Thermo-mechanical and tribological properties of phenolic polymers composites and C-C composites

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Abstract: *Formaldehyde resin-based composites have been an inaugural step in obtaining and using composite materials and they have grown rapidly because of their multiple uses, especially in electrical and aeronautical field.*

Phenolic matrix composites represent a preliminary study to obtain mezophase carbon-carbon composites for advanced materials as potential solutions for reentry shields of cosmic vehicles and launch subsystems, as elements of modern braking systems in aircraft or as potential solutions for the components of the combustion chamber of rockets and also as hypersonic transport solutions for the future. Both phenolic matrix laminated composites and C-C mezophase matrix C-C composites were obtained.

This paper presents an evaluation of the mechanical and tribological behavior of the obtained composites.

Key Words: Nanocomposite, mezophase, C-C composite, carbon fiber

1. INTRODUCTION

Composite materials based on formaldehyde resins are used most often as ablative materials for thermal protection systems (TPS - Thermal Protection Systems) of aerospace vehicles, as well as elements of braking systems for aircraft.

Phenolic matrix composites represent a preliminary study to obtain mezophase carbon-carbon composites for advanced materials as potential solutions for reentry shields of cosmic vehicles and launch subsystems, as elements of modern braking systems in aircraft or as potential solutions for the components of the combustion chamber of rockets and also as hypersonic transport solutions for the future. It is estimated that at speeds of 6.6 Mach the temperatures of critical areas (the radome or nose cone of the aircraft) will be of 10 500 C, and in other areas of 600-8000 C. At these temperatures superalloys or titanium alloys resist but are too heavy and have large expansion coefficients also inducing large voltages, the potential solutions being variants of C-C composites used as thermal protection systems.

For the shields of reentry and launch subsystems C-C composites are used as TPS materials due to ablation resistance at extreme temperatures.

Most TPS materials are reinforced composites where organic resins are used as matrices. When heated, the resins pyrolyzes generating gaseous products (mostly hydrocarbons) that permeate the solid diffusing toward the external heated surface and proceed into boundary layer, where the heat transfer processes take place. The resins pyrolysis also produces a carbonaceous residue, indicated as “char”. The process is typically endothermic and pyrolysis gases are heated as they percolate toward the surface, thus transferring energy from the solid state to the gas. [1]

The extreme heat and erosion of the burning propellant are controlled by the carbon-phenolic composite by means of ablation, a heat and mass transfer process in which a large amount of heat is dissipated by sacrificially removing material from a surface. Phenolic materials ablate with the initial formation of a char. The depth of the char is a function of the heat conduction coefficient of the composite. The char layer is a poor conductor so it protects the underlying phenolic composite from the high heat of the burning propellant. [2]

Experimental activities were oriented to the selection of both reinforcement and matrix materials. Two different composite materials were identified as possible TPS, and were tested and evaluated in terms of mechanical and tribological behavior.

2. EXPERIMENTAL

2.1 MATERIALS

The phenolic resin matrix is composed of CF-112 of which 68% is phenolic resin, the remaining being ethyl alcohol and isopropyl alcohol with a viscosity at 230^0 C: 80 seconds by 4 mm funnel and volatile content being of 38%. The gel-time is of 150 seconds at 1500 C. The SiC nano and the FC CARP 93 fabric were used as a reinforcement agent.

The petroleum pitch mezophase with a carbon content of 52-62%, viscosity of 250 ° C - 30-50 fps and softening point of 94-107 ° C was used as matrix for the C-C composites. The mezophase was obtained by ICPE-CA.

2.2. METHODS AND INSTRUMENTATION

To evaluate mechanical and tribological behaviour composites with different matrix and the same reinforcement agent were prepared and characterized.

The process of making phenolic matrix and CF laminated composites consist in formation of fabric folds, brushing on impregnation, prepolymerization to 700 C, formation of 15-folds laminated and pressing to 0.35 MPa with progressive heating of the press turntables up to 1600 C.The samples made of each composite variant were tested for strength by bending (three points system) with Instron 4301 installation.

