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Effect of the amount and location of phase change materials in a fibre reinforced composite matrix on ablative properties

Robert Szczepaniak[1*], Paweł Przybyłek[1], Katarzyna Krzysztofik[2]

[1] Faculty of Aviation, Polish Air Force University, ul. Dywizjonu 303 No. 35, 08-521 Dęblin, Poland
[2] Institute of Navigation, Polish Air Force University, ul. Dywizjonu 303 No. 35, 08-521 Dęblin, Poland
* Corresponding author's email: r.szczepaniak@law.mil.pl

ABSTRACT

For this work, fibre-reinforced composites were prepared using 14 layers of aramid fabric and 6 layers of carbon fabric. The matrix was composed of epoxy resin Epidian 52, cured with TFF hardener. The composite cross-linked at ambient temperature. Additionally, a phase change material (PCM) in the form of BASF's Micronal DS5038X powder was added to the resin. Three samples were prepared for each measurement run, varying in the amount of powder additive used in the resin. The composites prepared in this way were subjected to ablation tests lasting approximately 3 minutes, during which the samples were exposed to a hot gas mixture at around 1100 °C. The primary parameter measured during the experimental tests was the temperature of the back surface of the composite, recorded using thermocouples and a thermal imaging camera. The temperature of the ablated surface was also measured using a pyrometer, while the internal temperature of the material was recorded using thermocouples. Following the experimental tests, the ablative weight loss and ablation rate were analyzed. Additionally, an organoleptic evaluation of the individual layers of the composite structure was performed. The study revealed that the incorporation of phase change material altered the ablative properties of the composite. The average temperature on the back surface of the composite without the addition of microspheres was approximately 165 °C after 180 seconds of heating. With the addition of PCM, significantly lower temperatures were recorded, ranging from 86 °C to 106 °C. Conversely, the addition of powder in the epoxy resin resulted in an increase in ablative weight loss by 1–4%, depending on the amount of the additive. This may be due to the formation of a layer with a higher thermal conductivity barrier in the composite with PCM.

Keywords: composite, phase change material, ablative properties, ablative weight loss, Micronal DS5038X.

INTRODUCTION

Ablation is a dynamic process of heat and mass transfer that leads to permanent structural and chemical modifications in a material, triggered by both physical changes and chemical reactions, accompanied by the absorption of thermal energy. This process begins and is sustained by exposure to external heat sources. In the context of the physical model of ablation, several key phases can be identified, each contributing to the overall transformation [1, 2]:

- the ablative surface,
- the ablative layer, located between the ablation front and the ablative surface,
- the ablation front, separating the ablation layer from the virgin material,
- the virgin material.

Through the ablative surface, which occurs at the interface between the gas and solid phases, heating takes place. Chemical processes take place in the ablative layer, which can be divided into the following groups [2–4]:

- pyrolysis and chemical decomposition reactions,
- thermochemical transformations of solid and gaseous decomposition products,
- solid-phase chemical reactions between solid and gaseous decomposition products,

- phase transformations of undecomposed material components and chemical reaction products,
- transformations and reactions in the liquid phase.

Improved thermoprotective performance can be attained through the use of polymer composite coatings that incorporate traditional ablative composite matrices, such as epoxy resins. Research is being conducted to analyze the impact of resin application on the thermal (ablative) and mechanical properties of composites, utilizing both numerical methods [5, 6] and experimental approaches [7, 8]. The authors also aim to modify composites by introducing reinforcements such as fibers [9], as well as incorporating additives like nanopowders [10] and other powders [11–13]. Additives used in ablative composites must fulfill additional criteria for practical applications. Consequently, tribological studies of these composites are underway [14, 15], alongside thermal analyses aimed at enhancing the understanding of heat transfer processes and the variations in thermophysical parameters of the composite as a function of temperature [16], concluding with dynamic studies of the composites [17]. Alagar et al. [18] and Minkook et al. demonstrated promising results by integrating Kevlar49 and aramid fibers with honeycomb structures filled with phenolic foam [19]. Similarly, Kucharczyk et al. [20] explored the effectiveness of aramid fibers in thermo-protective ablation castings.

