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Composite material based on an ablative phenolic resin and carbon fibers

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Abstract: In this study, a technological procedure for the production of a molding compound based on short carbon fibers and an ablative phenol–formaldehyde resin for high temperature application was optimized. The starting raw materials were characterized and molding compounds with different fiber/matrix ratios and different fiber lengths were obtained. From the different laboratory samples, molded parts were made by thermocompression. The basic mechanical and thermal properties of the composites were determined. From the obtained results, the optimal fiber/matrix ratio was determined for a production of molding compound for high temperature application. The molding process of the composite material was optimized and all the parameters for good mechanical properties and high thermal stability of the composite were obtained. Optimization of the composite molding process was performed by the application of a numerical method for a planned experiment, *i.e.*, a full three-factorial experimental design with variance of all three parameters (fiber length, temperature and time of the press cycle) on two levels. The obtained mechanical properties (flexural strength: 247 MPa, modulus: 27.6 GPa, impact resistance: 110 (for test moldings 10 mm×10 mm) and 91 kJ/m^2 (for test moldings 15 mm×15 mm)) justified the application of this composite material in the automotive, leisure, military and other industries where high temperature resistance and high mechanical strength is required.

Keywords: molding compound; phenol–formaldehyde resin; carbon fibers; composites; thermocompression.

INTRODUCTION

Phenolic composites reinforced with carbon fibers are mostly used for the production of responsible parts for various industries, among which those for high temperature applications are of particular significance.[1]

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Phenolic resins are known for their excellent thermal properties and chemical stability. In the field of advanced composite materials, phenolic based composites are known for their excellent flame resistance and are excessively used in the rocket industry because of their ablative characteristics.

Carbon fiber-reinforced phenolic resins are particularly effective in resisting high temperatures, since the resin evaporates and burns at the surface creating a thermal protective layer.[2–4]

The gel time (B-time) of phenolic resins at 150 °C ranges from 1 to 3 min. The weight loss at temperatures higher than 500 °C is about 40 %.[5]

Phenolic bulk molding compound (BMC) composites have excellent dimensional stability at high temperatures, excellent strength and heat insulation properties and high durability.[6,7]

The properties of short fiber–polymer composites are strongly dependent on the volume fraction and orientation distribution of the fiber and on the adhesion between the fibers and matrices. The fiber volume fraction is usually fairly tight controlled, although some segregation of fibers and polymer may occur during fabrication. The fiber orientation distribution changes when the molding conditions change, but it is difficult to control.[8,9]

Thermosetting short fiber reinforced composites have unique property combinations. Thus, typical strength values are in the range from 150 to 200 MPa and Young's modulus values are in the range 10–18 GPa.[8] The differences in fiber orientation distribution usually occurs within the moldings, particularly through the wall thickness, and this can lead to a composite with unequal mechanical properties.[8]

In this study, the influence of the basic processing parameters and length of the carbon fibers on the basic mechanical and thermal properties of phenol–formaldehyde composites were investigated. According to the test results, the optimal processing parameters of the compound were determined. One of the possible applications of such a composite is expected to be for the production of load-bearing and high temperature resistant parts of anti-hail rockets, such as the nozzles.

EXPERIMENTAL

For the production of the molding compound, a resol-type phenol formaldehyde resin (under the trade name Borofen DX 30), see Table I, and carbon fiber type T800 (under the trade name Toray), see Table II, were used.

Thermal characterization of the resin was performed by thermogravimetry, TG, (Thermo Gravimetric Analyzer 980 of Du Pont de Numerous), differential scanning calorimetry, DSC, (Perkin Elmer DSC-7 analyzer) and through determination of the gel time at different temperatures.

The molding compound was produced by mixing resin and carbon fibers (cut at different lengths, 25 and 50 mm) in a universal mix and knead machine (Werner Pfleiderer, Germany). The produced molding compound was dried at 80 °C for 30 min. The content of volatile materials was kept at 2–3.5 %.

