

# **PROCESSING, PERFORMANCE, AND CHARACTERIZATION OF MONOLITHIC NANOCOMPOSITES FROM PRECERAMIC POLYMERS**

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## **ABSTRACT**

Ceramic matrix composite materials when reinforced with continuous ceramic fibers have found increased interest in many high temperature space applications such as aircraft structures, hot-gas nozzles, and jet-engine components where a higher inlet temperature is desirable. Fracture toughness is one of the important parameters that affects the mechanical properties and applicability of ceramics and ceramic matrix composites at high temperatures. Low fracture toughness in ceramic composites arises due to the very brittle nature of ceramic matrix. This can be prevented by inducing small load bearing nanoparticles in between the grain boundaries of the ceramic matrix, thereby resulting in good fracture toughness and non-catastrophic mode of failure. An optimization study to determine the required weight fraction of nanoparticles for enhanced mechanical performance in preceramic polymers is of utmost importance. The main objective of this research is to process, characterize, and evaluate the mechanical performance of monolithic ceramics from preceramic polymers with and without nanoparticles for use in high temperature space structures.

## **INCREASING MECHANICAL PROPERTIES OF CERAMICS WITH THE INSERTION OF NANOPARTICLES**

Many efforts have been spent on the development of high-performance ceramics, which are recognized as promising materials for severe engineering applications such as highly efficient gas turbines, as well as structures in space (e.g., re-entry vehicles), aerospace (e.g., high-speed airplanes), automobiles, etc. However, many problems still remain unresolved, for instance, low fracture toughness, degradation of mechanical properties at high-temperatures and poor creep, fatigue and thermal shock resistances, etc. Thus, many attempts have been made to break through these problems by incorporating second phases such as particulate, platelets, and whiskers in the micro-size level at the matrix grain boundaries, which produce so-called microcomposites. However, it appears to be difficult to sufficiently improve the above-mentioned problems of ceramic composites by such microcomposite technology (Yousefpour and Ghasemi Nejhada, 2001).

Nanocomposites are a novel class of composite materials where one of the constituents has dimensions in the range between 1 and 100 nm. Recent and on-going research on polymer/inorganic nanocomposites has shown enhancements in stiffness, strength, strain-to-failure, toughness, electrical, and thermal properties over those of polymers, without compromising on density or processibility. Major differences in behavior between conventional and nanostructured materials result from the fact that the latter have much larger surface (or interface) area per unit volume. Since many important chemical and physical interactions are governed by surfaces, a nanostructured material can have substantially different properties from a larger-dimension material of the same composition. In the case of fibers or foils, the area per

unit volume is inversely proportional to the fiber diameter or the foil thickness, respectively. Thus, the smaller these dimensions are, the larger are the surface areas per unit volume.

The aim of intragranular dispersions is the dislocation generation and pinning during the cooling down from the fabrication temperatures and/or the in-situ control of size and shape of matrix grains. The latter role is significant for the nonoxide ceramics such as  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  with strong covalent bonding even at high temperatures. The intergranular nanodispersoids must play important roles in the grain boundary structure control of oxide and nonoxide ceramics, which gives the improvement of high-temperature mechanical properties. Such a new materials design concept on nanocomposites can be also applied to the ceramic/metal, metal/ceramic, and polymer/ceramic composites systems. In addition, not only excellent mechanical properties but also attractive functions such as magnetic properties may be introduced. Thus, an "intermaterial," in which advanced functionalities and good mechanical properties are combined in one material, is expected to be realized via the nanocomposition technique. To develop such a material, understanding of roles of nanostructures, properties control, and nanostructural optimization should be performed aggressively.

Ghasemi Nejhad et al. (2000) developed CFCCs with micron-sized inclusions and demonstrated some improved mechanical performances and reduction in processing time. Gudapati et al. (2006, 2007) developed continuous fiber ceramic nanocomposites with improved mechanical performances. However, no work has yet been reported on monolithic ceramics made from preceramic polymers with nanoparticles as inclusion, which is the topic of this proposed work. This work would be of utmost importance as it has already been shown that nanoparticles improve the fracture properties of polymers as nanocomposites. This research work will mainly address the mechanical and fracture properties of ceramic matrices, used in fiber reinforced composites, as ceramic nanocomposites. These materials will have numerous high temperature applications in aircraft and spacecrafts.

