

Boron Nitride Composites

For this project, [Dr. Chris Mangun](#), President of [EKOS Material Inc.](#) has been working with our research group through a Phase I and Phase II SBIR from NSF

Several years ago we discovered that we could convert borazine oligomers, by heating at 1200°C, to a stable form (not attacked by moisture) of BN in 90% yield. The oligomer is derived from the self-condensation of borazine at 70°C, also in about 90% yield. We found that using the borazine oligomer we could prepare composites with PAN or pitch based fibers that displayed excellent mechanical properties, see Figure 1. One should remember that CVI is essential to produce a C/C composite with acceptable mechanicals. We postulated and were subsequently able to prove that the borazine oligomer formed a liquid crystalline phase, which tended to match the coefficient of thermal expansion of the fiber at the interface. Surprisingly with the pitch-based carbon fibers the composite displayed even on heating from 1200°C to 1500°C, see Figure 2.

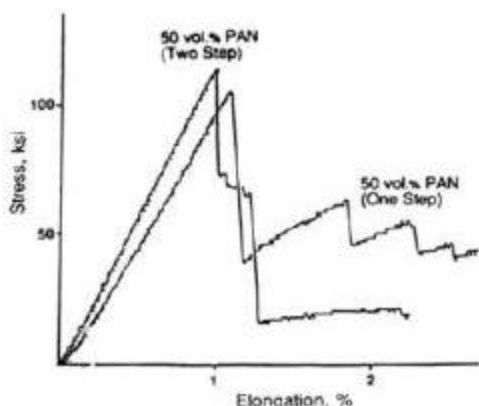


Figure 1. Stress-strain of composites

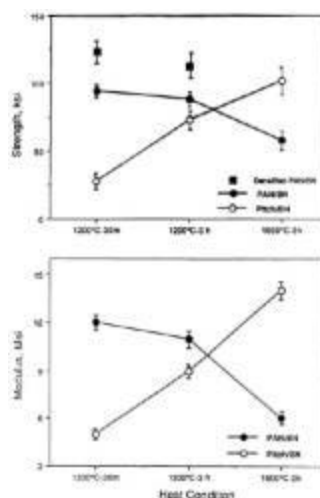


Figure 2. Higher mechanicals of composites

We have successfully prepared BN matrix composites with SiC, Al₂O₃ (both DuPont and Sumitomo grades), and Nextel fibers, see Table 1. We have also been able to infiltrate the borazine oligomer into C/C structures with densities up to 1.3 g/cc to obtain C/C/BN composites. The oxidative and hydrolytic stability of the C/BN and C/C/BN composites is greatly improved over the C/C composites, see Figure 3 and Figure 4. Previous researchers also demonstrated that the hydrolytic and oxidative stability of Boron nitride is dependent on the 002, or d-spacing, of the material. The dependence is shown in Figure 4.

(Annealed in Nitrogen 3 hours at 1200°C)

Fiber	Flexural Strength (MPa)	Flexural Modulus (GPa)	Strain to Failure (%)	Dielectric Constant (at 1 MHz)
PAN T300	610	80	0.90	NA
Pitch P25	500	60	0.95	NA
C-Nicalon	550	60	1.00	NA
Nicalon	420	80	0.50	58
Sumica	380	80	0.50	7.6
BN-Nextel 440	360	50	0.90	6.1
Nextel 440	190	65	0.35	6.1
FP Alumina	70	30	0.25	7.1

D. Kim, C. Cofer, and J. Economy, "Fabrication and Properties of Ceramic Composites with a Boron Nitride Matrix," *J. Am. Cer. Soc.*

