

# **Silicon Carbide Modified Carbon Materials. Formation of Nanocrystalline SiC from Thermochemical Processes in the System Coal Tar Pitch/Poly(carbosilane)<sup>1</sup>**

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Poly(carbosilane) or PCS,  $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\}_n$ , is used as a Si-bearing precursor in combination with a coal tar pitch to study thermally induced transformations toward SiC-modified carbon composites. Following mixing of the components in the molten pitch at 160°C, the mixture is heated under argon atmosphere at 500°C yielding a solid carbonizate that is further subjected to separate pyrolysis experiments at 1300°C or 1650°C. At temperatures up to 500°C, the PCS reacts with suitable pitch components as well as undergoing decomposition reactions. At higher temperatures, clusters of prevalingly nanocrystalline  $\beta$ -SiC are confirmed after the 1650°C pyrolysis step with indications that the formation of the compound starts at 1300°C. <sup>29</sup>Si MAS NMR, XRD, FT-IR, XPS, and elemental analysis are used to characterize each pyrolysis step, especially, from the viewpoint of transformation of silicon species to silicon carbide in the carbon matrix evolved from the pitch.

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**KEY WORDS:** Poly(carbosilane); nanocrystalline silicon carbide; SiC; carbonizate; carbon composites; carbon materials; <sup>29</sup>Si MAS NMR.

## **INTRODUCTION**

Studies on the utilization of appropriate Si-bearing precursors, including poly(carbosilanes) (PCS), as the source of silicon carbide in composite carbon materials have been anchored in the advantageous properties of SiC

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<sup>1</sup> Dedicated with heartfelt wishes, deep gratitude, and sincere regards to Prof. Richard L. Wells on the occasion of his retirement.

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such as its resistance to oxidation, high thermal conductivity, and robust mechanical behavior under a range of strained technological conditions. Extensive investigations in this area have been carried out mainly for the application of thin protective SiC layers on carbon matrices as well as on utilization of SiC fibers for composite reinforcement [1, 2]. In this regard, poly(carbosilanes) that already have the silicon-carbon backbone structure appear to be the most advantageous precursors to be considered in the system with various carbon sources.

It has now been more than two decades that Yajima *et al.* have shown the feasibility of PCS conversion toward silicon carbide leading to commercial Nicalon SiC fibers with significant quantities of incorporated oxygen [3–7]. The structure of the initial PCS consisting of alternating  $-(R_1)Si(R_2)-CH_2-$  fragments ( $R_1, R_2 = H, \text{alkyl, aryl}$ ) is particularly prone to thermally driven elimination-condensation chemistry since eventually leads to three-dimensional SiC structures [6].

In particular, utilizing IR, NMR, and chemical analysis methods, some carbosilane polymers and their thermally generated by-products have been characterized [4, 5] including a detailed study on an intermediate treatment in air at about 200°C [6]. According to the latter, in the first stage up to 550°C, two- and three-dimensional condensation of the Si and C atoms mainly due to  $H_2-$  and alkyl elimination chemistry takes place. This is followed at increased temperatures of 550–850°C by thermal cracking of the residual  $-CH_3$  and  $-CH_2-$  groups. The most pronounced chemical changes occur by 700°C as evidenced by dramatically decreasing quantities of the Si–H and Si– $CH_3$  moieties in the product. In the last heating stage above 850°C, the inorganic  $-Si-C-$  backbone predominates and the IR spectra show the new and strong bands at about 1090 and 800  $cm^{-1}$  for the Si–O and Si–C stretches, respectively. Such a sequence of thermochemical changes for poly(carbosilanes) has also been substantiated by others [1, 7–9]. It is worth mentioning that the observed Si–O species are apparently an artifact of the polymer's curing in air at 200°C and they play an important if not crucial role in determining the final properties of the synthesized SiC bodies. In this regard, pyrolysis of PCS without an intermediate curing in air has led to a highly porous, foamy residue of disadvantageous mechanical properties. This is due to an apparent massive evolution of volatiles including organosilicon fragments; consistent with this is lower ceramic yield of such a product compared with the air-cured SiC materials [10]. It has also been found that thermal treatment of PCS's initially leads to basic structural units composed of some 2–3 condensed  $(Si-C)_n$  rings about 3 nm large while the presence of oxygen is detrimental to this nucleation process. This stage is followed at 1000–1200°C by growth of nanocrystalline  $\beta$ -SiC and it has been suggested that the simultaneous

evolution of hydrogen from condensation reactions in the system has a retarding effect on the crystal growth [11]. The SiC nanocrystals (7–20 nm) are embedded in a highly turbostratic carbonaceous matrix and are shown to exhibit advantageous electrical properties [10, 12]. Still higher temperatures of the order of 1700°C result in the conversion of this in many respects “microscopically amorphous phase” to a mixture of microcrystalline  $\beta$ - and  $\alpha$ -SiC [13].