An emerging area of research is the incorporation of PCMs into these systems, with the goal of evaluating their potential in enhancing the thermal resistance of composites. Although the application of PCMs in high-temperature composites is relatively underexplored, research is being conducted to determine the energy storage capabilities of PCM materials [21, 22]. Additionally, studies are focusing on both the production methods of materials incorporating PCM [23] and the thermophysical properties of PCM-enhanced composites [24]. Experimental studies analyzing the ablation behavior of composites using phase change materials [25] are also underway, alongside comprehensive investigations into the thermophysical properties of PCM materials and others used in aviation technology. Detailed methodologies are presented in [26], with the mechanical properties discussed in [27].

EXPERIMENTS

Given the increasing demand for materials that are resistant to degradation during prolonged exposure to elevated temperatures [12], an effort was made to assess the impact of incorporating PCM into the resin matrix on the thermal resistance of fiber-reinforced polymer composites. To evaluate the ablative properties of the tested composite structure, the analysis focused on the following parameters:

- *Ts* – temperature on the rear surface of the test material,
- *Ta* – temperature on the ablative surface,
- *Ma* – relative mass loss due to ablation,
- *Ma* – relative ablation rate,
- *Ti* – internal temperature within the composite material.

These parameters were crucial in determining the composite's effectiveness under high thermal stress.

Material for ablative research

The presented composite has practical applications for ablative research, however this particular composite was modified by the use of a powder additive in the form of microcapsules in epoxy resin for research purposes. For the purposes of the study, four different types of composites were prepared three samples of each type: series 1 (Fig. 1a) without the addition of PCM in the matrix; series 2 (Fig. 1b) with the addition of 16 wt.% PCM in the matrix; series 3 (Fig. 1c) with the addition of 8 wt.% PCM applied to half the specimen thickness in the matrix; and series 4 (Fig. 1d) with the addition of 16 wt.% PCM applied to half the specimen thickness in the matrix. Epidian 52 epoxy resin was used as the matrix and TFF hardener produced by Zakłady Chemiczne "Organika - Sarzyna S.A. was used for crosslinking Epidian 52 at room temperature. A phase change material (PCM) in the form of MicronalDS5038X [28] was used as a powder resin additive in one batch of samples. As reinforcement of the composite, 14 layers of aramid fibres in plain weave and 6 layers of carbon fibres in twill weave were used production of G. Angeloni. The fundamental parameters of the materials used are presented in Table 1. The fibre-reinforced composite layer was designed to provide both stiffness and thermal stability to the polymer composite. The initial step in preparing the specimens for testing