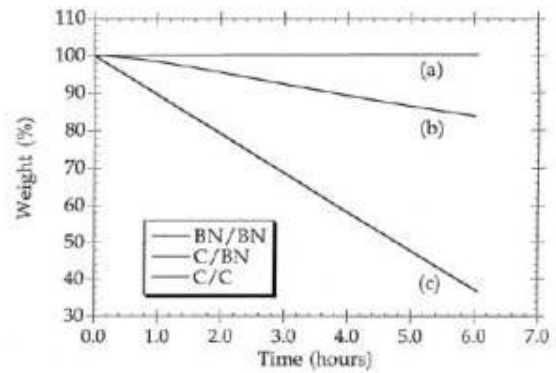


Figure 3. Isothermal Oxidation In Air At 700°C

Using high temperature pin on disk wear measurements we observed a five-fold improvement in wear resistance of C/BN over C/C, see Figure 5. More recently we have installed an inertial brake dynamometer, which provides friction and wear testing more suitable for the aircraft braking industry. Preliminary data confirms the excellent wear resistance of the C/C/BN as well as indicating that the wear film is far more stable than that formed in our test of C/C composites.

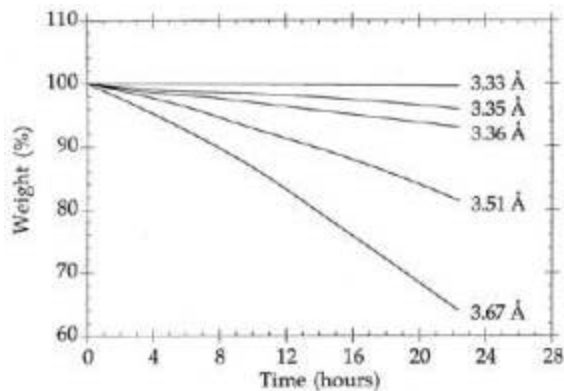


Figure 4. Effect of $d(002)$ spacing on BN; Hydrolytic Stability at 700°C

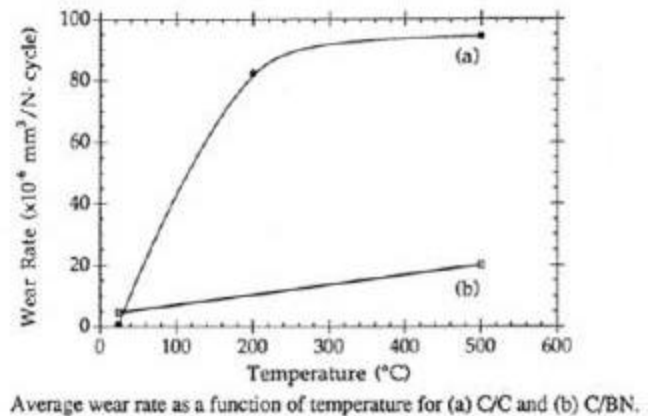


Figure 5: Pin On Disk Wear Testing

Potential Applications of Borazine Derived Boron Nitride

Matrix Material For Brakes

Presently, aircraft brakes are usually manufactured out of carbon/carbon, an expensive and relatively mechanically weak ceramic-matrix composite. The use of such an unwieldy and difficult material is necessary because of the extreme temperatures and loads seen by the brakes during landing cycles and rejected takeoffs. However, despite its high temperature strength, carbon/carbon is limited because carbon oxidizes at as low as 500°C. A typical aircraft landing cycle may heat a plane's brakes up to 800°C or higher. Hence, despite the

use of oxidation barriers, oxidation occurs in aircraft brakes and weakens the material, increasing the wear rate and reducing the useful lifetime of the brake.

Boron nitride has a higher oxidation temperature than the carbon matrices that make up present aircraft brakes, allowing the BN brake to retain more of its properties during an aircraft landing or rejected takeoff. In recent, members of our group have shown that the oxidation resistance of BN is dependent on the d-spacing of the material. The use of borazine as a polymeric precursor can lead to very small (and hence advantageous) d-spacings, partially due to the recently discovered liquid crystalline nature of borazine under certain conditions.

The C/C-BN composites with densities of 1.55g/cc displayed wear characteristics up to 50% lower than values observed with C/C samples with densities of approximately 1.75-1.8g/cc. These observations held over the entire energy spectrum typical of aircraft braking. In addition, the wear rates at low energy (taxiing conditions) and high wear rates (aggressive braking) were significantly reduced (see [Figure 6](#)). This behavior is attributed in part to the improved oxidation resistance of the BN and its ability to facilitate formation of a stable wear film.

