ANALYSIS OF THE POSSIBILITY OF INCREASING THE THERMAL RESISTANCE OF EPOXY RESIN WITH CWNT AND MMT

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Abstract

The need to provide thermal protection for sensitive aeronautical technology components exposed to high heat flux temperatures necessitates the emergence of new materials with high thermal protection properties. The research focused on a powder composite patterned with montmorillonite and carbon-walled nanotubes incorporated into epoxy resin LH145 and hardener H147. The specimens were exposed to a hot gas mixture of more than 900°C for a period of approximately 90 -180 seconds, depending on the thickness of the tested samples. The most important parameter determined from the experimental study was the temperature of the back surface of the specimen. The test material's average mass loss and mass ablation rate were also analyzed. The samples with the addition of montmorillonite had the lowest temperature of the rear wall surface, i.e., approximately 50ºC, ensuring maximum temperature reduction. The same can be observed in the ablation mass loss, which was approximately 45% for the average thickness of both samples, as well as in the ablation speed of approximately 24 μm/s.

Keywords: composite, matrix, montmorillonite, carbon walled nanotubes, ablation

1. Introduction

Ablative materials are able to absorb significant amounts of thermal energy through endothermic phase transitions. Therefore, they have been used for over fifty years [1] in numerous machine structural elements. Ablation is a self-regulating heat and mass transfer process, which, due to physical and chemical reactions, leads to irreversible structural and chemical changes in a material combined with heat absorption simultaneously. The process is initiated and sustained by external sources of thermal energy [2-8]. The exact description of chemical reactions and physical phenomena occurring in the composite material during combustion is difficult to define. Fig. 1 shows one of the proposed patterns of phenomena occurring during sample combustion.

The ablation process begins when the temperature of the ablation surface *Ta* reaches the temperature of the ablation front. Thermal decomposition of the ablative material matrix then occurs. Through the ablation process, the ablative thermal protective properties of composites can be determined. Belong to them:

- the temperature of the back surface of the insulating sample wall *Ts*,
- ablation surface temperature *Ta*,
- relative ablative mass loss *Ma* (sample mass loss caused by the impact of the gas stream),
- ablation speed v_a (average speed of displacement of the ablation front).

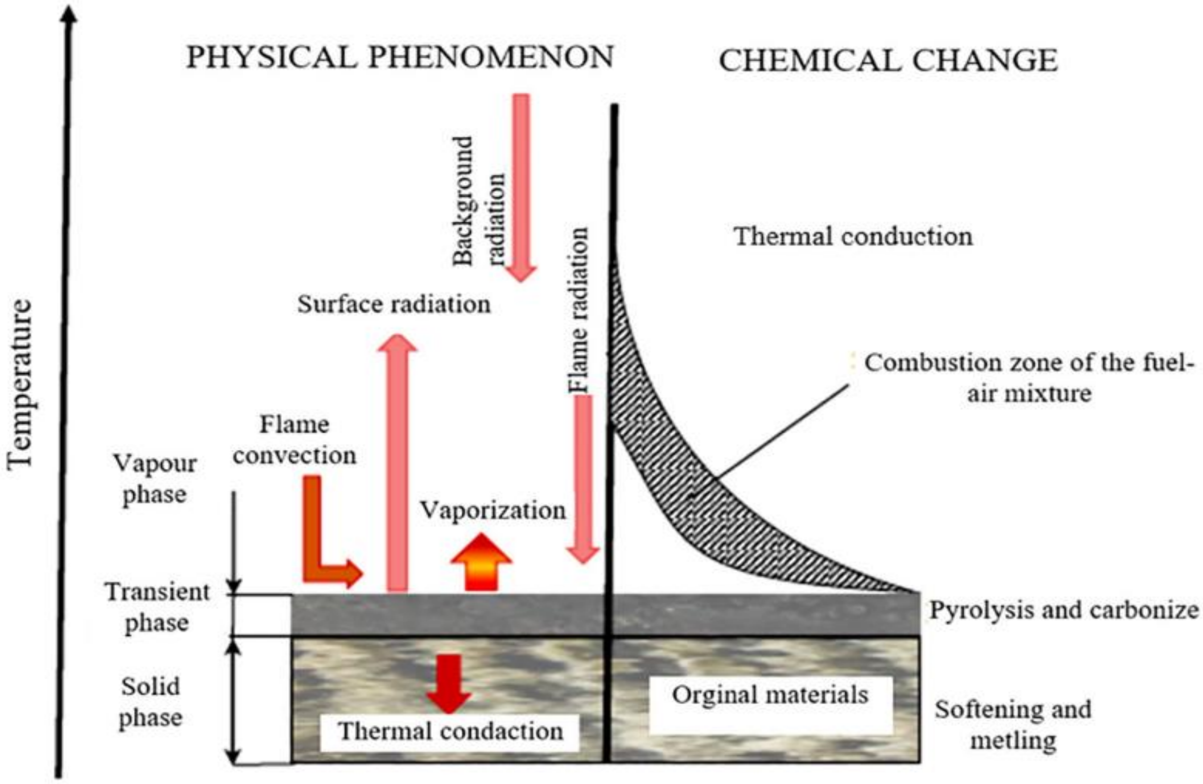


Fig. 1 – Scheme of phenomena occurring during sample combustion [5].

