

OPTIMIZATION OF THE POROUS CARBON MATRIX FOR PROCESSING OF CMCS BY THE LSI PROCESS

Günter Motz, Fushun Yang, Andreas Brendel and *Günter Ziegler

University of Bayreuth

Institute for Materials Research

**Friedrich-Baur-Research Institute for Biomaterials*

D-95440 Bayreuth, Germany

ABSTRACT: During the last decades fiber re-enforced CMCs have become increasing interest in high temperature applications in oxidizing and/or corrosive environments. The most economic process for manufacturing CMCs is the siliconization of carbon filled C-fiber fabrics (LSI process). During this process a number of problems can occur. The liquid silicon reacts with the C-fibers to SiC and can lead to very brittle C/SiC-composites. The thermal and chemical stability is limited by an incomplete reaction of the carbon matrix with the molten silicon, resulting in an inhomogeneous matrix which consists of the desired SiC as well as of unreacted carbon and silicon.

In order to generate a homogeneous SiC-matrix and to improve the melt infiltration process, it is necessary to develop a C-matrix with a tailored open porosity. This is possible by the combination of common carbon resins with chemically compatible C-polymers. These additional polymers are mixable but not soluble in the carbon resins. The different cross-linking mechanisms lead to various polymer structures and finally to differences in the ceramic yields. This results in an open porosity adjustable by the content and the type of the additional polymers.

In a first step the porosity of the tailored pure carbon matrices was investigated with Hg intrusion porosimetry and microscopical methods. Ceramic yield and pyrolysis behavior of the different compositions were determined by FTIR coupled TG-measurements. Differences in the type of the resulting carbon were determined with spectroscopic Raman method. Subsequent siliconization of the porous carbon specimens enables to screen the infiltration behavior and the formation of SiC. In a second step carbon fiber fabrics were infiltrated with the optimized polymer mixtures, then cross-linked and pyrolyzed to get porous carbon performs, and investigated with the methods mentioned above. The siliconization of the porous carbon preform demonstrates the better infiltration behavior and the formation of a homogeneous SiC matrix for CMCs with improved properties.

KEYWORDS: CMC, Carbon-Matrix, LSI-Process, Porosity

INTRODUCTION

Fiber re-enforced non-oxide CMCs have gained increasing interest especially for applications at high temperature and in oxidizing or corrosive environments. They offer the possibility to combine typical properties of ceramics like chemical and thermal stability, wear resistance as well as high hardness values with the tensile strength and flexibility of carbon or ceramic fibers. CMCs manufactured by the Liquid Polymer Infiltration (LPI)- and Chemical Vapor Infiltration (CVI)-process are distinguished particularly by better mechanical properties e.g. flexural and tensile strength, Young's modulus, fracture toughness and better strain values from CMCs made by the Liquid Silicon Infiltration (LSI)-Process [1]. Despite these drawbacks the LSI process is actually the most promising technique for manufacturing of CMCs in an industrial scale because of lower costs and shorter manufacturing times [2]. First LSI based CMC materials were manufactured for high temperature applications in future space transportation systems or for heat exchanger. Actually, the commercial activities are focused on

applications at lower temperatures, e.g., for automotive brakes but also for satellite communication systems (mirrors) due to the low coefficient of thermal expansion.