TABLE I. Characteristics of phenol–phormaldehide resin, Borofen DX30 resol type, dissolved in 2-propanol

Property		Value
Appearance		Clear dark red solution
pH		7.3–7.8
Dry material content, %		68–72
Viscosity (Ford, 4mm), s		140–160
Content of free phenol, %		Max. 6
Content of free formaldehyde, %		Max. 2
Gel-time, min	120 °C	8.0–11
	150 °C	1.0–1.5

TABLE II. Characteristics of carbon fiber

Property	Value
Trade name	“Toray” T800H
Producer	Toray Industries Inc., Tokyo, Japan
Filaments count	12000
Density, g/cm^3	1.81
Tex count, g/1000m	445
Filament diameter, µm	8
Tensile strength, MPa	5.49
Tensile modulus, GPa	294
Elongation, %	1.9

The composites, *i.e.*, moldings, were made by direct thermocompression on a semi-industrial press (Triulzzi, Italy).

The mechanical and thermal properties of the moldings, such as impact resistance (DIN 53453), compression strength (DIN 53454), flexural strength (DIN 53457) and the modulus (DIN 53452), were determined and the heat deflection temperature was analyzed (according to the Marthens method) (DIN 53 462). For all mechanical tests, a universal testing machine (Schenk and Frank, Germany) was used.

A numerical experimental design method, *i.e.*, a full three-factorial experimental design (Table III) was applied for optimization of the processing of the molding compound. The fol-

TABLE III. Plan-matrix for three-factorial experimental design

Characteristics (conditions of experiment)			Experimental design matrix							
X_1 (temperature, °C)	X_2 (fiber length, mm)	X_3 (curing time, min)	X_0	X_1	X_2	X_3	$X_1 X_2$	$X_1 X_3$	$X_2 X_3$	$X_1 X_2 X_3$
140	25	15	+1	–1	–1	–1	+1	+1	+1	–1
160	25	15	+1	+1	–1	–1	–1	–1	+1	+1
140	50	15	+1	–1	+1	–1	–1	+1	–1	+1
160	50	15	+1	+1	+1	–1	+1	–1	–1	–1
140	25	35	+1	–1	–1	+1	+1	–1	–1	+1
160	25	35	+1	+1	–1	+1	–1	+1	–1	–1
140	50	35	+1	–1	+1	+1	–1	–1	+1	–1
160	50	35	+1	+1	+1	+1	+1	+1	+1	+1

lowing parameters were varied: molding temperature (X_1), fiber length (X_2) and press cycle time (X_3). The base level for the first factor (X_1) was 150 and the interval of variance 10; for the second factor (X_2), the base level was 37.5 and the interval of variance 12.5; for the third factor (X_3), the base level was 25 and the interval of variance 10. This experimental design enables mathematical definitions, in form of regression equations, of the mechanical properties of the moldings as functions of the processing parameters. The regression coefficients were statistically determined by application of the student's criteria and the significance of the regression equations was tested according to Fisher's criteria.[10]

RESULTS AND DISCUSSION

The dependence of the gel time on temperature, in range from 120 to 180 °C, is presented in Fig. 1, from which it can be seen that the gel time of the resin ranged from 500 to 50 s for 120 and 180 °C, respectively. A drastic reduction of the gel time started at temperatures above 140 °C. From the technical point of view, the determination of the gel time is important because it gives an indication of the curing process of the resin and the phase transition from the liquid to the solid state.

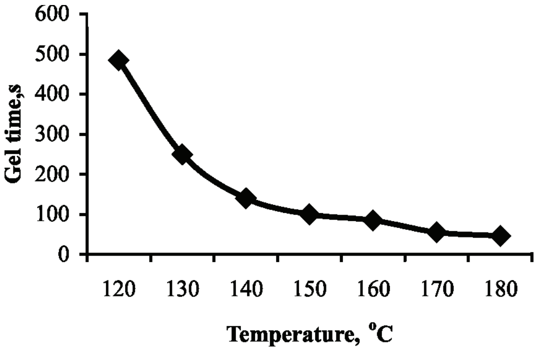

Fig. 1. Temperature dependence of the resin gel time.

