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Effect of initial cure time on toughness of geopolymer matrix composites

Patrick R. Jackson*, Donald W. Radford

Composite Materials, Manufacture and Structures Laboratory, Mechanical Engineering, Colorado State University, Fort Collins, 80523-1374 CO, USA

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ABSTRACT

The toughness of geopolymer matrix composites (GMC) has been identified as a limiting factor to their use in structural applications. Advanced ceramic matrix composites (CMC), which also are limited by brittle behavior, have shown gains in toughness through careful tailoring of the interface between fiber and matrix. This can create various crack dissipating mechanisms and prevent premature composite failure. Such interface modification has already been applied to a fiber reinforced geopolymer and while the resulting composite showed a reduction in brittle behavior, the modified interface produced an unacceptable loss in modulus without any other well-defined quantitative gains. Information gathered from other studies suggests the large decrease in modulus observed in the GMCs with the weakened interface may have been the result of poor matrix properties stemming from an inadequate cure. Therefore, this current study explores the effects of initial cure time on composite performance by measuring the mechanical properties GMCs with a modified interface. GMCs containing unidirectional Nextel 610 fiber were cured under two different sets of process conditions to better understand the influence of matrix properties. Additionally, specimens consisted of cleaned and carbon coated fiber surfaces, in an attempt to evaluate extremes of interfacial strength. Mechanical properties were then evaluated for comparison to determine if improved geopolymer matrix properties would allow a weakened interface to yield performance gains more in keeping with expectations based on CMC's. The results of the study indicate that specimens with carbon coating benefited from the longer initial cure time. The average increase in flexural modulus and strength over samples with one hour initial cure time was ~65% and ~170% respectively. Stress-strain behavior of the carbon-coated specimens with an extended cure time also indicated a greater degree of damage tolerance as compared to those without interphase.

1. Introduction

Inorganic, non-crystalline alumino-silicates, known as geopolymers, have emerged over the last several decades as a matrix material option in composites. Fiber reinforced geopolymers were first introduced by Davidovits in the 1980s [1]. Geopolymers are an appealing matrix material because they are capable of continuous operation at temperatures well beyond the upper use temperatures of organic polymers, yet share similar processing methods, requiring only relatively low temperatures. As such, geopolymer matrix composites (GMC) are produced at much lower temperatures than those of conventional ceramic matrix composites (CMC) therefore avoiding the development of thermally induced residual stresses at the fiber-matrix interface [2–4]. Sometimes good, sometimes bad, these residual stresses can be responsible for matrix cracking and modifications to mechanical bonding at the interface through tensile or compressive stresses [2,3]. In other words, these stresses can alter the degree of frictional shear stress where fiber and matrix meet. These factors, in addition to their relatively low densities, make geopolymer matrix composites (GMC) ideal candidates for use in intermediate temperature structural applications (up to approximately 800 °C).

Carbon fibers have often been the reinforcement of choice for GMCs, but for high temperature applications, in air, oxidation resistant fibers become imperative. For such elevated temperatures in an oxidative environment, SiC fibers have most commonly been utilized to reinforce the geopolymers. Only a handful of studies have explored the use of alumina-based ceramic fibers [5–8], which are also candidates for such applications. The limited number of studies using this type of fiber is most likely the result of the governing assumption, and evidence-based results from studies on CMCs, that the chemical similarity of the two constituents could result in the loss of a defined interfacial region due to diffusion at elevated temperatures. This concern is very appropriate. Both research generated at the Composite Materials, Manufacture, and Structures laboratory and a separate study have identified toughness as a limiting factor to the future use of these GMCs [6,9]. In an attempt to overcome this

* Corresponding author.
E-mail address: pjackson_04@yahoo.com (P.R. Jackson).

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limitation, research on weak interface concepts was conducted to understand whether this technique, successfully used in ceramic matrix composites, would be appropriate for GMCs [2,10]. Using a carbon coating to modify fiber surfaces, these studies demonstrated the potential of an interphase material to improve the damage tolerance of GMCs through pseudo ductility and non-catastrophic failure [7]. Unfortunately, the specimens with these altered fiber surfaces showed no gains in strength and a significant loss in composite modulus when tested in flexure. This reduction in modulus was troubling for any future efforts to promote toughness in GMCs via modified fiber-matrix interface properties.

The less than desirable result highlights a major consideration of the direct transfer of interphase technology from CMCs to GMCs. In CMCs, the bond is tailored to prevent strong bonding between the constituents. This allows crack energy dissipating mechanisms to be active in the composite and ultimately increases the toughness [11]. The trade-off of reduced interface strength is a reduction of load transfer from matrix to fiber, which ultimately affects composite modulus. However, for CMCs, with very similar constituent material moduli, this reduction in the interface strength has only a small effect on the composite modulus. As the disparity in moduli of the constituents increases, such is the case for GMCs (see Table 1), a stronger interface with a higher degree of load transfer is desirable in order to maintain effective reinforcement within the composite. The challenge in GMCs then is determining whether interfacial conditions exist that allow for both crack blunting and sufficient load transfer between the fiber and matrix to take advantage of the properties of the reinforcing fibers.