On the other end of carbon-based composite make-up is the choice of an appropriate carbon precursor to be combined with a silicon-bearing additive. In this regard, easily available and inexpensive coal tar and/or petroleum pitches that are poorly defined mixtures of complex hydrocarbons [14] have been commonly used in the carbon/graphite industry as binders. These materials are chemically convenient if not obvious candidates to be considered in combination with an appropriate precursor possibly leading to advantageous SiC-modified carbon/graphite materials. For example, a tar pitch has been modified with organosilicon and organo-aluminum compounds resulting in materials with improved oxidation resistance characteristics [15]. Similarly, pitch-derived fibers from 1200°C treatment of a petroleum pitch modified with poly(dimethylsilane) have been shown to exhibit advantageous oxidation behavior [16].

Our group has recently reported a study on the utilization of a typical coal tar pitch as the source of the C-reactant and C-matrix in systems with several silicon-bearing additives [17]. The current study is particularly concerned with the modification of a coal tar pitch with a commercially available poly(carbosilane) aimed at the formation at elevated temperatures of SiC-modified carbon materials with preferable technological parameters.

## EXPERIMENTAL

A coal tar pitch with the following characteristics was used: C, 93.5%; m.p. by Mettler, 101.5°C; toluene insolubles–TI, 20.9%). Poly(carbosilane),  $\{-\text{CH}_2\text{-SiH}(\text{CH}_3)\}_n$ , m.p. 79°C (Aldrich) was utilized as a Si-bearing additive at 15% wt. calculated per elemental Si in samples. The powdered ingredients were first homogenized in the solid state and, then, heated to 160°C to ensure a liquid medium of molten pitch, followed by a 0.5 hr mechanical stirring at this temperature. After cooling, the solidified material was ground/homogenized and samples for analyses were secured. The remaining bulk of the material was heat-treated under an Ar atmosphere at 500°C affording a non-melting solid carbonizate. After characterization this solid was pyrolyzed separately at 1300 or 1650°C under Ar flow for one hour followed by cooling to ambient temperature. In an identical fashion, a parallel series of two reference materials was

prepared; the first one starting with the non-modified, pure pitch and the second one of the pitch homogenized with a 15% wt. addition of commercial SiC (< 400 mesh, Aldrich) all heated under the same conditions as above. XRD measurements were carried out with a Bruker D8 Advance diffractometer operating with the Co-source,  $15^\circ < 2\theta < 150^\circ$ , step-size,  $0.01^\circ$ . Identification of crystalline phases was carried out with the help of available Bruker database as well as literature data [18].  $^{29}\text{Si}$  MAS NMR spectra were collected on a home-made pulse NMR spectrometer at 59.517 MHz (magnetic field 7.05 T). A Bruker HP-WB high-speed MAS probe was used to record spectra at the spinning rate of 4 kHz. The FID was recorded after a single  $3 \mu\text{s}$  rf pulse corresponding to  $\pi/2$  flipping angle. The  $^{29}\text{Si}$  longitudinal relaxation time measured in the model samples by saturation recovery method was 60 seconds and 200 seconds for PCS and SiC, respectively. Due to low signal intensity, the relaxation of  $^{29}\text{Si}$  nuclei in the mixtures with coal tar pitch was not measured but it was assumed to be the same as found in the pure Si-additives. Accordingly, the acquisition delay used in accumulation was 600 seconds and the number of acquisitions ranged from 32 to 220, depending on the signal strength. The frequency scale in ppm was referenced to the  $^{29}\text{Si}$  resonance in TMS. All NMR spectra were normalized to the same number of acquisitions and to the same mass of the sample. Additionally, the intensities of the pure reference samples were scaled down to 0.15 to account for the initial concentration of these additives, *i.e.*, 15% wt. per elemental Si, in the coal tar pitch. FT-IR spectra were collected for KBr pellets with a FTS-Biorad Analytical Digilab spectrometer in the  $400\text{--}4000 \text{ cm}^{-1}$  range. XPS data were obtained from a Vacuum Systems Workshop Ltd. instrument equipped with a  $\text{Al-K}_\alpha$  X-ray radiation source (1486.6 eV, 200 W) and chamber vacuum of  $10^{-8}$  mbar. Electron energies were determined in the fixed analyzer transmission mode with 22 eV electron pass energy. Spectral energies were referenced *vs.* that of carbon (284.6 eV).

