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POLY(BOROSILOXANES) AS PRECURSORS OF CERAMIC MATRIX IN CARBON FIBER COMPOSITES

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ABSTRACT

Ceramic matrix composites (CMC's) constituted of silicon boron oxycarbide (SiBCO) matrix and unidirectional carbon fiber rods as reinforcement phase, were prepared by pyrolysis of carbon fiber rods wrapped in polysiloxanes (PS) or poly(borosiloxanes) (PBS) matrices. The preparation of the polymeric precursors involved hydrolysis/condensation reactions of alkoxyxilanes in the presence or not of boric acid, with B/Si atomic ratio of 0.2 and 0.5. Infrared spectra of PBS showed evidence of Si-O-B bonds at 880 cm^{-1} , due to the incorporation of the crosslinker trigonal units of BO_3 in the polymeric network. X-ray diffraction analyses exhibited an amorphous character of the resulting polymer-derived ceramics obtained by pyrolysis up to $1000\text{ }^\circ\text{C}$, under inert atmosphere. The C/SiOC and C/SiBCO composites have good mechanical and thermal stability, in addition to good adhesion between the carbon fiber and the ceramic phase as observed by SEM microscopy.

KEYWORDS:

Precursors; Poly(borosiloxanes); Carbon fibers; Composites.

INTRODUCTION

Polymer-derived ceramics are presently being studied for application as protective coating (Didenko, 2000), fibers (Sutton, 1992) and ceramic matrix composites (Schiavon, 2004a) because they have outstanding high temperature properties. Indeed, the preparation of ceramic matrix composite (CMC's) from polymeric precursors has been a promising area, due to the possibility to obtain new ceramic materials, whose properties can be tailored to specific needs for long life service and load bearing applications (Krenkel, 2005).

Silicon oxycarbide-(SiOC) and silicon carbonitrides-(SiCN) derived glasses have attracted attention for their peculiar high temperature properties, such as low creep rate (Riedel, 1998) and high thermal stability (Ishikawa, 1998). They are easily produced by thermal degradation of polysiloxane and polysilazanes, respectively, which leads to a random network of covalent Si-C, Si-N and Si-O bonds. These materials showed excellent stability against crystallization. Amorphous SiCN led to β -SiC/Si₃N₄ nanocomposite only above $1450\text{ }^\circ\text{C}$ (Schiavon, 2002a) while SiCO starts to separate into amorphous silica and nanocrystalline (1 nm) β -

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SiC at lower temperature (1300 °C), with low crystallite growth rate. At 1500 °C β -SiC crystallites reach a maximum size of 2-3 nm (Turquat, 2001).

The incorporation of heteroatoms, such as boron, in these materials can be performed because the molecular structures of the polymeric precursors can be easily tailored (Klonczynski, 2004). Such approach is a recent strategy for structural and composition ceramic changes that improves the properties of the final materials, making possible new high demanding applications. In the SiCN system, the addition of B leads to the production of SiBCN glasses which may display the highest thermal stability ever shown for an amorphous phase under inert atmosphere with crystallization temperature above 1700 °C and decomposition temperatures even up to 2200 °C (Wang, 2001). The mechanism which can explain the role of boron in increasing the stability of the disordered SiCN network against devitrification is not completely understood yet. However, it has been proposed that B can form turbostratic BN layers which can act as a barrier for the diffusing atoms but also can increase the network disorder of SiCN making more difficult the structural reorganization toward crystalline phases (Wang, 2001).

Boron is also known to protect carbonaceous materials by carbon active site poisoning or by forming a boron oxide film on the surface of the carbonaceous material (Labruquère, 2002). In this field, the general consensus has been that substitutional boron act as an inhibitor of carbon oxidation, redistributing the π electrons, which inhibits the CO and CO₂ desorption, and enhancing the graphitization of carbon.

