

HYDROBORATION SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF NOVEL CYCLIC PRECERAMIC POLYMERS: TRANSITION TO SiBOC CERAMICS

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*Novel preceramic polymers were synthesized by hydroboration reaction and pyrolyzed under continuous nitrogen flow to obtain boron containing silicon oxycarbide (SiBOC) ceramics. The preceramic SiBOC polymers were synthesized with different cyclicsiloxane/borane molar ratios. Structure of the SiBOC polymers and transformation of them to the SiBOC ceramics investigated by Fourier Transform Infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), X-ray Diffraction (XRD) technique and Scanning Electron microscope (SEM). Since the cyclicsiloxanes used in smaller sizes according to literature, variations were observed in structure of obtained polymers and ceramics. During the pyrolysis of polymers, loss of the carbon was little. The transformation from amorphous form to the β -SiC crystal was achieved above 1200°C and consequently thermally stable SiBOC ceramics were obtained at higher temperatures. Antibacterial activity of SiBOC polymers were evaluated by disc diffusion method against *E. coli* ATCC 25922- for the first time. The new polymers inhibited the growth of Gram-negative bacteria well enough.*

INTRODUCTION

Preceramic polymers were first proposed for the production of silicon containing ceramics about 30 years ago [1]. The major advantage of these preceramic polymers is to give an opportunity for working with a lower reaction temperature and preparing amorphous or crystalline powder depending on the work. The synthesized preceramic polymers are pyrolyzed to transform the polymers to the ceramic materials. Preceramic materials shrink during pyrolysis due to the changes of the density from polymer materials ($1 \text{ g}\cdot\text{cm}^{-3}$) to ceramics ($2 - 3 \text{ g}\cdot\text{cm}^{-3}$) and the consisting of mass loss during pyrolysis [2].

The ceramic materials are improved by using boron and named as silicon boron oxycarbide (SiBOC) ceramics [3]. In these ceramics, the addition of boron to the structure results in an increase at the degradation temperature which means an increase in the thermal stability [4, 5]. These ceramics also behave like a hybrid material and thus offer the possibility of combining the properties of inorganic and organic materials in one material [2]. SiBOC ceramics can be produced cheaply from easily accessible poly(organoborosiloxanes) and obtained with shorter gelation time (t-gel) thanks to ultrasonic and microwave application [6, 7]. The common methods used for the synthesis of boron-

containing polyorganosiloxane are sol-gel method and hydroboration reactions [8]. Hydroboration reaction is a three-stage reaction and alkenes are converted to alcohols by the anti-Markovnikov hydration. In the first stage, boron hydride is added to alkene and then alkyl boron compounds consist at the end of the reaction which is following with the four-membered transition complex. In the second stage, alkyl boron compounds are oxidized to alkyl borate. In the third stage, the anti-Markovnikov alcohols are obtained by hydrolysis. The first two stages of the reaction are used for obtaining poly(organoborosiloxanes) [9, 10].

When the studies about cyclic SiBOC preceramic polymers are investigated, the following conclusions have been drawn. Liebau et al. [11] synthesized SiBOC polymers via hydroboration reaction of 1,3,5,7-tetramethyl-1,3,5,7-tetravinylcyclotetrasiloxane with borane dimethyl sulfide ($\text{BH}_3\cdot\text{S}(\text{CH}_3)_2$) using different molar ratios. In the mentioned study, the transformation of SiBOC polymers to ceramics occurred at 1000°C under nitrogen atmosphere and the obtained SiBOC ceramics were amorphous up to 1200°C. When it was reached up to 1300°C the β -SiC crystal phase occurred with degradation of the SiBOC matrix. In another study, Schiavo et al. [12] synthesized poly(organoborosiloxanes) by the following reactions. Hydrogen releasing reaction of the 1,3,5,7-tetramethyl-1,3,5,7-tetracyclotetrasiloxane (D_4H)

with boric acid, sol-gel reaction of vinyltriethoxysilane with boric acid and hydrosilation reactions of the D_4H with sol-gel reaction's product. As a result, black amorphous SiBOC materials were obtained by pyrolysis of poly (organoborosiloxanes) at $1000^{\circ}C$.

