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## **THERMO-PROTECTIVE PROPERTIES OF POLYMER COMPOSITES WITH NANO-TITANIUM DIOXIDE**

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### **ABSTRACT**

The present work investigates the ablative and thermal properties of an epoxy resin which was modified with titanium dioxide nanoparticles having different size. Prepared samples were submitted to temperatures above 1900°C and tested for their. The effect of epoxy composite components on thermo-protective and ablative properties: the maximum back side temperature and the average weight loss under intensive heat flow conditions, as well as temperature distribution on the ablation surface of the sample using a thermographic camera and a pyrometer have been established. A statistical analysis of the test results was made. It was confirmed that epoxy resin crosslinked with PAC hardener and modified with TiO<sub>2</sub> (21 nm) i TiO<sub>2</sub> (100 nm + 1%Mn) showed improved thermo-protective properties in comparison with unmodified epoxy matrix.

**Keywords:** epoxy Nanocomposites, ablative properties, thermal resistance.

### **INTRODUCTION**

The scope of experimental work is aimed at acquiring knowledge about basic phenomena occurring in ablation processes of epoxy nanocomposites, in the aspect of thermo protective properties of these composites as materials used under fire hazard or short-term intense thermal flux interaction conditions.

Ablation is a self-regulating process of heat and mass exchange leading to occurrence of physical changes and chemical reactions, irreversible structural and chemical changes of the material with the simultaneous heat absorption. This process is initiated and sustained from external sources of thermal energy. The thermal decomposition in the initial phase of the ablation process and the pyrolysis reactions at a higher temperature leads to the formation of a porous carbon layer with a very low thermal conductivity coefficient (so-called ablative layer) up to 2/3 of the initial matrix weight (Lin, 2005; Feng-Er, 2004; Dimitrienko, 1997).

The term ablation refers to the exchange of heat and mass in the body's upper layer in thermochemical and mechanical processes. There are many technical applications for ablative material. Polymeric ablation materials are increasingly used in the field of thermal protection systems. They can be used in the design of passive refractories for load-bearing structures of large-size buildings (NIST NCSTAR 1, 2005; Wilkinson, 2002), communication tunnels (Haack, 2004; Ono, 2006) and for protection of data stored on electronic, optical, magnetic, etc.

Modeling ablative thermo-protective properties consists in the selection of materials with high specific heat  $c_p(t)$  and high density  $\rho$ , high thermal capacity and with low thermal conductivity coefficient  $\lambda(t)$  (ie small thermal diffusivity  $\alpha(t)$ ) (Kucharczyk, 2007; Song, 2003). In polymeric composites, when the ablation temperature  $T_a$  is exceeded, there are endothermic reactions related to the thermal decomposition of the matrix material, which results in effective specific heat  $c_p$  with high values. In their pure form, polymers are good ablative materials (Bahramian, 2009; Bakar, 2016) with a very low heat conduction coefficient  $\lambda$ . However, due to their softening, low density and low thermal stability as well as the porosity and brittleness of the ablative layer formed in the ablation process, they need to be modified with mineral fillers (Bahramian, 2009; Lombardi, 2012) or reinforcing fibers wzmacniającymi (Jackowski, 1986; Bahramian, 2013; Kucharczyk, 2012; Patton, 2002) increasing their thermal stability, resistance to heat flow, and consequently the thermal insulation of the composite.

Epoxy composites and specific shells will protect machines, devices, components of building structures and people during incidental thermal loads much higher than expected, when the temperature increase, e.g. of carbon steel above 800°C, can cause a 6 - 8 fold decrease in its tensile strength and almost twice reducing its stiffness. Classical refractory materials do not protect against the temperature increase on the back surfaces of the protective layers as effectively as polymeric ablation materials, whose high thermal resistance of  $r_{kp}$  ( $\text{m}^2 \cdot \text{K}/\text{W}$ ), allows to reduce the temperature in the range from several dozen degrees to 2000°C, with the use of insulating walls of small thickness (Kucharczyk, 2018).

Ablative screens can also protect stored data of electronic, optical, magnetic carriers, etc. Classic materials and fire-fighting systems do not provide this possibility, because in emergency situations even rapid fire suppression does not reduce the heat transfer through the protective wall to the extent that it does not exceed the allowed operating temperature of the data carrier (Kucharczyk, 2010).

Recently, attempts have been made to obtain hybrid composites, among others based on epoxy resins, that contain more than one modifier. An important advantage of hybrid materials is a unique combination of mechanisms for properties improvement which may lead to synergistic effect unrealizable at all with traditional composites with one modifier (Bakar, 2014; Szymańska, 2017).

Due to the ease of processing and fairly good physical properties, there is an increasing interest in using not only thermoplastics but also thermosetting plastics as matrix for composite materials (Kucharczyk, 2013; Bakar, 2010; Szymańska, 2017).

Considering the subject of investigating such materials is particularly important for the researchers and industrialists, because in connection with the existing terrorist threat, this subject is becoming more and more important, which was included in the NATO-DAT (Defense Against Terrorism) program. Based on the analysis of the effects of terrorist attacks in Oklahoma City, on the World Trade Center (NIST NCSTAR 1, 2005; Wilkinson, 2002), the behavior of this type of materials is tested and analyzed using computer programs (Willam, 2004). These materials are beginning to be used to protect a few but important public utilities. Despite many years of use of ablative materials, there are still unexplored qualitative and quantitative relationships between the indicated type-phase composition and thermo-protecting properties of composites.

Conducting research will enable the development of assumptions for the constitution of polymer ablation composites to protect people, machines, devices and load-bearing construction structures against short-term exposure to high temperature flux, as well as to

describe the quantitative and qualitative impact of epoxy modifiers on the ablation process and their selected strength properties.

The results of the work can be application-oriented, form the basis for the design of thermal shields, especially for the protection of civil structures, and can be a preliminary stage for designing structures and developing technologies for modern aviation components with such systems.

The aim of the present study was to determine the effect of nanoparticles on the ablative properties, i.e the maximum temperature of the rear surface area  $T_{s\_max}$  and ablative weight loss  $U_a$  of epoxy composites containing two  $TiO_2$  nanoparticles with different particles size (21 nm and 100 nm). Prepared epoxy nanocomposites had to be used as thermal protective surfaces in machines and equipments.

## EVALUATION OF ABLATIVE PROPERTIES

On the basis of the developed research plan, the research works was carried out as follows:

1. Material samples were made for classical, thermo-protective ablative tests.
2. A classic ablation study was carried out using the effects of high temperature heat flux.
3. The effect of components on erosive and ablative material wear as well as the temperature of the back surface of the sample wall of the tested composites in classical ablation tests was assessed.
4. A statistical analysis of the test results was made.
5. Probable reasons for the interaction between the epoxy composites components and the possibilities of thermo-protective protection of the structures were discussed and established.