## RESULTS AND DISCUSSION

Figure 1 displays yields of the carbonizates (solid residues) produced at the applied pyrolysis temperatures from the poly(carbosilane) (PCS) modified materials as well as from the reference pure pitch and pitch modified with commercial SiC. The similar yields in the order of 70% are evident for the materials with the PCS and SiC while about 60% yield is determined for the pure pitch after the  $500^\circ\text{C}$  heating. These yield levels and observed differences between them can be attributed to the same kind of thermochemical changes taking place in the pitch component in all cases (distillation of low boiling constituents, decomposition and condensation of

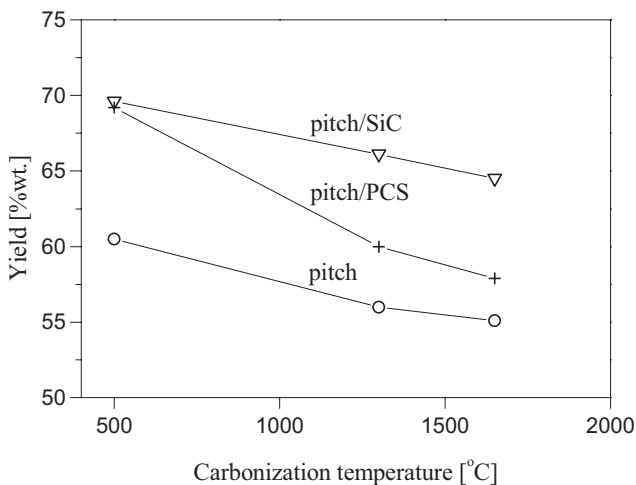
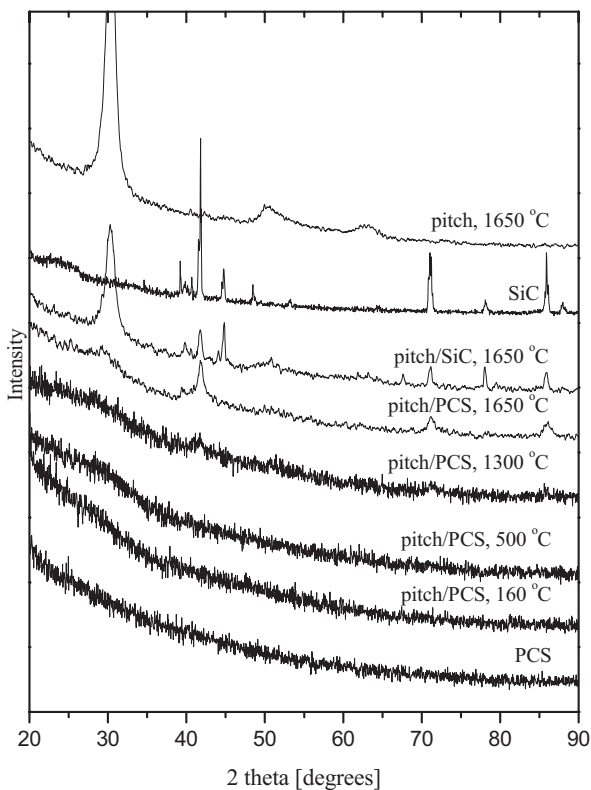


Fig. 1. Yields of carbonizates as function of pyrolysis temperature.

hydrocarbons) with insignificant mass balance impact of the essentially unchanged additives [14]. Under these conditions, in addition to the prevailing pitch decomposition chemistry associated with pronounced weight losses, the PCS-containing mixture with reactive Si-hydrides may also undergo elimination-condensation reactions involving some pitch constituents as well as self-condensation reactions with only small weight loss effects (hydrogen and/or low molecular hydrocarbon evolution).

In general, the weight losses for the pure pitch and SiC-modified pitch appear to parallel each other in the entire temperature range while for the PCS-modified pitch the losses are relatively larger, especially above 500°C. The latter can be explained by an additional evolution of volatiles in that system due to the pronounced elimination-condensation chemistry involving PCS at higher temperatures [7, 8]. It is worth mentioning that our analytical results support the retention of essentially all silicon introduced in the form of PCS at all applied pyrolysis temperatures, *i.e.*, 500°C-Si, 14.3%; 1300°C-Si, 14.8%, 1650°C-Si, 15.5%, and, therefore, indicate that the carbon-rich environment of the pitch prevents losses of low molecular Si-containing decomposition fragments. This can be compared with the outcome of the study on the pyrolysis of pure PCS when such losses were confirmed to take place [10].

The XRD patterns obtained for all investigated samples, including the reference materials, are shown in Fig. 2. It is apparent that the used SiC reference is a mixture of the 4H and 6H polytypes. First, it follows that the 1650°C treatment of both reference pure pitch and SiC-modified pitch



**Fig. 2.** XRD patterns for reference and modified materials that were obtained at increased pyrolysis temperatures in the system coal tar pitch/poly(carbosilane) (PCS).