Only two study have been seen about biological performance of SiOC preceramic polymers in the literature. The result of one of these studies confirmed a good biological performance of SiOC ceramic with both hard and soft tissue cell models. In the second study, the results indicated good biological performance of SiOC ceramics and confirmed citocompatibility [13, 14].

Best of our knowledge, in the literature, there are no study about biological performance of SiBOC preceramic polymers and ceramics. Furthermore, there are no available data in literature concerning antibacterial activity of SiOC and SiBOC preceramic polymers. So, it is not known how is antibacteriyel activity mechanism of the SiOC or SiBOC preceramic polymers. In many years, biological role of boron has been the subject of a number of biological studies. It is proven that a number of boron-containing compounds possess strong antibacterial activity specifically against the enteric group of gram-negative bacteria both in vitro and in animal infections. Also, the effect of the boron compounds to cells is defined as an abnormal form of growth in a cell envelope [15, 16]. So, in our study antibacterial activities of obtained SiBOC preceramic polymers were explained on the basis of boron feature.

In this study, novel SiBOC preceramic polymers were synthesized by using 1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane(siloxane)/boranedimethylsulfide ($BH_3 \cdot S(CH_3)_2$) (borane) with different molar ratios (3:4, 1:2 and 1:4) by hydroboration reaction. The antibacterial activity test of preceramic polymers at 3:4,1:2 and 1:4 molar ratios was performed by disc diffusion method for the first time. The novel preceramic polymer with 3:4 molar ratio was pyrolyzed at $700^{\circ}C$, $1200^{\circ}C$, $1400^{\circ}C$ to prepare novel SiBOC ceramics. Due to further cross-linking in 3:4 preceramic polymer by formation of intermolecular B-C linkages, only it was preferred for the pyrolysis among the preceramic samples. The obtained preceramic polymers and ceramics were characterized by Fourier Transform Infrared spectroscopy (FT-IR), Thermogravimetric analysis (TGA), X-ray Diffraction (XRD) technique and Scanning Electron microscope (SEM).

EXPERIMENTAL

Synthesis of SiBOC preceramic polymers

The synthesis of the preceramic polymers were carried out under nitrogen atmosphere using standard Schlenk technique. 3:4 molar ratios of SiBOC preceramic polymer was prepared according to the following route [11]: Firstly, the proper amount of 1,3,5-trimethyl-1,3,5-

trivinylcyclotrisiloxane (cyclic siloxane) was dissolved in 10 ml of hexane. The Solution was cooled to $0^{\circ}C$ and stirred for 30 min. Then, the proper amount of $BH_3 \cdot S(CH_3)_2$ was dissolved in 10 ml of hexane and added slowly into the previous solution. The final solution was stirred for 20 h at room temperature and solvent was removed by distillation under reduced pressure at $40^{\circ}C$. Finally, the white powders were obtained after drying in the vacuum oven at room temperature. Cyclicsiloxane/borane molar ratios of 1:2 and 1:4 of preceramic polymers were prepared according to the same procedure. The synthesized preceramic polymers were named as 3:4, 1:2 and 1:4 samples.

Antibacterial activity test

American Type Culture Collection (ATCC) quality control strain recommended by CLSI (Clinical and Laboratory Standards Institute) [17] and disc diffusion method were used to determine the antibacterial properties of all the prepared preceramic polymers. *E. coli* ATCC 25922- was used as tested bacterial strain.

E. coli bacteria species was first inoculated into *Mueller-Hinton Agar* (Merck KGaA, D-Darmstadt) and incubated at $37^{\circ}C$ over-night and checked for purity. Then bacteria suspension was prepared in 0.9 % NaCl solution by means of 0.5 *McFarland* (1×10^8 cells per ml, *BioMérieux*, Marcy l'Etoile, France) standard density. Prepared bacteria suspension was inoculated onto *Mueller-Hinton Agar* plates by sterile swab. 30 and 40 mg of all preceramic polymers were prepared under pressure (10 ton) as discs in 10 mm diameter, then they were placed on inoculated *Mueller-Hinton Agar* plates one by one. An inoculated *Mueller-Hinton Agar* plate without preceramic polymer was used to test the sterility. All plates were incubated at $37^{\circ}C$ for 24 h. The diameters of the inhibition zones were measured in millimetres.

