A Change of Length Has Consequences

The Coefficient of Thermal Expansion Can Help to Ensure Product Quality

The design of parts and components made of fiber-reinforced composites needs to take the coefficient of thermal expansion into account because it determines the extent to which a material changes in length when heated or cooled. Neglecting this quality criterion can have far-reaching consequences.

Fiber-reinforced composite materials, which combine the properties of fibers and a polymer matrix, have been around for decades. Fiber-matrix composites are stiffer, have a great strength-to-weight performance and have a much lower density than their metal counter parts. This makes them up to 60 % lighter than, for example, steel; a very desirable characteristic when it comes to components for the mobility sector and in particular the automotive industry, where the reduction of weight is important to improve fuel efficiency.

Similarly, electronic assemblies can also be regarded as composites. FR4 (FR= flame retardant) and its derivates (FR2, FR3, FR5) are by far the most widely used base materials for electronic circuit boards and electronic assemblies. The FR4's backing material exists of fiberglass

Thermomechanical analyzer TMA 402 F3 Hyperion Polymer Edition © Netzsch

woven into a thin, cloth-like sheet. The glass fabric is then impregnated with a flame-retardant epoxy resin. The resulting low cost composite is stiff, insulates reliably and performs well in most environmental conditions. On the flip side, the epoxy resin and the reinforcing glass fabric exert different material properties when going through several thermal cycles in the production process and potentially during use. This can lead to product failure.

An important property that needs to be considered during the design of parts and components made of composite materials is the coefficient of thermal expansion (α, or CTE), which determines how a material changes in length when being heated or cooled. The CTE can also be used as a quality control criterion.

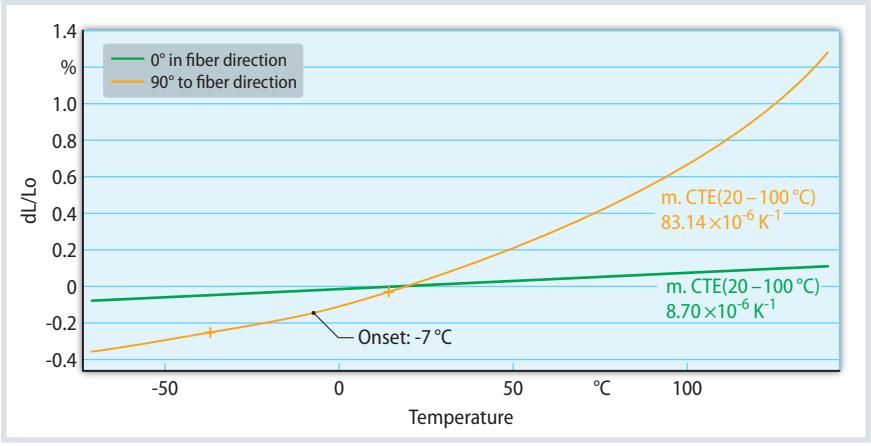

Fig. 1. TMA measurement on a PP-GF-UD composite material. Sample size 25 mm, heating rate 5 K/min from –70 °C to 140 °C, N_2 atmosphere, expansion sample holder made of fused silica

Source: Netzsch; graphic: © Hanser

TMA as Tool for Studying the Expansion Behavior

Thermomechanical analysis (TMA) is a perfect tool for studying the expansion behavior and softening temperature of various materials such as polymers, elastomers and composites. It provides fundamental information about the coefficient of thermal expansion (CTE), the glass transition temperature as well as about viscoelastic properties.

It is a very sensitive method and can be used to determine weak physical transitions that are associated with changes in modulus, curing, or delamination, which sometimes cannot be detected by Differential Scanning Calorimetry (DSC).In three case studies, it is highlighted how important the analysis of CTE and other key properties are in the design and manufacturing of high quality composite parts and components.

An Understanding of Anisotropy Is Critical to High-Performance Composites

There are several ways to incorporate fibers into the thermoplastic matrix:

- Randomly oriented fibers, also known as random fibers,
- unidirectional continuous fibers, or
- multidirectional fabrics.

While randomly oriented fibers increase the strength and stiffness compared to the neat polymer to some extent, the addition of oriented fibers in a preferential direction significantly increases the performance in this part direction. This preferential orientation gives the composite anisotropic properties, i.e. the properties in fiber orientation are dominated by the fiber properties and perpendicular to it, the matrix properties are more pronounced.

