

# Kinetic Model for the Pyrolysis of Polysiloxane Polymers to Ceramic Composites

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*A model describing the pyrolysis of an organo-silicate polymer (Blackglas polymer) to form a silicon oxycarbide glass was developed based on the known chemistry and architecture of the polysiloxane precursor. The objectives were to develop a plausible reaction pathway to explain the pyrolysis process, rate, and product spectrum, and to study the effect of various heating protocols on the pyrolysis process. The model successfully predicted the evolution rates of the major gases as a function of process temperature and the overall pressures reached during the process. The effects of various heating protocols on the outgassing kinetics were studied to develop an optimum protocol for a rapid pyrolysis process that gives a composite with desirable mechanical properties. Overall, the model appears to capture the essential characteristics of the process and is in good agreement with experimental results.*

## Introduction

The development of pyrolysis routes to form ceramic materials is attractive because the polymeric precursors can be molded easily at relatively low temperatures and then fired to produce near net shapes. These systems can also be adapted for rapid prototyping operations. One such process uses a polysiloxane precursor to form Blackglas, a refractory silicon oxycarbide, invented at Allied Signal (Leung et al., 1994; Annamalai et al., 1996). The Blackglas silicon oxycarbide offers the ease of fabrication of a polymer and the high temperature stability and capabilities of a ceramic. It is also envisioned to be an excellent candidate for use as a composite matrix to operate in the 260–1,200°C regime. A generic fabrication process for converting Blackglas or similar polysiloxane precursors to ceramics is shown in Figure 1. In these fabrication processes, the pyrolysis step is the bottleneck due to the slow diffusion and the low saturation concentrations of evolved gases in the resin (Dente and Ranzi, 1983). Proper control of the rate of pyrolysis and postcure temperature may enable one to minimize microcracks and pores and to relate changes in the composition of the matrix to the physical and mechanical properties of the final product (Hurwitz et al., 1995; Meador et al., 1996; Wang et al., 2000).

A lumped parameter model was previously developed (Annamalai et al., 1995, 1996) to enable one to control the rate

of mass loss as a function of time or temperature for a given heating protocol. However, the mechanical and thermal properties of the product and the composition of the evolved gases are functions of the processing variables and the chemistry of the precursor. The lumped model did not address these issues. This article describes how a mechanistic approach that considers the chemistry of the precursors, the chemical pathways for the dissociation and redistribution reactions leading to gas evolution, and the microstructure and properties of the product can be useful in designing a pyrolysis protocol for producing a useful ceramic part in minimal time.

## Model Development

Monitoring the changes in the chemical structure of the matrix during pyrolysis indicates plausible chemical pathways for generating the evolved gases and the ceramic product. Hurwitz et al. (1995) and Meador et al. (1996) used  $^{29}\text{Si}$  NMR (nuclear magnetic resonance) spectroscopy to study the high-temperature processing regime for these materials. Leung et al. (1994) used  $^{29}\text{Si}$  NMR to investigate the chemical composition of the polysiloxane precursor and then the final product after pyrolysis at 1,200°C. The  $^{29}\text{Si}$  NMR results indicated that the polymer precursor consists of  $\text{CH}_3\text{SiO}_2$  ( $\text{CH}_2\text{CH}_2$ ) (77%),  $(\text{CH}_3)_2\text{SiO}_2(\text{CHCH}_3)$  (12%),

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(CH<sub>3</sub>)<sub>3</sub>SiO (3%), CH<sub>3</sub>SiHO<sub>2</sub> (4%), CH<sub>3</sub>SiO<sub>3</sub>(1%), -CH<sub>2</sub>SiO<sub>3</sub> (3%), and C<sub>4</sub>H<sub>8</sub> (0.1%). The silicon environment in the final Blackglas ceramic consists of the following tetrahedral sites: SiO<sub>4</sub> (27.7%), SiCO<sub>3</sub> (16.2%), SiC<sub>2</sub>O<sub>2</sub>(22.6%), SiC<sub>4</sub> (33.5%).

The transformation of the polymeric network into an inorganic material is characterized by a loss of methane, hydrogen, and C<sub>2</sub> and C<sub>3</sub> hydrocarbons as detected by thermogravimetric analysis (TGA/EGA) (Leung and Porter, 1994). Elemental analyses indicate that all the silicon and oxygen present in the polymer remain in the ceramic Blackglas (Leung and Porter, 1994) after pyrolysis. Electron spin resonance (ESR) results, and the high temperatures involved during pyrolysis, suggest that this transformation occurs via a free radical mechanism. The energies for the various bonds present in the polymer are listed in Table 1 and provide for a simplistic representation of how the process might proceed. Cleavage of the Si-C and C-C bonds would likely occur first, at the lower temperatures, leading to the evolution of hydrocarbons. At temperatures above 600°C, the stronger C-H bonds would begin to break to form carbon and hydrogen (Leung and Porter, 1994). The silicon-oxygen bond is very strong and is stable to temperatures beyond, 1,450°C (Babonneau, 1995) even in the presence of excess carbon. This suggests that only Si-C, C-C, Si-H, and C-H bonds are broken to form radicals during the pyrolysis. There is no Si-Si to be formed during the pyrolysis (Soraru et al., 1990). Infrared (IR) spectra at 800°C suggest that only Si-C, Si-CH<sub>2</sub>-Si, Si-O-Si bonds exist in the solid matrix, indicating that the condensation process is completed through the formation of Si-CH<sub>2</sub>-Si in the transformation of the polymer to a ceramic (Yajima et al., 1978; Haregawa et al., 1980; Haregawa and Okamura, 1983, 1986).