The best thermal protection properties of composites result from their lowest values. In other words, the lower the ablative thermal protective properties values, the more excellent the resistance to an external heat source [3]. The nano-additive is the second element of the nanocomposite. The content of the nano-additive, or nanofiller, accounts for 1 - 5% of the mass of the entire nanocomposite [9]. The nano-additive improves the properties of the nanocomposite, e.g., tear strength, compressive strength, thermal expansion coefficient, and chemical resistance [10]. Ceramic materials are most often used as a nano-additive. Two types of nano-additives are presented below: montmorillonite (MMT) and carbon nanotubes. The first nano-additive, montmorillonite, belongs to the group of layered silicates. This group is the most popular and well-known nanofiller used to produce nanocomposites with thermal protective properties. Other layered silicates that also function as nano-additives are hectorite and saponite [11]. Montmorillonite belongs to three-layer clay minerals. The name of the mineral comes from the town of Montmorillon in France [12]. This mineral constitutes 60 – 95% of bentonite rock. Other components of this rock are quartz, mica, pyrites, feldspar, and calcium [9]. Montmorillonite comes in shades of brick red, pale yellow, and blue-gray [13] (Fig. 2). This mineral tends to swell. This is due to its layered structure. Swelling is important in producing polymer nanocomposites because it strongly stabilizes the Montmorillonite platelets with the polymer matrix particles. In this way, the strength of the nanocomposite increases [14].

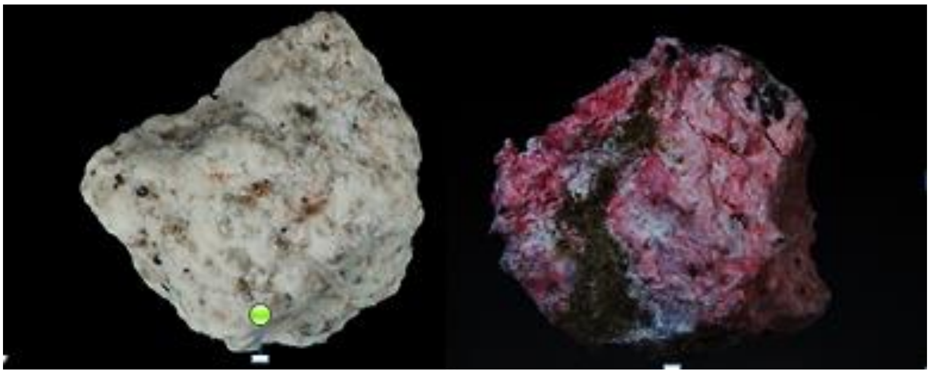


Fig. – 2 Colors of Montmorillonite [15, 16].

Montmorillonite is composed of three layers (2:1): two external layers, i.e., tetrahedral, and an internal layer - octahedral [9]. The outer layers are made of silicon dioxide crystals. Magnesium oxide or aluminum oxide crystals form the inner layer [12]. Between these layers, there is the so-called interlayer gallery. It is an interlayer of "loose" cations, primarily sodium, calcium, and hydrogen. The thickness of the Montmorillonite plate is 9.6 Å (Angstrom - a unit of length equal to 10^{-10} m). The sum of the plate thickness and the distance between two consecutive plates is the base distance d (Fig. 3) [9].

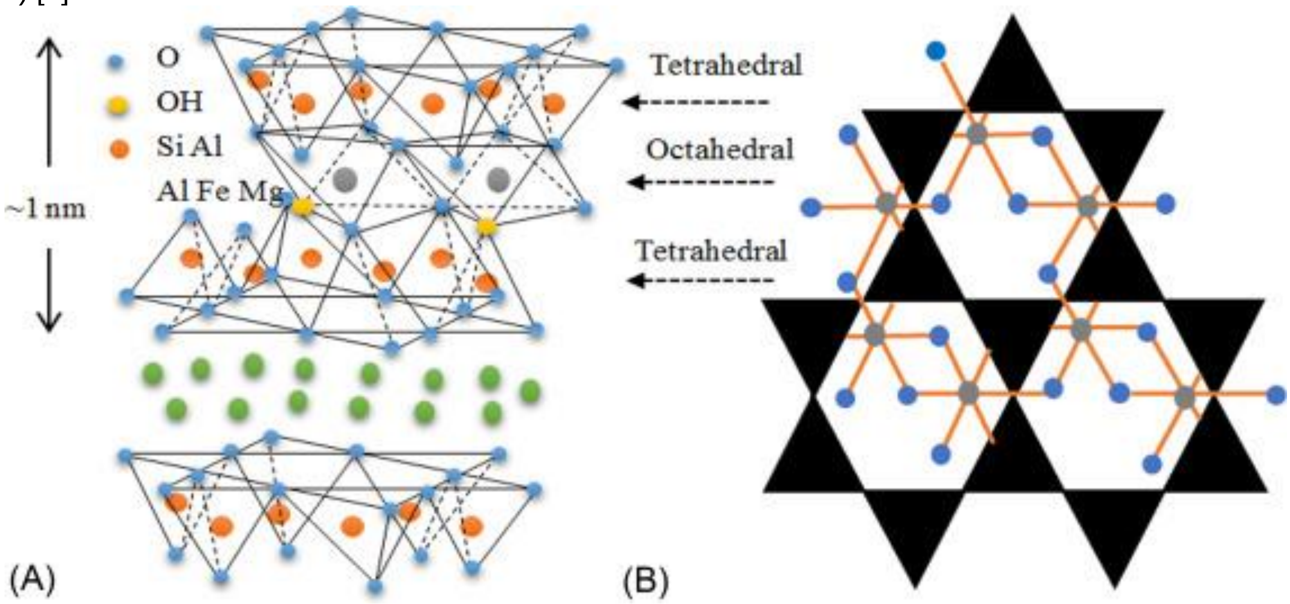


Fig. 3 – Schematic representation of the structure of Montmorillonite [17, 18].