Knowledge of this anisotropic behavior is required for the design and production of these composite components. Although the anisotropy of the mechanical properties is the first thing on everyone's mind, the material's expansion behavior also differs depending on the fiber direction. When the anisotropy of a material is overlooked, or is not known, it can cause major problems in the final product. For example, plane surfaces can buckle, or even worse, form cracks or break.

For this study, samples were prepared at Neue Materialien Bayreuth GmbH (NMB), Germany. Three layers of a PP-GF UD tape were stacked on top of each other and pre-consolidated in a double belt press in three heating zones from 180 to 190 °C. The blank was then preheated in a convection oven for 10 min and transferred in a hot press with a mold temperature of 80 °C. There, a pressure of 10 bar was applied for 5 min during solidification. The resulting thickness is 1 mm. While the tape has an average fiber volume content of 45 vol. %, the local variations in the plate were measured between 40 and 50 vol. % GF.

For the measurements with the aid of a thermomechanical analyzer (type: TMA 402 F3 Hyperion Polymer Edition; manufacturer: Netzsch-Gerätebau GmbH), samples of 25 x 5 mm were cut from the plate in two different directions: 0° in the fiber direction and 90° to the fiber direction. After an initial cooling step, the temperature was increased from –70 to 140 °C at a heating rate of 5 K/min in a N_2 atmosphere (gas flow rate 50 ml/min). The expansion sample holder, made of SiO_2, was used with a sample load of 50 mN. The thermal expansion coefficient was calculated using the mean CTE analysis (m. CTE), which computes the slope between two data points.

Different Coefficients of Expansion in Different Directions

The material exhibits different CTEs depending on the direction the material is measured. The CTE of these kinds of composites is a mixture between the matrix and the fiber contained in it. Therefore, the CTE of those materials differ considerably depending on direction. The measurement results of the CTE for the PP-GF in the two different fiber directions are shown in **Figure 1**. The green curve depicts the measurement in the fiber direction 0°. The low CTE value is in the range of the CTE of glass and shows that this measurement direction is dominated by the low thermal expansion of the glass fibers. The same material measured 90° to the fiber direction (orange curve), is dominated by the polypropylene matrix. It shows a much higher CTE and exhibits the known glass transition (T_g) of polypropylene at –7 °C, not observable in the green curve. »

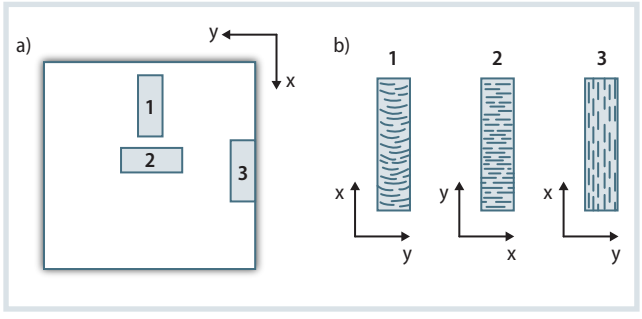

Fig. 2. a) Sample extraction location, b) dominant fiber orientation Source: Netzsch; graphic: © Hanser

In the matrix, the dominated direction of the CTE of a composite follows the rule of mixture:

$$a_c = v_f \cdot a_f + (1 - v_f) \cdot a_m$$

Where α is the linear thermal expansion coefficient (CTE), v is the volume fraction and the indices f and m denote the fibers and matrix, respectively. Assuming that the measured CTE in 0° fiber direction is the same as α_f and the CTE of the polypropylene matrix, α_m= 1.6 x10^{-4} K^{-1} (not measured here), the glass fiber volume fraction in the measured composite is calculated as

$$v_f = \frac{a_c - a_m}{a_f - a_m} = \frac{83.14 \cdot 10^{-6} K^{-1} - 1.6 \cdot 10^{-4} K^{-1}}{8.7 \cdot 10^{-6} K^{-1} - 1.6 \cdot 10^{-4} K^{-1}} \cdot 100\% = 50.8\%$$

How Does the Thermal Expansion Correlate to the Flow Field?

The orientation of a filler in the molded part influences materials' properties, like stiffness at different service temperatures. How fillers are oriented in the material depends strongly on the flow field during material processing, which describes how the material fills the mold.