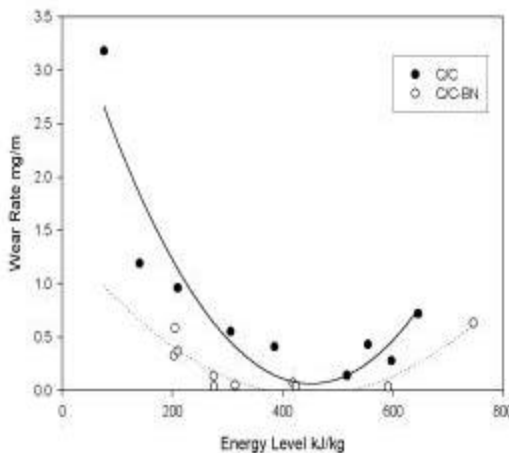


Figure 6. Dynamometer wear data for C/C-BN and C/C

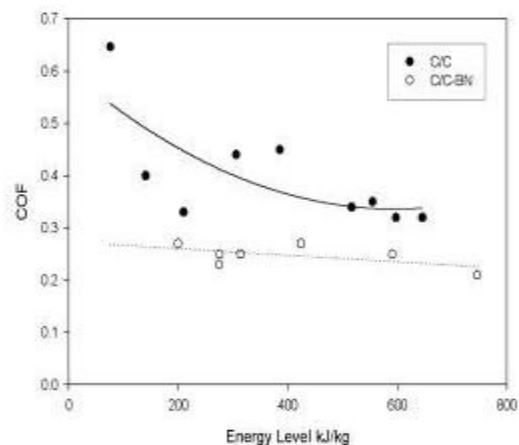


Figure 7. Comparison of COF for C/C and C/C-BN

The COF (see [Figure 7](#)), while being slightly lower than the values for C/C, appeared much less sensitive to changes in energy level. The significant decrease in wear rate at 300kJ/kg, and ensuing increase at 600kJ/kg, produced no subsequent change in the COF. This data, while preliminary, is extremely encouraging, especially considering the less than optimum nature of the samples.

The presence of the BN in the wear film ([Figure 8](#)) imparted increased stability at all energy levels. Further investigation of the low energy level wear film is required to understand the role of the BN under those conditions, although it appears the existence of a wear debris film on the surfaces could lead to reduced wear. The increased stability at high energy level is attributed to the improved oxidation resistance of the BN. BN does not display as low a COF as carbon but as a braking material appears to have lowered both the wear rate and COF in the low energy level regime.

The C/C-BN composites could be prepared to an average density of 1.55g/cc via a liquid infiltration technique using a borazine oligomer. Difficulties with processing led to non-uniform densities throughout the composites where the surface density was as high as 1.6g/cc. These difficulties are attributed to the less than ideal pore structure produced from the original charring of the phenolic resin. Improved processing techniques are now being developed to produce BN containing composites, which not only have a high density, but are uniform throughout the cross-section.

The d_{002} spacing was larger than desired. Further modification of the processing parameters is required to yield lower interlayer spacings, which will increase high energy level (temperature) performance of the composites by increasing their resistance to attack by water.

The fabrication and wear results of higher density carbon fiber/boron nitride composites (C/BN) and of C/C-BN reinforced with a 3-D weave of carbon fibers present the mechanism of wear at different energy levels.