Montmorillonite is usually opposed to polymers. In order for it to function as a nanofiller, it must be modified. Most often, it involves the exchange of interlayer cations with organic cations. The modification increases the interlayer distances, and the base distance d increases twice [9]. This allows polymers to get there. The introduction of layered silicate (Montmorillonite) into the matrix forms three basic nanocomposite structures: intercalated, exfoliated, and micro-composite.

In the intercalated structure, polymer molecules are located between single parallel silicate layers, forming an ordered, multi-layered structure. However, in the exfoliated structure, silicate layers are dispersed in different directions in the polymer matrix. When the introduction of polymer particles between the silicate layers is impossible, a micro-composite occurs [9].

A nanocomposite with an exfoliated structure has the best mechanical properties compared to the intercalated structure. Montmorillonite also increases thermal resistance. During combustion, a layer of charred matter is formed on the surface of the nanocomposite. This char cuts off oxygen access to the polymer matrix. The composite burns less, and thermal resistance increases [19]. Generally, nanofillers stop the combustion cycle. This cycle causes the destruction of the material, the release of flammable, volatile substances that are helpful in combustion, and the release of heat [20]. Advantages of Montmorillonite:

- increases heat resistance,
- results in good mechanical properties (tensile, compressive, and bending strength),
- absorbs water well,
- widely distributed (easily accessible).

Montmorillonite is used for commercial products. Many companies worldwide modify nanofillers, layered silicates, with various ammonium salts [14]. Montmorillonite is used in the ceramic, rubber, paper, pharmaceutical, chemical, metallurgical, and food industries. It is also a component of mineral fertilizers and drilling mud. It is used in the recultivation of areas contaminated with heavy metals, i.e., in restoring utility and natural values to areas that humans have degraded [12].

Another nano-additives are carbon nanotubes (CNTs). They have mechanical properties that favor polymer nanocomposites. Interest in them is constantly growing. They come from carbon nanostructures, which belong to organic chemistry. In addition to carbon nanotubes, carbon nanostructures include fullerenes. The structure of these nano-additives is formed by rolled graphene planes. Graphene is a single plane of graphite. By appropriately folding the graphene planes, the following carbon nanotube structures can be created (Fig. 4) [14, 21]:

- Single-Walled Carbon Nanotubes (SWCNTs), which are rolled from one plane of graphene,

- Double-Walled Carbon Nanotubes (DWCNTs), as the name suggests, are made of two graphene planes,
- Multiple-Walled Carbon Nanotubes (MWCNTs) are created by many rolled graphene planes.

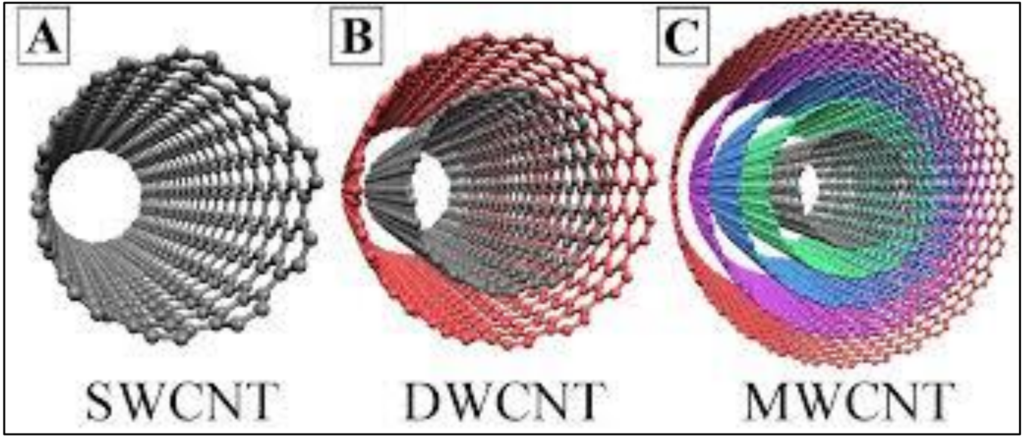


Fig. 4 – Types of carbon nanotube structures: A – single-wall carbon nanotube (SWCNT), B- double-wall carbon nanotube (DWCNT), C - multi-wall carbon nanotube (MWCNT) [22].

