

# COMPOZITE DE TIP ABLATIV PE BAZĂ DE MATRICE DIN RĂȘINĂ FENOLICĂ/NANOCARBURĂ DE SILICIU ȘI RANFORSARE DIN PÂSLĂ CARBONICĂ

## ABLATIVE TYPE COMPOSITES BASED ON PHENOLIC RESIN/NANO-SILICON CARBIDE MATRIX REINFORCED BY CARBON FIBER FELT

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The paper presents a study regarding obtaining, characterization and testing of carbon fiber felt-phenolic resin composite and nanocomposite materials with neat phenolic matrix and nanofilled with silicon carbide nanoparticles added in two different weight contents (1 and 2 wt. %). The effect of the nSiC presence and content is evaluated taking into consideration mechanical, tribological and thermal behavior. Mechanical testing consisted of compression and 3-point bending tests, the results indicating that the strength and stiffness are improved in the case of nanofilled sample. Tribological testing illustrated that friction coefficient increased with nSiC content increase. Thermal behavior was evaluated by TG-DSC analyses and thermal shock tests (at 1100°C), the post-test mass loss analyses showing that nSiC is able to act as a thermal protection agent, improving thermal resistance of these materials. The experimental results indicate that adding silicon carbide nanoparticles in the phenolic resin matrix of carbon fiber felt based ablative type materials improves their mechanical, tribological and thermal properties and recommends them as potential candidates for ablative applications.

Lucrarea prezintă un studiu privind obținerea, caracterizarea și testarea unor materiale compozite și nanocompozite pe bază de pâslă din fibră de carbon și rășină fenolică simplă și cu adaosuri de nanoparticule de carbură de siliciu, utilizând două concentrații masice diferite (1 și 2%). Efectul prezenței și concentrației de nSiC este evaluat luând în considerare comportamentul mecanic, tribologic și termic. Testarea mecanică a constatat din testarea la compresiune și la încovoiere în 3 puncte, rezultatele indicând îmbunătățirea rezistenței și rigidității în cazul probelor nanocompozite. Testarea tribologică a arătat creșterea valorilor coeficientului de frecare cu creșterea concentrației de nSiC. Comportamentul termic a fost evaluat prin analize TG-DSC și teste de șoc termic (la 1100°C), analiza pierderilor masice după testare a arătat că nSiC poate să acționeze ca un agent de protecție termică, îmbunătățind rezistența termică a acestor materiale. Rezultatele experimentale indică faptul că adaosul de nanoparticule de carbură de siliciu în matricea din rășină fenolică a materialelor de tip ablativ pe bază de pâslă din fibră de carbon le îmbunătățește proprietățile mecanice, tribologice și termice și le recomandă ca potențiale candidate pentru aplicații ablativă.

**Keywords:** carbon fiber felt, ablative materials, nano-silicon carbide, thermal shock resistance, TG-DSC

### 1. Introduction

The special conditions required by the aerospace environment lead to the necessity of developing complex systems based on a wide range of materials, in order to be able to meet the high standard level demands in this industry. Combining materials from different classes is required to cover all the high standard properties, to achieve high performance mechanically, thermally, weight related etc. The classes of materials extend from polymers (thermoset and/or thermoplastic resins), wood based compounds to carbon fiber based reinforcements and inorganic compounds with extreme temperature resistance.

Ablative materials are classified according to dominant ablation mechanism. There are three groups: subliming or melting ablators, charring ablators, and intumescent ablators, that are used in different types of applications, due to the basic thermal and physical differences between them. [1]. The selection of one material from the others depends on the properties of the hyperthermic environment that the thermal protection system is designed for [2].

Charring ablators are used in thermal environment at a higher extent than the other two classes, as they have the ability to sustain a higher thermal flux. During burning process, charring ablators absorb the incoming heat flux and

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generate a rapid increase of the surface temperature, and during endothermic chemical decomposition, the organic matrix pyrolysis occurs generating carbonized material and gaseous compounds. The absorbing heat gases that flow through the charred surface contribute to heat shielding performance and increase the boundary layer, reducing the convective flux. The charring/carbonization is a continuous process because the erosion of the surface due to extreme surface environment conditions leads to the formation of even more charred material [1]. This kind of material is often used in combination with subliming or melting reinforcing materials. One of the performance indexes of an ablator is the capacity of the matrix to form low density char, and phenolic resin fits into this class [3,4], while carbon fibers used as preforms offer mechanical resistance and can be successfully used as structural thermal shields. Carbon fiber reinforced phenolic materials are often used as part of thermal shields for high load space vehicles [5,6]. One of the most known ablative materials based on carbon felt is ASTERM (developed by EADS Astrium ST), that is a low density carbon-phenolic consisting of rigid graphite felt impregnated with phenolic resin [7]. Apollo capsules used materials based on epoxy resin with phenolic microbubbles and silicon fibers in a honeycomb structure made of glass fiber [8-10]. Entry vehicles used in the past numerous ablative type materials, based on phenolic resin impregnated silica fibers, phenolic resin impregnated short silica fiber felt, phenolic resin impregnated cork, silicone impregnated ceramic ablators [11, 12]. Different fillers (such as SiO<sub>2</sub>, MoSi<sub>2</sub> [13], ZrC [14], ceramic whiskers [15], etc.) can be added to improve the properties of the final ablative composite. Amongst them, silicon carbide in micrometric or nanometric form is a ceramic material with high hardness, wear resistance, thermal stability and chemical inertia, properties that made this compound suitable to improve the properties of thermoset matrix (epoxy or phenolic) [16-17] and thermoplastic (polyolefins, polystyrene) [18, 19]. One of the most known application of silicon carbide is to obtain C/SiC brakes, first developed by Porsche [20]. Silicon carbide is often used to improve thermo-oxidative properties [21, 22] and wear resistance [23, 24] of ablative materials.

