CMMT(MN)060

Characterisation of the Fibre-Matrix Interface by Thermal Analysis

The properties of the interface between fibre and matrix are critical to many properties of a composite material. This Measurement Note considers the use of two thermal analysis techniques, dynamic mechanical analysis and differential scanning calorimetry, for characterising the fibre-matrix interface. Previous work on this topic using these techniques is reviewed.

A series of glass fibre-vinyl ester composite materials has been manufactured using fibres with different surface coatings. Specimens from each material have been tested using both thermal analysis techniques. The results show that dynamic mechanical analysis is more sensitive to the interfacial properties than differential scanning calorimetry. A standardised procedure is presented for the use of dynamic mechanical analysis for the characterisation of the fibre-matrix interface.

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Introduction

Many properties of a composite material depend critically on the properties of the fibre-matrix interface. The properties of the interface are the result of many influences, such as the fibre roughness, the chemistry of the fibre surface and/or coating and the properties of the matrix. Qualities of the fibre that are thought to contribute to the development of the fibre-matrix interface have been considered in previous measurement notes [1, 2].

This measurement note considers two techniques that could provide information on the interface, rather than the fibre alone.

Thermal Analysis Techniques

The term "thermal analysis" covers a wide range of techniques that follow changes in material properties with temperature. This measurement note considers dynamic mechanical analysis (DMA), which monitors changes in the mechanical properties, and differential scanning calorimetry (DSC), which monitors changes in the heat flow. These two techniques are described below. Other thermal analysis techniques monitor the mass of the sample and the dielectric properties of the sample.

DMA

DMA equipment applies a sinusoidal load to a sample and the resulting deformation is measured during a controlled temperature programme. The response of the sample is interpreted as the storage (elastic) modulus and loss (viscous) modulus. The ratio of loss and storage modulus, tan δ, is also reported. The most common application of DMA is analysis of the glass transition which is affected by many aspects of the structure and processing of a material. DMA is far more sensitive to the glass transition than DSC. ISO 6721 is relevant to the use of this technique.

DSC

DSC is a technique in which the difference between the heat flux into a test specimen and a reference specimen is measured as a function of temperature and/or time while the specimens are subjected to a controlled temperature programme. There are two types of DSC instruments currently used; "heat flux" and "power compensation" instruments. Although they are fundamentally different in design, the data produced are comparable. DSC is probably the most versatile thermal analysis technique and can be used to study properties such as melting and crystallisation behaviour, glass transition temperature, curing behaviour and specific heat capacity. ISO 11357 is relevant to the use of this technique.

Studies Of The Fibre-Matrix Interface By Thermal Analysis

There are many research papers that report the use of DMA to investigate the fibre-matrix interface of a composite material, usually through changes in the glass transition. For example, one of the more recent papers [3] reports on DMA of carbon fibre-epoxy composites. This paper recommends that the single cantilever mode should be used. This work also confirms an earlier statement [4] that the longitudinal mode is the most appropriate for investigating fibre, and therefore interface, properties.

Generally, the tan δ curve is considered in these studies since it is normalised with respect to the specimen stiffness, so direct comparison between specimens with minor variations in the volume fraction of fibre is possible.

The study of the fibre-matrix interface by this technique is not without pitfalls. Thomason [5] described how an effect of the heating rate caused artefacts which had been incorrectly interpreted as evidence of the interphase. However, the author was able to detect genuine effects of the interface using this technique.

DSC has been successfully used to investigate the fibre-matrix interface in composite materials [6]. However, the materials contained fibres which melted at a lower temperature than the matrix, which is generally not the case for composite materials.

In principle, it should be possible to detect changes in the glass transition by DSC, similar to those detected by DMA. However, in practice DSC is less sensitive to the glass transition and is unlikely to provide enough detail to distinguish effects of the fibre-matrix interface.

Materials

The composite material system chosen for investigation was a glass fibre reinforced vinyl ester resin, using four types of glass fibre. (N.B. This range of fibres was also used for wetting measurements, see Measurement Note CMMT(MN)055 [2].) In addition, a separate material was manufactured with fibre with complete sizing that had been sprayed with PTFE.

The composite specimens were manufactured using a silicone mould. A number of glass fibre tows were attached longitudinally within the mould and resin was poured into the mould and allowed to impregnate the fibre tows. The resin was cured at 100°C for 3 hours. An unreinforced resin sample was manufactured in the same way. The six types of material are listed in Table 1.

