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THE ANALYSIS OF THE PROPERTIES OF ABLATIVE COMPOSITES WITH CARBON AND MMT NANOFILLER REINFORCEMENT

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Abstract

One of the most important parameters in the selection of composite materials used for the protection of avionics instruments exposed to high temperatures are ablative properties. They constitute the main criterion in determining the composition and thickness of the protective material. In this article, the authors determine the ablative properties of a polymer matrix with carbon reinforcement and check the effect of using the MMT additive (montmorillonite) on the change in the resistance to the impact of a high heat flux. The tested materials play an important role in the defence, aviation and space industry. Ablative materials are the only ones to protect the rear wall surface from an excessive temperature rise while using a thin insulation wall. For the sake of the research, we prepared a series of samples of the composite produced with epoxy resin LH 145, H 147 hardener, carbon fibre mats and the addition of MMT. The prepared samples were tested on a unique stand in laboratory conditions. The findings obtained from the experimental testing after a detailed analysis were tabulated and presented in the form of graphs. The authors determined the ablative loss of mass of the individual samples, compared their internal temperatures, which had been measured with thermocouples, as well as the temperature on the backside of the sample. In addition, in order to complement the experimental studies of determining the temperature rise on the rear surface, the authors used a thermal imaging camera. Besides, they took photos of different layers of the examined structure, which had been exposed, to a heat stream, by means of a scanning microscope.

Keywords: *composite, ablative properties, nanotubes, carbon fibre, ablation*

1. Introduction

The use of modified plastics as ablative materials protecting against an excessive temperature increase was connected with the middle of 20th century, directly with arms industry as well as aeronautical, rocket and space technologies. These materials can also be used in the design of passive fireproof protections for large cubature supporting elements in building structures, communication tunnels and for the protection of data stored in electronic, optical and magnetic carriers. This article reports results of studies on ablative and thermal properties of epoxy composites with reinforcement carbon fibres filled with a mixture of epoxy resin and mineral nanoclays (layered silicates). The composites were treated with hot combustion gases to detect the temperature profiles across the studied samples, the back side temperature of specimen t_s, the average linear rate of ablation v_a, and their mass waste U_a during ablation processes. The article briefs assumptions and requirements on research how to create ablative and thermal properties of epoxy composites with fabrics reinforcement [17] as well as the modification of composite structures through the addition of nanofillers or aerogels structure [3, 13]. The effect of additives on the properties of ablative composites has been more and more widely studied due to significant changes in their structures and thus the ablative properties of a composite, resulting from the impact of the heat flux. These changes occur dynamically, usually in the nano-scale.

2. Description of the method

Ablation is a self-regulating heat and mass transfer process, which, due to physical and chemical reactions, leads to irreversible structural and chemical changes of a material combined with heat absorption at the same time. The process is initiated and sustained by external sources of thermal energy [10].

Once an ablation surface interacts with a high-temperature heat stream, an ablation process is initiated. This is when the ablation surface, under the influence of temperature, undergoes internal structural changes, which protect lower layers and affect thermo-protective properties of a material. If an ablation shield has a multi-surface structure, the process takes place in cycles: the external layer is sometimes burned, falling off the larger part; subsequently another layer undergoes ablation changes. Among the factors, which are not directly linked with the ablation layer, the cohesion of native material plays a tremendous role in its exploitation reliability, particularly in the case of thermal interactions. The need to assess mechanical properties of a native ablative material is connected with the fact that high mechanical stresses arising in a non-degraded layer of polymer composites, during a process of high-temperature heat transfer and heat conduction exerts a much stronger influence on composite cohesion rather than heat stresses in a degraded ablation layer. Thermo-mechanical stresses of the native material are responsible for the damage of a composite. Therefore, it is vital also to evaluate the basic mechanical properties of the composites in question [4, 5, 6]. Despite numerous years of applying ablation materials, there is still room to fully determine the quality and quantity relationships between the type-phase composition and ablation properties, in the context of other exploitation features of composites used for thermos-protective shields [9, 14].Polymer composites with fibre reinforcement in the form of glass fibres and carbon fibres have been quite thoroughly investigated, also in connection with various powder fillers [2, 7, 8]. It is also true of composites with reinforcement in the form of carbon fibre as well as multilayer composites with hybrid reinforcement [16, 18].