Despite many relevant studies regarding the role of substitutional boron in carbon oxidation protection (Lee, 2003), controversial understanding still remains, and much more experimental results must be discussed. Indeed, different approaches have been used to produce B-doped carbon materials (Ehrburger, 1986; Labruquère, 2002). Although each study has used different materials and experimental conditions, the final goal for them was the improvement of the carbon oxidation stability with the introduction of B in the system.

Taking in account the above ideas, this work reports the synthesis and thermal characterization of polysiloxanes (PS) and poly(borosiloxanes) (PBS), aiming the use of these polymers as precursors of ceramic matrix for protection of carbon fibers in ceramic matrix composites (CMC). C/SiOC and C/SiBOC composites were prepared by impregnation of the liquid precursors in uni-directional sets of carbon fibers followed by cure, drying and pyrolysis. The results regarding the preparation and polymer-to-ceramic conversion, as well as the properties of the resulting CMC's involving carbon fibers will be discussed.

EXPERIMENTAL

Preparation of the polymeric precursors

Poly(borosiloxane) gels (PBS) were synthesized by adding to methyltriethoxysilane, CH₃Si(OCH₂CH₃)₃, MTES (Aldrich) or vinyltriethoxysilane, CH₂CHSi(OCH₂CH₃)₃, VTES (Aldrich) an appropriate amount of boric acid, B(OH)₃ (Vetec Brasil), following by stirring until its complete dissolution (Sorarù, 2000; Schiavon, 2004b). Compositions having a nominal B/Si atomic ratio of 0.2 and 0.5 were prepared. The clear solutions were then cast in plastic tubes and left open for gelation. Wet gels were dried for at least 10 days at 60 °C. For comparison purposes, gels without B (polysiloxane, PS) were prepared from both methyltriethoxysilane or vinyltriethoxysilane. MTES or VTES was hydrolyzed using a ratio H₂O/(OCH₂CH₃) of 1, at 70 °C for 15 minutes under acidic conditions (HCl, pH = 1). Afterward the solution was cooled to room temperature, and the sol was gelled and dried at 70 °C for at least 10 days.

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Glass preparation

Gel fragments of PS and PBS were converted into the SiOC and SiBOC glasses, respectively, through pyrolysis in flowing Ar (100 mL/min) at 1000 °C. The pyrolysis was carried out in a tubular furnace (EDG10P-S) by placing the sample in an alumina crucible, and then in an alumina furnace using a heating rate of 10 °C/min with a holding time of 1 h at the maximum temperature. For the polymer-to-ceramic conversion studies the gel samples were heated, with the same heating schedule, at 300 and 700 °C. Ceramic yield was determined by thermogravimetric analysis.

Ceramic matrix composite preparation

C/SiCO and C/SiBCO composites were prepared by impregnation of ex-PAN carbon fiber tows with the corresponding sol precursor. The carbon fibers were manufactured by Hexcel Co. The fiber tows were left immersed in the sol for a period of 24 hours. The polymeric-impregnated fiber tows were then passed through cylindrical polyethylene tubes (10 mm length and 3 mm of internal diameter), and kept inside it for seven days to complete the cure of the polymeric precursor. After that, green bodies were additionally dried at 60 °C for seven days. Finally, they were pyrolysed, under inert atmosphere of argon, using the heat schedule described previously.

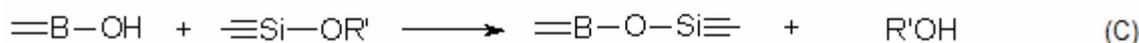
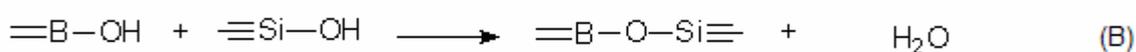
Characterization techniques