Generally, the LSI process consists of three steps [3]. It starts with the infiltration of mostly C-fiber fabrics with a preferably very liquid, cross-linkable organic resin. After cross-linking of the polymer and the formation of a carbon fiber re-enforced plastic, subsequent pyrolysis of the polymer matrix should lead to a porous carbon matrix in a carbon yield as high as possible. The resulting C/C composite shows a high content of open porosity, due to the separation of gaseous products and the shrinkage of the carbon matrix during pyrolysis. In the final step the porous C/C body is infiltrated with liquid silicon at temperatures higher than 1420 °C. The exothermic reaction between liquid silicon and carbon finally leads to an SiC/C composite with an open porosity lower than 3 %. Therefore, an additional re-infiltration step is not required. Especially for applications at higher temperatures and in strongly oxidizing or corrosive environments an effective protection of the C-fibers is important. But also a quantitative reaction of the C-matrix with the infiltrated liquid silicon to SiC can improve the high temperature properties. If the siliconized matrix contains an excess of carbon, the strength of the CMC decreases by burnout of carbon already at 400 °C in air or in strongly oxidizing environments like nitric or sulfuric acid. If the matrix contains unreacted silicon the strength of the CMC decreases at temperatures beyond 1400 °C. Besides parameters like reaction temperature, the type of the formed carbon or specially tailored Si-alloys, also the type and the content of the porosity of the carbon matrix is very important [4]. A large reaction surface of the solid carbon in combination with a suitable porosity will promote for a quantitative and homogeneous reaction to SiC.

This paper discusses the formation of a carbon matrix based on a polycyanurate resin and experiments to tailor the porosity of the matrix by addition of a suitable organic polymer with low ceramic yield as well as by variation of the temperature program during pyrolysis. Firstly, to exclude the influence of the fiber fabric on the properties and on the structure of the resulting matrix the pure or modified polycyanurate resin was used. Subsequently, it was tried to transfer the achieved results on the processing of C/C bodies with tailored porosity for an improved LSI process.

EXPERIMENTAL

Wax like, meltable cyanate esters with low molecular weight were cross-linked by cyclotrimerization reaction at 130 °C (4 - 6 h) by using 1 wt% of a copper catalyst [5] to an unmeltable polycyanurate resin (PCR) as carbon precursor. 10 and 20 wt% polybutadiene ($M_n = 1800$, Aldrich) was added to the untreated cyanate ester to generate an additional porosity during pyrolysis.

Rheological measurements to determine the optimal infiltration temperature and the cross linking behavior were conducted with a rotational rheometer (Rheolab MC 100, Physica,) at a shear rate $\dot{\gamma} = 15 \text{ s}^{-1}$. For processing suitable specimen, the pure cyanate ester or the modified system and the catalyst were mixed, casted into a teflon container (130x110x10) mm and cross-linked. The resulting PCR bodies were cutted with a wire saw to samples of (30x15x8) mm and pyrolyzed with different temperature rates (0.1 up to 2 K/min) up to 1600 °C in a nitrogen atmosphere.

The pyrolysis process of the PCR was characterized by thermogravimetric measurements (STA 409, Netzsch), FTIR (Vector 22, Bruker) and Raman (Olympus BX41, Jobin Yvon) spectroscopy, X-ray diffraction (XRD3000P, Seifert) and elemental analysis.

Microstructural characterization of all carbon monoliths, C/C materials and LSI based CMCs in the polymer as well as in the ceramic state was examined by scanning electron microscopy (JSM 6400, Jeol). The porosity of selected samples were investigated by Hg-Porosimetry (Macropores Unit 120 and Porosimeter 2000, Carlo Erba Instruments) and by He-Pyknometry (AccuPyc 1330, Micromeritics).