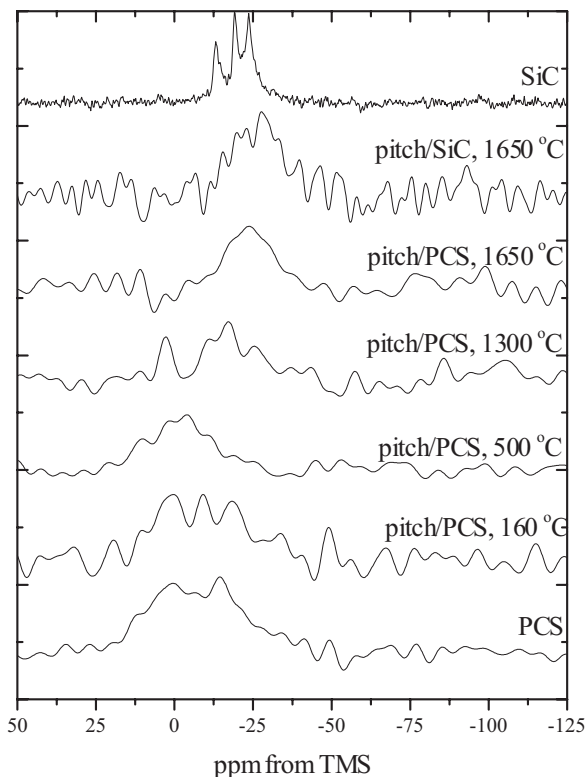
results in an increased ordering of graphitic carbon layers as evidenced by the evolution of the relatively broad peak at about  $2\theta = 30^\circ$  that is characteristic for graphite-like domains. On the other hand, for the PCS-modified material after  $1650^\circ\text{C}$ , only a very broad and weak halo is detected in this region supporting either highly amorphous carbon species [19] and/or agglomerates consisting of only a few condensed C-rings [11]. This observation suggests an inhibitive effect on the C-ordering processes of the *in-situ* formed SiC nanocrystallites that are distributed throughout the carbon matrix. Such a high temperature structural property of the C-domains in the system with PCS can further be linked to some plausible chemical reactions at  $500^\circ\text{C}$  or lower. Namely, the poly(carbosilane) reactive hydride functionalities may react with pitch constituents containing the  $-\text{OH}$  and/or other heteroatom groups on the surface of liquid mesophase

spheroids before their thermal decomposition and conversion to the solid body. This would prevent mesophase droplet coalescence and, thus, have a constraining impact on the subsequent graphite-like domain growth at higher temperatures. Similar arguments have been invoked to explain the inhibitive effect of the primary  $\alpha_2$  pitch constituents (quinoline insoluble) on the graphitization processes of pitches [20, 21]. Also, the pitch/PCS-derived carbonizate after the 500°C step has a microscopic foam-like structure with very thin walls similar to the structure of the material obtained from the thermal decomposition of pure PCS without curing in air [10].

Second, the XRD patterns for the pitch/PCS-derived carbonizates clearly confirm the formation of silicon carbide after the 1650°C pyrolysis step with indications that this process may have begun at 1300°C. Even in the former case, the relevant diffraction lines are rather weak and broad suggestive of the presence of nanocrystalline SiC and a detailed analysis of the pattern provides with the prevalingly regular  $\beta$ -SiC phase (3C) and some minor  $\alpha$ -SiC phase (6H) in this case. The occurrence of the latter can be understood in terms of the actual temperature conditions since the hexagonal phase is thermodynamically stable at high temperatures [19, 22]. Utilizing the Scherrer's equation ( $K = 1.0$ ), the average crystallite sizes of the SiC phases are estimated indicating the nanosized regime of the crystallites in the 1650°C pyrolyzed material, i.e., 28 nm for the regular  $\beta$ -SiC phase and 8 nm for the hexagonal  $\alpha$ -SiC phase.

The  $^{29}\text{Si}$  MAS NMR spectra for the materials are shown in Fig. 3 stacked in the order matching the respective XRD patterns in Fig. 2. It should be stressed that in contrast to the XRD measurements, which are sensitive to crystalline phases only, the NMR spectrum reflects all Si atoms in the sample independent of their long range ordering. Differences in the local arrangement of atoms surrounding a given silicon atom result in crystallographically nonequivalent sites which are characterized by different chemical shifts. Therefore, NMR provides different yet supplementary structural information to the XRD studies.

This fact is well illustrated by the spectra for the reference commercial SiC and pure PCS compounds shown at the top and bottom of Fig. 3, respectively. At the top, the three peaks of roughly the same intensity at  $-14.8$ ,  $-20.8$ , and  $-25.2$  ppm represent the A, B, and C types of silicon atom environment, respectively, that are observed in the 6H polytype of SiC [13, 23]. These types correspond to specific stacking sequences of successive atom layers labeled for A, *bCcAaBb*; B, *cBbAaBb*; and C, *aCcAaBb*, where the italicized letters *ABC/abc* (herein, the capital letters A, B, and C not to be confused with the A, B, and C labels for the types of silicon above) determine the first (*A/a*) and subsequent (*B, C/b, c*) Si/C atom