#### Decompositions of -CH<sub>2</sub>-CH<sub>2</sub>-, CH<sub>3</sub>- and -CH<sub>2</sub>-

In the final silicon oxycarbide ceramic, some silicon is bonded to both oxygen and carbon while carbon is bonded either to silicon or carbon. There are no carbon-oxygen bonds found in the material (Renlund and Prochazka, 1991). The silicon oxycarbide structure is envisioned to be a random network of silicon-oxygen tetrahedra with an occasional silicon bonded to one or two carbons. These carbons are, in turn, tetrahedrally bonded to other silicon atoms. Although redistribution reactions between Si-C and Si-O bonds are likely during the pyrolysis, the number of Si-O bonds remains approximately constant. The redistribution reactions lead only to the change of atoms surrounding Si. Therefore, any outgassing or mass loss with respect to temperature or time is caused by the cleavage of Si-C, C-C, Si-H, and C-H bonds. This suggests that the functional groups in the precursor involved in the pyrolysis reactions are CH<sub>3</sub>, -CH<sub>2</sub>-CH<sub>2</sub>-, and -CH<sub>2</sub>-.

Table 2 shows that the functional group -CH<sub>2</sub>-CH<sub>2</sub>- can be thermally decomposed to form ethylene by reaction (1), benzene (C<sub>6</sub>H<sub>6</sub>) and hydrogen by reaction (2), carbon and hydrogen by reaction (3), 1-hexene (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>CH = CH<sub>2</sub>) by reaction (4), or carbon and methane by reaction (5). The methyl (-CH<sub>3</sub>) group can be thermally decomposed to form methane (CH<sub>4</sub>) and methylene (-CH<sub>2</sub>-) by reaction (6), carbon and hydrogen by reaction (7), or ethane (C<sub>2</sub>H<sub>6</sub>) by reac-

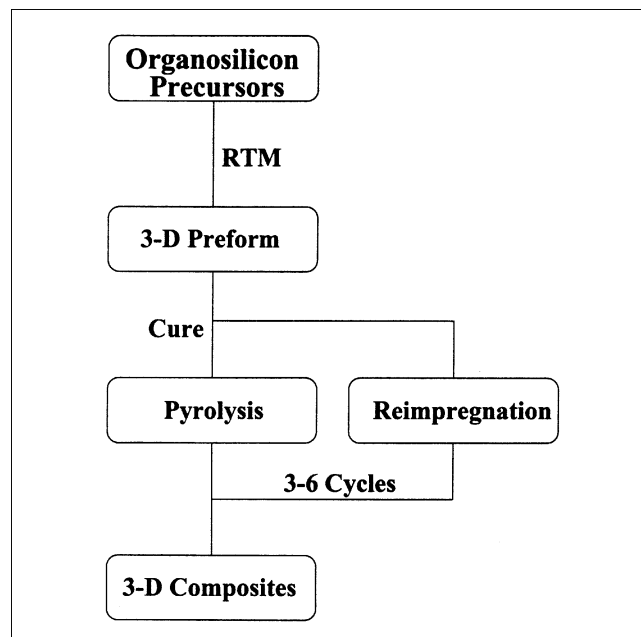


Figure 1. Process for making composite from pre-ceramic polymer.

tion (8). The methylene (-CH<sub>2</sub>-) group can be thermally decomposed to form carbon and hydrogen by reaction (9) or to form carbon and methane by reaction (10). The Gibbs energies for reactions 1–10 are shown in Figures 2, 3, and 4, and indicate which reactions from that set are possible at a given temperature.

As shown in Figure 2, the -CH<sub>2</sub>-CH<sub>2</sub>- group can be decomposed to form ethylene above 400°C, to form benzene and hydrogen, or to form 1-hexene above 300°C. Benzene and 1-hexene are not observed in mass spectroscopy (TGA-MS) or residual gas analysis (TGA-RGA) thermogravimetric experiments (Leung and Porter, 1994), and so, while reactions 2 and 4 are thermodynamically favorable, they appear unlikely to occur in the transformation of the polymer to a ceramic. The slow diffusion of the -CH<sub>2</sub>-CH<sub>2</sub>- group in the solid may kinetically limit the formation of these bigger molecules. The -CH<sub>2</sub>-CH<sub>2</sub>- group can also be decomposed to form carbon and hydrogen or to form carbon and methane above 300°C. <sup>13</sup>C NMR of the semi-ceramic, intermediate material indicates that free carbon forms around 600°C. At higher temperatures, the -CH<sub>2</sub>-CH<sub>2</sub>- group is most likely decomposed to form carbon and methane, because the Gibbs energy of reaction 5 is more negative than the other four decomposition pathways and diffusion through the solid provides ample opportunity for hydrogen and carbon to react and form methane.

Table 1. Bond Energies of Various Bonds Present in the Polymeric Precursor

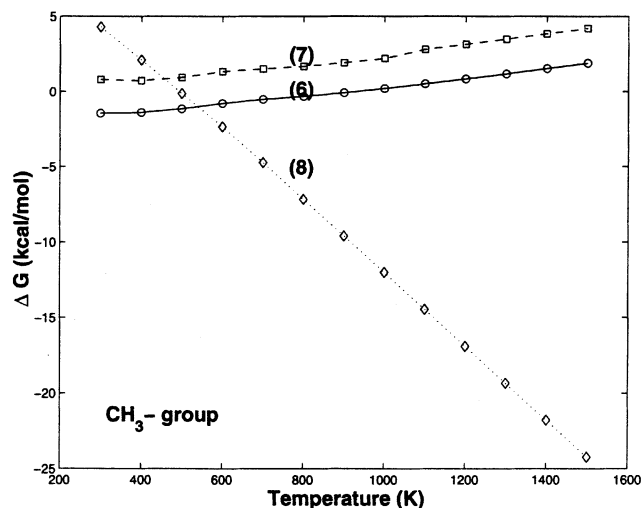
Bond	Si-C	C-C	Si-H	C-H	Si-O
Bond energy (kcal/mol)	75	80	80–90	100	127–195