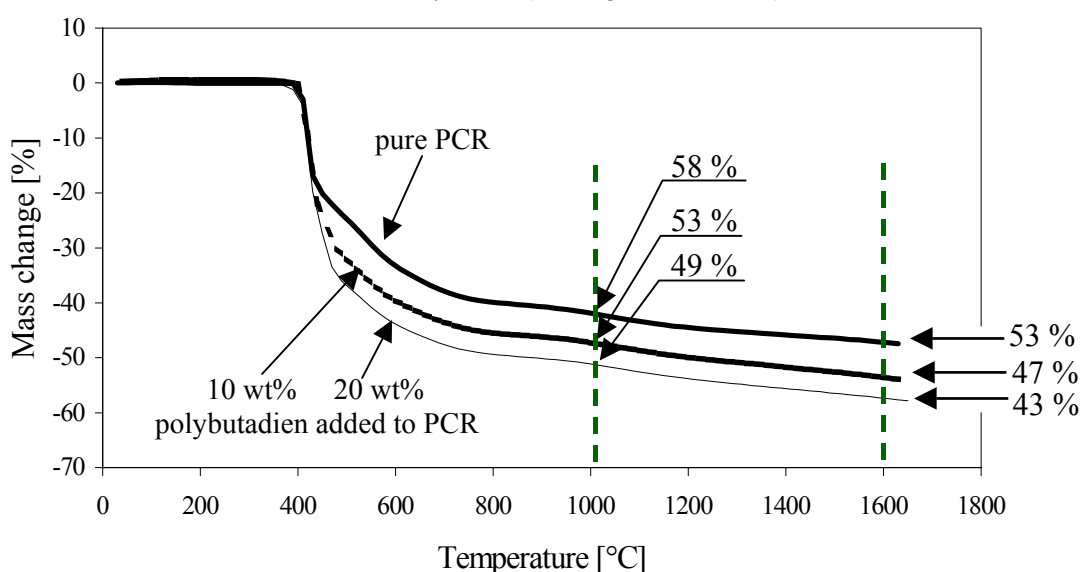
RESULTS AND DISCUSSION

A large variety of polycyanurate resins on the basis of cyanate esters were developed as thermoset polymer especially for manufacturing of fiber re-enforced plastics. The cross-linking is initiated thermally or by a catalyst. In both cases the $-O-C\equiv N$ groups of three cyanate esters form in an exothermic reaction a six-member triazine ring. During this addition reaction no volatile species evaporate. This leads to void free plastics with an outstanding thermal stability up to more than 400 °C without mass loss depending on the polymer. The high degree of cross linking and the high amount of carbon in the thermoset is also a precondition for a high char yield after pyrolysis in an inert atmosphere. Therefore polycyanurate resins are very interesting as carbon matrix materials for the LSI process.

For processing of monolithic materials but especially for manufacturing of the fiber re-enforced C/C bodies it is very important to investigate the resin regarding the rheological behavior and the cross linking. The viscosity of a polymer during the infiltration should be lower than 100 mPa•s without cross-linking effects. In the case of the used pure and modified cyanate esters this value is already reached at 80 °C. At 90 °C the viscosity decreases for the pure system up to 38 mPa•s and is lowered by addition of 10 wt% PB up to 30 mPa•s. Also the cross linking behavior of the two systems was investigated via rheological measurements at 140 °C. In contrast to the viscosity values at 90 °C the addition of PB influences the start and the process of cross linking. The pure precursor reacts after 40 minutes very vigorously in a strong exothermic reaction. In contrast, the addition of 20 wt% PB leads to a slow and controllable increase in viscosity from 400 mPa•s after a curing time of 100 min up to 600 mPa•s after 120 min.

With the objective to use the wax like meltable cyanate ester as carbon matrix for the LSI process, the educt was cross-linked with copper catalyst. The subsequent TG-measurement (Fig. 1) demonstrates the high thermal stability of the PCR. A remarkable mass loss starts only but very rapidly at 410 °C. The char yield at 1000 °C (N_2 -atmosphere) is 58 % and decreases to 53 % after pyrolysis up to 1600 °C. This char yield is high enough for modification of the PCR with an polymeric hydrocarbon like polybutadiene (PB) ($-CH_2CH=CHCH_2-$)_n. The liquid PB is a linear polymer, shows no reaction with the cyanate ester and is mixable but not soluble therein. A phase separation of the PB and the molten PCR takes place only after a couple of days at 80 °C. Pure polybutadiene has a very low char yield. In combination with the PCR this polymer can act as pore forming agent during pyrolysis. The TG-measurements for mixtures of PCR with 10 and 20 wt% polybutadiene demonstrate (Fig. 1) that the char yields decreases up to 53 and 49 % (1000 °C), respectively. The differences between the char yields of the different polymers remain constant also up to the pyrolysis temperature of 1600 °C. Char yields of 47 and 43 % are high enough to form a suitable carbon matrix for the LSI process.