The aim of the present study was to determine the effect of phase composition on the ablative properties, i.e the maximum temperature of the rear surface area  $T_{s\_max}$  and ablative weight loss  $U_a$  of epoxy composites containing two nano-modifiers ( $TiO_2$  (21 nm) and  $TiO_2$  (100 nm + 1%Mn)). The prepared epoxy based composites had to be used as thermal protective surfaces in machines and equipments, from their phase components after 120 s of exposure to the high-temperature flammable gases.

The so-called “ablative gun” (Song, 2003) of our own design (Kucharczyk, 2007) was used or the classical ablation tests of thermo protective properties, allowing the effect of high temperature, stabilized, homogeneous flammable gas stream on the sample. The temperature distribution was recorded on the ablation surfaces and the back surfaces of the sample walls by using the available pyrometers, thermovision camera and thermocouples. Ablation weight loss were determined.

The research on ablation properties of thermo protecting epoxy hybrid nanocomposites, was carried out on the basis of the developed statistical program of the first-order experimental test of type  $2^3$  with repetitions (Montgomery, 2009; Leszek, 1997).

## MATERIALS USED AS COMPONENTS OF EPOXY-NANOCOMPOSITES

Considering the differences of some specific physicochemical, technological and utility properties, susceptibility to processing, production costs or availability of components, and

results of literature analysis, epoxy nanocomposites modified with titanium dioxide nanoparticles were selected for the study.

A liquid epoxy resin Epidian 52 produced by Sarzyna Chemical Company (Nowa Sarzyna, Poland) was chosen as a matrix for nanocomposites. It is a mixture of a low-molecular diglycidyl ether of Bisphenol A and an active diluent which reacts with the hardener during the epoxy resin curing process. A polyaminoamide hardener with the trade name PAC produced by ZCh Ciech-Sarzyna in Nowa Sarzyna (Table 1) was used as crosslinking agent.

Table 1 - Epoxy resin and curing agent characteristics (Ciech-Sarzyna Co, 2014)

Resin - Epidian 52	Curing agent - PAC
<p>Mixture of diglycidyl ether of Bisphenol A having an average molecular weight of 700 g/mol and <i>butyl glycidyl ether</i>:</p> <ul style="list-style-type: none"> <li>• melting temperature (cured): 150°C;</li> <li>• density (20°C): 1.12 g/cm<sup>3</sup>;</li> <li>• viscosity (25°C): 400 - 800 mPa.s.</li> <li>• ignition temperature: 64°C.</li> </ul>	<p>Polyaminoamide:</p> <ul style="list-style-type: none"> <li>• pH = 12,3;</li> <li>• it doesn't undergo boiling (temp. &gt; 250°C)</li> <li>• coagulation temperature: 3 - 4°C;</li> <li>• density (20°C): 1.10 - 1.20 g/cm<sup>3</sup>;</li> <li>• viscosity (25°C): 10 000 - 25 000 mPa.s;</li> <li>• ignition temperature: ~170°C.</li> </ul>

The hardener (PAC) is mainly used for the modification and curing of low molecular weight epoxy resin. It is a low-reactive, viscous liquid that can be used in a wide range of weight ratios. The lifetime of the epoxy composition with PAC hardener is several hours, and complete curing takes place within 4 - 7 days.

Two types of Sigma-Aldrich titanium nanodioxide were selected to modify the epoxy matrix (Sigma-Aldrich Co, 2014):

- molecular weight: 79.87 g / mol;
- density at 25°C: 4.26 g / cm<sup>3</sup>;
- pH = 5 - 8.5;
- melting point: 1250°C;
- particle size: TiO<sub>2</sub> (21 nm) 21 nm and TiO<sub>2</sub> (100 nm + 1% Mn) 100 nm (containing 1% Mn additive).

Titanium oxide occurs naturally in many types of rocks and minerals in three crystalline forms, as rutile, anatase or brookite (Figure 1). It is the ninth most common element in the Earth's crust. Additionally, it absorbs UV rays in the range of 290 - 400 nm and is usually considered as chemically inert (Anselme, 2013; Bowers, 2012).

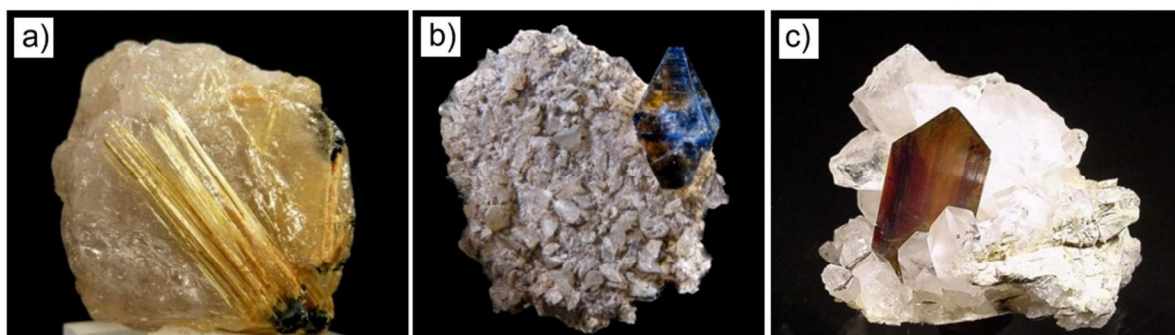


Fig. 1 - Titanium oxide crystalline forms: a) rutile, b) anatase, c) brookite (Anselme, 2013; Bowers, 2012)

The titanium oxide in the nano form with particles has a size less than 100 nm has been selected in the present study. The particles are strongly bound or connected with each other by means of chemical bonds, forming aggregates, i.e. particles of micro scale size (Anselme, 2013).

Titanium dioxide is characterized by: high refractive index in the range of 2.616 - 2.903 (higher than for diamond); low optical absorption in the visible range; good chemical stability; high chemical resistance; high hardness of about 6 on the Mohs scale; high permeability (120 for rutile); high resistance (Sigma-Aldrich Co, 2014).

Titanium dioxide has been used for several decades in many industries, including in the production of fibers, printing inks, adhesives, varnishes, rubber composites, LCD screens, self-cleaning glass and ceramics, antibacterial materials, resistant to UV rays and conductive, food packaging, air and sewage treatment processes, and also in the metallurgical and aerospace industries and cosmonautic (Rao, 2012; Fujishima, 2006; Hu, 2003; Li, 2003).