**Table 2. Decomposition Reactions of Functional Groups in Blackglas Resin**

Group	Products Formed	Reaction No.
-CH <sub>2</sub> -CH <sub>2</sub> -	C <sub>2</sub> H <sub>4</sub>	(1)
	1/3 C <sub>6</sub> H <sub>6</sub> + H <sub>2</sub>	(2)
	2C + 2H <sub>2</sub>	(3)
	1/2 CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH = CH <sub>2</sub>	(4)
	C + CH <sub>4</sub>	(5)
-CH <sub>3</sub>	1/2 (CH <sub>4</sub> + -CH <sub>2</sub> -)	(6)
	C + 3/2 H <sub>2</sub>	(7)
	C <sub>2</sub> H <sub>6</sub>	(8)
-CH <sub>2</sub> -	C + H <sub>2</sub>	(9)
	1/2 (C + CH <sub>4</sub> )	(10)

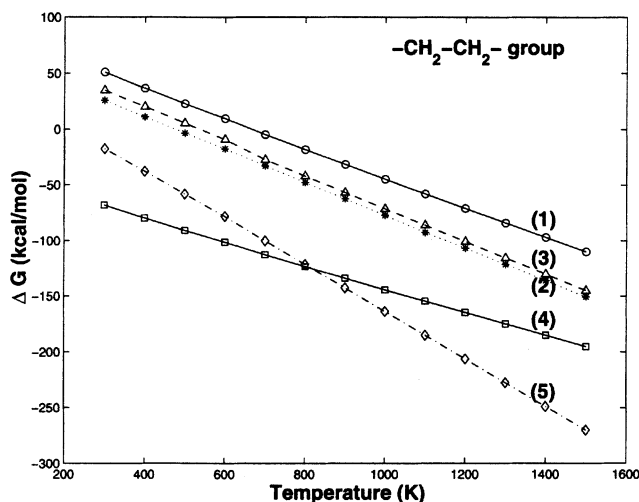
Figure 3 shows that the CH<sub>3</sub>- group can be thermally decomposed to form methane and methylene (-CH<sub>2</sub>-) at temperatures below 600°C. The CH<sub>3</sub>- group is not favored to decompose to form carbon and hydrogen directly, because the Gibbs energy of reaction 7 is always positive above room temperature. Two methyl (CH<sub>3</sub>-) groups are strongly favored to combine to form ethane (C<sub>2</sub>H<sub>6</sub>) at all temperatures. Since the CH<sub>3</sub>- group in the polymer resin is stable to about 600°C, it is expected that ethane (C<sub>2</sub>H<sub>6</sub>) might be formed at temperatures below 600°C.

The decomposition of the -CH<sub>2</sub>- group to form either car-

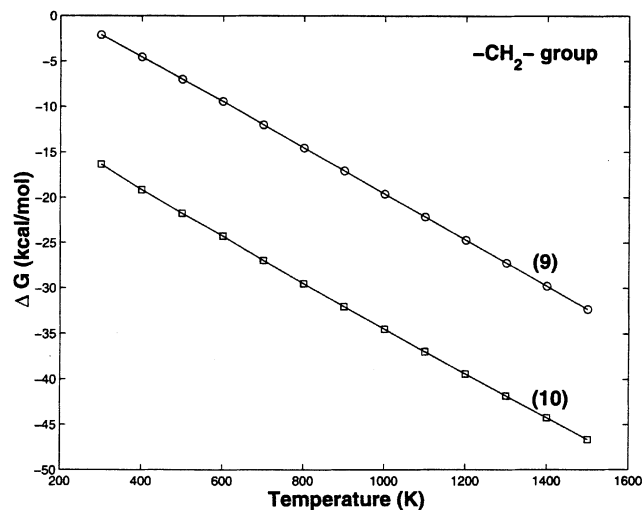


**Figure 3. Calculated Gibbs energies of reactions 6–8 with temperature.**

bon and hydrogen or carbon and methane is thermodynamically favored, as shown in Figure 4. As the pyrolysis temperature increases, the decomposition to carbon and methane is more strongly favored since the Gibbs energy for reaction 10 is more negative.



**Figure 2. Calculated Gibbs energies of reactions 1–5 with temperature.**



**Figure 4. Calculated Gibbs energies of reactions 9–10 with temperature.**

**Table 3. Mechanical Tests of 2D Nextel 312 Composite Panels**

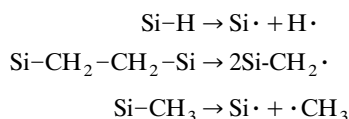
Sample Thickness	3-Pt Flex Test	Temp./Pyrolysis Cycle Time			
		5.0C/min (4.2 h)	2.0C/min (6.8 h)	Beta Cycle (22.4 h)	0.2C/min (46.7 h)
0.070 in. (v <sub>f</sub> = 50%)	Ult. Stress Modulus % Strain	42.0 KSI 11.5 MPsi 0.5%	40.0 KSI 11.4 MPsi 0.4%	41.0 KSI 11.9 MPsi 0.4%	37.0 KSI 11.4 MPsi 0.4%
0.140 in. (v <sub>f</sub> = 50%)	Ult. Stress Modulus % Strain	Delam 2nd Pyro	Delam 4th Pyro	45.0 KSI 11.2 MPsi 0.5%	35.0 KSI 11.4 MPsi 0.3%

Actual TGA/RGA experiments during Blackglas pyrolysis (Leung and Porter, 1994) indicate that methane ( $\text{CH}_4$ ) and hydrogen ( $\text{H}_2$ ) are the major evolved gases. These would be the gases having the highest diffusivity in the solid. There are two peaks for methane at 590°C and 730°C, and one broad peak for hydrogen at 800°C. Thus, on the basis of the thermodynamic decomposition analyses for the functional groups  $-\text{CH}_2-\text{CH}_2-$ ,  $\text{CH}_3-$  and  $-\text{CH}_2-$ , we expect that the methyl group ( $\text{CH}_3-$ ) would be responsible for the first methane peak via reaction 6. The intermediate ( $-\text{CH}_2-$ ) would be responsible for the second methane peak via reaction 10. The carbon and hydrogen are likely formed via reactions 9 and 10.