Thermogravimetric analysis (TGA) of the gels and green bodies were performed on a thermoanalyzer (TA Instruments 2950), equipped with an alumina tube furnace and alumina crucibles. Typically, tests were performed in flowing argon or synthetic air, with a heating rate of 10 °C/min up to 1000 °C. Fourier transform infrared spectra (FTIR) were recorded using Bomem MB series equipment. FTIR spectra were obtained on KBr pellets in the transmission mode, recording 32 scans with a resolution of 4 cm⁻¹. XRD spectra were recorded on a diffractometer (Shimadzu, model XD3A), using Cu K α radiation ($\lambda = 0.15418$ nm). Microstructural characterization was performed by scanning electron microscopy (SEM), using an electronic microscopy (LEO 435VPI), operating with an accelerating voltage of 20 kV, and optical microscopy (OM), using an Olympus BH microscope.

RESULTS AND DISCUSSION

Synthesis and characterization of the polymeric precursors

The reactions involved in the synthesis of the polymeric precursor network PS and PBS can be represented by the equations (A), (B) e (C):



where R' is the ethyl group (-CH₂CH₃).

B(OH)₃ shows low solubility in alkoxy silane system. However, it has been shown (Irwin, 1987) that reaction (A) occurs first, and it is followed by reactions (B) and (C). As B-OEt are formed by reaction (A) the solubility of B(OH)_{3-x}(OEt)_x (1 < x < 3) species increases in the course of the reaction. In addition, the alcohol formed in step (C) also helps the dissolution of boric acid. The gelation time for the hydrolysis of methytriethoxysilane, CH₃Si(OEt)₃, with boric acid in the B/Si atomic ratio of 0.2 e 0.5 was ~13 e 10 days,

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respectively. Such times suggest that the boric acid takes part in the slowest step of the gel network formation. The same behavior was observed for the gels derived from VTES. All the hybrid gels were monolithic and transparent.

FTIR spectra of the hybrid gels derived from MTES and VTES are shown in Figure 1 and 2, respectively. The free-boron gel (PS) spectrum displayed two broad and intense absorptions in the range of ~ 1200 to 1000 cm^{-1} , which are related to Si-O-Si bonds. Other bands related to the Si-CH₃ group appeared at 1275 cm^{-1} ($\delta\text{C-H}$, Si-CH₃) and 770 cm^{-1} ($\rho\text{C-H}$, SiCH₃), in addition to the $\nu\text{C-H}$ at 2975 cm^{-1} (not shown), and $\nu\text{Si-C}$ at $\sim 800\text{ cm}^{-1}$. For the gel derived from VTES, absorptions at ~ 1600 and 1410 cm^{-1} were assigned to $\nu\text{C=C}$ and $\delta=\text{CH}_2$, respectively. For the gels obtained in the systems containing boron, the broad absorptions between 1300 and 1500 cm^{-1} were assigned to $\nu\text{B-O}$, and that at 1195 cm^{-1} was associated to the $\delta\text{B-OH}$. The band at 540 cm^{-1} correspondent to the $\delta\text{O-B-O}$ was also observed. The most important band in the gels was the one observed at $\sim 880\text{ cm}^{-1}$ due to the Si-O-B bonds (Soraru, 1999). This band was observed in all compositions of the gels with boron. The symbols: δ , ν e ρ means, respectively, the vibration modes: angular deformation, stretching and “rocking”.

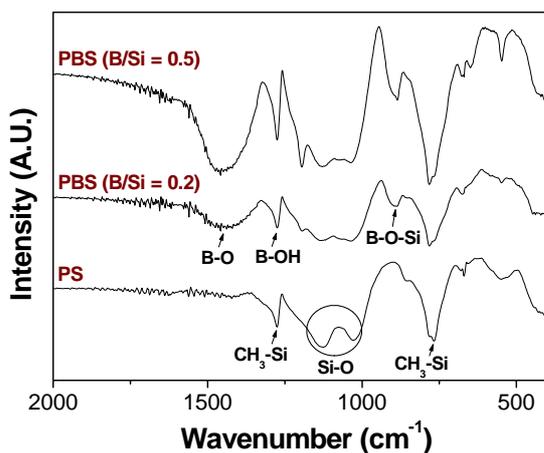


Figure 1 - FTIR spectra of PS and PBS gels derived from MTES.

