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ABLATIVE AND ABRASIVE WEAR OF PHENOLIC-FORMALDEHYDE GLASS LAMINATES WITH POWDER FILLERS

ZUŻYWANIE ABLACYJNE I ŚCIERNE LAMINATÓW FENOLOWO-FORMALDEHYDOWYCH – SZKLANYCH Z NAPEŁNIACZAMI PROSZKOWYMI*

This paper reports the results of wearing out polymer composites: the ablative wear, after 30 s of treating with hot combustion gases, as well as the abrasive wear, after 1000 s of friction using the loose abradant in the T-07 tester. The specimens were made of phenolic-formaldehyde matrix, glass fabrics-reinforcement and powder fillers: the corundum Al_2O_3 and the carbon powder C. It was qualified the qualitative and the quantitative effect of components on the average linear rate of ablation v_a and the average mass intensity of abrasive wear I_z. It was proved, that composites with the smaller intensity of abrasive wear I_z are characterized by bigger rate of ablative using up.

Keywords: *ablation, abrasive wear, powder fillers, glass laminates.*

Przedstawiono wyniki badań zużywania kompozytów polimerowych: ablacyjnego, po 30 s oddziaływania wysokotemperaturowego strumienia gazów palnych oraz ściernego, po 1000 s tarcia próbki luźnym ścierniwem w testerze T-07. Doświadczeniom poddano szklane laminaty fenolowo-formaldehydowe z napełniaczami proszkowymi: korundem Al_2O_3 oraz pyłem węglowym C. Określono jakościowy i ilościowy wpływ komponentów na wartości zużywania: średnią liniową szybkość ablacji ν_α oraz średnią masową intensywności zużywania I_z. Stwierdzono, że kompozyty o składach fazowych zapewniających mniejszą intensywność zużywania ściernego charakteryzują się większą szybkością zużywania ablacyjnego.

Słowa kluczowe: *ablacja, zużywanie ścierne, napełniacze proszkowe, laminaty szklane.*

1. Introduction

Modified polymer composites as ablative materials to prevent the excess rise in temperature has been mostly used in armament industry as well as aircraft, rocket and space technology [7, 6]. Such materials can also be used as passive fire protection of load-bearing structures in large-volume buildings [12, 19], tunnels [5, 13], as well as in electronic, optic and magnetic data protection systems, etc.

The development of compositions, manufacturing technologies and research into the characteristics of ablative materials has become of great importance due to the threat of terrorists attacks. It is in the USA that the analysis of the causes and consequences of such disastrous events as Oklahoma City or World Trade Center attacks [12, 19] has brought about a thorough scientific investigation into the behavior of such materials. Ablative materials are beginning to be used in protection of public facilities and structures [12, 19, 5, 13] which can be exposed to fire hazard or short-term, intensive erosive heat flux.

Thanks to autonomous shields and ablative shielding we can protect building structures and people's lives in heat load incidents with temperatures much exceeding permissible standards since the classical flameproof materials cannot prevent the increase in temperature at the rear side of protective shields as effectively as ablative materials whose high characteristics of substitute heat resistance r_{kp} [$m^2 \cdot K/W$] allows the reduction of temperatures by anything from several dozens degrees to ~ 2 000 °C with the use of relatively thin insulation shields.

The ITA (International Tunneling Association) guidelines, for example, recommend flameproof shielding in transport tunnels that should reduce the temperature of concrete down to 350 °C (exceeding this value results in the drop of its rigidity by 50% of the nominal value [20]) and prevent it from peeling and splitting off. The temperature of steel elements used in such constructions must not exceed 300 °C [5, 13] as this is the value beyond which the strength of steel decreases dramatically [2].

Despite the fact that ablative materials have been used for many years we still do not know the dependencies between the quality and contents of a given phase composition of and its ablative characteristics in relation to other operational features of the composites that are used in thermo-insulating shields. [8, 4 , 21].

This paper attempts to answer the question of the influence of the quantitative and qualitative phase composition of phenolic-formaldehyde glass laminates with powder fillers on ablative wear (average linear rate of ablation ν_α [μm/s]) and whether the ablative wear of a composite is related to abrasive wear resistance of the basic material (mass intensity of abrasive wear I_z [mg/s]).

