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Investigation of the thermal protection ablative properties of thermosetting composites with powder fillers: the corundum Al_2O_3 and the Carbon Powder C

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Phenol formaldehyde resins were filled with mixtures of corundum Al_2O_3 and carbon C powders to produce thermo-protective composites. The composites were treated with hot combustion gases to determinate the temperature profiles across rectangular samples of dimensions 10x25x35 mm. The carbonization of the thermosetting matrix was observed. It was qualified the qualitative and the quantitative effect of components on the ablation surface temperature, the back side temperature of specimen and the mass waste under intensive heat flow after 120 s of treatment with hot combustion gases. The composites with higher matrix content (more liquid resin and less adhesive resin) and with predominance of corundum Al_2O_3 over carbon powder C showed the best insulating properties.

Keywords: ablative shields and coats, thermosetting polymer composites, high-melting fillers, thermo-protective materials.

INTRODUCTION

Modified plastics were introduced as ablative protecting materials against excessive temperature in the middle of the 20th century, finding applications in the arms industry as well as aeronautical, rocket and space industries[1]. These materials can also be used in the design of passive fire-proof protections for large cubature supporting elements in building structures[2], communication tunnels[3–4] and for the protection of data stored in electronic, optical and magnetic carriers[5].

Autonomous shields and ablative shielding are also used to protect building structures and people's lives in heat load incidents with temperatures much exceeding permissible standards. 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} allows the reduction of temperatures from several dozen degrees to ~2000°C with the use of relatively thin insulation shields[1, 5–9].

Endothermic reactions associated with thermal decomposition of polymer matrix take place in polymer composites at temperatures higher than the ablation temperature t_a, which lead to high values of effective specific heat c_p. In their pure form, polymers are considered to be good ablative materials[1, 5–9] having very low heat conductivity coefficient λ. However, due to their softening, low density and low heat stability as well as brittleness which are induced during the ablation of ablative layer, there is a need to combine these materials with mineral powders or fiber reinforcements which improves the thermal stability, resistance to heat flux and consequently the thermal insulation of composites.

Despite many years of experience with ablative materials, the relationship between the phases type and composition with ablative properties, within the context of others operational properties of the composites used as thermal protection shields, remains still not evaluated qualitatively and quantitatively[5, 6, 9].

The present work investigates the effect of quantitative and qualitative phase composition of phenol formaldehyde composites with chosen powder fillers (corundum Al_2O_3 and carbon C) on ablative thermo-protective properties of these composites, especially on the back side temperature of specimen t_s and the mass waste U_a.

MATERIALS AND DESIGN OF EXPERIMENTS

Materials

Materials were chosen on the basis of the thermo-physical properties of powder fillers, their commonness in applications to provide thermal protection as well as good ablative properties, high thermal stability, incombustibility and lack of toxic products of thermal decomposition of the resin. Based on bibliography[5–14] the following materials have been used to prepare the specimens of polymer composites: thermosetting matrix, resins (*Modofen 54S* and *Nowolak MR*); powder fillers, corundum Al_2O_3 (*ALO G5-4*) with grains of 2 to 5 μm with the minimal contents of aluminium oxide of 99.5% (95% α Al_2O_3) manufactured by Ajka Amumina, Hungary and fine grain carbon powder C of 5 μm and purity of 98% manufactured in Poland.

Samples preparation

Experimental samples for thermoprotective investigations were created in a six-step procedure:

1. Preparing a mixture of fillers (homogenization of the mixture of both powders).
2. Adding appropriate mass of grain damper (liquid resin *Modofen 54S* increasing adhesion of the binder to fillers) and mixing it to homogenize the mixture.
3. Adding weighted amount of the binder powder (powder resin *Nowolak MR*) and mixing everything until uniform, powdery material is formed. One obtains a semi-finished product consisting of loose groups of grains covered with two resin coatings: grains of the fillers in the inner coating of liquid resin (the grain damper) are covered with loose powder (the binder).
4. Filling the metal grid with the obtained powder and increasing its density under pressure of approximately 0.4 MPa.

5. Closing sides of the metal mould and keeping it in 150°C for 60 minutes to allow gelation of the resin, filler supersaturation and crosslinking the matrix. Moulds had air channels allowing for degasification of the hardening samples.

