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Thermal conversion of carbon fibres/polysiloxane composites to carbon fibres/ceramic composites

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Abstract

The aim of this work is to investigate the thermal conversion of carbon fibres/polysiloxane composites to carbon fibres/ceramic composites. The conversion mechanism of four different resins to the ceramic phase in the presence of carbon fibres is investigated. The experiments were conducted in three temperature ranges, corresponding to composite manufacturing stages, namely up to 160 °C, 1000 °C and finally 1700 °C.

The study reveals that the thermal conversion mechanism of pure resins in the presence of carbon fibres is similar to that without fibres up to 1000 °C. Above 1000 °C thermal decomposition occurs in both solid (composite matrix) and gas phases, and the presence of carbon fibres in resin matrix produces higher mass losses and higher porosity of the resulting composite samples in comparison to ceramic residue obtained from pure resin samples. XRD analysis shows that at temperature of 1700 °C composite matrices contain nanosized silicon carbide. SEM and EDS analyses indicate that due to the secondary decomposition of gaseous compounds released during pyrolysis a silicon carbide protective layer is created on the fibre surface and fibre–matrix interface. Moreover, nanosized silicon carbide filaments crystallize in composite pores.

Owing to the presence of the protective silicon carbide layer created from the gas phase on the fibre–matrix interface, highly porous C/SiC composites show significantly high oxidation resistance.

Keywords: Polysiloxanes; Carbon fibres; Ceramic matrix composites; Black glass ceramics

1. Introduction

The field of application of ceramic matrix composites (CMCs) reinforced with carbon fibres mainly concerns aerospace technology and avionic applications. Recently, these composites have also been applied to automotive engineering and brakes systems [1–6]. CMCs represent an advantageous combination of thermal and mechanical properties and are lightweight and chemically resistant as compared to metals and alloys. Industrial application of CMCs reinforced with continuous fibres is still a long way off due to processing difficulties, particularly with regard to obtaining materials with reproducible properties and high manufacturing costs [7–9].

Generally, three methods are used for the preparation of continuous fibre-reinforced ceramic matrices, i.e., chemical vapour infiltration (CVI) or pressure pulsed chemical vapour infiltration (P-CVI), reactive melt infiltration (RMI) and polymer impregnation followed by pyrolysis (PIP) [10–15]. CVI and P-CVI processes are relatively slow and require expensive equipment. Composites obtained by these methods have some residual porosity and density gradient. Unlike both CVI methods, the RMI method is fast; however the process is limited by fibre-damaging chemical interactions between the fibre and the matrix at elevated temperatures. The PIP method is based on precerams (polymeric precursors of ceramics) that can be transformed into ceramic phases during heat treatment (pyrolysis). In comparison to the CVI, P-CVI and RMI methods, the use of precerams offers opportunities for broadening the application of continuous fibre-reinforced ceramic matrix composites. This method is the most economical from the point of view of matrix precursor prices and energy saving (lower processing temperatures). Moreover, it does not damage fibres and allows for obtaining pure homogenous

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composite matrices with tailored matrix structure and microstructure.

Organosilicon polymers, which are commercially applied as a source of ceramic compounds and composites, e.g., polycarbosilanes, are well documented in the literature [16–19]. On the contrary, there are limited works concerning the use of polysiloxanes as precursors of ceramic materials [20–23], and as precursors for the manufacture of CMCs containing carbon fibres as a reinforcement. The polysiloxanes are widely applied to protect building materials against moisture. A cross-linked polysiloxane resin during pyrolysis up to 1000 °C can be transformed into a silicon oxycarbide (black glass), structure containing Si–O–Si bonds. Such a resin seems to be a particular advantageous precursor as a matrix in the manufacture of CMCs. Our previous work indicate that depending on the structure of polysiloxane resins there is possible to obtain pore-free bulk ceramic samples with high ceramic yield, i.e., from 82 to 86 wt% at 1000 °C and 61 to 70 wt% at 1700 °C [23]. The aim of this work is to investigate the thermal conversion process of carbon fibres/polysiloxane composites to carbon fibres/ceramic composites. Ceramic matrix composites containing continuous carbon fibres were manufactured by the PIP technique, using four types of polysiloxanes, differing in carbon to silicon molar ratio and oxygen concentration. The cured pure resin samples and carbon fibres – based resin composites were heated up to 1700 °C. Structure, microstructure, mass losses and dimensional changes of the samples were analysed with the aim to assess usability of selected polysiloxane resins as ceramic matrix precursors.