Three types of single-wall carbon nanotubes exist armchair, zigzag, and chiral. They are created by rolling the graphene plane at a different angle in relation to the nanotube axis [14]. The first three methods are the main ways to produce carbon nanotubes. All methods use catalysts [23]. A catalyst is required for single-wall nanotubes. However, for multi-walled nanotubes, a catalyst is only sometimes needed [9]. A catalyst causes a chemical reaction to speed up. They may be metals, semiconductor compounds, and porous metal oxides. Essential factors in producing carbon nanotubes are temperature, pressure, and the type of carbon source. Most importantly, the nanotubes produced are of high quality and low cost [23]. The most important are straight nanotubes that grow perpendicular to the substrate. They can be obtained using the CVD method. Existing swirling nanotubes were also obtained using these methods [9].

Removing defects in the resulting nanotubes, such as catalyst residues, amorphous carbon, or incorrect structure, is essential. Catalyst residues are chemically removed, and the use of solvents excludes amorphous carbon. However, the abnormal structure of nanotubes is heated to a high temperature, i.e., 3000 K. Purification is a critical process to further modify the nanotubes [14].

Introducing carbon nanotubes into the matrix (polymer) improves the properties of the resulting nanocomposite. They are more resistant to stretching and bending. The modulus of elasticity (Young's) also increases. On the contrary, the elongation at break is reduced [14].

Carbon nanotubes conduct heat very well, which is why they are worth using in polymer nanocomposites. They also increase the fire resistance of polymers [24] and are characterized by good electrical conductivity. The remaining structures of nanotubes, i.e., zigzag and chiral, are semiconductors [14].

Carbon nanotubes are used in fuel and solar cells, electronic devices, sensors, composite materials (as fillers), nano-electronic devices, and car body elements [9].

2. Experiment

2.1 Material for ablative research

In the experimental study, HAVEL COMPOSITES POLAND LH 145 epoxy resin was used, acting as a matrix in the powder composite. It is a mixture prepared from bisphenol A and epichlorohydrin with an average molecular weight ≤ 700 (85 – 90%) and trimethylolpropane-triglycidyl ether (0 – 30%). Hardener H 147 was used in a weight ratio of 100:30. Industrial Grade Carbon Walled Nanotubes (IGCWNTs) used in industry were used as powder additives and Bentonite. This mineral mainly contains montmorillonite - MMT (approximately 75 %) as well as smectites, calcite, dolomite, feldspar, kaolinite, and quartz. The volume proportion of the powder additives in the composite was 1, 2, 3, and 5 % for MMT and 1, 2, 3, and 5 % for IGCWNT. In addition, samples with a volume proportion of 2.5 MMT and 2.5 % IGCWNT were also made for comparison (Fig. 5 and 6).

Table 1 Names, masses, and overall thickness and layer thickness of samples

Series no	Name	Type of supplement	Volume fraction of additive [%]
0.	0.1, 0.2	0	0
1.	1.1, 1.2	MMT	1
2.	2.1, 2.2		2
3.	3.1, 3.2		3
4.	4.1, 4.2		5
5.	5.1, 5.2	IGCWNTs	1
6.	6.1, 6.2		2
7.	7.1, 7.2		3
8.	8.1, 8.2		5
9.	9.1, 9.2	MMT + IGCWNTs	2.5+2.5

The samples were prepared by hand mixing, and the ultrasonic method was used to ensure better dispersion of the powder additive and to remove air bubbles from the composite. Ten series of samples were prepared (20 in total according to Table 1), two in each series, differing in thickness (one sample was about 12 mm thick and the other about 6 mm) for each percentage of nano-additives (Fig. 6).

During their production, thermocouples were placed in each sample to measure the temperature during the tests. Thermocouples were mounted on the back surface of the sample - temperature measurements *Ts1* (Fig. 5), which recorded the temperature only for the first seconds of measurement due to rapid burning due to the direct impact of the flammable gas stream. The temperature of the ablation surface was also measured using an optical pyrometer *Ta*.

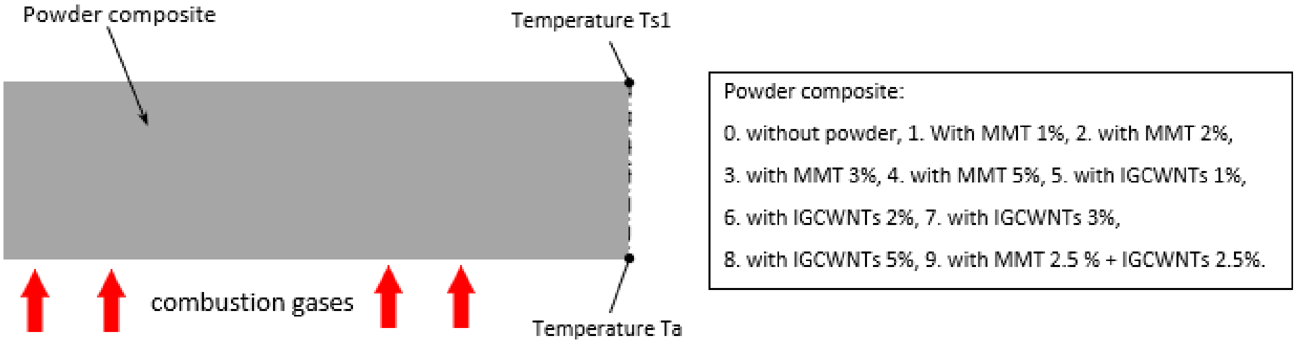


Fig. 5 – The shape of the sample subjected to ablation testing, along with the location of the measurement sites for individual temperatures (10 types of composite)