(*) Tekst artykułu w polskiej wersji językowej dostępny w elektronicznym wydaniu kwartalnika na stronie ***www.ein.org.pl***

2. Ablation of polymer composites

The ablation process is the process of exchanging of heat and mass which, due to physical changes and chemical reactions, results in chemical and structural changes of the material with simultaneous heat absorption, which reduces heating up of the material below the front of ablation (Fig. 1). The heat influx causes relocation of the ablation front deeper into the material and thickening of the porous ablative surface [8].

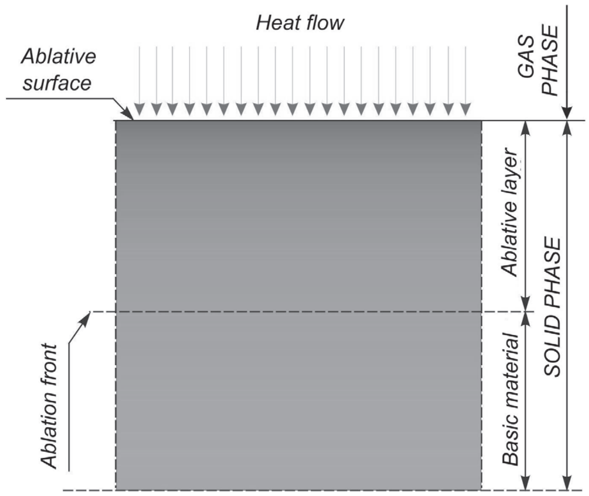

Fig. 1. Physical model of ablation [8]

In polymer composites, when the ablation temperature has been exceeded, there occur endothermic reactions involved in the thermal decomposition of the matrix material due to which the effective specific heat of c_p resins reach very high values. In their pure form such resins are a very good thermo-insulating ablative material [6, 4, 21]. However, due to their softening as well as the porosity and brittleness of the formed ablative surface they require an addition of high-melting fibre fillers [7, 6, 14] or powder fillers [17, 1].

In his paper [3] Yu. I. Dimitrienko proposed a classification of ablation processes in composites treated with heat fluxes (Fig. 2). The process of mass loss $m = \rho \cdot V$ (where ρ is density and V is volume) due to the heat and thermo-mechanical impact of gas fluxes may result in a change in either density or volume as well as in a simultaneous change of both values [3].

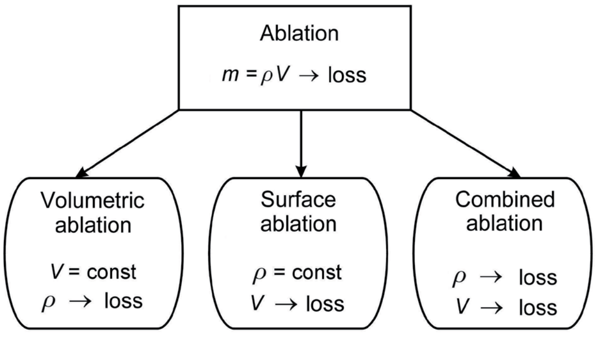

Fig. 2. Classification of main ablation processes of materials: m - mass ρ - density and V - volume [3]

The process of density loss where the volume remains unchanged is a pyrolysis which occurs in temperatures 500 ÷ 1000 °C and is characteristic for polymer composites. Such a process is called *volumetric ablation*. The process in which there occurs a volume loss with unchanged density is called *surface ablation*. It is typical for oxidization o graphite, metals and their alloys, glass as well as some types of fusible ceramic materials. A simultaneous occurrence of both processes of thermal degradation is referred to as *combined ablation*. Combined ablation usually takes place in high temperatures (1000 ÷ 1500 °C) and results from thermal and erosive gas impact. In all of the above-mentioned cases there occur ablative wear (which is sometimes purely erosive) of the basic material [3].