This present work, investigating GMCs toughness through the use of a modified interface, is a follow-on from a pair of recent studies using the same geopolymer resin system, MEYEB, supplied by Pyromeral Systems. One recent study found that a weakened fiber-matrix interface resulted in a significant reduction in flexural modulus, while the other study indicated improvements in the mechanical properties of the neat geopolymer matrix material with extended duration hydrated cures [7,19,21]. The previous studies investigating the effectiveness of a weak interface in unidirectional Nextel 610/MEYEB composites used the recommended 1-h cure at 80 °C [7]. The use of cure times exceeding one hour is common in the literature involving a variety of unreinforced geopolymers and longer cure times have also been reported in many studies involving reinforced geopolymers [8,12,14,22,23]. After investigations of cure cycle modifications for neat MEYEB geopolymer resin, it was determined that longer duration hydrated cures could result in as much as a 42% reduction in pore diameter and a 30% improvement in compressive strength [19,21]. These improvements were credited to sufficient time in humid environment, thus preventing drying and allowing for more complete poly-condensation. Other researchers have also noted significant variations in mechanical properties of geopolymers with variations in cure time and methods, and have related these variations in properties to changes in the concentration of porosity [8,13,24].

The goal of the present work is to reexamine the effect of interphase coatings on the mechanical performance of Nextel 610 reinforced MEYEB GMCs as a function of the geopolymer degree of cure. Fiber surfaces are modified from the as-received condition to create different interfacial properties and the composite specimens are subjected to different cure cycles prior to flexure testing to evaluate the process-induced response.

2. Experimental

2.1. Materials

Nextel 610 (N610) unidirectional fiber tows were used in the fabrication of composite samples. The chemical composition of the Nextel 610 fiber is > 99% alumina (Al_2O_3). The sizing on the fiber is 100% organic and mostly composed of poly-vinyl alcohol (PVA) [25]. This sizing is generally removed for CMC applications; however, it has been found that the PVA can be converted to a form of carbon through pyrolysis in an inert environment. For this geopolymer matrix composite research effort, fiber surfaces were modified from the as-received condition by heating in; (a) air or (b) N_2 to create two different fiber surface conditions: cleaned (CL) and carbon coated (CC) respectively. In both cases, groups of fiber tows were placed in an oven, heated to 700 °C at 5 °C/min and held at temperature for 15 min prior to cooling to room temperature.

A liquid inorganic polysialate polymer resin system, referred to as MEYEB, supplied by Pyromeral Systems was used as the geopolymer matrix. In general, the chemical make-up of a geopolymer is a network of 3D silicate (SiO_4) and aluminate (AlO_4) tetrahedrals charge balanced by a positive alkali ion [1]. MEYEB is charge balanced by potassium (K^+). MEYEB was shipped in a cryogenic state from the manufacturer and subsequently stored at −25 °C to increase the usable life. Upon removal from storage, the material has an approximate working time of about 30 min at room temperature and a viscosity similar to many commercial epoxies.

2.2. Fabrication

The MEYEB resin was removed from storage, stirred, and then poured onto a premeasured number of tows with a goal of 50% fiber volume fraction (V_f). The fibers were wet out using hand lay-up techniques. The wetted fiber tows were then placed in the cavities of a stainless steel die which had been pretreated with Frekote NC-770 release agent (Fig. 1).

After placing the T-bars in the corresponding cavities, the complete die assembly was placed in an evacuated bag for two to three minutes to draw out excess resin and remove entrapped air. Remaining in a sealed bag to reduce moisture loss, but no longer under vacuum, the die was moved to a hot press where heat and pressure were applied. The applied pressure was required to close the die to a fixed stop, generating constant cross-sectional dimensions. The temperature was allowed to rise from room temperature at 1 °C/min to 80 °C. Still in a sealed bag in the hot press, the die containing the samples was held at 80 °C for either one or five hours to evaluate cure duration effects. After this initial 80 °C cure, the bag was vented to atmosphere and the stainless steel die was moved to an oven where samples remained at 80 °C, for several more hours, before beginning the follow-on post cure.

Table 1
Properties of GMC and CMC matrix materials and fibers.

	Tensile strength (MPa)	Young's Modulus (GPa)	Compressive strength (MPa)	Flexural strength (MPa)	Flexural Modulus (GPa)	Ref.
Geopolymers	3.7	5–10	39–45	1.7–16.8	5–11	[8,12–19]
SiC	310	400–440	4600	–	–	[3,20]
Alumina	250–300	360–400	3000	400	–	[3,20]
SiC type fibers	2000–3500	200–400	–	–	–	[3]
Alumina type fibers	1000–3100	100–380	–	–	–	[3]
Carbon type fibers	2000–3450	230–700	–	–	–	[3,20]