2. Materials and methods

HTS 5131 (Tenax Fibre) carbon fibres in the form of roving consisted of 3000 filaments were used as reinforcement. Four types of commercially available polysiloxane resins produced by Lucebni zavody, Kolin (Czech Republic) were used as ceramic matrix precursors. The basic characteristics of pure polysiloxane resins are presented in Table 1. The additional details related to the polysiloxane resins properties, their thermogravimetric analyses, and the elemental compositions after pyrolysis to 1000 °C are given elsewhere [21,23].

The unidirectional composite samples were manufactured according to the PIP procedure. Carbon fibre roving was wrapped onto a rotating cylindrical drum to form (1D) unidirectional fibre prepreg tapes. The carbon fibre tapes were then impregnated with polysiloxane solution. After drying, the impregnated fibre prepreg tape was removed from the drum, cut into the desired shape, stacked in a metallic mould in the required orientation (1D) and compression moulded under a pressure of 10 MPa. Polymer – based composite samples with different matrix precursors were then cured in an autoclave under an air pressure of 0.9 MPa. Nonporous crack-free polymeric composites were prepared under optimal curing conditions. The processing parameters were selected on the basis of thermogravimetric measurements [23] and the following assumptions: adequate conditions of curing should lead to obtaining bulk nonporous polymeric matrices; the composites should retain their shape during moulding and curing. Thus, composite samples were cured at lower temperatures and in longer time than those recommended by resin supplier, i.e., at 160 °C in an air atmosphere for 7–14 days, depending on the type of polymer.

C/polymer composites were then subjected to the first stage of thermal treatment in an inert atmosphere up to 1000 °C. In this way composites with silicon oxycarbide matrix were obtained (denoted as C/Si–C–O composites). The C/Si–C–O composites were subjected to further heat treatment in an inert atmosphere up to 1700 °C in order to obtain composites with silicon carbide matrices (denoted as C/SiC composites).

The apparent density and open porosity of as-received composites were determined by the hydrostatic weighing method.

The mass losses of resin and composite samples after heat treatment were determined by comparing the sample weights before and after heat treatment.

The fibre volume and weight fractions were determined from the weight and dimensions of the samples, the known amount of fibres in the matrices and densities of fibres and cured resins.

Linear transverse shrinkage of composites due to thermal conversion was measured perpendicularly to the fibre

Table 2
Composite characteristics.

Type of composites	Apparent density [g/cm^3]	Fibres volume fraction [vol%]	Fibres weight fraction [wt%]	Open porosity [vol%]
C/polymer	1.42 ± 0.02	0.50 ± 0.03	0.60 ± 0.03	1 ± 1
C/Si-C-O	1.46 ± 0.02	0.55 ± 0.03	0.70 ± 0.03	20 ± 2
C/SiC	1.17 ± 0.02	0.60 ± 0.03	0.82 ± 0.03	35 ± 2

Table 1
Characteristics of polysiloxane resins - labels are derived from the approximate carbon to silicon molar ratio in resin [23].

Trade name	Labelling	Type of resin	Molar ratio		Ceramic yield at 1000 °C [wt%] ± 1%	Ceramic yield at 1700 °C [wt%] ± 1%
			O/Si	C/Si		
Lukosil 150 X	**P5**	Polymethylphenylsiloxane resin	2.00	4.87	47	27
Lukosil 4102	**P3.1**	Polymethylphenylsiloxane resin	1.17	3.11	86	61
Lukosil 901	**P3.2**	Polymethylphenylsiloxane resin	1.42	3.14	85	61
Lukosil M 130	**P1**	Polymethylsiloxane resin	1.54	1.14	82	70

axis in the matrix using a graphite dilatometer, in an argon atmosphere at temperatures ranging from 500 °C to 1700 °C. During these measurements, shrinkage of composites along the fibres was negligible.

The microstructure of the composites was observed by JEOL 5400 scanning electron microscope (SEM) equipped with EDS (LINK AN 10000 microanalyser). X-ray diffraction

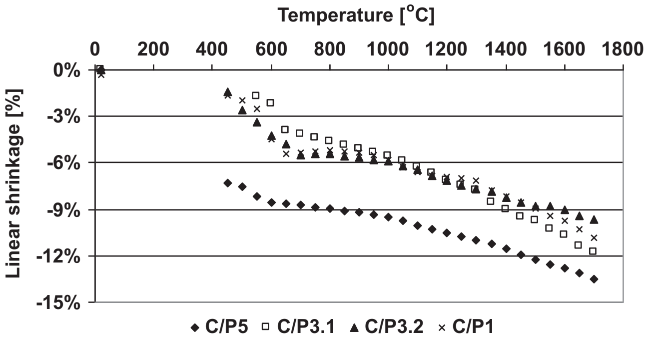

Fig. 1. Linear shrinkage measured perpendicular to the fibre axis for C/polymer composites heat treated up to 1700 °C.