Fig. 1: TG-measurement (N_2 -atmosphere) of the pure PCR and the polybutadiene modified PCR systems (heating rate 5 K/min)



The thermal decomposition behavior of cyanate resins was very intensively investigated by Ramirez et al. [6,7]. To explain the mass loss of the pyrolysis products between 1000 and 1600 °C the TG-measurement was coupled with FTIR spectroscopy to determine the formed gaseous species in this temperature range. Additionally, at 1000 and 1600 °C pyrolyzed PCR samples were analyzed regarding their chemical composition (Tab. 1). With FTIR spectroscopy only oxygen containing molecules like H₂O, CO₂ and CO were detected. But the results of the elemental analysis demonstrate that the nitrogen content decreases remarkably from 3.7 (1000 °C) up to 0.6 wt% (1600 °C). Both the absence of peaks for nitrogen containing gases in the IR spectra and the decreasing nitrogen content in the pyrolysis products suggest the formation of IR inactive N₂ molecules.

Tab.1: Chemical composition of the PCR pyrolysis products

Pyrolysis temperature	Pyrolysis atmosphere	C [wt%]	H [wt%]	N [wt%]	O [wt%]	Formula
1000 °C	N ₂	93.5	0.4	3.7	1.9	C ₁₀₀ H _{5.1} N _{3.4} O _{1.5}
1600 °C	N ₂	98.2	< 0.1	0.6	0.2	C ₁₀₀ H ₀ N _{0.53} O _{0.15}

As mentioned above the char yield of polybutadiene is very low. Therefore, chemical composition of the pyrolyzed PB modified polycyanurate resin shows no significant differences to the pure PCR char. Commonly the pyrolysis of organic resins up to 1000 °C leads to non-graphitic carbon with hexagonally arranged carbon atoms [8]. The formed layer planes are very limited in dimension and highly defective. Heteroatoms like nitrogen and oxygen are mostly located at the edges of the lamellae and structure defects. Pyrolysis at higher temperatures and the loss of the heteroatoms should lead to higher orientated crystalline regions detectable by Raman spectroscopy and X-ray diffraction.

Raman spectroscopy is one of the most sensitive methods for the characterization of the different modifications of carbon [9-15]. In the spectrum recorded on PCR char pyrolyzed at 1000 °C, two broad signals with low intensity centered at about 1280 and 1600 cm⁻¹ are observed. The same two bands with increased intensity were detected for the PCR pyrolysis product at 1600 °C.

The two Raman bands mentioned above are the most striking features of disordered graphitic-like carbon and are assigned to the D and G bands [9,10]. The higher energy G band is due to the vibrational mode (E_{2g}) of graphitic layers, which usually shifts to higher frequencies and shows an increased line width when the graphitic layers become less ordered. The appearance of the D and the G band in the Raman spectra of the PCR chars indicates disordered or nanocrystalline graphitic clusters. Both the line width of the G band (115 cm⁻¹ → 43 cm⁻¹) as well as of the D band (200 cm⁻¹ → 51 cm⁻¹) reduces with increasing pyrolysis temperature from 1000 up to 1600 °C. As published the intensity ratio (I_D/I_G) is inversely proportional to the domain size of nanocrystalline graphite [10,11]. For the PCR chars decreasing (I_D/I_G) values of 1.74 (pyrolysis at 1000 °C) and 1.19 (pyrolysis at 1600 °C), respectively, were determined. The decreased line widths and (I_D/I_G) values refer to structural rearrangements by formation of an increased number of crystallites and/or an increase in size and ordering of existing nanocrystallites.

