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Strength retention of fire resistant aluminosilicate–carbon composites under wet–dry conditions

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Abstract

The results of an experimental investigation of the durability of inorganic matrix–carbon composites are reported. The matrix, which can sustain temperatures up to 1000°C, is being evaluated for applications that require fire resistance, such as the interior of aircraft. The original matrix formulation, which had a high ratio of silica to alumina, was found to weaken when subjected to wet–dry cycles. Preliminary tests indicated that an efficient way to increase water-stability was to increase the amount of alumina in the matrix. Therefore, a systematic evaluation was carried out to obtain the optimum silica/alumina ratio for improving stability of composites in water. In-plane shear strengths were used as an indicator of strength retention after the specimens were subjected to 50 wet–dry cycles. The results indicate that silica/alumina ratio between 18 and 20 provide the best results. In this range, strength loss is negligible.

Keywords: A. Ceramic matrix composites; Fire-proof composites

1. Introduction

Flammability of organic matrices limits the use of fiber reinforced composites in applications where fire is an important design parameter, such as the interior of aircraft. Many of the commonly used organic matrix materials soften and ignite at 400–600°C [1]. This is unacceptable in structures where egress is restricted. Composites made using inorganic matrices can be utilized when high use temperatures are expected. Research on Geopolymer materials is being conducted at Rutgers, The State University of New Jersey. The primary focus of this research is to characterize the mechanical properties of composites made with this new inorganic matrix.

Extensive evaluation of the mechanical properties has been carried out and the results are reported in Refs. [1–4]. The major findings can be summarized as follows:

Geopolymer composites have fire properties that are superior to all organic matrix composites currently available. The fire properties, that were obtained from an oxygen consumption calorimeter, are: weight loss, time to ignition, peak heat release rate (HRR), 300 s average HRR, total heat release, and smoke production. Table 1 compares Geopolymer's fire properties to organic matrix materials that are currently used in aircraft interiors. In addition to these properties, perhaps the best indicator of fire resistance is the predicted time to flashover value that is obtained from the ISO 9705 room corner test. Flashover occurs in closed compartments when flammable gasses from material combustion are finally heated to a point where they ignite. This event marks the end of human survivability in post-crash scenarios. Fig. 1 shows the time to flashover of the aforementioned composites. The Geopolymer composite had an infinite time to flashover. This is the logical result for an inorganic matrix composite. There is no flammable material in the composite; hence there can never be a flashover.

Composites made with 3k plain weave carbon fabric and Geopolymer had a tensile strength of 327 MPa and a flexural strength of 245 MPa. Both of these values are comparable to the strengths from similar organic matrix composites. Geopolymer composite samples retained 63% of their flexural load carrying ability after 1 h of exposure at 800°C. In shear, Geopolymer samples had a strength of 14 MPa. This strength decreases to a value of 4.6 MPa for samples heated to 1000°C for 1 h.

Under fatigue loading, composites made with Geopolymer matrix can sustain about 10 million cycles at a stress

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Table 1
Fire property data [1]

Resin family	Weight loss (%)	Time to ignition (s)	Peak HRR (kW/m^2)	300 s Average HRR (kW/m^2)	Total heat release (MJ/m^2)	Smoke (m^2/kg)
Thermosets	24	68	175	99	33	1077
Advanced thermosets	19	124	115	86	43	538
Phenolics	11	206	111	66	23	142
Engineering thermoplastics	8	207	35	22	15	310
Geopolymers	0	∞	0	0	0	0

range of 40% of ultimate strength and a minimum stress of 10% of ultimate strength. This gives an average stress of 30% of ultimate. The endurance limit for these Geopolymer composites is 35%, meaning that the composite can sustain infinite cycles if the stress range is less than 35% of the ultimate strength.

When these carbon–inorganic matrix composites were subjected to wet–dry cycles, the flexural strengths were found to deteriorate rapidly. Since carbon fibers do not degrade in water, the matrix was assumed to contribute entirely to the degradation of the composite strength, and an experimental investigation was undertaken to improve the matrix performance. In order to eliminate the contribution of strength from the carbon fabric, but maintain the fiber–matrix interaction, it was decided that interlaminar shear strength of the composite would be used as a response variable for the study of degradation. In this mode of loading, the shear strength of the matrix is measured, but at the same time there is interaction between the fiber and the matrix. More details of the test can be found in ASTM D-3518 test procedure [5].