3. Experimental verification

3.1. Preparation of samples for research

On the basis of the analysis of thematic publications [1, 11, 15], we selected phase components of the composites: composed of a reinforcement with 30 layers of a carbon fabric, 200 g/m^2 in weight and approximately 40 mm in diameter, which were laid out in the matrix of epoxide resine LH 145 cured with H 147 hardener at room temperature.

The properties of the composite were modified by changing the volume share of MMT in the matrix, which equalled as follows 10%, 18%, 24% [wt.] (Tab. 1.). We prepared samples which had simultaneously been fixed, in-between the layers, K-type thermocouples (between layers five and six) and J-type thermocouples in-between layers 10 and 11. In order to measure the temperature rise on the surface of the rear surface, we placed the J-type thermocouple there. The composite samples prepared in this way were left to harden for 7 days.

3.2. Laboratory stand

The thermos-protective ablative research was realized on the author's own construction stand (Fig. 1), in accordance with the assumptions and methodology described in the available studies [11, 12].

The ablative specimens (composite cylinder of 40×11) were placed in a fire resistant insulating board made with plasterboard, where they were treated with a stabilized stream of combustible gases for a time period of τ = 180 s. The source of heat was burning a mixture of liquid gases – propane butane, which gave off a flame temperature of 900ºC.

Tab. 1. Composition of individual samples with their geometrical values, density and mass

Sample number	Reinforcement	Before the test				After the test		
	MMT [% wt]	Mass of sample [g]	Diameter [mm]	Thickness [mm]	Density [g/cm^3]	Mass of sample [g]	Thickness [mm]	Density [g/cm^3]
1	0.0	16.8	39.68	10.17	1.34	11.30	8.59	1.06
2	0.0	15.10	39.89	9.39	1.28	11.40	8.90	1.02
3	10.0	17.23	39.90	11.40	1.20	11.50	8.75	1.05
4	10.0	17.42	40	12	1.15	12.40	9.58	1.03
5	18.1	17.34	39.68	9.80	1.43	12.20	9.65	1.02
6	18.1	15.28	40.14	9.70	1.24	11.00	8.70	1.01
7	23.6	17.80	39.70	10.15	1.42	12.82	9.50	1.09
8	23.6	15.50	40.10	10.05	1.22	11.40	8.18	1.02

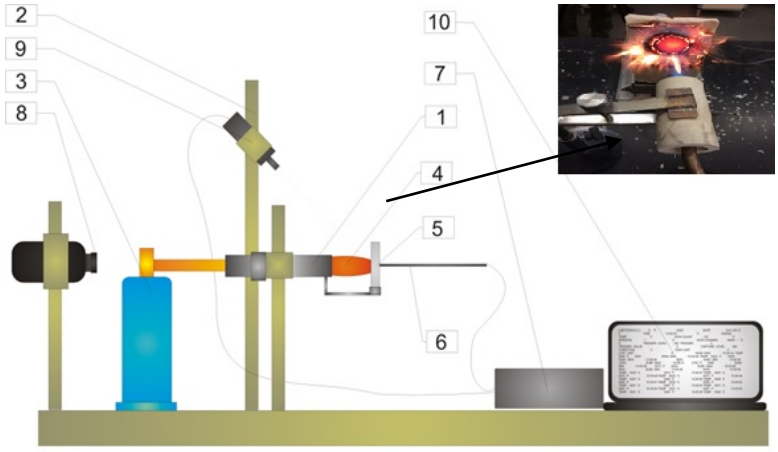


Fig. 1. Laboratory research stand

The flame was stabilized in the burner nozzle and also by means of an ablation gun – a fire resistant cylinder 40 mm in diameter, which reduces the flow rate of the exhaust gas streams. Thus, the temperature of the ablation surface T_{pa} over the whole surface of the sample reaches almost the same level.

