APPLICATION NOTE

No. V241

Dynamic mechanical thermal analysis (DMTA) on polymer nanocomposites

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Keywords
DMTA, Solids clamping tool, Glass transition

Introduction

Polymer nanocomposites (PNC) are materials that consist of a polymer matrix with embedded particles with a size of 100 nanometers or smaller. Typical nanoparticles are nanoclays, carbon nanotubes or nanofibers and graphenes. Compared to unfilled polymers, polymer nanocomposites show improved properties that make them interesting for various technical applications. In particular, the greater mechanical strength of polymeric materials combined with low weight are desired properties. Additionallythe incorporation of nanocomponents can lead to an improved heat and chemical resistance as well as electric conductivity. Nowadays, polymer nanocomposites are frequently used in the automotive and aviation industries, as well as in construction materials for windmill blades.

Polymer nanocomposites can be produced by mixing the nanoparticles into the molten polymer matrix using extrusion. One way to achieve proper mixing during the extrusion process is to use nanoparticles that are predispersed in a carrier liquid and to feed the dispersion into the extruder. Only when the particles are distributed homogeneously inside the polymer matrix and no larger clusters are formed, the composite material exhibit the desired properties.

For testing the mechanical properties of a polymer nanocomposite, dynamic mechanical thermal analysis (DMTA) can be used. DMTA can be performed in torsion with a rotational rheometer. The material is exposed to oscillatory shear while the temperature is changing continuously. The obtained data is used to identify characteristic phase changes such as the glass transition or the occurring of

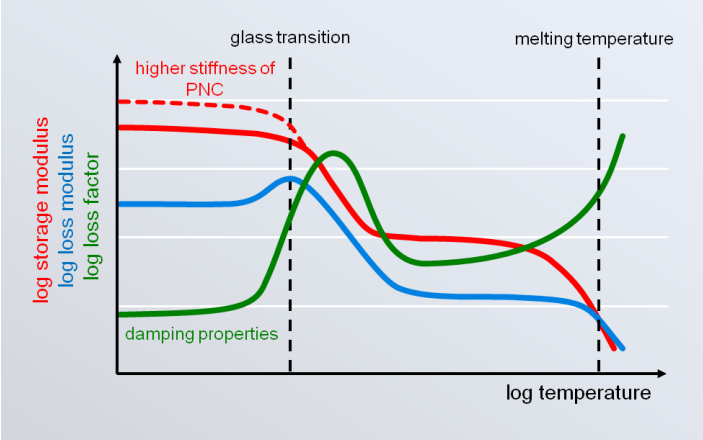

Figure 1: Schematic drawing of dynamic mechanical thermal analysis results of a semi-crystalline polymer.

melting and crystallization. In addition to this, DMTA is used to determine the solid material's mechanical performance with important application related properties such as stiffness, brittleness, damping or impact resistance. The rheological parameters storage modulus (G'), loss modulus (G") and the loss or damping factor (tan δ) are obtained from DMTA. The storage modulus represents the elastic, and the loss modulus represents the viscous properties of a material. For solids, the storage modulus is larger than the loss modulus and vice versa for fluids. The loss factor is the ratio of G" and G' and is also a measure for the damping properties of a material. Figure 1 shows the schematic diagram for DMTA on a semi-crystalline polymer. The glass transition can be identified using different

approaches. The most common approach for rheological tests uses the maximum of the loss modulus (Figure 1). The onset of the decrease of the storage modulus or the maximum in the tan δ (G"/G') are two alternative methods. At room temperature, polymer nanocomposites are usually in the glassy state and show high values for G', indicating the high stiffness of the material. Compared to the unfilled polymers, polymer nanocomposites show higher G' values in the glassy state indicating their greater mechanical strength.

Smaller phase transitions at temperatures way below the main glass transition can occur for copolymers and polymers that carry side chains. The additional peak in the damping factor can improve the impact resistance of a polymer. An example for such a material would be high impact polystyrene (HIPS), an engineering plastic with a polystyrene backbone and rubber side chains.

Figure 2: Solids clamping tool with carbon fiber enforced composite sample.

Material and methods

To extend its range of testing methods into the field of composites and other solids, the Thermo Scientific™ HAAKE™ MARS™ Rheometer can be equipped with a solids clamping tool [1]. The temperature control for this setup is provided by the Controlled Test Chamber (CTC) (Figure 2).

The patented design of the CTC, which uses a combination of radiation heating and convection heating, creates a large uniform heating zone inside its gold plated test chamber (see Figure 2) thus allowing testing of larger samples under uniform temperature conditions. The solids clamping tool can be equipped with special jaws for soft, medium or hard samples.

With the latter, the jaws are even able to fix hard composite materials with smooth surfaces during oscillatory testing. Due to the unique design with two moving jaws, the solids clamping tool automatically positions the sample in the axis of the rheometer, which is mandatory to avoid any error from eccentric placement.