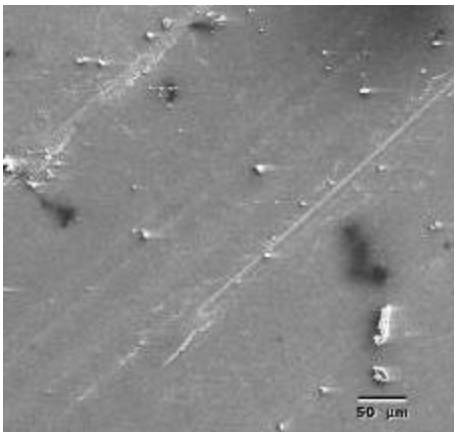


Figure 8. SEM of Film-Type Wear Debris of C/C-BN

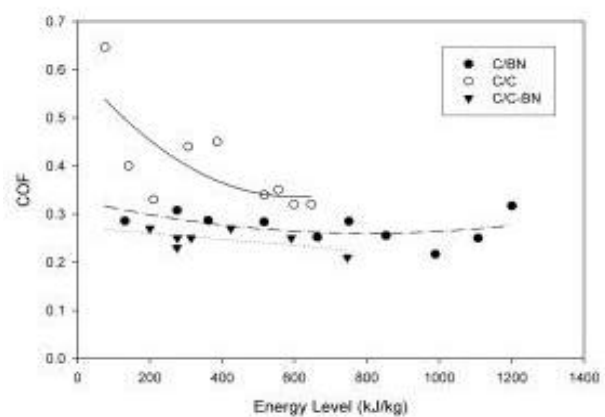


Figure 9: Dynamometer COF data for C/BN, C/C-BN and C/C

The 3-D needled reinforcement in the C/C system, coupled with the deposition of the matrix via CVI, yielded a material with greatly increased wear resistance. Wear rate dependence on energy appeared to remain unchanged, with wear rates higher at low energy levels and eventually increasing at the onset of oxidation. The changes in reinforcement and matrix appeared to have a modest effect on COF. The COF still varied from approximately 0.5 at low energy levels to approximately 0.25 at the onset of oxidation. (see [Figure 9](#)).

In the case of the 3D C/BN, little effect was observed in the wear rate behavior with the addition of the 3-D needled carbon fiber, implying the wear rate is dominated by the matrix material in the case of the composites with a complete matrix of BN (see [Figure 10](#)). The one improvement noted was a shift in the energy level at which oxidation begins. It is believed increased thermal conductivity in the thickness direction, provided by the 3-D weave accounts for this increase. The 3-D reinforcement did have the effect of significantly increasing the COF. With the exception of the initial data point at low energy level the 3D C/BN displayed a value of approximately 0.45. As with all the composites containing BN the COF was found to be relatively insensitive to the energy level.