Preceramic polymer pyrolysis

SiBOC preceramic polymer of 3:4 molar ratio was converted into SiBOC ceramic by pyrolysis under continuous nitrogen flow at $700^{\circ}C$, $1200^{\circ}C$, $1400^{\circ}C$. The pyrolysis was carried out in a LENTON tube furnace using alumina and ceramic crucibles. Pyrolysis temperature ($700^{\circ}C$, $1200^{\circ}C$ or $1400^{\circ}C$) was reached using a heating rate of $10 K \cdot min^{-1}$. The samples were held 1 h at pyrolysis temperature and cooled to room temperature. Obtained three SiBOC ceramics were stored in dessicator at room temperature until further analysis.

Characterization techniques

The structural evolution from the preceramic polymer to the ceramic was investigated by FT-IR using a Bruker Tensor 27 spectrometer operating between 4000 and $400 cm^{-1}$. Thermogravimetric analysis was performed

with TA Instruments TGA Q500. This analysis was carried out with a heating rate of $10 \text{ K}\cdot\text{min}^{-1}$ up to the maximum temperature under nitrogen. X-ray diffraction (XRD) patterns were recorded on a PANalytical X'Pert Pro MPD using $\text{CuK}\alpha$, $2\theta = 15 - 95^\circ$. The microstructural analysis was carried out using scanning electron microscope (SEM, LEO 440) operating at 20.00 kV.

RESULTS AND DISCUSSION

The hydroboration reactions of siloxanes with borane were given in Figure 1, 2 and 3 with different molar ratios of 3:4, 1:2 and 1:4, respectively. The obtained SiBOC preceramic polymers and 3:4 SiBOC ceramics characterized by Fourier Transform Infrared spectroscopy (FT-IR) were introduced in Figure 4 and 5. The pyrolyzed preceramic polymers (SiBOC ceramics) at 700°C , 1200°C , 1400°C were also introduced in Figure 5 named as 3:4-700, 3:4-1200, 3:4-1400.

The spectra of 3:4, 1:2, 1:4 samples were introduced in Figure 4, together. In the spectrum of 1:4 sample, the absorption peaks at 2264 cm^{-1} and 543 cm^{-1} assigned to the B–H stretching vibration are sharper than B–H peaks of the other spectra. These results indicate that amount of borane in 1:4 sample was more than the other samples. In

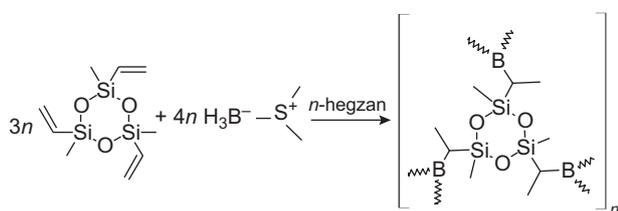


Figure 1. Synthesis of poly(organoborosiloxane) preceramic with 3:4 siloxane/borane molar ratio via hydroboration reaction.

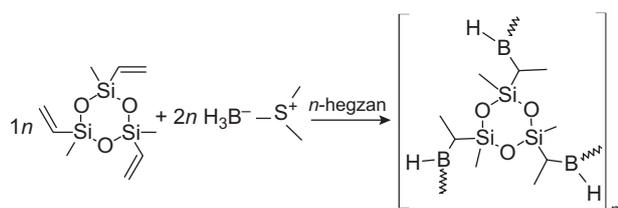


Figure 2. Synthesis of poly(organoborosiloxane) preceramic with 1:2 siloxane/borane molar ratio via hydroboration reaction.

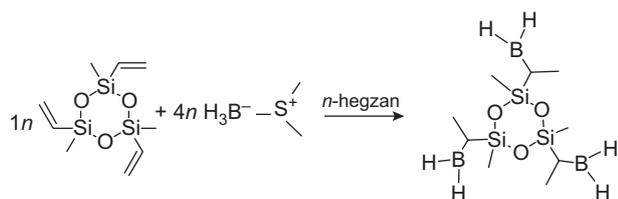


Figure 3. Synthesis of poly(organoborosiloxane) preceramic with 1:4 siloxane/borane molar ratio via hydroboration reaction.