Two different composite materials were tested using the HAAKE MARS Rheometer, CTC and solids clamping tool. The first sample was a lightweight carbon fiber enforced material, which could be used, for instance, in airplane construction. The second sample was a glass fiber enforced polyphenylene-sulfide (PPS). Such materials are used for applications where a high mechanical and thermal stability are required.

DMTA was performed with both samples. The carbon fiber enforced material was tested in a temperature range between -100 °C and +240 °C. A constant oscillatory deformation γ of 0.1% was applied with a frequency of 1 Hz. During the entire test, a constant axial force of -1 N (pulling force) was applied.

The glass fiber enforced PPS was tested from 30 °C to 250 °C. A constant oscillatory deformation of 0.01% was applied at a constant frequency of 1 Hz. The axial force was kept constant at zero Newton during the tests. All tests were performed with a heating rate of 2 °C/min.

Results and discussion

Figure 3 shows the results of the DMTA tests with the carbon fiber enforced sample. The data reveals the high stiffness of the material at room temperature, with a storage modulus G' of more than 3 x 109 Pa. The results also show three transition temperatures of the sample represented by the local maxima of the loss modulus G". The biggest change of the rheological properties occurs between 80 and 150 °C. The two maxima of G" at 99 °C and 115 °C indicate the glass transitions of two different components in this temperature range. The excellent reproducibility of the test results was shown by comparing the results of two independent tests run with two different specimens of the same material. The two sets of curves shown in Figure 3 are almost perfectly identical.

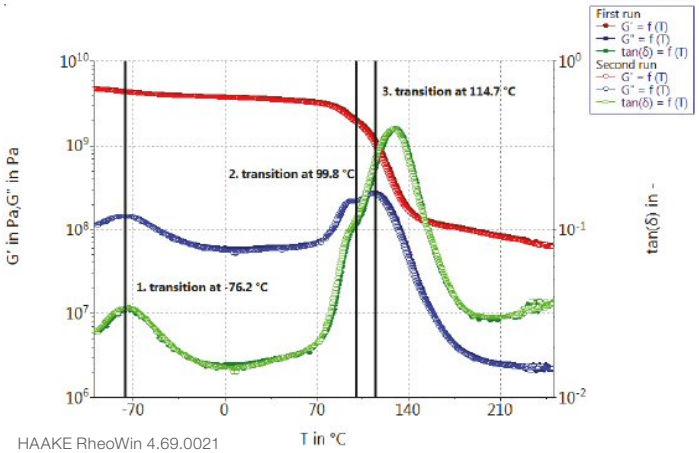

Figure 3: Storage modulus G' (red), loss modulus G" (blue) and tan (δ) (green) as a function of temperature for the carbon based sample. The glass transition temperature T_G is indicated by the green line. The results of 2 independent tests (open and filled symbols) run on fresh samples each, show the excellent reproducibility of the results.

During the measurement, the rheometer applied a constant small pulling force on the sample to compensate for any thermal expansion or contraction (see black curve in Figure 4). This results in a lift motion of the rheometer, that reacts to any change in sample length. This information can be used to check whether the clamps were able to hold the sample or might have lost their grip. In a plot of the sample length as a function of temperature, any slipping of the sample between the jaws of the clamps would show as a step-change. The smooth progression of the orange curve in Figure 4 documents the clamp's steady grip even on such a hard material.

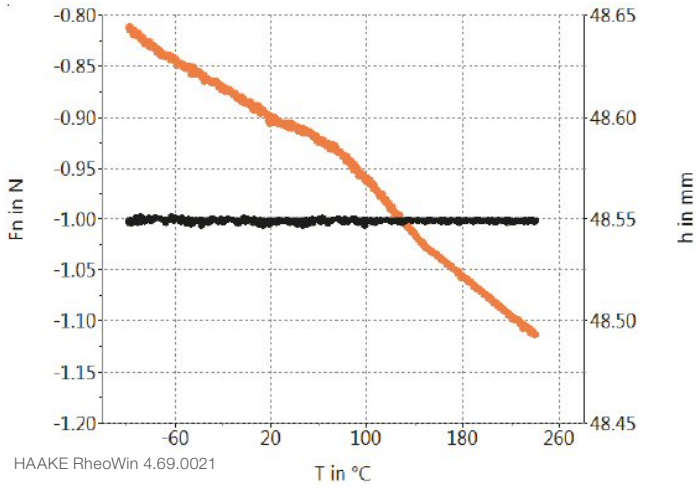

Figure 4: Constant normal force (black) and decreasing sample length (orange) during a temperature increase from -100 °C to 240 °C on the carbon fiber enforced sample.

Apart from its diagnostic value, the data shown in Figure 4 contains valuable information about the sample itself.

The length decrease with increasing temperature reflects the negative temperature expansion coefficient (α) some carbon fiber enforced materials show in fiber direction. One can even see from the change in slope, that the material's α changes around the major transition temperatures starting at 80°.

