Using Thermogravimetric Analysis to Determine Carbon Fiber Weight Percentage of Fiber-Reinforced Plastics

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ABSTRACT

The fiber content φ of fiber-reinforced plastics (FRPs) is a dominant influence on the mechanical performance and is therefore an essential quality measure. There is a lack of cost-efficient but precise measurement methods to determine φ of randomly distributed long-carbon-fiber-reinforced materials. Macro thermogravimetric analysis (TGA) is widely used for glass-fiber-reinforced plastics (GFRPs) as it is less labor-intense than sulfuric acid digestion. However, this method is not standardized for carbon-fiber-reinforced plastics (CFRPs). In this study, several macro TGA measurements of raw materials and FRPs were performed to measure degradation in relation to temperature, time and atmosphere. Conditions were found and validated which degraded the polymer but not the carbon fiber. Using macro TGA, it is possible to measure φ of a CFRP with an absolute error of less than 0.5 wt% compared to the actual value measured by weighing the raw materials.

1. Introduction

Chopped glass and carbon fiber sheet molding compounds (GF-SMCs and CF-SMCs) offer excellent characteristics of complex part geometry, function integration, material utilization and productivity for a relatively low price. To analyze the results of mechanical characterization and processing parameters such as mold coverage, knowledge of the local fiber content is essential. For GF-SMCs, adequate methods to determine the fiber content are widely reported, standardized and applied in the automotive industry [1]. For carbon fiber materials a standard of the aerospace industry has to be used, which is labor intensive. It is therefore a priority to develop a cost-effective, automatable and accurate method for measuring the fiber content of CF-material.

2. State of the art

To determine the fiber content (φ in wt%) of fiber-reinforced plastics (FRPs), two different methods are established, depending on whether glass (G) or carbon (C) fibers are used [2]. For GFRPs, thermogravimetric analysis (TGA) is recommended and described in national and international standards [3–6]. For CFRPs, the standard to determine the fiber content is to measure the mass difference before and after extraction of the resin by sulfuric acid digestion [7,8].

TGA is used to measure a sample's reduction of mass in relation to a temperature profile and/or time. The mass reduction occurs during sublimation, evaporation, decomposition, chemical reaction, magnetic transformation or electrical transformations [9]. TGA is simple to use, low in operating costs and high in sample throughput. By contrast, acid digestion requires chemical laboratories and experienced laboratory staff, which increases the costs of the procedure. Several studies have therefore been carried out concerning the possibility of widening the use of TGA towards CFRP:

- Yee et al. [10] compares measurements of micro TGA (sample mass 20 mg) to acid digestion measurements. The samples were small slices cut from filament wound carbon fiber epoxy FRP (about eight pieces for one 20 mg sample). Nitrogen is used to prevent oxidation of the carbon fibers. The temperature is set to 600 °C for 40 min. The sizing is included in the weight of the epoxy resin. The error is determined to be +1% compared to acid digestion, but this is only achievable with a uniform sample geometry.

- Moon et al. [11] compares micro TGA measurements (sample mass 15 mg) to acid digestion measurements. The samples were cut from autoclave-cured epoxy prepreg laminates. The temperature is set to 550 °C for 300 min. A factor of 1.21% is introduced to correct for the fiber weight loss due to moisture and decomposition of the sizing. The error is determined to be 1% compared to acid digestion.
- Jakob [12] describes a method to measure the carbon fiber content using macro TGA (sample mass 1−2 g). The sample consists of carbon- and glass-fiber-reinforced epoxy FRP. To measure the CF content a temperature of 450−500 °C is recommended for 120−180 min. The publication gives no information about the error, but indicates a possible influence of CF oxidation.

In summary, there are few scientific works on measuring the fiber content of CFRP using TGA, and most of them are based on micro TGA. Micro TGA is appropriate for homogeneous materials such as prepregs, but not for chopped fiber SMC due to its resin- and fiber-rich areas on a millimeter scale. All papers address the issue of CF-weight loss during the measurement, and compensate for this through a significant effort in sample preparation, or through sample-specific heating periods. Where the results are validated, the measurements are compared to other destructive measurements and not to absolute values.