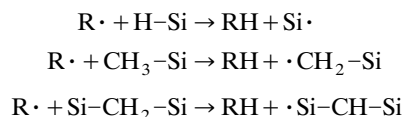
### Thermal decomposition of the Blackglas organo-silicon polymer

The transformation of organo-silicon polymers to a ceramic in an inert atmosphere proceeds via a free radical reaction mechanism as supported by ESR, IR, TGA-DTA, and TGA-MS experimental results (Yajima et al., 1978; Hasegawa et al., 1980; Hasegawa and Okamura, 1983, 1986). The Gibbs energy of formation for the generic Blackglas polymer (approximately  $\text{Si}_{10}\text{C}_{12}\text{O}_{11}$ ) is on the order of -116 kcal/mole at 300°. Thus, considerable energy input is required to decompose it. The polymer survives intact at temperatures up to 450°C. As the pyrolysis temperature increases beyond 450°C, the concentrations of C-H, Si-H and Si- $\text{CH}_3$  bonds decrease and hydrogen and methane are evolved. New bridging species, Si- $\text{CH}_2$ -Si, form at the same time, and these bonds eventually break down above 800°C. The reactions of  $-\text{CH}_2-$  in the Si- $\text{CH}_2$ -Si lead to the formation of Si-CH(Si)-Si and finally to Si-C(Si) $_2$ -Si, resulting in the formation of a three-dimensional (3-D) network.

The stability of a chemical bond in an organo-silicon polymer depends primarily on its bond energy and this provides one plausible route for developing a reaction pathway for the pyrolysis process. Based on the bond energies for Si-H, Si-C, C-C, C-H and Si-O bonds listed in Table 1, the Si-H, Si-C and C-C bonds would be broken first and so the proposed initial decomposition reactions are

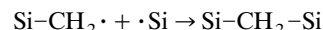


The radicals formed from these reactions may then abstract hydrogen atoms to give  $\text{H}_2$  and  $\text{CH}_4$ . Tetra-substituted atoms such as silicon or carbon are almost never abstracted by free radicals. Similarly, the abstraction of an entire group such as  $\text{CH}_3$  or  $\text{SiR}_3$  is also unlikely. Therefore, hydrogen abstraction probably occurs at Si-H bonds or C-H bonds via

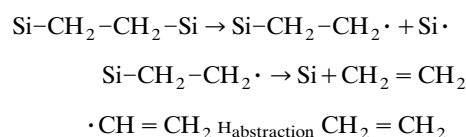


where  $\text{R}\cdot = \text{H}\cdot$ ,  $\cdot\text{CH}_3$ ,  $\text{Si}\cdot$  or  $\cdot\text{CH}_2\text{-Si}$ . The abstraction of hydrogen attached to carbon should take place at higher temperatures since the C-H bond is stronger than the Si-H bond.

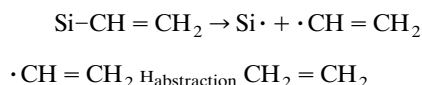
The combination of the various Si and C radicals formed in the above reactions may lead to the formation of Si-Si, Si-C, and C-C bonds. At higher temperatures, the probabilities of Si-C and Si-H bond cleavage are higher, the concentrations of radicals become significant and combination reactions cannot be neglected. However, the Si-Si bonds are unstable at the temperatures required by those cleavage reactions ( $T > 500^\circ\text{C}$ ), and any Si-Si bonds formed are likely to reform to more stable Si- $\text{CH}_2$ -Si bonds. This latter species may be formed according to



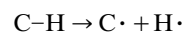
The evolution of ethylene may be due to the degradation of Si- $\text{CH}_2$ - $\text{CH}_2$ -Si bridges via a two-step mechanism—cleavage of Si-C bonds followed by a radical rearrangement and hydrogen abstraction according to



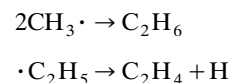
Residual vinyl groups may also account for the formation of ethylene according to



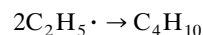
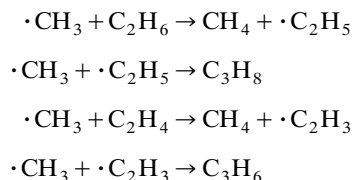
The C-H bond is the second strongest bond present in the polymer resin. The cleavage of this bond requires higher temperatures. It probably accounts for most of the hydrogen formed above 600°C, and for the formation of free carbon



In addition to hydrogen radicals abstracting hydrogen to form molecular hydrogen, methyl and ethyl radicals also abstract hydrogen to form methane and ethylene. The decomposition of the  $\cdot\text{C}_2\text{H}_5$  radical may be another source of ethylene