Figure 4, the absorption peaks at 668 cm^{-1} and 1194 cm^{-1} assigned to the B–C stretching vibration and the absence of the peak of C=C bond ($1680 - 1620 \text{ cm}^{-1}$) demonstrate the formation of binding between borane and siloxane in all samples [11].

In the spectrum of 3:4 sample in Figure 5, the absorption peaks at 2964 cm^{-1} and 2876 cm^{-1} are assigned to the C–H stretching vibration. The absorption peaks at 1259 cm^{-1} and 786 cm^{-1} are assigned to the Si–C; at 671 cm^{-1} and 1194 cm^{-1} are assigned to the and B–C stretching vibration. The absorption peaks at 1047 cm^{-1} and 424 cm^{-1} are assigned to the Si–O stretching vibration. B–H stretching vibration at 2258 cm^{-1} and 549 cm^{-1} de-creased in 3:4-700, 3:4-1200 samples and disappeared in 3:4-1400 sample spectra in Figure 5. In the spectra of 3:4-700, 3:4-1200, 3:4-1400 samples, C–H stretching vibration have completely disappeared. Disappearing of C-H bond peak in 3:4-1400 sample

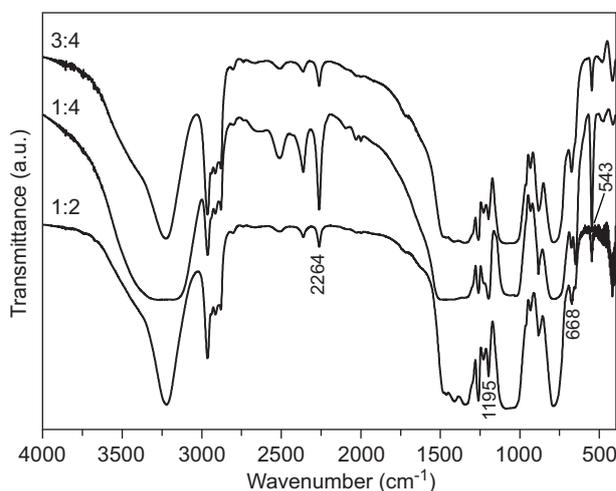


Figure 4. FTIR spectra of poly(organoborosiloxanes) with 3:4 1:2 and 1:4 siloxane/borane molar ratios.

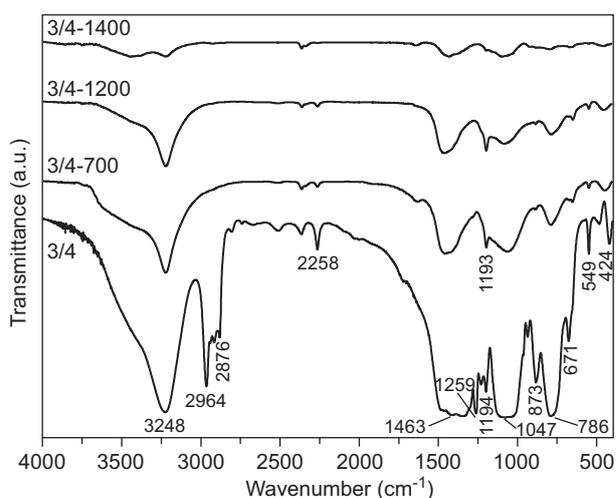


Figure 5. FTIR spectra of poly(organoborosiloxane) preceramic with 3:4 siloxane/borane molar ratio and the samples formed by its pyrolysis at 700, 1200 and 1400°C .

supports to form β -SiC crystallization [12].

XRD patterns collected from the samples formed by pyrolysis of 3:4 sample at 700°C, 1200°C, 1400°C are reported in Figure 6. The spectra of 3:4-700 and 3:4-1200 samples show sharp peaks at $2\theta = 28^\circ$ (002) which are assigned to the presence of crystalline $B(OH)_3$. In the spectrum of 3:4-1400, the appearance of the four peaks at $2\theta = 35.7^\circ$ (111), 41.3° (200), 60.1° (220), and 71.8° (311) prove the existence of β -SiC crystallization. In addition, a broad halo with a maximum centered at $2\theta \sim 23^\circ$ is associated with amorphous silica in all spectra. As shown in XRD spectra, $B(OH)_3$ occurred until 1400°C and combined to the silica network in