**Fig. 3.**  $^{29}\text{Si}$  MAS NMR spectra for coal tar pitch samples modified with poly(carbosilane) (PCS) and pyrolyzed at indicated temperatures. The two top spectra are for reference untreated SiC and pitch/SiC mixture pyrolyzed at 1650°C. The bottom spectrum is for pure PCS modifier.

layers in SiC. For the bottom spectrum, the two broad and overlapping peaks at 0 and -18 ppm correspond, respectively, to the  $\{-\text{CH}_2-\text{Si}(\text{CH}_3)_2-\text{CH}_2-\}$  and  $\{-\text{CH}_2-\text{SiH}(\text{CH}_3)-\text{CH}_2-\}$  units that are plausible in this system [24, 13] or, more generally, to the  $\text{SiC}_4$  and  $\text{SiC}_3\text{H}$  units in the initially linear and, progressively, more and more cross-linked PCS [25].

It can be seen that the initial process of mixing/homogenization of the PCS and coal tar pitch with a concurrent heating at 160°C does not visibly effect the shape of the NMR spectrum except for the reduction of its overall intensity. On the other hand, a significant reduction of the -18 ppm peak's intensity ( $\text{SiC}_3\text{H}$  units) as compared to that of the 0 ppm peak ( $\text{SiC}_4$  units) is observed in the sample pyrolyzed at 500°C. This is likely caused by a significant reduction of Si-hydrogen content in the material due to



condensation reactions between the individual poly(carbosilane) chains and/or involving the carbonaceous matrix which, in effect, result in replacement of the  $\text{SiC}_3\text{H}$  units with new  $\text{SiC}_4$  units. A similar effect on the  $^{29}\text{Si}$  NMR shifts has been reported for pure poly(carbosilane) pyrolyzed at  $500^\circ\text{C}$  [13].

A large change can be observed in the spectrum for the sample subjected to the pyrolysis at  $1300^\circ\text{C}$ . Apart from the relatively narrow peak at about 0 ppm representing the original  $\text{SiC}_4$  units, a broad feature centered at about  $-15$  ppm develops which can be attributed to a microscopically "amorphous" SiC phase. Analogous low crystallinity phases were found in the SiC-modified materials prepared from TMOS and phenol resin at  $800^\circ\text{C}$  [26] as well as in the poly(silylenemethylene) and poly(carbosilane) systems both pyrolyzed at  $1000^\circ\text{C}$  [27, 10]. Interestingly, a similar transition from the initially crystalline to a low crystallinity SiC phase is also observed in the present study for the reference sample with the 15% SiC additive in the pitch pyrolyzed at  $1300^\circ\text{C}$  (not shown; see discussion below).

Profound changes occur in the sample pyrolyzed at  $1650^\circ\text{C}$  as can be seen in the relevant NMR spectrum in Fig. 3. The line at 0 ppm disappears completely and the one at approx.  $-15$  ppm shifts toward lower chemical shifts. The latter line is now very broad (FWHM, approx. 900 Hz) and centered at about  $-25$  ppm both for the PCS and SiC additives, corresponding to the prevailing hexagonal  $\alpha$ -SiC phase. In the crystalline  $\alpha$ -SiC phases the number of nonequivalent Si-sites ranges from one to four, depending on a polytype, and the NMR spectrum consists of one to four peaks in the  $-14$  to  $-25$  ppm range. On the other hand, in the crystalline  $\beta$ -SiC phase all Si sites are crystallographically equivalent and its NMR spectrum consists of a single peak at  $-18.4$  ppm [28]. Due to the poor S/N ratio in the present case, it is difficult to unequivocally tell whether the spectrum represents a single SiC phase or, perhaps, superposition of various SiC polytypes that would all have the lines in the same frequency range. Although more than 200 polytypes of SiC have been reported in the literature, the number of crystallographically nonequivalent Si-sites is at most four [28], each of them characterized by a unique but slightly different chemical shift in the NMR spectrum. We are aware of only one successful analysis of the  $^{29}\text{Si}$  NMR line as the superposition of two components arising from the cubic and hexagonal phases of SiC. This was possible for the SiC prepared by selective area laser deposition [29] that produced microtwinned crystals of 1 to  $2\ \mu\text{m}$  size. Hence, they were at least an order of magnitude larger than in the present study.

