# POLYMER DERIVED ARCHITECTURED CERAMICS AND CERAMIC MATRIX COMPOSITES

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## ABSTRACT

Ceramics are very attractive engineering materials because of their high compressive strength, low density and high thermal resistance. Their range of applicability, however, is currently limited by their brittleness. Natural hard materials such as nacre and tooth enamel, on the other hand, are mainly made of brittle minerals and yet show interesting combinations of stiffness, strength and toughness. This outstanding performance is rooted in their architecture which results in toughening mechanisms such as crack bridging, deflection and process zone. Creating architectures within ceramics is therefore a promising pathway towards mitigating the effects of damage, and in turn improving their toughness. In this study, we show that pre-ceramic resins can be effectively used to fabricate low porosity architectured ceramics and ceramic matrix composites with improved fracture toughness. The ceramic materials were obtained using nano-sized active fillers and hydrostatic pressure during the pyrolysis. Using pre-ceramic resin eliminates the shape limitations in the traditional ceramic processing techniques and results in time-efficient near-net-shape manufacturing of novel classes of ceramics with interesting combinations of properties and functionalities, effectively pushing the current envelope of materials. The resulting materials are of interest in protective armor (body, vehicle and aircraft), propulsion, thermal protection, device packaging, and bio-material systems.

## **1** INTRODUCTION

Ceramics are promising materials used in structural applications involving high service temperatures (e.g., engine components, high temperature furnaces, exhausts), due to their high strength, low density, excellent thermal stability, oxidation resistance, and corrosion resistance [1]. The main weaknesses of ceramics compared to

advanced metals and alloys are their low fracture toughness, susceptibility to thermal shocks and low production rates [2]. To improve reliability, fracture toughness and durability of ceramics, ceramic matrix composites (CMCs) have been developed [2, 3]. Today, CMCs have diverse applications in aerospace structures, automotive components, gas-turbine engines, and other structures operating at high temperatures [4]. As a result, in 2015, General Electric (GE) aviation announced \$200 million investment to build two new factories in Huntsville, Alabama to make CMCs primarily for gas turbine engines whose sales was estimated at ~US\$39 billion globally in 2015 [5].

There are different types of CMCs such as particulate, whisker, short fiber, or continuous filler- reinforced ceramics [2]. Recently, there has been an increased interest to toughen CMCs by continuous ceramic fibers. Continuous ceramic fiber reinforced ceramics (CFCCs) benefit from all the advantages of ceramics and are concurrently reaching the toughness of metals [6]. There is therefore a major shift in industry to replace super-alloys with CFCCs for high temperature applications such as engine components in hypersonic vehicles subjected to high temperatures, lightweight superconductors for computers, sensors and actuators, heat exchangers, turbochargers, high temperature furnaces, and valve systems.

Techniques such as chemical vapor deposition (CVD), chemical vapor infiltration (CVI), powder processing, sol-gel processing, and pre-ceramic pyrolysis (PCP) have been developed to make CFCCs [5]. PCP has several particular advantages: (i) all the manufacturing techniques originally developed for processing of polymer based composites (e.g., resin transfer molding, fiber-placement, etc.) can be used to develop CFCCs with some modifications in the process such as cure-on-the-fly at the green stage, (ii) the process results in near-net-shape manufacturing of CFCCs with complex shapes, (iii) the pyrolysis of the polymeric precursor occurs at lower temperatures compared to other methods, (iv) having high-temperature applications in mind, complex and advanced cooling systems can be implemented in the product so that higher operating temperatures and in turn higher efficiency can be achieved, (v) low viscosity of pre-ceramic polymer enables the addition of reinforcing agents (e.g., passive fillers, nano/micro fibers) to the CMCs, to address their relatively low toughness. The main drawback of PCP is however excessive gas release and shrinkage during chemical transformation of pre-ceramic polymer to ceramic [3].

Processing of pre-ceramic polymers has two stages. In the first stage, the polymer is covalently cross-linked (cured) to a green state. In the second stage (pyrolysis), the temperature in increased (usually to  $\geq 1000$  °C) so that the organic moieties, typical of a polymer (e.g., methyl group attached to the Si atoms in a Polysilazane) will be eliminated and a ceramic residue called "polymer-derived ceramic" is obtained. The elimination of organic moieties is accompanied by a significant gas release which can induce porosity in the resulting material [7]. In order to decrease the porosity, three main approaches have been followed [4, 5]: (i) adding nanometer sized active fillers, (ii) adding nanometer sized passive fillers such as carbon nanotubes, and (iii) using pressure during pyrolysis. Passive fillers simply dilute the pre-ceramic polymer and therefore decrease the amount of gas generated and the associated volume shrinkage, reducing the possibility of forming cracks/voids during pyrolysis. Active fillers on the other hand react with the decomposition gases generated during pyrolysis and therefore reduce the amount of shrinkage. Pressurizing the polymer during pyrolysis also possibly increases the flow of the materials into the cavities resulted from the gas release and decrease the possibility of having voids. In this study, we used a combination of all these three strategies to improve the quality of the polymer-derived ceramics. We then used the pre-ceramic polymers

(modified by addition of nanometer-sized fillers) to infiltrate continuous ceramic fiber pre-forms. Followed by a pyrolysis step, CFCCs with reduced porosity were achieved.