Table 3
Total linear and volumetric shrinkages of composite samples after heat treatment to 1000 °C and 1700 °C.

Type of composite sample	Linear shrinkage, 1000 °C [%]	Calculated volumetric shrinkage, 1000 °C [%]	Linear shrinkage, 1700 °C [%]	Calculated volumetric shrinkage, 1700 °C [%]
C/P5	10.0	19.0	13.0	24.3
C/P3.1	5.5	10.7	11.8	22.2
C/P3.2	5.9	11.5	9.7	18.5
C/P1	5.8	11.3	10.8	20.4

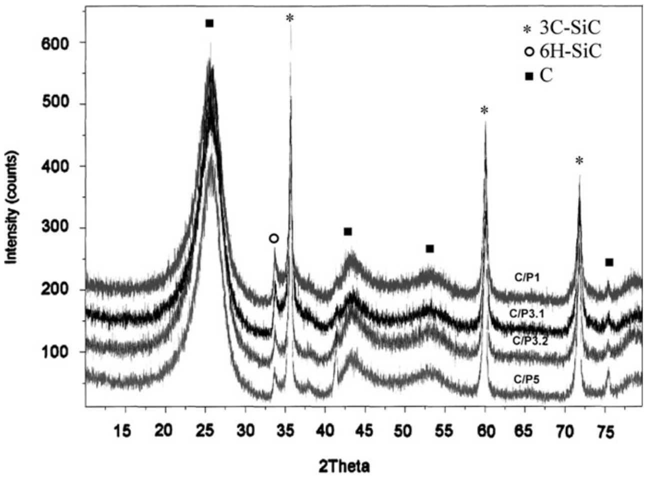

Fig. 3. XRD patterns of C/SiC composites.