In this respect, the  $^{29}\text{Si}$  NMR spectra reported for the ambiguous "amorphous" SiC display a single broad line (FWHM, approx. 1.1 kHz)

with a shift ranging from  $-14.5$  ppm for the ceramic fiber [26], to  $-15$  ppm for the silicon and graphite powder mixture prepared by high energy milling [30], up to  $-16$  ppm for the ceramics obtained from pyrolysis of pure PCS at  $1700^\circ\text{C}$  [13]. In the latter case, the material was believed to be crystalline in nature, mainly  $\beta$ -SiC, with some traces of  $\alpha$ -SiC. Finally, a broad line at  $-18$  ppm was reported for rice hulls pyrolyzed at  $1450^\circ\text{C}$  and it was assigned to the  $\beta$ -SiC phase based on XRD results [31]. We prefer to think about our materials and many relevant cases of the reported "amorphous"/low crystallinity, precursor-derived SiC in terms of their nanocrystalline rather than amorphous nature, which is consistent with our as well as others XRD results. For example, in the materials derived from the pyrolysis of pure PCS [13] and PCS-derived fibers [32, 33], it has been found from XRD measurements that the average crystallite sizes of the resulting SiC range from 2 to 16 nm if the pyrolysis temperature changes from 1000 to  $1700^\circ\text{C}$ . This can be compared with the 8–28 nm size range for the synthesized SiC in this study after the  $1650^\circ\text{C}$  heating step (see above). The presence of such small crystallites cannot be convincingly discriminated from an amorphous phase solely on the basis of the  $^{29}\text{Si}$  MAS NMR spectra due to the line broadness and line overlap problems. Therefore, in our case the NMR does not provide clear-cut evidence of the nature of SiC phases obtained by the pyrolysis of the PCS-modified coal tar pitch under conditions resulting in extremely low molecular weight clusters of SiC toward their nanocrystalline size regime. From a different angle, it is also likely that the formation and crystallization processes of SiC, given the relatively short carbonization time of 1 h, are limited only to a fraction of the silicon bearing additive. It would thus require longer carbonization times at  $1650^\circ\text{C}$  in order to transform the entire SiC to a unique and stable crystalline phase. Only then would the  $^{29}\text{Si}$  NMR together with XRD provide a definite answer regarding the quantitative aspects of the SiC phase composition.

The FT-IR spectra for the investigated materials are included in Fig. 4. The observed bands are in the typical regions for characteristic chemical bonds and can be helpful in identification of the starting compounds as well as intermediate and final materials [5–9, 14]. For example, in our samples, alkyl C–H stretches are seen in the  $2900$ – $2970$   $\text{cm}^{-1}$  region and the medium intensity bands at about  $1355$  and  $1400$   $\text{cm}^{-1}$  that can be assigned, respectively, to the  $-\text{CH}_3$  and  $-\text{CH}_2-$  groups in the carbonaceous phase. In addition, the infrared vibrations in poly(carbosilane) fragments are identified at  $830$  and  $1256$   $\text{cm}^{-1}$  ( $\text{Si}-\text{CH}_3$ ),  $1024$   $\text{cm}^{-1}$  ( $-\text{CH}_2-$  in  $\equiv\text{Si}-\text{CH}_2-\text{Si}\equiv$ ), and  $2104$   $\text{cm}^{-1}$  ( $\text{Si}-\text{H}$ ). Already after the  $160^\circ\text{C}$  treatment in the pitch/PCS system, a new band at  $1089$   $\text{cm}^{-1}$  appears that is characteristic of Si–O stretches [6, 7]. Such groups can be envisioned to result in

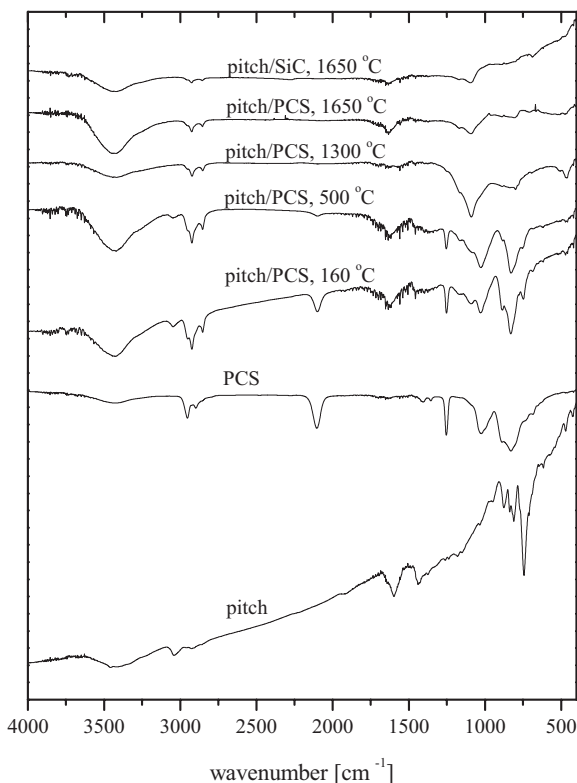


Fig. 4. FT-IR spectra for pure pitch, pure poly(carbosilane) (PCS), and modified materials that were obtained at increased pyrolysis temperatures in the system coal tar pitch/poly(carbosilane).

