

Thermogravimetric analysis of epoxy-based carbon fiber reinforced polymers modified by carbon fillers

Burkov M V^{1,2} and Eremin A V^{1,2}

¹Institute of Strength Physics and Materials Science, Akademicheskiiy avenue 2/4, Tomsk, 634055, Russia

²Tomsk Polytechnic University, Lenin avenue 30, Tomsk, 634050, Russia

Corresponding author: burkovispms@mail.ru

Abstract. The paper presents the results of thermogravimetric/differential scanning calorimetry investigation of hybrid thermoset CFRPs modified by the addition of single-wall carbon nanotubes and milled carbon fibers. Specimens were tested using NETZSCH STA 409 PC/PG with the following parameters: heating from ambient temperature to 873 K with a rate of 15 K/min; Ar flow rate of 50 ml/min. The content of the carbon filler in CFRP was varied allowing to establish some regularities in thermal and physical properties.

1. Introduction

Composite materials are applied in many fields such as aerospace, marine, and mechanical engineering. Carbon fiber reinforced polymers (CFRPs) are one of the most versatile materials among composites with polymer matrices. They have outstanding properties: high specific strength, good fatigue resistance, etc. One of the novel ways to improve mechanical and physical properties is associated with the addition of nano- or micropowders. Thus hybrid composites where carbon continuous fibers or fabric is additionally reinforced by such dispersive fillers are obtained. It has been shown that hybrid composites demonstrate higher mechanical properties under tension, compression, bending and fatigue [1]; impact properties are investigated in [2-4].

In [2] Dong Quan et al reported about the improvement of the fatigue properties and toughness. It was found that the addition of the 0.5 and 1 wt% of multi-walled carbon nanotubes (MWCNTs) increase mode-I and mode-II fracture energy. The study [3] investigated the effect of adding multi-walled carbon nanotubes to the epoxy matrix of CFRP on impact resistance and impact damage progression. It has been shown that the absorbed impact and shear punch energies in the punch tests are higher for composite filled with MWCNTs by almost 21.3% which is connected with increased interlaminar fracture toughness, damping, and the alleviated crushing/buckling strength of the fibers.

The modified CFRPs laminates with 1.5 wt.% MWCNTs were subjected to low-velocity impact at three impact energy levels (8, 15 and 30 J) and directly compared with the unmodified laminates in the paper [4]. In terms of the CFRPs impact performance, the compressive strength of nanomodified composites was improved for all energy levels with the incorporation of 1.5 wt.% MWCNTs compared to the reference material.

It is important for proper investigation and comparison of properties to assess fiber-to-binder ratio. One of the robust methods is thermogravimetric analysis that is described in [5-7]. The present paper is devoted to the investigation of hybrid CFRPs modified by different carbon filler. Thermogravimetry is used to evaluate thermal properties of hybrid CFRPs and establish fiber content.



2. Materials and testing technique

The specimens were carbon fiber reinforced polymers with additional carbon fillers. The lay-up was balanced, symmetric and pseudoisotropic: $[0/90/+45/-45]_{4s}$. Hybrid CFRP components:

- CBX300 biaxial fabrics made of PAN carbon fiber (Mitsubishi Pyrofil TR50S 12K);
- R&G Epoxy L with GL2 hardener;
- single-wall carbon nanotubes (SWCNT) TUBALL™ by OcSiAl (denoted as CNT) or;
- MATRIX 201 by OcSiAl – commercially available 10%CNT+90%Alcohol solution modifier for epoxy resin (denotes as MTRX) or;
- milled carbon fibers (denoted as uCF).

The resulting thickness of the blank was ~4 mm and the specimens were cut from the blank using a milling machine to obtain nearly cube-shaped specimens: the thickness of the specimens was as-moulded; length and width were 4×4 mm. The content of the fillers was varied resulting in the formation of 10 specimens; the compositions tested are summarized in Table 1. The additive concentration is calculated for the total epoxy weight, not for the resulting CFRP. For each composition 3 blanks were prepared.

Specimens were tested using NETZSCH STA 409 PC/PG. Testing parameters are heating from ambient temperature to 873 K with a rate of 15 K/min and Ar flow of 50 ml/min.