The  $\text{C}_3$  and  $\text{C}_4$  hydrocarbons, if any, may be formed via





**Table 5. Kinetic Data for the Mechanistic Kinetic Model**

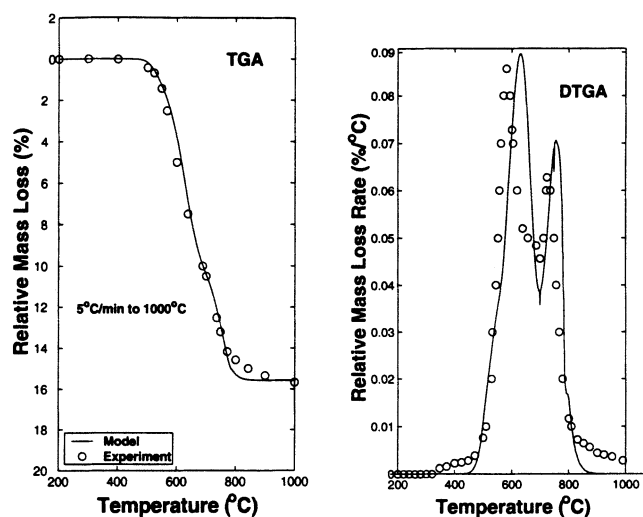
Reaction No.	Forward Reaction		Reverse Reaction	
	$\log(A_f)$	$E_{if}$ (kcal/mol)	$\log(A_r)$	$E_{ir}$ (kcal/mol)
1	16	60.0	10	0.0
2	16	62.0	10	0.0
3	16	64.0	10	0.0
4	10	0.0	15	85.0
5	10	0.0	15	85.0
6	10	0.0	15	85.0
7	15	45.0	15	80.0
8	15	45.0	15	80.0
9	15	48.0	15	80.0
10	15	50.0	15	80.0
11	10	0.0	15	60.0
12	10	15.0	9	10.0
13	10	0.0	15	45.0
14	10	0.0	15	45.0
15	14	40.0	10	0.0
16	9	15.0	9	8.0
17	10	0.0	15	95.0
18	10	0.0	15	45.0
19	15	64.0	10	0.0
20	15	66.0	10	0.0
21	15	68.0	10	0.0
22	15	45.0	15	80.0
23	15	48.0	15	80.0
24	15	50.0	15	80.0
25	15	62.0	10	0.0
26	10	0.0	15	80.0
27	15	64.0	15	80.0
28	6	2.0	15	80.0
29	6	37.0	0	0
30	6	37.0	0	0
31	6	38.0	0	0
32	6	40.0	0	0
33	6	42.0	0	0
34	6	35.0	0	0
35	10	36.0	0	0

are determined, these can be fed into the model and used to constrain the optimization. We are primarily interested in determining whether the set of proposed reactions is sufficient to describe the pyrolysis process, whether our set of parameters allow us to match experimental mass loss, gas evolution, and pressure data, and whether the model can give us some insight into how best to operate the pyrolysis process to produce useful product in a minimum amount of time. Table 3 relates mechanical properties to the pyrolysis cycle used.

## Results and Discussions

Simulations of the pyrolysis process were done for the initial concentrations of species determined from the  $^{29}\text{Si}$  NMR results (Leung et al., 1994) on the Blackglas polymer precursor. The initial concentrations of the  $\text{Si-CH}_3$ ,  $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ ,  $\text{Si-CH(CH}_3\text{)-Si}$  were 10.4, 8.35 and 1.11 (mole/L), and the concentrations of all the other species were set to zero initially. A linear temperature ramp was used in the simulation and the experiments. The concentrations of various groups were calculated at different temperatures or times using the DASSL (Petzold) integration package.

The percentage of initial mass lost from the model was compared with the experimentally observed value (Leung and Porter, 1994), shown in Figure 6. The rates of evolved gases

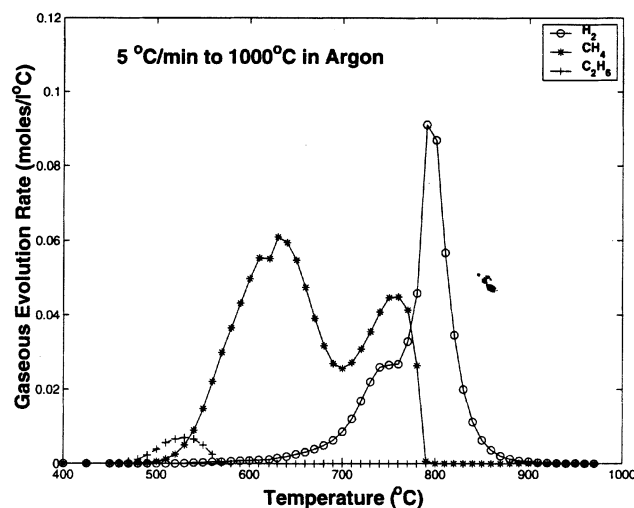


**Figure 6. Comparison of mechanistic model with experiment.**

TGA errors are  $\pm 5\%$ .

with respect to temperature are shown in Figure 7. Methane is the primary gas evolved in both the experiments and in the simulation. Hydrogen is the second most abundant gas followed by a minor amount of ethane. Similar observations on gas evolution were made in the Grumman studies (Leung, 1996; Leung and Porter, 1994). Other studies conducted by Allied Signal indicate  $\text{C}_2$ 's as the second most abundant gas group after methane (Leung, 1996; Leung and Curran, 1994). The model predicts two peaks for methane and one broad peak for hydrogen. Both predictions are in good agreement with observations from TGA-RGA experiments.