In case of getting the mezophase matrix C composites, the moulding was obtained in steel molds. The volume ratio was 60% FC and 40% mezophase. 11 plies of CF and micronized mezophase were put into the mold in alternating layers, so that the first and the last layer be of mezophase. They were heated to 360° C and pressed for 1.5 h at 0.55 MPa. Then the mold was transferred into a controlled atmosphere furnace and heated gradually to 10 ° C /h in argon environment to 550º C, and maintained at this temperature for 1 hour .The roast was made by coke wrapping in an inert environment

The samples were mechanically and tribologically tested and evaluated.

The instrument Instron 4301 was used for mechanical tests, which were performed after 7 days from composites preparation.

Tribological testing was made with INCAS installation- Timken type.

3. RESULTS AND DISCUSSIONS

Phenolic matrix composites represent a preliminary study to obtain mezophase carbon-carbon composites for advanced materials as potential solutions for reentry shields of cosmic vehicles and launch subsystems, as elements of modern braking systems in aircraft or as potential solutions for the components of the combustion chamber of rockets and also as hypersonic transport solutions for the future. It should be noted that compared to epoxy resin composites /FC (the strength is of 658 MPa and the elasticity modulus is of 25 GPa) the mechanical strength is lower while the elasticity modulus is higher. It is useful to note that the phenolic matrix can be used both for making structural composites with fiberglass or carbon fiber stiffening and for carbon-carbon composites. The mezophase is utilized as a matrix to obtain the carbon-carbon composites that are superior to those with phenolic matrix. Table 1. shows the main mechanical characteristics (flexural strength and elasticity modulus) of the achieved composites. For comparison mechanical values of the composites with epoxy resin and fiberglass and carbon fiber reinforcement have been added.

The mechanical characteristics of phenolic matrix composites Table 1.

Crt.No	Composite material	Flexural strength MPa	Elasticity modulus GPa
1	GF + P401	368.1	14.7
2	CF + P401	658.1	25
3	GF +PHR (CF-112)	336.8	15.5
7	CF + PHR (CF-112)	535.5	48.2

where:

- P401- epoxy resin
- GF- glass fiber fabric E_{18} –FIROS
- CF- carbon fibre fabric CARP 93
- PHR-phenolic resin (CF-112) - commercialized by Isovolta

The mechanical tests of phenolic matrix composites were made on Instron 4301. In Figures I.1-I.4 representative diagrams are shown based on which the mechanical properties of the composites were calculated. The values of mechanical characteristics are suggestively presented in histograms in Figures 1-3. Table 1.