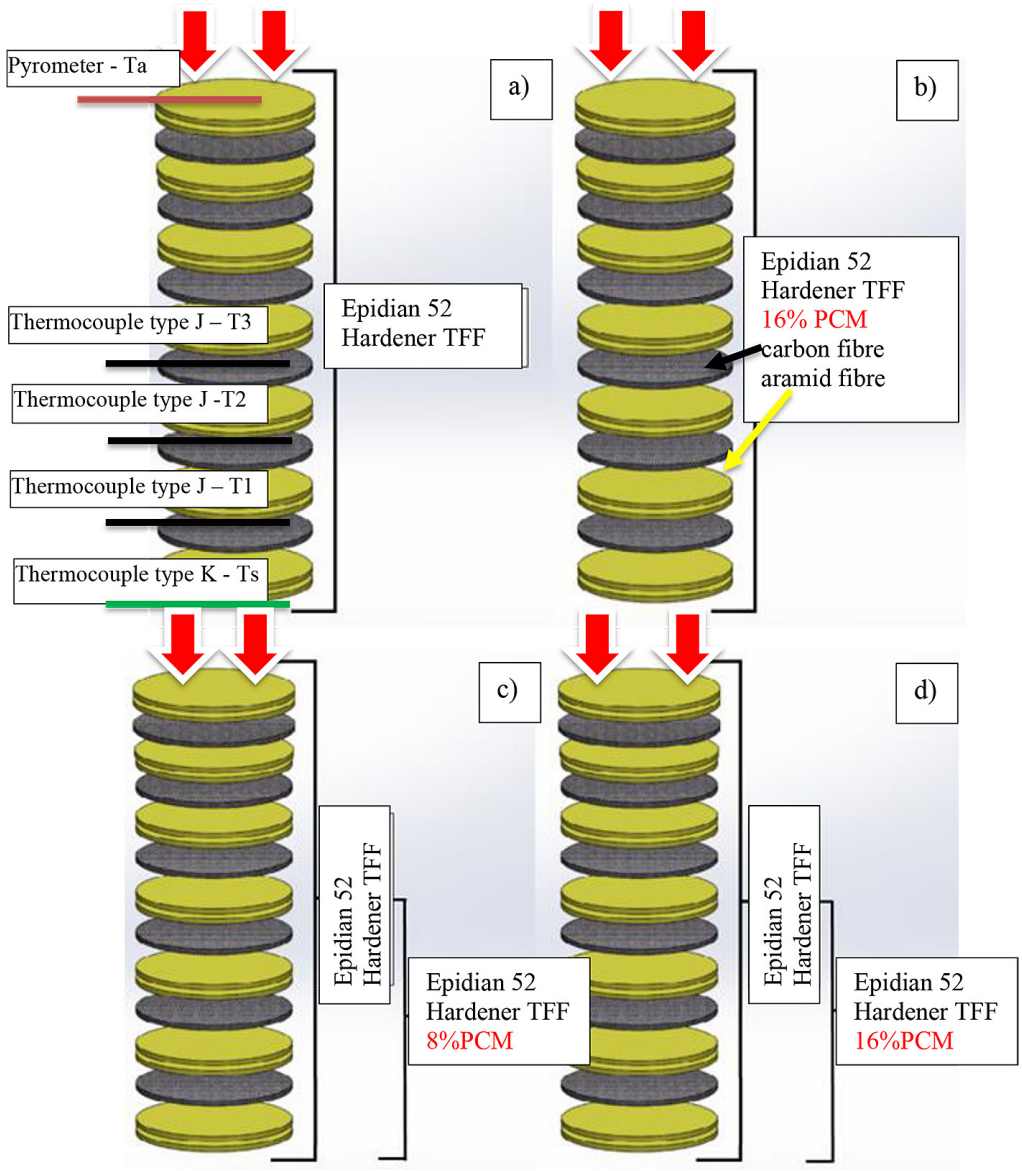


Figure 1. Schematic of the constructed composite with the location of the thermocouples measuring, the green line indicates the K-type thermocouple, the black line indicates the J-type thermocouple, and the red line represents the pyrometer measurement on the surface. The red arrows show the direction of flame impact on the tested material (a) without the addition of PCM – series 1, (b) with the addition of 16% PCM in the matrix – series 2, (c) with the addition of 8% PCM in the matrix to the middle of the sample – series 3, (d) with the addition of 16% PCM in the matrix to the middle of the sample – series 4

Table 1. The main parameters of the materials used in the tested composite

Epidian 52	Density ρ (g/cm³)	Value ph	Flash-point (°C)
	1.12–1.13	~7	64
Hardener TFF	Density ρ (g/cm³)	Value ph	Melting point (°C)
	1.15–1.20	~12	8
MicronalDS5038X	Bulk density (G/cm³)	Particle size (μm)	Melting point/crystallisation temperature (°C)
	0.3–0.4	50–300	24/25
Fibre	Grammage (g/m²)	Thickness (μm)	Wide (mm)
Carbon twill weave G. Angeloni	160 ±5%	0.16 ± 2.5%	1000 ± 2.5%
Aramid twill weave G. Angeloni	220 ±5%	0.28 ± 1.5%	1000 ± 2.5%

involved cutting circular layers of carbon fiber and aramid fiber. The composites in group 1 did not include the PCM Micronal DS5038X, allowing for an assessment of the additive's impact on the ablative properties of the polymer fiber composites (Fig. 1). The samples were fabricated using the hand lay-up method, and the stacking order of the various fabric layers was also established (Fig. 1).

The samples prepared for testing were cylindrical, with a diameter of 38 mm, a thickness of approximately 10 mm, and a weight of around 11 gram. After fabrication, the samples were left to cure for 7 days to allow the resin to crosslink. Thermocouples were then affixed inside the samples according to the schematic (Fig. 1). Each sample was encased in a refractory shell made of plasterboard. If any gaps were detected between the sample and the enclosure, Ceresit's high-temperature filler, which has a thermal resistance of up to 1500 °C, was applied to ensure a tight seal.

Test stand

The author's test stand (Fig. 2) was used to study the ablative properties. The composite samples produced were exposed to a high-temperature gas flow at approximately 1,100 °C. A comprehensive description of the apparatus and the testing procedure is provided in the article [24]. For clarity, a schematic diagram of the laboratory test rig utilized in the experiments is presented (Fig. 2).