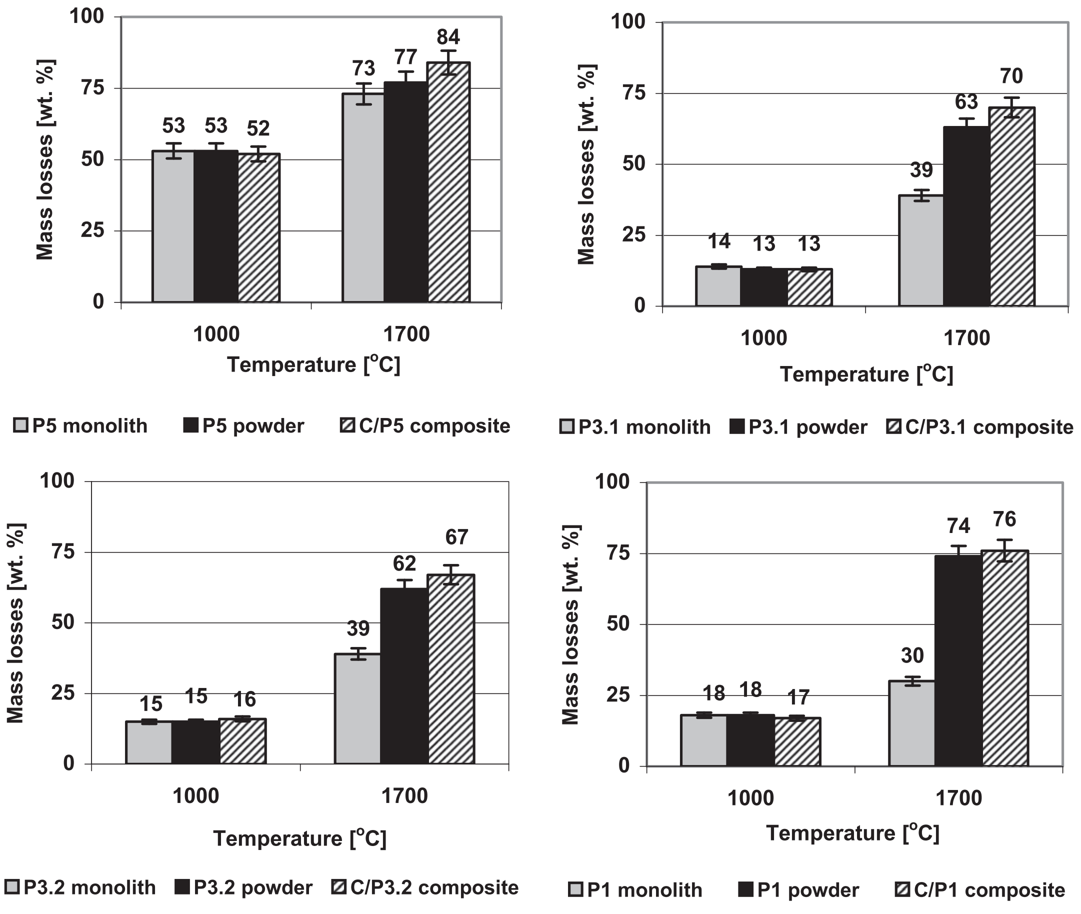

Fig. 2. Comparison of mass losses of different forms of polymeric matrices after heat treatment at 1000 °C and 1700 °C; monolithic sample, powdered polymer and polymer with carbon fibres (composite).

(XRD) studies of the ceramic composites were also carried out (Ni-filtered CuK_α, radiation). The apparent crystallite size was calculated using the Scherrer equation:

$$L_c = k\lambda/(B\cos\theta)$$

where L_c is the apparent crystallite size; k – the Scherrer constant; λ – the wavelength of the CuK_α-radiation; B – the peak width at half maximum; and θ – the Bragg diffraction angle.

Oxidation resistance was examined by mass losses of composite samples heated in air at 600 °C for 2 h. In this experiment pure carbon fibres were used as a reference.

3. Results and discussion

The properties of the investigated composites are given in the Table 2. During heat treatment the density changes