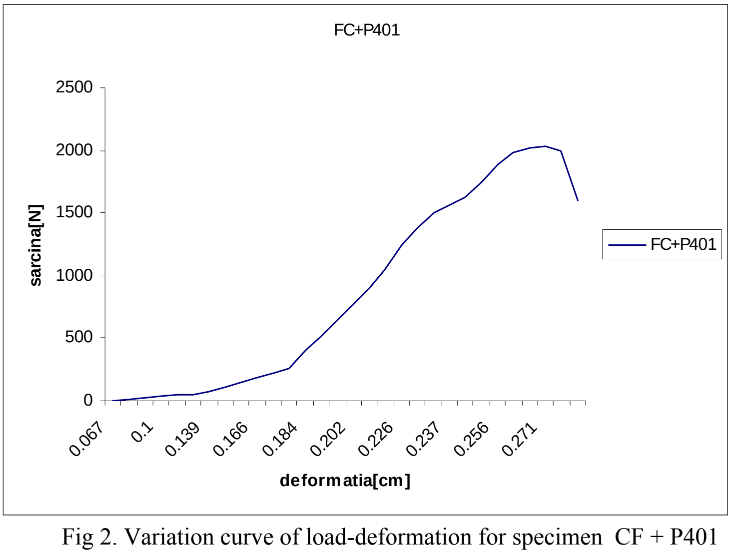

Fig 2. Variation curve of load-deformation for specimen CF + P401

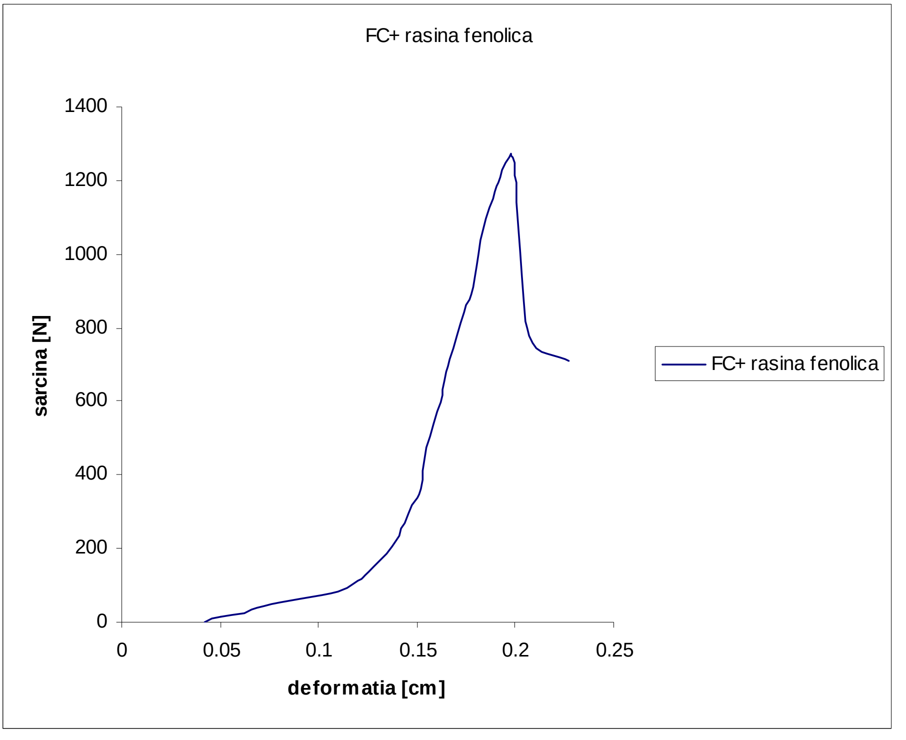

Fig 3. Variation curve of load-deformation for specimen FC + phenolic resin

Fig. 4 Carbon fiber composite CF 112

The C-C composites are considered as a category of new materials consisting essentially of a carbon fiber reinforcement (in various forms, as chop, unidirectional fibers, two and three dimensional fabrics) embedded in a phenolic resin or in a mass of a special petroleum or coal pitch (of mesophase type similar to liquid crystals), and which, through an appropriate heat treatment are also converted into carbon.

The density of the C - C composites which are obtained is of 1.6 ÷ 1.9 g/ cm^3.

The Main characteristics of carbon -carbon composites as advanced tribological materials are the following:

- very high ablation heat (20,000 Kcal / Kg)
- favorable report strength /density, superior to conventional carbon materials

- high strength at high temperatures (above peste 1000°C ÷ 1500°C)
- low thermal expansion coefficient
- light specific weight ((~ 1,6 ÷ 1,9 Kg/dm^3)

Phenolic resins have the following characteristics:

a) carbon content of coke: 50-70% of weight. This content does not increase even by carbonization under pressure.

b) structure of coke (by carbonization) is amorphous and up to 3000° C do not lead to graphitizing.

c) coke density is low (= 1.5 g/cm3)

d) during carbonisation they suffer large shrinkage. The resins carbonized at high pressure do not lead to shrinkage cracks as those carbonized at low pressures, but give less carbon as when carbonised at atmospheric pressure (47%).

e) applying pressure of about 42.2 MPa at a temperature of 400-600°C during carbonisation can lead to graphitized carbon at over 2300°C.

f) phenolic resins polymerize at relatively low temperatures (= 250°C)

g) they have the advantage that being thermostable after polymerization they do not flow when carbonized.

h) coke contains 50 ÷ 56% carbon.

From the tribological point of view, the parameters that govern the phenomenon of friction are speed, pressure and temperature. For the aircraft brakes their values are situated in the following field

v = 25 m/s÷100 m/s

p = 1.5 MPa

t = 700 ÷ 800°C or even 1000°C in limit situations.