3. Approach of the current study

The aim of this study was to examine whether there is an environment in which thermosets degradate completely while carbon fibers remain constant in total weight for samples of ~1 g. This enabled the definition of a test method for characterizing the CF weight content of CF-SMC by macro TGA. This test method was then validated on the basis of absolute values.

3.1. Equipment

The macro-TGA (TGA701 by Leco Corporation) was modified to prevent short-circuits on the electronics board caused by CF particles. The device is equipped with 20 crucibles of 25 mm inner diameter and 34 mm height for simultaneous measurements. Air, oxygen and nitrogen are available as purge gas. Furthermore a high-precision scale (SI-234 by Denver Instrument) and an air convection oven (UT 6420 by Heraeus GmbH) are available. A scanning electron microscope (SEM) (Supra 55 VP by Carl Zeiss AG) was used to analyze the samples.

3.2. Sample preparation

For a more detailed understanding of the relationship between temperature and mass reduction, samples of raw materials are needed (see Table 1). The raw materials are stored in a standard climate and the sample weight is 0.8–1.5 g.

Vinylester (VE) and unsaturated polyester polyurethane hybrid (UPPH) were used as thermoset matrix materials. The formulations were mixed in batch sizes of ~200 g and hardened in the air convection oven. Afterwards the thermosets were sawed into samples of 0.8−1.5 g.

The composite samples were prepared by combining glass (GF_1) or carbon (CF_1) reinforcement fibers of ~1.5 g with ~1.5 g VE matrix in a test tube. The weight gain of the test tube was measured before and after compounding to calculate the absolute fiber weight content φ. The test tubes were then sealed and the compound was hardened in the air convection oven.

Table 1
Details of raw material samples.

| Sample	Product name		Supplier
VE	resin:	ZW 014042	Aliancys
	additives:	9076	BYK
		9085	BYK
		A530	BYK
	peroxide:	Trigonox 117	AkzoNobel
	thickener:	Luvatol MK 25	Lehmann & Voss
UPPH	resin:	Daron AQR 1009	Aliancys
	additives:	L-powder	UOP
		pBQ	Fraunhofer ICT
	peroxide:	Peroxan BEC	Pergan
	accelerator:	Borchi Kat 0243	Borchers
	thickener:	Lupranat M20R	BASF
CF_1	PX3505015T-13		Zoltek
CF_2	PX3505015W-13		Zoltek
CF_3	T700SC-12000-FOE		Toray
GF_1	Multistar 272		Johns Manville

4. Results and discussion

4.1. Purge gas

The atmosphere inside the measuring chamber influences the mass reduction mechanism. Oxygen or air leads to thermooxidative decomposition (oxidation). To determine purely thermal decomposition (pyrolysis), inert purge gases such as helium, nitrogen, and argon are needed [9].

Fig. 1 shows the sample mass reduction of carbon fibers and glass fibers during macro TGAs using different purge gases. Both fiber materials show a reduction in mass of ~1.5 wt% during heat-up. This behavior is independent of the purge gas. Afterwards, the glass fibers stay constant in their weight for the remaining testing period (20 h at 430 °C), whether the purge gas is air or nitrogen. For carbon fibers an ongoing decomposition is measured. Fig. 2 shows the samples' mass degradation rates. For the testing period between 11 h and 29 h the average carbon fiber degradation rate is $-2.5\text{E-}05\%\ s^{-1}$ for air and $-8.8\text{E-}6\%\ s^{-1}$ for nitrogen.

