COMPREHENSIVE THERMAL CHARACTERIZATION OF FIBER-REINFORCED PLASTICS (FRP)

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Abstract

The measurement results presented clearly demonstrate the high capabilities of the selected thermoanalytical and thermophysical techniques for comprehensive thermal characterization of different carbon fiber-reinforced plastics (CFRPs). By means of Differential Scanning Calorimetry (DSC) and Dielectric Analysis (DEA), the curing behavior of thermosetting resins can be investigated. DMA (Dynamic-Mechanical Analysis) is ideal for the determination of the glass transition temperature Tg and the stiffness and damping behavior of the composite. With Laser or Light Flash Analysis (LFA), the thermal conductivity can be determined according to the fiber orientation, which rounds out a comprehensive thermal characterization program for fiber-reinforced plastics.

1. Introduction

Lightweight fiber-reinforced plastics (FRPs) are ideal substitutes for heavier metal constructions in a variety of industries. Especially carbon fiber-reinforced plastics (CFRPs) are being used increasingly in the aircraft/aerospace and marine industries as well as for high-volume productions in the automotive industry [1]. The main objective is to save energy by lowering fuel consumption. Often, fiber-reinforced plastics exhibit better performance than their conventional predecessor materials in the application range of interest. In order to guarantee a long lifetime, an FRP has to be tested under various conditions including thermal treatment, mechanical stress and different atmospheres. Selected thermoanalytical and thermophysical techniques are the best-suited testing tools for such investigations since they only require small FRP sample sizes or quantities. The measurement results for different CFRP samples are demonstrated in this paper.

2. Methods and Instrumentation

With DSC (Differential Scanning Calorimetry), the glass transition and the exothermal curing reaction of a thermosetting resin as the polymer matrix for an FRP can be determined and quantified. Here, the DSC 214 *Polyma*, along with many accessories for reproducible sample preparation, is used (Fig. 1). This DSC is specialized for polymer analysis from -170°C to 600°C and offers unique software features such as *AutoEvaluation* and *Identify* for the identification of unknown materials by an editable and expandable library.

Figure 1: Work station with a DSC 214 *Polyma* with automatic sample changer, PC with touch screen for pre-defined methods and several tools for sample preparation

Cure monitoring by DEA (Dielectric Analysis) is not restricted to a lab environment; it can also be employed for in-process curing of thermosetting resins and composites [2]. The multi-channel DEA 288 *Epsilon* (Fig. 2) with its fast data acquisition rate can be connected with disposable IDEX (interdigitated electrodes) comb sensors (Fig. 3, right) or reusable sensors such as a TMS (Tool Mount Sensor, Fig. 3 left). These are positioned, for example, in a mold for resin transfer molding (RTM), or in a press for prepregs or for sheet molding compounds (SMCs), or they are used for infusion processes or in autoclaves at elevated temperatures and pressures. For CFRP the DEA sensor has to be protected for avoiding a short circuit caused by the conductive carbon fiber.

Figure 2: DEA 288 *Epsilon*, industrial version with up to 8 DEA modules (channels)

Figure 3: Reusable TMS sensor (left) and disposable IDEX comb sensor (right) for DEA

With DMA (Dynamic-Mechanical Analysis), the glass transition, possible post-curing, and stiffness and damping behavior of an FRP specimen can be measured as a function of temperature, time and frequency. The DMA 242 E *Artemis* (Fig. 4) operates between -170°C and 600°C. It can be equipped with various sample holders for bending, tensile, compression/penetration and shearing measurements. Specially designed sample holders for high-modulus materials are available (Fig. 5) and, when used with a 5-dimensional system stiffness calibration, yield precise quantitative data.

Figure 4: DMA 242 E *Artemis* for the viscoelastic properties of polymers and composites

Figure 5: DMA sample holder; single/dual cantilever bending with free push-rod for FRP

An increasingly used non-contact method for the determination of thermal conductivity in and perpendicular to the fiber orientation is LFA (Light/Laser Flash Analysis). The LFA 467 *HyperFlash* (Fig. 6) offers measurements on up to 16 samples at a single defined isothermal temperature across a wide temperature range from -100°C to 500°C. Various sample holders and accessories are available for in-plane and through-plane measurements on different geometries of the FRP (Fig. 7).