Table 1. Overview of the tested compositions

Additive	Amount, wt%	Designation
Non-modified CFRP	0	NM CFRP
CNT	0.1	CNT-001
	0.2	CNT-002
	0.3	CNT-003
	0.5	CNT-005
uCF	0.5	uCF-005
	1	uCF-010
	2	uCF-020
	5	uCF-050
MTRX	2	MTRX-020

3. Experimental results and discussion

Figure 1 presents TG and DSC curves obtained for the NM CFRP specimen. The weight loss curve has 3 stages that can be identified. The first stage is from the start of the test till 320-350 °C and it is associated with the less than 1 wt% loss of the weight. Within this temperature range, the thermoset epoxy binder in the neutral Ar atmosphere is stable and no significant changes occur. Then after 330-360 °C a sharp drop associated with binder decomposition can be seen. This process of decomposition depends on the heating rate and gas flow and it can be seen that the weight loss slows down at 450-500 °C. The rate of heating used (15 K/min) is higher than 10 K/min used in investigations by different researchers thus it can be concluded that the process of decomposition does not finish completely at 600 °C. Thus the transition between the second and the third stage is nonlinear.

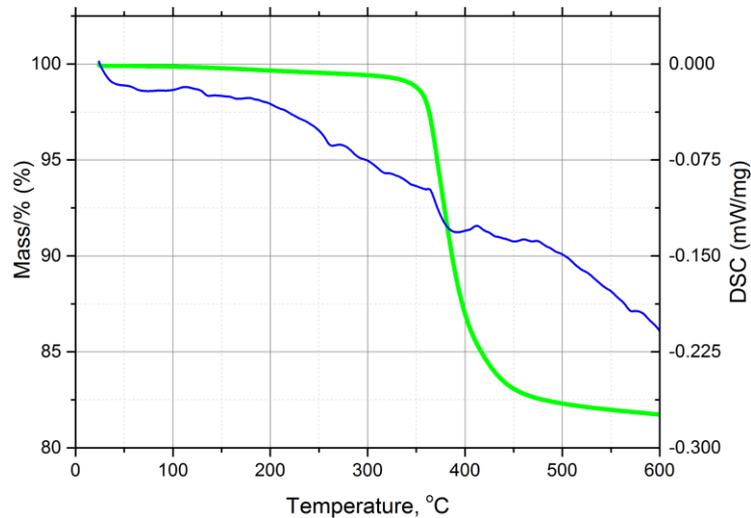


Figure 1. Typical TG (green) and DSC (blue) dependencies for non-modified CFRP specimen

Figure 2 shows the plot combining weight loss curves obtained for all specimens. Two insets describe detailed images of two areas: the transition from the first to the second stage and the second part of the stage 2. The former one describes the initial of the binder decomposition process and the latter one – its ending. It can be seen from Figure 2 that the first stage is characterized by the lower slope of all weight loss curves for CNT and MTRX specimens. Thus it can be concluded that the SWCNT modified epoxy binder has higher thermal stability. However, the transition from the first to the second stage (left inset in Figure 2) shows that non-modified CFRP and uCF specimens are grouped more on the right side, i.e. the process of decomposition of these specimens starts later than for CNT and MTRX specimens. It seems that the presence of SWCNT promotes the initial binder decomposition while the rates are nearly the same. The third stage is finished with a small slope of weight loss curve thus, as it was noted above, the binder decomposition is not completely finished.