Curing of thermosetting resins are highly exothermic processes. This is most critical when thick sections are molded. Addabbo *et al.*[11] studied the curing of a thermoset in a heated mold and showed the existence of a critical thickness below which the cycle time was not dependent on the thickness of the part. Williams *et al.*[12] found that the hottest plane does not always coincide with the centerline and that the cure cycle time is not necessarily proportional to the thickness of the part, as is often asserted. It is important to select the optimal wall temperature so that the mold can be filled without premature gelling, and so that the maximum temperature in the part remains below a ceiling temperature, when degradation or undesirable side reactions may occur. When the cycle time is determined by curing at the wall, it is important not to overestimate the critical conversion needed to eject the part from the mold. The material must reach a critical conversion level at which it is dimensionally stable and can be removed from the mold without losing its shape or blemishing its surface. This is often described as the end of the cure, though there will normally be further reaction ("curing") after this time.

The results of the weight loss of the resin, obtained at a constant heating rate of 20 °C/min in an inert atmosphere, are presented in Fig. 2. From the TG curve, four temperature ranges of weight loss of the resin DX 30 can be noticed. In the first range 0–130 °C, the weight loss was insignificant, 3 %; in the second range 130–230 °C, there was a sharp decline of the curve, *i.e.*, the weight loss of the resin was higher, approximately 15 %, and in the third range 230–400 °C, the weight loss of the resin was again insignificant. At a temperature of 400 °C, the weight loss was approximately 18 %. From 400 to 600 °C there was again a sharp decline of the weight loss curve, *i.e.*, the destruction of the resin rapidly increased. At a temperature of 550 °C, the weight loss of the resin was 33 %.

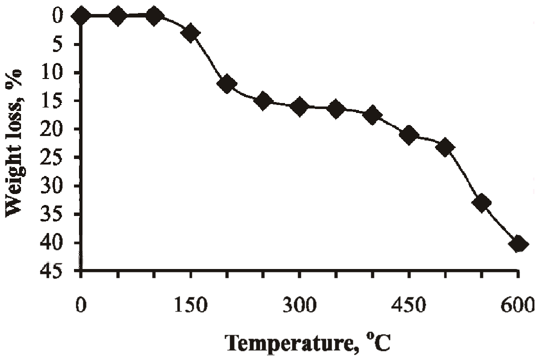

Fig. 2. Thermal degradation (TG) of the resin DX 30.

The preliminary characterization on the resin DX 30 was performed by DSC analysis. The basic temperature transitions: glass transition temperature, t_g, the cure reaction temperature, t_r, and the corresponding effects within these transitions, ΔC_p and $\Delta_r H$, were determined. The onset temperatures of the glass transitions and the curing reactions were also determined. All the obtained values are presented in Table IV.

TABLE IV. DSC results for t_g and t_r of the resin DX 30

t_g, °C	t_g (onset), °C	ΔC_p, J/g K	t_r, °C	t_r (onset), °C	$\Delta_r H$, J/g
73.5	67.7	0.60	189.8	155.4	83.4

According to the DSC results, the curing reactions of the phenolic resin begin at 155 °C. Based on these results, as well as on previous experience, the processing conditions for all samples were determined as follows: molding pressure, $p = 75$ bar, molding temperature, $t = 160$ °C and processing cycle time, $\tau = 20$ min.

Under the influence of the heat flux, the resin becomes viscous (vitrification proceeds) and as heating progresses, it begins to degrade, producing a foaming carbon-mass and ultimately a porous carbon char. The char is a thermal insulation; the interior is cooled by the volatile material percolating through it from the decomposing polymer. Thus, a char forming resin acts as a self-regulating ablation radiator, providing thermal protection through cooling and insulation of the interior.[2,3,13,14]

From the molding compounds made with different fiber/matrix ratios (25/75, 45/55, 57/43, 67/33 and 75/25) and with different fiber lengths (25 and 50 mm), test samples were prepared and the basic mechanical and thermal properties of the composites were determined.