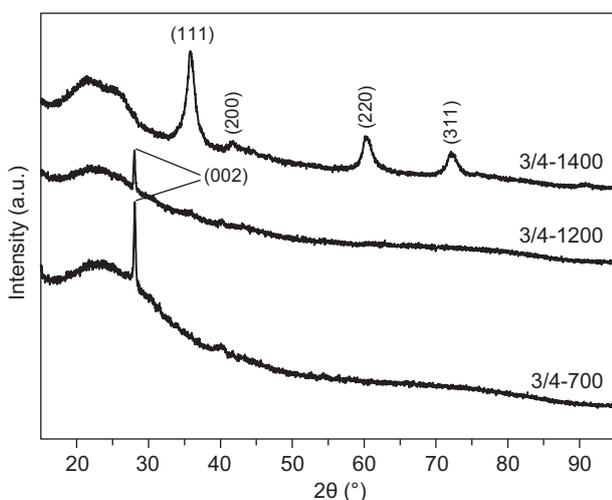


Figure 6. XRD spectra of SiBOC ceramics formed by pyrolysis of poly (organoborosiloxanes) with 3:4 siloxane/borane molar ratio at 700, 1200 and 1400°C.

the structure, then at 1400°C β -SiC crystal structure occurred [18-20].

The TGA curves of 3:4, 1:2 and 1:4 samples were shown in Figure 7, Figure 8 and Figure 9, respectively. These curves indicate that weight loss in 1:4 sample is lower than 1:2 sample and the ceramic yields increase with rising of boron amount. However, the curve of 3:4 sample in Figure 7 indicate that weight loss doesn't increase with further decreasing of boron amount. According to these results, organoborosiloxane structures in 3:4 sample are more interconnected than the other samples. Moreover, obtained structure in 3:4 sample is exactly a polymer, so the structure shows more resistant against weight loss. According to the TGA curves of all samples it can be said that the weight losses occur between 300 and 400°C due to releasing of organic groups and H_2 [11].

Scanning Electron microscope (SEM) images of 3:4 and 3:4-1400 samples were shown in Figure 10 and 11, respectively. When the SEM images are evaluated, it is observed that 3:4 sample has an amorphous structure and 3:4-1400 sample has a crystal structure with 1 micron-

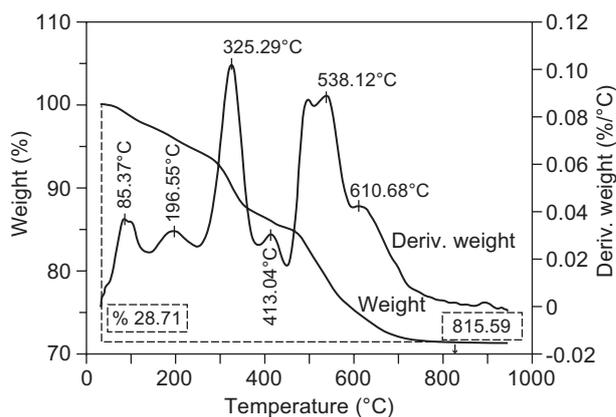


Figure 7. TGA and DTG curves of poly(organoborosiloxane) preceramic with 3:4 siloxane/borane molar ratio.

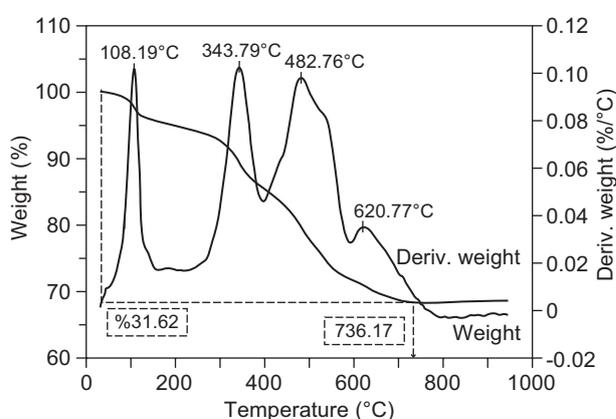


Figure 8. TGA and DTG curves of poly(organoborosiloxane) preceramic with 1:2 siloxane/borane molar ratio.

