APPLICATION NOTE

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Inspire the Next

DMA7100 & NEXTA DSC

Thermal analysis of carbon fiber reinforced epoxy prepreg

INTRODUCTION

Prepreg is the term given to composite materials, such as glass fiber or carbon fiber, that have been pre-impregnated with a resin, such as epoxy or polyester. They provide an easy way for manufacturers to make complex and intricate components from lightweight materials, such as carbon fiber.

Carbon fiber reinforced epoxy resin prepreg is made by combining carbon fiber with an epoxy resin system, comprising of resin and curing agent. The material comes in semi-cured laminated fabric form and requires no extra resin or curing agent during the manufacturing process. To fully cure the material, heat and pressure are applied within a large autoclave. Prepreg is used where advanced, strong and lightweight materials are needed, from sporting equipment like golf clubs, to formula 1 body panels and aircraft parts.

Prepregs are delivered partially cured, and because of this they need to be stored at low temperature to prevent the curing process from continuing. However, even at relatively low temperatures, the curing process can still progress and prepregs usually have a short shelf life because of this. Before using the stored prepreg fabric, it's necessary to check the curing level to make sure the composite can still be used. Also, the mechanical properties of the carbon fiber composite will depend on the level of curing, and for many applications a full cure is not desirable. Manufacturers have to determine the right cure time and temperature to ensure the finished components have the right properties.

Thermal analysis using dynamic viscoelastic analysis and differential scanning calorimetry are ideal ways of establishing both the curing status of the prepreg prior to use, and to fine tune the curing process to achieve the desired level of curing within the final manufacturing process.

The Hitachi DMA7100 and NEXTA DSC200 instruments are ideal for these measurements due to their low noise, high sensitivity and advanced application capabilities.

Hitachi High-Tech Analytical Science's family of thermal analyzers have been employed in the field for more than 45 years, delivering world-class performance for precise materials and process characterization measurements, including thermal analysis of carbon fiber reinforced epoxy prepreg.

HITACHI INSTRUMENTS FOR THERMAL ANALYSIS OF PREPREG

DMA7100

The Hitachi DMA7100 (dynamic mechanical analyzer) is versatile, high-performance instrument that's ideal for dynamic viscoelastic analysis within production, applied research and R&D for many different kinds of materials, including partially cured prepregs. The instrument includes Hitachi's easy to use software that makes understanding and interpreting DMA results easy for fast evaluation of materials. Using the built-in wizard, even the untrained analyst will get the best results every time. Suitable for soft and stiff samples, the DMA7100 is customizable for different types of applications, such as TMA analysis, and has optimized CPU performance for increased measurement count and better accuracy.

NEXTA DSC

The NEXTA DSC200 is an advanced differential scanning calorimeter that's designed to meet the most advanced DSC applications today, both within production and applied research. However, like other Hitachi instruments, the NEXTA DSC200 is easy to use and robust enough for high-volume operation within a production or development environment. High sensitivity and world-class baseline performance mean the analyzer can detect minute changes of state when evaluating partially cured composite materials.

In this application, we've taken advantage of the high sensitivity of the DMA7100 to detect curing levels in carbon fiber reinforced epoxy prepreg. We've then used the NEXTA DSC200 to verify the results obtained with the DMA7100. Both of these instruments have very low levels of noise, which allow for precise analysis – essential for determining curing levels.

ALL-INCLUSIVE SOFTWARE WITH CAPACITY FOR NEW APPLICATIONS

Both analyzers come with Hitachi's intuitive and advanced NEXTA TA software, which gives you options for how you need to operate the instrument. New users are able to get reliable and accurate results and experienced operators can use these instruments for more advanced analysis. All modules are included with the instruments, so if you decide to expand your use into new applications, you won't have to purchase additional modules. The software includes three modes of operation:

- Guidance mode for step by step measurement and analysis including a calibration wizard.
- Simple mode for more experienced users carrying out routine analysis that requires a simple interface. All important features are available on the main screen.
- Standard mode where all modules are included, and all the flexibility you need for a variety of analysis.

PERFORMANCE AND RESULTS

The Hitachi DMA7100 was used in film shear mode to evaluate the sample and the Hitachi NEXTA DSC was used to provide reference data. Analysis was carried out twice, the first to determine the curing level of the sample and the second to establish the profile of the sample when fully cured.

