Microstructure and Indentation Fracture Behavior of SiC−BN Composites Derived from Blended Precursors of AHPCS and Polyborazylene

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A novel method of preparing multiphase ceramic materials from mixtures of preceramic polymers is described. This method employs the typical immiscibility of polymer blends to prepare two-phase SiC−BN ceramic composites by co-pyrolysis of a mixture of two polymeric precursors, allylhydridopolycarbosilane (AHPCS) (nominally, $[Si(CH_2CH{=}CH_2)_2CH_2]_{0.05}[SiH_2CH_2]_{0.95}$) and polyborazylene (PBz) $[B_3N_3H_{4-x}]_n$, which serve as the sources for the SiC and BN phases, respectively. Two different proportions of these polymers (80:20 and 50:50 wt %) were mixed in glyme solution, and, after removal of the solvent, heated to 1000 °C to obtain amorphous SiC−BN ceramic composites whose microstructure resembles that of an immiscible polymer blend. Studies of the composition (by electron microprobe analysis), microstructure (by SEM), and Vickers hardness of these samples were carried out as a function of annealing temperature up to 1600−1700 °C. The hardness of the SiC−BN composite was found to decrease with increasing PBz addition, with both mixtures exhibiting a lower hardness than that of the AHPCS-derived SiC alone. Particularly in case of the 50:50 SiC−BN sample prepared at 1600 °C, evidence was obtained for debonding and crack deviation at the interface between the two phases, suggesting possible interest in this system as a tough two-phase ceramic composite or as a weak interphase material in fiber-reinforced ceramic matrix composites.

Introduction

The widespread use of polymer blends and alloys (polymer blend is a mixture of at least two polymers or copolymers; and polymer alloy is an immiscible polymer blend having a modified interface and/or morphology (ref 1)) in modern technology has generated an extensive body of knowledge about the factors that determine the microstructure and physical properties of such systems.[1] A characteristic feature of most of these polymer mixtures is their tendency to undergo phase separation due to the intrinsically low entropy of mixing for high-molecular-weight linear molecules. This feature, along with the ability to change the interfacial interactions between the constituent polymer phases by means of reactive processing or with certain additives (or “compatibilizers”), has enabled the production of polymer blends with controlled microstructures and physical properties. Among the various types of polymer blends that have found widespread use in industry are mixtures of hard and soft polymers (e.g., polystyrene and polybutadiene) that, when properly formulated, serve as strong, tough thermoplastics. In these cases, the use of a compatibilizer that migrates to the interface between the constituent polymers (analogous to an emulsifier in classical emulsion technology), thereby causing a reduction in the dispersed phase dimensions and stabilization of the microstructure, is often critical to the realization of the desired microstructure and properties.

When two such dissimilar polymers are connected to form a block copolymer, and when at least one of the blocks is uniform in size (i.e., has a polydispersity close to 1.0), this tendency of the two polymer chain sections to separate from one another leads to specific, well-defined nanometer-scale structures that depend on the

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(1) (a) Utracki, L. A. *Polymer Alloys and Blends*; Hanser Publishers: Munich, 1989. (b) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer−Polymer Miscibility*; Academic Press: New York, 1979.

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relative sizes of the component polymers.[2] Such block copolymers have been used previously to control the nanostructure of inorganic/organic composites and, in some cases, after elimination of the organic phase by pyrolysis or in an oxygen plasma, to generate nanostructured ceramic materials.[3−6] However, in these cases the final result after removal of the organic component is a single-phase ceramic, such as alumina or silica, in the form of a nanoporous solid or as nanosized objects, rather than a composite of two different ceramics.

In the course of our prior efforts to prepare protective C/SiC interface coatings for SiC fibers in SiC_f/SiC_m composites, a mixture of a SiC precursor (AHPCS[7,8]) with pitch as a C precursor was pyrolyzed to form a two-phase SiC/C ceramic mixture.[9] This mixture was found to survive oxidation of the embedded C phase at 1300 °C in air and was effective in inhibiting degradation of the composite's mechanical strength after air exposure at 800 °C for >5 days. In the case of this SiC/C system, the microstructure and properties of the ceramic product was found to vary with the pitch source used, but in both of the cases investigated, a two-phase (SiC_x/C) polymer-blend-type microstructure was observed by SEM. We now report the extension of this approach to the preparation of SiC/BN composites with similar polymer-blend-type microstructures and unusual mechanical properties by pyrolysis of AHPCS/polyborazylene mixtures.[10] These microphase-separated SiC/BN composite materials are also of interest in connection with the considerable research activity that has been focused in recent years on precursor-derived ceramics that combine these same four elements in a more homogeneous, single-phase, amorphous, microstructural arrangement.[11] Such ceramics have shown extraordinary thermal stability, especially in inert atmosphere environments, and have been suggested for use as fibers, matrixes, and coatings for high-temperature ceramic matrix composites.

Experimental Section

All manipulations were carried out using standard high vacuum or inert atmosphere techniques as described by Shriver.[12] Allylhydridopolycarbosilane (AHPCS), a partially allyl-substituted polycarbosilane of the approximate composition $[Si(CH_2CH{=}CH_2)_2CH_2]_{0.05}[SiH_2CH_2]_{0.95}$,[7] was obtained from Starfire Systems, Inc.[13] as a yellowish liquid and used as received. Polyborazylene (PBz) was prepared as previously described[14] and was obtained as a white solid. Ethyleneglycoldimethyl ether (glyme) was distilled from a sodium benzophenone ketyl prior to use. To prepare the AHPCS−PBz polymer blend, in a typical reaction AHPCS (typically 2−3 g) and PBz (0.6−1.5 g) were charged into two separate preweighed Schlenk flasks in a glovebag. The flask containing the PBz was then moved to a vacuum line and evacuated, and 15 mL of dry glyme was added by vacuum transfer. At room temperature the PBz dissolved to produce a clear, colorless solution. The PBz/glyme solution was then transferred with stirring into the flask containing AHPCS via a syringe under nitrogen. After stirring the clear yellow reaction mixture at room temperature for 6 h, the solvent was removed under vacuum. As the solvent was removed the solution turned cloudy, and upon complete removal of solvent a cloudy, yellow gel resulted. Individual reaction conditions are presented in Table 1.