The paper presents the obtaining, characterization and testing of carbon fiber felt-phenolic resin based ablative type materials with neat phenolic matrix and nanofilled with silicon carbide nanoparticles added in two different weight contents (1 and 2 wt. %). The materials were subjected to compression and 3-point bending mechanical test, friction coefficient measuring tribological test, TG-DSC analyses, thermal shock tests and further post-testing investigations. The experimental results indicate that adding silicon

carbide nanoparticles in the phenolic resin matrix of carbon fiber felt based ablative type materials improves their mechanical, tribological and thermal properties.

## 2. Experimental procedure

### 2.1. Materials

The advanced composite materials were composed of a nanofilled phenolic matrix and carbon preform. The matrix was ISOPHEN 215 SM (solid mass) 57 wt.% resole type phenolic resin, provided by ISOVOLTA S.A. Bucharest, with a density value of 1.135 g/cm<sup>3</sup>. The resin was nanofilled with silicon carbide nanoparticles ( $\beta$ -nSiC) with 3.22 g/cm<sup>3</sup> true density, purchased from Nanostructured & Amorphous Materials Inc., USA. The material used as preform was carbon fiber felt, Sigratherm GFA10) purchased from SGL Group - The Carbon Company, GmbH, with 11.5 mm thickness, 1000 g/m<sup>2</sup> area weight and 2000°C maximum application temperature in vacuum or inert gas.

### 2.2. Obtaining procedure

The obtaining procedure was established after a trial session in which the main factors influencing the process were identified (resin curing temperature and dwell time, pressure, mold material and treatment, solvent evaporating temperature etc.). Different nSiC nanoparticles weight contents (0, 1 and 2 wt.%) were added to the liquid resin, the obtained mixtures were afterwards mechanically stirred for 3-5 minutes and homogenized by ultrasonication for 15 minutes using an ultrasound probe. The carbon fiber felt was cut to the mould dimensions into samples for each of the mixtures and it was soaked into the prepared mixtures. For a proper impregnation, the soaked felt samples were maintained for 24 h at 2 bar pressure. Afterwards, the samples were kept in an oven at 65-70 °C for 30 min for solvent (methanol) evaporation and decrease gas bubbles formation process rate that occurs during resin curing. The samples were transferred into the moulds, that were previously cleaned with ethanol and acetone and their surface was covered with demoulding agent. The moulds were placed in a hydraulic Carver press at 70°C and the temperature was increased according to the curve in Table 1. When the temperature reached 90°C, the pressing of the platens was initiated, and the pressure of 3 kg/cm<sup>2</sup> was maintained until the sample was cooled down to room temperature (12 h).

The following nomenclature for the nanofilled ablative type materials will be used: PR/Felt for the control sample based on carbon fiber felt preform and phenolic resin with no nanofiller and PR+1%nSiC/Felt and PR+2%nSiC/Felt for the samples based on carbon fiber felt preform and phenolic resin with 1 and 2 wt.% nSiC content into the matrix.

Table 1

Thermal pressing program steps of the obtaining process of PR/nSiC/Felt materials  
*Etapele programului de presare termică din procesul de formare a materialelor RF/nSiC/Păslă*

Temperature/ Temperatură, °C	Tim de menținere/ Dwell time, min	Pressing force/ Forța de presare, kg/cm <sup>2</sup>
70	30 (in the oven)	0
70	20 (between platens)	0
90	20 (pressed between the platens)	3
110	20 (pressed between the platens)	3
130	20 (pressed between the platens)	3
150	20 (pressed between the platens)	3
150-25	720 (cooled between the platens)	3

### 2.3. Testing and characterization

The neat and the ultrasonicated nanofilled resin mixtures viscosities were measured at 25°C using Ubbelohde capillary tube viscometer (Cannon CT-1000). The composite samples were subjected to 3-point bending (SR EN ISO 178) and compression (ASTM 1074-11) tests using INSTRON 5982 mechanical testing machine, and the fracture cross section was visualized by scanning electron microscopy (SEM) using FEI Inspect F50 High Resolution Scanning Electron Microscope with field emission gun and 1.2 nm resolution and energy dispersive X-ray spectrometer (EDS). Tribological tests measured the friction coefficient using CETR UMT 3 (Universal Macro Materials Tester) block-on ring module (35 mm diameter steel role, 10 N load and 60s testing time, 1000 and 1500 rpm). Thermal properties were measured TG-DSC and thermal shock tests. TG-DSC tests were performed on Netzsch TG 449C STA Jupiter equipment, using 10 K/min heat rate, in Ar flow in the 25-900°C temperature range and in air flow in 900-1000°C range. Thermal shock tests were performed at 1100°C in air, at three different dwell periods (30, 60, 120s) using a carbonization oven (Nabertherm). FTIR spectroscopy analyses were performed on the grinded samples before and after subjecting them to thermal shock at 1100°C, using Nicolet iS50 Spectrometer in ATR (Attenuated Total Reflectance) mode.