Titanium dioxide in the nano form is characterized by significantly better properties and a wider range of use compared to standard titanium oxide.

Al-Ajaj et al. (Al-Ajaj, 2013) as well as Rajabi (Rajabi, 2013) conducted research on the influence of micro and titanium dioxide on the properties of epoxy resin. Both research groups have shown that the use of titanium nanodioxide increases the flexural strength, Young's modulus and resistance to cracking, as well as an increase in glass transition temperature. This is caused by a reduction in the distance between the nanofiller and the polymer chain, the polarity of the particles, the strength of the van der Waals bonds in the matrix and the length of the polymer chains, as confirmed by Merad (Merad, 2011), Hsieh and others (Hsieh, 2010).

Chen (Chen, 2007) and Chatterjee (Chatterjee, 2008) and their research groups showed that as the content of the nanofiller in the EP / TiO<sub>2</sub> composite increases, the stiffness of the sample increases. This is mainly attributed to increased limitations of the polymer chains movement due to the presence of solid particles.

In addition, Chatterjee *et al.* showed significantly improved thermal, mechanical and viscoelastic properties of the epoxy resin with the addition of titanium dioxide nanoparticles.

Chang *et al.* (Chang, 2005) investigated the effect of the addition of titanium dioxide on the tribological properties of epoxy resin. They showed that the small addition of the nanofiller visibly reduces the coefficient of friction.

Wetzel *et al.* (Wetzel, 2006) modified epoxy resin by using titanium dioxide and aluminum oxide nanoparticles, focusing mainly on the strengthening, cracking mechanism and improvement of thermal resistance of the composite. The controlled dispersion process was obtained by using high energy to reduce the size of agglomerates and to obtain a homogeneous distribution of individual nanoparticles in the resin.

## EXPERIMENTAL RESEARCH PLAN

The number of sample phase compositions, equal to the number of scheduled experiments ( $N = 8$ ), was determined on the basis of the experiment plan described by an orthogonal 1<sup>st</sup> order full-factorial matrix of the type  $2^3 = 8$  (Table 2). It included single replications, where two state levels (lower level -1 and upper level +1) and three independent input variables ( $x_i$ ) ( $i = 1, 2, 3$ ) occur (Montgomery, 2009; Leszek, 1997):

- $x_1$  proportion of PAC hardener relative to Epidian 52 resin ([phr] - number of parts by weight of the hardener per 100 parts of resin).  
 (-) 60 ns i (+) 100 ns,  $x_{1(sr)} = 80$  ns,  $\Delta x_1 = 20$  ns;
- $x_2$  volume fraction of the mixture of both TiO<sub>2</sub> nanofillers in the composite [%]  
 (-) 2% i (+) 5%,  $x_{2(sr)} = 3.5\%$ ,  $\Delta x_2 = 1.5\%$ ;
- $x_3$  weight fraction of TiO<sub>2</sub> (21 nm) to the sum of the weight of both nanofillers TiO<sub>2</sub>(21 nm) / [TiO<sub>2</sub>(100 nm + 1%Mn) + TiO<sub>2</sub>(21 nm)], [%].  
 (-) 60% i (+) 90%,  $x_{3(sr)} = 75\%$ ,  $\Delta x_2 = 15\%$ .

The components of the response variable  $y$  (the output parameters) are the average maximal temperature of the rear surface of specimen  $T_{s\_max}$ , (°C) and an average relative ablative (erosive) weight loss  $U_a$ , (%) after 120 s of treatment with hot combustion gases.

Table 2 - Full-factorial planning matrix type 2<sup>3</sup> with repetition (Montgomery, 2009; Leszek, 1997)

$j$	$x_0$	$x_1$	$x_2$	$x_3$	$x_1x_2$	$x_1x_3$	$x_2x_3$	$x_1x_2x_3$	$\bar{y}$
1	+	-	-	-	+	+	+	-	
2	+	+	-	-	-	-	+	+	
3	+	-	+	-	-	+	-	+	
4	+	+	+	-	+	-	-	-	
5	+	-	-	+	+	-	-	+	
6	+	+	-	+	-	+	-	-	
7	+	-	+	+	-	-	+	-	
8	+	+	+	+	+	+	+	+	
	$b_0$	$b_1$	$b_2$	$b_3$	$b_{12}$	$b_{13}$	$b_{23}$	$b_{123}$	

The regression and interaction coefficients ( $b_i$ ) of all function components have been calculated. The statistical analysis of the test results enabled to determine the threshold relevance of the regression coefficients ( $b_i$ ) and estimation of their effect on the output parameters ( $y$ ). The output value was calculated from the following equation of the experiment objective (1) (Montgomery, 2009; Leszek, 1997):

$$y = (b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3) \pm s(y) \quad (1)$$

Moreover, the variance  $s(y)$ , regression error and interaction coefficients  $s(b_i)$ , as well as the level of their statistical significance ( $b_{sign} \geq b_i$ ) have been determined on the basis of t-Student test at the confidence level  $\alpha_p = 0.05$  (Montgomery, 2009; Leszek, 1997).

## SAMPLES PREPARATION

The polymer matrix of the composite samples was Epidian 52 epoxy resin, cross-linked at room temperature with PAC hardener (curing time - 14 days). The ablation properties of the resins were modified by adding high density bulk nanofillers (titanium dioxide with a grain size of 21 nm and 100 nm).

The weight fraction of the hardener ( $x_1$ ) and the content of powder fillers ( $x_2$  - the volume fraction of the mixture of both fillers in the composite and  $x_3$  - the weight fraction of TiO<sub>2</sub> (21 nm) in the total weight of both nanofillers) were independent variables of the Type I test plan with repetition and were presented using an orthogonal full-matrix matrix. The weight compositions of the obtained composites are summarized in Table 3.

Table 3 - The mass phase compositions of the composites

№	x <sub>1</sub>	x <sub>2</sub>	x <sub>3</sub>	Resi -n, (g)	Curing agent, (g)	TiO <sub>2</sub> (21 nm + 100 nm), (g)	TiO <sub>2</sub> (21 nm), (g)	TiO <sub>2</sub> (100 nm), (g)
1	-	-	-	14.898	8.939	1.896	1.138	0.758
2	+	-	-	11.823	11.822	1.896	1.138	0.758
3	-	+	-	14.442	8.665	4.741	2.845	1.896
4	+	+	-	11.460	11.461	4.741	2.845	1.896
5	-	-	+	14.898	8.939	1.896	1.706	0.190
6	+	-	+	11.823	11.822	1.896	1.706	0.190
7	-	+	+	14.442	8.665	4.741	4.267	0.474
8	+	+	+	11.460	11.461	4.741	4.267	0.474

The epoxy composite samples were prepared as follows:

- appropriate amount of TiO<sub>2</sub> (21 nm) was added to epoxy resin Epidian 52 and mixing of ingredients was carried out by using a Hielscher UP200H homogenizer (cycle: 1, amplitude: 100%) during 15 min;
- addition of a second nanofiller TiO<sub>2</sub> (100 nm + 1% Mn) to the mixture;
- mixing of ingredients using homogenizer during additional 15 min;
- cooling of obtained mixture to room temperature;
- addition of the curing agent;
- mechanical mixing of obtained composite for 5 min;
- pouring the mixture into previously prepared forms;
- curing of samples at room temperature during 14 days.