The most important parameter of the research is the temperature value on the rear surface of the test sample and the temperature distribution within the composite. In order to measure the temperatures we used the K type thermocouple (NiCr-NiAl) placed in-between 5th and 6th layer of the carbon mats in the composite and type J (Fe-CuNi) placed on the surface of the back and in-between layer 10 and 11. In order to read the measurements, we used the SCB- A meter device manufactured by National Instruments equipped with a card, which reads the difference in voltage potential.

Furthermore, in order to have an image of the temperature field on the rear surface and read the temperature in points on the back surface of the sample, we used a thermal imaging camera Infrared camera series VarioCAM HD research 980. The camera captures the image in a resolution of 640×480 pixels. The accuracy of the examination equals ± 2 K.

3.3. Findings, discussion of experimental research

The conducted research allowed an assessment and analysis of structural changes of the examined composites (Fig. 2). Under the influence of high temperature, it was noted that the epoxy resin was

Fig. 2. View of the surface of the ablative test samples

burned, resulting in a reduction in the density and mass of the composite (Tab. 1). We also observed partial frontal decomposition of the layers of carbon fibre.

While comparing the density of the samples prior to ablative testing and after it, it was found that they differ from each other by approximately 20% of the values for individual samples (Fig. 3).

In order to ensure similar boundary conditions, while conducting the ablative research, we used a special ablation gun. In order to verify the correctness of its use, we measured the temperature of the ablation surface of the examined sample T_{pa} [ºC] by means of a pyrometer. This temperature for each sample reaches a value of above 900ºC (Fig. 4), whereas the test time τ is approximately 180 seconds.

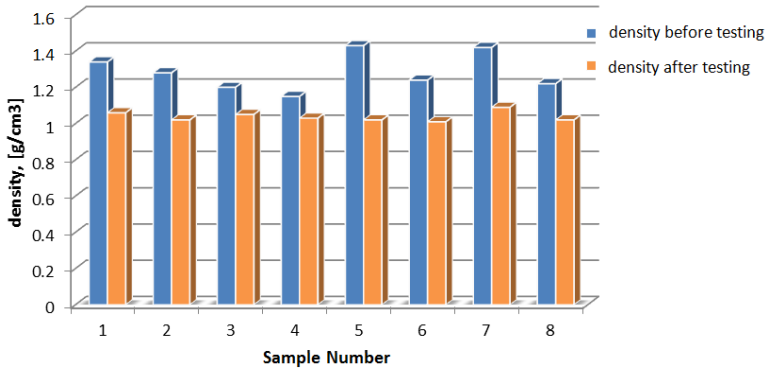


Fig. 3. Comparison of density of the composite samples before and after ablation testing

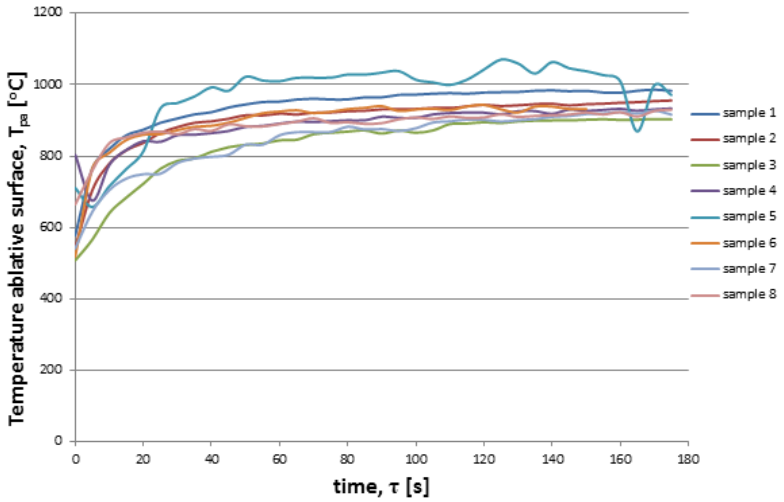


Fig. 4. Ablation layer temperature of individual samples

After comprehensive testing, we specified the relative ablative loss in mass (Fig. 5) for all test samples of the composite, using a dependence (1).

$$U_a = \frac{|m_1 - m_0|}{m_0} \cdot 100\%, \tag{1}$$

where:
U_a – relative ablative loss of mass [%],
m_0 – initial mass of the original material [g],
m_1 – remaining overall mass of ablation layer and the original material [g].