In a typical pyrolysis of the AHPCS and the AHPCS/PBz blends, an aliquot of the polymer (or blend) was weighed, under inert atmosphere, into a graphite crucible and transferred into a tube furnace that was being flushed with argon. The sample was then heated under argon to 1000 °C at 5°/min and held at temperature for 4 h before cooling to room temperature.

The AHPCS-derived SiC material and the AHPCS/PBz-derived SiC−BN samples were further heat treated to 1400

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(2) (a) Hadjichristidis, N. *Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*; J. Wiley and Sons: Hoboken, NJ, 2003. (b) Noshay, A.; McGrath, J. E. *Block Copolymers*; Academic Press: New York, 1977. (c) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52* (2), 32−38. (d) Matsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29* (4), 1091. (e) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.

(3) (a) Simon, P. F. W.; Ulrich, R.; Spiess, H. W.; Wiesner, U. *Chem. Mater.* **2001**, *13* (10), 3464. (b) Finnefrock, A. C.; Ulrich, R.; Du Chesne, A.; Honeker, C. C.; Schumacher, K.; Unger, K. K.; Gruner, S. M.; Wiesner, U. *Angew. Chem., Int. Ed.* **2001**, *40* (7), 1208. (c) Ulrich, R.; Du Chesne, A.; Templin, M.; Wiesner, U. *Adv. Mater.* **1999**, *11* (2), 141. (d) Kulbaba, K.; Resendes, R.; Cheng, A.; Bartole, A.; Safa-Sefat, A.; Coombs, N.; Stöver, H. D. H.; Greedan, J. E.; Ozin, G. A.; Manners, I. *Adv. Mater.* **2001**, *13*, 732. (e) Kulbaba, K.; Cheng, A.; Bartole, A.; Greenberg, S.; Resendes, R.; Coombs, N.; Safa-Sefat, A.; Greedan, J. E.; Stöver, H. D. H.; Ozin, G. A.; Manners, I. *J. Am. Chem. Soc.* **2002**, *124*, 12522. (f) Massey, J. A.; Winnik, M. A.; Manners, I.; Chan, V. Z.-H.; Ostermann, J. M.; Enchelmaier, R.; Spatz, J. P.; Möller, M. *J. Am. Chem. Soc.* **2001**, *123*, 3147. (g) Temple, K.; Kulbaba, K.; Power-Billard, K. N.; Manners, I.; Leach, A.; Xu, T.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2003**, *15*, 297.

(4) (a) Chan, V. Z.-H.; Hoffman, J.; Lee, V. Y.; Latrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D. *Science* **1999**, *286* (5445), 1716. (b) Nguyen, C. V.; Carter, K. R.; Hawker, C. J.; Hedrick, J. L.; Jaffe, R. L.; Miller, R. D.; Remenar, J. F.; Rhee, H.-W.; Rice, P. M.; Toney, M. F.; Trollsas, M.; Yoon, D. Y. *Chem. Mater.* **1999**, *11* (11), 3080.

(5) (a) Avgeropoulos, A.; Chan, V. Z.-H.; Lee, V. Y.; Ngo, D.; Miller, R. D.; Hadjichristidis, N.; Thomas, E. L. *Chem. Mater.* **1998**, *10*, 2109. (b) Chan, V. Z. H.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286* (5445), 1716.

(6) (a) Yang, P.; Zhao, D.; Melosh, N.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater*. **1998** *10*, 2033. (b) Yang, P.; Zhao, D.; Margolese, D. I.; Chmelka, B. F.; Stucky, G. D. *Chem. Mater.* **1999**, *11*, 2813.

(7) (a) Whitmarsh, C. W.; Interrante, L. V. *Organometallics* **1991**, *10*, 1336. (b) Whitmarsh, C. W.; Interrante, L. V. *Carbosilane Polymer Precursors to Silicon Carbide Ceramics*; U.S. Patent 5,153,295, October 6, 1992. (c) Rushkin, I.; Shen, Q.; Lehman, S. E.; Interrante, L. V. *Macromolecules* **1997**, *30*, 3141.

(8) (a) Berbon, M. M.; Dietrich, D. R.; Marshall, D. B.; Hasselman, D. P. H. *J. Am. Ceram. Soc.* **2001**, *84* (10), 2229. (b) Moraes, K.; Jacobs, J. M.; Sherwood, W. J.; Interrante, L. V. *Ceram. Eng. Sci. Proc.* **2000**, *21* (3), 289. (c) Interrante, L. V.; Jacobs, J. M.; Sherwood W.; Whitmarsh, C. W. *Fabrication and Properties of Fiber- and Particulate-Reinforced SiC Matrix Composites Obtained With (A)HPCS as the Matrix Source*; Key Engineering Materials Vol. 127−131; Transtec Publications: Zurich, Switzerland, 1997; p 271. (d) Interrante, L. V.; Whitmarsh, C. W.; Sherwood, W. *Ceram. Trans.* **1995**, *58*, 111. (e) Interrante, L. V.; Whitmarsh, C. W.; Sherwood, W. *Mater. Res. Soc. Symp. Proc.* **1994**, *346*, 593.

(9) Interrante, L. V.; Moraes, K.; Sherwood, W.; Jacobs, J.; Whitmarsh, C. W. Low-Cost, Near-Net Shape Ceramic Composites by Polymer Infiltration and Pyrolysis. In *Proceedings of the 8th Japan-U. S. Conference on Composite Materials*; Technomic Publishing: Lancaster, PA, 1998; pp 506−515.

(10) A preliminary report of some of these findings has appeared in the proceedings of the 5th Conference on Solid State Chemistry, Bratislava, Slovakia. *Pure Appl. Chem.* **2002**, *74*, 2111.

(11) (a) Weisbarth, R.; Jansen, M. *J. Mater. Chem.* **2003**, *13*, 1926. (b) Baldus, H.-P.; Passing, G.; Sporn, D.; Thierauf, A. *Ceram. Trans.* **1995**, *58*, 75. (c) Riedel, R.; Kienzle, A.; Dressler, W.; Ruwisch, L. M.; Bill, J.; Aldinger, F. *Nature* **1996**, *382*, 796. (d) Baldus, H.-P.; Jansen, M.; Sporn, D. *Science* **1999,** *285*, 699. (e) Muller, A.; Gerstel, P.; Weinmann, M.; Bill, J.; Aldinger, F. *Chem. Mater.* **2002**, *14*, 3398. (f) Muller, A.; Peng, J.; Seifert, J.; Bill, J.; Aldinger, F. *Chem. Mater.* **2002**, *14*, 3406.