This pyrolysis system is extremely complex with numerous chemical reactions taking place simultaneously. The total moles of evolved gases generated per gram of sample vs. temperature is compared with the experimental data shown in Figure 8. A closed system of fixed volume was used to cap-



**Figure 7. Simulation results for the gas evolution rate during pyrolysis.**

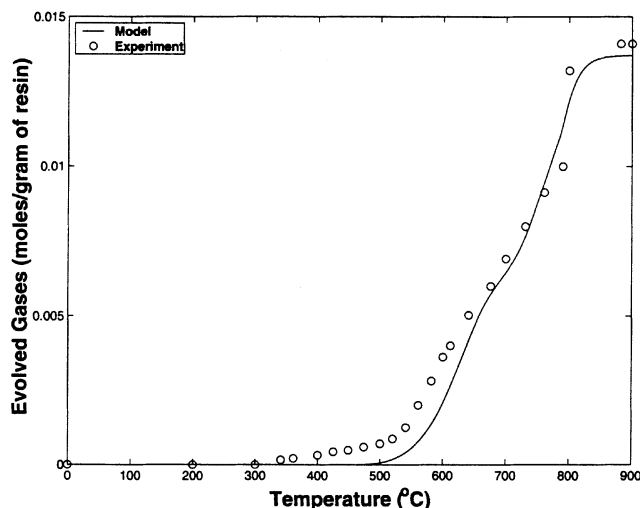


Figure 8. Total moles of evolved gases vs. temperature. TGA errors are  $\pm 5\%$ .

ture the evolved gases during polymer decomposition. This approach was a useful way of estimating the pressure that may be built up in the closed pores of a composite and checking to see that gas production from the model matched the experiment. As shown in Figure 9, the pressure buildup is significant and the model is in reasonable agreement with the experiments (Leung, 1996).

The consumption of the initial functional groups ( $\text{Si-CH}_3$ ,  $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ ) in the resin and the appearance of the intermediate functional group ( $\text{Si-CH}_2\text{-Si}$ ) are shown in Figure 10. At temperatures above  $400^\circ\text{C}$ , the functional groups ( $\text{Si-CH}_3$ ,  $\text{Si-CH}_2\text{-CH}_2\text{-Si}$ ) rapidly decrease, the functional group ( $\text{Si-CH}_2\text{-Si}$ ) is formed, and the latter group survives up to  $800^\circ\text{C}$ . These model predictions are in a good agreement with  $^{29}\text{Si}$  NMR observations. Carbon in the forms of silicon carbide and graphite can also be predicted, as shown in Figure 11.

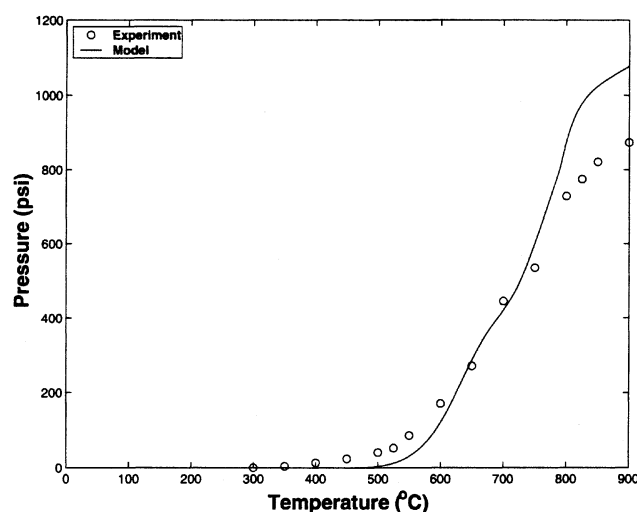


Figure 9. Pressure vs. temperature in the closed system. Experimental errors are  $\pm 10\%$ .

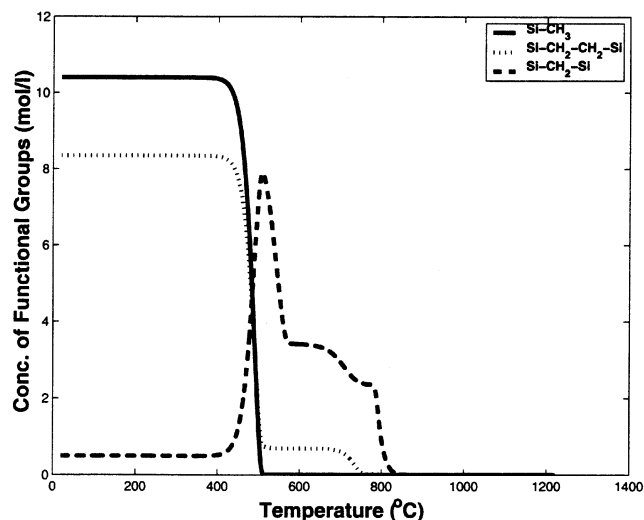


Figure 10. Calculated concentrations of functional groups vs. temperature.

Free carbon is deposited above  $600^\circ\text{C}$ , which is in a good agreement with the experimental observation that the color of the sample changes from transparent to brown. Free carbon comprises about 55% of the total carbon in the Blackglas ceramic. This prediction is also in good agreement with compositions determined from  $^{13}\text{C}$  NMR observations of Blackglas ceramic pyrolyzed at  $900^\circ\text{C}$ . A small percentage of carbon exists in the form of  $\text{Si-C(Si)-Si}$ , which suggests that a connection between the network of silicon oxycarbide and the free carbon is possible.

### Application of the Model

The major cost associated with the manufacture of composites is the pyrolysis process. This is due to the long cycle time required to obtain the desired properties and the extremely slow heating rate necessary. We were interested in determining if our model could predict the rate of gas evolution with respect to time, identify the critical outgassing regions in the pyrolysis cycle, and help to identify process changes required to slow down a fast reaction zone or to accelerate a slow reaction zone. Due to the complexity of the pyrolysis process, a multistep heating protocol is indicated. Such a protocol, called a  $\beta$  cycle, was designed to control the fabrication of 2D Nextel 312 composite. This protocol is shown in Figure 12 along with the evolution rate of methane, ethane, and hydrogen. The experimental tests were performed by Northrup Grumman.