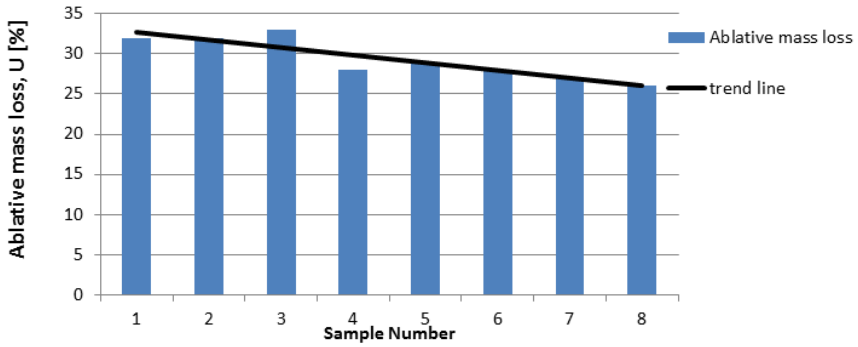
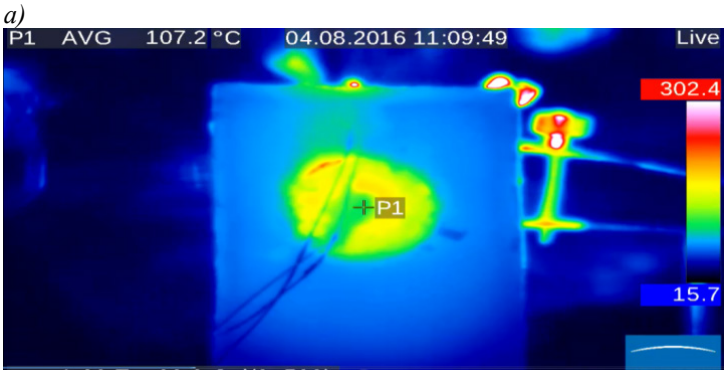


Fig. 5. Relative ablative loss of mass [%]

Based on the obtained results we can see that with the increase in the amount of the used MMT, the relative ablation mass loss is becoming smaller. However, we used high temperature silicone to seal and isolate the thermocouple wires coming out of the sample, therefore remains of the silicone after the examination may have been left over on the samples, which slightly affected the measurement of the masses of samples after ablative investigations, which at the same time lowers the value of the ablative loss of mass (these values are burdened with an error no higher than 3%).

The most important parameter of the research is the temperature value on the rear surface of the test sample and the temperature distribution within the composite. In order to measure the temperatures we used the K type, the J type thermocouples, and a thermal imaging camera. The use of the camera was to visualize the temperature field over the entire back surface (Fig. 6a) while the use of thermocouples allowed exact reading of the digitalised temperature values in the selected areas of the sample (Fig. 6b). They were marked in following way: T_1 – temperature between layers 5 and 6, T_2 – temperature between layers 10 and 11, T_3 – temperature on the back surface.

a)



b)

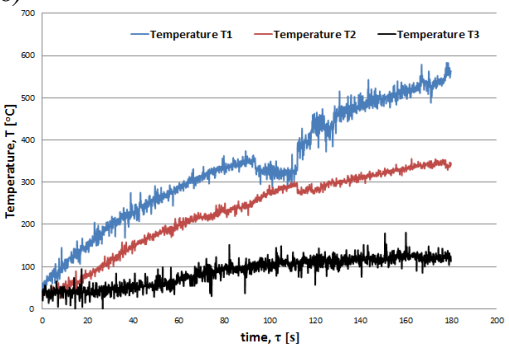


Fig. 6. a) Exemplary distribution of the final temperature on the rear surface of the wall, sample no 5 – view of the thermal imaging camera, b) temperature distribution in the exemplary sample no 8

In the article, we presented only one chart with full temperature measurement during the testing (Fig. 6b) and a collective graph showing the maximum temperatures read out at individual thermocouples (Fig. 7). Thus, the highest temperature in sample 8, which was recorded between layer 5 and 6 was approximately 575ºC after approximately 180 seconds from the start of burning the sample's surface (Fig. 6b). On the other hand, the rear surface of the sample reached the temperature of approximately 121ºC. Basing on the read data, it was found that the reduction in temperature between surface 6 and 30 of the sample equalled approximately 450ºC.