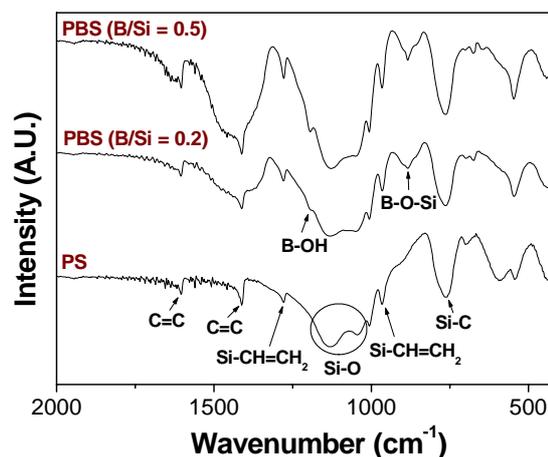


Figure 2 - FTIR spectra of PS and PBS gels derived from VTES.

The polymer-to-ceramic conversion was followed up by FTIR (spectra not shown). In these spectra, the decrease of the relative intensities of the organic group absorptions and the broadening of the Si-O-Si absorptions were observed with the increase of the pyrolysis temperature. The disappearance of the band assigned to the Si-O-B bond was due to the simultaneous broadening of the Si-O and Si-C bands. These structural rearrangements in the materials led to the formation of silicon oxycarbide ($\text{SiO}_x\text{C}_{4-x}$) and boron oxycarbide (BO_xC_{3-x}), homogeneously dispersed in these ceramics (Gervais, 2001).

TGA curves recorded on the PS and PBS gels derived from MTES and VTES during pyrolysis in flowing argon are shown in Figures 3 and 4, respectively. The boron-free gels displayed the same thermogravimetric profiles and three main degradation steps were observed for these samples. The first one, in the range of ~ 120 e $250\text{ }^\circ\text{C}$ was probably associated to the evolution of free oligomers trapped in gels. The second step in the temperature range of ~ 260 e $500\text{ }^\circ\text{C}$ was associated with the cleavage of Si-O, Si-C bonds, and the third step, in the temperature range of ~ 500 e $800\text{ }^\circ\text{C}$ was related to mineralization of the material, with formation of the silicon oxycarbide glasses (SiOC) (Schiavon, 2002b). For the PBS gels, TGA curves displayed similar behaviour, with significant weight losses at the range of 110 to $150\text{ }^\circ\text{C}$, due to the boron evolution. The intensity of such loss was proportional to the boron content. The ceramic yield of the boron-free gels and the

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ones with B/Si ratio of 0.2 were higher than that observed for the sample with B/Si ratio of 0.5, due to the more intense boron losses at low temperatures.

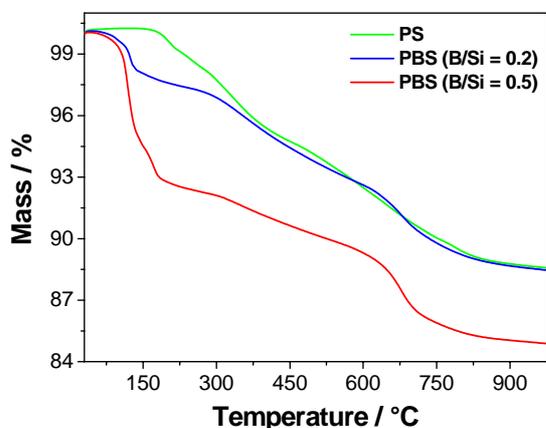


Figure 3 - TGA curves for PS e PBS gels derived from MTES (Ar, 10 °C/min.).