The “reference” samples (unmodified, cured epoxy resins) were prepared by adding appropriate amounts of hardener to the epoxy resin followed by mixing the ingredients.

Sample 01 contained 60 phr of PAC hardener, while sample 02 contained 100 phr of hardener. The curing time of the samples in the molds was 4 days at room temperature and then post-cured at 70 °C for 72 hours.

Samples for ablative tests were formed in laboratory conditions. A total of 20 composite samples with dimensions of 12 x 35 x 26 mm were prepared for the tests.

## ABLATIVE TESTS AND THEY RESULTS

Composite samples were weighed and mounted on plasterboard shields on a stand designed for ablation research prior to ablation test. Next, in a test which lasted  $t = 120$  seconds, the samples were exposed to a stabilized stream of combustible gases (Figure 2). The heat source was a burning of propane-butane mixture (65% propane and 35% butane) with temperature of flammable gases above 1900°C. The flame was stabilized with an ablation gun (Fig. 2b), whose axis was set perpendicularly to the front surface of the sample (26 x 35 mm). The gun nozzle was set at a distance of 30 mm away from the surface of the ablation surface. The above configuration of the ablation test stand allows stabilizing the flame, unifying the temperature on the ablation surface as well as ensuring the repeatability of results for all test samples.

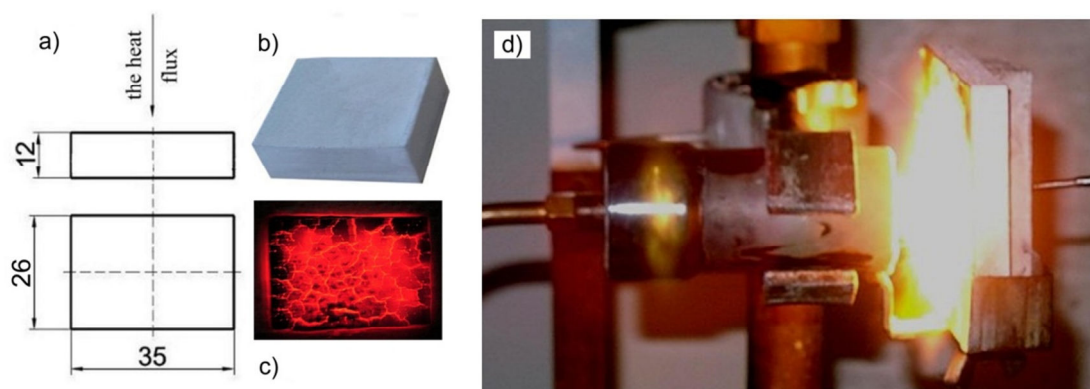


Fig. 2 - The tested samples: (a) size and direction of the exposition of the heat flow, (b) the shape, (c) at the moment after ablative test, d) during the test with the ablative gun

During the tests, the following temperatures were measured and recorded on the measurement stand (Figure 3):

1. The ablative surface  $T_{pa}$  with a thermovision camera Thermo Tracer NEC H2640 at the 60<sup>th</sup> second of each test.
2. The ablative surface  $T_{pa}(t)$  using an optical pyrometer OPTCT2MHCF by Optris GmbH, set at an emissivity of  $\varepsilon = 0.95$  and featuring a continuous electronic recording of temperature variations using Compact Connect 1.7.3 software.
3. The rear sample wall surface  $T_s(t)$  by means of TP-204N (NiCrSi-NiSi) thermocouple by Czaki Thermo-Product using a measurement module USB-4718 by Advantech.

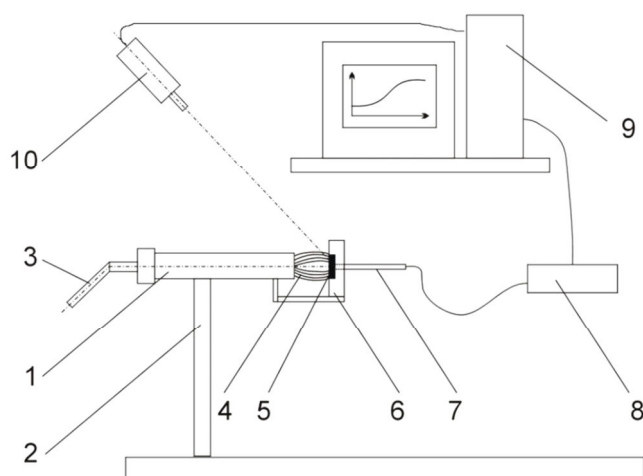


Fig. 3 - Measurement stand: 1 - the ablative gun with flammable gases stabilization, 2 - a tripod, 3 - a torch, 4 - a flame, 5 - the testing sample, 6 - a sample casing, 7 - the thermocouple, 8 - the temperature measurer of  $T_s(t)$ , 9 - a computer, 10 - the pyrometer or the thermovision camera to  $T_{pa}(t)$  measurement

Using a thermovision camera, the temperature distribution on the ablation surfaces of the tested samples was recorded. Figure 4 shows sample results of temperature measurement on the surface of the sample № 8, in the 60 second of the ablation sample. The brightest area in the upper part of the sample (point A) corresponds to the highest temperature on the surface - equal to 961.5 °C. The darker areas (points B and C) correspond in turn to its lower values, 780.7 °C and 616 °C. Further away from the hot spot of the sample, the lower temperature values. The position of the point A in the upper area of the sample is caused by the rising of the hot gas jet upwards.



