clamped between the two sample arms. The sample–arm–pivot system is oscillated at its resonant frequency by an electomechanical transducer. The frequency and amplitude of this oscillation are detected by a linear variable differential transformer (LVDT) positioned at the opposite end of the active arm. The LVDT provides a signal to the electromagnetic transducer which in turn keeps the sample oscillating at constant amplitude. The resonant frequency of the specimen (Hz) and the necessary transducer voltage (mV), which also is called the damping voltage and is proportionally related to the dissipation energy, are measured as functions of temperature at discrete time intervals. The dynamic Young's modulus of the sample can be obtained from the resonant frequency by using the relation

$$E = \frac{4\pi^2 f^2 J - K}{2W[(L/2) - D]}\left(\frac{L}{T}\right)^3$$

where, L, W and T are the length, width and thickness of the specimen, respectively, f the DMA frequency and J, K, D the moment of inertia of the arms (kg m^2), the spring constant of the pivot (N m rad^{-1}) and the clamping distance of the system (m), respectively. The

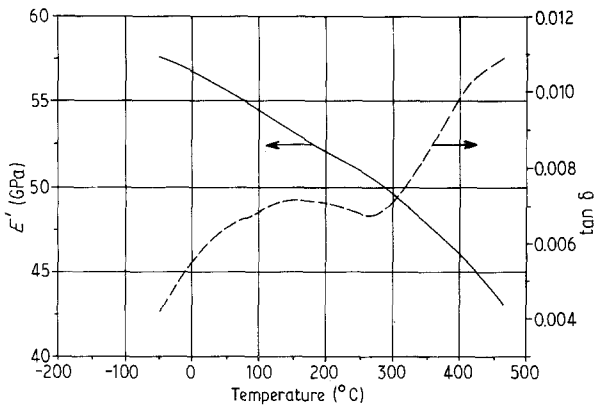

Figure 2 Dynamic mechanical characteristics of a weft direction cut unprotected C–C composite plotted against temperature.

parameters are related to the DMA and reflect its influence on the measurement.

The ratio of the loss energy to the storage energy expresses the ratio of the imaginary part of the dynamic modulus of elasticity to the real part, and is defined as tanδ. It is a quantitive measurement of the material's internal damping. This parameter is evaluated using the equation

$$\tan\delta = VC/f^2$$

where V is the damping voltage (mV), f the DMA resonant frequency (Hz) and, C a system constant ($Hz^2\,mV^{-1}$) which affects the measuring value.

During testing, a sample of known dimensions is deformed in a sinusoidal low-strain displacement of 0.04 mm and the resonant frequency as well as the damping signal are recorded as a function of temperature. A constant heating rate of $10\,^{\circ}C\,min^{-1}$ was applied over the entire temperature region under consideration. A calibration procedure was followed for the DMA based on the DuPont software for DMA *calibration* for securing the accuracy of the measurements. More precisely, the phase-lag calibration was performed at the beginning of each test because of the low-loss character of C–C material.

The material is reinforced in two dimensions and made of stacked 0°/90° laminates densified with carbon matrix and bought from Schunk Kohlenstofftechnik (Germany). Initially the fibre preform is liquid-phase impregnated with a typical phenolic resin system [3] at a pressure of about 6 bar. Then a carbonization process is applied at about 1200 °C under an inert atmosphere to allow decomposition of the resin, followed by a graphitation process at about 2000 °C. A repetition of 5–7 densification cycles (impregnation/carbonization/graphitization) is necessary to arrive at the final C–C material which has a density of $1.6\,g\,cm^{-3}$ and a porosity less than 10%. A material plate of 350 mm × 220 mm was investigated with respect to its quality using an ultrasonic scanner and five specimens of each direction, weft and warp, were cut out using plate regions having the acceptable porosity (less than 10%). Another amount of six specimens (three of each direction) were cut and antioxidation-protected at XyCarb, a Dutch company dealing with surface treatment. Again all specimens were checked after machining to identify any possible damage produced during the cutting procedure.

The antioxidation protection is applied via a chemical vapour deposition of SiC. To overcome the mismatch of thermal expansion coefficient between SiC and the carbon matrix, a thin gradient layer is applied on the specimen starting with carbon-rich and ending with stoichiometric SiC. Both protected and unprotected samples are placed in the DMA support grips with special care for alignment.