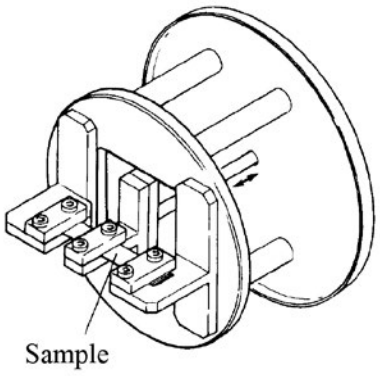

Figure 1 Film shear measurement head used in DMA7100

Sample information

The sample is carbon fiber reinforced epoxy resin in a film configuration with a thickness of 150 µm.
It is a continuous fiber, with the carbon fiber stretched in one direction.

DMA measurement conditions:
Temperature range: -120ºC — 280ºC
Heating rate: 2ºC / min
Oscillating frequencies: 0.5, 1, 2, 5 and 10 Hz

DSC measurement conditions:
Temperature range: -30ºC — 240ºC
Heating rate: 10ºC / min
Sample weight: 10 mg

DMA Viscoelastic spectrum after 1st heating at 1Hz

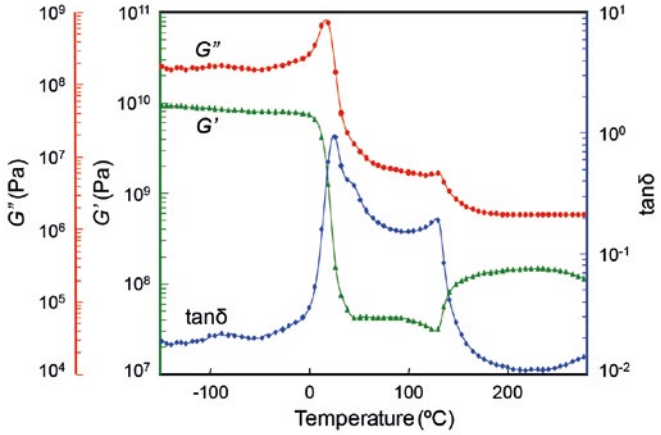

Figure 2 Viscoelastic spectrum of Carbon fiber reinforced epoxy prepreg (1st heating) Frequency: 1Hz

In figure 2, a decrease in G' and a peak in G" and tanδ from 0 to 50ºC is seen. Because the deformation mode in this case is shear mode, we use shear storage module (G') and shear loss modulus (G"), rather than E' and E" which are more commonly used for DMA results. This can be attributed to the primary dispersion, or glass transition, of the epoxy resin. The increase of G' from 130ºC to 150ºC is assumed to indicate the curing of the uncured portion of the resin.

The primary dispersion peak seen in the G' and tanδ curves shows a shoulder peak towards the high temperature side of the curve. This is attributed to the restraining of the molecule motion within fibre reinforced composites due to the polymer being caught between the fibers[1].

DMA Viscoelastic spectrum after 2nd heating at 1Hz

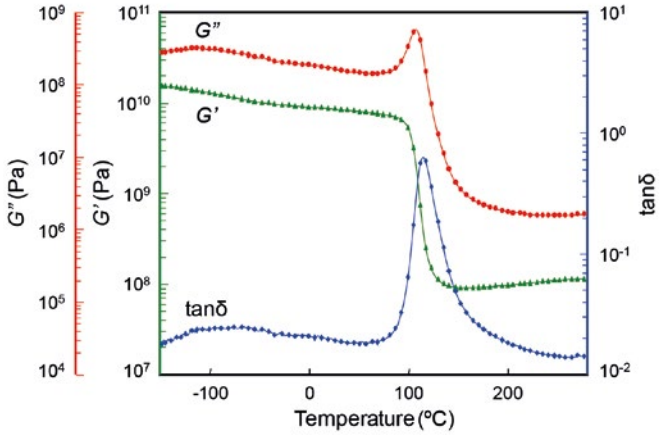

Figure 3 Viscoelastic spectrum of Carbon fiber reinforced epoxy prepreg (2nd heating) Frequency: 1Hz

In figure 3, the decrease of G' and dispersion peaks of G" and tanδ at around 80 — 120ºC are due to the primary dispersion (glass transition) of the cured epoxy resin. No further curing is seen in the G' curve which shows the sample was fully cured.