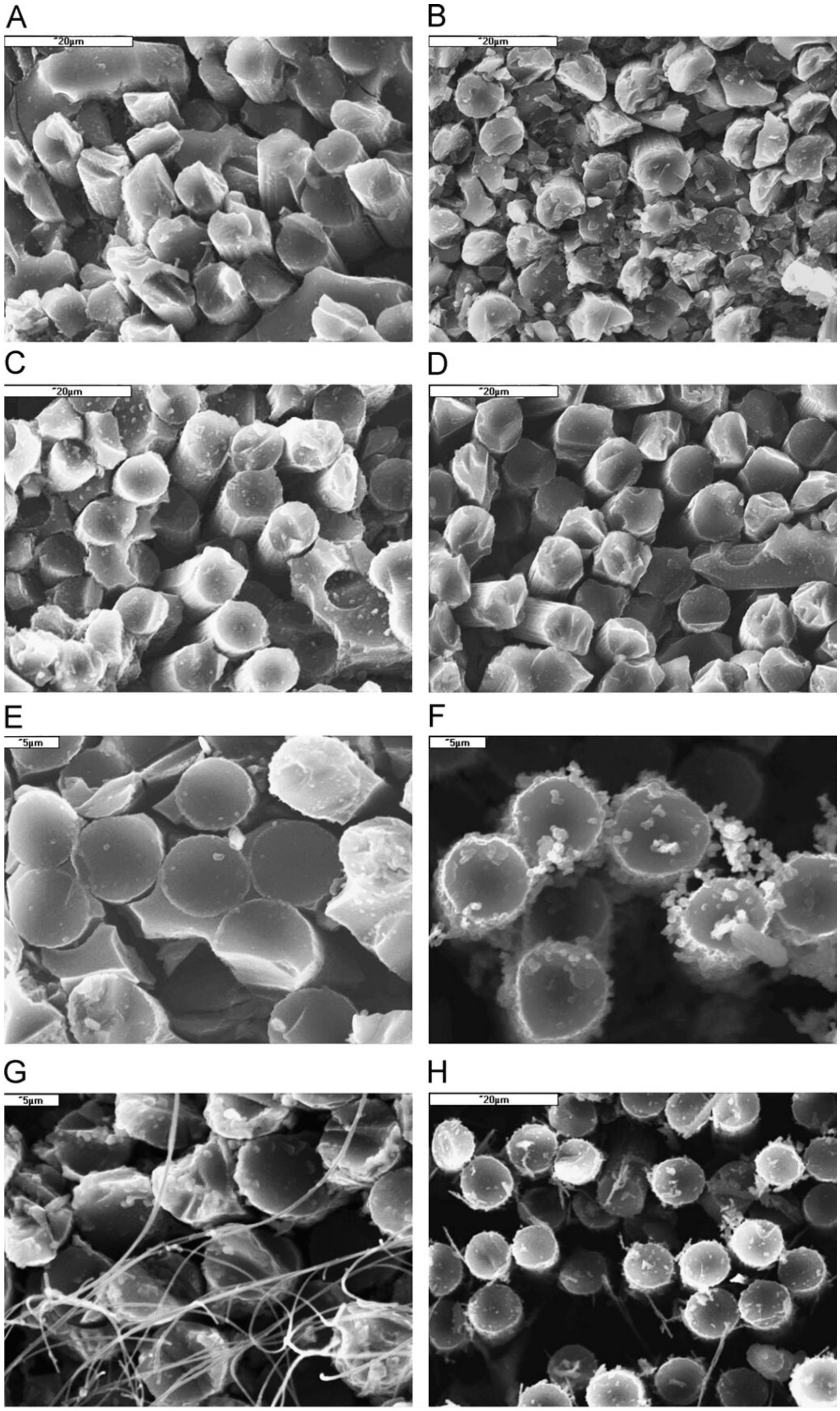

Fig. 4. SEM microphotographs of composite cross-sections, (A–D) C/Si–C–O composites; (E–H) C/SiC composites. (A) C/P5, (B) C/P3.1, (C) C/P3.2, (D) C/P1, (E) C/P5, (F) C/P3.1, (G) C/P3.2 and (H) C/P1.

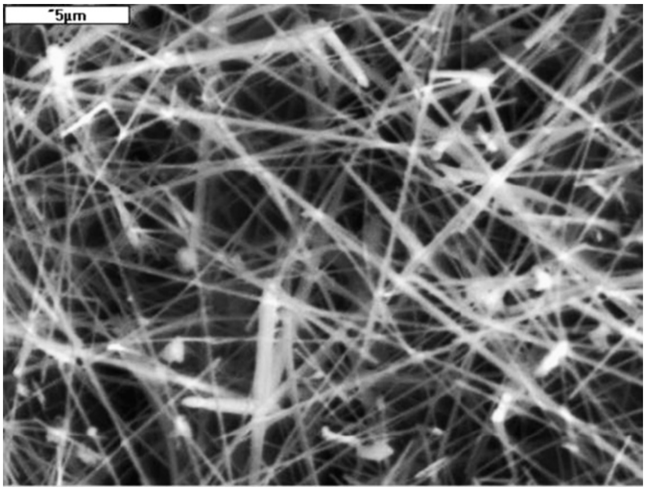

Fig. 5. SEM microphotograph of SiC nanofilaments in the C/SiC composite pores.

of composites were observed. The density of C/Si–C–O composites is higher in comparison with the density of C/polymer composites, whereas the density of the final composites C/SiC obtained at 1700 °C is very low (Table 2). Such a behaviour suggests that two mechanisms may occur during conversion of C/polymer composite to C/SiC composites. The first one proceeds in solid phase and is associated with the pyrolysis of polymeric matrix and its conversion into SiC matrix. The second one is associated with the formation of gaseous products containing carbon, silicon and oxygen-containing volatile compounds. This last mechanism leads to a distinct decrease in apparent density of the composite samples. Because apparent density decreased significantly above 1000 °C, it is evident that the formation of gaseous products dominates in the temperature range from 1000 °C to 1700 °C. Fig. 1 shows shrinkage-temperature relationships for different composite samples, and Table 3 lists the total linear and volumetric shrinkages.

Two ranges of substantial dimensional changes are observed during heat treatment of the composites. The highest transverse shrinkage of the samples takes place within the temperature range from 20 °C to 650 °C, and from 1200 °C to 1700 °C. The magnitude of these changes is roughly proportional to the value of porosity (compare the porosity of C/Si–C–O and C/SiC composites in Table 2) and to fibre amount (up to 60% in C/SiC samples, Table 2). The highest shrinkage was obtained for P5 polymer-based composite, i.e., for the resin with the highest C/Si molar ratio.

Further information has been obtained from the evaluation of the mass losses of pyrolysed composite samples. This parameter has been measured for the following samples: the cured pure resins in the form of monolithic plates, resins containing carbon fibres (composite samples), and mechanically powdered cured resins, which possess a higher surface area in comparison to monolithic polymers. The results of these measurements are shown in the form of diagrams in Fig. 2.

The diagrams indicate that during the treatment to 1000 °C the mass losses of pure polymers and polymers containing carbon fibres are comparable. Above 1000 °C, the mass losses of the composite samples and resin powders are higher as compared to the cured monolithic resins (Fig. 2). During further treatment above 1000 °C up to 1700 °C, due to the presence of fibres/matrix interface creating an additional internal surface in composite samples, the structural changes in the matrix proceed in a different way in comparison to the monolithic resin samples. It can be assumed that the presence of carbon fibres in the composite facilitates the thermal decomposition of a silicon oxycarbide structure accompanied by releasing gaseous products as well as formation of pores. The P5 polymeric precursor, having the highest C/Si molar ratio, was found to have the highest mass loss (see Table 1). On the contrary, the P1 polymeric precursor exhibits the lowest mass loss at 1700 °C (Fig. 2) and the highest differences in mass losses between its monolithic (30 wt%) and powdered form (74 wt%). The P3.1 and P3.2 polymers showed the lowest mass losses among the powdered samples (63 an 62 wt% respectively). The highest mass losses during heat treatment of the resins are in a good correlation with the highest dimensional changes (shrinkage) – (see Fig. 1 and Table 3). Hence, these results indicate that P3.1 and P3.2 polysiloxanes seem to be advantageous matrix precursors for the manufacture of CMCs at 1700 °C.