The main characteristics of carbon -carbon composites - utilized as friction materials are: [1, 2, 8]

- specific weight much lower than that of conventional materials (1.9 g/cm3, compared to 7.8 ÷ 8g/cm3 for ceramics or bimetallics)
- very good dimensional stability even at high temperatures (thermal expansion coefficient max. 2x10- 6 against 10-5 for steel);
- stability of friction coefficient up to 1000°C
- moderate strength (100 ÷ 300daN/cm2)
- very high ablation heat (20,000 Kcal / Kg)

To achieve the carbon-carbon composite with friction properties also applicable to brake systems, the INCAS team utilized additions of silicon carbide powder, which, on one hand, can give wear resistance and an appropriate coefficient of friction to the C-C composite and, on the other hand, can stand the treatments of carbonization and of forging if need be.

Materials and technology used are as follows:

<u>Reinforcement materials</u>

Two-dimensional CF fabric CARP 193 with the following features:

- cable 3 K (3000 filaments)
- carbon content 100%
- weight 193 g/m2
- thickness 250 mm
- finite 1,1 dtex

Chopped CF, INCAS

- cable 6 K (6,000 filaments)
- filament diameter 7 mm
- chopped CF length 3.5 mm
- carbon content 97%

Impregnating material (matrix) - mezophase provided by the coordinator (ICPE-CA):

- coal pitch precursor
- carbon content 85%
- softening point 350 ° C
- irreversible solidification point 520° C ÷ 530° C

Breaking Strength -Mezophasic Composites Table 5

Crt No	Composite	*Breaking Strength* MPa		
		After pressing	After carbonization	After graphitizing
1	CARP 193 fabric+ mezophase powder	-	260	200
2	CARP 193 fabric +liquid mezophase	-	263	200
3	Chopped CF+ mezophase powder	-	140	105
4	Chopped CF +liquid mezophase	-	136	78

Every couple of friction worked during three stages of 15 minutes. During the same stage the machine worked in cycles of one minute followed by a pause of 5 minutes for cooling.

After accumulation of 15 minutes the block were removed and the wear was determined, gravimetrically on an analytical balance. The obtained results of the tribological experiments are summarized in Table 6:

The coefficient of friction and wear of the steel/ mezophasic composite couple Table 6

Nr. crt	Materials	Coefficient of friction	block wear gr.		
			15'	30'	45'
1.	CARP fabric + Micronized mezophase	0.145	0.035	0.06	0.093
2.	CARP fabric + Liquid mezophase	0.145	0.04	0.073	0.1
3.	Chopped CF+ Micronized mezophase	0.143	0.038	0.07	0.09
4.	Chopped CF+ Liquid mezophase	0.141	0.041	0.075	0.098
1'	1 Graphitized	0.131	0.042	0.075	0.11
2'	2 Graphitized	0.130	0.04	0.087	0.108
3'	3 Graphitized	0.132	0.0405	0.086	0.13
4'	4 Graphitized	0.132	0.04	0.082	0.12

Note: - Tests 1, 2, 3, 4 refer to the composite after roasting (1000 ° C) - Tests 1 ', 2', 3 ', 4' refer to the same graphitized composites (2800 ÷ 3000° C)

4. CONCLUSIONS

It is useful to note that the phenolic matrix is to be used both for making structural composites with fiberglass or carbon fiber reinforcement and carbon-carbon composites. Superior behavior is to be remarked both in terms of strength and modules of composites with carbon fiber reinforcement against those reinforced with glass fiber (σ_{CF} = 535 MPa, E_{CF} = 48.2 GPa against σ_{GF} = 336.8 MPa si E_{GF} = 15.5 Gpa. The modules of elasticity when using phenolic matrices were higher than for epoxy resins. For the carbon fiber reinforcement the mechanical strength was higher when using epoxy resins than when using phenolic resins. The elasticity modules were higher in phenolic resins than with epoxy resins (E = 48.2 GPa versus 25 GPa).

In case of the C-C composite specimens with mezophase a sharp strength decrease is found after roasting (t = 1000° C) and also after graphitization (260 MPa and 200 MPa respectivelly). In case of reinforcement with chopped CF the mechanical resistance values are much smaller (~ 45 ÷ 50%) than in case of fabric reinforcement. The mechanical behavior of C-C composites made by using solid micronized mezophase was similar to that of the corresponding C-C composites with liquid mezophase. Mezophase carbonized composites (1000° C) showed higher friction coefficients and lower wear than graphitized composites. The coefficients of friction and wear of the composites with two dimensional fabric or chopped fibers were practically of same values.

5. REFERENCES

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