RESULTS AND DISCUSSION

The temperature of the surface directly exposed to the flame was measured using a CT pyrometer at a frequency of 0.1 Hz. The measurement results for all samples are presented in Figure 3. The most critical parameter for analyzing the impact of powder additives on the ablative

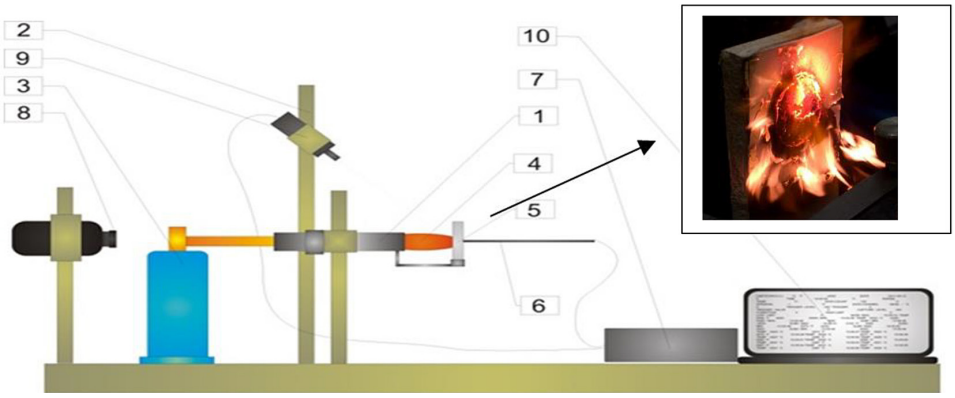


Figure 2. Laboratory research stand [2] 1-ablative gun, 2-stand, 3-the gas cylinder with burner nozzle, 4-flame, 5-speciment, 6-thermocouple, 7-measurement data acquisition system, 8-thermal imaging camera, 9-pyrometer, 10-computer

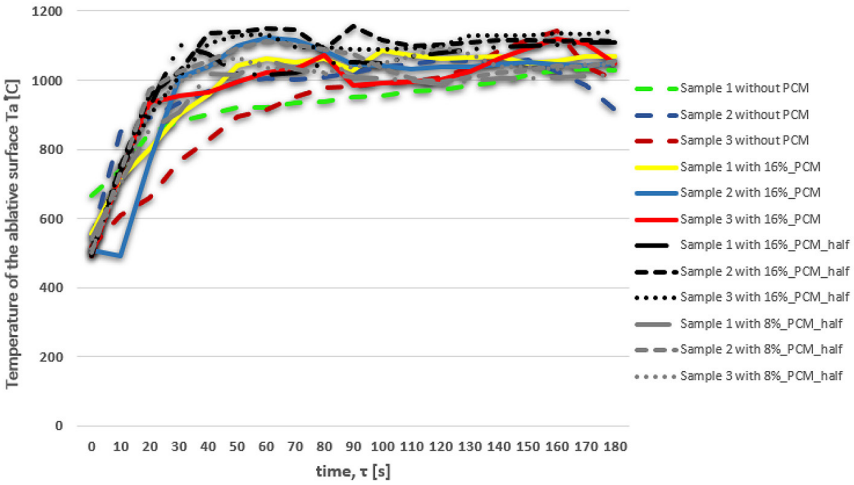


Figure 3. Temperature measurements of the ablative surfaces in all evaluated composites

properties of the polymer composite with fiber reinforcement was the temperature on the rear surface of the tested material, denoted as *Ts*. Additionally, to compare the influence of the powder additives, the authors recorded and presented the average temperature Ts for all four series, obtained in the final second of the test (after 180 seconds), in Table 2. Furthermore, the change in this temperature throughout the test was illustrated, showing the average value for three samples from the same series in Figure 4.

Based on the results obtained, it can be concluded that incorporating the PCM into the composites significantly enhances their thermal resistance (Fig. 4). The use of PCM led to a reduction in the average temperature of the rear surface of the tested materials by approximately 60 to 80 °C.

To better illustrate the temperature distributions on individual thermocouples, Figure 5a presents the results obtained for sample no. 3.2 as an example: (composite with the addition of 8% PCM in the composite matrix up to half the specimen thickness). There is a large increase in temperature at the ablated surface until about 100 seconds, when the temperature stabilises. This is also evident in the temperature measurement inside sample *T3*, when a decrease in growth dynamics is visible. This may be due to delamination of the first layers of aramid fibres at the front of the material. The temperature then stabilises and increases almost linearly until the end of the measurement (Fig 5 b).