this system from reactions of the Si-hydrides in the PCS with  $\text{-OH}$ -containing species in the pitch *via*  $\text{H}_2$ -elimination chemistry, *i.e.*,  $\equiv\text{Si-H} + \text{HO-} \rightarrow \equiv\text{Si-O} + \text{H}_2$ , an advantageous process competing with the simple thermal self-decomposition of PCS associated with losses of low molecular mass fragments. The presence of the hydroxy groups and possibly  $\text{-NH}$ -groups [34] in the pitch is supported by the broad bands at  $3200\text{--}3600$  and  $1020\text{--}1280$   $\text{cm}^{-1}$ . Additional support for such a reactivity of the Si-hydrides at increased temperatures is found in the vanishing intensity of the characteristic Si-H stretches at about  $2100$   $\text{cm}^{-1}$  through the  $500^\circ\text{C}$  pyrolysis step with a simultaneous appearance and growth of the bands at about  $1090$   $\text{cm}^{-1}$  (Si-O bonds) and  $800$   $\text{cm}^{-1}$  (Si-C bonds). It appears that the former persist up to the  $1650^\circ\text{C}$  heating step with the latter then prevailing. This is consistent with the progressing carbothermal reduction of

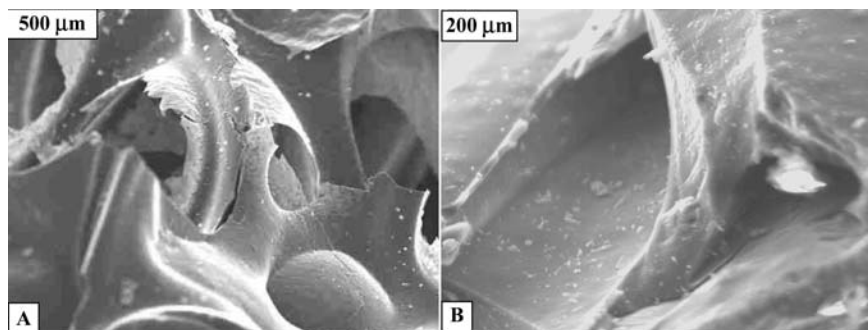


Fig. 5. Typical SEM micrographs for the carbonizates obtained at 1300 °C (A) and 1650 °C (B) in the system coal tar pitch/poly(carbosilane) (PCS).

the Si–O bonds above 1300°C according to an idealized reaction  $\text{Si-O} + 2\text{C} \rightarrow \text{Si-C} + \text{CO}$  that helps in formation of low oxygen content silicon carbide materials in the system with abundant carbon source.

It has already been mentioned that the PCS's Si–hydrides show pronounced reactivity toward oxygen during air-curing of the polymer at about 200°C yielding low porosity materials indicative of intensive cross-linking processes under these conditions [7]. On the other hand, if the PCS is pyrolyzed with exclusion of air/moisture, the materials are highly porous foams suggesting a massive evolution of volatiles from thermal cracking of the polymer in such a case [10]. In our study, the 500°C product in the pitch/PCS system is also foamy in appearance while the pure pitch or pitch modified with commercial SiC both yield much more compact residues under the same processing conditions. Furthermore, such a foam structure is preserved in the 1300 and 1650°C carbonizates. Typical SEM pictures for these carbonizates are shown in Fig. 5.

In an attempt to better elucidate the chemical nature of the materials obtained after each pyrolysis step, a XPS study was undertaken. One has to be aware, however, that this technique is surface sensitive and, especially, in the current case of powders, requires special attention as far as the interpretation of results is concerned. Figure 6 presents selected XPS results including the changes of the Si 2p (a) and C 1s (b) binding energies with pyrolysis temperature. The initial PCS shows a symmetrical Si 2p peak at 101.5 eV. This peak becomes gradually more and more deformed for the materials heated in the 160–500°C range with an apparent shoulder developing on the low-energy side and base widening on the high-energy side, the latter consistent with the formation of Si–O species. This is in good agreement with the earlier FT-IR results, thus, supporting the intermolecular elimination-condensation reactions between the PCS and suitable