XRD analysis of composite samples obtained at 1700 °C showed the presence of carbon phase and nanosized 3C and 6 H silicon carbide structures (Fig. 3). The calculated SiC crystallite size is in the range of 25–40 nm for all examined samples.

Further evidences that the presence of carbon fibres develops porosity in the composite matrix above 1000 °C are provided by the study of composite microstructure (Figs. 4–6) and oxidation resistance assessments (Table 4).

SEM microphotographs of the cross-section surface areas of C/Si–C–O and C/SiC composites are shown in Fig. 4. C/Si–C–O composites show a highly porous and relatively uniform microstructure (Fig. 4A–D). No differences are observed between C/Si–C–O composites derived from various resins. Subsequent heat treatment of these composites to 1700 °C causes further decomposition of the matrix with creating solid deposits on the fibre surfaces (Fig. 4F,H). Moreover, the microphotographs revealed the presence of 0.1–0.5 μm thick filaments, which crystallized within the porous space between the carbon fibres (Fig. 4G,H). Such highly porous C/SiC composites consist of carbon fibres (Fig. 4E–H), nanosized SiC filaments (Fig. 4G,H) and small amounts of SiC in the form of grains (Fig. 4F,H). High mass losses at this stage indicate that the thermal decomposition process of Si–C–O matrices is accompanied by formation of silicon-containing volatile compounds. Silicon is released from the matrices, probably as SiO gaseous compounds, while formation of silicon carbide in the form of nanosized filaments and discontinuous layers on