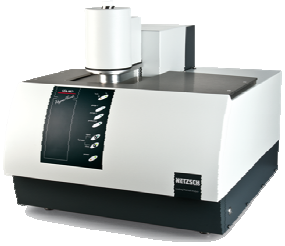

Figure 6: LFA 467 *HyperFlash* for thermal diffusivity and thermal conductivity measurements on FRPs

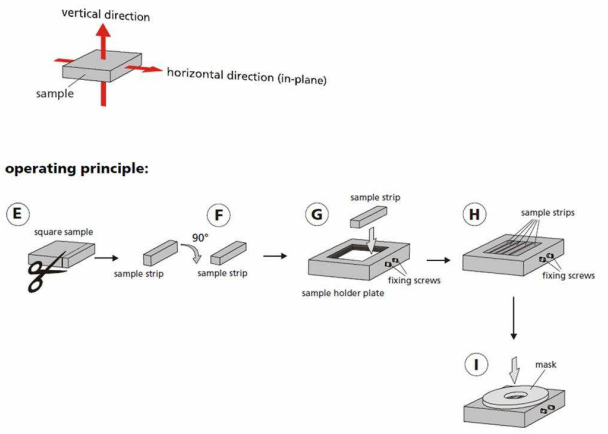

Figure 7: LFA sample holder for laminates for measurements in various fiber directions

3. Measurement Results and Discussion

In Fig. 8, the 1st heating (blue curve) of an uncured 2-component epoxy resin with DSC (heating rate 10 K/min, N_2 atmosphere, Al pan) is displayed. The Tg can be evaluated at -28°C. The exothermal 2-step curing starts at 40°C with a peak at 113°C and a shoulder at approx. 150°C. The heat release amounts to 415 J/g. The black dotted curve shows the calculated conversion curve for the reaction until a 100% degree of curing is achieved at 240°C.

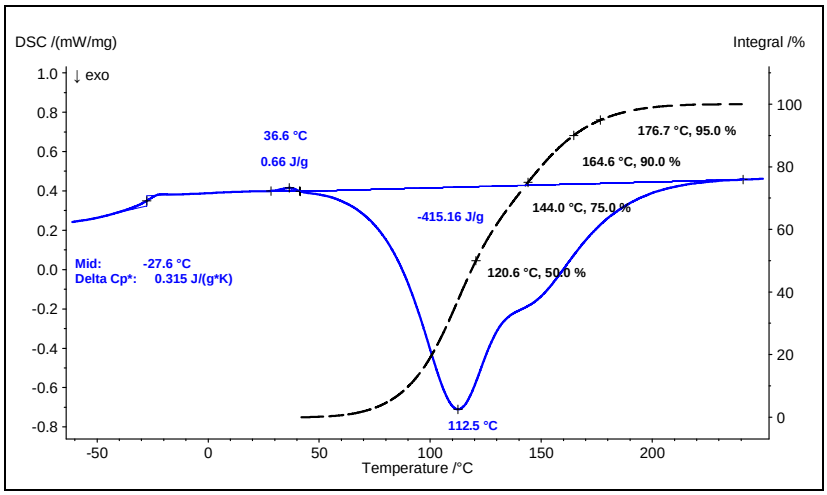

Figure 8: 1st heating (blue curve) of an uncured 2-component epoxy resin with DSC and calculated conversion curve for degree of curing (black curve); heating rate: 10 K/min, N_2 atmosphere, aluminum pan with pierced lid

Fig. 9 shows the 1st (blue curve) and 2nd (green curve) heating segments for a CFRP. In the 1st heating, the glass transition temperature Tg is 113°C since post-curing can be detected starting at approx. 170°C as well as some residual moisture at approx. 70°C. The 2nd heating exhibits a higher Tg at 117°C with Δc_p of 0.13 J/(g*K).