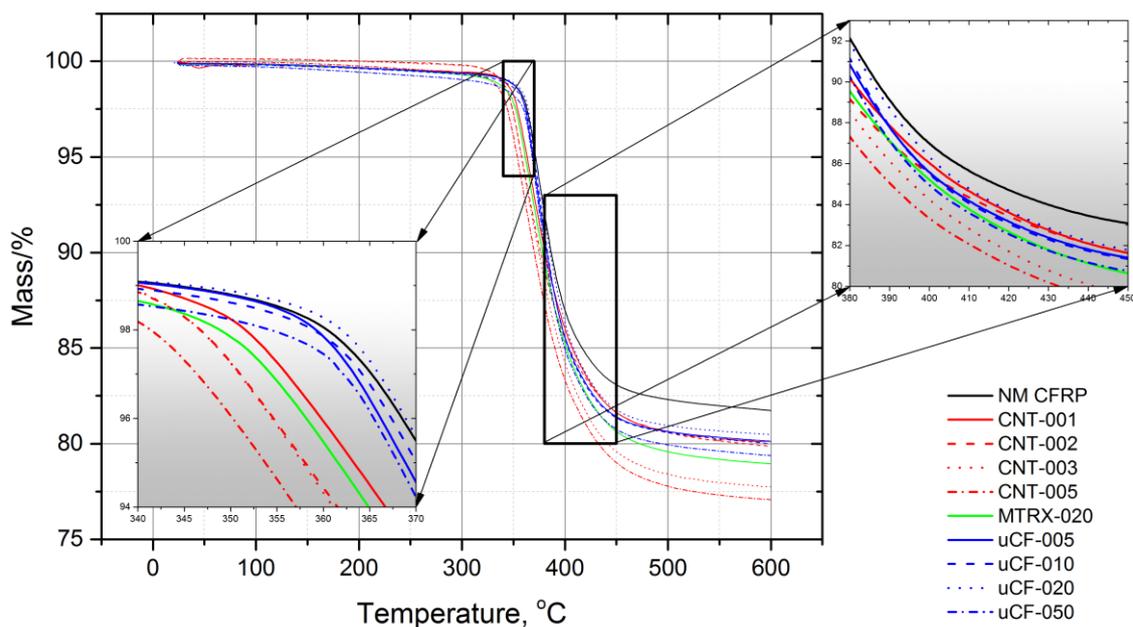


Figure 2. Weight loss curves obtained after TG for all investigated specimens

Final weight residue after TG testing (at 600 °C) was used to calculate the fiber content in fabricated and tested CFRPs. For these calculations we used datasheet density values of fiber end epoxy binder which are 1.82 g/cm³ and 1.15 g/cm³ correspondingly. The following equation was used for CF_{content}:

$$CF_{content} = \frac{w_R - 100\mu_A + w_R\mu_A}{\rho_{CF}/\rho_E(100 - w_R - 100\mu_A + w_R\mu_A) + w_R} \quad (1)$$

where w_R – weight residue after the TG test; μ_A – amount of additive; ρ_{CF} – density of carbon fibers; ρ_E – density of epoxy binder. The results of the CF_{content} depending on the type and the amount of the filler are shown in Figure 3.

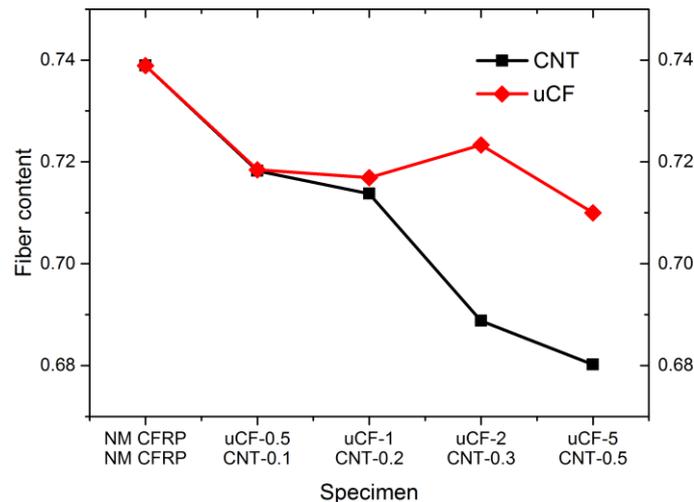


Figure 3. Fiber content vs type and amount of filler

4. Conclusion

Experimental TG/DSC testing of hybrid CFRPs modified by the addition of single-wall carbon nanotubes and milled carbon fibers was performed. It was shown that the weight loss (decomposition) curves have some differences. The rate of decomposition in the second stage does not differ and it is nearly constant but the initial of decomposition is shifted to the lower temperatures for SWCNT modified CFRPs. The residual weight of the specimens was used to assess the fiber content in the moulded CFRPs.

Acknowledgements

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