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Functional Geopolymer Composites for Structural Ceramic Applications

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Submitted by

Christian Defazio *
Research Assistant

Mohamed Danish Arafa*
Research Assistant

Dr. P.N. Balaguru*
Professor

* Center for Advanced Infrastructure & Transportation (CAIT)
Rutgers, the State University of New Jersey
Piscataway, NJ 08854-8014

Project Manager
Balakrishnan Nair

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16. Abstract

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ABSTRACT

The results of an experimental investigation on the behavior of milled and short-fiber reinforced composite plates are presented in this paper. The target operating temperature for the plates was 1300°C. The principal variables were the type and volume fraction of fibers and the matrix composition. Three fiber types and five fiber contents ranging from 2.5 to 10 weight percent were evaluated. The density of the samples varied from 1500 to 2800 kg/m^3. For the matrix, the ratio between alumina and silica was varied from 1:1 to 5:1. The flexural tensile strength, (modulus of rupture) varied from 10 to 95 MPa. The modulus of elasticity varied from 5 to 60 GPa. There is a strong correlation between the unit weight and the mechanical properties of strength and modulus. Load-deflection response in flexure, strength and stiffness for the various mix formulations and their relation to unit weight are presented.

1. INTRODUCTION

Composite materials are widely used in all types industries. The requirements depend on the type of application. Ceramic composites are popular in applications where materials are expected to encounter high temperatures; such as engine components, exhaust systems and fire barriers. The low density as compared to metals makes them attractive in applications where weight is a critical design parameter. Most of the ceramic composites are fabricated using heat treatment and often the operating temperatures are lower than the temperatures used for the fabrication of the component. For the research reported in this paper a modified version of an inorganic resin known as Geopolymer was used. Typical Geopolymer can sustain temperatures up to 800°C. This composition was evaluated for a number of applications that require fire-resistance, such as the interior of an aircraft (1). This low-cost, inorganic polymer is derived from naturally occurring geological materials, namely silica and alumina, hence the name Geopolymer. Geopolymer is a two-part system consisting of a silicate liquid and a silica powder and cures at a reasonably low temperature of 150ºC. Hardeners can be added to achieve room temperature curing (22ºC). The matrix has been used to fabricate standard laminate composite plates with carbon, glass, and silicon carbide fibers, sandwich structures using syntactic foam, and strengthening of brick, masonry, and reinforced concrete elements (2).

The primary objective of the current investigation was to develop a composite that can sustain at least 1350ºC and have a flexural strength of 75 MPa. Additional objectives were to keep the fabrication temperature to a minimum and use commercially available economical materials. Modifications were made to the basic Geopolymer to attain a higher operating temperature. The modified composition can sustain 1400ºC for long term exposure. Alumina fibers were added to the base matrix for obtaining higher flexural strengths. Three types of alumina fibers were evaluated. The first one was in a paper form and the second fiber type consisted of randomly distributed very short fibers. These fibers were designated as milled fibers. The third type consisted of discrete short fibers that were much more uniform as compared to the second type. The third type of fibers was more expensive than the second. Approximately one hundred coupon samples were tested in flexure with varying alumina to silica ratios, fiber content,

fabrication methods, and curing temperatures. The primary focus of the results presented in this paper was to evaluate the effects of fiber percentages and fabrication methods on the density and flexural properties of the coupons.

2. RESEARCH PROGRAM

The research program was designed to obtain high temperature composites with different densities. As expected the lower density compositions had a lower flexural strength. But these formulations provide a better insulation and hence might be useful in applications that require low heat conductivity. The primary variables were matrix composition, fiber type, fiber content and fabrication method. Curing temperatures were also evaluated but the results are not presented in this paper. The following sections provide a brief discussion regarding these variables. Summary of all the variables and specimen designations are presented in Table 1.

2.1 Matrix Composition and Fibers

Geopolymer was used as the base mix. Silica/Alumina ratio was changed to improve high temperature resistance. For the samples with papers, a higher Alumina/Silica ratio was used as compared to other samples. The stability of the composition was verified by exposing the samples to 1400ºC for a minimum of 30 minutes. Three different types of fiber reinforcements namely: reformatted alumina, milled alumina, and short ceramic fibers were evaluated. All of the three forms are commercially available for purchase. The reformatted alumina fiber is a paper type material that is available as rolls or cut sheets. Thicknesses of 1.6mm and 6.35mm were used to fabricate the samples. The two thicknesses resulted in fiber contents of 9 and 13%. The second type of reinforcement was milled alumina fibers. This material had cotton-like consistency and was bulky. The fiber contents for these fibers were: 4.4, 4.5, 6.5 and 9.6%. The short ceramic fibers were 3 mm long and were very uniform. Fiber contents for these fibers were: 6.5, 8.5, 9.6 and 11.3%. Sample details: such as density and fiber content, are presented in Table 1. The sample designation represents a single coupon cut from an entire plate. It should be noted that only about 25 to 30 percent of the total number of coupons tested are presented in the tables. The samples tested had densities ranging from 1095 to 2901 kg/m^3. The fiber content, as well as, the fabrication processes is also shown for the various samples.