(12) Shriver, D. F.; Drezdzon, M. A. *Manipulations of Air-Sensitive Compounds* 2nd ed.; Wiley: New York, 1986.

(13) Starfire Systems, Inc., 877 25th St., Watervliet, NY 12180.

(14) (a) Fazen, P. J.; Beck, J. S.; Lynch, A. T.; Remsen, E. E.; Sneddon, L. G. *Chem. Mater.* **1990**, *2*, 96. (b) Fazen, P. J.; Remsen, E. R.; Beck, J. S.; Carroll, P. J.; McGhie, A. R.; Sneddon, L. G. *Chem. Mater.* **1995**, *7*, 1942. (c) Chan, V. Z.-H.; Rothman, J. B.; Palladino, P.; Sneddon, L. G.; Composto, R. J. *J. Mater. Res.*, **1996**, *11*, 373. (d) Wideman, T.; Fazen, P. J.; Lynch, A. T.; Su, K.; Remsen, E. E.; Sneddon, L. G. *Inorganic Synthesis, Vol. 32*; Darensbourg, M., Ed.; Wiley: New York, 1998; pp 232−242. (e) Wideman, T.; Remsen, E. E.; Carroll, P. J.; Sneddon, L. G. *Chem. Mater.* **1998**, *10*, 412.

Table 1. Weight Ratios and Ceramic Yields for AHPCS and AHPCS/PBz Mixtures

sample	rel. wt. % AHPCS/PBz (actual weights used in g)	SiC_x/BN molar ratio	ceramic yield (wt %) after 4 h at 1000 °C
AHPCS	100% AHPCS		67.0%
AHPCS/PBz 80:20	80:20 (2.62/0.66)	2.25/1	84.9%
AHPCS/PBz 50:50	50:50 (2.87/2.91)	0.56/1	88.5%

and 1600 °C as follows. Chunks of the 1000 °C pyrolyzed material were placed in molybdenum boats and heated to 1400 and 1600 °C at 3 °C/min and then held at these temperatures for 4 h under an argon atmosphere. An additional sample of the 50:50 AHPCS/PBz mixture, which was used for electron microprobe analysis (EMPA) and X-ray diffraction (XRD) studies, was heated directly to 1700 °C at 3°C/min followed by a 1-h hold at 1700 °C.

Large chunks, 3−4-mm size, of the 1000, 1400, and 1600 °C SiC and SiC−BN materials were potted separately in epoxy. After cutting them with a diamond saw, a flat face suitable for hardness testing was polished to a 1-μm finish. Hardness was measured using a Leco 400 microhardness tester fitted with a Vickers indenter under a load of 1000 g for 10 s. A minimum of fifteen indentation tests were performed for each condition of material and temperature. Vickers Hardness (HV) (in GPa) was calculated as

$$HV = 0.0018544\left(\frac{P}{d^2}\right)$$

where P is the load (in N) and d is the average length of the two diagonals (in mm).

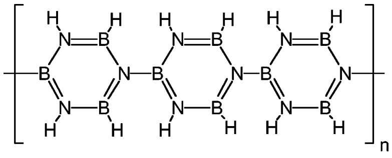
Several of the indents in each sample were studied at high magnification by using a SEM.

Elemental analyses of the epoxy-mounted samples were carried out by using a focused beam on a JEOL 733 electron microprobe automated with dQant software from Geller MicroAnalytical, at a current of 25 nA and an accelerating voltage of 15 kV, using the Heinrich ZAF correction model.[15] Standards included BN, SiC, and Al_2O_3, which were calibrated under the same operating conditions. Samples and standards were simultaneously coated with a thin film (roughly 300 Å) of Cr metal to eliminate charging from the electron beam. Analyses were performed by analyzing the Kα X-ray lines using an STE crystal for B, an LDE1 crystal for C, N, and O, and a TAP crystal for Si.

X-ray diffraction data were collected for the 1700 °C treated 50:50 polymer mixture on a RINT-1100 (Rigaku International Corporation, Tokyo, Japan) diffractometer operated at 50 kV and 24 mA. The X-ray system used copper Kα_1 and Kα_2 radiation. Samples were ground in a silicon nitride mortar and pestle, and the resultant powder was mounted by pressing it into a recess (20 × 15 × 1 mm) on a glass holder. X-ray patterns were scanned between 10 and 90° 2θ.

Results and Discussion

Polymer Precursors. Previous studies of allylhydridopolycarbosilane (AHPCS, nominally $[Si(CH_2CH{=}CH_2)_2CH_2]_{0.05}[SiH_2CH_2]_{0.95}$), and its all-hydrido analogue HPCS, have indicated a hyperbranched structure of the type $[R_3SiCH_2-]_x[-SiR_2CH_2-]_y[-SiR(CH_2-)_{1.5}]_z -[-Si(CH_2-)_2]_l$ (R = H (HPCS), $-CH_2CH{=}CH_2$ (APCS)), with a typical M_n of 600−1000 AMU, corresponding to about 15 monomer units, and a polydispersity of 2−6.[7] These low-molecular-weight, hydrocarbon-soluble, liquid carbosilanes, have relatively low viscosities and undergo cross-linking on heating in the range 200−400 °C to form a hard glass. Further heating to 1000 °C yields an amorphous "SiC_x" (x = 1.0−1.1) which undergoes partial crystallization to β-SiC above ca. 1300 °C.[16,17] The BN precursor used in this study, polyborazylene, is obtained from borazine ($B_3N_3H_6$) by thermally induced dehydrocoupling.[14] The product of this reaction is a low-molecular-weight (typically, M_n = 500−1500 AMU) solid having a $[B_3N_3H_{4-x}]$ composition and a complex structure, with linear, branched, and fused-ring (naphthyl-like) segments in addition to the all para-linked units of the type represented below.[18]



Polyborazylene

This hydrolytically sensitive, solid polymer is soluble in ether solvents, such as THF and ethyleneglycoldimethyl ether (glyme) and converts in high yield to a turbostratic BN on pyrolysis to 1000 °C. It has been used as a precursor for BN fibers, a matrix source for fiber-reinforced, BN matrix composites, and to deposit BN films on ceramic fibers and Si or SiO_2 substrates.[19]