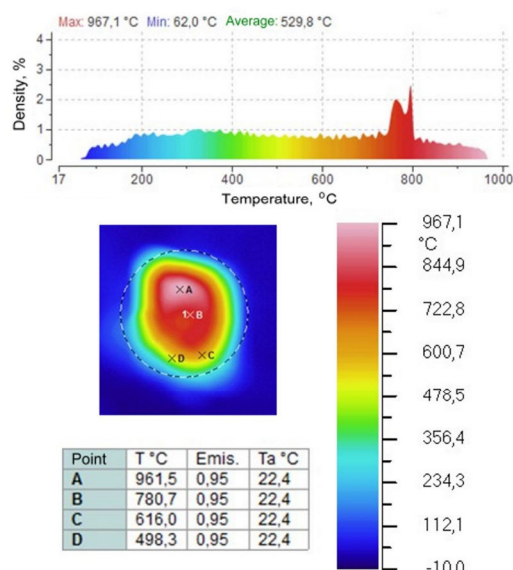


Fig. 4 - Example of the temperature field on the ablative surface at 60 s of the heat flow exposition (sample № 8)

The temperature of ablative surface (shown in Figure 5) resulted from the heat transfer at boundary between gas and solid state material, the heat conduction through the wall of the composite and the ablative processes taking place on surface layer (endothermic chemical reactions, polymer degradation and different structural changes). The value of this temperature depended on physical properties of solid material and gas, as well as insulating wall geometry. Ablative surface temperature  $T_{pa}$  was considered as an indirect input testing parameter and was assumed as first type boundary condition for *Dirchlet* (determined by the temperature distribution anytime on the surface of the body), enabling in the future the resolution of Fourier Kirchhoff differential equation of unsteady heat conduction in solids (Kucharczyk, 2007; Bakar, 2016).

The average value of all measured maximum temperature  $T_{pa\_max}$  was 875°C with a standard deviation of 14°C (Figure 6).

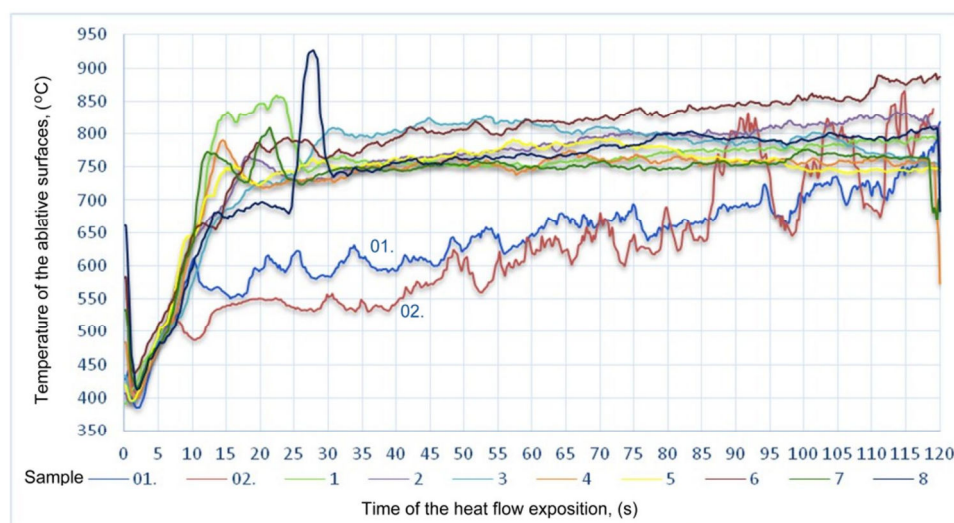


Fig. 5 - Temperature on the ablative surfaces  $T_{pa}(t)$  during 120 s of the heat flow exposition

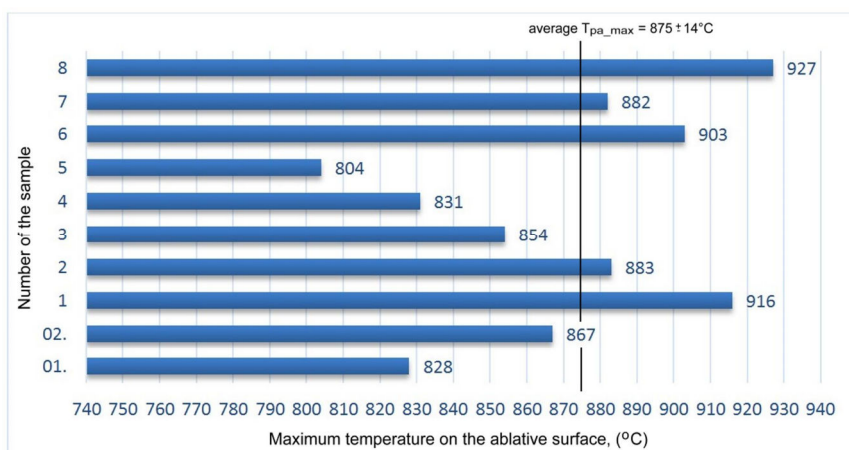


Fig. 6 - Average maximum temperature on the surface of ablation  $T_{pa\_max}$  for particular phase compositions after 120 s of the heat flow exposition

The temperature values obtained on the surface of the rear wall  $T_{s\_max}$  depend upon the possibility of using the material as a protective shield for a wide range of applications. The temperature of the surface on the rear  $T_s(t)$  wall was measured for a period of 120 seconds. Figure 7 shows temperature curves on the surface of the rear wall of the samples for each phase composition of the ablative composite.

The highest temperature  $T_{s\_max}$  of unmodified epoxy resin crosslinked with 100 phr of PAC hardener (composition № 2) was almost three times higher than epoxy composite samples. During the last seconds of the test, the sample was destroyed as recorded by a sharp increase in temperature on its back surface (Figure 7). However, the reduction of the hardener content to 60 phr (composition № 1) resulted in decrease of  $T_{s\_max}$ , which still remained almost 30% higher than for the epoxy nanocomposites (Figures 7 and 8).

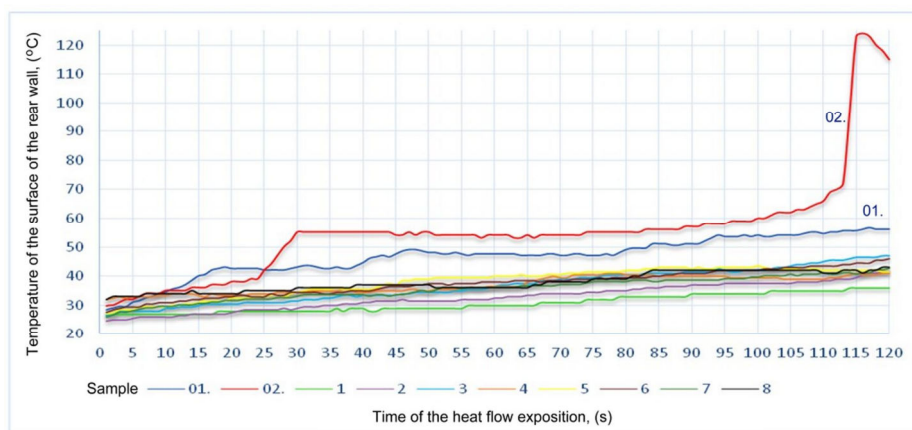


Fig. 7 - Changing of the rear surface temperature  $T_s(t)$  during 120 s of the heat flow exposition

Resin Epidian 52 modified with a nanofiller showed better thermo-protective properties. Composition № 1 based on 60 phr of hardener PAC, with a content of 2% by volume of a mixture of titanium dioxides, including 60% by weight  $TiO_2(21\text{ nm})$ , reached the lowest temperature  $T_{s\_max}$  from all tested composites.