It can be seen that after only a short exposure to temperature, neither oxidation nor pyrolysis of the glass fibers occurs. However, carbon fibers show both mass reduction mechanisms for the same testing period. Here the impact of oxidation is higher than the impact of pyrolysis. To minimize the error in measuring φ of CFRP materials, it is thus necessary to use inert purge gases.
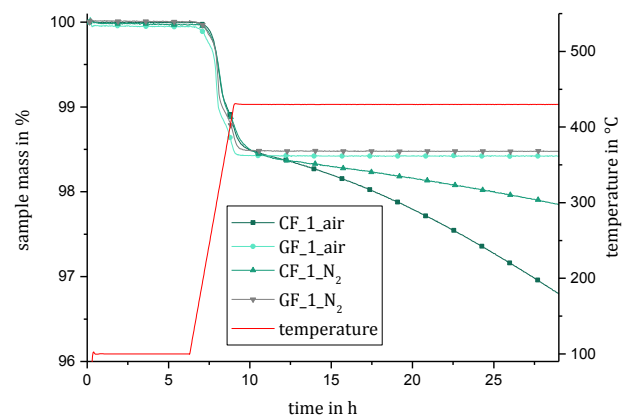
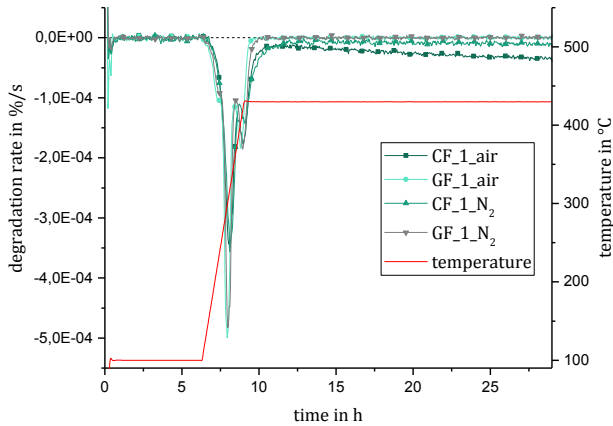**Fig. 1.** Sample mass reduction of carbon fibers and glass fibers using different purge gases.

Fig. 2. Sample mass degradation rate of carbon fibers and glass fibers using different purge gases.

However, the highest weight loss (~1.5 wt%) was observed during heat-up, independent of the fiber material and purge gas. As the shipping certificate of the carbon fibers [13] specifies a sizing content of 1.47 wt% and the data sheet of the glass fibers [14] a sizing content of 1.5 wt%, it is clear that this should be examined in more detail. Fig. 3 shows SEM pictures of the fibers before and after

TGA. Fibers before TGA (Fig. 3, top) are coated and show a smooth surface. Some glass fibers are partially bound together by the sizing. After TGA (430 °C for 20 h; Fig. 3, middle and bottom) the surface of the fibers is rough. For carbon fibers no residue of the sizing is visible. For glass fibers a porous structure remains. The observed decomposition of sizing is independent of the fiber material and purge gas and has to be taken into account when determining the fiber weight content φ by TGA. This result was further confirmed by TGA measurements of carbon fibers with different sizing amounts (CF_2: 1.53 wt% sizing [15], CF_3: 0.7 wt% sizing [16]). These fibers also showed a sample mass reduction equivalent to the sizing amount.

4.2. Temperature profile

Temperature in conjunction with time determines the samples' mass loss in thermogravimetric analysis. Insufficient heat will result in incomplete pyrolysis of the thermoset material. Excessively high temperature supports an unintentional pyrolysis of the carbon fibers. Thus measurements at different temperature levels were performed to determine the temperature required for a complete decomposition of the matrix (see Fig. 4). UPPH was chosen as matrix material as it has a higher thermal resistance than VE. Carbon fibers were measured simultaneously, as a reference.