As shown in Table 1, the prepared mixtures of AHPCS and PBz show enhanced ceramic yields compared to the additive yields of the component polymers. As the proportion of PBz is increased to 50 wt %, this combined yield approaches quite closely the yield that would be expected if these two polymers were losing only H_2, while retaining the initial Si, C, B, and N content of the starting polymer mixture. This observation, along with the results of the electron microprobe chemical analysis of the final ceramic mixture (see below), strongly suggests that the two polymers are interacting chemically with each other during pyrolysis, thereby limiting the loss of the low-molecular-weight, volatile byproducts that are typically evolved during the pyrolysis of the individual polymers (particularly AHPCS). A similar enhancement in ceramic yield has been previously observed for mixtures of the Yajima polycarbosilane (nominal composition, $[Si(CH_3)(H)CH_2]$) with PBz, where an increase in the pyrolysis yield of the PCS from 63 to 78% was observed after heating with 1% PBz at 70 °C for 10 h,[20] as well as for samples of AHPCS which had been modified by hydrosilation of some of the allyl

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(15) Goldstein, J. I.; Newbury, D. E.; Echlin, P.; Joy, D. C.; Fiori, C.; Lifshin, E. *Scanning Electron Microscopy and X-Ray Microanalysis*; Plenum Press: New York, 1981; 673 pp.

(16) Moraes, K.; Interrante, L. V. *J. Am. Ceram. Soc.* **2003**, *86* (2), 342.

(17) Interrante, L. V.; Moraes, K.; MacDonald, L.; Sherwood, W. *Mechanical, Thermochemical, and Microstructural Characterization of AHPCS-Derived SiC*. In *Advanced SiC/SiC Ceramic Composites: Developments and Applications in Energy Systems*; Kohyama, A., Singh, M., Lin, H.-T., Katoh, Y., Eds.; *Ceram. Trans.* **2002**, *144*, 125.

(18) Gervais, C.; Maquet, J.; Babonneau, F.; Duriez, C.; Framery, E.; Vaultier, M.; Florian, P.; Massiot, D. *Chem. Mater.* **2001**, *13*, 1700.

(19) (a) Kim, D.-P.; Economy, J. *Chem. Mater.* **1993**, *5* (9), 1216. (b) Kim, D.-P.; Coffer, C. G.; Economy, J. *J. Am. Ceram. Soc.* **1995**, *78* (6), 1546. (c) Kho, J.-G.; Moon, K.-T.; Kim, J.-H.; Kim, D.-P *J. Am. Ceram. Soc.* **2000**, *83* (11), 2681. (d) Kho, J.-G.; Moon, K.-T.; Noet, G.; Ruterana, P.; Kim, D.-P. *Thin Solid Films* **2001**, *389* (1, 2), 78.

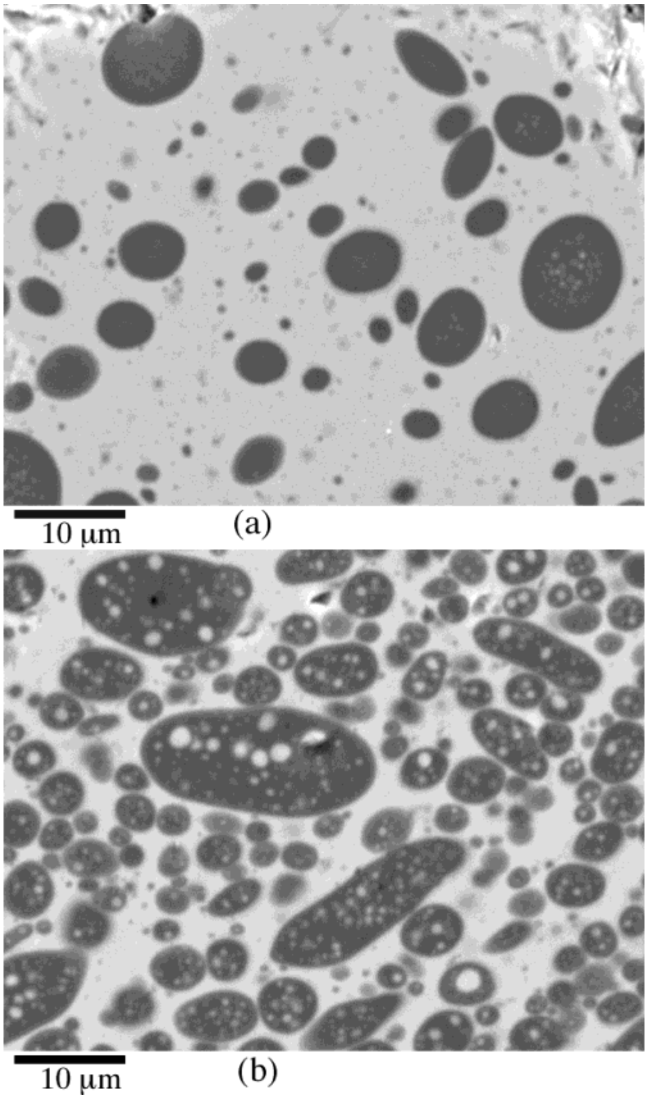

Figure 1. Microstructure of (a) an 80:20 and (b) a 50:50 AHPCS−SiC/PBz−BN composite heat-treated to 1000 °C for 4 h.

groups with 9-borabicyclo^{3,3,1}nonane.[21] Several possible reactions, including hydroboration of the AHPCS allyl groups by the PBz B−H bonds[21] or intermolecular cross-linking via dehydrocoupling reactions of the type Si−H + N−H → Si−N + H$_2$,[22] could be responsible for the enhanced ceramic yields.

Table 2. Electron Microprobe Composition of the Ceramic Composite Derived from the 50:50 and 80:20 AHPCS−PBz Mixtures[a]

sample (atm%)	%Si	%C	%B	%N	%O
50:50 1000 °C dark region	2.4 (0.7)	3.0 (1.1)	41.7 (1.4)	41.4 (1.5)	11.4 (0.8)
50:50 1000 °C light region	29.5 (1.2)	36.7 (1.5)	14.6 (1.9)	15.8 (0.4)	3.4 (0.9)
50:50 1700 °C dark region	2.6 (0.2)	3.0 (0.5)	45.2 (0.7)	46.8 (1.2)	2.4 (0.3)
50:50 1700 °C light region	27.7 (0.8)	35.1 (1.3)	17.4 (1.6)	16.7 (1.1)	3.0 (0.2)
80:20 1000 °C dark region	9.0 (0.2)	11.8 (0.4)	39.2 (1.1)	39.2 (1.4)	0.8 (0.1)
80:20 1000 °C light region	34.8 (1.3)	41.0 (1.9)	12.0 (2.6)	9.4 (1.1)	2.8 (0.1)

[a] Each value cited is the average of multiple analyses in the “light” and “dark” regions of each sample. The one-sigma standard deviations of these analyses are given in parentheses.