Histograms of temperature changes  $T_{pa}(t)$ , for samples from unmodified resins (compositions № 1 and № 2), are well below the graphs for epoxy nanocomposites (Figure 5). Under fixed conditions, the heat transfer between gas and solid depends on the resistance of heat transfer

$r_{kp}$ , ie the value that include the physical properties of the material and gas with the geometry of the insulating wall. Thus, from the analysis of histograms temperature  $T_{pa}(t)$ , and  $T_s(t)$  (Figures 5 and 7), it follows that the lower temperature of the ablation surface  $T_{pa}$  is due to higher rates of heat transfer at the border gas-solid, and thermal conduction through the wall of the composite, which is equivalent to an increase in the temperature of the rear face of the wall  $T_s$  of a given material and depends directly on its phase composition. The greatest degree of reduction in temperature difference or  $T_{pa}(t) - T_s$ , the characterized nanocomposite epoxy compositions № 1 and № 8. According to the laws of Pécleta have the greatest resistance to heat transfer replacement  $r_{kp}$  of the test materials. From the point of view of thermo-protecting properties, it is important that the temperature of the rear face of the wall  $T_s$  of the ablative shield (s) is the lowest after a given time of exposure to the heat flux. However, composites with a higher temperature on the ablation surface and a lower temperature on the back surface of the sample wall (higher temperature gradient) are subjected to higher thermo-mechanical stresses, which can lead to the destruction of the ablation shield (Kucharczyk, 2010).

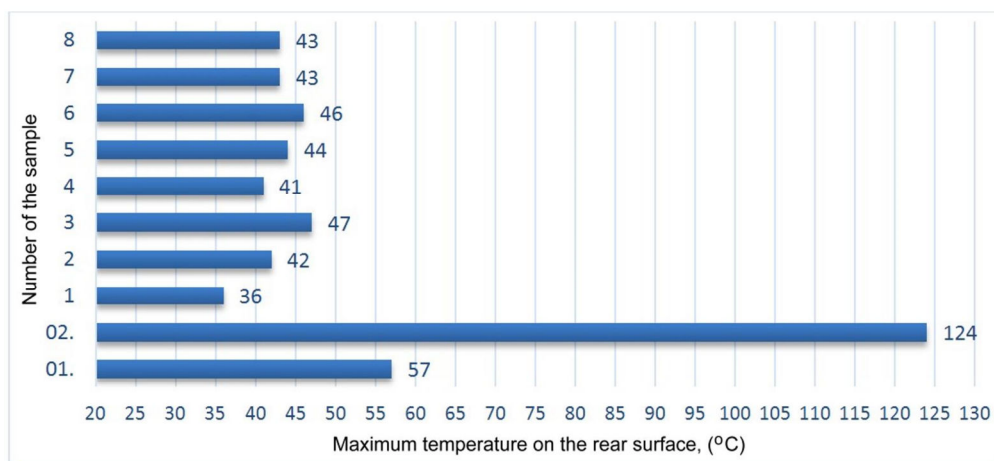


Fig. 8 - Average maximum temperature on the rear surface  $T_{s\_max}$  for particular phase compositions after 120 s of the heat flow exposition

In this context, the ablation (erosive) weight loss of the  $U_a$  composite becomes more important. The smaller loss of mass of the ablation layer, indicates higher thermal stability of the composite and a thicker operating top layer (Kucharczyk, 2010) with a low thermal conductivity coefficient  $\lambda(t)$ . The smallest erosive wear after 120 s during the impact of the stream of combustible gas, the composition of the sample has suffered phase № 4 (Table 4), which is characterized by a second in order  $T_{s\_max}$  low temperature (Figure 9).

The average values of ablative results of the tests (i.e the maximum surface temperature of the ablation  $T_{pa\_max}$ , the maximum temperature of the back surface area of an ablative sample  $T_{s\_max}$  and ablative weight loss  $U_a$ ) are shown in Table 4.

Table 4 - The results of thermal protective tests after 120 s of treatment with hot combustion gases

Parameter	Number of specimen, №									
	01	02	1	2	3	4	5	6	7	8
$T_{pa\_max}$ (°C)	828	867	916	883	854	831	804	903	882	927
$T_{s\_max}$ (°C)	57	124	36	42	47	41	44	46	43	43
$U_a$ (%)	65.2	90.7	67.1	58.8	37.7	34.0	47.7	65.3	38.8	37.1

The lower weight loss is exhibited by composites containing a higher amount of nanofillers, i.e. 5% by volume fraction - phase compositions № 3, № 4, № 7 and № 8 (Figure 9). Samples № 4 and № 8 were cross-linked with a higher amount of hardener (100 phr). The smallest weight loss (34%) was shown a composite № 4, containing less  $\text{TiO}_2$  (21 nm), than composite № 8. Sample "reference" № 2, cross-linked (similarly to composite № 4) 100 phr of hardener PAC, reached the largest ablation fat loss, upto about 90%. This indicates the adverse effect of a larger amount of PAC hardener on the thermal stability and thermo-protective ablative properties of pure, unmodified Epidian 52 epoxy resin.