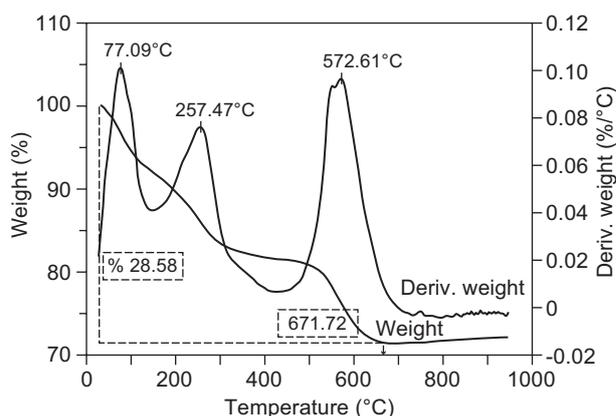


Figure 9. TGA and DTG curves of poly(organoborosiloxane) preceramic with 1:4 siloxane/borane molar ratio.

size crystals. These results prove that the crystal form of SiBOC ceramics are achieved at 1400°C.

Antibacterial activities of SiBOC preceramic polymers of 3:4, 1:2 and 1:4 molar ratios were determined against the bacterial strain (*E. coli* ATCC 25922) by disc diffusion method as mentioned above. The results of the antibacterial activity test were shown in Table 1

as the diameters of inhibition zones. The results show that the antibacterial activity of 1:4 sample is higher than others and 3:4 samples is the lowest in both 30 mg and 40 mg preceramic polymers. These cases originate from different polymerization of the samples. For instance, 1:4 sample is not a polymer and polymerization of 1:2 sample is lower than 3:4 sample. Antibacterial activities of the

samples increase with decrease of the polymerization. Because, without polymerization, release of boron atom from the structure can be more easily. Boron atoms in all samples have occupied three coordination sites and one empty coordination site. Nitrogen of the proteins can easily coordinate with boron's empty coordination site. Besides, steric effect of polymeric structure of 3:4 sample