To be able to take the full advantage of ablative materials we need to be aware of their ablative wear characteristics, which have to be taken into consideration at the early stage of the technological design. This includes a loss in active volume of the material that is not subject to ablation. The effect is characterized by linear ablation rate ν_α [μm/s] defined as the average rate of dislocation of the ablation front i.e. the average rate of formation of ablative surface and so-called *vitreous slag*. If we determine the rate of ablation it is possible to determine the temporary location of the ablation front and, in consequence, to determine the thickness of active insulating layer [6, 1, 3, 11].

Processes of ablative wear of thermo-insulating shielding of structures and machinery, which can be exposed to fire hazard, or short-term, intensive erosive heat flux usually occur in failure situations which are incidental by assumption. Throughout the course of its normal operation in the usual operating temperatures, the ablative thermo-insulating shielding of the machinery is exposed to service and mechanical loads (including abrasive wear), which have a negative influence of the ablative characteristics of the materials [7, 21, 3].

3. Choice of materials

Based of bibliography [7, 14, 21], the following materials have been used to prepare the specimens of glass fibre laminate with powder fillers:

1. Thermosetting matrix: PF resins (*Modofen* 54S and *Nowolak MR* used in 1:1 weight ratio) manufactured by Organika-Sarzyna Chemical Works.

2. Fibre reinforcement: balanced glassfibre fabric STR-022 of 250 g/m^2 manufactured by Krosno Glassworks SA.

3. Powder fillers: *corundum* Al_2O_3 (ALO G5-4) with grains of 2 to 5 μm with the minimal contents of aluminum oxide of 99,5% (95% α Al_2O_3) manufactured by Ajka Amumina, Hungary; fine grain carbon powder *C* of 5 μm and purity of 98%.

4. Design of experiments

The number of experiments and the phase compositions of specimens have been determined on the basis of the experimental design, (Table 1) [10, 15] i.e. 2-level orthogonal full factorial design for replicated 2^3 factorial experiments. The composite materials constitute the three input parameters x_i with 2-level coding (–1 as low value and +1 as high value):

x_1 – mass contents of the matrix: 24% (– 1) and 30% (+1);
x_2 – number of fibreglass fabric layers: 8 (– 1) and 12 (+1);
x_3 – proportion of Al_2O_3 corundum to the total mass of both fillers $Al_2O_3/(Al_2O_3 + C)$: 20% (– 1) and 80% (+1).

The components of the response variable *y* (the output parameters) are the average linear rate of ablation ν_α [μm/s] and the average mass intensity of abrasive wear I_z [mg/s].

Table 2 shows the factual phase compositions of the tested phenolic- of formaldehyde laminates and their coding. The regression indexes b_1, b_2, b_3 and the interaction indexes b_{12}, b_{13}, b_{23}, b_{123} determine the influence of a given input value (or several input values i.e. interactions) on $\bar{y}$ which is the output value in the equation of the experiment objective (1) [10, 15]:

$$\bar{y} = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 + b_{123} x_1 x_2 x_3 \quad (1)$$

The values of regression indexes are achieved from the equation (2):

$$\frac{\sum_{j=1}^{8} x_{ij} \cdot \bar{y}_j}{N} \qquad i = 0, 1, 2, 3 \qquad (2)$$

The statistical analysis of the results aims at determining the significance of regression indexes b_i and assessing their influence on the value of output parameter $\bar{y}$ with the following equations [10, 15]. Variance (3) and error in determination of regression indexes (4) are:

$$s(\bar{y}) = \sqrt{\frac{\Sigma\, d_j^2}{2N}} \quad (3) \qquad s(b_i) = \sqrt{\frac{s^2(\bar{y})}{N}} \quad (4)$$

where:

$d_j = \bar{y} - y_{jk}$ ($\bar{y}$ - the average of k number of measure ments; y_{jk} - value of the k^{th} measurement in the j^{th} test; $k = 1, 2$; N - number of tests).