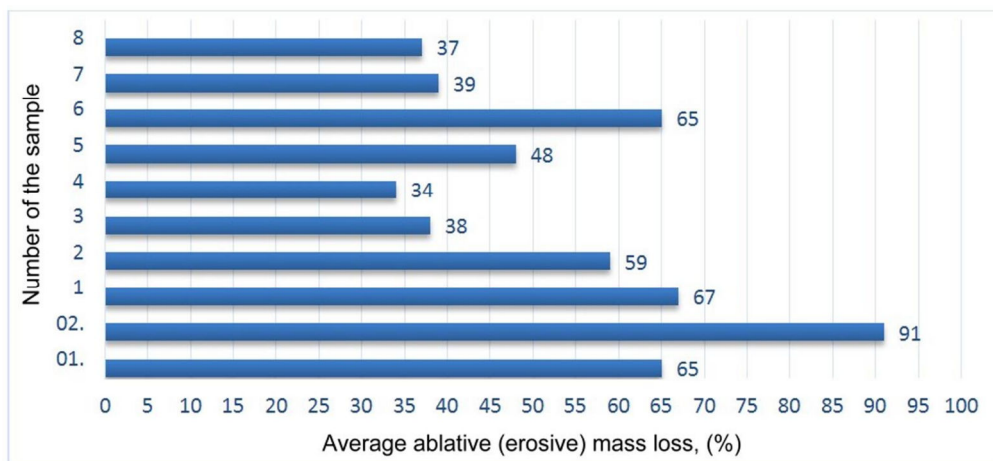


Fig. 9 - Average ablative (erosive) mass loss  $U_a$  after 120 s of the heat flow exposition

Epoxy composites have undergone intensive decomposition and pyrolysis during the ablation process with harmful volatiles products to human health. The formed ablative layer during the process was not consistent but brittle, very porous and automatically separated from the original material (Table 5). This constituted a negative phenomenon, which reduced both the strength and durability of coatings and their thermal protective characteristics.

Composites based on epoxy resins have undergone intensive decomposition and pyrolysis during the ablation process with harmful volatiles products to human health. The formed ablative layer during the process was not consistent but brittle, very porous and automatically separated from the original material (Table 5). This constituted a negative phenomenon, which reduced both the strength and durability of coatings and their thermal protective characteristics.

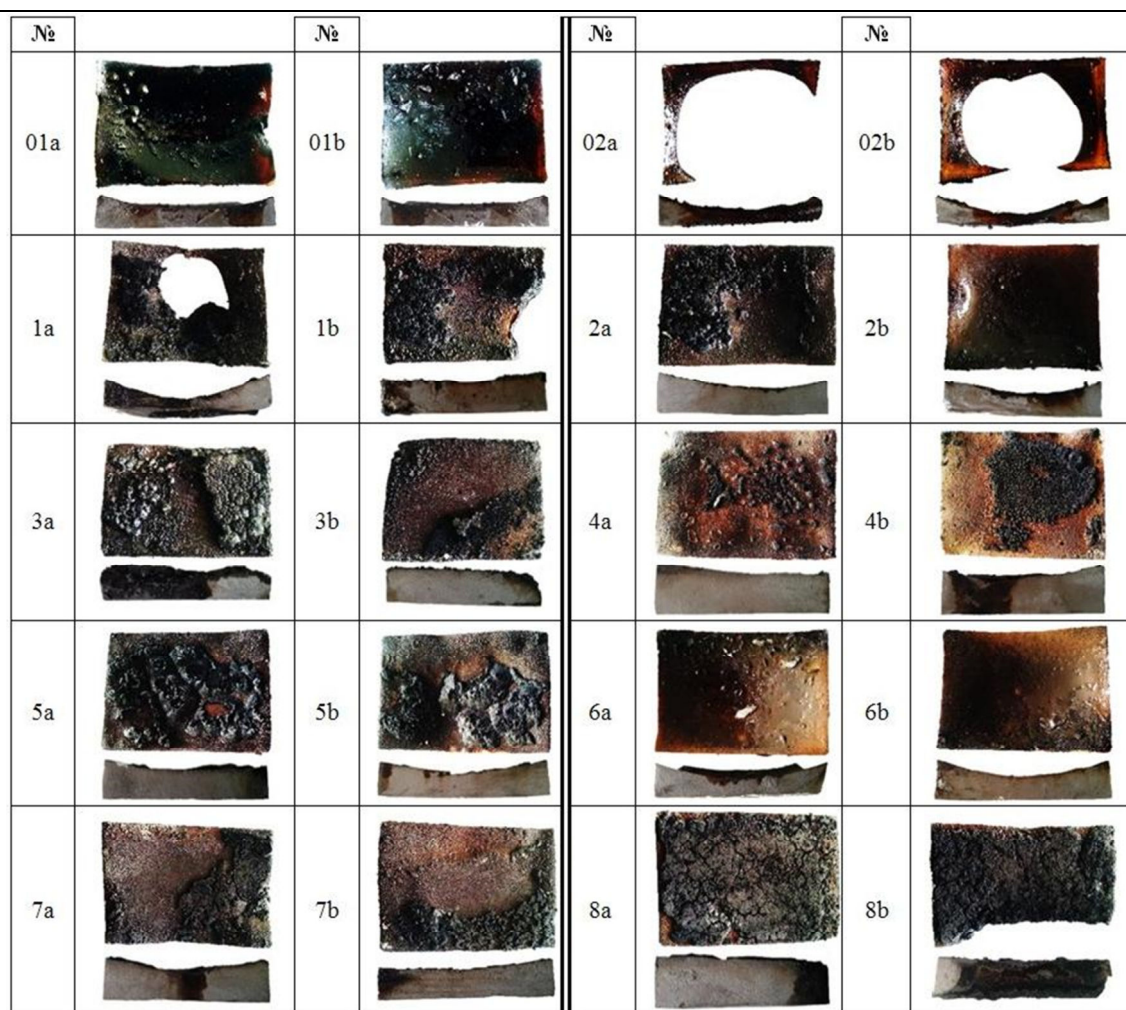
In summary, the smallest weight loss  $U_a$  is characterized by a composite № 4 (i.e. Epidian 52 + 100 phr PAC + 5% by volume of  $\text{TiO}_2$  (21 nm) and  $\text{TiO}_2$  (100 nm + 1% Mn), including 60 wt% of  $\text{TiO}_2$ (21 nm).

The lowest end temperature of the back wall surface of the sample  $T_{s\_max}$  was obtained by the composite sample № 1 with the following composition: Epidian 52 + 60 phr PAC + 2% by volume of  $\text{TiO}_2$  (21 nm) and  $\text{TiO}_2$  (100 nm + 1% Mn), including 60 wt% of  $\text{TiO}_2$  (21 nm).

The best thermoprotective properties were exhibited by the composite which reached the lowest value of the maximum surface temperature of the sample wall  $T_{s\_max}$  (provides the greatest temperature reduction) and the smallest ablation weight loss  $U_a$  (has the highest thermal stability and is the thickest and most consistent internally, good adhesion to the original, ablative material exploitation layer with low thermal conductivity). Both conditions are best met by a sample with phase composition № 4.