The CTE is sensitive to the orientation of the filler in the molded part. This orientation depends strongly on the flow field, which describes how the material fills the mold. Therefore, different values for the CTE are to be expected in the molded part. This articles aims to investigate this assumption. For this study, a low-viscosity PEEK resin with 40 vol.% short carbon fibers was injection molded in a plate mold of 80 x 80 mm and 2 mm thickness at Neue Materialien Bayreuth. A film gate was used to get a more uniform flow front and reduce fiber breakage, which could occur through a thinner gate.

Due to the velocity gradient, different forces and moments act on the fibers and lead to a characteristic fiber orientation within the part. In the center of the part, the fibers are oriented perpendicular to the flow direction due to extensional and transverse flow. Due to the high shear rates at the wall or frozen layer, the fibers are aligned parallel to the flow.

For the TMA measurements at Netzsch Analyzing & Testing, samples were cut according to **Figure 2** to study the effect of fiber orientation on the thermal expansion coefficient. The expected dominant fiber orientation is depicted in the samples.

The samples were measured with the new TMA 402 F3 Hyperion Polymer Edition. After an initial cooling step, the temperature was increased from –70 to 300 °C at a heating rate of 5 K/min. The thermal expansion coefficient was calculated using the mean CTE analysis (m. CTE), which computes the slope between two data points.

As expected, the CTE above the T_g is higher than below the T_g; for these samples it is about double. It can be seen that the CTEs of sample 3 are the lowest and sample 2 has the highest values. Sample 1 is in between. The same trend between samples is observable in the T_g. Sample 2 that is most dominated by the matrix behavior compared to the other samples has the same T_g of 143 °C as listed in the datasheet (measured with a DSC). Sample 1 that shows more effect of the fiber in the CTE has a higher T_g of 152 °C, which indicates the higher stiffness introduced by the fibers. This can be detected in a TMA, because it measures a mechanical response. Sample 3 is strongly dominated by the fibers and therefore, the T_g is hardly visible and was not analyzed (**Fig. 3**).

Thermomechanical Analysis

Thermomechanical analysis (TMA) is a method for determining dimensional changes in solids, liquids or pasty materials as a function of temperature and/or time under a defined mechanical load (DIN 51005, ASTM E831, ASTM D696, ASTM D3386, ISO 11359 – Parts 1 to 3). Linear thermal expansion is an important quantity for assessing the dimensional behavior of a material in response to a change in temperature. It indicates the extent to which a material contracts or expands during processing, whether dissimilar materials can be combined, or at what temperature the phase change occurs and the CTE changes.

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From the CTE measurements as well as the theory of fiber orientation in the flow field, the dominant fiber orientation in the samples can be deduced. It can be seen that due to the thin samples, the effect of the frozen layer seems to be dominant in samples 2 and 3. The majority of the fibers are oriented in the flow direction. Therefore, sample 3 yields the lowest CTE (measurement in the flow and in the fiber direction) and sample 2 the highest values (measurement perpendicular to the flow and fiber direction).

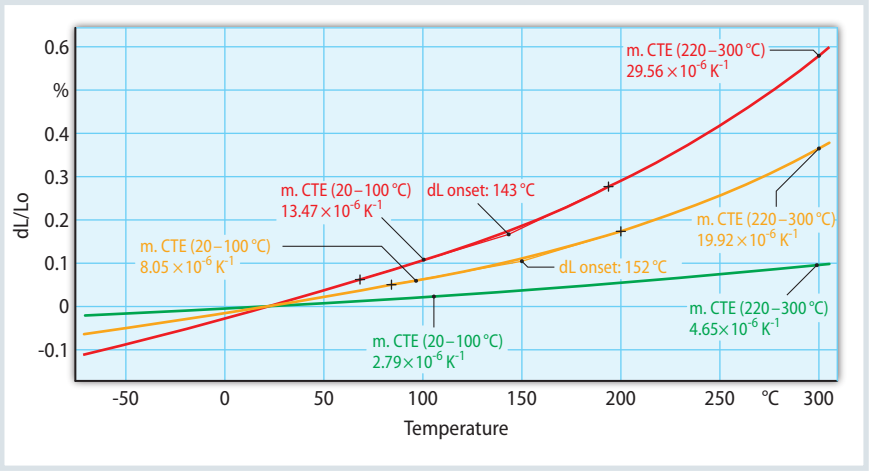

Fig. 3. TMA measurement results of PEEK with short carbon fibers from different part locations; sample 1 = orange; sample 2 = red; sample 3 = green Source: Netzsch; graphic: © Hanser

Determining Time to Delamination of Electronic Assemblies

To ensure that electronic assemblies and thus circuit base boards conform to a certain quality, IPC standards were put into place that require measurement of the thermal expansion, glass transition and softening point [see IPC-TM-650 2.4.24.1 Time to Delamination (TMA Method)].