6. Cooling and removing of the forms to obtain an experimental sample.

Design of experiments

The evaluation of ablative thermal protection properties of ablative thermosetting polymer composites were carried out on the basis on a first order 2^3 full experimental design with repetitions[15] (Table 1). 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: 20% (–1) and 40% (+1);

x_2 – mass proportion of liquid resin *Modofen 54S* to the total mass of both resins *Modofen* 54S/(*Modofen 54S + Nowolak MR*): 30% (–1) and 70% (+1);

x_3 – mass proportion of Al_2O_3 corundum to the total mass of both fillers $Al_2O_3/(Al_2O_3 + C)$: 60% (–1) and 80% (+1).

The components of the response variable *y* (the output parameters) are the average maximal back side temperature of specimen $t_{s\ (max)}$ [°C] and the average mass waste U_a [%] after 120 s of treatment with hot combustion gases.

The regression coefficients b_i of all function components have been calculated. The statistical analysis of the tests results allowed for the determination of the threshold relevance of the regression coefficients b_i and estimation of their effect on the output parameters *y*. The output value is signed in the equation of the experiment objective (1)[15]:

$$(\bar{y}) = (b_0 + b_1x_1 + b_2x_2 + b_3 x_3 + b_{12}\, x_1x_2 + b_{13}\, x_1x_3 + b_{23}\, x_2x_3 + b_{123}\, x_1x_2x_3) \pm s(\bar{y}) \qquad (1)$$

Moreover, the variance $s^2(\bar{y})$, error in determination regression coefficients $s(b_i)$ and their level of statistical significance b_{istot} have been determined on the basis of *t-Student* test at confidence level 95%[15].

Evaluation of ablative properties

The so-called "ablating gun"[16] (Fig. 1) of own construction[5, 7] was used for the classical tests of ablative thermal protection properties, enabling thus the interaction of steady and uniform streams of inflammable gases on the samples at high temperatures. The specimens (of size 10x25x35 mm) were placed in a shielding made of flameproof plaster-cardboard panel and exposed to gas heat flux for τ = 120 seconds. Burning of Methyl Acetylene and Propadiene mixture (MAPP gas) in an ablating gun blowpipe provided the source of heat (Fig. 2).

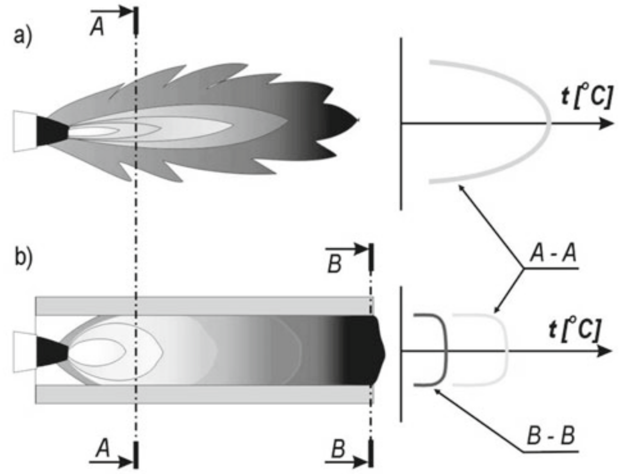

Figure 1. Temperature of combustion gases using[5]: a) typical blowpipe – without stabilization of temperature, b) ablating gun blowpipe – with stabilization of temperature

The registration of decomposition temperatures on the ablative surface t_{pa} (Fig. 3 – typical sample) and back surface t_s (Fig. 4 – average, for all phase compositions) of ablative partition of the tested samples have been performed using pyrometer (*OPTCT2MHCF Optris GmbH*) and thermocouple (*TP-204N* (NiCrSi-NiSi)

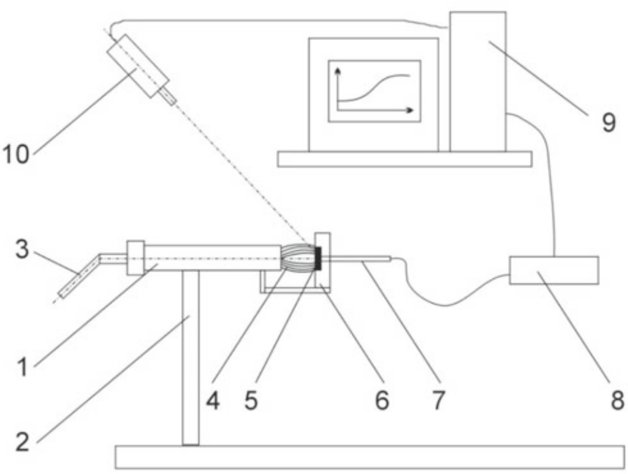

Figure 2. Schematic of the ablation equipment[5, 7]: 1 – ablating gun, 2 – rotating device, 3 – MAPP gas blowpipe, 4 – hot combustion gases, 5 – ablating sample, 6 – handle for sample, 7 – thermocouple on the back of the sample, 8 – temperature measuring instrument, 9 – computer, 10 – multiwavelength pyrometer