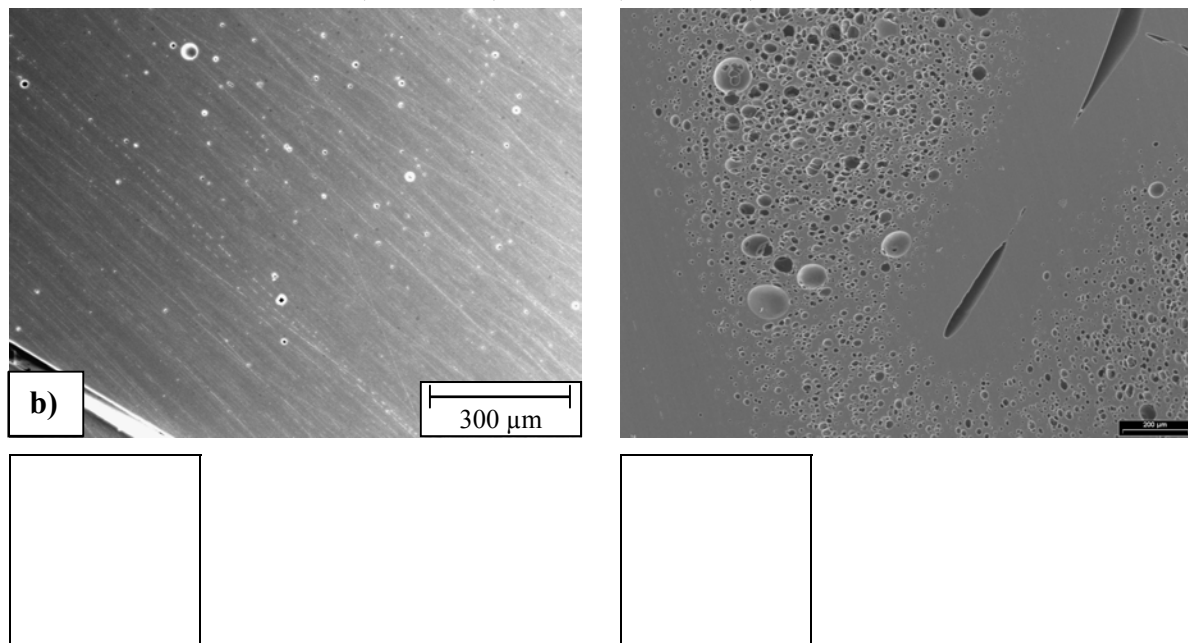
Only amorphous carbon structure was demonstrated with X-ray diffraction at both 1000 and 1600 °C which suggest that the formed crystallites are too small for detection with XRD.

Beside a high char yield and the type of the char (reactivity) a suitable interconnecting pore network by the formation of cracks and open pores during pyrolysis is very important for processing of CMCs via the LSI process. Especially, the diameter (capillary forces, reaction surface) and the distribution of the pores (thickness of the pore walls, homogeneity) influence the reaction with liquid silicon and the properties of the resulting CMC. The formation of larger pores is preferred by faster heating rates. As showed in Fig. 1 the release of gaseous species during pyrolysis of the PCR starts very rapidly at 410 °C. Whereas after heat treatment at 350 °C the polymer is almost dense, already at 370 °C the gaseous pyrolysis products are responsible for the formation of first pores (Fig. 2b). Additionally, thermal stresses into the pure PCR result in slot pores surrounded by a very dense matrix. Further heating up to 400 °C leads to an increase in the total porosity from 11 up to 44 %. The pore structure

is similar to the material pyrolysed at 370 °C but the number and the average diameter of pores increase rapidly. After heat treatment at 1000 °C the matrix structure is still unchanged. Only the pore diameters and the total porosity (40 %) are decreasing by further compaction of the char. The resulting porous char shows a very inhomogeneous structure consisting of pores with very large diameters and dense regions up to 250 µm in thickness around the slot pores. Therefore, this matrix leads to undesired unreacted silicon and carbon after siliconization.

A further drawback is the high volume change of the matrix at faster heating rates during pyrolysis (Fig. 3). After an increase in volume of approx. 70 % after heating up to 400 °C further pyrolysis leads to the expected shrinkage of about 40 % related to the original size. In the case of an infiltrated fiber fabric this extreme change in volume can lead to delamination effects.