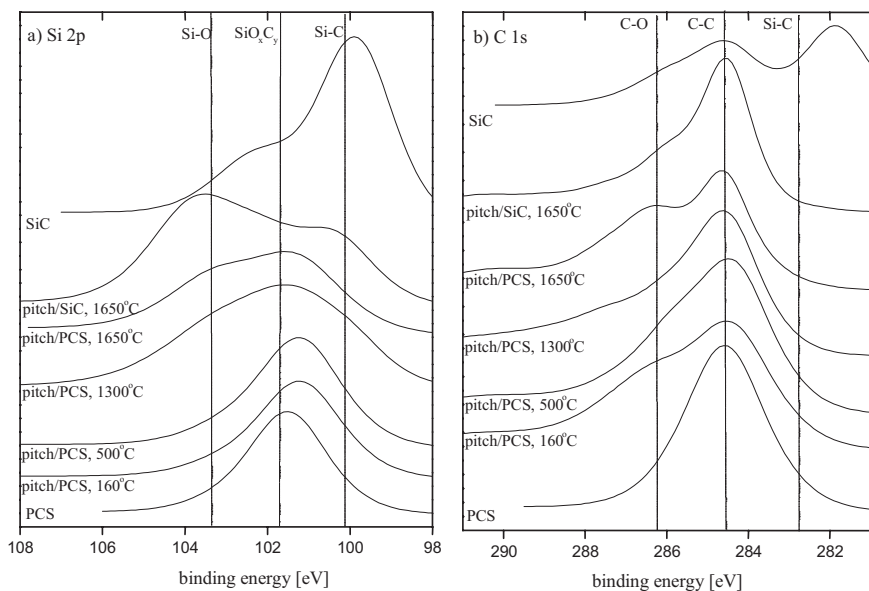
pitch components taking place in this temperature range. Dramatic spectral changes are apparent for the material after the 1300°C pyrolysis step. They are associated with a relatively large shift of binding energies both toward the initial peak's lower energy side (Si–C bonds) and higher energy side (Si–O bonds) significantly broadening the resulting peak. This is again consistent with the conclusions drawn from the IR measurements about co-existence of the Si–C and Si–O species in the 1300°C carbonizate, as discussed above. The XPS spectrum for the material after the 1650°C pyrolysis step shows this Si 2p peak becoming even broader. The peak's deconvolution (not shown) yields a component at 103.5 eV that can be assigned to Si–O species [8] and the major peak at 101.8 eV that is in the range for the Si–C bonds while some authors have suggested its association with the C–Si–O type of species as well [8, 35]. Again, the presence of the Si–O bonds in this carbonizate is supported by the relevant IR results. It is also worth to note that the pitch contains about 1% wt. nitrogen and it is probable that in addition to the SiC and SiO<sub>x</sub>C<sub>y</sub> phases the product may include silicon bound nitrogen. In this regard, the Si 2p binding energy in Si<sub>3</sub>N<sub>4</sub> is 101.9 eV being in the range of energies for the observed Si–C bonds.

The surface reactions of SiC with the pitch components providing reactive O- and N-sites that lead to Si–O and, possibly, Si–N species could explain the actual position and broadened shape of the Si 2p peak for our reference system pitch/commercial SiC pyrolyzed at 1650°C. It is clear that the overall chemical bonding environment for the silicon atoms here is complex and cannot be simply reconciled with the initially assumed neutral chemical relationship in the pitch/SiC system. Additionally, credence is lent for the surface interactions between the SiC and pitch by the broadened <sup>29</sup>Si MAS NMR peaks and some small discrepancies of the relevant XRD spectrum vs. that of pure SiC for this material. However, the bulk of the reference SiC appears to be unchanged after the pyrolysis.

The symmetrical C 1s peak at 284.6 eV for pure PCS shown at the bottom of Fig. 6 is typical for the C–H carbon environment in the polymer. The broadening of this peak and its shift toward higher energies for the composite system after the 160°C stage is likely associated with the presence of abundant carbon environment in the pitch including C–O groups. After the 1650°C pyrolysis step, a well defined peak component at 286.4 eV is observed typical for the C–O bonds, perhaps, in the plausible SiO<sub>x</sub>C<sub>y</sub> structures emerging from the earlier discussion of the Si 2p peaks as well. Interestingly, none of the spectra clearly show a definite feature expected at about 283 eV that could be associated with “pure” Si–C bonds in either intermediate precursors or final SiC-containing composite [8, 28]. This spectral property could possibly result from the relatively small quantity of

the SiC species in the carbon matrix, the latter known also to influence shifting the C 1s peak to higher energies in such systems [36]. It has been suggested, too, that some preferential carbon segregation and enrichment at grain surfaces of this kind of material may happen and somewhat artificially enhance the C(-C) and C(-O) signals *vs.* that of the weak C(-Si) 1s peak [37].

In summary, based on the result of the characterization techniques applied to study the coal tar pitch/poly(carbosilane) system, it can be concluded that (i) in addition to pitch cracking processes, some specific chemical reactivity is apparent already in the low temperature range of 160–500°C that can be linked to the condensation reactions between the PCS Si-hydrides and heteroatom functionalities in the pitch and that (ii) the formation of nanocrystalline SiC in the pitch-derived carbon matrix is pronounced after the 1650°C pyrolysis step with some data supporting the beginning of the process at 1300°C. Investigations of technological properties of such C/SiC composite materials are in progress and will be reported elsewhere.



**Fig. 6.** Selected XPS spectra for starting materials, reference compounds, and carbonizates obtained at increased pyrolysis temperatures in the system coal tar pitch/poly(carbosilane) (PCS).

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