Based on the chemistry of dissolution in water, it was expected that lowering the silica/alumina ratio in the matrix would improve its stability in water. In the first set of samples, a wide range of silica/alumina ratios were evaluated by testing a single layer of 3k plain weave carbon in $\pm 45^\circ$ tension [6]. The use of single ply specimens does not comply with ASTM standards, but as so many samples had to be considered, following ASTM standards for each sample would have been too time consuming. The results of this preliminary testing provided good initial indications of strength degradation. Sample preparation, wet–dry exposure, and testing were done using the same procedures for phase 2 of the investigation, described in subsequent sections.

Based on the results of phase 1, five sets of samples with multiple layers were made for a more systematic evaluation. In this phase, in addition to altering the silica/alumina ratio, the effect of a water repellent was evaluated. Preliminary tests indicated that the water repellant not only reduced the affinity for water absorption in the cured sample but also provided better flowing characteristics in the uncured matrix resulting in less air voids and reduced water permeability.

The details of the composition of all five-sample sets are presented in Table 2. The first set had the same composition as the matrix that was used to determine the mechanical and temperature resistance properties. Sample sets 2 and 3 had higher alumina contents. The alumina contents were chosen based on the preliminary tests that covered a wider range of silica/alumina ratios. Sample set 4 was chosen to evaluate whether water repellant could have a synergistic effect with the lowered silica/alumina ratio. Finally, sample set 5 was chosen to determine whether the water repellant alone could improve durability.

As mentioned previously, in-plane shear tests were used to determine the strength retention of the matrix because they measure only the matrix strength [7]. With fibers aligned at $\pm 45^\circ$ to the axis of testing, none of the load carrying ability of the specimens can be attributed to the fabric.

2. Sample preparation

The samples were prepared using hand pre-preg and vacuum bagging technique [8]. The matrix consisted of a liquid component of potassium silicate, and a powder component of alumino-silicate. These two components were mixed using a high shear mixer for 1 min to obtain a smooth uniform mix. The mix was stored for 30 min at 5°C for maturation and release of entrained air bubbles. The 3k PAN based carbon fabric layers were impregnated with matrix manually then stacked in a $[\pm 45]_{2s}$ pattern for a total of 8 layers and placed in the vacuum bag setup. In the vacuum bag, the stacked fabric was covered with a Teflon release ply and a breathing layer to allow for the continued removal of entrained air. Next, the bag was placed into a heated press at 80°C and 3 MPa. The temperature was ramped from 80 to 150°C over 1 h. The sample was maintained at 150°C for 1 h, and then cooled to room

Table 2
Sample information

Sample designation	Silica/ alumina ratio	Water repellant added	Density (g/cm^3)
1	27.0	No	1.85
2	18.2	No	1.82
3	19.7	No	1.84
4	19.7	Yes	1.92
5	27.0	Yes	1.88

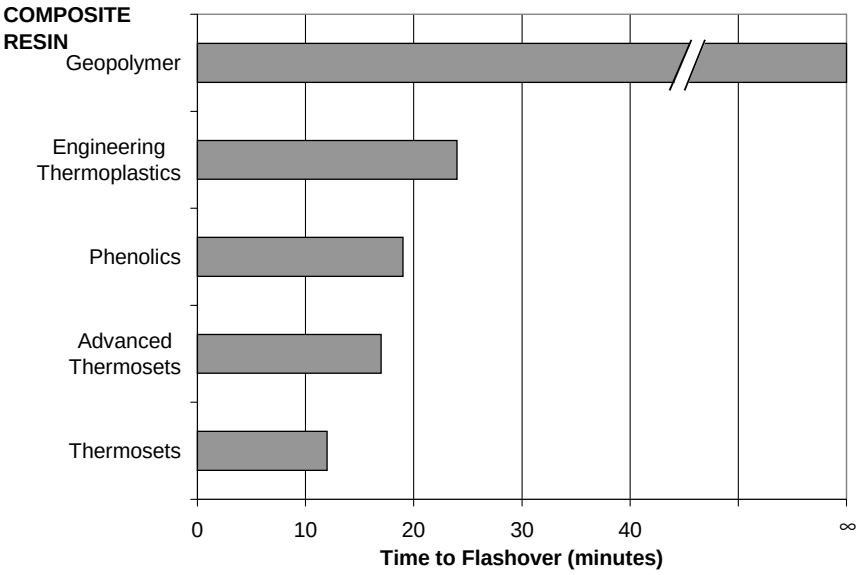

Fig. 1. Time to flashover [1].

temperature in approximately 4 h. Specimens were cut from the sample using a diamond saw blade. The thickness of the specimens was checked to assure uniformity and density measurements were taken using water displacement method.

3. Sample conditioning: wetting and drying

Sample conditioning for wetting and drying consisted of a stainless steel container for storing water, a high velocity fan for drying, electronic switches to control water inflow and outflow, and a mechanism to control water temperature (Fig. 2). A special support system was fabricated to suspend the specimens in the container to prevent specimens touching each other or the side of the container.