## 3. Results and discussion

### 3.1. Resin viscosity measurements

The neat and nanofilled resin viscosity is very important for the composite development process, as it influences the interaction with the carbon felt preform regarding the matrix interpenetration into the felt pores and wetting of the preform, consequently influencing the interphase of the system. If the used modified resin has too high viscosity, it will not be able to uniformly impregnate the carbon felt preform, this will generate both voids and weak interphase areas, that drastically damage the composite mechanical performance. On the other hand, if the modified resin has too low viscosity, it will drain through the felt preform impregnating it with a low quantity of matrix, resulting in high resin material loss during processing, poor impregnation and too high matrix/fiber content that will also lead to poor

adhesion and consequently low mechanical properties.

As the results illustrate, the neat phenolic resin viscosity has a viscosity value that can be labeled as situated in the low viscosity range. Adding silicon carbide nanopowder generates a minor increase in the resin viscosity, the increase has a linear trendline with nSiC content increase. Nevertheless, the highest viscosity value in the sample series (211.06 cSt) corresponding to the highest nSiC content (2 wt.%) is still in the low-to-medium range.

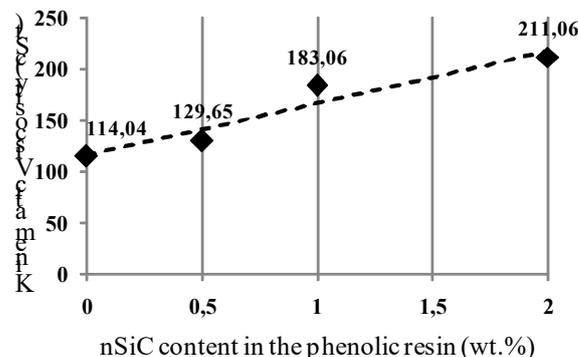


Fig. 1 – Liquid phenolic resin viscosity as a function of nSiC content/ Viscositatea rășinii ifenolice în funcție de conținutul de nSiC.

These results indicate that there should be no impregnation issues arising when the carbon fiber felt will be impregnated with the nanofilled resin.

### 3.2. Mechanical testing

Compressive properties were determined according to ASTM D 1074 standard, at 1.3 mm min<sup>-1</sup> testing speed, on cylindrical specimens, with 12.7 mm diameter and 4 mm height, using 5 specimens per sample. The testing was conducted until the failure of the specimens, which occurred through crushing, due to the brittle nature of the materials. The compression strength and elasticity modulus variation was evaluated as a function of nanofiller weight content and the mean values of the mediated replicas are presented in Table 2.

The results show the positive effect of the nSiC presence regarding the compressive performance of the PR/Felt materials, but it is influenced by the nanoparticles weight content. It can be observed that compared to the control

Table 2

Mechanical properties in compression of PR/nSiC/Felt/ *Proprietățile mecanice la compresiune ale RF/nSiC/Păsle*

Sample/ Probă	Compression strength/ <i>Rezistența la compresiune</i> , MPa ± StdDev	Compression elasticity modulus/ <i>Modulul la compresiune</i> , MPa ± StdDev
PR/Felt	50.79 ± 2.6	585.47 ± 19.9
PR+1%nSiC/Felt	62.62 ± 1.2	664.98 ± 9.3
PR +2%nSiC/Felt	52.94 ± 4.8	659.64 ± 14.6

Table 3

Mechanical properties in 3-point bending of PR/nSiC/Felt/ *Proprietățile mecanice la încovoiere în 3 puncte ale RF/nSiC/Păsle*

Sample/ Probă	Bending strength/ <i>Rezistența la încovoiere</i> , MPa ± StdDev	Bending elasticity modulus/ <i>Modulul la încovoiere</i> , MPa ± StdDev	Strain/ <i>Alungirea</i> , %
PR/Felt	20.92 ± 0.23	2190.21 ± 38.9	0.94
PR+1%nSiC/Felt	24.13 ± 0.33	2393.32 ± 68.5	0.92
PR +2%nSiC/Felt	22.05 ± 0.29	2469.1 ± 112,5	0.89

samples, the highest increment of the compressive strength and modulus is presented by the samples with 1 wt.% nSiC weight content into the matrix. PR+1%nSiC/Felt sample has 23% higher compressive strength and 15 % higher elasticity modulus, while PR+2%nSiC/Felt sample has only a 4% higher strength and 13% higher elasticity modulus.

3-point bending tests were performed according to SR EN ISO 178, at 2 mm min<sup>-1</sup> testing speed, using nominal span length (16 x specimen thickness), on rectangular specimens (80x15x4 mm), using 5 specimens per sample.

Likewise compression testing, during 3-point bending the materials fractured before conventional deflection was reached. The strength variation as a function of nSiC nanoparticles, follows the same trend as in the case of compressive properties, PR+1%nSiC/Felt sample has 15% higher strength and PR+2%nSiC/Felt sample has 5% higher strength. Regarding modulus of elasticity,

the difference between the nanofilled samples is less significant, both presenting approximately 10% higher values.

### 3.3. Scanning electron microscopy analysis

Scanning electron microscopy was performed on the fracture cross section of the mechanically tested PR/nSiC/Felt samples, and prior to this the carbon fiber felt and silicon carbide nanopowder were also subjected to SEM investigations. Figure 2-a, b illustrate the carbonic filaments with 1.7-2.8μm diameters that form bundles that the carbon fiber felt is composed of. It can be noticed that the bundles have diameters between 22-24μm and they are irregularly displaced. Figure 2-c illustrates the nSiC nanopowder, distinguishing both separated and agglutinated nanoparticles. It can be noticed that the nanoparticles have irregular shapes, and their diameter range is between approximately 30-150nm.