To monitor the temperature distribution on the rear surface of the tested material, a FLIR

Table 2. Evaluation of the ablative properties of the analyzed composites

Batch number	Sample number	Temperature *Ts* (°C)	Mass before test (g)	Mass after test (g)	Thickness before test (mm)	Thickness after test (mm)	Ablative mass loss (%)	Average mass ablation rate (mg/s)
1	1	164.6	10.92	7.73	10.52	9.53	31.7	18.8
	2		10.26	7.08	9.74	10.57		
	3		10.82	7.05	10.44	9.25		
2	1	106,1	11.78	8.07	11.23	9.35	32.9	21.8
	2		12.12	7.84	10.57	9.57		
	3		11.83	8.05	10.78	10.22		
3	1	101.2	14.33	10.32	10.32	10.50	35.3	28.5
	2		14.85	10.85	10.90	10.19		
	3		14.38	10.48	10.37	10.45		
4	1	88.4	15.03	11.33	11.86	11.07	35.8	30.3
	2		15.45	11.81	11.47	10.82		
	3		15.35	11.42	11.38	11.80		

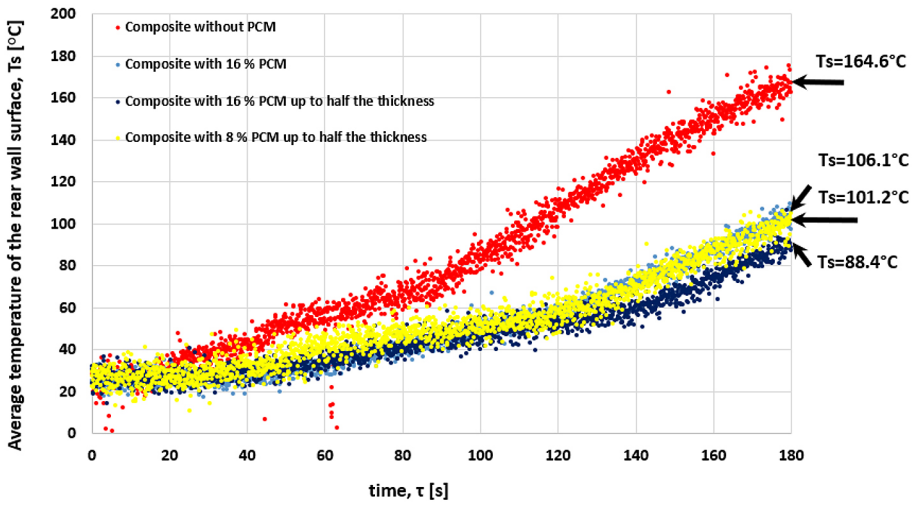
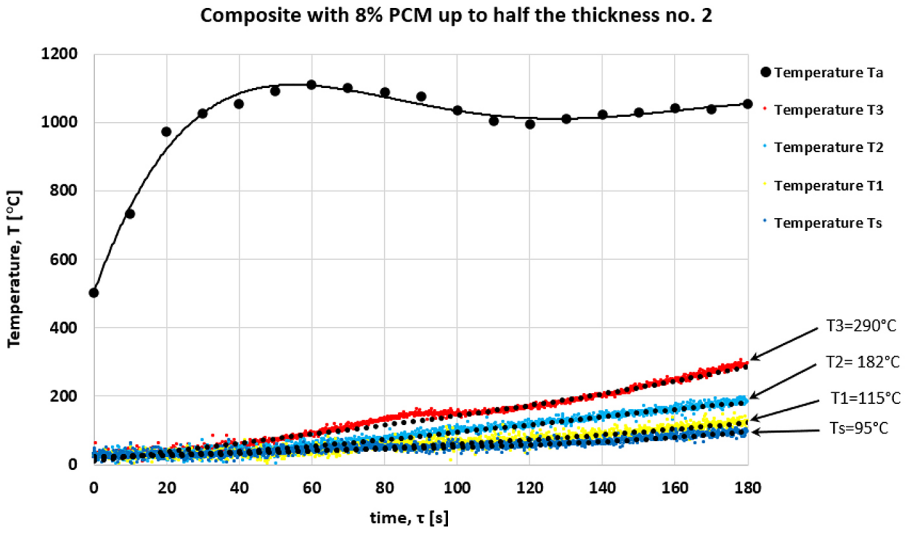