The most widely used base material for printed circuit boards are FR4 (FR= flame retardant) and its derivates (FR2, FR3, FR5). In the production process of PCBs, the parts gets subjected to thermal stress during assembly, for example, in the reflow soldering oven. The time to delamination is important when it comes to the material selection for a certain application. **Figure 4** shows a measurement on an FR4 sample in which the time to delamination was recorded. Two measurements were conducted. In both, the sample was heated to the testing temperature. Then one was kept at an isothermal temperature of 260 °C (according to IPC standard) and a second one with an isothermal temperature of 300 °C.

In the first measurement at 260 °C (green line), the TMA did not detect delamination as the curve stays flat until the end of the measurement. However, at the higher temperature of 300 °C, degradation of the product is visible. The second measurement, records a time to delamination at 18.1 min after being held at an isothermal temperature of 300 °C, which was reached 28 min after the start of the measurement. The TMA clearly detects the delamination, where the physical inspection of the sample only shows some discoloration.

This test has become especially important ever since the "Restriction of Hazardous Substances Directive" 2002/95/EC (RoHS 1) took effect in the European Union. In the case of electronic and electrical equipment, this affects, for example, the use of lead-containing solders. Equipment produced or sold to the EU market now has to be lead-free. This had a major effect on the required thermal stability of all components – including FR4.

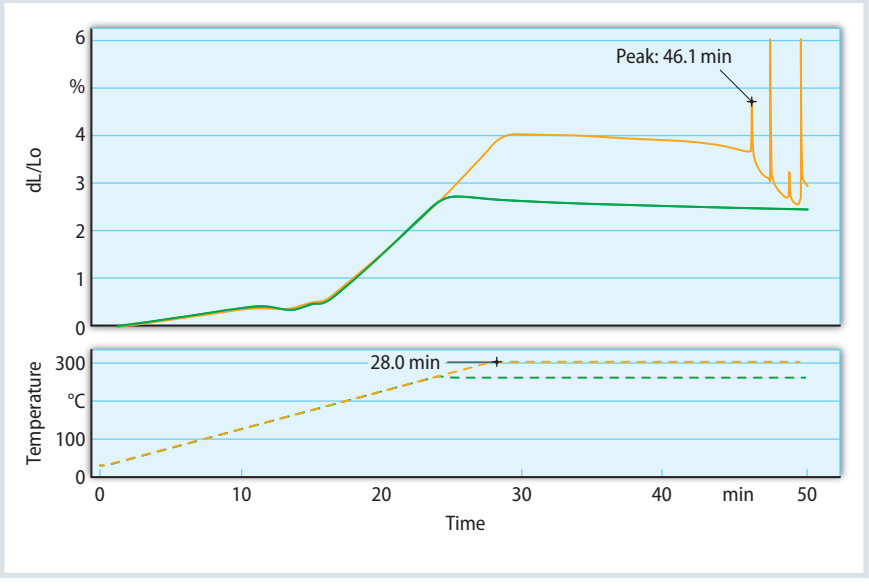

Fig. 4. Determination of time to delamination on an FR4 composite circuit board. Sample size 6.35 mm^2 as defined by IPC standard, dried for 2 h pre-measurement at 105 °C, heating rate 10K/min, N2 atmosphere, sample holder made of fused silica Source: Netzsch; graphic: © Hanser

The processes to produce lead-free solders now require reflow temperatures of up to 260 °C. Prior reflow temperatures were only at 240 °C. The FR4 used for this study would be suitable for both the leaded and the lead-free solders, as the delamination effects were not detected until a temperature of 300 °C was reached. However, not all materials that are currently used as base materials for electronic circuit boards and electronic assemblies may withstand the new requirements of lead-free processes.

Conclusion

The above investigations and case studies show how important knowledge of thermomechanical properties are in the design, manufacturing and quality control of polymer composites. It gives insights into the anisotropy of fiber-reinforced polymers, explains how the flow field correlates with the stiffness of materials and ensures that electronic assemblies and thus circuit base boards conform to a certain quality. ■