1 M.Kodama, J.Appl.Polym.Sci., 20, 2853 (1971)

Activation energy of glass transition

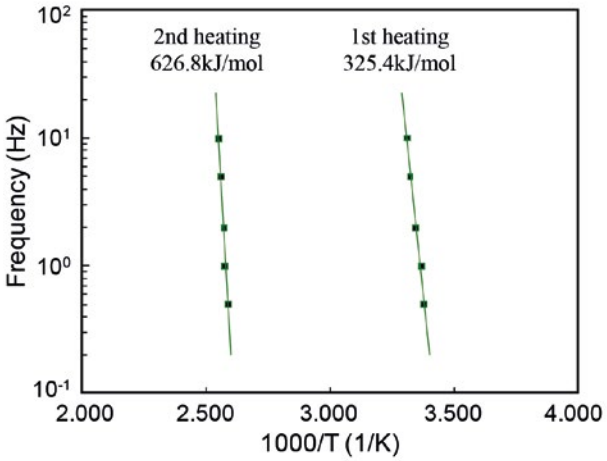

Figure 4 Apparent activation energy of primary dispersion of 1st and 2nd heating

Figure 4 gives the results of the activation energy calculated from the tanδ peaks of the glass transition seen during the first and second heating (figure 2 and figure 3 respectively). The activation energy of the first heating is 325.4 kJ/mol, and 626.8 kJ/mol for the second heating. These results imply that all the dispersion peaks seen are due to the glass transition of the epoxy resin.

DSC curves for 1st and 2nd heating of sample

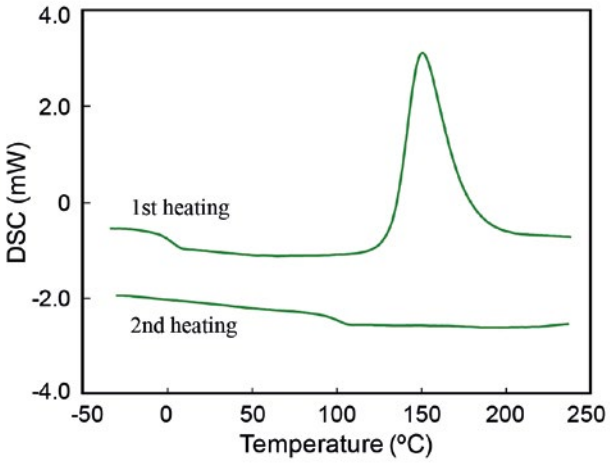

Figure 4 DSC curves of Carbon fiber reinforced epoxy prepreg Heating rate: 10°C/min

In figure 5, you can see the DSC results for the first and second heating. For the first heating, a reduction in the baseline can be seen between -5ºC and 10ºC due to the glass transition, and an exothermic peak seen between 120ºC to 200ºC that correlates to the curing of the epoxy resin. The curve for the second heating indicates a higher glass transition temperature between 90ºC and 110ºC. These results help explain the results seen with DMA in the previous graphs; the decrease in G' and peaks of G" and tanδ are due to glass transition and increase of G' is due to the curing of the epoxy.

As mentioned previously, level of curing is important to know if the materials are still useable and to get the right mechanical properties. It can easily be measured using a DSC. Uncured and partially cured samples are analyzed and the area under the exothermic peak is measured for the uncured (ΔH0) and sample (ΔH1). The level of cure can then be calculated using this equation:

Curing level (%) = ((ΔH0 - ΔH1)/ ΔH0) x 100.

SUMMARY

The **DMA7100** and **NEXTA DSC200** can be used together to determine curing level and final curing profiles of composite materials, such as carbon fiber reinforced epoxy prepreg. Low noise and high sensitivity ensure that the glass transition temperature can be accurately determined, as can whether the material had undergone complete curing.

Many applications have been optimized for Hitachi High-Tech Analytical Science's thermal analyzers. For more information on other applications, please contact our experts at **contact@hitachi-hightech.com**.

DMA7100: ULTRA-SENSITIVE MECHANICAL CHARACTERIZATION

Our dynamic mechanical analyzer range is engineered for ultra-low noise and high sensitivity, making it ideal for precise viscoelastic measurements of polymers, rubbers, thin films and other materials within a production or research environment.

The DMA7100 range offers:

- Ease of use with simple sample clamping mechanism and step by step guidance software
- Low operating costs with auto LN2 cooling unit that reduces nitrogen consumption
- Ability to perform sinusoidal and synthesis wave oscillations, stress-strain, creep/recovery and stress relaxation measurements.
- Ultra-low noise and Lissajous monitoring ensures reliability of the results for every measurement
- Supports a variety of deformation modes: tension, dual-cantilever bending, 3-point bending, shear, film-shear and compression.

NEXTA DSC: HIGH ACCURACY MATERIALS CHARACTERIZATION

Designed for accurate determination melting point, glass transition and crystallisation temperatures, our range of differential scanning calorimeters deliver excellent sensitivity and baseline flatness.

The NEXTA DSC range offers:

- High sensitivity and baseline performance, with unique furnace design for accuracy
- Real View camera system that allows you to watch material behaviour on screen
- Intuitive, easy to use software, with advanced functionality for specific applications
- Reliable auto-sampler testing and auto analysis function for faster testing
- High degree of flexibility, allowing for addition of options after installation

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