Fig. 2: SEM micrographs of different PCR products pyrolyzed at different temperatures (N₂-atm.)
a) 350 °C, b) 370 °C, c) 400 °C, d) 1000 °C



Heating rate program: RT-300 °C 2 K/min; 300-600 °C 1 K/min; 600-1000 °C 2 K/min

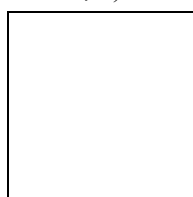
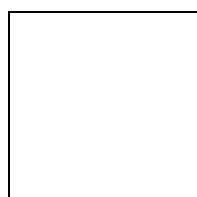
The first experiment to get a more homogeneous matrix and to reduce the change in volume was to lower the heating rate especially in the very sensitive temperature range from 350 up to 450 °C. The lower degassing rate lower the thermal stresses and should lead to a uniformly distributed porosity. Fig. 4 illustrates that pores just formed again after heat treatment at 400 °C, but no dense walls are formed around the slot walls. Also after pyrolysis at 1000 °C the nature of the porosity remains unchanged. In comparison to faster heating rate the porosity of the chars is homogeneously distributed and the diameters are similar. Due to the controlled evaporation of the gaseous pyrolysis products only shrinkage during pyrolysis within the expected limit was determined (Fig. 3).

Fig. 3: Change in volume of different PCR pyrolysis products



◆	Pure PCR	RT-300 °C 2 K/min; 300-600 °C 1 K/min; 600-1000 °C 2 K/min
■	Pure PCR	RT-200 °C 1K/min; 200-350 °C 0.5 K/min; 350-450 °C 0.1 K/min; 450-1000 °C 0.5 K/min
▲	PCR/PB = 10 : 1	RT-300 °C 2 K/min; 300-600 °C 1 K/min; 600-1000 °C 2 K/min
×	PCR/PB = 10 : 1	RT-350 °C 0.5 K/min; 350-400 °C 0.3 K/min

Fig. 4: SEM micrographs of PCR products pyrolyzed at different temperatures (N₂-atm.) and reduced temperature rates a) 400 °C, b) 1000 °C

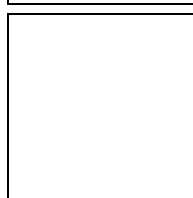
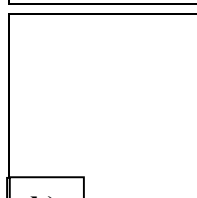
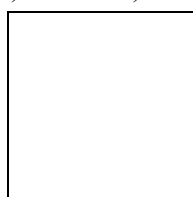
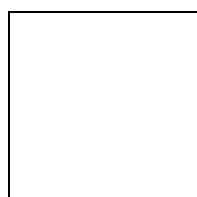


Heating rate program: RT-200 °C 1K/min; 200-350 °C 0.5 K/min; 350-450 °C 0.1 K/min; 450-1000 °C 0.5 K/min

Singh et al. [16] reported that microporous carbon materials with controlled porosity can be fabricated by addition of a liquid pore forming agent to the carbon resin. To avoid processing problems by use of such solvent like liquids the polymeric hydrocarbon polybutadiene (PB) was used.

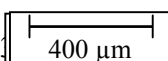
The modification of the PCR with polybutadiene leads to similar results like the pyrolysis experiments with the pure resin at different temperature rates (Fig. 5). The expansion of the modified PCR body up to 400 °C is only 30 % (Fig. 3). Reduced temperature rates lead even to shrinkage up to 400 °C. Therefore, in both cases delamination effects during the processing of CMCs are improbable. The distribution of the pores and the reduced pore wall thickness should enable an improved siliconization process by using this polycyanurate resin.