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

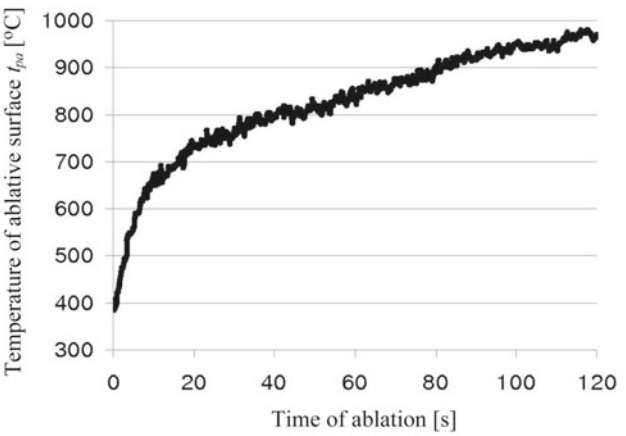

Figure 3. Typical increase of ablative surface temperature t_{pa} during 120 s of treatment with hot combustion gases

Czaki Thermo-Product). Furthermore, the ablation weight loss of composites U_a has been also evaluated.

The temperature on the ablative surface increased more rapidly the first 10 s, followed by a low rate of temperature increase for the rest of the test (Fig. 3). Fast increase of temperature during first 10 seconds is caused by rapid heating of the sample surface. Next, temperature grows slower, because apart from taking the heat and conducting it deeper into the sample, endothermic ablation processes start (heat is used i.e. to decompose resins).

The temperature of the back side increased with increasing time of ablation. Specimens 7 and 8 exhibited the highest and lowest back side temperature (Fig. 4).

The average results of ablation tests and the relation of both response variables (the output parameters) to the phase variables are presented in Table 2 and their graphic interpretations in Figure 5.

Shaping the thermal protective ablative properties of polymer composites can be done by choosing such phase composition which: guarantees the possibly most significant reduction of the temperature on the thickness of the protective wall; ensures the emergence of the ablative layer which is coherent, thermally stable, characterized by good adhesion to the basic material with a low coefficient of thermal conductivity; increases the thermal stability of the basic material and its endurance to withstand thermal-mechanical strain which appears because of the impact of the heat flux; ensures the lack of combustibility, smoke and toxicity of the appearing ablation products.

The aim of the experiment was to find such a composite whose values of the average maximal back side temperature $t_{s\ (max)}$ and the average mass waste U_a are the lowest and it gives good reduction of temperature and good thermal stability of the material. These conditions have been met by specimen 8 whose phase composition consists of 40% matrix (28% *Modofen 54S* and 12% *Nowolak MR*), 48% corundum Al_2O_3, and 12% carbon powder C (Fig. 5).

STATISTICAL ANALYSIS OF TEST RESULTS

The regression coefficients and their significance, the variance $s^2(\bar{y})$, and the determination error $s(b_i)$ were calculated based on the data provided in Table 2 and were presented in Table 3. The bold print marks b_i – values, which is lower than b_{istot} but burdened with the error $s(b_i)$ which allows to assess the b_i as statistically significant. The lack of data in the Table means that the given index is

Table 2. The factual phase compositions of the composites and the results of ablation tests

Parameter		Number of tests (number of specimens 1 – 8)							
		1	2	3	4	5	6	7	8
matrix [%]	*Modofen 54S*	6	12	14	28	6	12	14	28
	Nowolak MR	14	28	6	12	14	28	6	12
powder fillers [%]	Al_2O_3	48	36	48	36	64	48	64	48
	C	32	24	32	24	16	12	16	12
$t_{pa\ (max)}$ [°C]		1 146	1 146	1 101	1 115	1 124	1 069	1 054	1 110
$t_{s\ (max)}$ [°C] (after 120 s)		52.0	53.6	60.9	52.1	67.7	52.4	89	46.7
U_a [%] (after 120 s)		13.5	13.0	11.3	15.5	9.7	12.4	10.7	9.8