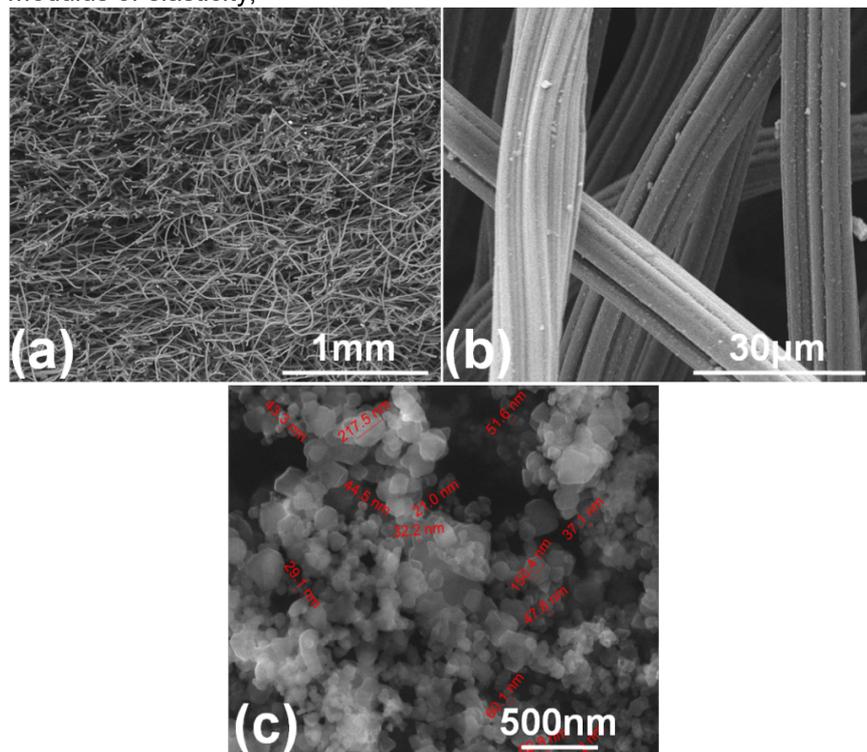


Fig.2 – SEM images of (a, b) carbon fiber felt and (c) nanoparticles of silicon carbide/ *Imagini SEM ale (a, b) păslei carbonice și (c) nanoparticulelor de carbură de siliciu.*