Figure 5 shows the results of the DMTA tests with the glass fiber enforced material. Also this material shows a high stiffness at room temperature with a storage modulus G' of above 3 x 109 Pa. The glass transition temperature, indicated by the maximum in the loss modulus G", was occurring at 101 °C. At temperatures above the glass transition, the material transformed into a rubber elastic condition, where the moduli data changed less with increasing temperature.

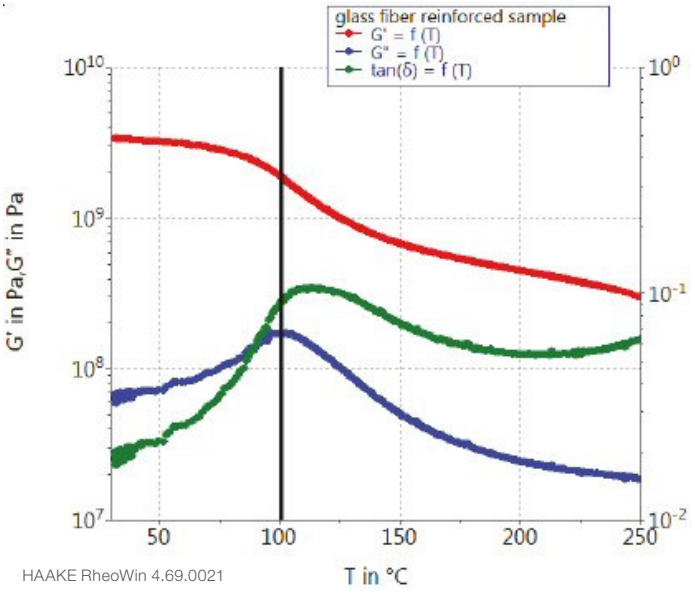

Figure 5: Storage modulus G' (red), loss modulus G" (blue) and tan (δ) (green) as a function of temperature for a glass fiber enforced PPS sample. The glass transition temperature T_G is indicated by the black line.

Also for this measurement, the sample length over temperature plot shows the perfect grip of the solids clamping tool. Compared to the carbon fiber enforced sample, this material has a positive thermal expansion coefficient, which does not change around the glass transition temperature. From the data in Figure 5, a constant coefficient of approximately $\alpha = 3.3 \times 10^{-6}\ K^{-1}$ can be calculated.

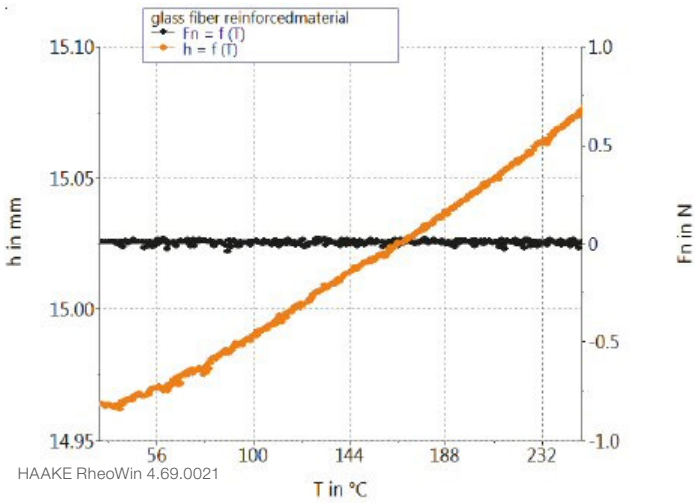

Figure 6: Constant normal force (black) and increasing sample length (orange) during a temperature increase from 30 °C to 250 °C on one of the glass fiber enforced PPS samples.

Summary

The special design of the solids clamping tool accessory for the HAAKE MARS Rheometer combines easy handling with high precision and perfect reproducibility of test results. Different composite samples with very hard and smooth surfaces have been tested with both yielding very good results.

Using the rheometer's lift and normal force sensor in combination with the solids clamping tool provides an easy way to verify the perfect grip on the sample and thus the reliability of the data collected. Due to the unique precision of both lift and normal force sensor, important data about the thermal expansion of the samples can be collected simultaneously. This allows, for example, the calculation of the sample's thermal expansion coefficient.

With the Controlled Test Chamber and solids clamping tool, the HAAKE MARS Rheometer is able to extend its range of testing capabilities into the field of dynamic mechanical thermal analysis. In combination with a classical rheological setup like a Peltier temperature control module and cone & plate geometries, the HAAKE MARS Rheometer is an ideal and cost-effective solution for testing polymer composites and their liquid base materials on one instrument.

Reference

1. Cornelia Küchenmeister-Lehrheuer, Fabian Meyer and Klaus Oldörp, Thermo Scientific Product Information P004 "Solids clamping tool for Dynamic Mechanical Thermal Analysis (DMTA) with HAAKE MARS Rheometers"

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