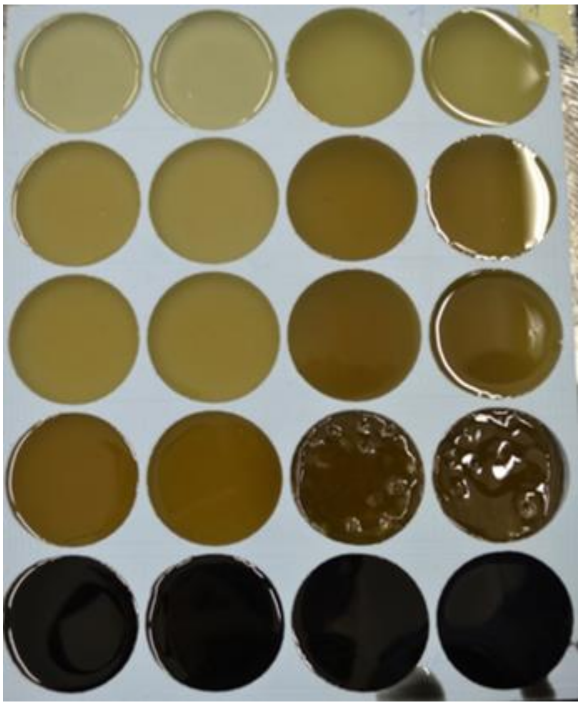
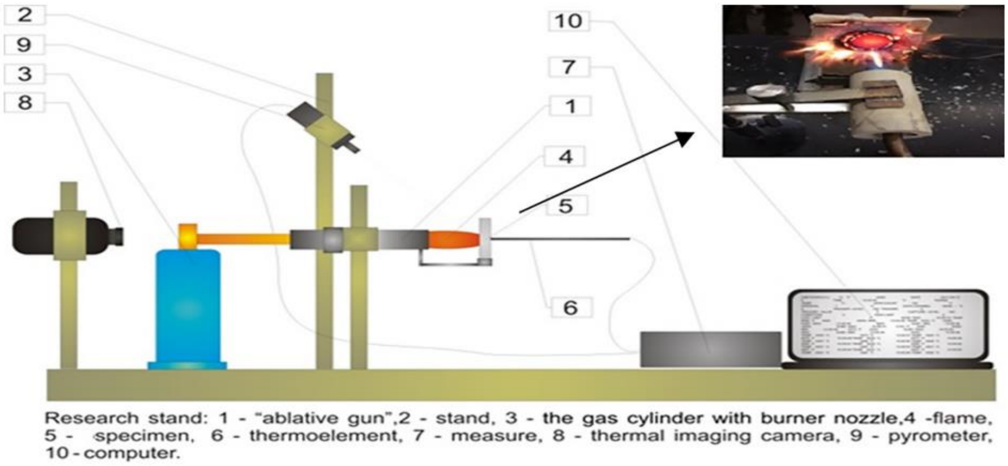


Fig. 6 – Composite samples in silicone form.

2.2 Test stand and research methodology

The manufactured samples were subjected to a high-temperature heat flux (approximately 900 °C) on the test stand developed by the authors (Fig. 7). The test duration time equaled 90 - 180 s for each sample. Due to the temperature range, the authors decided to measure the temperature on the rear surface of the composite sample wall using J-type and K-type thermocouples. The temperature of the tested sample's ablation surface (exposed to a flame) was measured using a pyrometer made by Optris, model CT.



Research stand: 1 - "ablative gun",2 - stand, 3 - the gas cylinder with burner nozzle,4 -flame, 5 - specimen, 6 - thermoelement, 7 - measure, 8 - thermal imaging camera, 9 - pyrometer, 10 - computer.

Fig. 7 – Laboratory research stand [5].

3. Results and discussion

The most crucial parameter for analyzing the impact of powder additives on the ablative thermal protective properties of the powder-reinforced polymer composite was the change in temperature on the back surface of the tested material Ts (Table 2 and Fig. 8 a; b). However, most of the 6 mm thick composite samples burned out in less than 120 seconds under the influence of the heat flux (Fig. 8 c), as did the 12 mm thick samples, where the average burning length was about 150 seconds (Fig. 8 d), only the sample with 5% MMT withstood burning for 180 seconds (Fig. 9).