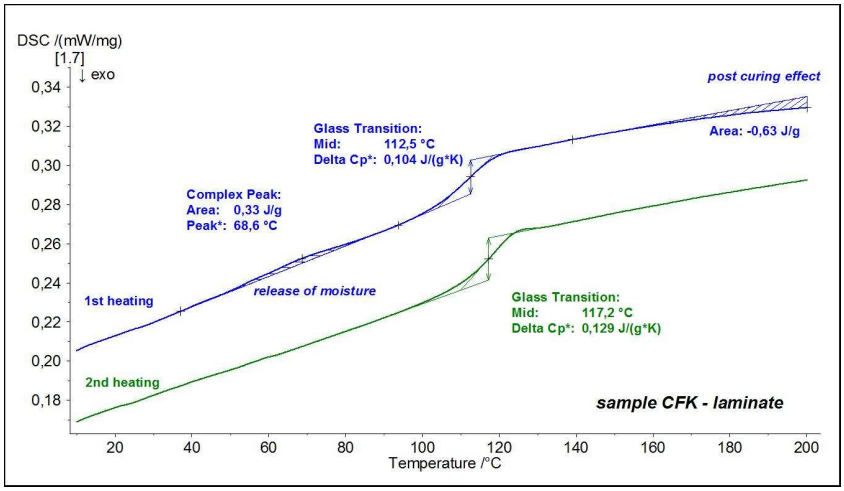

Figure 9: 1st (blue curve) and 2nd (green curve) heating segments for a CFRP laminate sample with DSC; heating rate: 10 K/min, N_2 atmosphere, aluminum pan with pierced lid

The curing of a carbon fiber-reinforced epoxy prepreg in a press at 120°C is measured with DEA at a frequency of 10 Hz by using a filtered IDEX sensor between two carbon fiber

layers. It is necessary to protect the sensing area of the IDEX sensor with a glass-fiber filter to avoid a short circuit due to the conductive carbon fiber. Fig. 10 shows the so-called ion viscosity (green curve) as the reciprocal value of the ion conductivity, which is derived from the loss factor ε'' (blue curve). The ion viscosity increases as curing progresses and reaches a horizontal level, signaling a 100% degree of curing, after 14 min. The temperature (red curve) was simultaneously recorded on the same DEA channel and exhibits a peak at 167°C after 5.9 min due to the exothermal curing effect.

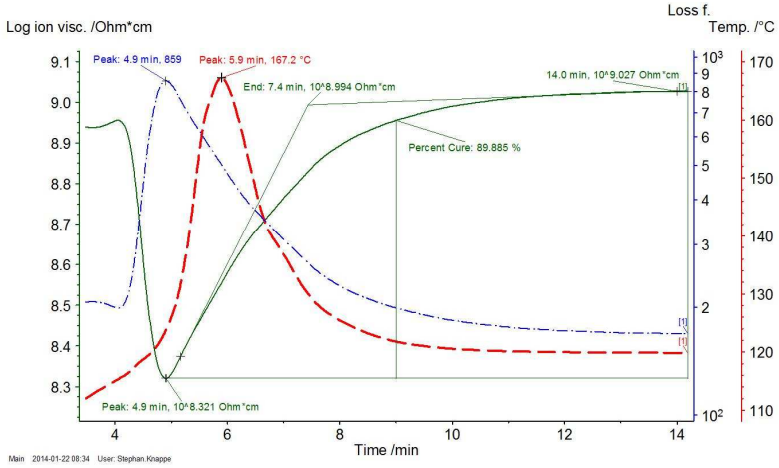

Figure 10: Curing of a carbon fiber-reinforced epoxy prepreg in a press at 120°C with DEA and filtered IDEX comb sensor; measurement frequency: 10 Hz

In Fig. 11, the viscoelastic properties of a CFRP specimen measured in the bending mode at 10 Hz are displayed with storage modulus E' (green curve), loss modulus E'' (red curve) and damping factor tan δ (blue curve). At 158°C (extrapolated onset), E' drops down from approx. 140 GPa (which is stiffer than even titanium) to only 30 GPa at 250°C due to the glass transition of the polymer matrix. The glass transition temperature can also be evaluated as peaks of the E'' curve at 180°C and of the tan δ curve at 188°C.