Mechanical properties

The analysis of the mechanics of short fiber composites is much more difficult than for continuously aligned fiber composites. There are two reasons for this. Firstly, the stress transfer between the fiber and the matrix is not uniform along the fiber, and there are fiber-end effects that can be neglected in continuous fiber composites but that are important in short fiber composites. Secondly, in short fiber composites, the fibers are never exactly parallel and may even have random orientation.[8,12,15]

Tables V and VI present the impact strength, *an* 10 and *an* 15, respectively, for the test sample-moldings as a function of the content and the length of the carbon fibers.

TABLE V. Impact strength *an* 10 (σ_{10} / kJ m^{-2}) of the moldings; x_{sr} – average value of 5, *SD* – standard deviation and C_v – coefficient of variation

Property	Fiber length: 25 mm				
	Fiber content, %				
	25	45	57	67	75
x_{sr}	105	120	136	122	133
SD	7.90	7.30	4.00	9.60	8.50
C_v	7.50	6.00	2.90	7.80	6.40
	Fiber length: 50 mm				
x_{sr}	128	130	163	125	156
SD	6.90	6.00	4.50	7.90	4.10
Cv	5.40	4.60	2.80	6.30	2.60

TABLE VI. Impact strength *an* 15 (σ_{15} / kJ m^{-2}) of the moldings; x_{sr} – average value of 5, *SD* – standard deviation and C_v – coefficient of variation

Property	Fiber length: 25 mm				
	Fiber content, %				
	25	45	57	67	75
x_{sr}	87.5	98.7	85.1	105	94.2
SD	5.20	9.50	7.80	14.9	7.50
C_v	5.90	9.60	9.20	14.2	8.00
	Fiber length: 50 mm				
x_{sr}	78.3	87.2	116	109	98.0
SD	9.90	5.30	9.20	9.90	7.60
C_v	12.6	6.10	7.90	9.10	7.70

The total impact energy that can be absorbed by the test specimens per unit area was determined. The absorbed energy is spent for the work done against friction in displacing the fibers relative to the matrix, or the work required to cause elastic debonding is the principal source of this fracture energy. In short-fiber composites, the situation is often slightly clearer because the ends of many fibers must inevitably be nearer to a crack face than half the critical transfer length and these ends will therefore be pulled from the matrix as the composites separates into two or more pieces.[16–20]

The impact strength was higher for the composites with the longer fibers length. A certain deviation was noticed for the impact strength *an* 15 of the composites with fiber contents of 25 mass % and 45 mass % and a fiber length of 50 mm. The higher value for the coefficient of variation (C_v = 12.6) of the first test sample shows that the probable cause for this is the difference in the fiber orientation distribution through the wall thickness of the sample. The composite material with a higher fiber content becomes more rigid, which results in a lower impact strength. The best impact strength exhibited the test sample with 57 mass % fiber content and 50 mm fiber length.

The composites with the shorter fiber length had a higher compression strength, as can be seen inTable VII.

TABLE VII. Compression strength (σ_C / MPa) of the moldings

Property	Fiber content, %				
	25	45	57	67	75
Fiber length: 25 mm					
x_{sr}	153	159	164	179	143
SD	1.50	0.80	1.40	2.40	5.20
C_v	1.00	0.50	0.90	1.30	3.60
Fiber length: 50 mm					
x_{sr}	135	128	172	132	141
SD	3.40	6.40	18.5	10.0	6.20
C_v	2.50	5.00	10.8	7.50	4.40

On compression, the matrix is called upon to bear a large fraction of the applied load. Since the reinforcement is not continuous, local shear failure in the matrix initiates a buckling type of rupture as the interface begins to fail and fiber strengthening of the matrix is lost. In composites with poor fiber/matrix bonding, longitudinal splitting occurs but in a well-bonded composite, a substantial proportion of the compression strength may be retained.[13,15]

The highest value for the compression strength is registered for composites with fiber contents of 57–67 mass %, *i.e.*, 164–170 MPa (with fiber length of 25 mm). The deviation of the composite with longer fibers and with a fiber content of 57 mass % is probably the result of non-homogeneity and non-uniformity of the material. A proof for this is the value of the coefficient of variation (C_v = = 10.8), which is higher than the ones for the other composites. In the other composites, the distribution of the fibers was more uniform, which resulted in more uniform compression strengths.