Table 2. Individual data for each sample

Series no	Name	addition	Share	Mass before burning [g]	Mass after burning [g]	Thickness before burning [mm]	Thickness after burning [mm]	Loss of layer thickness [%]	Ablative loss of mass [%]	Temperature Ts [°C]
0	0.1	No addition	0	7.41	2.18	5.55	none	100	70.58	309
	0.2			13.80	5.87	10.96	2.93	73	57.46	96
1	1.1	MMT	1	8.65	2.94	6.64	3.27	51	66.01	295
	1.2			14.67	8.91	11.05	7.32	34	39.26	50.4
2	2.1		2	7.80	3.29	5.80	3.58	38	57.82	247
	2.2			15.17	10.52	11.74	9.31	21	30.65	40.3
3	3.1		3	6.75	Brak	5.61	none	100	100	350
	3.2			14.67	Brak	11.09	none	100	100	172
4	4.1		5	7.49	2.59	6.05	none	100	65.42	341
	4.2			14.68	10.86	12.98	7.93	39	26.02	58.5
5	5.1	IGCWNTs	1	5.79	2.40	5.27	none	100	58.55	256
	5.2			12.20	7.81	9.48	4.85	49	35.98	86.2
6	6.1		2	5.95	3.42	4.98	none	100	42.52	254
	6.2			13.46	6.57	10.89	4.88	55	51.19	60.5
7	7.1		3	6.96	2.02	5.97	none	100	70.98	351
	7.2			14.26	7.79	11.95	4.56	62	45.37	49.5
8	8.1		5	6.60	1.71	5.39	none	100	74.09	230
	8.2			13.23	6.28	10.55	5.31	50	52.53	95.6
9	9.1	MMT + IGCWNTs	2.5+2.5	7.75	2.04	6.52	none	100	73.68	330
	9.2			14.26	7.73	11.56	4.55	61	45.79	77

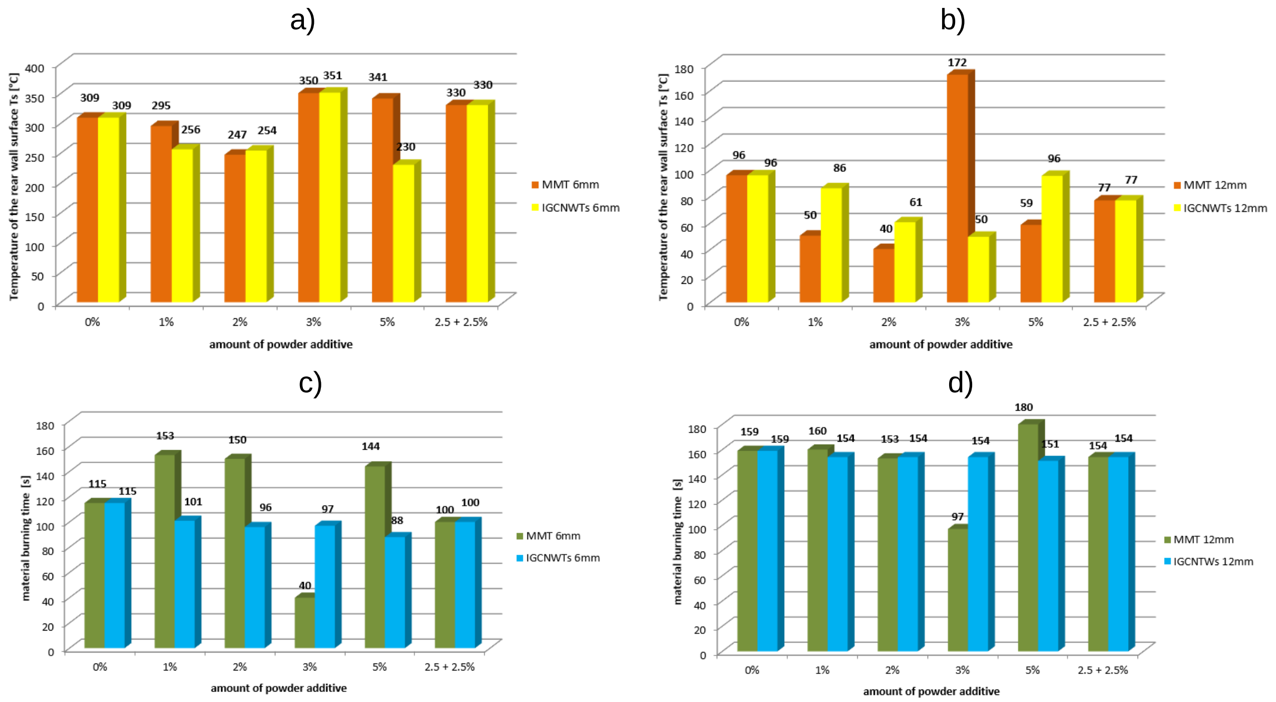
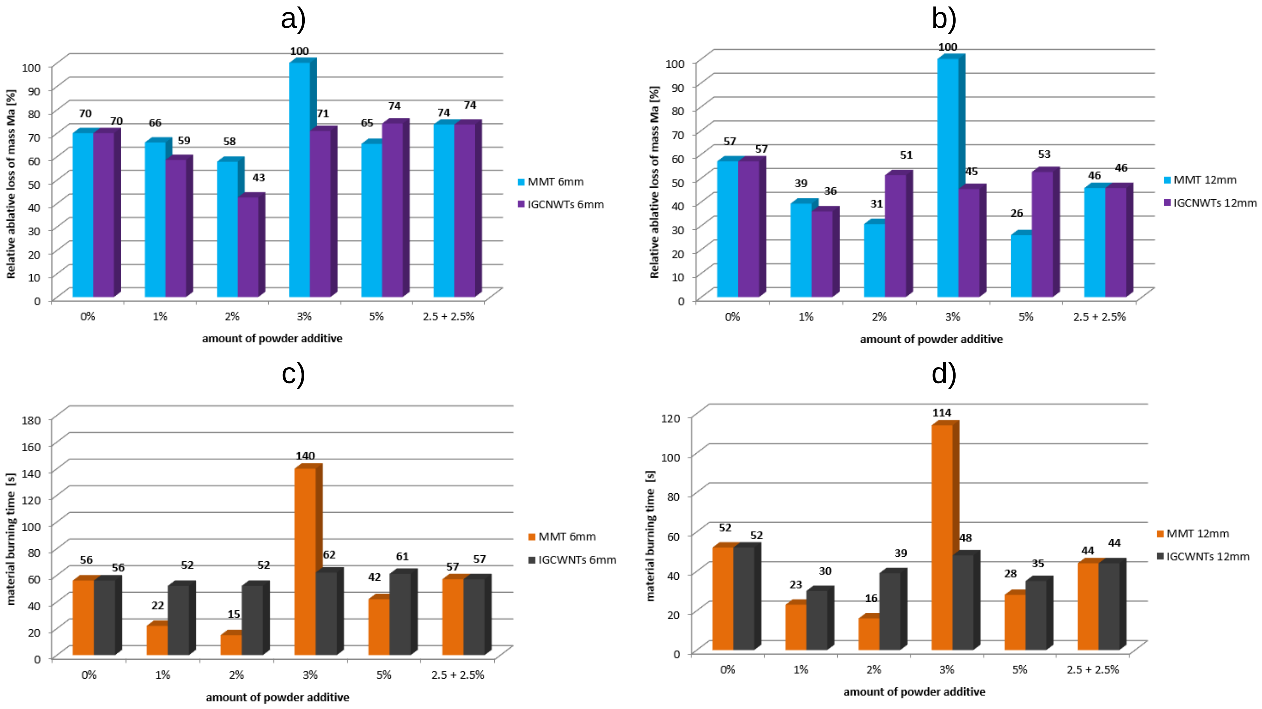