Procedures

The DMA procedure is described below.

DSC Procedure

Approximately 20 mg of sample was accurately weighed into an open aluminium crucible. The sample was heated from ambient to 200°C at a heating rate of 10°C/minute with a dry nitrogen purge gas.

The step transition corresponding to the glass transition was analysed; inflection point, extrapolated onset, extrapolated endset and the value of the step transition were determined.

Table 1. Materials.

Material code	Type of size on glass fibre
Size 1	Water size
Size 2	Epoxy compatible size
Size 3	Polyester compatible size
Size 4	Complete size: polyester and epoxy compatible size
Sprayed	Size 4 sprayed with PTFE
Resin only	-

Standardised procedure for characterisation of the fibre-matrix interface by dynamic mechanical analysis

1 Scope

This procedure describes the use of dynamic mechanical analysis (DMA) equipment to characterise the fibre-matrix interface of a polymer composite material. The tan δ values for the material are sensitive to the properties of the interface.

2 Apparatus

2.1 Dynamic mechanical analyser, capable of heating at 3°C/minute and testing at a frequency of 1 Hz. The load capability of the analyser shall be sufficient for the samples tested.

2.2 Vernier callipers, capable of measuring to an accuracy of 0.05 mm.

2.3 Standard reference materials: as required by the manufacturer's procedures.

3 Calibration

3.1 Mechanical Calibration: Mechanically calibrate the instrument according to the manufacturers' recommendations. The mechanical calibration will generally involve measurement of the compliance of the instrument using a stiff, usually steel, bar.

3.2 Temperature Calibration: No temperature calibration method is currently recommended for these measurements.

Note 1:
It is recommended that no temperature calibration is applied because there is currently no single method that is satisfactory for all types of instrument. Consequently, it is not possible to compare values from different instruments or laboratories.

NPL is contributing to the development of an ISO standard for temperature calibration of DMA equipment.

4 Sample

4.1 Composite samples containing unidirectional continuous fibres shall be used. The fibres shall be oriented longitudinally within the sample to maximise the influence of the fibre-matrix interface on the specimen response. Suitable sample dimensions will vary depending on the particular instrument being used.

4.2 A sample with a relatively small cross sectional area is recommended to reduce thermal lag effects. A square section has been found to be suitable.

5 Procedure

5.1 Single cantilever mode shall be used

5.2 A heating rate of 3°C/minute shall be used.

5.3 A frequency of 1 Hz shall be used.

5.4 The strain on the sample shall be selected so that it is within the linear elastic range of the material being tested.

5.5 The temperature range of the test is from at least 50°C below the region of interest to at least 50°C above the region of interest.

Note 2:
This procedure is based on the NPL Measurement Good Practice Guide "Thermal Analysis Techniques for Processing of Composites and Adhesives", which can be obtained from NPL.

6 Analysis of Results

6.1 The tan δ curve has been identified as the most relevant property for assessing the fibre-matrix interface. There are four quantities derived from the curve which can provide information:

a) The peak tan δ temperature.

b) The value of tan δ at the peak.

c) The full-width-half-maximum (FWHM) of the tan δ peak

d) The area under the curve.

These quantities are illustrated in Figure 1.

6.2 The peak tan δ temperature and value can be reproducibly assigned without difficulty.

6.3 The FWHM shall be taken as width of the peak parallel to a straight baseline, connecting a point on the tan δ curve 50 °C below the peak tan δ temperature to a point on the tan δ curve 50°C above the peak tan δ temperature, at half the height of the peak with respect to the baseline. The result will be a temperature value.

6.4 Similarly, the area under the peak shall be taken as the area bounded by the tan δ curve and a straight baseline (constructed in 6.3), connecting a point on the tan δ curve 50 °C below the peak tan δ temperature to a point on the tan δ curve 50°C above the peak tan δ temperature. This area will again be a temperature value, because tan δ is a dimensionless quantity.

Note 3:
In general, the tan δ curve is not recommended for determining the thermal properties of a composite material, because it is not a good guide to the usable properties of the material.However, for assessment of the fibre-matrix interface, the energy storage and dissipation are more relevant than the service properties, so the tan δ curve is analysed.