A typical value for the compression strength of phenolic resin/carbon fabric composites is 359 MPa. The obtained values for the compression strength of the BMC-based moldings were half of that of fabric-based composites. Continuous fibers composites show the best mechanical properties, due to the continuous form of the reinforcement and the fiber orientation distribution.[3]

The flexural strength and the modulus of the test moldings as a function of content and length the carbon fibers are presented in Figs. 3 and 4. As is known, the fiber length was selected in accordance with the composite application. The composites with shorter fibers have higher flexural strength and modulus. Generally, for the best mechanical properties, the fiber length should exceed a critical value but if the composite is overloaded, fiber fracture occurs until the fibers degrade to this value. The analysis showed that the fiber length and the aspect ratio should be as large as possible. The dimensions of the short fibers for reinforced composites must be chosen accordingly and steps must be taken during processing to maintain the lengths at adequate levels. The fiber length should not be too long or the fibers becomes entangled, causing problems with dispersion; if it is too short, the stress transfer area is too small and the fibers do not provide effective reinforcement.[8,15]

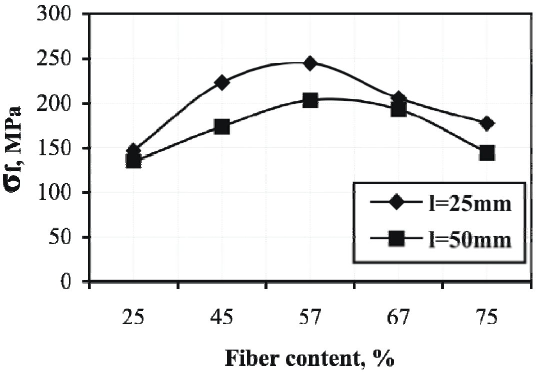

Fig. 3. Flexural strength of the moldings as a function of the fiber content.

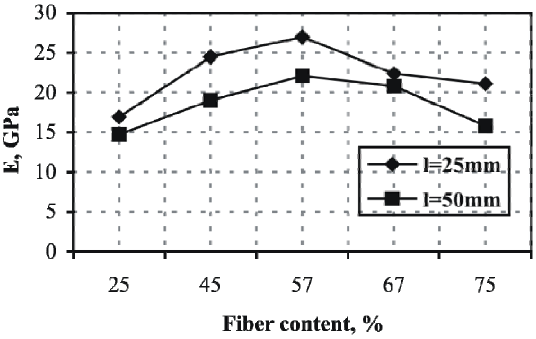

Fig. 4. Flexural modulus of the moldings as a function of the fiber content.

The composites with a fiber content of 57 mass % had the highest values for the flexural strength and the modulus.

Full factorial experimental design

In order to determine the optimal processing parameters and optimal fiber length, full factorial experimental design was applied. In accordance with the plan matrix, eight experiments with the variation of three parameters on two levels were performed. The results showed that the optimal fiber content is 60 mass %.[21] Some test results are presented in Figs 5 and 6.

The impact strength of 10 mm×10 mm test (σ_{10}) moldings *vs*. different fiber lengths at a constant temperature and curing time is presented in Fig. 5.