The specimen's dimensions are 60 mm × 10 mm × T where T has the original plate thickness of about 2.5 mm. In the case of protected samples the width and thickness were increased due to the protection thickness, but all the properties were normalized to the unprotected dimensions, assuming that the protection layer is not bearing material.

3. Results

In the present work four different groups of C–C samples were tested. They consisted of weft and warp cut specimens, both protected against oxidation and unprotected. Representative results for each group of experiments are given in Figs 2 to 5, where both the dynamic modulus of elasticity E' and loss factor tanδ are shown.

In general, a very good reproducibility of the results obtained over the entire temperature range were shown to be within 5% for the unprotected specimens

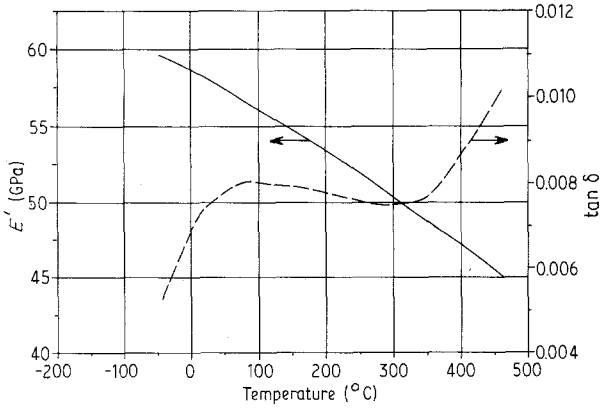

Figure 3 Dynamic mechanical characteristics of a warp direction cut unprotected C–C composite plotted against temperature.

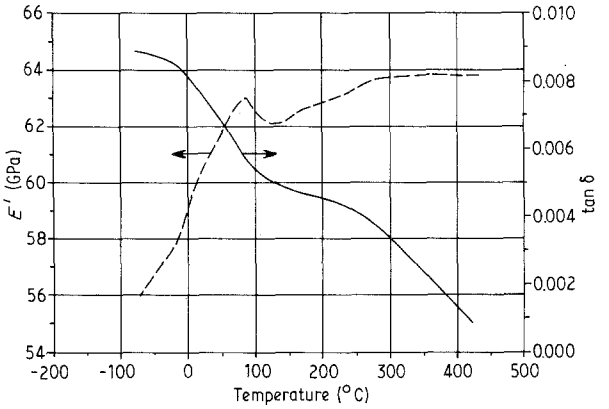

Figure 4 Dynamic mechanical characteristics of a weft direction cut protected C–C composite plotted against temperature.

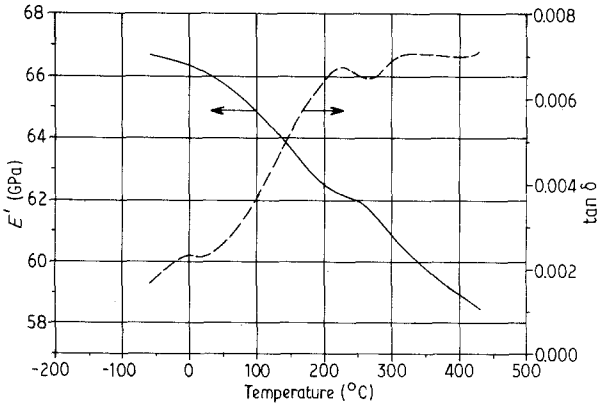

Figure 5 Dynamic mechanical characteristics of a warp direction cut protected C–C composite plotted against temperature.

and 7% for the protected ones concerning the modulus of elasticity, while the relative reproducibility for the loss factor was within 10% for both cases. Good reproducibility is probably due to the initially applied quality control. Specimens having delaminations or porosity higher than 10% were rejected.

As was expected in all cases, the storage modulus decreases as the temperature increases while an opposite behaviour is exhibited for the material loss factor. More precisely, in Fig. 2 the behaviour of a weft direction cut specimen is plotted against temperature. The dynamic modulus of elasticity yields a bilinear behaviour within the investigated temperature range, having a more intensive rate of decrease at temperatures higher than 350 °C. The total decrease of the storage modulus within the said temperature range is about 25%.