The significance of regression indexes b_i was value for the t-Student's distribution, where $t_{obl} >> t_{tabl}$ ($t_{tabl} = 2{,}306$ with probability $P = 0{,}95$). The equation (5) is thus fulfilled and following transformations we achieve equations (6) and (7):

$$\frac{b_i \cdot \sqrt{N}}{s(\bar{y})} = t_{obl.} \quad (5) \qquad b_i = \frac{2{,}306 \cdot s(\bar{y})}{\sqrt{N}} \quad (6)$$

$$b_{istot} \geq b_i = \frac{2{,}306}{\sqrt{8}} \cdot s(\bar{y}) = 0{,}8153 \cdot s(\bar{y}) \quad (7)$$

5. Ablation and abrasive wear tests

5.1. The ablation testing conditions

The ablation tests of the composites were carried out with the following assumptions: thermophysical characteristics of the materials are solely the temperature function; the heat flux during the test is of constant value; the isothermal surface of the ablation front constitute the ablation surface (Fig. 1); the heat exchange of the outer surface with the environment is omitted [7, 8].

The specimens (10 x 25 x 35 mm cubes) were placed in a shielding of flameproof plaster-cardboard panel and exposed to gas heat flux for $\tau = 30$ seconds. Burning of acetylene and oxygen mixture (with the oxygen/acetylene ratio of 1:1,2) in a *PU-241A* blowpipe provided the source of heat. The blowpipe was equipped with Attachment 3 to ensure so-called neutral flame. The blowpipe was placed perpendicular to the surface of the laminate (in the middle of the 25 x 35 mm side). The ablation surface was situated at the end of the flame reducing zone i.e.

Table 1. Two-level full factorial design for replicated 2^3 factorial experiments [10, 15]

j^*	x_0	x_1	x_2	x_3	x_1x_2	x_1x_3	x_2x_3	$x_1x_2x_3$	y_j
1	+	−	−	−	+	+	+	−	
2	+	+	−	−	−	−	+	+	
3	+	−	+	−	−	+	−	+	
4	+	+	+	−	+	−	−	−	
5	+	−	−	+	+	−	−	+	
6	+	+	−	+	−	+	−	−	
7	+	−	+	+	−	−	+	−	
8	+	+	+	+	+	+	+	+	
	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}	

* **j-value is a test number and also the number of the composite whose phase composition is determined by function of x_i**

Table 2. Coding of variables and the factual phase compositions of the composites

Test no.	Mass ratio of materials in a composite [%]						
	matrix (x_1)		fibreglass fabric (x_2)		powder fillers (x_3)		
						Al_2O_3	C
1	–	24	–	18	–	11,6	46,4
2	+	30	–		–	10,4	41,6
3	–	24	+	25	–	10,2	40,8
4	+	30	+		–	9,0	36,0
5	–	24	–	13	+	50,4	12,6
6	+	30	–		+	45,6	11,4
7	–	24	+	19	+	45,6	11,4
8	+	30	+		+	40,8	10,2

Table 3. Parameters and condition for tribological tests [18]

Load of specimen against counterspecimen: $P = 44$ N	Counterspecimen: a steel roll covered with rubber (hardness of 78 ÷ 85 Sh A)
Rate of rotation of counterspecimen: $n = 60$ r.p.m.	Abradant: electrocorundum no. 90 (PN-76/M-59115)
Duration of test (number of counterspecimen rotations): $\tau = 1000$ s ($N_b = 1000$ rotations)	Output value: Wear intensity I_z [mg/s]

10 mm from its cone. The flame temperature at the ablation surface was approx. 2 500°C [8, 17, 1, 16].

After the heat treatment tests the cross sections of the specimens were made and the measurements of the ablation front and the depth of its relocation were taken to determine the average linear ablation rate v_α.

5.2. Assessment of the intensity of abrasive wear

A modified *T-07* tester for assessment of the abrasion resistance of materials and metal coatings to friction against loose abradant was used do determine the mass intensity of abrasive wear I_z (the change in mass in relation to wearing period) complying with the testing condition and parameters recommended by the manufacturer (see Table 3) [18, 22].

The shape and dimensions of the specimens [9, 22] are shown in Figure 3a while Figure 3b depict a specimen after the abrasive test. The sliding surface and the direction of the friction force were set perpendicular to the glass layers of the laminate (see Fig. 3a) [9].