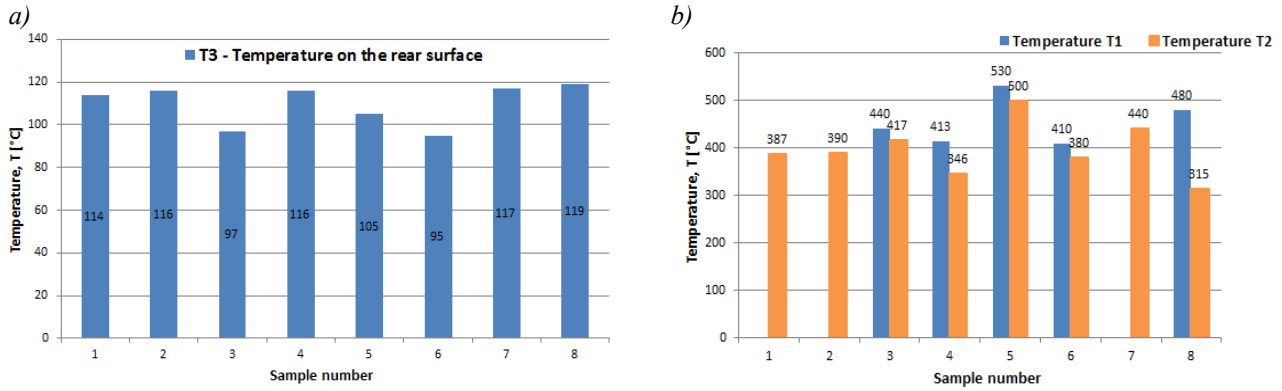


Fig. 7. The listing of the maximum temperature: a) rear wall of T_3 wall, b) internal temperature T_1 T_2 of the examined samples during the examination time of 145 seconds.

On the other hand, while analysing a collective listing of the maximum temperatures, one may notice that it was made for the impact of the heat flux for 145 seconds for the sake of comparison (not all the samples had a full range of 180 seconds of measurements for technical reasons). With regard to the temperature on the back wall surface, the lowest value reported to be equal to 95ºC for the composite containing 18% MMT, whereas the highest temperature of the rear surface, equal to 119ºC, was achieved in the composite that contained 24% MMT (Fig. 7a). On the other hand, the extreme temperature values inside the samples were visualised in Fig. 7b.

However, the increase in temperatures in terms of the amount of the additives used is uneven. This may result from such causes as:

– it was not possible to keep perfectly parallel layers of carbon fibre since they had been made manually,
– there appeared small amounts of air bubbles at the time of preparing the samples,
– there were uneven increases in the surface temperature, which can be observed in thermal camera images.

There was no significant decrease in the temperature on the backside surface of the examined composite through the addition of MMT to the resin. This addition might only have caused a faster and more uniform propagation of the heat flux inside the sample, thus reducing the temperature of the rear surface. However, it cannot be stated definitely, since the distribution and supersaturation of the matrix were not uniform in the sample; we made only readings of three temperatures, which is insufficient to confirm the exact effect of the addition on the ablative properties of composite materials.

3.4. Microscopic examination after the ablation

In order to visualise the structure of the examined material, we took a series of images using the Hitachi TM3030+ electron microscope both prior to the testing (Fig. 8) and after the ablation investigation (Fig. 9 – without the addition of MMT) and with its addition (Fig. 10). The images were taken on the first few layers of the composite material, counting from the front of the flame.