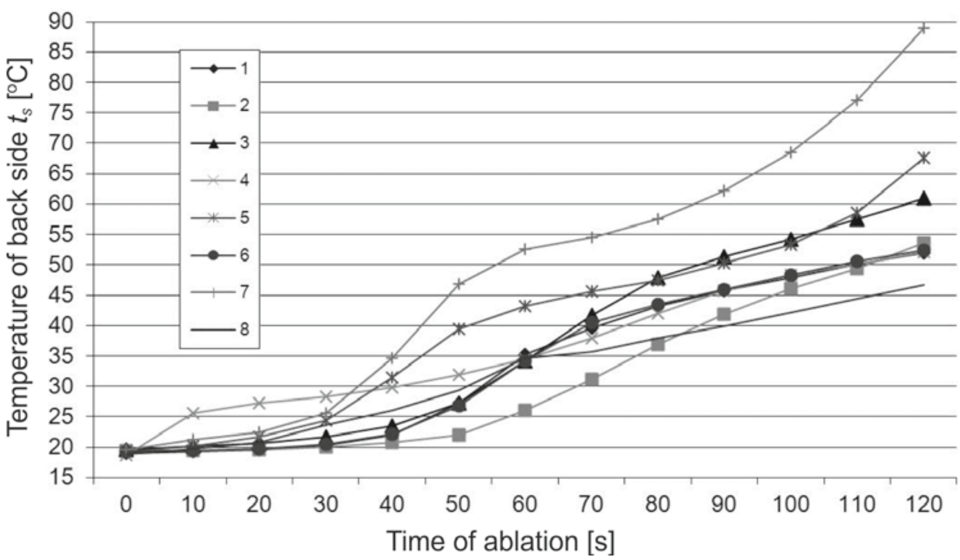

Figure 4. Increase of back side temperature t_s during 120 s of treatment with hot combustion gases

Table 3. 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}	$s^2(\bar{y})$	$s(b_i)$	b_{istot}
$t_{s\,(max)}$ [°C]	59.30	–8.10	2.88	4.65	–4.68	–6.30		**–2.08**	11.02	1.17	2.71
U_a [%]	11.96	0.82		–1.23		–0.36	–0.35		0.102	0.11	0.26

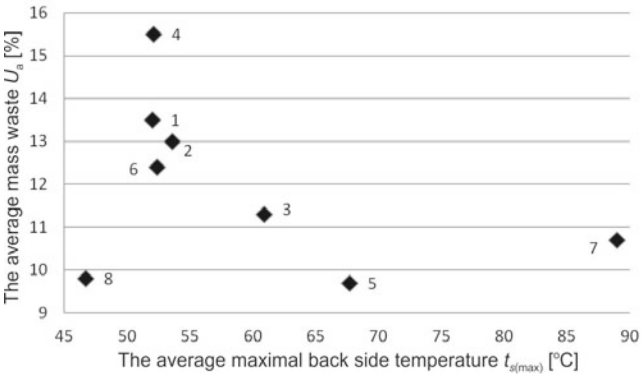

Figure 5. The average maximal back side temperature $t_{s\,(max)}$ [°C] and the average mass waste U_a [%] after 120 s of treatment with hot combustion gases

not statistically significant at 95% confidence level and has therefore been omitted.

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

With the increase in matrix contents, the temperature $t_{s\,(max)}$ decreases, but the weight loss U_a increases (coefficient b_1).

The increase in the corundum share Al_2O_3 (the decrease in the carbon powder share C) results in the decrease of ablative weight loss U_a, but at the same time leads to the increase in temperature $t_{s\,(max)}$ (coefficient b_3).

When the increase in the matrix content is related to the increase in the *Modofen 54S* share (negative value of b_{12} in case of $t_{s\,(max)}$), with the higher content of Al_2O_3 and smaller content of carbon powder C (negative value of b_{23} in the case of U_a as well as negative values of b_{13} in the case of $t_{s\,(max)}$ and U_a), this type of phase composition of the composite ensures the top thermo-protective properties, that is the lowest temperature $t_{s\,(max)}$ and the lowest ablative weight loss U_a.

STRUCTURES OF ABLATIVE SAMPLES

Experimental samples after the ablation process were covered with chemically crosslinked resin in cylindrical moulds (plastic tubes). After hardening the resin, it was cut along the heat flux direction in the symmetry axis of the ablative surface. Samples were cut mechanically at slow speed and with cooling to avoid temperature increase in the cross-section, which could affect the structure and thermal stability of the polymer. Next, the samples were wet polished using sandpaper with decreasing grain size and then wet polished using felt with polishing paste (corundum). No corrosives were used. Then pictures of the ablative layer structures and the basic material were taken using an optical microscope.