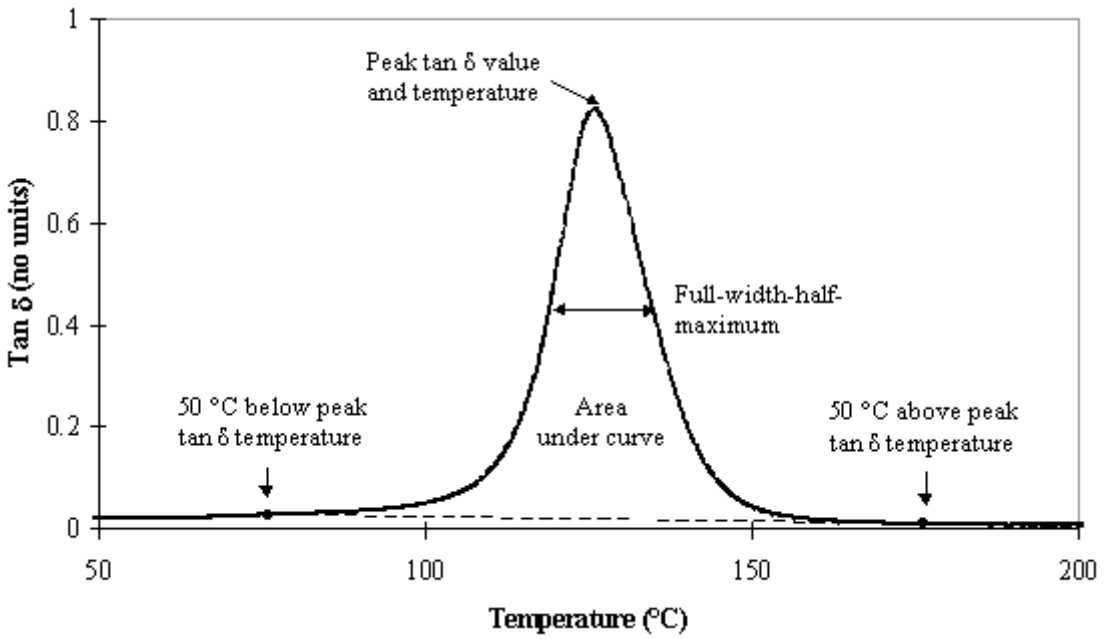

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Figure 1. Example of a tan δ curve showing the four quantities identified in this procedureand their construction.

Results And Discussion

The aim of this investigation is to determine which techniques can be used to characterise the properties of the fibre-matrix interface. Four of the materials ("Size 1", "Size 2", "Size 3" and "Size 4") contain fibres that are sized. Although there may be differences in the details of the size, they should all show reasonably good adhesion to the matrix. A further sample containing fibres coated with PTFE (the "Sprayed" material) would be expected to show poor adhesion.

The results of the DMA testing are shown in Table 2. The DMA response reflects the energy absorption by the material; a higher tan δ value indicates more energy absorbed. Each of the four composite materials tested has a unique value of both peak tan δ value and the full-width-half-maximum. This can be seen clearly in Figure 2, which shows the appearance of the tan δ curves. Although they rank the materials slightly differently, these two quantities could indicate the efficiency of the fibre-matrix interface.

It can be seen from Table 2 and Figure 2 that the results for the "Sprayed" material are significantly different to those for the other four composite materials. The peak tan δ temperature and value are lower than the other composite materials, while the width of the peak is greater. The results for the "Sprayed" material appear to be inconsistent with the results for other composite materials, since it indicates this material has the most efficient bonding. A possible explanation is that although the PTFE coated fibres are poorly bonded, they are lubricated by the PTFE, so little energy is absorbed at the interface.

Table 3 shows the results of the DSC testing. Minor variations are observed, but these are not significant for this technique and do not appear to correlate with the interfacial properties.

Table 2. Dynamic mechanical analysis results.

Material	Peak tan δ temperature (°C)	Peak tan δ value (no units)	Full-width-half-maximum (°C)	Area under tan δ peak (°C)
Size 1	126.0	0.867	15.8	16.4
Size 2	126.9	0.773	17.7	16.1

Size 3	129.8	0.522	20.8	11.9
Size 4	128.7	0.616	23.2	16.2
Sprayed	116.3	0.443	45.8	20.1
Resin	122.2	1.028	16.2	20.0

Table 3. Differential scanning calorimetry results.