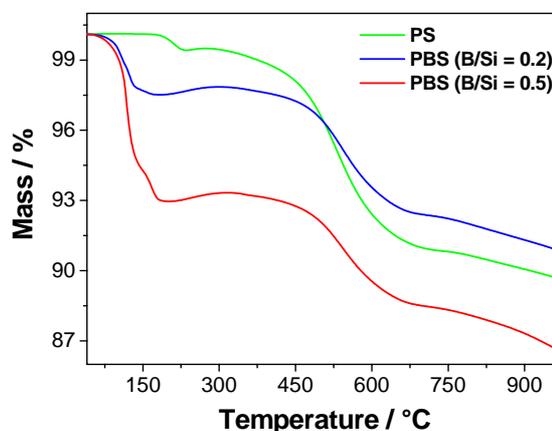


Figure 4 - TGA curves for PS e PBS gels derived from VTES (Ar, 10 °C/min.).

Typical XRD patterns of amorphous materials were observed for PS- and PBS-derived glasses, obtained at 1000 °C from MTES and VTES gels, as shown in Figures 5 and 6, respectively. In addition, a broad halo with maximum centered at $\sim 23^\circ$ (2θ) was observed, which was associated with silica domains at the beginning of the organization stage. For the sample derived from the gels with B/Si ratio of 0.5, besides this halo, peaks at 14.7° and 28.2° (2θ) were assigned to the boron oxide crystalline phase. As the B/Si ratio increased from 0.2 to 0.5, the formation of boron oxide crystalline phase was favored, suggesting the formation of the BO_3 -clusters units in the gels with atomic ratio of B/Si = 0.5.

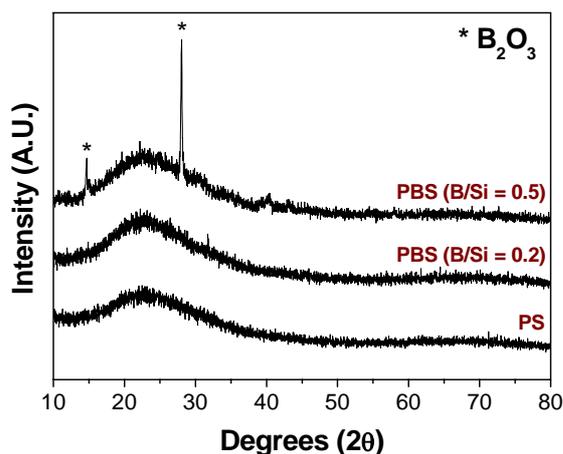


Figure 5 - X-ray diffraction patterns of PS- and PBS-derived MTES glasses obtained at 1000 °C.

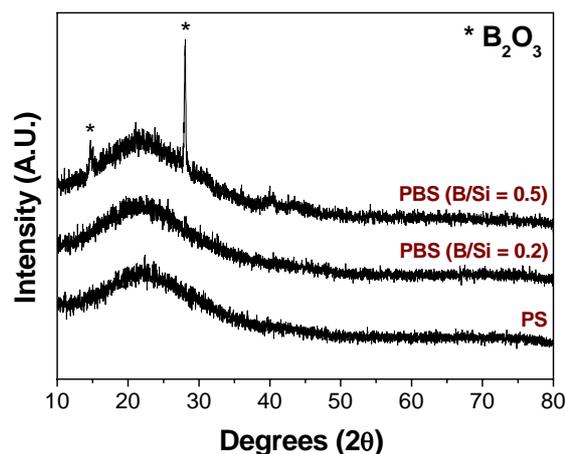


Figure 6 - X-ray diffraction patterns of PS- and PBS-derived VTES glasses obtained at 1000 °C.