The cylindrical storage chamber had a capacity of 150 l. Cold and hot tap water was mixed before entering the chamber, and the proportions were controlled to achieve a water temperature of 50°C in the chamber. The specimens were soaked for 2 h. After this, the electronic control opened the outlet valve to drain the chamber, and at the same time turned on the high velocity fan to begin the drying process. A drying cycle time of 3 h was chosen to assure complete drying of all specimens. After the 3 h drying process, the electronic control closed the outlet valve and turned off the fan. Next, the inlet valve was opened and the chamber was again filled with warm water. One full cycle occurred every 6 h.

Wetting in warm water and drying under the high velocity fan provided an extremely corrosive environment, causing visible rust to steel bars in about three cycles. All of the fixtures were made of stainless steel or plastic to prevent corrosion. It should be noted that the water was not

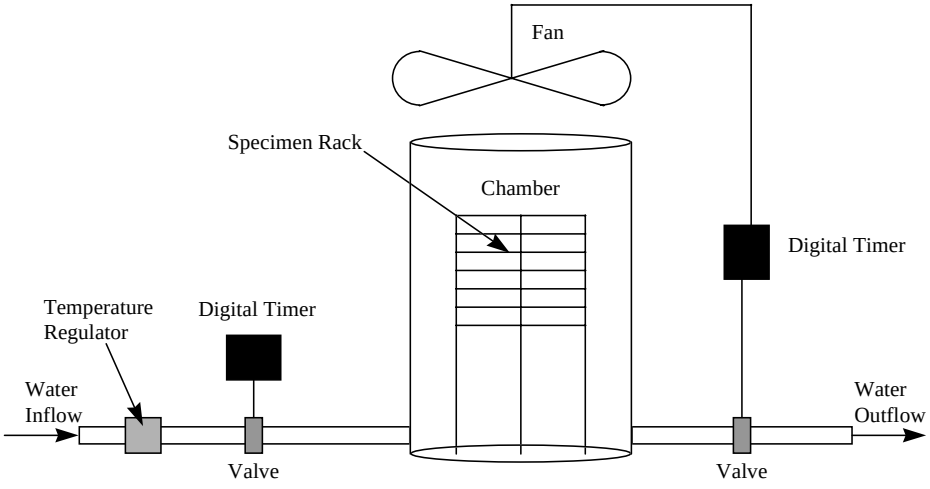

Fig. 2. Schematic diagram of wet–dry chamber.

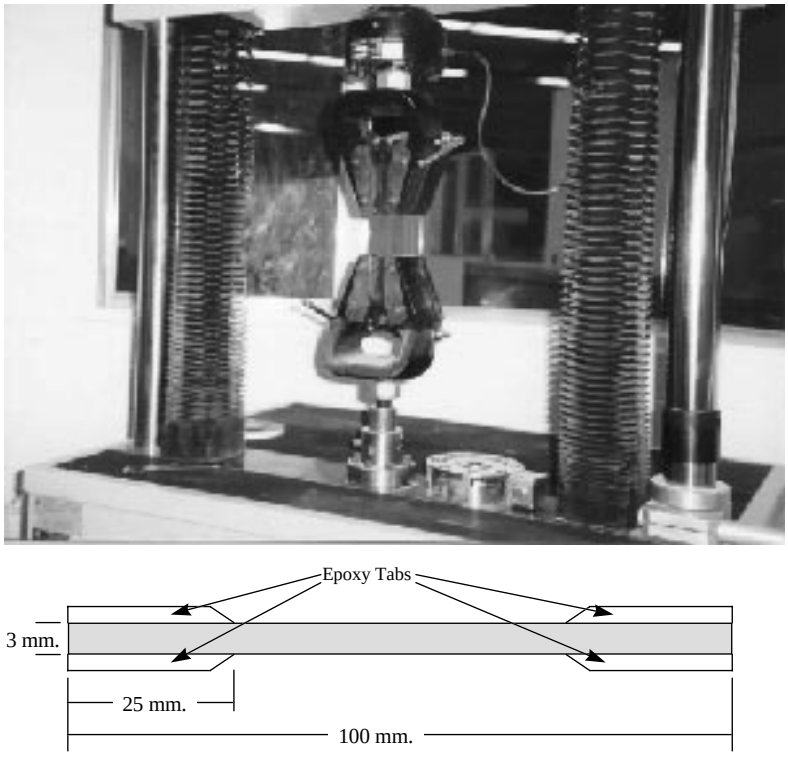

Fig. 3. Test sample and setup.

recirculated and thus any chemicals that were leached from the samples did not influence the water quality of the subsequent cycles.