Material	Onset temperature (° C)	Inflection temperature (° C)	Endset temperature (° C)	Change in Cp (J/g/° C)
Size 1	106.8	114.0	120.2	0.191
Size 2	104.8	112.6	116.5	0.219
Size 3	106.2	115.0	121.4	0.187
Size 4	106.0	113.0	114.5	0.322
Sprayed	109.1	112.4	114.3	0.187
Resin	104.4	110.9	111.2	0.206

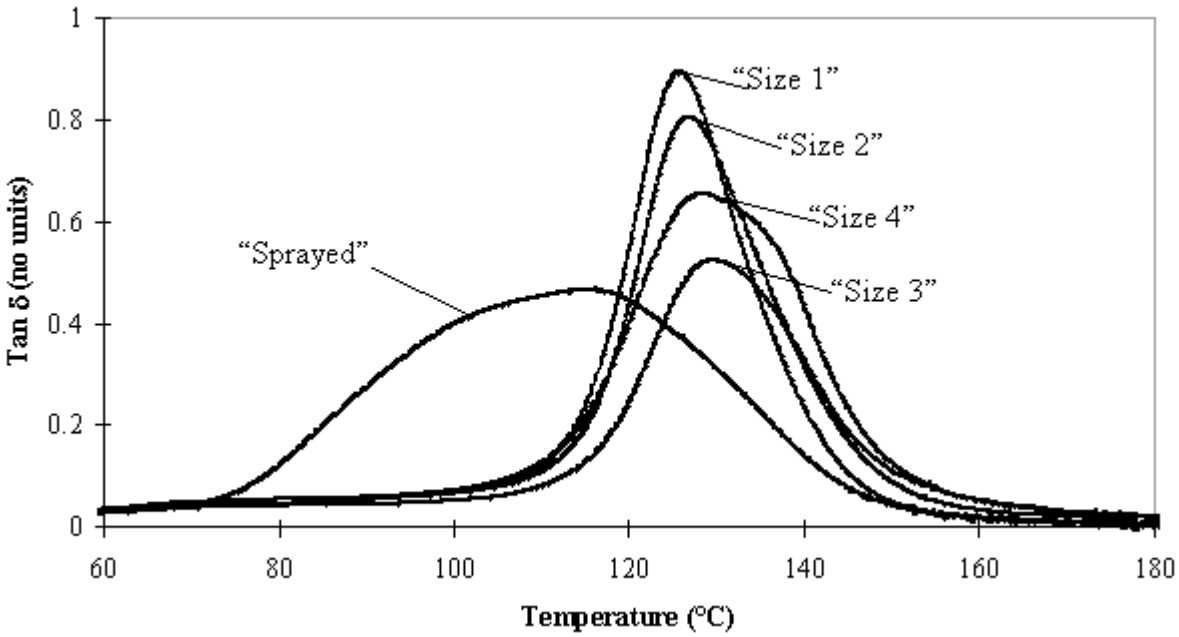

Figure 2. Tan δ curves for the five types of composite material tested.

Concluding Remarks

Thermal analysis for characterisation of the fibre-matrix interface

The results of this investigation show that DMA is sensitive to interfacial properties. Of the quantities that are sensitive to the interface, the peak tan δ value and full-width-half-maximum are identified as the most promising indications of the properties of the fibre-matrix interface.

A complicating factor is that DMA is sensitive to the energy absorption by the material, which may be influenced by factors other than the properties of the fibre-matrix interface. For instance, energy can also be absorbed by defects, cracks and residual stresses. DMA could be a useful quality assurance test as these features are as undesirable as poor bonding at the interface.

As anticipated, DSC does not appear to be sensitive to the fibre-matrix interface in composite materials. There is some variation in the results, but this does not appear to correlate with the properties of the fibre-matrix interface. This is reasonable because the volume of the interface is a very small component of the volume of the sample.

Comparison with other techniques

It is not clear how the variations observed in DMA relate to other properties of the fibre-matrix interface. For instance, the DMA response provides information on the energy absorption at the interface, but it is not clear if this can be related to the strength of the interface, a quantity required by many models for composite material properties.

In this area of study there are a number of techniques which each provide a single piece of information about the interfacial properties, but it is not clear how these correlate with each other. A further Measurement Note will be produced comparing the techniques investigated within this project.

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