Specimen Microstructure. AHPCS−SiC, without any PBz, as expected, is monolithic and homogeneous. AHPCS−SiC/PBz−BN, on the other hand, is composed of two distinct phases. These show up in backscattered electron images (Figure 1) as a lighter-colored matrix phase and a darker embedded phase which occurs as droplets. In both the 50:50 and 80:20 samples, the lighter-colored phase forms the continuous (matrix) phase and the darker one forms the embedded phase. The darker droplets are generally in the 1−10 μm range, although much smaller and somewhat larger droplets can also been seen, especially in the case of the sample obtained from the 50:50 polymer mixture. Particularly in the latter case, small droplets of the light-colored phase can be seen dispersed within the larger droplets of the dark phase. Such droplet-within-droplet micro-emulsions have been evidenced for mixtures of two thermodynamically incompatible homopolymers to which a block copolymer of the two homopolymers has been added.[23] In these cases, the block copolymer apparently segregates at the interface between the homopolymer phases, thereby reducing the interfacial tension to the point where droplets of the matrix phase can form within the larger dispersed phase droplets.

Electron microprobe chemical analysis of the two regions, carried out for both the 50:50 and 80:20 polymer mixtures after pyrolysis to 1000 °C, and for the 50:50 sample after ramping directly to 1700 °C (Table 2), shows that the dark regions are predominantly composed of boron and nitrogen with small amounts of silicon and carbon. In the case of the 50:50 AHPCS/PBz sample, there is apparently also a significant amount (11 mol %) of oxygen present in the BN-rich phase of the two-phase material obtained after the 1000 °C pyrolysis. On the other hand, the oxygen level in the other (lighter) phase in this sample, and for both phases of the other sample obtained by using the 80:20 AHPCS/PBz ratio, is substantially lower (2−3%). Moreover, in a separate sample that was heated to 1700 °C directly from the precursor mixture the oxygen level in this dark phase of the 50:50 sample is also quite low. Other than the difference in the oxygen content, the changes in elemental composition for the sample heated to 1700 °C relative to the same mixture heated to 1000 °C do not appear to be substantial (except possibly for N, which is 6 mol % higher[24] in the dark phase for this sample). If we assume that the oxygen in the BN-rich phase of the 50:50 AHPCS/PBz-derived ceramic is due to inadvertent exposure of the PBz polymer to moisture, perhaps during handling of the sample of the precursor mixture during transfer to the furnace, it is likely present in the form of a boron oxide after pyrolysis to

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[20] Cao, F.; Li, X.-D.; Ryu, J.-H.; Kim, D.-P. *J. Mater. Chem.* **2003**, *13*, 1914. Cao, F.; Kim, D.-P.; Ryu, J.-H.; Li, X.-D. *Korean J. Chem. Eng.* **2001**, *18* (5), 761.

[21] Puerta, A.; Remsen, E. E.; Bradley, M. G.; Sherwood, W.; Sneddon, L. G. *Chem. Mater.* **2003**, *15*, 478.

[22] Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley: New York, 2000; p 365.

[23] (a) Hillmyer, M. A.; Maurer, W. W.; Lodge, T. P.; Bates, F. S. *J. Phys. Chem. B* **1999**, *103* (23), 4814. (b) Bates, F. S.; Maurer, W. W.; Lipic, P. M.; Hillmyer, M. A.; Almdal, K.; Moretensen, K.; Fredrickson, G. H.; Lodge, T. P. *Phys. Rev. Lett.* **1997**, *79* (5), 849.

[24] Note that all of these mol % values for a particular sample are normalized to 100%; therefore, only the ratios of these values and not the absolute percentages should be taken as significant, within the error limits of the measurements.

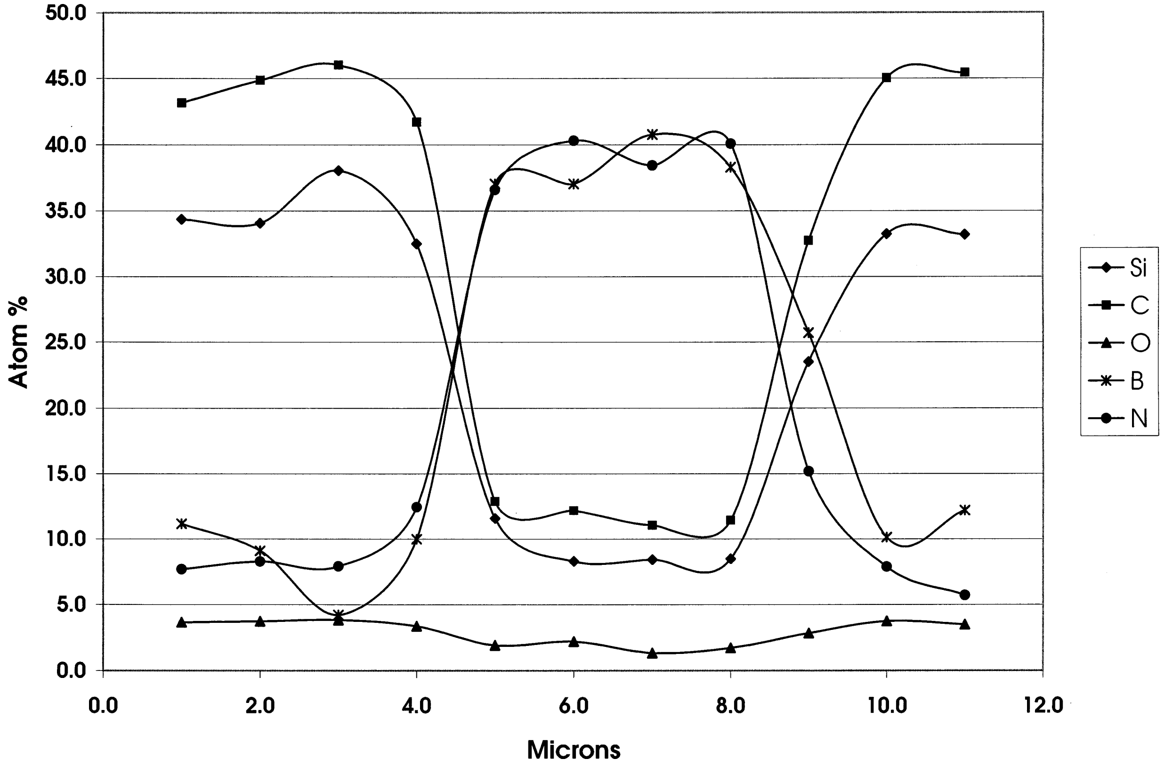

Figure 2. Electron microprobe line scans for a 50:50 SiC−BN composite heated to 1000 °C for 4 h.