After a drying period the samples were heated up to 370 °C with a holding time of 5 h. This temperature level already causes a >60% mass reduction of the UPPH. Complete decomposition of the UPPH
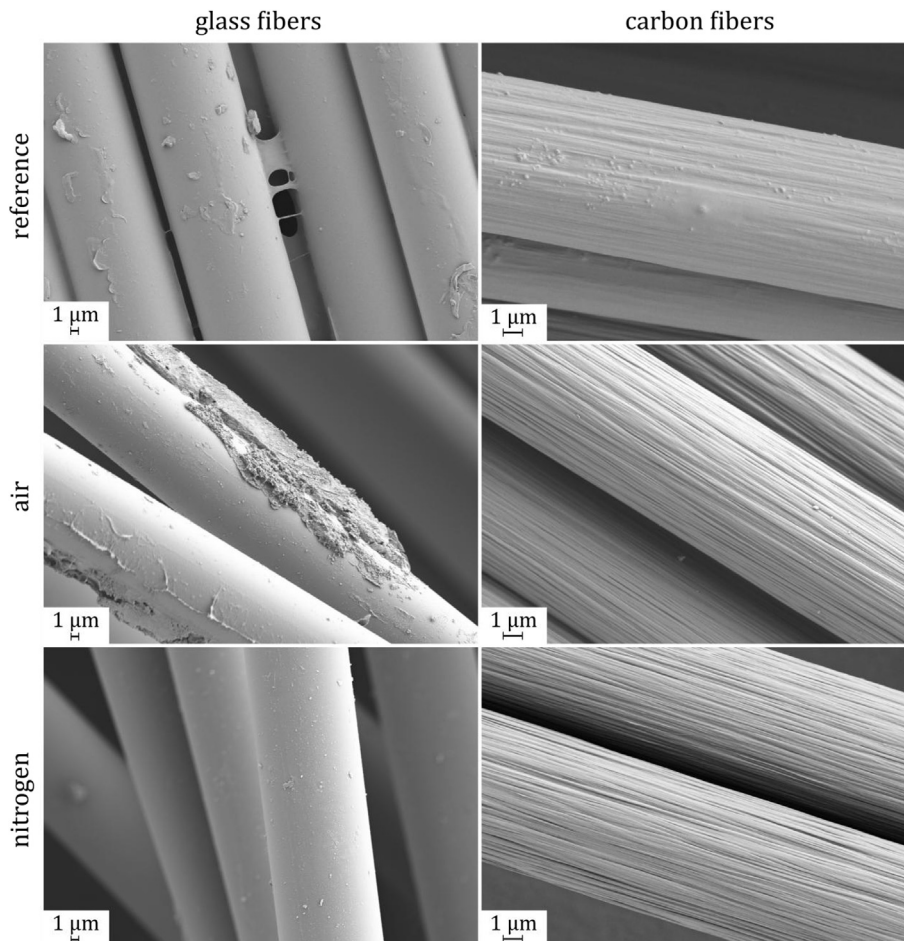

Fig. 3. SEM pictures of carbon fibers (CF_1) and glass fibers (GF_1) before and after TGA with different purge gases.
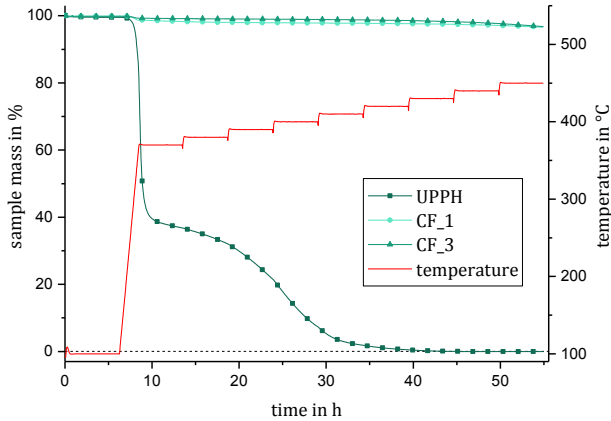
Fig. 4. Raw material TGA to determine the required pyrolysis temperature.

is achieved at 430 °C.

4.3. Measurement duration

Where measurement periods are too long a slow but continuing carbon fiber mass reduction occurs and machines are occupied unnecessarily. In contrast, where measurement periods are too short this leads to incomplete pyrolysis of the matrix material. As a consequence the measurement duration has to be chosen carefully. Fig. 5 and Fig. 6 show that a heating period greater than 13 h at 430 °C is needed to ensure full pyrolysis of the matrix material for a large sample weight of up to 1.5 g. At the same time all the investigated fiber materials and types show only very small degradation rates. If the measurement were stopped automatically once the degradation rate nears zero, this would be ideal to prevent further pyrolysis of the carbon fibers. But this is not applicable for all materials. In some cases the thermal decomposition leads to chemical intermediates with higher thermal resistance than the original substance (for example UPPH, compare Fig. 5).