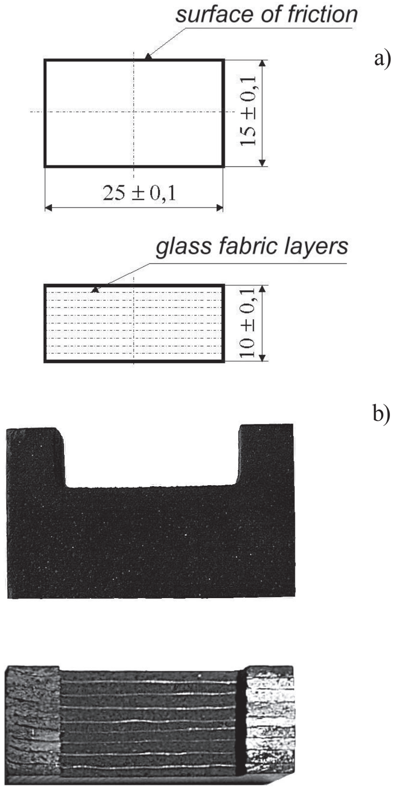

Fig. 3. A tested specimen [9, 22]: a) structural drawing, b) after the test

5.3. The results of ablation tests and tribological tests

The results of ablation tests (the average linear ablation rate v_α) and tribological tests (the average mass intensity of abrasive wear I_z) are presented in Table 4 while Figure 4 shows its graphic interpretation.

The aim of the experiment was to find such a composite whose values of the average linear ablation rate v_α the average mass intensity of abrasive wear I_z are the lowest. These conditions have been fairly met by specimen 4 whose phase composition consists of 30% matrix, 25% fibre glass fabric reinforcement, 9% corundum Al_2O_3, and 36% carbon powder C (fig. 4).

5.4. Statistical analysis of test results

The regression indexes and their significance, the variance, and the determination error were calculated based on the data provided in Table 4 and with formulas (2), (3), (4), and (7). The results are presented in Table 5. The **bold print** marks b_i values, which are lower than b_{istot} but burdened with the error $s(b_i)$ which allows to assess the b_i as statistically significant. The empty cells in the Table mean that the given index is not of any statistical significance and has been omitted. The analysis of the values of b_i - coefficients and the signs preceding them let us assess the influence of independent variables x_i on the output values (response variable). The graphic interpretations of the relation of both response variables (the output parameters) to the phase variables are presented in Figures 5 to 7.

Having analysed the values and preceding signs of the regression and interaction indexes, we can confirm that for the assumed range of independent variables, there exist the relation of the wear parameters to the coding variables that is to the phase composition of the composite.

The higher content of the matrix results in a significant decrease in abrasive wear I_z while the average rate of ablation v_a rises (negative and positive coefficient b_i for both components of the response variable respectively). The content of matrix influences the abrasive wear values in the most significant manner. Thus if its content is lower, the increase in the content of hard corundum must follow.

The change in the number of the fibreglass fabric layers (the change of the content of glass reinforcement) does not have any significant influence on any of the examined wear parameters (insignificant values of b_2). However, the increase in the content of glass reinforcement (x_2) together with the content of matrix (x_1) i.e. the decrease in the content of powder fillers results in a noticeable drop in the ablation rate and a slight increase in the wear resistance (negative b_{12}).

With the higher content of Al_2O_3 (i.e. the lower content of powder carbon C) the wear intensity I_z slightly drops (negative b_3 and b_{13}) but there is a considerable rise in the rate of ablation v_α (positive b_3). The higher number of fibreglass fabric layers (x_2) with simultaneous increase in the content of Al_2O_3

Table 4. The results of ablation tests and tribological tests

Parameter		Number of test							
		1	2	3	4	5	6	7	8
matrix [%]		24	30	24	30	24	30	24	30
fibreglass fabric [%]		18		25		13		19	
powder fillers [%]	Al_2O_3	11,6	10,4	10,2	9,0	50,4	45,6	45,6	40,8
	C	46,4	41,6	40,8	36,0	12,6	11,4	11,4	10,2
v_a [μm/s]		121	158	125	128	130	166	157	172
I_z [mg/s]		1,11	1,28	1,50	0,89	1,40	0,70	1,31	0,83