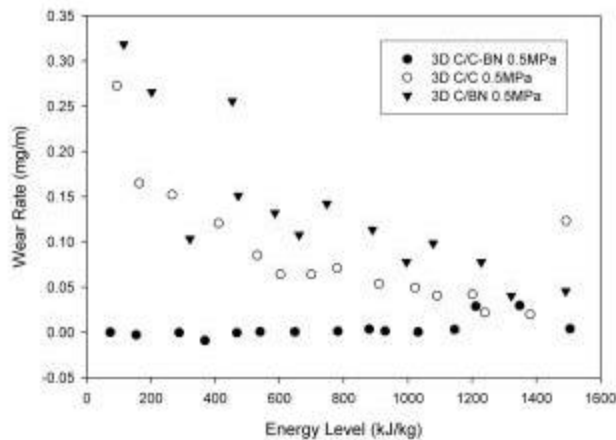


Figure 10. Dynamometer Wear Rate Data for 3-D Reinforced Composites

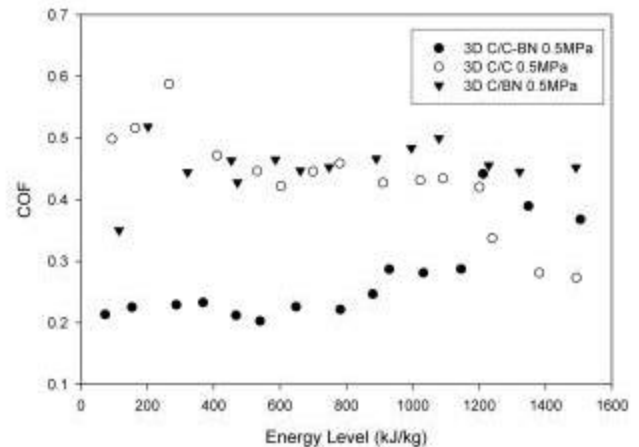


Figure 11. Dynamometer COF Data for 3-D Reinforced Composites

The best results were obtained for the 3D C/C-BN, which displayed little or no wear across the entire energy spectrum tested. Based on the previously reported data for C/C-BN the excellent wear resistance of these composites was expected in the medium (low wear) energy level regime. The outstanding wear resistance at high energy level is attributed to the improved oxidation resistance of the BN and the increased thermal conductivity of the 3-D reinforced composites (see [Figure 11](#)). In the low energy level regime the BN facilitates the formation of the film-type wear debris immediately, allowing extremely low wear rates. Interestingly, the greatest wear resistance is realized only when the hybrid matrix is used. The 3D C/C-BN also displays a COF that is relatively constant throughout the normal use range (up to 1000 kJ/kg) and then increases with increasing energy level thereafter. Thus if one imagines that 3D C/C-BN was used as an aircraft brake it would perform consistently, displaying nearly constant wear rates and COF, from taxiing conditions up to and including RTO.

Thin Films and Adhesives

A second phase of our research involves creating high-temperature adhesives and dielectric thin films from BN derived from borazine. BN has promise as a material for dielectrics in microelectronics because it has a very high thermal conductivity and yet a low dielectric constant. Earlier work in this group measured the dielectric constants in the lateral and transverse directions of a thin film of boron nitride derived from borazine. However, presently, in order to stabilize the borazine into boron nitride, a high-temperature (1200°C) heat treatment is required. This is realistically too high for microelectronics applications, because substrate materials like Si and GaAs cannot be processed at such temperatures. However, the liquid crystalline behavior of the borazine may lead to alignment of the borazine when in a thin film configuration, which could allow the borazine to be stabilized at a much lower temperature. Current research hopes to show that good-quality thin films of boron nitride can be processed at temperatures compatible with present-day microelectronics packaging.

It was noticed that the liquid crystalline behavior of the borazine also has the effect of "matching" the coefficient of thermal expansion of the reinforcement material in a borazine-derived BN-matrix composite. Such behavior may prove be useful if the borazine can be used

as an adhesive. This thermal expansion "matching" behavior could lead to an adhesive that could successfully be used to bond dissimilar materials. The adhesive, being a ceramic, would be stable at high temperatures. Such a high temperature adhesive could prove useful in countless applications.

Related Publications

1. D-p. Kim, C. G. Cofer, J. Economy, "*Fabrication and Properties of Ceramic Composites with a Boron Nitride Matrix*", **Journal of the American Ceramics Society** 78, 1546-1552 (1995)
2. D-p. Kim, J. Economy, "*Fabrication of Oxidation Resistant Carbon fiber / Boron Nitride Matrix Composites*", **Chemical Materials** 5, 1216-1220 (1993)
3. C. G. Cofer, J. Economy, "*Oxidative and Hydrolytic Stability of Boron Nitride - A New Approach to Improving the Oxidation Resistance of Carbonaceous Structures*", **Carbon** 33, 389-395
4. D-p. Kim, J. Economy, "*Occurrence of Liquid Crystallinity in a Borazine Polymer*", **Chemical Materials** 6, 395-400 (1994)
5. C. G. Cofer, et al., "*Characterization of Fiber / Matrix Interfaces in Composites with Boron Nitride Matrix*", **Composites Science and Technology** 50, 967 (1996)
6. C. G. Cofer, A. W. Saak, J. Economy, "*Carbon/Boron Nitride Composites: An Alternative to Carbon/Carbon*", **Ceramic Engineering and Science Proceedings** 16, 663-671 (1995)
7. C. G. Cofer, J. Economy, "*Inorganic Polymer Liquid Crystals*", **Polymer Liquid Crystal Series**, vol. 3, Chapter 3.

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