4.4. Developed method

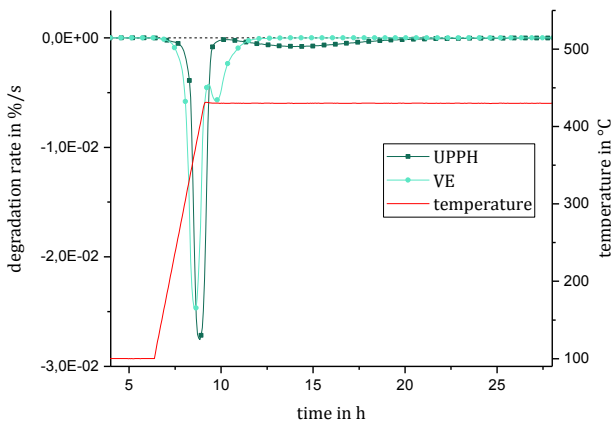The investigations performed led to the development of the following measuring procedure:

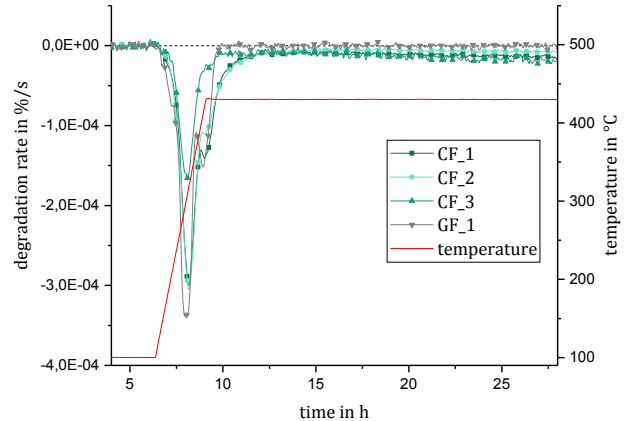**Fig. 5.** Matrix mass degradation rate for isotherm TGA at 430 °C.

Fig. 6. Fiber mass degradation rate for isotherm TGA at 430 °C.

- Preparation of samples (1 g–3 g; max. 20 mm in diameter).
- Drying of samples inside TGA or with external device (6 h at 100 °C).
- Pyrolysis of samples:
  o Purge gas: Nitrogen
  o Heating rate: 2 °C min^{-1}
  o Final temperature: 430 °C
  o Pyrolysis time: 20 h

4.5. Validation measurements

To identify the accuracy of the method, samples of FRP with known fiber content and matrix formulation are needed. Thus VE resin and both carbon fibers and glass fibers were combined as described in Section 3.2. Fig. 7 shows the CFRP mass degradation in relation to the testing period. Fig. 8 shows the mass reduction of GFRP samples as a reference.

4.6. Calculation of carbon fiber content

A composite sample consists of carbon fibers *CF*, a matrix *M* and water *W* according Equation (1). The carbon fibers can be divided
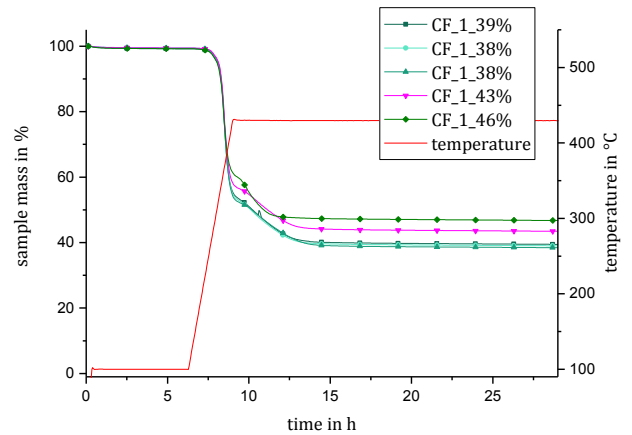