1000 °C. The volatility of boron oxide at the final temperature of 1700 °C[25] could then account for the loss of this oxygen in the higher temperature sample. Alternatively, as these two samples were separately heated to their final pyrolysis temperatures, it is possible that exposure to moisture occurred only in the case of the 1000 °C sample.

The light region is richer in silicon and carbon, but also contains a significant amount of boron and nitrogen. The proportion of C/Si in this phase is somewhat higher than is typically observed for AHPCS-derived SiC, suggesting that the allyl groups in AHPCS are more effectively incorporated into the cross-linked polymer mixture than in the case of AHPCS alone.[26] Because there is no overlap of elements (other than H) between the two starting precursors, and because the composition of the composite preserves the stoichiometry of the starting precursor, it is reasonable to assume that the light regions were formed from a mixture of AHPCS and PBz which was richer in AHPCS than PBz and the dark regions were formed predominantly from PBz. The electron microprobe chemical analysis suggests that some level of mixing has occurred between the two polymers, particularly in the continuous SiC-rich areas. The much smaller atomic percentage of silicon and carbon in the dark BN-rich regions, compared to the boron and nitrogen in the SiC-rich regions, suggests that the PBz is significantly more soluble in the AHPCS phase than AHPCS is in the PBz phase. The relative amounts of the other two elements in the majority "SiC_x" and "BN" phases appears to change somewhat on going from the 50:50 to the 80:20 AHPCS/SiC mixture, with the proportion of SiC_x in the BN-rich phase increasing and the proportion of BN in the SiC-rich phase decreasing by a few %. It should also be noted that, although considerable effort was made to find regions of the sample for EMPA spot analyses that were well within a "dark" or "light" phase region and free from internal droplets, the depth and breadth of the X-rays emanating from the EMPA sampling beam (estimated as between 1 and 2 μm) could result in a sampling of some of the second phase during these analyses. Nonetheless, much of the uncertainty reported as the standard deviation of the average (Table 2) can be attributed to analytical error (counting statistics), which is roughly three percent for Si, C, B, and N values at the highest reported concentrations (35 to 42 atm%), with uncertainties increasing with decreasing element concentration. Where the standard deviation on the mean exceeds that expected from analytical uncertainties, the beam likely sampled more than one phase. These considerations notwithstanding, in view of the consistency in the findings from region to region and particle to particle within these samples, the measured differences in composition of the "dark" and "light" regions in these two (50:50 and 80:20) samples are significant.

In addition to these "spot" analyses, a line scan across a BN-rich droplet was also taken in the case of the 80:20 sample (Figure 2). The values for %B, N, Si, and C across the "light" and "dark" regions of this sample are generally consistent with the results of the "spot" analyses given in Table 2. This line scan, along with the relatively sharp outlines of the droplets observed in the BSE images, suggest that little or no gradation in composition occurs at the interface between these two phases.

It is notable that in both the 50:50 SiC−BN and the 80:20 SiC−BN samples, the continuous phase is formed by the SiC-rich composition. In the 80:20 (by weight)

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[25] Yoon, S. J.; Jha, A. *J. Mater. Sci.* **1995**, *30*, 607.

[26] EMPA on a sample of AHPCS−SiC prepared in the same manner gave the following values: atomic% Si: 45 ± 1; %C = 54 ± 1.

AHPCS/PBz mixture, SiC−BN are in a 2.25:1 molar ratio.[27] As might be expected due to the higher proportion of SiC, the SiC-rich composition forms the continuous phase. The actual composition of this lighter colored phase is 76% SiC_x (with a 6% excess of C over Si) and 21% B + N. In contrast, in the 50:50 (by weight) AHPCS/PBz mixture, SiC−BN are in a 0.56:1 molar ratio. This higher proportion of BN also correlates with the microstructure of this sample, where it is seen that there is a much higher (>50%) proportion of the darker, BN-rich phase (with only 5 mol % SiC_x) compared to the lighter colored, SiC-rich phase (with a B + N concentration of 30 mol %). However, the continuous phase is still the SiC-rich phase, although present in a smaller proportion. On annealing to 1700 °C, the compositions remain approximately the same, with an apparent slight increase in the proportion of BN in both phases. The fact that smaller droplets of the lighter (SiC-rich) phase are frequently observed in the larger BN droplets are suggestive of a low interface surface tension, perhaps due to a reaction of the two starting polymers which generates some type of copolymer at the interface.[23] Such a reaction between the starting polymers is, in fact, evidenced by the significantly enhanced ceramic yield observed for the polymer mixtures, relative to the additive combination of the separate polymers, as well as by the formation of a gel upon evaporation of the solvent from the mixed polymer solution. This interface reaction, as well as the high overall yield of the polymer mixture-to-ceramic conversion, may also be important in preserving the original, polymer-blend-type microstructure through the considerable overall changes in density and volume that must accompany the polymer-to-ceramic conversion process as these samples are heated to 1000 °C. The relative compositions of BN and SiC_x in the two phases obtained for the 50:50 and 80:20 AHPCS/BN mixtures do not vary greatly, although in the 80:20 mixture there does appear to be a somewhat higher proportion of BN in the SiC_x phase, and vice versa.

A similar type of two-phase microstructure, consisting of droplets of a C-rich phase in a predominantly “SiC” matrix was observed previously in the case of SiC/C composites that were obtained by mixing AHPCS with certain pitch samples (which served as the C source), followed by thermal cross-linking and pyrolysis.[7] In both cases the appearance of the resultant microstructure resembles strongly that observed for mixtures of two immiscible liquids, or for blends of high-molecular-weight polymers.