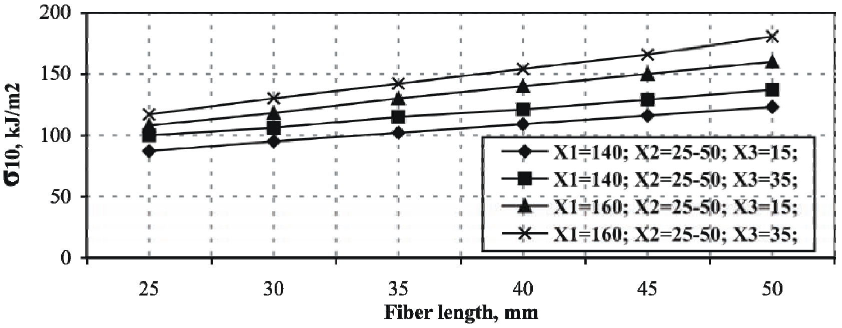

Fig. 5. Impact strength *vs*. fiber length (25–50 mm) at constant temperature and curing time.

Impact strength was higher for the composites with the longer fibers for both types of test moldings (10 mm×10 mm and 15 mm×15 mm). The regression equation (1) shows the individual contribution of the parameters: fiber length, press cycle temperature and press cycle time on the response function, *i.e*., impact strength.

$$y(X) = -32.80 + 0.46X_1 - 1.40X_2 - 0.66X_3 + 0.02X_2X_3 \quad (1)$$

The fiber length had the largest contribution to the impact strength, the contribution of the press cycle temperature was lower and the press cycle time had the lowest contribution. By increasing the fiber length and keeping the press cycle temperature at the upper level, an increase of the impact strength can be achieved at a shorter time.

The flexural strength *vs*. different fiber lengths at a constant temperature and curing time is presented in Fig. 6. An inverse dependence of the flexural strength as a function of the fiber length was found, Eq. (2):

$$y(X) = 58.76 + 1.65X_1 - 3.80X_2 - 0.83X_3 + 0.06X_2X_3 \quad (2)$$

The compression strength for all the tested moldings was also inversely dependant on the fiber length. All the results were in the 147 to 245 MPa range.[22]

From the regression equations, it can be seen that the fiber length had the greatest influence on the mechanical properties of the moldings, next the press cycle temperature and the smallest the press cycle time.

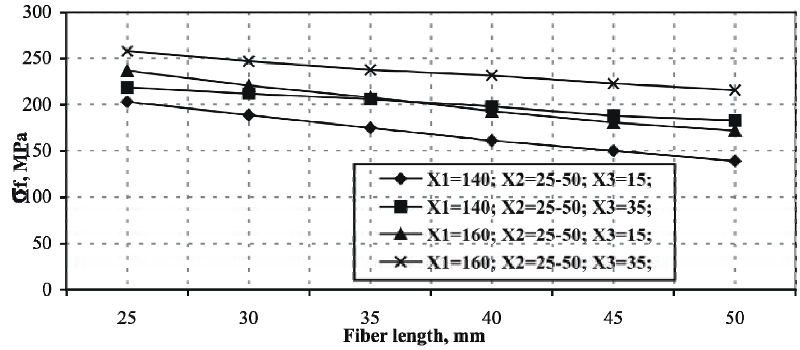

Fig. 6. Flexural strength *vs*. fiber length (25–50mm) at constant temperature and curing time.

Thermal properties

Thermogravimetry of the composites with carbon fiber contents of 25, 45, 57, 67 and 75 mass % and with a fiber length of 25 and 50 mm was performed (Table VIII).

From Table VIII, it can be noticed that the fiber content had a certain influence on the thermal degradation: the composites with the highest fiber content degraded at a higher temperature (the temperature of the excessive thermal degradation occurred at 350 °C, compared to 250 °C for the composite with lowest fiber content). The weight loss of the pure resin was higher compared to that of the fiber-reinforced resins. In addition, the weight loss of the composites with the highest fiber content was lower in comparison with the composites with the lowest fiber content: at 500 °C, the weight loss of the composite with a fiber content of 75 % was 14.6 %, and for the composite with a fiber content of 25 %, it was 22.8 % (see Fig. 7).