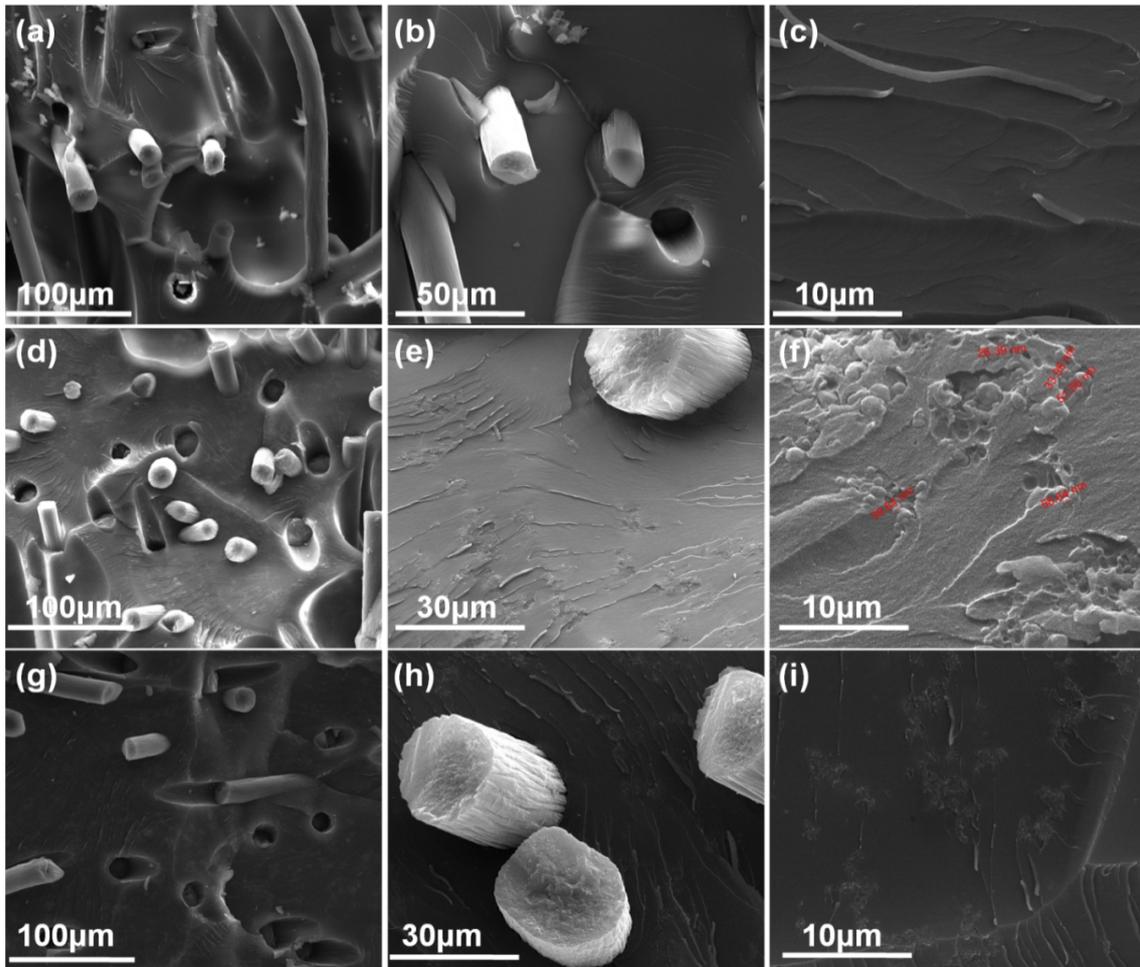


Fig. 3 – SEM images of fracture cross section of ablative composites (a, b, c) PR/Felt, (c, d, f) PR+1% nSiC/Felt, (g, h, i) PR+2% nSiC/Felt  
 /Imagini SEM ale secțiunii de rupere a compozitelor ablative (a, b, c) RF/Păslă, (c, d, f) RF+1% nSiC/Păslă (g, h, i) RF+2% nSiC/Păslă

SEM analysis images of the carbon felt based ablative composites at different magnification level are illustrated in Figure 3. Lower magnification levels (Fig. 3-a, d, g) show the filaments that compose the carbon fiber felt preform embedded into the simple and nanofilled respectively matrix, and there are visible areas where the filaments were ripped out of the polymeric cover. However, the majority of filaments remained strongly embedded into the matrix layer around them (Fig. 3- b, e, h). At higher magnification levels (Fig. 3-c, f, i) only the polymeric phase can be visualized, and the silicon carbide nanoparticles can be distinguished in the nanofilled samples (Fig. 3-f, i), and it can be observed that they are uniformly dispersed into the phenolic resin matrix, on the entire area visualized.

### 3.4. Tribological test

As it is well known carbon fiber is an anti-frictional nature material [25, 26], therefore the felt preform, composed of carbon fiber filaments has an anti-frictional nature, as well. On the other hand, silicon carbide is a well-known abrasive compound [23, 24]. Tribological testing focused on the friction

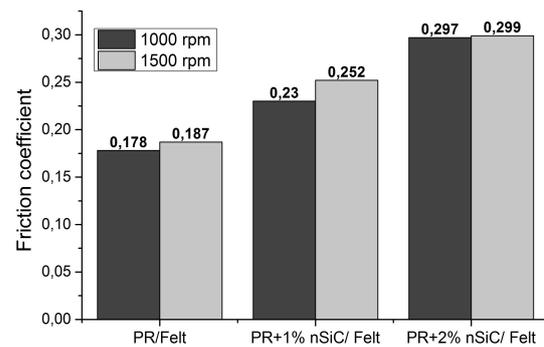


Fig.4 – Friction coefficient variation of PR/nSiC/Felt at 1000 and 1500 rpm/ Variația coeficientului de frecare al RF/nSiC/Păslă la 1000 și 1500 rpm.

coefficient variation as a function of nSiC weight content into the phenolic resin matrix of the PR/Felt composites. The results are presented in Figure 4 and they illustrate the increased friction coefficient values of the nanofilled samples. Friction coefficient increased with nSiC weight content into the matrix

increase, for both speed rates. At 1000 rpm, adding 1 wt.% and 2 wt.% respectively generated an increase of 29 and 67% respectively of the friction coefficient, while at 1500 rpm, 1 wt.% nSiC generated an increase of 35% while 2 wt.% nSiC generated an increase of 60% compared to the control sample with no nanofiller.

### 3.5. TG-DSC analysis

TG-DSC analyses were performed to evaluate the thermal behavior of the materials during linear controlled temperature increase. TG analysis was performed from room temperature to 900°C in inert atmosphere (Ar gas) and from 900-1000°C in air, to perform the combustion of the carbonaceous mass resulted in the previous stage.

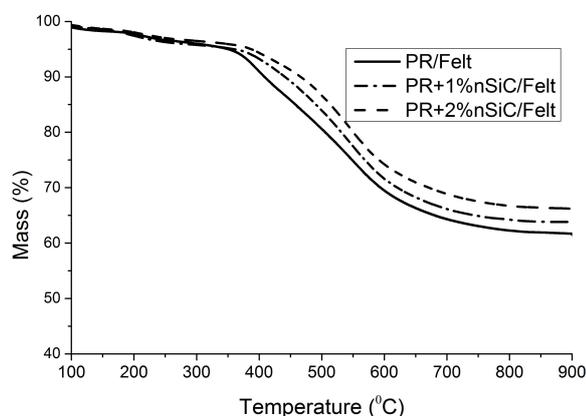


Fig. 5 – TG curves of PR/nSiC/Felt registered in Ar gas between 25-900°C/ Curbele TG ale probelor RF/nSiC/pâslă înregistrate în Ar în domeniul 25-900°C.

The curves registered in the 25-900°C range are presented in Figure 5 and they illustrate the weight loss recorded during this stage. In the 100-350°C temperature domain, the weight loss occurs slowly and smoothly, as it is the domain corresponding to the decomposition of organic compounds from the matrix. Between 350-700°C, the highest weight loss occurs, probably due to the processes of thermal degradation of all the rest of the compounds from the system. The TG curves registered in the 25-900°C illustrate that nSiC nanofiller addition generates an increase of the initial degradation temperature, the control sample showing higher weight losses than the ones presented by the nanofilled samples, at the same temperature value.