Fig. 5: SEM micrographs of PB modified PCR products pyrolyzed at different temperatures (N₂-atm.) a) 350 °C, b) 400 °C, c) 600 °C d) 1000 °C



b)

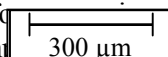
Heating rate program: RT-350 °C 0.5 K/min; 300-600 °C 1 K/min; 600-1000 °C 2 K/min



CONCLUSIONS

PCR system is very suitable for fiber re-enforced plastics. For application as carbon for the LSI process an improved pyrolysis behavior regarding the formation of a suitable porosity and a reduced volume extension is very important. Dense carbon walls with a thickness more than 200 μm are a difficult problem for a complete transformation into SiC. The variation of the pyrolysis program and the addition of a polymer with a very low char yield as pore

d)



former offer possibilities to overcome the named problems. Further research will deal with transferring the achieved results to the conditions of carbon fiber re-enforced materials.

ACKNOWLEDGEMENTS

This work has been supported bei the Bayerische Forschungsstiftung, Bayerisches Staatsministerium für Wissenschaft, Forschung und Kunst (Bavaria, Germany). In addition, Th. Kabelitz, University of Bayreuth, as well as L. Weisensel, University of Erlangen, are acknowledged for their support.

REFERENCES

- [1] A. Mühlratzer, M. Leuchs, "Applications of Non-Oxide CMCs", High Temperature Ceramic Matrix Composites, 288-298 (2001)
- [2] R. Kochendörfer, N. Lützenburger, "Applications of CMCs Made via the Liquid Silicon Infiltration (LSI) Technique", High Temperature Ceramic Matrix Composites, 277-287 (2001)
- [3] E. Fitzer, R. Gadow, *Am. Ceram. Soc. Bull.*, **65** [2] 326-335 (1986)
- [4] R. Gadow, M. Speicher, *Ceram. Eng. Sci. Proc.*, **21** [4] 485-492 (2000)
- [5] J. Schillgalies, H.-G. Reichwein, A. Palinsky, A. Kaffee, German Patent DE 19905448A1
- [6] M.L. Ramirez, R. Walters, E.P. Savitski, R.E. Lyon, „Thermal Decomposition of Cyanate Ester Resins“, *DOT/FAA/AR-01/32, FAA William J. Hughes Technical Center*, September 2001
- [7] M. L. Ramirez, R.N. Walters, R. E. Lyon, E. P. Savitski, "Thermal decomposition of cyanate ester resins", *Polymer Degradation and Stability* **78** 73-82 (2002)
- [8] B. Rand, "Matrix Precursors for Carbon-Carbon Composites" in *Essentials of Carbon-Carbon Composites* 67-90 (1993)
- [9] Y. Wang, D. C. Alsmeyer, R. L. McCreery, "Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra," *Chem. Mater.*, **2** 557-563 (1990).
- [10] R. O. Dillon, J. A. Woollam, V. Katkanant, "Use of Raman scattering to investigate disorder and crystallite formation in as-deposited and annealed carbon films," *Phys. Rev. B*, **29** [6] 3482-3489 (1984).
- [11] T. Jawahari, A. Roid, J. Casado, "Raman Spectroscopic Characterization of some Commercially Available Carbon Black Materials", *Carbon*, **33** [11] 1561-1565 (1995)
- [12] W. A. Yarbrough, R. Messier, "Current Issues and Problems in the Chemical Vapor Deposition of Diamond," *Science*, **247** 688-696 (1990).
- [13] F. Tuinstra, J. L. Koenig, "Raman Spectrum of Graphite," *J. Chem. Phys.*, **53** [3] 1126-1130 (1970).
- [14] R. J. Nemanich and S. A. Solin, "First- and second-order Raman scattering from finite-size crystals of graphite," *Phys. Rev. B*, **20** [2] 392-401 (1979).
- [15] M. I. Nathan, J. E. Smith Jr., and K. N. Tu, "Raman spectra of glassy carbon," *J. Appl. Phys.*, **45** [5] 2370 (1974).
- [16] M. Singh, S.C. Farmer, "Morphological characterization of microporous carbon materials", *J. Mater. Sci. Let.*, **16** 946-949 (1997)