#### 2 Fabrication of polymer derived ceramics and CFCCs

A polysilazane (commercial name Ceraset® PSZ 20) from KiON industries was used as the pre-ceramic polymer. 3 wt% of a radical initiator (dicumyl peroxide, 99% ACROS Organics) was added to the polymer to decrease the thermoset (curing) time to the solid (green) state. We found that when oxygen is absent (in inert environment or in vacuum) the curing time for this polysilazane is extremely long (up to 24 hours) in the absence of radical initiator. By adding the 3 wt% dicumyl peroxide, the curing time was reduced to 15 min in vaccum at 150  $^{\circ}$ C. In order to study the effects of active fillers on the polymer derived ceramics, Al<sub>2</sub>O<sub>3</sub> nano-powder (13 nm primary particle size, 99.8% trace metals basis, Singma Aldrich) with different concentrations of 2, 6, 18 wt %, was added to the polysilazane. Concentrations beyond 18 wt% resulted in a very viscous paste which was hard to process. Prior to mixing, the nano-powder was dried in vacuum at 150 °C for two hours. The powder was then cooled down and was mixed with the polymer using a planetary mixer (Thinky ARE-310) at 2000 rpm for 3 mins. The degassing of the mixture was done in two stages: the first stage was done in the planetary mixer at 2500 rpm for 3 mins. The second step was done under vacuum for 1 hour. After degassing, 10 g of the mixture was poured into an aluminum circular mold (diameter d = 6 cm). The materials were then cured at 150 °C for 15 min (Figure 1a) and were removed from the mold. The resulting cured samples were heated at 2 °C/min up to 400 °C at which temperature they were kept for four hours to finish the cross-linking of the polymer. Under iso-static pressure of 30 MPa, the temperature was then increased to 1600 °C (at 2 °C/min). The material was kept at 1600 °C for four hours to finish pyrolysis [8]. At 800 °C, the polymer to ceramic conversion starts, and at about a 1000 °C the decomposition gases resulted from the polymer-ceramic conversion start to react with alumina nano-particles. The alumina-polysilazane reaction is fully done at 1600 °C [9]. The samples were then cooled down to room temperature at 2 °C/min.

The samples containing no alumina nano-filler or low concentrations of it (i.e., 2 wt %) cracked during pyrolysis (Figure 1b) and reducing the heating rate did not prevent cracking. On the other hand, higher concentrations of filler eliminated cracking and resulted in solid samples with relatively retained shape (Figure 1c). We also measured the weight reduction after pyrolysis as a function of addition of alumina nano-filler (Figure 1d). The samples containing no filler lost 27 % of their weight during pyrolysis. Increasing the concentration of the filler linearly decreases the weight reduction to 20 % at 18 wt % filler. This reduced weight reduction is rooted in the reaction of the decomposition gasses with alumina. Detailed optical microcopy of the pyrolyzed samples with low concentrations of filler shows that there are some large cracks within each of the pieces (Figure 2a, b). However, the images of the samples containing higher concentrations of filler show that the resulting material is free of defects observable with the optical microscope (Figure 2c). For optical microcopy, the samples were embedded in low viscosity epoxy which was then cured, cut and polished.



Figure 1: Nano-modified pre-ceramic polymer, (a) samples with different concentrations of alumina nano-filler before the pyrolysis, (b,c) after the pyrolysis, (d) weight reduction as a function of concentration of alumina nano-filler filler



Figure 2: microscopic images of the ceramics samples with different concentrations of alumina nano-filler, (a) no filler, (b) 2 wt% alumina nano-filler, (c) 6 wt% alumina nano-filler. The cross-section of the samples with 18 wt% alumina nano-filler was very similar to the one with 6 wt% filler.

Existing advanced manufacturing technologies initially established for polymer matrix composites can possibly be adapted to develop cost-effective near-net-shape CCFCs. In this study, an automated process based on preceramic polymer impregnation of a ceramic fiber preform was employed to fabricate near net-shape CFCCs. The ceramic fiber pre-form was initially formed on a CNC-machined aluminum mold. This pre-from was then placed in a vacuum bag in which the pre-ceramic polymer (nano-modified as well as plain) was injected (similar to vacuum assisted resin transfer molding process). The sample went through the same curing-pyrolysis process used for the pre-ceramic polymer. Figure 3 shows the pictures of the vane before and after pyrolysis. The presence of fibers would hypothetically improve the toughness of the ceramic [10]. Our initial inspections show that adding the nano-filler improves the density and quality of the CCFCs after a single infiltration-pyrolysis process. However, the part still needed to be infiltrated-pyrolyzed multiple times to make a void free component. In terms of processing, the methods developed here can be further improved to make dense CCFCs in a single impregnation-pyrolysis process significantly decreasing the manufacturing time.



Figure 3: small vein made by polymer derived CCFFs, (a) before pyrolysis, and (b) after pyrolysis

# **3** CONCLUSIONS

This study shows how active nano-fillers and hydrostatic pressure during pyrolysis of pre-ceramic polymers can improve the integrity and as a result the mechanical properties of the resulting ceramic. The nano-modified pre-ceramic resin was also used to fabricate CFCCs through a ceramic fiber pre-form infiltration-pyrolysis process. The results show that using nano-active fillers can result in reducing the number of infiltration-pyrolysis cycles required for making dense CCFCs. Detailed quasi-static, cyclic, and impact testing of developed CCFCs at room and elevated temperatures are required for the optimization of CCFCs, which is the subject of future studies. The high temperature stability and environmental resistance of the resulting CCFCs will also be tested. In longer term, next generation of large and complex aerospace structures with improved performance can be fabricated at significantly lower manufacturing costs using the methods developed here. This study can also lead to the expansion of CFCCs applications to areas not anticipated today due to the cost prohibition.

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