## **MANUFACTURING MONOLITHIC CERAMICS WITH AND WITHOUT NANOPARTICLES**

KiON Ceraset® preceramic polymer was used to manufacture the monolithic ceramic samples. To manufacture the monolithic ceramic nanocomposites, silicon carbide nanoparticles were mixed with the preceramic polymer. When the nanoparticles were added, the mixture became highly viscous. As the weight percent of nanoparticle reinforcement was increased, it became difficult to mix the nanoparticles with the polymer without any agglomerations. The nanoparticles employed were obtained from Sigma Aldrich and had a mean diameter of 55nm. To assist in the mixing process, a solvent was used to make the resulting polymer less viscous. Isopropyl alcohol (IPA) and tetrahydrofuran (THF) were experimented with, as solvents. The Ceraset,  $\text{SiC}$  nanoparticles, and solvent were slowly mixed either by a magnetic stirrer or by hand using a glass stirring rod. After sufficient mixing, 1 wt% of dicumyl peroxide obtained from Aldrich Chemical was used as the free radical initiator to lower the required cure temperature to 150 °C. The mixture was then poured into a 2" x 2" x 1/4" pre-sanded aluminum mold coated with a release agent to ensure the sample would not adhere to the mold. The aluminum plate was then placed in the convection oven. The oven was set to heat the sample to 150°C at a rate of 0.5°C/min.

The second step in converting a preceramic polymer into a ceramic involves in pyrolyzing the sample at a high temperature in inert atmosphere using argon gas. Initially, samples from pure Ceraset were pyrolyzed to 1100 °C. As can be seen from Figure 1a, the

polymer, although converted into ceramic, broke up into small pieces. To prevent this, the next batch of samples was pyrolyzed to a lower temperature of about 550°C. As can be seen from Figure 1b, although the samples broke into larger pieces, it had not been completely converted into SiC ceramic.



Figure 1. (a) Pyrolysis of pure ceramic at 1100°C, (b) Pyrolysis of pure ceramic at 550°C

The next batch of pyrolysis samples contained samples from pure Ceraset, and Ceraset + 2.5 wt% SiC nanoparticles + 20 wt% 2-Propanol (IPA). These samples were heated to 450°C to enhance the yield and reduce the breakage of samples. Although the samples after pyrolysis remained in one piece (see Figure 2), cracks started appearing at this point. These cracks could be filled by reinfiltrating them with the base polymer and curing it again. However, establishing test results from such samples would not provide valid data to interpret results from it. To establish strength variations between samples with and without nanoparticles in Ceraset polymer, mechanical tests were to be interpreted at B-Stage (an intermediate stage where the sample is solidified but has not reached the final curing stage).



Figure 2. Samples pyrolyzed at 450°C, top sample contains 2.5 wt% nanoparticles & bottom sample is from pure polymer.

The increase in wt% of nanoparticles within the preceramic polymer was observed to have increased the strength of the material. For the polymer without nanoparticles, the sample fractured in the mold during the curing process. As shown in Figure 3, as the wt% of nanoparticles increased, fewer cracks were present in the samples during the curing process. This clearly shows that increasing the wt% of nanoparticles increased the strength of the material.

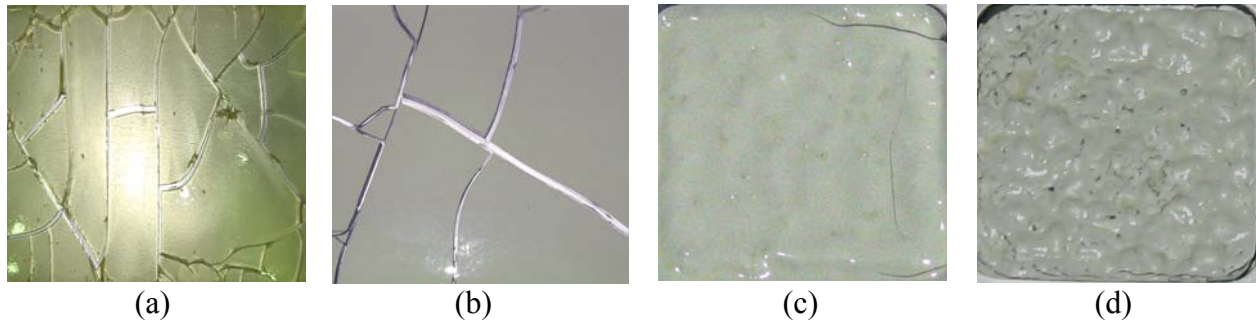


Figure 3. (a) Polymer with no nanoparticles, (b) polymer with 2.5 wt% nanoparticles, (c) polymer with 10 wt% nanoparticles, and (d) polymer with 15 wt% nanoparticles.