TABLE VIII. Weight loss (Δm / %) of the resin and the composites with fiber lengths of 25 and 50 mm

t / °C	Weight loss of Resin DX 30 mg	Fiber content, %							
		25	57	67	75	25	57	67	75
		Composite with *l* = 25 mm				Composite with *l* = 50 mm			
0–250	15	9.7	4.4	2.4	1.6	5.4	3.8	2.0	0.9
250–325	1.2	2.4	3.6	2.4	1.4	4.0	3.4	1.6	1.5
325–400	1.3	3.7	5.6	3.2	2.3	3.8	5.3	3.2	2.0
400–500	5.7	7.0	6.6	10.3	9.3	6.2	8.3	10.4	10.2

The heat deflection temperature was measured according to Martens for all moldings and it was found that, in all cases, the value exceed 210 °C, as reported earlier.[23]

The results of the thermal analysis of the composites show that they meet the criteria necessary for high temperature application.

As a result of the investigations, a rocket nozzle was produced and tested under real application conditions. It satisfied all service requirements.

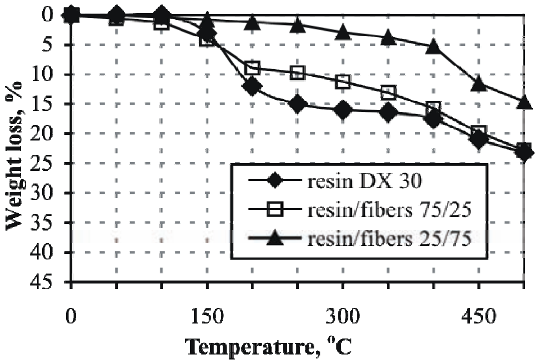

Fig. 7. Thermal decomposition (TG) of the resin DX 30 and composites with 25/75 and 75/25 fiber/matrix ratio.

CONCLUSIONS

The basic mechanical and thermal properties of phenolic resin composites with different fiber contents and fiber lengths were tested. The optimal results were obtained for composites with a carbon fiber content of approx. 60 %. The optimal processing parameters, determined using full factorial experimental design, were found to be: press cycle temperature: 160 °C, press cycle time: 25 min and fiber length: 25 mm.

The composite material based on the ablative phenolic resin and carbon fibers, produced using these processing parameters and a fiber length of 25 mm had the following mechanical properties: flexural strength, 247 MPa; modulus, 27.6 GPa; impact resistance 110 and 91 kJ/m^2 for test moldings of 10 mm×10 mm and 15 mm×15 mm, respectively.

The final composite parts based on this molding compound are recommended for various application in the automotive industry, military (for anti-hail rocket nozzles), leisure, *etc*.

ИЗВОД

КОМПОЗИТНИ МАТЕРИЈАЛ НА БАЗИ АБЛАТИВНЕ ФЕНОЛНЕ СМОЛЕ И УГЉЕНИЧНИХ ВЛАКАНА

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У раду је извршена оптимизација технологије за производњу пресованих композита на бази високотемпературне аблативне фенол–формалдехидне смоле и кратких угљеничних влакана. Окарактерисани су почетни материјали, као и добијени узорци композита са различитом количином и дужином угљеничних влакана. Применом термокомпресије израђени су узорци, чија су основна механичка и термичка својства испитивана у раду. На бази добијених резултата одређен је оптималан однос влакно–матрица за производњу прес-масе за високо-температурну примену. На основу оптимизације процеса пресовања композитног материјала одређени су параметри процеса адекватни за добијање композита са високим механичким својствима и термичком стабилношћу. За оптимизацију процеса примењена је нумеричка метода планираног експеримента са варирањем три основна фактора: дужина влакна, температура и време пресовања. Механичке карактеристике композита (чврстоћа савијања од 247 MPa, модул од 27,6 GPa, ударна отпорност од 110 (за тест узорка 10mm×10 mm) и 91 kJ/m^2 (за тест узорка 15mm×15mm)) потврђују да је добијени материјал адекватан за примену у аутомобилској, војној и другим индустријама где су неопходне висока температурна издржљивост и задовољавајућа механичка чврстоћа.

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