The experimental test used a 4 in.  $\times$  6 in. (102 mm  $\times$  152 mm) panel made from Nextel 312 fiber with a volume fraction of 50% fiber. Panels were made in two thicknesses (0.070 in. and 0.14 in., 1.78 mm and 3.56 mm) to determine the effect of the thickness on the final mechanical properties. All panels were made by a standard curing process (Annamalai et al., 1996). Three linear heating protocols (0.2, 2.0 and 5.0  $^\circ\text{C}/\text{min}$ ) and one step-heating protocol ( $\beta$  cycle) to  $1,000^\circ\text{C}$  were used to control the pyrolysis. The process also involved five reinfiltration-pyrolysis cycles. Three-point flexure tests at

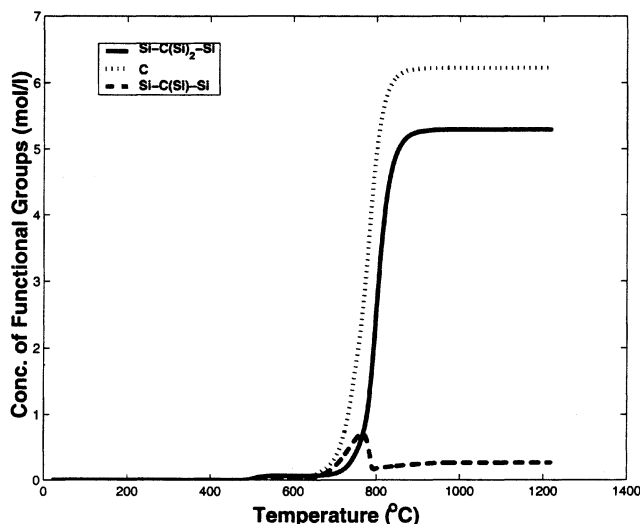


Figure 11. Calculated concentrations of carbon species vs. temperature.

room temperature were used to measure changes in mechanical properties. The results of these flexure tests are summarized in Table 3.

For the thinner panels (0.07 in.), the flexure properties are fairly uniform except for the 0.2 C/min cycle where there is about a 10% drop in ultimate strength. In thinner panels, the generated gases can easily diffuse out of the sample for all heating protocols. Thus, there is no pressure built up in the composite. The reason for the 10% drop for 0.2 C/min cycle is that some trace oxygen from the ambient environment may have been incorporated in the ceramic and this reduced the carbon load in the silica network. For the thicker panels (0.14 in.), delamination developed during the 4th cycle at a heating rate of 2.0 C/min and during the 2nd cycle at a heating rate of 5.0 C/min cycle. The  $\beta$  cycle outperformed the fixed 0.2

C/min cycle by producing panels with 20% higher ultimate strength in less than half the time of the fixed cycle process.

Considering the mechanical test results from the 2-D Nextel 312 composite panels shown in Table 3, the optimal temperature protocol for making 0.140 in. 2-D Nextel 312 composite panels is 5.0°C/min for the first cycle, 2.0°C/min for the 2nd and 3rd cycles, and the  $\beta$  cycle for the 4th and 5th cycles. The total pyrolysis time of 62.6 h for the five cycles using this protocol is nearly half the time required (112 h), if the  $\beta$  cycle alone is used.

## Conclusions

A plausible reaction pathway and kinetic model has been developed to describe the transformation of a polysiloxane polymer to a silicon oxycarbide ceramic. Resin compositions determined by  $^{29}\text{Si}$  NMR were used to determine the initial conditions for solving the rate equations.

- The model can be used to predict the mass loss and the rates and composition of evolved gases as a function of temperature and time.

- The model predicts that free carbon is formed above 600°C, and this prediction is in good agreement with the experimental observation that the resin turns from transparent to brown at 600°.

- The model can be used to design various step-heating protocols for optimizing the pyrolysis fabrication process for low cost ceramic composites.

The uniqueness of the model is based on the breakage and the formation of chemical bonds present in the resin. This methodology should be very useful for predicting the thermal degradation of very complex organic matter such as biomass or thermoset polymers.

The model can be expected to predict the evolution of gases and the formation of specific chemical bonds during the pyrolysis of polycarbosilane, because that pyrolysis process is similar to that for polysiloxane.

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## Literature Cited

- Annamalai, J., W. N. Gill, and A. Tobin, "Modeling, Analysis and Kinetics of Transformations During Blackglas™ Polymer Pyrolysis to Blackglas™ Ceramic," *Ceramic Eng. & Sci. Proc.*, **16**, 225 (1995).
- Annamalai, J., W. N. Gill, A. Tobin, J. Madsen, and T. M. Donnellan, "Pyrolysis Behavior of Blackglas™ Composites," *Ceram. Eng. & Sci. Proc.*, **17**, 401 (1996).
- Babonneau, F., "NMR Characterization of Ceramic Materials Derived from Pre ceramic Polymer," *Application of Organometallic Chemistry in the Preparation and Processing of Advanced Materials*, J.F. Harrod and R.M. Laines, Kluwer Academic Publishers, Boston, pp. 103–123 (1995).
- Benson, S. W., *Thermochemical Kinetics, Methods for the Estimation of Thermochemical Data and Rate Parameters*, 2nd ed., Wiley, New York, pp. 63–64 (1976).
- Dente, M. E., and E. M. Ranzi, "Mathematical Modeling of Pyrolysis Reactions," *Pyrolysis—Theory and Industrial Practice*, Albright, Crynes and Corcoran, eds., Academic Press, New York (1983).
- Hasegawa, Y., and K. Okamura, "Synthesis of Continuous Silicon Carbide Fiber: 3. Pyrolysis Process of Polycarbosilane and Structure of the Products," *J. of Materials Sci.*, **18**, 3633 (1983).