In Figure 6, the border between the basic and secondary ablation is visible (mark by an arrow). In the structure of the ablative layer we can see the so-called *vitreous slag* – the porous substance of low thermal conductivity, which is the solid product of pyrolysis and ablation processes (the dark area of the secondary ablation). It is visible below the congealed/solidified ceramic compounds (the light area of the secondary ablation). Above it, one can observe a congealed, fine-grain ceramic structure which is the transition as well as secondary reactions zone, almost free from solid products of pyrolysis. It can be stated that the resin matrix of the composite got decomposed below the border of the secondary ablation.

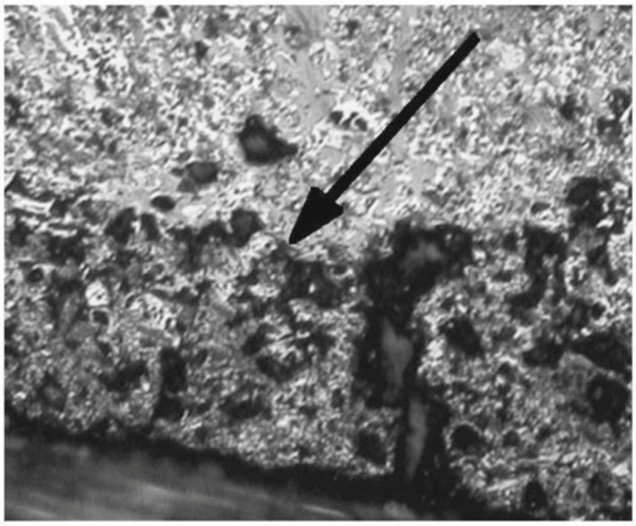

Figure 6. Basic and secondary ablation border, x100

Figure 7a shows the composite basic material, which has not become the subject of ablation. One can easily see big, light, angular grains of corundum Al_2O_3 against the background of black carbon powder and structural defects – pores which appeared in the technological process.

In Figure 7b, we can see the fine-grained structure of solidified ceramic (secondary ablation) with a typical dendrite type of grain (light areas), against the dark background of porous, glassy slag (the substance that remained after the secondary ablation). Instead of having sharp edges, the grains of ceramic have ovoid ones, which proves that they emerged in result of chemical reactions from substrates of the secondary ablation process (on the basis of carbon and corundum) and then got solidified due to the termination of the impact of the heat flux.

CONCLUSIONS

The composites containing higher amount of matrix (more liquid resin *Modofen 54S* and less adhesive resin *Nowolak MR*) have the best thermo-protective ablation proprieties when corundum Al_2O_3 is predominant in the filler mixture (over carbon powder C). Both temperature of specimen t_s and average mass loss U_a are the lowest (tested sample 8).

The kind and the content of powder fillers are the most important phase composition parameters, as they

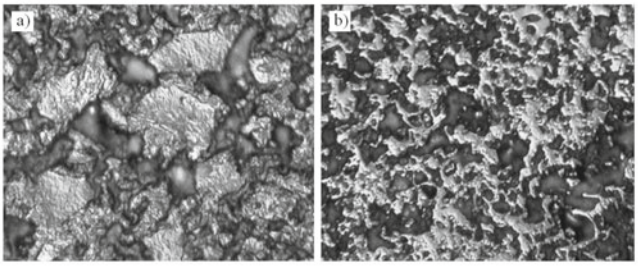

Figure 7. Structure of ablative sample, x250: a) basic material, b) ablative layers

give the highest effect on the improvement of thermal stability and resistance to heat flux. The higher amount of corundum Al_2O_3 (the lower content of carbon powder C) the lover ablation weight loss of composites U_a.

The statistical analysis – for the first order experimental plan – allows us to quantify the influence of each level of the factor variables on both response variables. The signs of the regression coefficients show if the response is increasing or decreasing, while their absolute values inform us about the strength of the dependence. Coupling this information with technological constraints influencing the values of the input variables indicates the way towards optimal phase composition of ablative thermal-protective composites.

The ablation layer is porous. In the zone of secondary reactions it has fine-grained dendrite structure made of ceramic compounds, which were created from fillers and products of polymer pyrolysis of the composite matrix under high-temperature heat flux. In the primary ablation zone we observe high-melting grains of fillers covered in solid products of resin pyrolysis.

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