As the wt% of nanoparticles increased, more solvent was required. This created bubbles within the samples with surface finishes that were not smooth, as shown in Figure 4. This poses a problem in testing the samples as the test data would not be valid because the samples do not meet the ASTM (American Society for Testing and Materials) standards.



Figure 4. Pictures of a sample with 15 wt% nanoparticles and 40% solvent. Left: Top view of the sample. Right: Side view of the sample cross-section.

### TESTING B-STAGED SAMPLES FOR FLEXURE STRENGTH

The main objective of this part of the study is to experimentally evaluate the mechanical performance of different specimens in flexure after B-staging. A three-point bend fixture test was used to measure the flexural load-deflection responses of the specimens loaded in three-point bending. The test specimens were selected so that they had a span to depth ratio ( $L/d$ ) that produces tensile and compressive failures at the outer surfaces of the samples under the bending loading. In this study, the recommended  $L/d$  value is greater than 8. The specimens were nominally 45 mm long, 4 mm wide and 3 mm thick on an average. Three samples were tested for each type. The tests were conducted using an Instron testing machine.

Figure 5 shows a schematic of the three-point bending test. The test specimen rests on two supports, the distance between which is called support span. The specimen is loaded at the center by a loading roller.

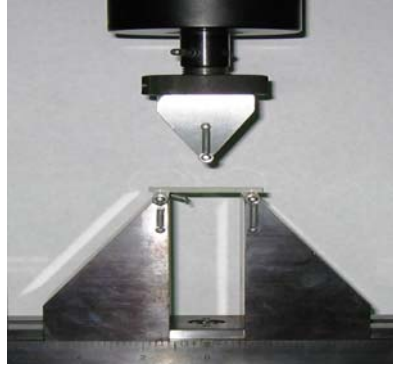


Figure 5. Three point bend fixture used to test the samples.

All the samples tested fractured inside the uniformly stressed region of the flexure specimens (i.e., between the inner loading points of the fixture), eliminating uncertainties about failures due to stress concentrations outside the uniform loading region as well as the shear failure of the specimens (see Figure 6).

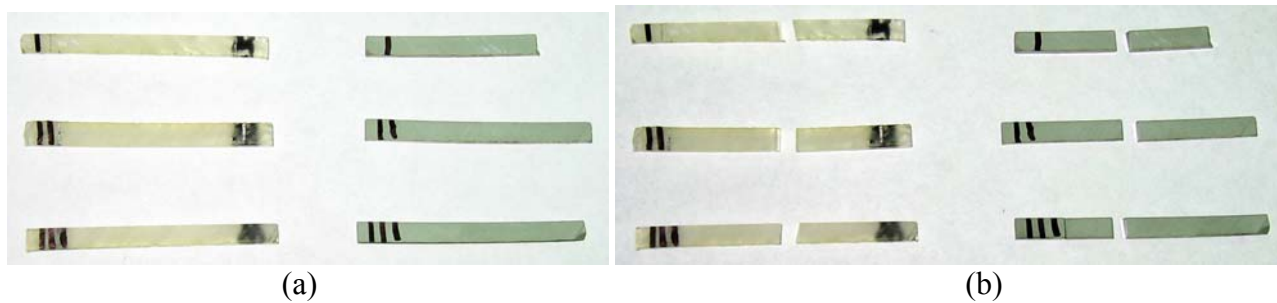


Figure 6. (a) Samples before testing, (b) Samples after testing

The samples seen on the left-hand-side of Figures 6a and 6b represent pure pre-ceramic polymer samples. The samples seen on the right-hand-side have nanoparticle loading of 2.5 weight % and 40 wt% of IPA solvent. It should be noted that the samples with the nanoparticles also have 40% IPA, and hence their strengths are affected by the IPA, which tend to lower the strength. However, a control sample with 40% IPA and pure polymer could not be manufactured for comparison purpose since they broke in pieces. However, as evident from Figure 3, nanoparticles definitely aid in better binding of the polymer and result in better structural integrity.

## CONCLUSIONS

The effects of reinforcing nanoparticle inclusions on the flexural mechanical properties of monolithic ceramic composites at B-stage are experimentally investigated. Although, no conclusive result could be interpreted from the test results, good specimen shape retention, compactness of the material, and good dispersion of the nanoparticles in the samples was achieved at the B-stage level. The above mentioned process seems more appropriate for continuous fiber ceramic composites and other manufacturing techniques such as compression molding with higher weight loading of nanoparticles could be a viable solution for manufacturing monolithic ceramic nanocomposites.

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