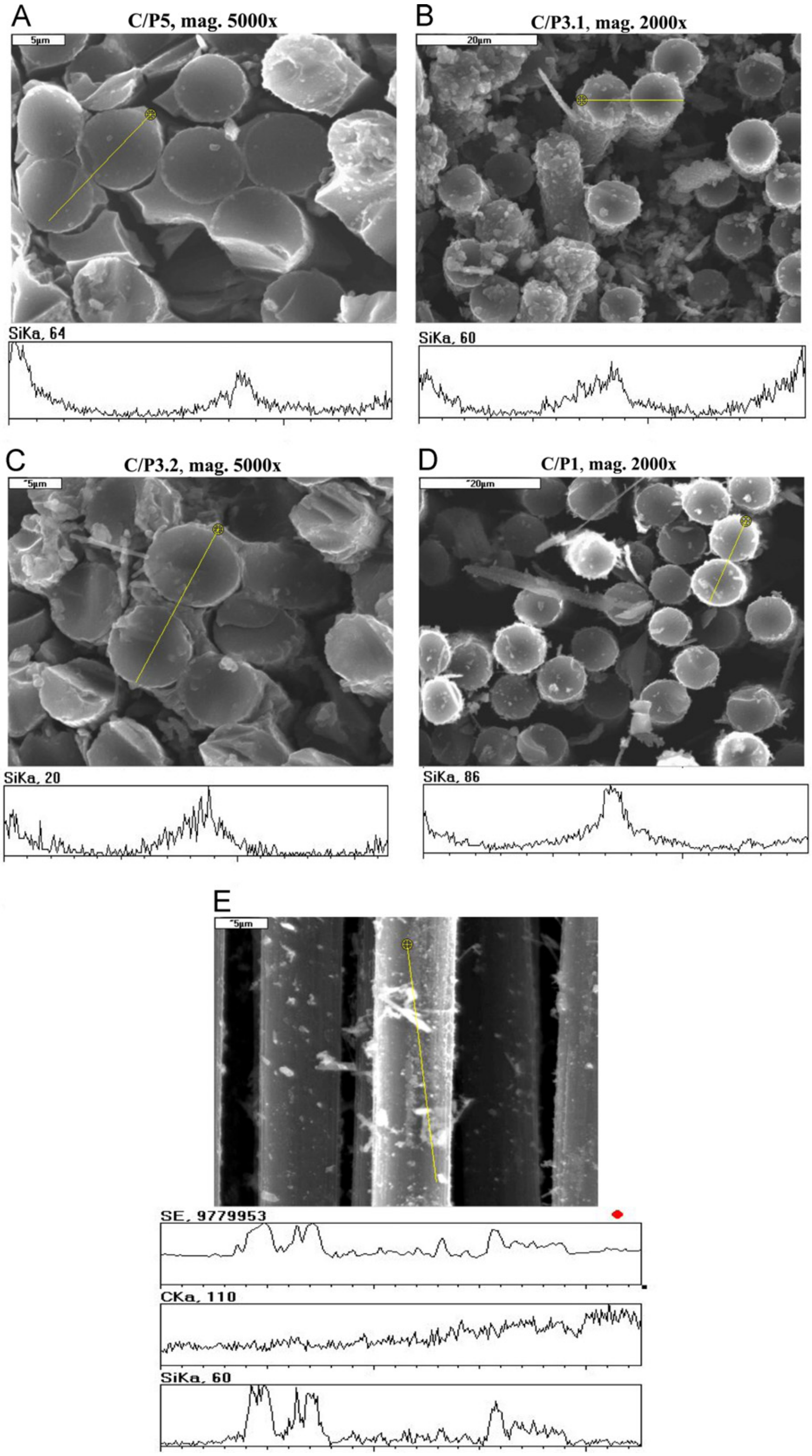

Fig. 6. SEM microphotographs of C/SiC composites with EDS linear analyses, (A–D) cross-sections; (E) linear analysis of the fibre surface. (A) C/P5, mag. 5000x, (B) C/P3.1, mag. 2000x, (C) C/P3.2, mag. 5000x, (D) C/P1, mag. 2000x.

the fibres surface occurs due to reaction of these molecules with carbon. C/SiC composites contain nanosized SiC filaments, that deposit in composite pores (Fig. 5). The microphotographs demonstrate dense network of SiC filaments within the composite matrix. A similar network of SiC filaments was obtained for C/C composites that were impregnated with polysiloxane preceram and heat treated at 1700 °C [24].

Microscopic observation of silicon carbide deposits crystallizing during thermal decomposition of Si–C–O matrix indicates that this process takes places via the gas phase [24,25]. The probable growth process of SiC filaments is by VS mechanism as the temperature of the crystallization process is higher than 1350 °C. The SiO molecules released from the oxycarbide matrix diffuse to the carbon fibre surface and are condensed to form SiO_2. Subsequently, silicon carbide filaments are synthesized by the carboreduction reaction [24,25]. EDS analysis showed that SiC is also deposited on the surface of carbon fibres in the form of small grains and layers (Fig. 6).

Table 4 contains the results of oxidation resistance tests of C/Si–C–O and C/SiC composites.

C/SiC composites represent distinctly higher oxidation resistance, in comparison with C/Si–C–O composites; mass losses of C/SiC composites in the oxidation test are below 10 wt% (Table 4). Under the same oxidation conditions carbon fibres used as a reference were totally burned (99% mass loss, Table 4). Notwithstanding that the composite samples obtained at 1700 °C have higher porosity (open porosity 35%), their oxidation resistance is distinctly higher than that of samples with Si–C–O matrices. The high oxidation resistance of C/SiC composites, combined with low matrix volume and weight fractions (see Table 2), may be explained by the formation of a silicon carbide protective barrier layer (below 0.2 μm) on carbon fibres, which was also confirmed by SEM observations and EDS analysis. The analysis from the fibre surface does not reveal any presence of oxygen (see Fig. 7), which could be expected due to possible formation of amorphous SiO_2 layer on silicon carbide during oxidation tests (passivation). However, oxidation of SiC layer in air and formation of SiO_2 barrier on its surface occurs with a noticeable rate above 900 °C [26,27], whereas our experiments were led at 600 °C for 2 h. Therefore, due to relatively short time and low temperature the passivation process of SiC was not observed. Thus, the improved oxidation resistance results from the presence of silicon carbide layer.

Table 4
Mass losses of C/Si–C–O and C/SiC composites after oxidation.