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Characterization of ceramic matrix composites

Figure 7 shows TGA curves, recorded under oxidant atmosphere, of the carbon fiber, and of the CMC's, derived from the PS and PBS with atomic ratio of B/Si = 0.2, obtained at 1000 °C, both prepared from MTES. For carbon fibers only one degradation process was observed between 400 and 700 °C, due to the evolution of volatile products such as CO. The activation energy of this degradation process, determined by the dynamic thermogravimetric method (Ozawa, 1965) was $112.8 \pm 0.8 \text{ kJ mol}^{-1}$, which agrees with the most values reported in literature for similar fibers (Howe, 2004).

CMC's showed better thermal stability than the carbon fiber. For the composite obtained from PBS (B/Si = 0.2), a slightly gain in stability was observed in relation to the CMC obtained from the parent boron-free polysiloxane (PS). Such increase of stability was probably related to the boron content in the material.

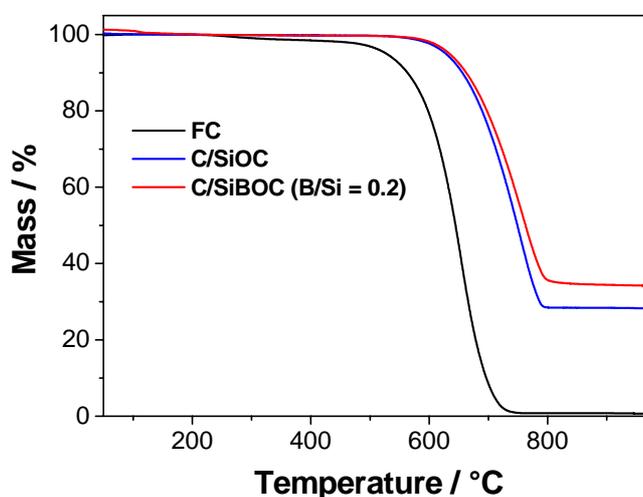


Figure 7 - TGA curves of the carbon fiber, and the CMC's obtained at 1000 °C for the PS e PBS derived-MTES (Ar, 10 °C/mim.).

The resulting composites, obtained at 1000 °C, C/SiCO and C/SiBCO, were stable and crack-free monolithics. Such characteristics were observed for all composites obtained from the PBS and PS precursors. Figure 8 illustrates a micrograph for the green body and CMC's obtained from VTES-derived PS. Figures 9 and 10 illustrate SEM and optical micrographs, respectively, for CMC obtained from MTES-derived PBS (with B/Si of 0.2).

Both polymeric and ceramic matrices displayed good adhesion to the carbon fibers specially for CMC's obtained from precursors containing boron (B/Si = 0.2), as can be seen in Figures 9 and 10. However, in the micrograph of the pyrolysed composite can also be seen pores and micro-cracks, which is a result of the weight loss during the pyrolysis process.

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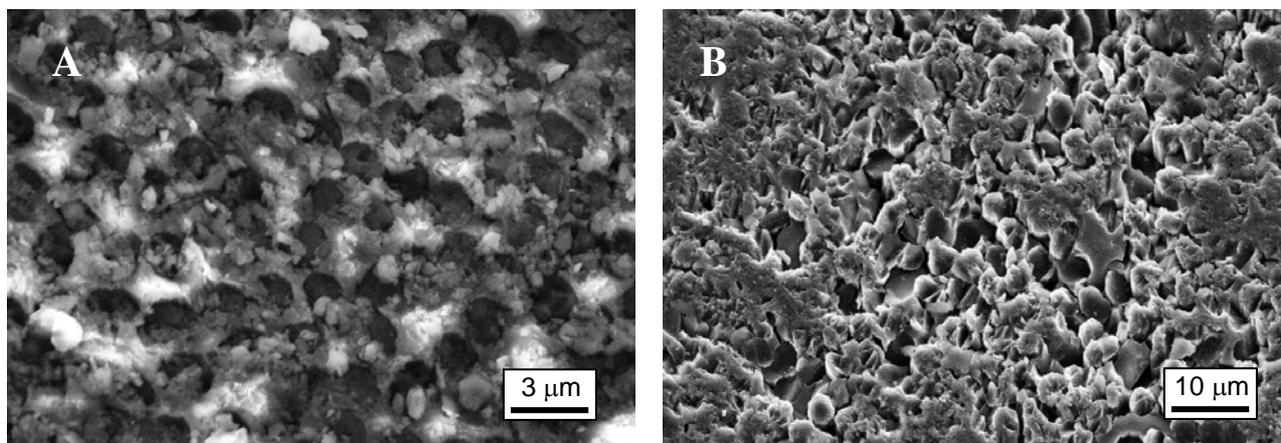