The carbonaceous mass resulted in the 25-900°C temperature range stage was subjected to combustion, from 900-1000°C. The curves registered in this domain, in air flow, are presented in Figure 6. Although, the differences between the final residual mass are significant, the values are rather large, due to the thermal resistant carbon fiber felt preform that the materials have as reinforcement. The control sample showed the highest mass loss, the final residual mass being 18.38 %, while the nanofilled samples showed

significantly higher residual mass values, approximately 25% for PR+1%nSiC/Felt and approximately 35% for PR+2%nSiC/Felt. It is very important to mention that the differences between residual mass values corresponding to the nanofilled samples, are not owned only to the nSiC higher weight content in the matrix of PR+2%nSiC/Felt, as the residual mass increase is not proportional to the nanofiller content. This suggests that the additional residual mass corresponding to PR+2%nSiC/Felt corresponds both to the higher nSiC quantity as well as residual composite mass, indicating an improved thermal resistance of the PR/nSiC/Felt composite material.

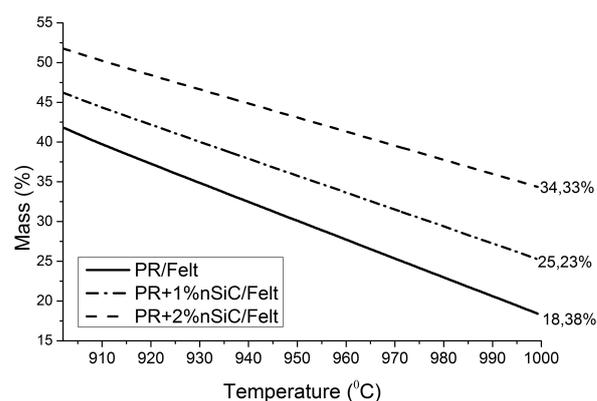


Fig. 6 – TG curves of PR/nSiC/Felt registered in air between 900-1000°C/ Curbele TG ale probelor RF/nSiC/pâslă înregistrate în aer în domeniul 900-1000°C.

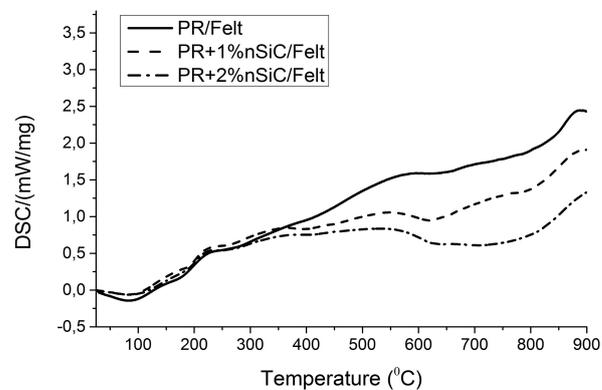


Fig. 7 – DSC curves of PR/nSiC/Felt samples registered in Ar between 25-900°C/ Curbele DSC ale probelor RF/nSiC/pâslă înregistrate în Ar în domeniul 25-900°C.

DSC analysis was performed together with TG analysis in the 25-900°C temperature range in Ar gas and the resulting curves are illustrated in Figure 7. It can be observed that the degradation of the three samples starts simultaneously, but the curve subsequent evolution presents some differences. The control sample curve slope is more abrupt than the one corresponding to the nanofilled samples, indicating a stronger exothermic effect. At higher temperature in the 600-900°C, nSiC added in 2 wt.% content is able to reduce the thermal degradation effect.

Therefore, TG-DSC analyses illustrate that nSiC compound seems to act as a thermal protection agent, reducing exothermic effects and resulting in higher residual composite mass.

### 3.6. Thermal shock test

Thermal shock tests were performed to evaluate the mass loss and material degradation exposing the materials from room temperature directly at an extreme temperature (1100°C). This experiment represents a preliminary test that precedes the in-flame test characteristic for ablative behavior evaluation, and it gives information regarding the ablative capacity of these materials.

The samples were introduced directly at 1100°C and maintained for 3 different periods of time: 30, 60 and 120s. The mass loss was evaluated after each of the exposure periods and it was correlated with the nanofiller content (Fig. 8). It can be observed that exposure time (at 1100°C) increase generates mass loss for all the samples, by organic compounds in the structure decomposition, as was also shown by DSC. In a clear conjunction with TG-DSC results, thermal shock test results in terms of mass loss illustrate that nSiC presence in the PR/Felt composites generates a lower weight loss at as nSiC contents increase, due to the excellent thermal resistance of this compound [27].

The same phenomenon of disproportionality is observed regarding residual mass and nSiC content, confirming once again that the remaining mass is not owned only to the higher nSiC content, but also to a more thermal resistant composite, protected by the nSiC nanoparticles. The thermal protection provided by silicon carbide nanoparticles suggests that PR/nSiC/Felt materials can exhibit improved ablative properties.