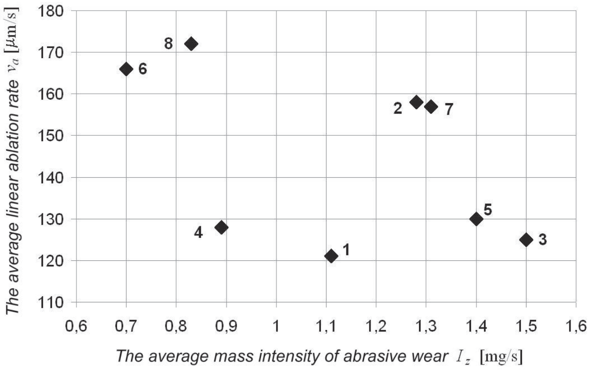

Fig. 4. The tests results: the average linear ablation rate v_a and the average mass intensity of abrasive wear I_z

Table 5. Statistics of coefficients the equations of the response variable

	b_0	b_1	b_2	b_3	b_{12}	b_{13}	b_{23}	b_{123}	$\bar{y}$	$s(b_i)$	b_{istot}
v_a [μm/s]	144,5	11,4		11,5	-6,9		7,5		6,9	2,4	5,6
I_z [mg/s]	1,13	-0,21		**-0,07**	**-0,07**	**-0,09**		0,13	0,11	0,04	0,1

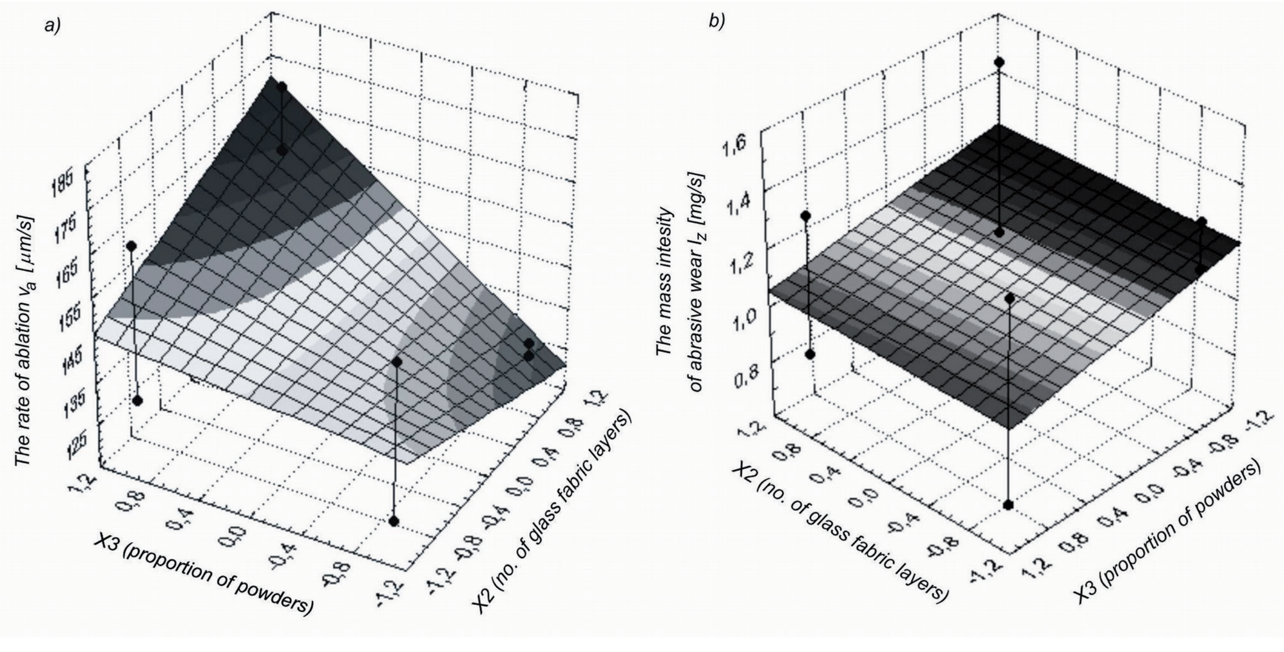

Fig. 5. Relation of abrasive wear to phase composition for variable $x_1 = 0$, (27% resin): a) the average linear rate of ablation v_a, b) the average mass intensity of abrasive wear I_z.