Fig. 8 – Rear surface temperature for composite samples with a) 6 mm thickness, b) 12 mm thickness, and material burning time for samples with c) 6 mm thickness, d) 12 mm thickness.

Fig. 9 – Photo of an example of a sample after ablation testing with 5% MMT.

The following parameters determined were the ablation mass loss M_a (Fig. 10 a, b) and the ablation rate v_a (Fig. 10 c, d). There is a visible tendency for ablative mass loss to decrease when the amount of MMT additive in the composite is increased, while in the case of the addition in the form of IGCWNTs, the decrease is only up to 2% of this additive. The MMT share significantly impacts the ablation mass loss and thus reduces the material's flammability; however, the different measurement lengths need to be clarified from the charts below. Therefore, the ablation speed parameter is also presented. Analyzing this parameter, it can be concluded that for samples with a thickness of 6 mm, the lowest ablation speed, i.e., 15 µm/s, was achieved by the sample with 2% MMT content. For samples with a thickness of 12 mm, the lowest ablation speed, i.e., 16 µm/s, was also achieved by the sample with 2% MMT. This means that the share of MMT had a more significant impact on the thermal protective properties of the composite.


a)

b)

c)

d)

Fig. 10 – Relative ablative loss of mass Ma a) for samples with a thickness of 6 mm, b) for samples with a thickness of 12 mm and ablation speed, c) for samples with a thickness of 6 mm, and d) for samples with a thickness of 12 mm.

The ablation surface temperature *Ta* was measured using a pyrometer. A summary of an exemplary increase in the ablation temperature and the back surface measured during burning for a composite sample with the addition of 2.5% MMT and 2.5% IGCWNTs is shown in Fig. 11. The ablation temperature after about 100 seconds of burning was about 800ºC, and after about 40 seconds of burning this value oscillated around 700ºC. However, the temperature of the rear surface of the sample increased more rapidly after exceeding 60 seconds of the test.