4. Test procedure

All tests were conducted in accordance with ASTM D-3518 using a 50 kN MTS Sintech test frame. The load was applied under displacement control at a rate of 2.5 mm/min (Fig. 3). Epoxy tabs were applied to the specimens to allow for better gripping. Since the primary interest was the in-plane shear strength, only the peak load was recorded for each test. The shear stress was obtained from the equation:

$$\tau = \frac{P}{2A}$$

where τ is the in-plane shear stress (MPa), P the maximum tensile load (N), and A the cross-sectional area (mm^2).

5. Test results and discussion

The strength results are presented in Table 3 and Fig. 4. As expected, the failure plane in all tested specimens was inclined at 45° to the axis of loading. A typical failed sample is shown in Fig. 5. A careful study of Table 3 and Fig. 4 and observations made during the sample preparation lead to the following discussion.

Addition of water repellant made the matrix more flowable and therefore the matrix filled the air voids during curing. This resulted in a higher density for silica/alumina ratios of 27 and 19.7 when the water repellent was added.

Table 3
Test results

Sample designation	Silica/alumina ratio	Initial strength		Strength after 50 cycles		Shear strength retained (%)
		Shear strength (MPa)	Standard deviation (MPa)	Shear strength (MPa)	Standard deviation (MPa)	
1	27.0	13.3	0.5	7.8	0.3	58.6
2	18.2	20.3	1.0	21.5	0.7	105.9
3	19.7	16.8	0.3	15.3	1.3	91.1
4	19.7	16.7	1.4	17.0	1.2	101.7
5	27.0	12.5	1.4	7.6	1.3	60.8

Fig. 4. Tested specimen.

However, the shear strengths decreased in both cases. The initial shear strength increased from 13.3 to 16.8 and 20.3 MPa when the silica/alumina ratio was decreased from to 27 to 19.7 and 18.2, respectively. These results concur with those seen in the preliminary phase of the investigation. Further increase in alumina was found to decrease the strength of the matrix, and it was observed that the matrix became chalky with the addition of more alumina. Silica/alumina ratios in the range of 18–18.5 seem to be optimal.

After wetting and drying, the contribution of higher alumina content was much more substantial. While samples in set 1, with the ratio of 27, lost about 41% of their strength, samples in set 2 continued to gain about 6% strength. The authors believe that the matrix continues to cure in spite of the adverse exposure conditions.

Reduction of the ratio to 19.7 was not sufficient to completely prevent strength loss, but the addition of water repellent had a synergistic effect and prevented strength degradation. However, strength values were still lower than that obtained using a ratio of 18.2. When the silica/alumina ratio was high, the water repellant did contribute to the stability under wet–dry conditions, but the effects were not substantial.

6. Conclusions

Based on the results obtained from this investigation, it is clear that the silica/alumina ratio has a significant effect on both the strength and water stability of Geopolymer matrices. Reduction of the silica/alumina ratio of the inorganic matrix increases the shear strength by as much as 53%. Another observation is that reduction in the silica/alumina ratio results in consistent improvement in the residual strength after wet–dry cycling and that the optimum ratio is 18.2. Using an inorganic matrix with the correct

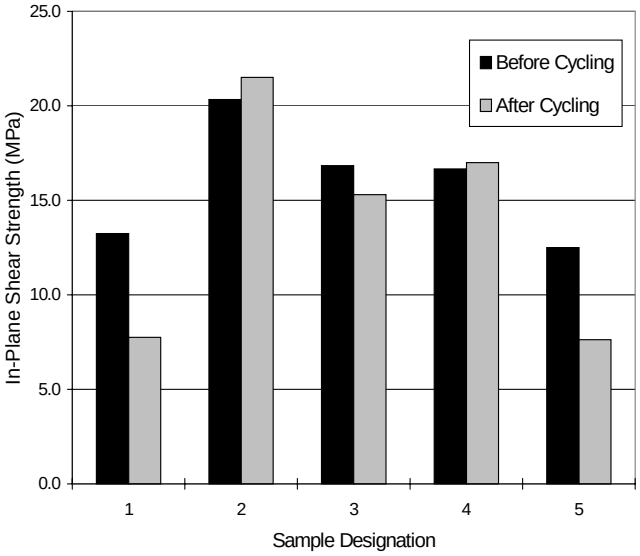

Fig. 5. In-plane shear strength both before and after cycling.

silica/alumina ratio, it is possible to obtain water stable composite.

Further research is currently being conducted to investigate the effect of silica/alumina ratio on the fire response and mechanical properties of Geopolymer composites.

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