On the other hand, the material loss factor shows a more complicated behaviour having an initial increase up to 100 °C, then an almost constant value up to 350 °C and a final increase with about the same constant rate as in the first part of the curve. An analogous behaviour appeared for the warp direction samples, both concerning the storage modulus and the loss factor (Fig. 3). The higher values of dynamic modulus of elasticity obtained in the warp direction are not statistically significant.

In Figs 4 and 5 the corresponding results concerning the SiC-protected samples are presented. Again there is a slight superiority of the storage modulus obtained from the warp direction but with no statistically significant difference. However, comparison of the results presented in Figs 4 and 5 with those of Figs 2 and 3 exhibits a significant difference. The storage modulus of the protected samples shows a more stable behaviour, having a total decrease within the temperature rate under consideration of almost 15%, while the loss factor exhibits a smoother behaviour compared to that of the unprotected samples and an approximately constant value at temperatures higher than 100 °C. On the other hand, the storage modulus of the protected samples shows a transition zone between 100 and 200 °C, possibly connected with the properties of the protection layer.

The higher absolute values of the storage modulus in the case of protected specimens are fictitious and due to the normalization of the obtained results to the dimensions of the unprotected specimens. So the presence of the SiC protection layer, even in a very fine thickness, influences the material stiffness.

In Fig. 6 the results of the weft direction protected samples are plotted against temperature and the real sample dimensions have been used. As mentioned above, there is a significant decrease of the storage modulus compared to the respective value of Fig. 4, while the corresponding value of the loss factor is slightly decreased. But the most important difference between the results obtained from the unprotected and the protected specimens is shown by comparison of the plots of the loss factor against temperature (Figs 2 to 6). It is obvious that in the case of protected samples no loss factor increase appears over 350 °C. This fact, combined with the higher decrease of storage modulus of unprotected C–C samples, may be caused by a burning process which initiates in unprotected coupons tested over 350 °C. This effect does not occur in the case of SiC-protected specimens. Further investigation is proposed by the authors for clarifying the reasons for such behaviour of the unprotected samples at relative low temperature.

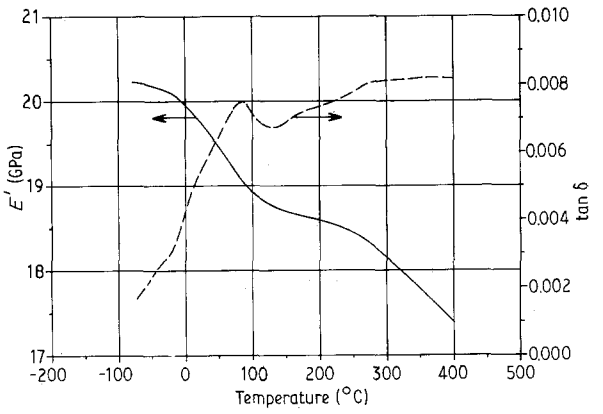

Figure 6 Unnormalized dynamic mechanical characteristics of a weft direction cut C–C composite plotted against temperature.

4. Conclusions

The dynamic mechanical analysis technique has been applied to analyse samples of two-dimensional carbon–carbon material over a wide temperature range. This technique leads to an excellent reproducibility of the measured dynamic characteristics of the material, in the case of quality-controlled specimens. This technique can therefore be used as a non-destructive test method for ensuring the acceptable quality of C–C specimens.

Regarding the C–C material analysed, antioxidation protection does not affect the dynamic characteristics and especially the loss factor of the protected samples as possibly may be expected. The protection layer works well under the test conditions described and secures the sample's stability.

In addition, there are no statistically significant differences in dynamic mechanical properties of the ceramic material under consideration, in weft and warp direction, and this was expected due to the method of its production.

Future application of the DMA technique at higher temperatures should be a promising method for also evaluating the quality of an antioxidation protection on various substrate materials.

Acknowledgements

The authors want to thank Dr Leis of Deutsche Aerospace (DASA) for the supply of C–C materials and his useful suggestions, as well as XyCarb Helmond and especially Mr M. Michorius for machining and application of the antioxidization protection on the samples. Part of this work was carried out within the frame work of BRITE/EURAM project BE-3243-11/91.

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Received 9 October
and accepted 17 November 1992