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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.

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- 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 −2.5E-05% s^{-1} for air and −8.8E-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.

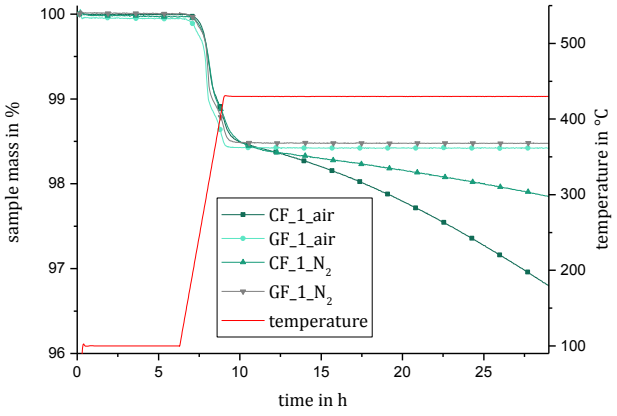

Fig. 1. Sample mass reduction of carbon fibers and glass fibers using different purge gases.