The samples appearance after different exposure periods at 1100°C is illustrated in Figure 9. As carbon fiber felt preform is a high temperature resistant material, the samples "erosion" is not so visible at a macroscopic level. However, after exposure for 120s at 1100°C, it can

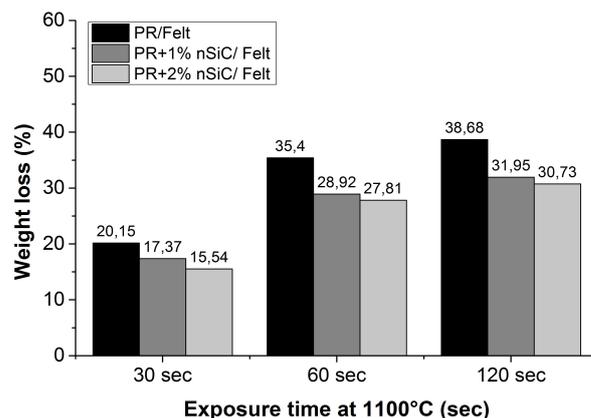


Fig. 8 – Mass loss of PR/nSiC/Felt samples after 30, 60, and 120s dwell time at 1100°C/ Pierdereă masică înregistrată de probele RF/nSiC/Pâslă după menținere timp de 30, 60 și respectiv 120s la 1100°C.

be observed that the control sample shows some cracks on the peripheral area. None of the nanofilled sample present cracks or fractured areas that can be observed macroscopically, the samples only change their color appearance through surface carbonization.

The overall structure of the PR/nSiC/Felt materials does not suffer mechanical degradation after thermal shock testing, all samples maintain their integrity. This confirms once again these composites potential as thermal protection materials.

### 3.7. FTIR spectroscopy after thermal shock tests

FTIR spectroscopy analyses of the PR/nSiC/Felt materials were performed before and after thermal shock test at 1100°C.

Figure 10 illustrates the spectra of the simple and nanofilled PR/Felt samples, before exposure at 1100°C. nSiC presence is difficult to observe, as in the 750-820 cm<sup>-1</sup> range, where the nSiC characteristic peak is situated, some of the benzene ring (from phenolic resin) characteristic

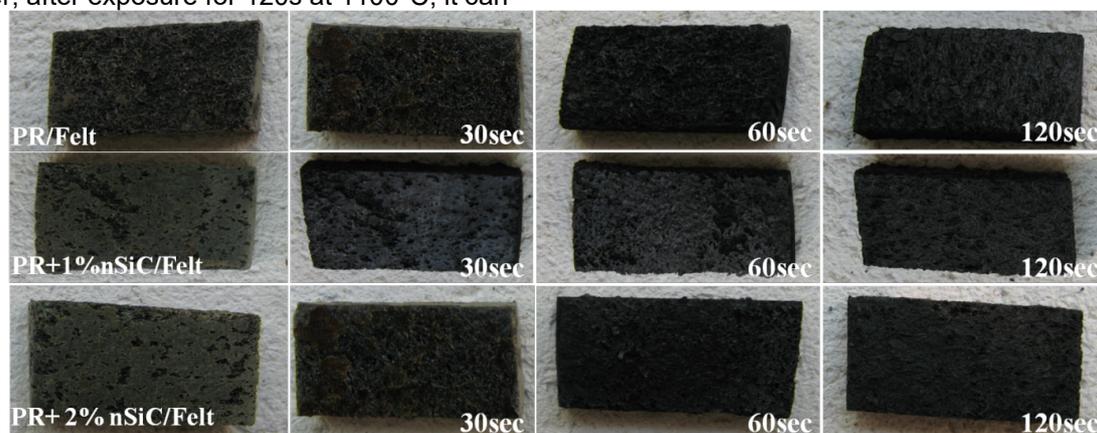


Fig. 9 – PR/Felt, PR+1%nSiC/Felt, PR+2%nSiC/Felt samples before and after thermal shock treatment at 1100°C for 30, 60, and 120s respectively/ Probele RF/Pâslă, RF+1%nSiC/ Pâslă, RF+2%nSiC/ Pâslă înainte și după tratamentul de șoc termic la 1100°C timp de 30, 60 respectiv 120s.

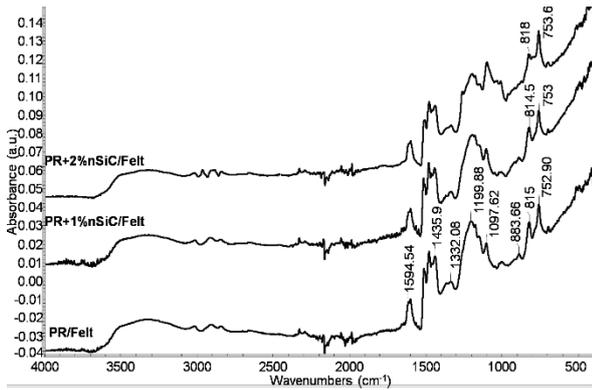


Fig. 10 – FTIR spectra of PR/Felt, PR+1%nSiC/Felt and PR+2%nSiC/Felt ablative materials samples/ *Spectrele FTIR ale compozitelor de tip ablativ RF/Pâslă, RF+1%nSiC/Pâslă și RF+2%nSiC/Pâslă înainte de testarea la șoc termic.*

peaks are present [28]. Nevertheless, in the spectra of 2 wt.% nSiC sample a minor modification in the 750-818  $\text{cm}^{-1}$  domain can be noticed, through the appearance of a low intensity peak at approximately 800  $\text{cm}^{-1}$  that could be owned to the nSiC presence.

Figure 11 and Figure 12 illustrate the comparison of the spectra of PR/Felt and PR+1%nSiC/Felt respectively, before thermal shock and after exposure at 1100°C for 60s and for 120s.