Type of C/polymer composite	Heat treatment temperature 1000°C [wt%]	Heat treatment temperature 1700°C [wt%]
C/P5	45 ± 1	8 ± 1
C/P3.1	47 ± 1	6 ± 1
C/P3.2	47 ± 1	8 ± 1
C/P1	45 ± 1	8 ± 1
Carbon fibres (reference)	99 ± 1	99 ± 1

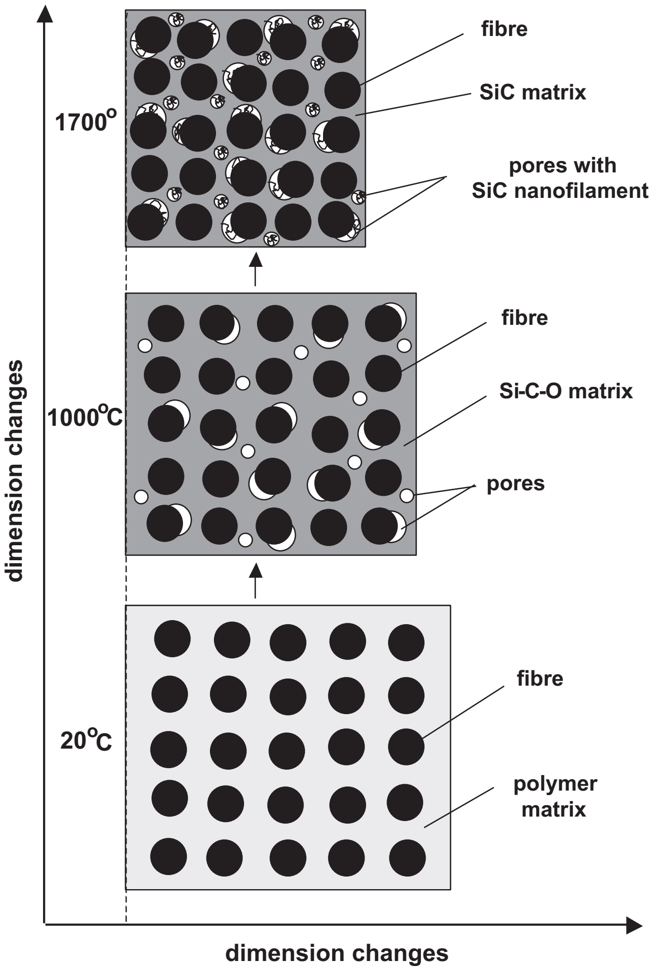

Fig. 8. Thermal conversion of C/polymer composites to C/SiC composites.

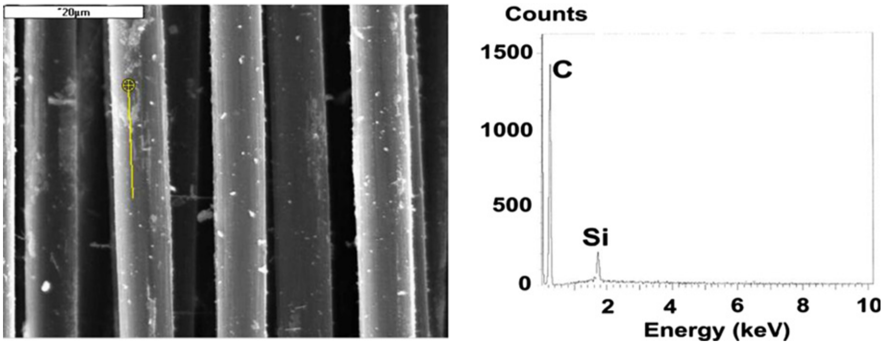

Fig. 7. SEM microphotograph of C/SiC composite with EDS point analysis – sample after oxidation.

Fig. 8 illustrates a probable scheme of dimensional changes accompanying thermal conversion of C/polymer composites to C/SiC composites.

The transverse dimensional changes of composite samples caused by mass losses are accompanied by structural transformation of polymeric precursors into Si–C–O compound (black glass, [21,23]) at about 1000 °C, followed by transformation of the matrix into silicon carbide at 1700 °C, [23]. Because the matrix is constrained by carbon fibres along their axis, longitudinal dimensional changes of the composite samples are not observed. Silicon carbide nanofilaments crystallize within the pores formed during heat treatment. Such a mechanism is observed only for the composite samples heated above 1000 °C.

4. Conclusions

The study shows that the mechanism of decomposition of investigated resins up to 1000 °C is similar both in composite samples with carbon fibres and without fibres. Heat treatment leads to transversal shrinkage of the samples and pores formation in the ceramic matrix. Above 1000 °C up to 1700 °C decomposition of the matrix in the presence of carbon fibres is more intense – the process proceeds with formation of solid ceramic residue and silicon-containing volatile products, resulting in mass losses and porosity formation in the composite matrix. SiC layers onto the fibres surfaces and nanosized silicon carbide filaments are formed as a result of carboreduction of silicon-containing volatile products. All the investigated composites obtained at 1700 °C contain 3C and 2 H SiC structures.

Owing to the presence of protective silicon carbide layer created from the gas phase at the fibre–matrix interface, highly porous C/SiC composites represent a significantly high oxidation resistance.

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