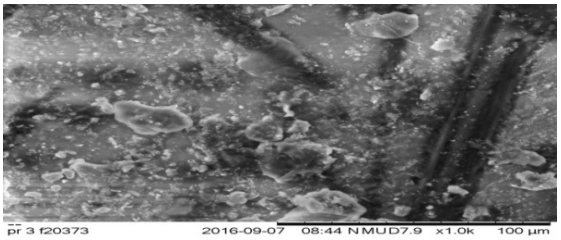


Fig. 8. Image of an electron microscope, 1000 times magnification on sample no 1 before the exposition to flame

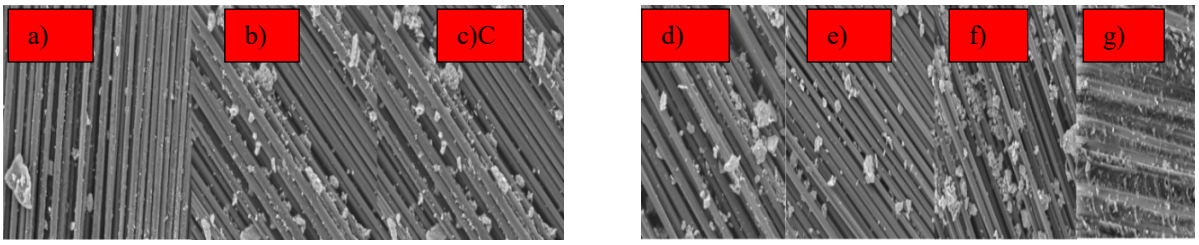


Fig. 9. Image from the electron microscope, 1000 times magnification, after exposure to heat flux without MMT, a) the first layer, (b) the third layer, c) the fifth layer, d) the seventh layer, e) the ninth layer, f) the eleventh layer, g) the sixteenth layer

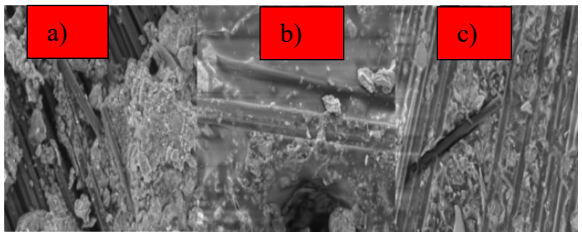


Fig. 10. Image from the electron microscope, 1000 times magnification, upon sample 5, after exposure to heat flux-containing MMT, a) the second layer, b) the fourth layer, c) the sixth layer

The presented images of the samples are complementary to the results of the ablation investigation, i.e. the influence of the heat flux on the composite. In the sample's structure before testing (Fig. 8) the composite matrix is visible. On the other hand, after the ablation tests, a complete burnout of the matrix in the first layers of the composite is visible (Fig 9a-c) and until the sixteenth composite layer (Fig. 9g) where no ablation can be observed since individual carbon fibres in the resin matrix had not burned. For comparative purposes, the composite samples with the addition of MMT are depicted, which is noticeable in the matrix structure of the composite (Fig. 10). The addition caused the growth of the sample's resistance to the dislocation of the layers.

4. Conclusions

The aim of the conducted experimental studies was to assess the thermos-protective properties of composites with carbon reinforcement. The performed tests and the obtained findings allowed formulating a number of conclusions, which are useful in the creation of future composites.

Above all, investigating the thermos-protective properties was difficult in terms of its execution with regard to methodology. A crucial element, which exerts a significant impact on the correctness of the results, is a meticulous and accurate setting of the ablation gun towards the central part of the sample's surface in order to burn evenly the whole front, at a simultaneous impact of the flame. It is also important to protect the thermocouple wires by using sealing and thermal insulating silicone when assembling the test specimens in the laboratory stand (in the plasterboard) to prevent their burning during the investigation.

The primary conclusion resulting from the analysis of the obtained findings is the fact that the layers of carbon fibre satisfy their features of heat resistance during the impact of high temperatures. The addition of a layered silicate MMT did not reduce the temperature on the side of the composite, but certainly had a significant impact on the duration of the sample. On the other hand, the ablation mass loss in each of the samples decreased in a linear manner while the amount of the used MMT additive grew.

With such a measurement, we determined the drops in temperatures between the ablation layers 6, 11 and the rear one of a given sample, which brings some additional information on the temperature distribution inside the sample.

In order to obtain more reproducible test results, it is necessary to perfect the technique of hand-made samples as well as perfecting exact pressure on each of the individual samples in order to obtain materials with very similar parameters (perhaps by applying a vacuum bag with particular attention to the non-breaking of thermocouples assembled into the sample).

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