Figure 8 - SEM micrograph of the CMC obtained from VTES-derived PS: A) green body; B) CMC obtained at 1000 °C in argon atmosphere.

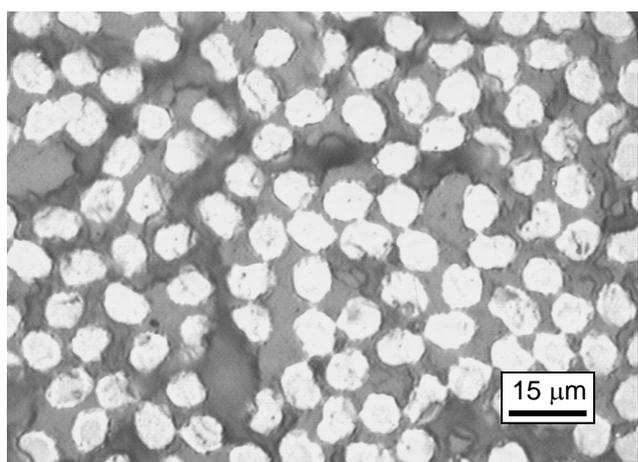


Figura 9 - Optical micrograph of the CMC obtained from MTES-derived PBS (B/Si of 0.2).

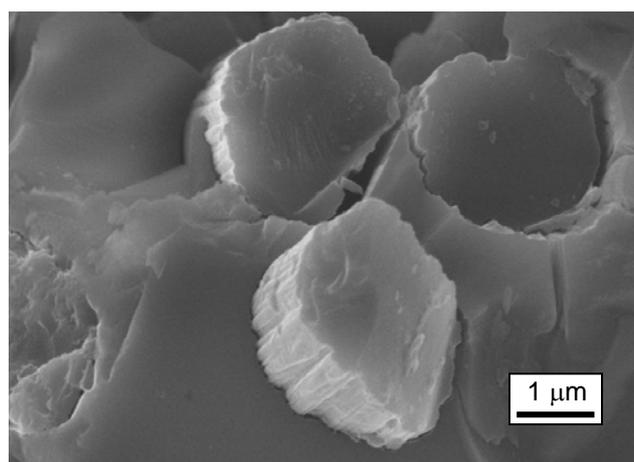


Figura 10 - SEM micrograph of the CMC obtained from MTES-derived PBS (B/Si of 0.2).

CONCLUSION

In this study, it was possible to demonstrate that poly(borosiloxane) network prepared are excellent precursors of ceramic materials in the SiBOC system. Gels bearing homogeneously Si-O-B bonds in the structure can be easily prepared using boric acid as precursor of trigonal BO_3 units in the siloxane network. The ceramic obtained at 1000 °C from poly(borosiloxanes) can be considered as silicon and boron oxycarbide. It was also observed that poly(borosiloxanes) prepared with B/Si ratio of 0.5 displayed phase segregation of boron oxide phase after pyrolysis at 1000 °C, probably due to formation of BO_3 -cluster units in the precursor. The polymeric precursors were adequate wrapping carbon fibers, giving rise to CMC's. The resulting materials exhibited better thermal stability in relation to the carbon fiber. This study showed that poly(borosiloxanes) are promising materials for oxidation protection of carbon fiber material.

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