Prior powder X-ray diffraction (XRD), differential scanning calorimetry (DSC), and electron diffraction (ED) studies of AHPCS-derived SiC have indicated that pyrolysis to 1000 °C (or even 1200 °C) yields an amorphous, apparently homogeneous, material.[17] The onset of crystallization (to β-SiC) at around 1250 °C is apparent in the DSC and is also supported by ED studies; however, even after several hours at temperatures up to 1600−1700 °C, crystallization is far from complete and the crystallite sizes are typically in the nm range.

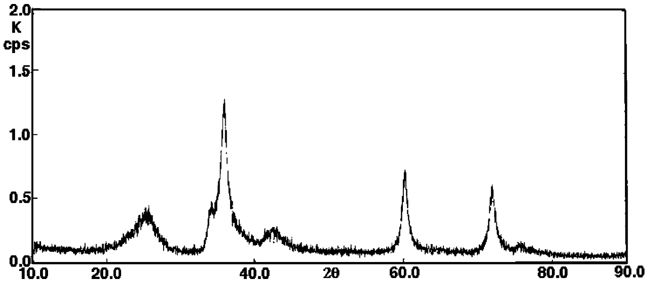

Figure 3. XRD pattern of 50:50 mixture heated to 1700 °C for 1 h.

Table 3. Vickers Hardness of the Samples (in Gpa)

heat-treatment temperature °C	AHPCS−SiC 100%	AHPCS−PBz 80:20	AHPCS−PBz 50:50
1000	14 ± 1	12 ± 1	8 ± 1
1400	15 ± 1		6 ± 1
1600	13 ± 1	10 ± 1	5 ± 1

Figure 3 shows the XRD pattern obtained for the 50:50 AHPCS/PBz-derived ceramic mixture after annealing at 1700 °C for 1 h. The three major peaks at $2\theta = 35.6°$ (111), 60.2° (220), and 72.0° (311), along with the weaker ones at 42° (200) and 75° (222), are attributable to β-SiC, and the shoulder at 34° is assigned to stacking faults (alpha-SiC like) in β-SiC. Such stacking faults are usually observed in precursor-derived SiC materials just after crystallization and, in general, this part of the XRD pattern resembles quite closely that observed for AHPCS-derived SiC after heating to 1600−1700 °C. This leaves only the broad, relatively strong peak at ca. 25° unassigned, which is attributable to the main (002) diffraction peak of turbostratic boron nitride. The second prominent line in the t-BN pattern, due to the (100) reflection, is expected at about the same position as the SiC (200) line at 42°, and is therefore probably overlapped with that peak. Thus, there is strong evidence for the presence of both nanocrystalline[28] β-SiC and t-BN in this sample after heating to 1700 °C, but no sign of any of the several other possible crystalline phases that could occur in the Si−C−B−N system.

Hardness. Vickers hardness results, measured at a load of 1000 g for the samples obtained after the 4-h heat treatment at 1000, 1400, and 1600 °C are shown in Table 3. For the AHPCS−SiC it is seen that compared to samples heat-treated to 1000 °C, hardness increases on heat treatment to 1400 °C and decreases on further heat treatment to 1600 °C. Although the variation in Vickers hardness is small, the trend seen is significant ($p \leq 0.05$). Moreover, at each condition measured, increasing the concentration of the polyborazylene-derived BN phase resulted in a decrease in hardness compared to that of the similarly prepared AHPCS−SiC material. The reduction in hardness as the BN concentration in the ceramic is increased presumably relates to the expected lower hardness of the “BN” component[29] of the ceramic mixture, either as an intimate mixture with the precursor-derived “SiC” in the light colored phase, and/or as the separate dark phase. The fact that the area sampled by the diamond indenter in these measurements was much larger than the sizes of the individual light and dark phase regions

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[27] This assumes loss of only hydrogen (as H_2) from both precursors on pyrolysis, and the chemical formulas $[SiH_2CH_2]_{0.95}[Si(C_3H_5)_2CH_2]_{0.05}$ ($SiC_{1.3}H_{2.5}$) and $[B_3N_3H_4]$ for AHPCS and PBz, respectively.

[28] As deduced from the relatively broad line widths; the half-height line width ranges from ca. 0.15 to 0.24 for all peaks.