Fig. 7. Mass degradation of VE composite samples with known carbon fiber content φ in wt%.
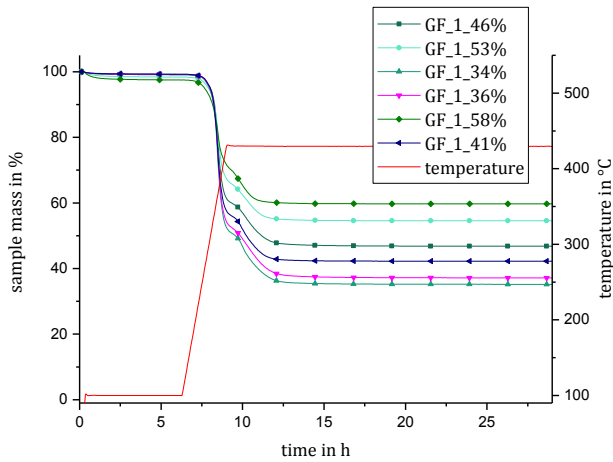
Fig. 8. Mass degradation of VE composite samples with known glass fiber content φ in wt%.
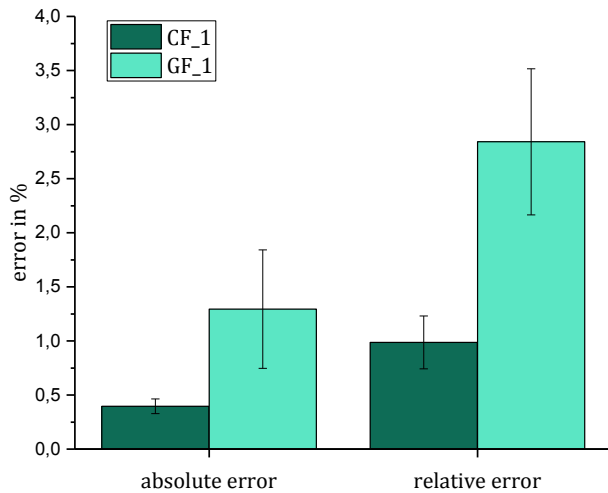

Fig. 9. Absolute and relative error of the developed method in determining the fiber content φ.

into filaments F and sizing S, see Equation (2). The matrix can be divided into the polymer P and inorganic additives IA, see Equation (3). The residue R at the end of the measurement contains filaments

and inorganic additives which are dependent on the initial polymer mass, see Equation (4). In total this delivers four equations to determine the four unknowns CF, M, F, P with the help of the measured values W, R and the known values for S and IA. Solving the system of equations for CF leads to Equation (5).

$$100 \ wt\% = CF + M + W \tag{1}$$

$$CF = F + S{*}CF \tag{2}$$

$$M = P + IA{*}P \tag{3}$$

$$R = F + IA{*}P \tag{4}$$

$$CF = \frac{1 - W + R{*}\left(1 - IA^{-1}\right)}{2 - S - IA^{-1}{*}(1 - S)} \tag{5}$$

[CF, M, W, R, F, P] = wt% relative to initial sample mass.[S] = wt% relative to CF mass.[IA] = wt% relative to P mass.

The glass fiber content GF is calculated accordingly by Equation (6):

$$GF = \frac{1 - W + R{*}\left(1 - IA^{-1}\right)}{2 - S - IA^{-1}{*}(1 - S)} \tag{6}$$

[GF] = wt% relative to initial sample mass.

Using Equations (5) And (6) for the macro TGA measurements shown in Section 4.5 leads to a measured value φ for each sample. Comparing this value with the known real fiber content of each sample allows the calculation of an absolute error of φ and an error of φ relative to the real fiber content (see Fig. 9).

Both the absolute error and the relative error are less for carbon fiber materials than for glass fiber materials. Furthermore the method delivers fiber contents that are slightly too high, especially for glass fiber composites. Comparing SEM pictures of the samples after TGA (see Fig. 10), the glass-fiber-reinforced-composite samples show a higher amount of residue despite the identical matrix formulation.