Figure 4. The average temperature of the rear surface of the wall, denoted as Ts, for the tested materials

a)



b)

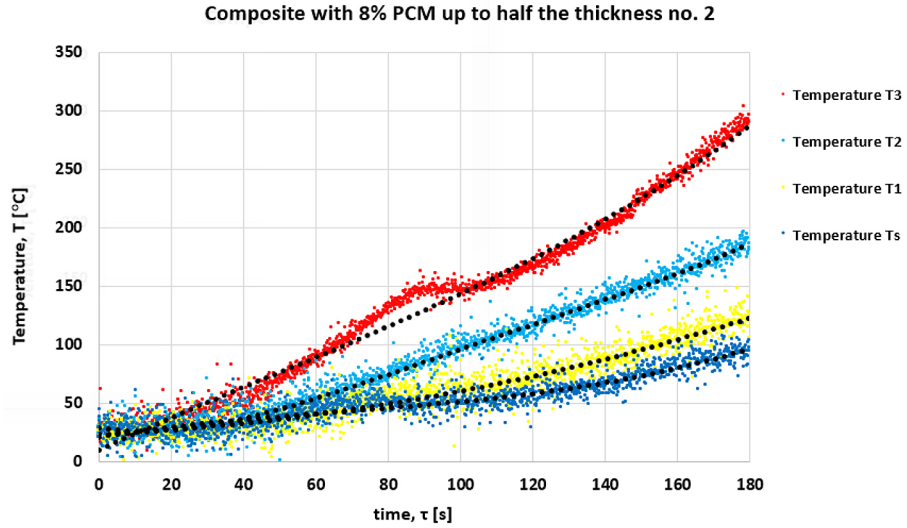


Figure 5. a) exemplary temperature on the rear sample wall *Ts* and on the ablative surface *Ta* and temperature inside the composite *Ti*, b) without the temperature ablation surface

i60 thermal imaging camera was utilized. Figure 6 illustrates an example of the temperature distribution on the rear wall of the sample (sample 3.2 - composite with 8% PCM added to the composite matrix up to half the specimen's thickness). Based on the images captured by the thermal camera, an evaluation of the proper fixation of the samples within the protective plate was conducted (Fig. 6 a–c). Temperature readings from the thermal imaging camera, taken from a point near the center of the sample (corresponding to the thermocouple measurement point), were recorded every 30 seconds. Delamination of the top layers of the fiber composite was observed during exposure to a stream of hot flammable gases, as shown in Figure 7. This stratification extends up to the sixth layer, which consists of carbon fabric. Microscopic images were taken from layer 4 onwards due to the stable structure of the sample after the tests. But nevertheless, cracks in the aramid fibres are visible due to the hot gas exposure of layers 4 and 5. Layer 7 (aramid fabric) showed little thermal damage despite the burning of the epoxy resin the fabric did not degrade completely. The PCM additive in the second part of the composite can also be seen in the pictures, and it can be observed that it did not degrade, but only some of the circles cracked, due to exceeding the exposition temperature for this additive. The relative ablative mass loss (expressed as a percentage)

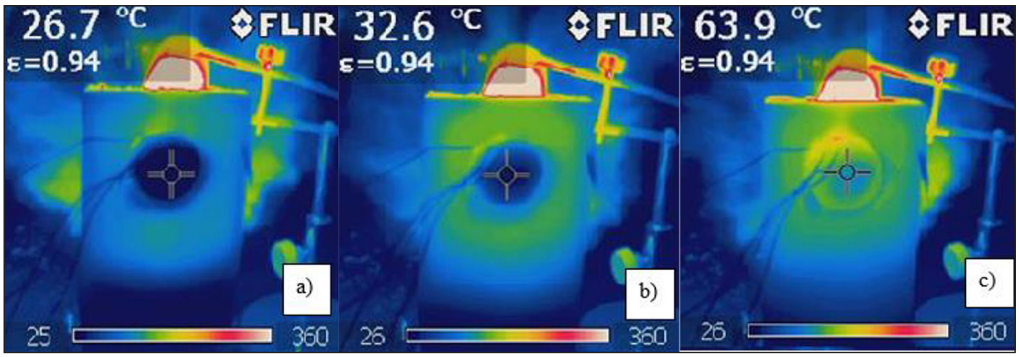


Figure 6. Measurement of the rear surface temperature using a thermal imaging camera (a) at 30 seconds, (b) at 60 seconds, (c) at 90 seconds