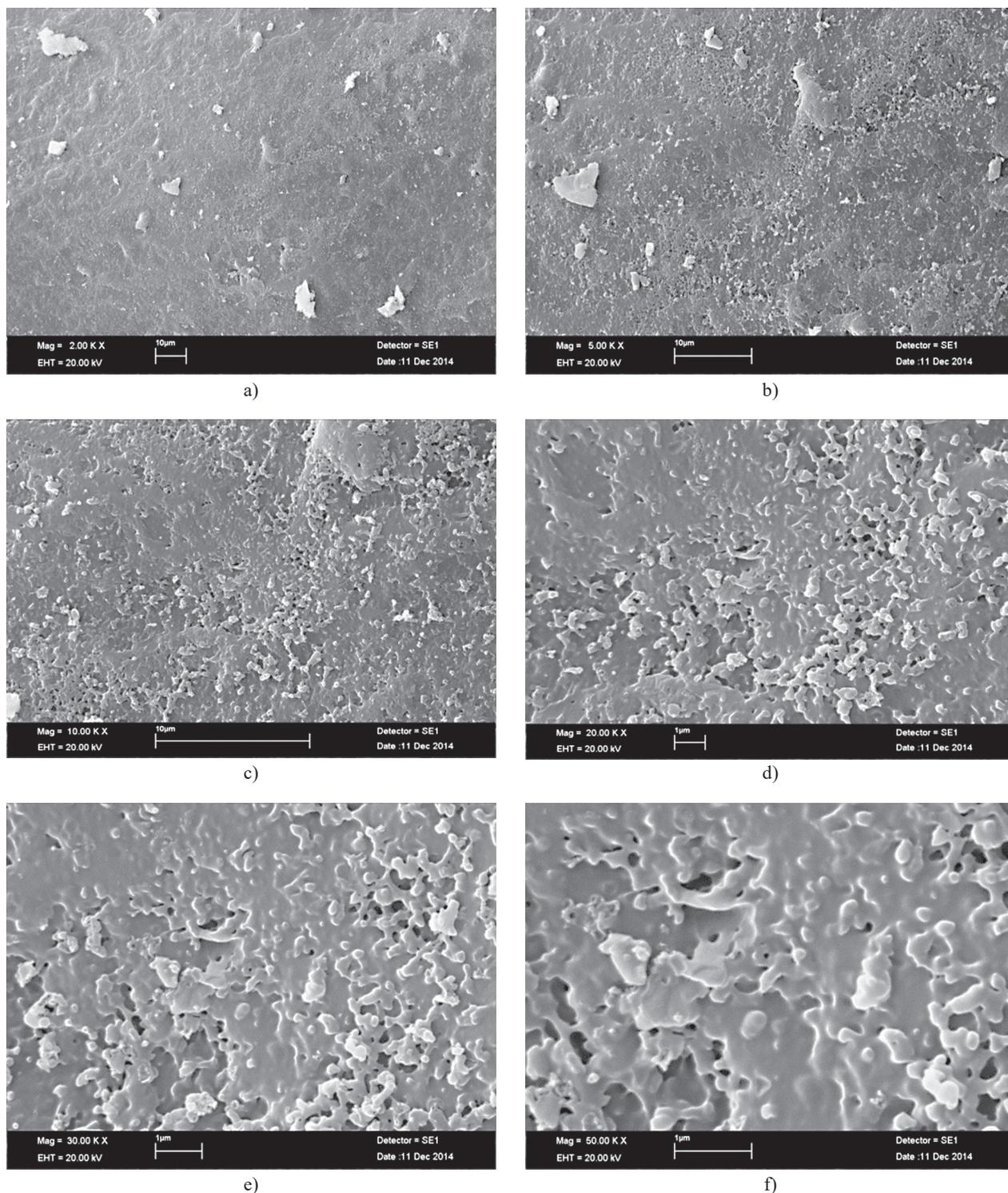
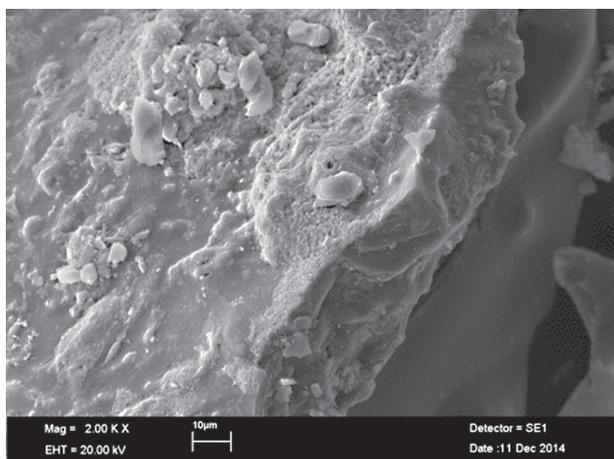


Figure 10. SEM images of poly(organoborosiloxane) preceramic with 3:4 siloxane/borane molar ratio in images 1-6 at 10 µm and 1 µm sizes with different magnifications.

Table 1. Antibacterial activities of 30 mg and 40 mg preceramic polymers with 3:4, 1:2 and 1:4 molar ratios against the bacterial strain (*E. coli* ATCC 25922) tested based on disk diffusion method.

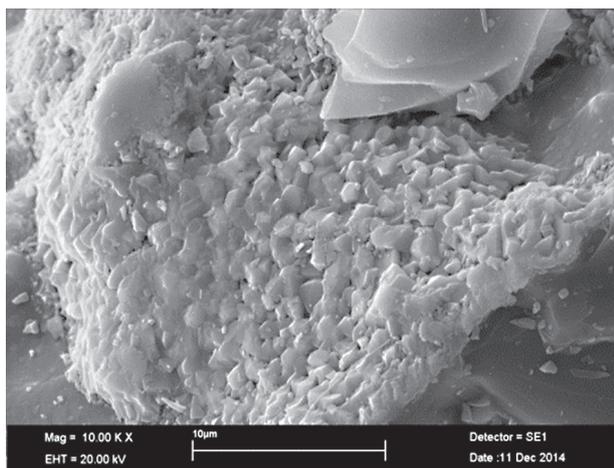
Molar ratios	30 mg	40 mg
3:4	19 mm	23 mm
1:2	21 mm	26 mm
1:4	26 mm	32 mm