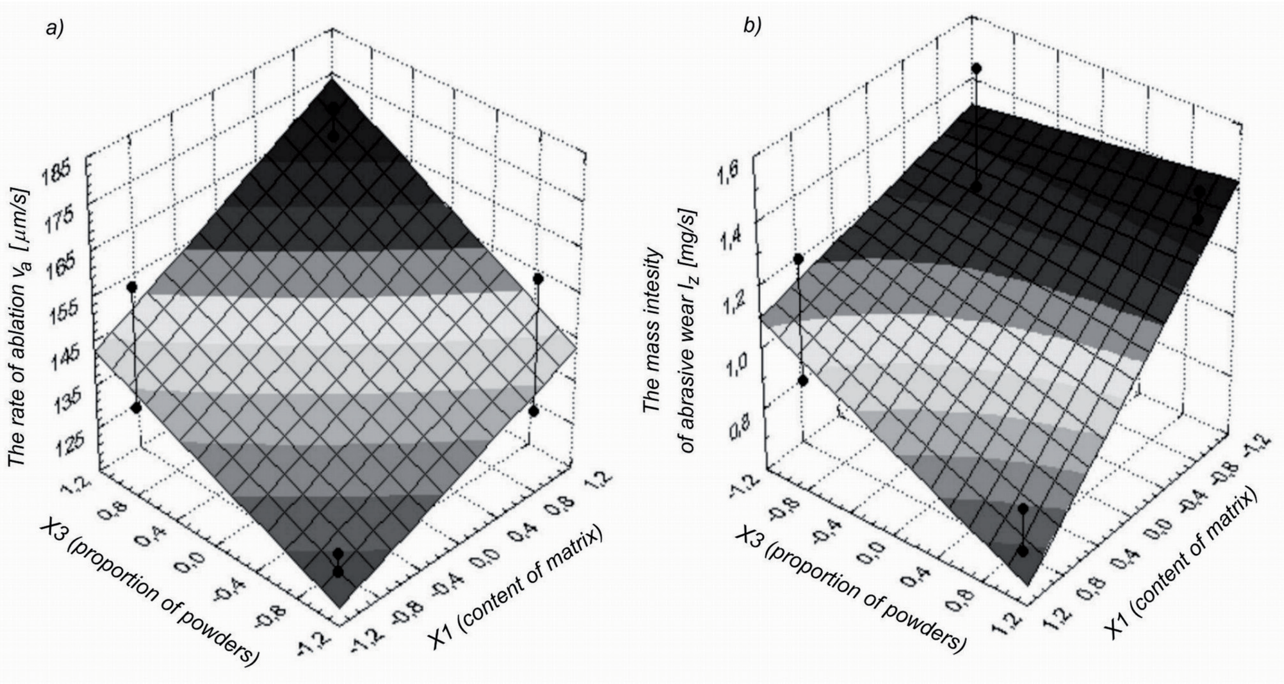

Fig. 6. Relation of abrasive wear to phase composition for variable $x_2 = 0$, (10 layers of glass fabric): a) the average linear rate of ablation v_a, b) the average mass intensity of abrasive wear I_z.

