

Inspired by Abalone Shell: Strengthening of Porous Ceramics with Polymers

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INTRODUCTION

Alumina ceramics have long been of technological importance. However, their brittleness limits their potential for use in structural applications.¹ Traditional approaches proposed to improve the strength and reliability of ceramics include: decrease flaw size, improve fracture toughness and flaw insensitivity, and decrease applied stresses.² Polymers on the other hand, although weak, possess very large inelastic strain. Mixing of polymers and ceramics on the molecular level can be thought of as a route to enhance the brittleness of ceramics or the strength of polymers. Polymer-ceramic nanocomposites are divided into two categories: 1) polymer matrix reinforced with nanosize ceramic particles and 2) polymer chains molecularly dispersed into ceramic matrix. Recently, strength enhancement of porous ceramic matrices through infiltration of polymers into their porous structure has been observed for hydroxyapatite ceramics, intrinsically weak bio-ceramics,³⁻⁶. However, the strength of this ceramic is similar to or lower than the strength of the polymer used for impregnation, thus strength enhancement is expected by the simple addition of a stronger material. In this study, we present an approach to enhance the mechanical properties of strong alumina ceramics through impregnation with acrylate based polymers ranging from homopolymer (poly(methyl methacrylate) (PMMA) to a zwitterionic ionomers with two nonionic monomers, a cationic monomer and an anionic monomer. The pristine alumina ceramic is at least five times stronger than the polymers used. Therefore, in this case a weaker material is used to strengthen a stronger one. The strength enhancement we observe correlates with polymer-alumina interactions on their interface.

EXPERIMENTAL

Alumina Bars. 52% dense laminated alumina tapes were prepared by tape-casting from 750 nm alumina-particle suspension and sintering at 1300°C for 1 h. Bar dimensions are 25x5x2 mm.

Polymer Synthesis. Ionomers (cationic, anionic and zwitterionic), poly(methyl methacrylate), polystyrene and polypropylene were used for the impregnation of partially sintered alumina bars. These polymers were prepared by free radical polymerization at 60°C using thermal initiator (Vazo 52). Table 1 shows the monomers and the molar ratio of each monomer for the polymers used in the infiltration of the porous alumina bars.

Infiltration of Polymers into Alumina. 3 different methods have been used to infiltrate the above-mentioned polymers into the pores of the alumina bars including: solvent infiltration, melt infiltration, and monomer and initiator infiltration followed by in-situ polymerization inside the alumina pores. In both solvent and in-situ polymerization methods, the alumina bars were initially vacuumed for 1 h, and the polymer solution or the monomers were then introduced through dropping funnel. The polymerization starts by heating the monomer solution to 60°C. In melt infiltration, the alumina bars covered by solid polymer films were vacuumed for 1 hr, and then heated to 150-200°C allowing the polymer to flow into the alumina pores.

Mechanical Properties. 3-point bending test was used to measure the mechanical strength of the pristine and polymer infiltrated alumina bars. On average of 3 to 9 bars are tested for each sample.

Table 1. Composition of Polymers used in the Infiltration of the Partially Sintered Alumina. Last column shows method of infiltration method (S=solvent, I=In-situ polymerization, M= melt)

#	Butyl methacrylate	Methyl Methacrylate	Methacrylic Acid	Amonium Chloride-Acrylate	Styrene	Propylene	Infiltration method
1	-	-	-	-	-	-	
2	41	52	4	3	-	-	S
3	41	52	4	3	-	-	I
4	41	52	7	-	-	-	I
5	41	52	-	7	-	-	I
6	-	84	8	8	-	-	I
7	-	91	9	-	-	-	I
8	-	91	-	9	-	-	I
9	-	100	-	-	-	-	I
10	-	-	-	-	100	-	M+I
11	-	-	-	-	-	100	M
12	-	100	-	-	-	-	I*

RESULTS AND DISCUSSION

The 52 v/o alumina has fracture strength of 74±7 MPa as measured by 3-point bending test. The infiltration of polymers into the pores of the alumina bars leads to reduction in their porosity, as expected. Moreover, there is significant enhancement of the fracture strength of the alumina bars upon infiltration. The degree of enhancement depends on both the amount of the polymer infiltrated (the final open porosity) and the polymer chemistry. Figure 1 shows the fracture strength of the alumina bars before and after infiltration with different polymers. Numbers on the Figure represent the sample number as described in Table 1. Samples 2 through 8 were infiltrated with different ionomers including anionic (samples 4 and 7) cationic (samples 5 and 8) and zwitterionic (samples 2, 3, and 6) polymers. Samples 2 through 5 have the same nonionic monomers, butyl methacrylate and methyl methacrylate. On the other hand, samples 6 through 8 have methyl methacrylate as the nonionic monomer. In general, for samples 2 through 8 there is up to 80% increase in the fracture strength of the alumina that is also dependent on the amount of polymer added. Moreover, non-ionic polymers such as PMMA (sample 9), polystyrene (sample 10) and polypropylene (sample 11) strengthened the alumina to different extents in the order: PMMA > poly(styrene) > poly(propylene). Poly(propylene) showed no significant effect on the strength of the alumina bars.

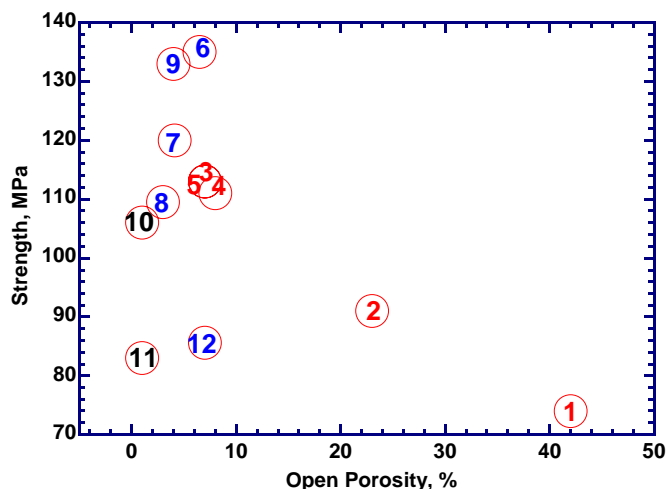


Figure 1. Fracture strength of pristine and polymer-impregnated alumina tapes. Number corresponds to the polymer structure and composition indicated in Table 1. Note sample 12 is the same as sample 6 except the alumina surface was modified by chloro-trimethyl silane

An important and very interesting observation is that the treatment of the alumina surface with chloro-trimethyl silane had a large impact on the strength enhancement. Infiltrating the alumina bars whose surface was pretreated with chloro-trimethylsilane (sample 12) resulted only in a slight increase in the strength after infiltration with PMMA (sample 12). Without passivating the alumina surface with the silane, the strength enhancement would be expected to be nearly 80%.

CONCLUSIONS

The tensile strength of the polymers used in this study (5-20 MPa) is much lower than the strength of the alumina (74 MPa). Therefore, the strength enhancement is attributed to interactions between the polymer and the alumina at the alumina-polymer interface. The level of enhancement also suggests these interactions are most pronounced when acrylate based polymers. The affect of chlorotrimethylsilane surface treatment impacts the alumina-polymer interface and thus the strength enhancement is eliminated. Ongoing research is focusing on the nature of the polymer-alumina interface interactions, and the mechanism by which these surface interactions translate into enhanced mechanical strength.

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