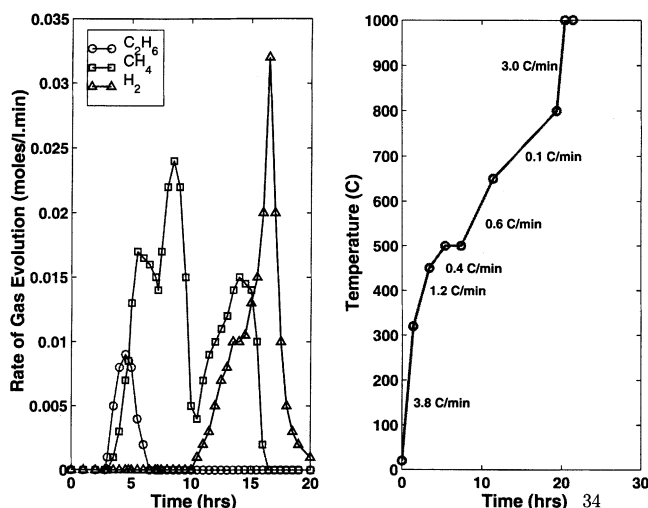


Figure 12. (a) Calculated gas evolution rate with respect to the designed heating protocol; (b)  $\beta$  cycle protocol.



- Hasegawa, Y., M. Imura, and S. Yajima, "Synthesis of Continuous Silicon Carbide Fiber. 2. Conversion of Polycarbosilane Fiber into Silicon Carbide Fibers," *J. of Materials Sci.*, **15**, 720 (1980).
- Hasegawa, Y., and K. Okamura, "Synthesis of Continuous Silicon Carbide Fiber: 4. The Structure of Polycarbosilane as the Precursor," *J. of Materials Sci.*, **21**, 321 (1986).
- Hurwitz, F., P. Heimann, and T. Kacik, "Redistribution Reactions in Blackglas<sup>TM</sup> During Pyrolysis and their Effect on Oxidative Stability," *Ceramic Eng. & Sci. Proc.*, **16**, 217 (1995).
- Leung, R. Y., S. T. Gonczy, M. S. Shum, and J. J. Zupancic, "Carbon Containing Black Glass Monoliths," U.S. Patent 5,328,976 (1994).
- Leung, R. Y., and W. Porter, "Thermal and Evolved Gas Analysis of Blackglas<sup>TM</sup> 493 Resin Pyrolysis," LC<sup>3</sup>7, ARPA LC<sup>3</sup> Program, Report LC<sup>3</sup>7, Adv. Res. Projects Agency LC Program, Report issued by Northrop Grumman Corp., Bethpage, NY (1994).
- Leung, R. Y., and S. Curran, "Characterization of Blackglas<sup>TM</sup> Intermediate & Pyrolyzed Products," LC<sup>3</sup> 19, ARPA LC<sup>3</sup> Program, (1994).
- Leung, R. Y., "Pyrolysis Process Pressure and Composition of Evolved Gases," LC<sup>3</sup> The 4th Semiannual Review and Phase II Kick-off Meeting, Wright Patterson Air Force Base, OH, published by WPAFB, 26-27 (1996).
- Libanati, C., "Monte Carlo Simulation of Complex Reactive Macromolecular Systems," PhD Diss., University of Delaware (1992).
- Meador, M. A. B., F. Hurwitz, and S. T. Gonczy, "NMR Study of Redistribution Reactions in Blackglas<sup>TM</sup> and their Influence on Oxidative Stability," *Ceramic Eng. & Sci. Proc.*, **17** (3), 394 (1996).
- Petzold, L. R., *This code solves a system of differential/algebraic equations of the form  $G(T, Y, YPRIME) = 0$* , Computing and Mathematics Research Division, Lawrence Livermore National Laboratory (1995).
- Renlund, G. M., and S. Prochazka, "Silicon Oxycarbide Glasses: Part II. Structure and Properties," *J. Mat. Res.*, **6** (12), 2723 (1991).
- Soraru, G. D., F. Babonneau, and J. D. Mackenzie, "Structural Evolutions from Polycarbosilane to SiC Ceramic," *J. of Mat. Sci.*, 3886 (1990).
- Walsh, R., "Thermochemistry," *The Chemistry of Organic Silicon Compounds*, Part-I, Patai and Rappaport, eds., Wiley, New York, p. 372 (1989).
- Wang, F., "Modeling and Experimental Characterization of Blackglas<sup>TM</sup> Polymer Pyrolysis to Ceramic and Thermodynamic Characterization of Blackglas<sup>TM</sup> Ceramic," PhD Diss., Rensselaer Polytechnic Institute, Troy, NY (2000).
- Wang, F., W. N. Gill, C. A. Kirk, and T. Apple, "NMR Characterization of Postcure Temperature Effects on the Microstructures of Blackglas<sup>TM</sup> and their Influence on Oxidative Stability," *J. of Non-Crystalline Solids*, **275**, 210 (2000).
- Wang, F., T. Apple, and W. N. Gill, "Thermal Redistribution Reactions of Blackglas<sup>TM</sup> Ceramic," *J. of Applied Polymer Sci.*, **81** (1), 143 (2001).
- Yajima, S., Y. Hasegawa, J. Hayashi, and M. Imura, "Synthesis of Continuous Silicon-Carbide Fiber with High Tensile Strength and High Young's Modulus 1. Synthesis of Polycarbosilane as Precursor," *J. of Mat. Sci.*, **13**, 2569 (1978).

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