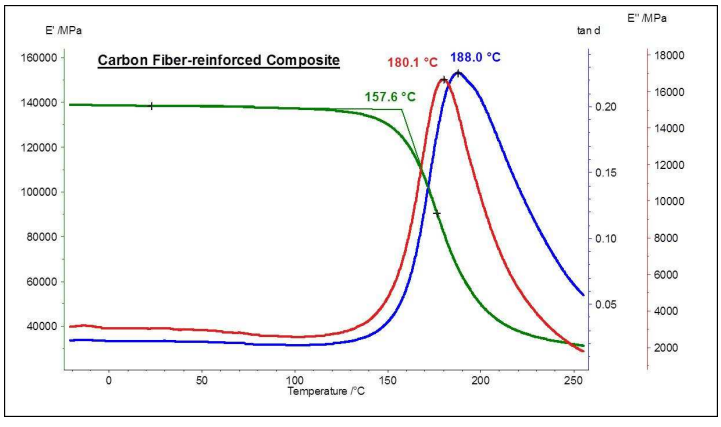

Figure 11: DMA result of a CFRP measured in the bending mode; frequency: 10 Hz, heating rate: 3 K/min

Fig. 12 presents the LFA results of a unidirectional (UD) CFRP sample with a density ρ of 1.5 g/cm³ and a carbon fiber volume content of 60%. The 2.0-mm-thick sample was measured in the direction of the fiber orientation at defined isothermal temperatures between 120°C and 200°C. The measured values of the thermal diffusivity a (red dots) decrease slightly as temperature increases.

With the following equation according to W. J. Parker et al from 1961

$$\lambda(T) = \rho \cdot c_p(T) \cdot a(T) \tag{1}$$

the calculated thermal conductivity λ (blue) increases with increasing temperature as the values for specific heat c_p (black) also increase.

Fig. 13 shows a direct comparison of two different CFRP samples with unidirectional (UD, black dots) and bidirectional (BD, red dots) fiber orientations. Both samples were measured in the fiber direction (UD_1 and BD_1) and perpendicular to the carbon fiber direction (UD_3 and BD_3). As expected, the thermal conductivity values are higher for the measurements in the fiber direction. The unidirectional arrangement of the carbon fiber (UD_1) provides the highest λ values.

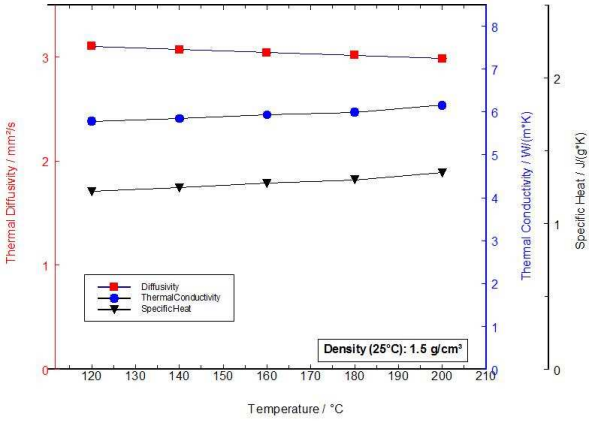

Figure 12: LFA results for a unidirectional (UD) CFRP with regard to thermal conductivity (blue), thermal diffusivity (red) and specific heat (black)

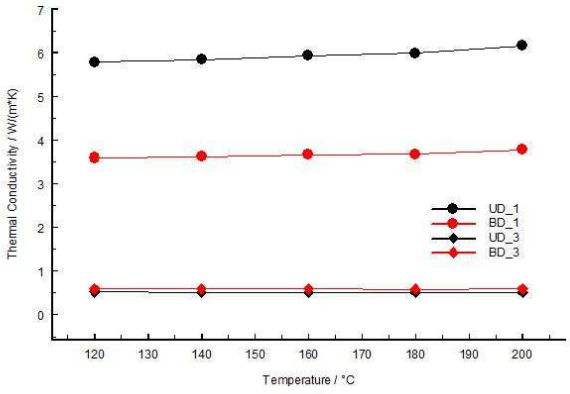

Figure 13: Comparison of UD CFRP (black) with BD CFRP (red), both measured in the fiber direction (_1, dots) and perpendicular to the fiber direction (_3, rhombi)

4. Conclusion

The measurement results clearly demonstrate the high capabilities of the different thermoanalytical and thermophysical techniques for the comprehensive thermal characterization of fiber-reinforced plastics (FRPs) such as carbon fiber-reinforced plastics (CFRPs).

References

[1] G. Kaiser, S. Schmölzer, S. Knappe, D. Rapp, M. Meyer and A. Lindemann. Characterizing High-Tech Composites by Means of Thermal Analysis. In *SAMPE Journal*, Volume 50, No.1, p. 7-12, January/February 2014.

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