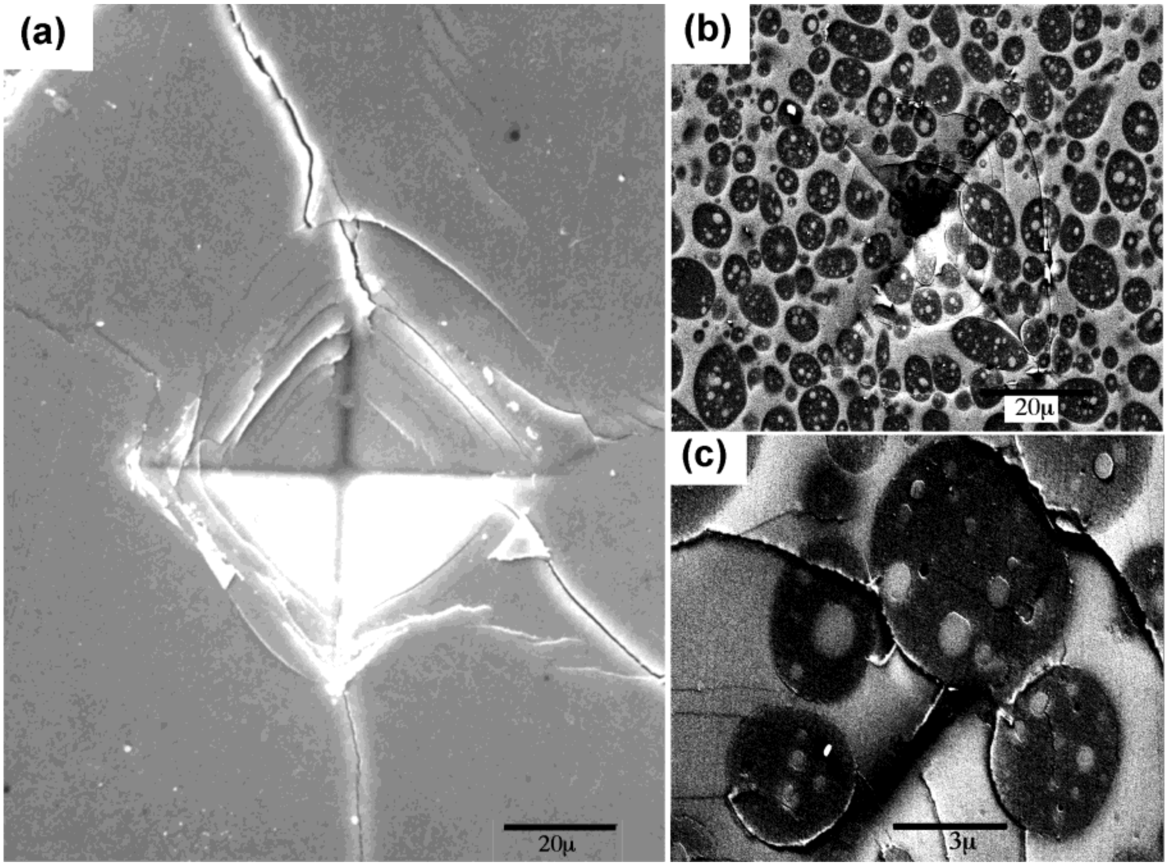

Figure 4. SEM micrographs of Vickers indents at a load of 1000 g on samples heated to 1600 °C. (a) AHPCS−SiC sample (no PBz) showing several large radial cracks emanating from the corners of the indent; (b) and (c) SiC/BN 50:50 composite at two magnifications (a 20 and a 3 *μ* bar, respectively, is shown for reference) showing no radial cracks, and the deviation of the Hertzian conc-type indentation cracks at the debonded BN phase.

and effectively encompassed both regions (see Figure 4) allows for both possibilities. On the basis of our earlier studies of AHPCS-derived SiC alone[16] it seems likely that the apparent reduction in hardness observed for the SiC/BN mixtures with increasing annealing temperature is due to the effects of increased internal porosity (and/or free volume), which arises from the weight loss and shrinkage occurring overall as these precursor-derived ceramics are heated to higher temperatures.

Indentation Behavior. Typical SEM micrographs of cracks produced by a Vickers indenter, at a load of 1000 g, are shown in Figure 4 for both AHPCS-derived SiC alone, and the SiC/BN composite obtained from a 50:50 mixture of the component polymers. Indentation of AHPCS-derived SiC heat-treated to 1000 and 1600 °C results in radial cracks that propagate quite some distance from the indent (Figure 4(a)) in addition to the cracks that form around the circumference of the indent. It was observed that, in general, the size of the indent is larger and cracking is more extensive in the AHPCS−SiC material heat-treated to 1600 °C compared to that heat-treated to 1000 °C. Indentation impressions produced in the 50:50 and 80:20 SiC−BN material heat-treated to 1000 and 1600 °C are significantly larger than those in the AHPCS−SiC material, as would be expected from their lower hardness. Compared to the AHPCS−SiC samples, few signs of radial cracks are observed under these indentation conditions (Figure 4(b)). Both the 50:50 and the 80:20 SiC−BN samples heat-treated to 1000 °C show no clear evidence of crack deviation or debonding at the interface between the two "phases". In contrast, in the case of the 50:50 SiC−BN sample heat-treated to 1600 °C, considerable debonding and separation of the two phases at their interface can be seen in the region of the indent. Also, as is clear in the higher magnification picture of the same sample as in Figure 4(b) (Figure 4(c)), indentation cracks produced by the indent deviate around, and sometimes terminate at, the weakly bonded second phase. This separation at the interface between the BN- and SiC-rich phases may reflect the differing amount of shrinkage of the two phases that accompanies the increasing densification/crystallization of the component materials as they are heated to 1600 °C. Indeed, XRD measurements carried out on this system, as described above, have indicated that partial crystallization of both the SiC and BN components occurs after heating to 1700 °C.

Thus, it appears that as the proportion of the BN phase is increased, and as the annealing temperature is raised to 1600 °C, there is increasing evidence of debonding between the BN-rich and SiC-rich phases in these composites. The observation of such interface debonding, and its apparent dependence on the composition and annealing temperature, does promise the potential to vary the mechanical properties of this SiC−

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(29) Edgar, J. H., Ed. *Properties of Group III Nitrides*; EMIS Datareviews Series No. 11; INSPEC, the Institution of Electrical Engineers: London, 1994; p 12. Mott, B. W. *Micro-Indentation Hardness Testing*;Butterworth Scientific Publications: London, 1956.

BN composite through control of its composition and/or processing. Moreover, on the basis of prior work on polymer blends, it seems likely that one can also control the sizes and distribution of the two component phases in this system, and therefore its properties, through control of the interface between these phases, perhaps through addition of certain reagents that will migrate to that interface, or by control of chemical reactions occurring at that interface during the thermosetting of the constituent polymers.

Clearly much remains to be determined about the processes of phase separation, cross-linking, pyrolysis, and crystallization that occur during the conversion of this polymer mixture to the two-phase BN- and SiC-rich phases; however, it is clear that this approach of using mixtures of immiscible polymer precursors has quite general applicability and that it offers unique opportunities for microstructural (and thereby property) control in ceramic composites.

Conclusions

The copyrolysis of a mixture of two different polymer precursors, to SiC and BN, respectively, has been found to yield a two-phase ceramic mixture which possesses a highly unusual microstructure that resembles closely that observed for certain polymer blends. This microstructure appears to derive from a phase separation occurring in the precursor mixture that is driven by the inherent immiscibility of the component polymers. Moreover, diamond indentation studies of this ceramic mixture demonstrate a reduced hardness of the SiC-rich phase, and an enhanced resistance to crack formation upon indentation. Finally, after annealing the 50:50 polymer mixture to 1600 °C, clear evidence for separation at the interface between the two component phases is obtained, and, when sufficient loads are applied to induce the formation of indentation cracks, in some cases these cracks were observed to terminate at such an interface. These results are suggestive of unusual toughness for this precursor-derived SiC/BN mixture. Further studies are needed to verify these preliminary conclusions; however, if this is indeed the case, such a system would be of considerable interest as either an interphase or as the matrix phase in ceramic-fiber-reinforced, ceramic matrix composites (such as SiC_f/SiC_m).

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