5. Conclusions

The investigations performed led to the development of a measuring method suitable for determining the carbon fiber weight content of FRP with a VE or UPPH matrix. The absolute error achieved with this method is less than +0.5 wt% and thus competitive to labor intense methods like acid digestion or micro TGA [10,11]. Furthermore macro TGA allows the analysis of large samples with various geometries. The method is therefore suitable
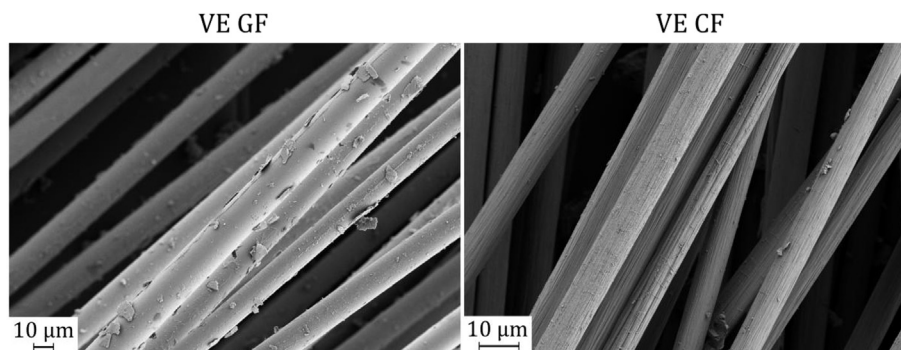

Fig. 10. SEM pictures of composite samples after TGA.

for the investigation of inhomogeneous materials such as SMCs and characteristic samples taken directly from components, such as ribs.

Acknowledgements

References

[1] Volkswagen AG. GF-UP-Harz für Abschirmkapseln: werkstoffanforderungen (TL52342 1989-11). 1989.

[2] Assmann W, Witten E. Handbuch faserverbundkunststoffe - composites: Grundlagen, Verarbeitung, Anwendungen. fourth ed. Wiesbaden: Springer Fachmedien; 2013.

[3] Normenstelle Kunststoffe (FNK) im DIN Deutsches Institut für Normung e. V. Prepregs, Formmassen und Laminate: Bestimmung des Textilglas- und Mineralfüllstoffgehalts (DIN EN ISO 1172:1998).

[4] Plastics: thermogravimetry (TG) of polymers part 1: general principles (ISO 11358-1:2014-07).

[5] E37 Committee. Test method for compositional analysis by thermogravimetry (ASTM E1131-08(2014)). West Conshohocken, PA: ASTM International. doi: 10.1520/E1131.

[6] Thermische Analyse (TA): Thermogravimetrie (TG): Grundlagen (DIN 51006: 2005-07).

[7] D30 Committee. Test methods for constituent content of composite materials (ASTM D3171-15). West Conshohocken, PA: ASTM International; 2015. http://dx.doi.org/10.1520/D3171-15.

[8] Normenstelle Luftfahrt (NL) im DIN Deutsches Institut für Normung e. V. Kohlesntofffaser-Laminate: Bestimmung der Faser-, Harz- und Porenanteile (DIN EN 2564:1998-08).

[9] Ehrenstein GW, Riedel G, Trawiel P. Thermal analysis of plastics: theory and practice. Munich, Cincinnati: Hanser; Hanser Gardner Publications [distributor]; 2004.

[10] Yee RY, Stephens TS. A TGA technique for determining graphite fiber content in epoxy composites. Thermochim Acta 1996;272:191–9.

[11] Moon C, Bang B, Choi W, Kang G, Park S. A technique for determining fiber content in FRP by thermogravimetric analyzer. Polym Test 2005;24(3): 376–80.

[12] Jakob M. Faservolumengehalt in Kunststoffen per Makro-TGA bestimmen. February 09, 2016. Available from: http://de.leco-europe.com/files/2014/07/Laborpraxis_Juni14_TGAFaser.pdf.

[13] Zoltek. Certificate of analysis: PX3505015T-13. 2015.

[14] Johns Manville. Technical data sheet MultiStar 272.

[15] Zoltek. Certificate of analysis: PX3505015W-13. 2015.

[16] Toray carbon fibers Europe. Statement of conformity: T700SC-12000-FOE. 2015.