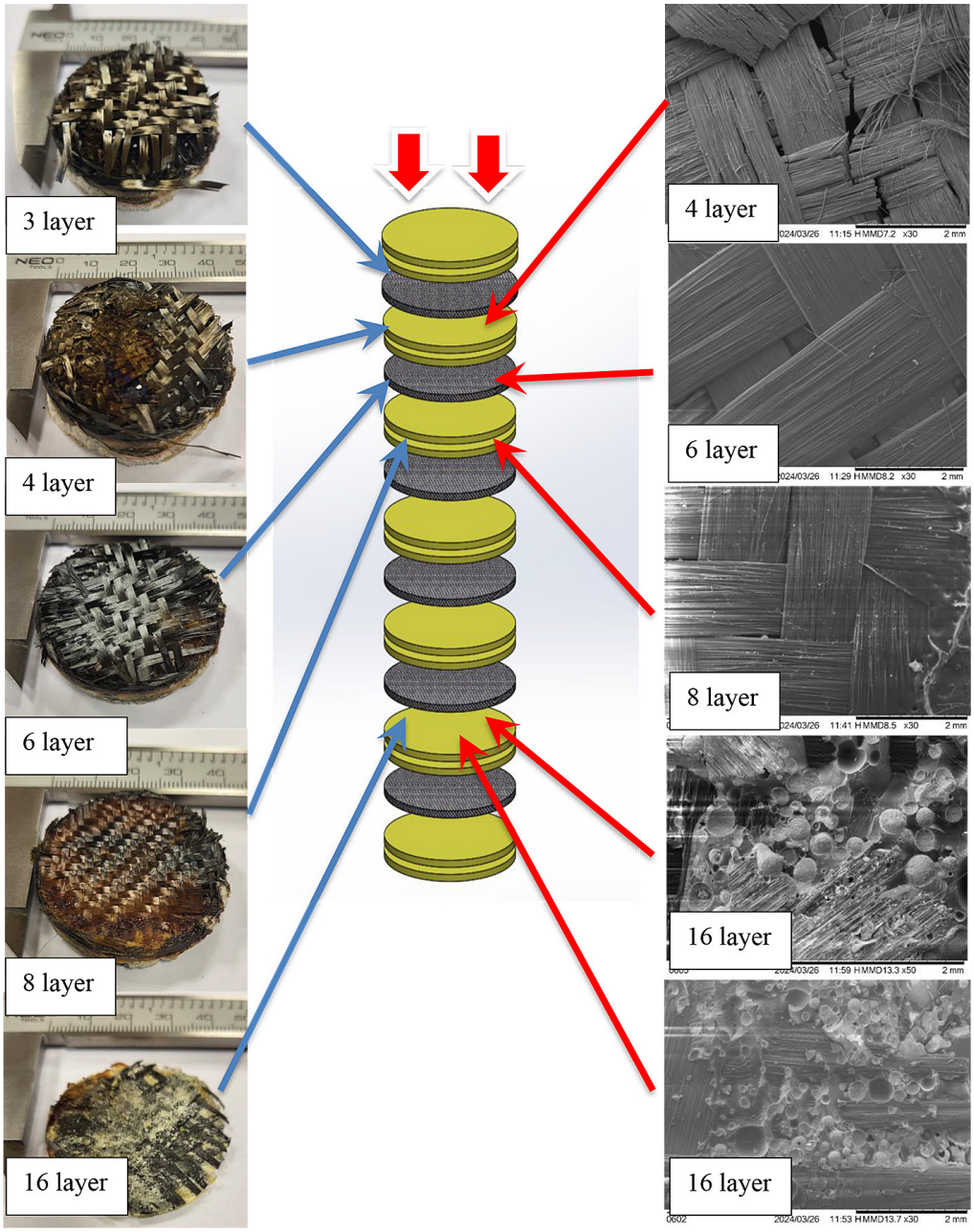


Figure 7. Illustration of selected composite layers by means of photographs and SEM microscopic images with marked areas on the specimen diagram