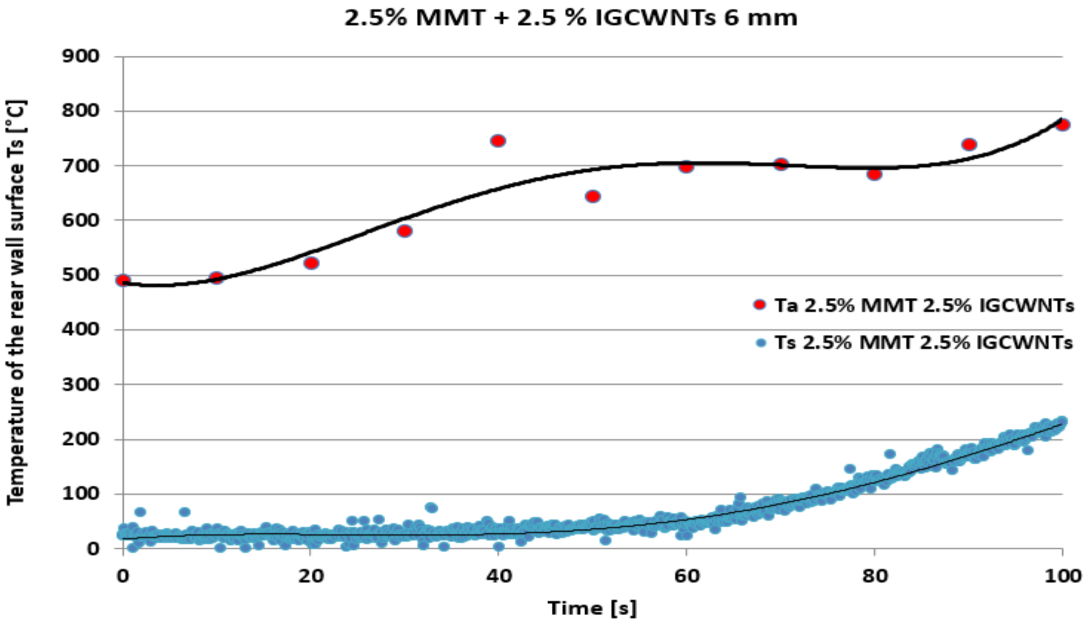


Fig. 11 – Example of temperature increase on the back wall of the *Ts* sample and the ablation surface Ta for a powder composite with 2.5% MMT and IGCWNTs addition

An example of the results of temperature increase tests on the back surface for a powder composite with the addition of IGCWNTs with a thickness of 6 mm is also illustrated (Fig. 12). It can be seen that a more dynamic increase in the rear surface temperature is noticeable for all samples after approximately 60 seconds from the start of the test. At the same time, all of them were burned out within 120 seconds of exposure to the hot gas stream.

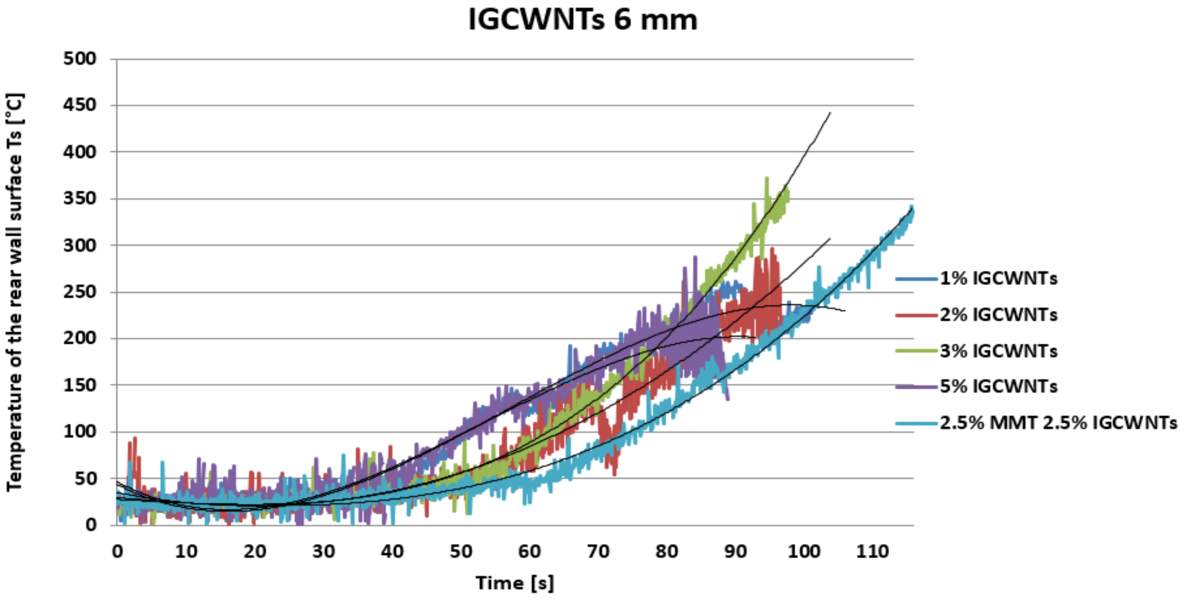


Fig. 11 – Temperature of the rear wall surface *Ts* of the examined materials for IGCWNTs 6 mm.

4. Conclusions

The best ablative thermal protective properties are those of composites that obtained the lowest parameter values, such as the rear wall surface temperature, ablative mass loss, and ablation speed. The addition of MMT had the most beneficial effect on the mentioned thermal protective properties.

When comparing composite samples in terms of thickness, 12 mm thick samples are more resistant to heat flux than 6 mm thick samples. This applies to both groups of composites. Unfortunately, not all samples achieved the same measurement time because the 6 mm thick samples burned completely faster, achieving a shorter measurement time. The lowest temperature of the back surface of the wall, *Ts*, was obtained for the sample with 2% MMT addition, i.e., approx. 50 ºC, ensuring the maximum temperature reduction. The same can be observed in the ablation mass loss U_a, which was approximately 45% for the average thickness of both samples, as well as in the ablation speed v_a, i.e., 24 μm/s. Generally, the 2% amount of the nano-additive had the best effect on all measured parameters determining the ablative thermal protective properties. These parameters provide the most excellent thermal stability.

Cured LH 145 resin samples are not an excellent ablative material. However, during this work, an improvement in the ablative properties was demonstrated by the use of nanofibers. A particularly favorable change in properties was achieved by a linear increase (by volume) of the addition of MMT to the LH 145 resin.

Samples of ablative composites with two nano-additives, i.e., MMT and IGCWNTs, showed no particular heat flux resistance. The obtained results can be used to continue ablation research using nanofillers, especially with a significant increase in the mass share of nano-additives. The authors of the paper see a much better tendency to use MMT in subsequent cycles of testing the ablation properties of nanocomposites.

5. Copyright Statement

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