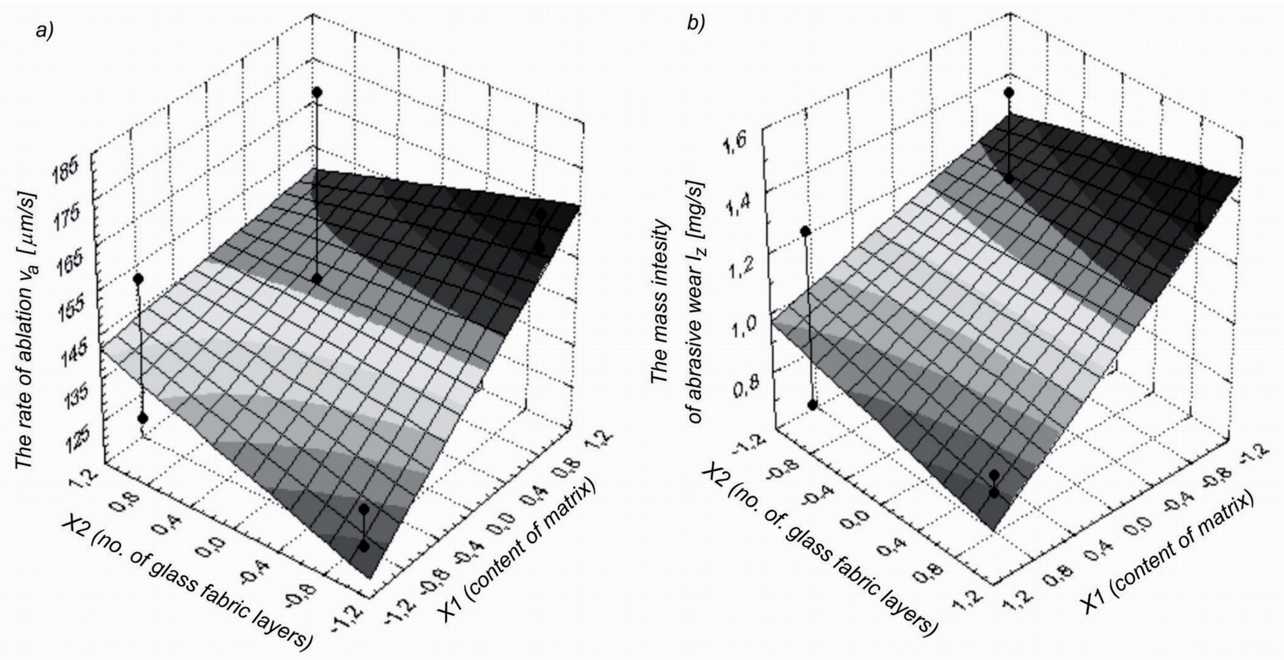

Fig. 7. Relation of abrasive wear to phase composition for variable $x_3 = 0$, (50% C and 50% Al_2O_3): a) the average linear rate of ablation v_a, b) the average mass intensity of abrasive wear I_z.

(a drop in the content of $C - x_3$) results in increasing ablation wear of the composite (b_{23}). The abrasive wear is more intense if both the content of matrix and of the fibreglass reinforcement is higher, despite the predominance of hard corundum in relation to powder carbon when the content of fillers has been decreased (b_{123}).

6. Conclusions

1. Composites whose phase composition provides lower wear intensity I_z have higher ablation rate v_α.

2. The wear intensity decreases when the content of matrix is higher or when corundum Al_2O_3 is predominant in the filler mixture. A high amount of resins, which guarantees the adequate solutioning and hardening of the composite, prob-

ably hinders the removal of filler grains in the abrasion process while a high content of corundum increases the resistance to abrasion.

3. An opposite dependence can be observed for the rate of ablation ν_α which decreases due to either a lower content of matrix i.e. the constant content of fibreglass reinforcement and the higher content of a given powder filler, or due to predominant content of powder carbon *C*. A lower content of pyrolytic carbon (the main component of the thermoinsulating ablation layer), which is a product of the matrix decomposition process, is compensated by higher amounts of carbon dust due to the higher content of powders as well as its proportion to corundum.

4. The slow rate of ablation v_a can be also achieved by decreasing the content of powder fillers maintaining the minimum amount of corundum Al_2O_3 and maximum amount of powder carbon *C*, which involves more matrix and glass reinforcement.

5. Within the scope of the assumed independent variables, the composite, which is the most resistant to abrasion, contains the maximum amount of corundum Al_2O_3 (minimum amount of powder carbon *C*) with the highest possible solutioning of resins and 10 layers of glass fabric.

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