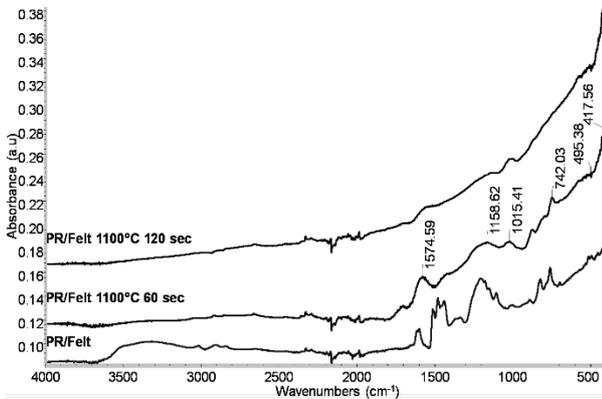


Fig. 11 – FTIR spectra of PR/Felt before and after thermal shock at 1100°C for 60 and 120s/ *Spectrele FTIR ale compozitelor de tip ablativ RF/Pâslă înainte și după testarea la șoc termic cu menținere 60 și respectiv 120s la 1100°C.*

It can be observed that exposure at 1100°C leads to a decrease in intensity of the phenolic resin representative peaks, this decrease becoming more pronounced with exposure time period increase, suggesting the material carbonization phenomenon. In the control sample case, the spectrum registered on the sample exposed at 1100°C for 120s is rather smooth, with some low intensity peaks, suggesting that the material is almost entirely carbonized.

In the case of PR+1%nSiC/Felt sample, some peaks characteristic to the matrix can be observed even after exposure at 1100°C, and at

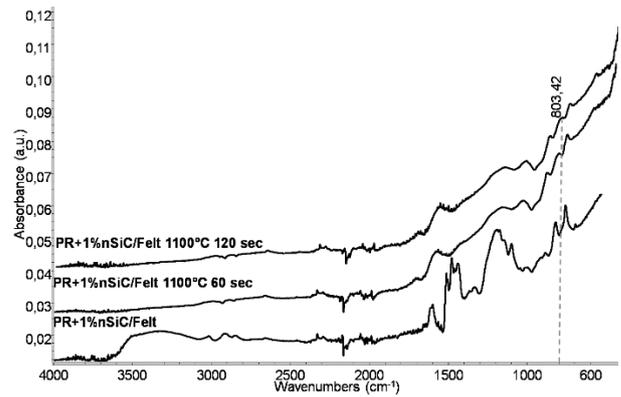


Fig. 12 – FTIR spectra of PR+1%nSiC/Felt before and after thermal shock at 1100°C for 60 and 120s/ *Spectrele FTIR ale compozitelor de tip ablativ RF+1%nSiC/Pâslă înainte și după testarea la șoc termic cu menținere 60 și respectiv 120s la 1100°C.*

approximately 803  $\text{cm}^{-1}$  the registered peak can be attributed to nSiC compound.

The differences between the control sample PR/Felt and nanofilled sample PR/nSiC/Felt can be corroborated with SEM analysis as well as TG-DSC and thermal shock test results, all information offered by these experimental trials indicating the protection agent role that the silicon carbide nanoparticles exhibit in the PR/nSiC/Felt materials.

#### 4. Conclusions

The study presented in this paper focuses on obtaining, characterization and testing of carbon fiber felt-phenolic resin based ablative type materials and the effect of silicon carbide nanofiller (added in 2 different weight contents relative to the phenolic resin matrix: 1 and 2 wt.%) has on these materials properties. The materials were tested in terms of mechanical, tribological and thermal behavior. Mechanical test results indicate that, both compression and 3-point bending strength and stiffness are improved in the case of nanofilled materials compared to the unfilled PR/Felt. The mechanical strength and elasticity modulus values suggest that to obtain higher mechanical performance it is indicated to use lower nSiC contents, as 1 wt.% nanofiller showed the best results. This could be owned to eventual agglomeration that could result when using higher nSiC nanoparticles contents (2 wt.%) that can act as defects during mechanical testing.

Nevertheless, tribological and thermal test results indicate that the materials performance increases with nSiC content increase. The abrasive nature of nSiC generates higher friction coefficient values of the PR/nSiC/Felt materials, while the excellent thermal resistance of these nanofiller improves thermal stability and thermal shock resistance. TG-DSC analyses and thermal shock test results show that silicon carbide

nanoparticles seem to act as a thermal protection agent of the carbon fiber felt- phenolic resin based materials, the weight loss suffered by the nanofilled samples during this tests decreasing with nSiC content increase. However, the mass loss decrease is not proportional to the nanofiller content, suggesting that the additional residual mass corresponds to composite mass that withstood thermal degradation. FTIR spectroscopy analyses confirm the thermal protection effect of nSiC suggested by the other experimental results.

Overall, the results conclude that adding silicon carbide nanoparticles in the phenolic resin matrix of carbon fiber felt based ablative type composites can lead to materials with improved mechanical, tribological and thermal properties and therefore, make them potential candidates for ablative applications.

#### Acknowledgements

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Ministry of European Funds through the Financial Agreement POSDRU/159/1.5/S/134398. The authors are immensely grateful to PhD Eng Roxana Truşcă from University Polytechnica of Bucharest for all SEM analysis and to SR II PhD Phys Adriana Ştefan and SR I Eng Ion Dincă from National Institute for Aerospace Research and Development "Elie Carafoli" from Bucharest for all their support regarding composite processing and testing techniques.

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