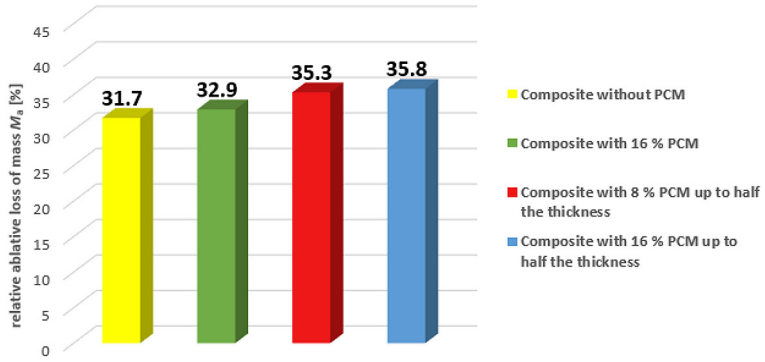


Figure 8. Relative mass loss due to ablation M_a [%]

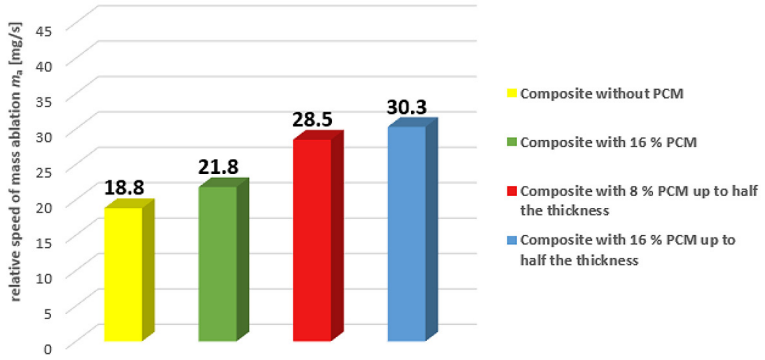


Figure 9. Relative ablation rate m_a [mg/s]

was calculated by analyzing the weight changes of the tested samples before and after the heat resistance tests. The results are illustrated in Figure 8, while the relative mass loss rate [mg/s] is depicted in Figure 9.

CONCLUSIONS

By analyzing the experimental results and observing the research process (which involved the phase-change additive PCM in the resin matrix), the following conclusions can be drawn:

The addition of PCM to the epoxy resin resulted in a decrease in the back surface temperature of the material to approximately 96 ± 10 °C for all tested samples, from an initial average of about 165 °C for the sample without the powder additive, measured 180 seconds after the start of the hot gas stream exposure. The differences in temperature values for the samples marked with light blue and yellow are insignificant, while for the samples marked with dark blue they are significant. This is particularly noticeable after 120 seconds from the start of the test, where a clear decrease in the temperature difference was noted. After 180 seconds, this difference is about 10–15 °C compared to the other two series.

Of the composites tested, the fibre composite with 16% PCM up to half the thickness of the sample showed the highest heat resistance and obtained the lowest rear wall temperature of the sample *Ts* of about 88 °C after 180 seconds. This may indicate very good thermal insulation of the PCM additive and blocking the heat flow to the rear surface.

Delamination of the initial composite layers was observed due to aerodynamic erosion resulting from the direct impact of the flame on these layers, which indicates the ablative properties of the tested material.

The temperature distribution on the rear surface of the sample was generally uniform; however, the observed fluctuations could be attributed to variations in sample thickness, which did not significantly affect the final measurements.

Two types of fiber composites with the addition of PCM reached the temperature of the rear surface of the sample wall at a similar level. The composite with 8% PCM added to half the thickness reached a temperature of the rear surface of the sample wall of approximately 101 °C, while

the fibrous composite with 16% PCM added throughout the thickness reached a temperature of the rear surface of the sample wall of approximately 106 °C.

Analyzing the results of the ablative mass loss tests, it can be concluded that the highest relative mass loss was achieved by the composite with 16% PCM added to half the thickness, with a value of 35.8%. In contrast, the composite with 16% PCM added to the entire thickness of the sample recorded the lowest relative mass loss at 32.9%. The incorporation of PCM as a powder additive in the epoxy resin resulted in a slightly higher mass loss compared to the composite without PCM, with values ranging from 1% to 4%.

The obtained results are promising and can be used as a basis for further analysis of the use of various types of PCM in ablative materials.

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