Table 5 - The ablative surfaces and the mass waste of composites after 120 s of heat flux exposition



### STATISTICAL ANALYSIS OF THE RESULTS

Statistical calculations of both the component response functions  $T_{s\_max}(x_i)$  and  $U_a(x_i)$  were conducted using the results of ablative testing. Table 6 shows the calculated values of regression coefficients  $b_i$  and variance  $s(y)$ , errors of regression coefficients  $s(b_i)$ , and significance levels of regression coefficients  $b_{istot}$ . The parameter  $b_i$  is shown in **bold** - it is lower than  $b_{sign}$  but subject to error  $s(b_i)$  which, once taken into account to compute  $b_i$ , helps to estimate the sum total of  $b_i$  and  $s(b_i)$  as larger than  $b_{istot}$ , that is, still significant statistically (Montgomery, 2009; Leszek, 1997).

Table 6 - Regression and interaction coefficients of model (1) after 120 s of ablative tests

	$b_0$	$b_1$	$b_2$	$b_3$	$b_{12}$	$b_{13}$	$b_{23}$	$b_{123}$	$s(y)$	$s(b_i)$	$b_{sign}$
$T_{s\_max}$ (°C)	42.56		<b>0.81</b>	1.19	-1.69		-1.81	1.19	1.34	0.47	1.09
$U_{as}$ (%)	48.31		-11.41			<b>3.49</b>		<b>-2.99</b>	4.73	1.67	3.86

Based on the calculated coefficients of regression and interaction ( $b_i$ ) and considering level of their significance ( $b_{sign} \geq b_i$ ), regression equations of the component response functions (2) and (3) are formulated:

$$T_{s\_max}(x_i) = (42.56 + \mathbf{0.81}x_2 + 1.19x_3 - 1.69x_1x_2 - 1.81x_2x_3 + 1.19x_1x_2x_3) \pm 1.34^\circ\text{C} \quad (2)$$

$$U_a(x_i) = (48.31 - 11.41x_2 + \mathbf{3.49}x_1x_3 - \mathbf{2.99}x_1x_2x_3) \pm 4.73\% \quad (3)$$

Analysis of numerical results of statistical calculations for the maximum back side temperature of tested samples  $T_{s\_max}$  are presented in Table 6 and coefficients of response function  $T_{s\_max}(x_i)$  equation (2) indicates the following rules:

1. A significant effect on decreasing the temperature of the back surface of the sample wall  $T_s$  has two input variables  $x_2$  and  $x_3$  (negative coefficient  $b_{23}$ ). They determine respectively: the content of the mixture of  $\text{TiO}_2(21\text{ nm}) + \text{TiO}_2(100\text{ nm} + 1\%\text{Mn})$  in the composite and the amount of  $\text{TiO}_2(21\text{ nm})$  in the filler mixture. Increasing the number of nanofillers with a higher  $\text{TiO}_2(21\text{ nm})$  content in the mixture resulted in the reduction of the maximum temperature  $T_{s\_max}$ . This interaction does not occur when using a larger amount of hardener (changing the sign to positive at the  $b_{123}$  coefficient).
2. Simultaneous application of larger quantities of hardener and a mixture of nanofillers, resulted in a lower  $T_{s\_max}$  temperature. This is evidenced by the negative value of the interaction factor  $b_{12}$ .
3. Increasing the content of fine-grained oxide  $\text{TiO}_2(21\text{ nm})$  (without increasing the amount of mixture of oxides and hardener content) will increase the temperature  $T_{s\_max}$  (positive coefficient  $b_3$ ).
4. Input variable  $x_2$ , denoting the amount of  $\text{TiO}_2(21\text{ nm}) + \text{TiO}_2(100\text{ nm} + 1\%\text{Mn})$ , in the individual interaction (without taking into account the amount of hardener and composition of the nanopowder mixture), does not significantly affect the temperature of the back surface of the sample wall.

Analysis of numerical results of statistical calculations for the ablative weight loss of test samples  $U_a$  presented in Table 6 and coefficients of response function  $U_a(x_i)$  equation (3) indicates the following rules:

1. The input variable  $x_2$  (negative value of the coefficient  $b_2$ ) has the most important influence on the ablation reduction of  $U_a$  parameter, which means that increasing the amount of  $\text{TiO}_2(21\text{ nm}) + \text{TiO}_2(100\text{ nm} + 1\%\text{Mn})$  decreases ablation weight loss. The value of coefficient  $b_2$  is over three times higher than the coefficients  $b_{13}$  and  $b_{123}$ .
2. Input variables  $x_1$  and  $x_3$ , denoting the amount of hardener and  $\text{TiO}_2(21\text{ nm})$  in the mixture of nanofillers, in mutual interaction (positive value of  $b_{13}$ ), as well as the interaction of all three variables (negative value  $b_{123}$ ) do not significantly affect the value of the response function  $U_a(x_i)$ . In addition, the opposite signs, with both of these coefficients, indicate the mutual abolition of influence.

## CONCLUSIONS

Based on obtained results, it can be concluded that:

1. Composite based on epoxy resin Epidian 52 cross-linked with 60 phr of PAC hardener, with a 2% by volume of a mixture of  $\text{TiO}_2(21\text{ nm}) + \text{TiO}_2(100\text{ nm} + 1\%\text{Mn})$ , including 60% by weight of  $\text{TiO}_2(21\text{ nm})$ , characterized by the lowest temperature of the rear wall surface.

2. Epoxy resin Epidian 52 cross-linked with 100 phr of PAC hardener, with 5% by volume of a mixture of nanofillers  $\text{TiO}_2$  (21 nm) +  $\text{TiO}_2$  (100 nm + 1%Mn), including 60 wt% of  $\text{TiO}_2$  (21 nm), shows the smallest abrasive weight loss  $U_a$ , i.e. the best thermal stability of the virgin material and cohesion of the ablative layer, which improves the resistance to thermomechanical stresses of the composite and ensures the formation of a passive thermo-protective layer.
3. Increasing the amount of PAC hardener in Epidian 52 resin-based composites and increasing the amount of both  $\text{TiO}_2$  (21 nm) and  $\text{TiO}_2$  (100 nm + 1%Mn) led to increase of the maximum temperature of the back wall surface  $T_{s\_max}$  but at the same time contributed to the reduction of ablative weight loss  $U_a$ .
4. Considering the values of both parameters ( $T_{s\_max}$  and  $U_a$ ), it should be noted that the best thermal protection properties were shown by composite № 4, which was characterized by a very low, maximum temperature of the wall surface of the sample  $T_{s\_max}$  (40°C) as well as the lowest value of ablation weight loss  $U_a$  (35%).
5. Epidian 52 epoxy resin composites crosslinked with PAC hardener and modified with  $\text{TiO}_2$  (21 nm) i  $\text{TiO}_2$  (100 nm + 1%Mn) showed better thermo-protective properties compared to virgin unmodified epoxy resins.

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