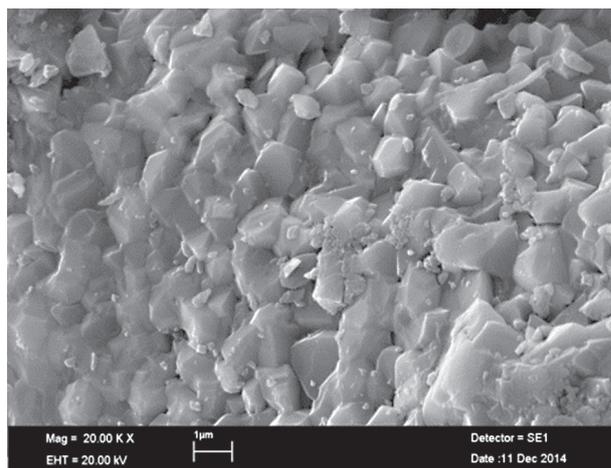
a)



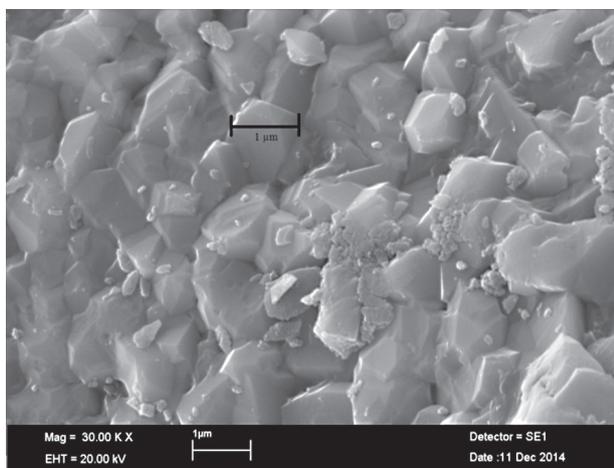
b)



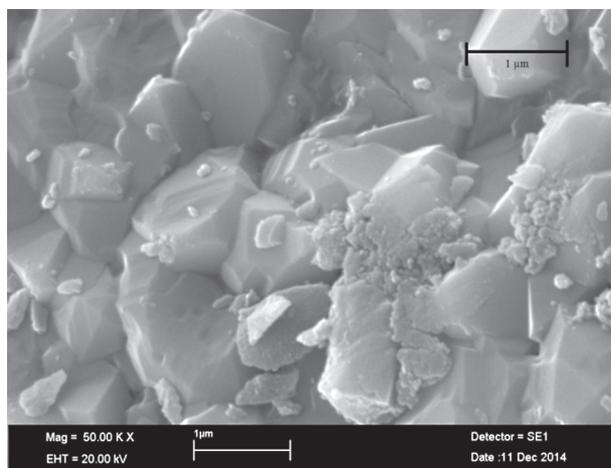
c)



d)



e)



f)

Figure 11. SEM images of SiBOC ceramics formed by pyrolysis of poly(organoborosiloxane) with 3:4 siloxane/borane molar ratio at 1400°C (images 1-6 at 10 μm and 1 μm sizes with different magnifications).

inhibits the reaction between B atoms and proteins of bacteria cells, thus antibacterial activity of polymeric 3:4 preceramic sample is lower. The antibacterial activities of the preceramic polymers were evaluated in terms of sample amount. When 40 mg preceramic polymer was used for the disc preparation, antibacterial activity of the preceramic polymer was found to be higher owing to more boron amount.

CONCLUSIONS

In this study, novel SiBOC preceramic polymers and SiBOC ceramics have been synthesized by hydroboration reaction with different molar ratios of cyclic siloxane and borane. Reducing of ring size in the cyclic vinylsiloxanes altered the structure of obtained preceramic polymers and ceramics. According to the TGA results, carbon loss was little during the pyrolysis of preceramic polymers, thus obtained ceramics should provide better electrical resistance. 3:4 molar ratios of cyclic siloxane/borane preceramic sample showed better polymerization than 1:2 and 1:4 molar ratios of preceramic samples. As is seen from XRD and SEM analysis, the transformation from the amorphous structure to the β -SiC crystal form was achieved above 1200°C and consequently at higher temperatures thermally stable SiBOC ceramics were obtained. Antibacterial activity of preceramic sample was examined for the first time on SiBOC preceramic polymers. The best antibacterial activity among the preceramics was observed in 1:4 sample which has no polymerization.

Acknowledgments

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