Table 1 Details of the Specimens						
Sample ID	**Density (kg/m^3)**	**Width (mm)**	**Depth (mm)**	**Fiber Type**	**Fiber Content (%)**	**Fabrication Series**
P1	1159	13.84	3.82	Paper	9	I*
P2	1181	13.85	3.64	Paper	9	I*
P3	1095	13.92	3.98	Paper	9	I*
P4	1731	13.62	2.54	Paper	13	I
P5	1672	13.03	2.69	Paper	13	I
P6	1717	13.40	2.63	Paper	13	I
M1	2777	10.06	4.17	Milled	4.4	II
M2	2688	9.91	3.59	Milled	4.4	II
M3	2748	13.03	3.85	Milled	4.5	II
M4	2703	12.86	4.07	Milled	4.5	II
M5	2754	12.90	4.10	Milled	4.5	II
M6	2654	12.81	3.96	Milled	6.5	II
M7	2675	13.21	3.93	Milled	6.5	II
M8	2901	12.60	2.38	Short Ceramic	6.5	II
M9	2695	9.04	3.13	Short Ceramic	10.5	II
V1	2573	13.43	3.10	Milled	9.6	III
V2	2733	13.58	2.49	Short Ceramic	9.6	III
V3	2735	13.68	2.40	Short Ceramic	9.6	III
V4	2890	13.41	2.63	Short Ceramic	11.3	III
V5	2770	12.69	2.64	Short Ceramic	11.3	III
V6	2856	12.55	2.60	Short Ceramic	11.3	III

*No pressure applied while curing

2.2 Fabrication Methods

Three fabrication techniques were investigated for the sample preparation. These include hand lay-up, vibration, and a hot-press process.

2.2.1 Series I

For samples made with 1.6 and 6.35 mm alumina reformatted fiber, wet lay-up with hand impregnation technique was used. The Geopolymer was prepared and poured onto alumina ply with an area of about 230 cm^2. Squeegees, brushes, and grooved rollers were used to impregnate the matrix into the paper and hence wet the fibers. This process was also helpful for removing most of the entrapped air. The impregnated plies were stacked one on top of the other until the designated thickness was achieved. The laminate was then placed in a standard vacuum bagging system and placed in a heated pressed at a pressure of 48 MPa and a temperature of 150ºC for a minimum of 3 hours. After the plate was cured, it was cut into 12 mm wide and 63.5 mm long coupons using a wet-saw with a diamond tipped blade.

2.2.2 Series II

For the samples with milled and short fibers, the matrix was mixed with fibers using a high shear mixer. The fiber reinforced mixture was placed on a plastic mold and vibrated using a table vibrator for 10 minutes. A 6 mm thick rubber plate was placed in between the mold and the vibrating table. A bungee was used to secure the mold to the table during vibration. This vibrating technique allows entrapped air to travel up through the matrix and escape from the top surface. The plates were left in the molds for 2 days to cure at room temperature. After 2 days the plates were removed from the molds and cured at 200ºC for 24 hours. After the plates have cooled down, they were cut into coupons.

2.2.3 Series III

The last fabrication technique undertaken was a vacuum bagging system in conjunction with a heated-press process. Fibers were mixed with the matrix using high shear mixer and poured into a stainless-steel mold with approximate dimensions of 150 by 150 by 20 mm. The mold filled with the fiber-reinforced mixture was placed in the standard vacuum bagging system, Figure 1. Grooved rollers were used to gently distribute the mix within the mold. The vacuum pump was turned on and again the mix was rolled to ease the distribution. The entire system was then placed into a heated-press at a pressure of 48 MPa and temperature of 80ºC. The plate would remain in the machine for 4 days while the vacuuming, pressure and heat were regulated during this time. Again, the plate was left to cool to room temperature and then cut to coupons. This process resulted in a uniform plate thickness with much lower imperfections as compared to plates made using the simple vibration technique.

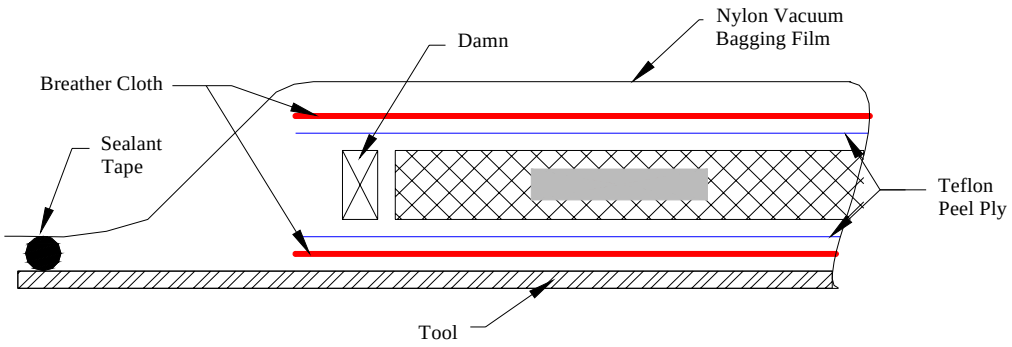

Figure 1 Vacuum bagging setup for composite plate

3. TEST SETUP

The flexure tests were conducted over a simply supported span of 50 mm with a center point load in accordance with ASTM D790 (3). The span-to-depth ratios ranged from approximately 6:1 to 11:1, both of which fell within the acceptable limits of the standard flexure test. The tests were conducted on an MTS TestWorks® system under deflection control with a mid-span deflection rate of 0.25 mm/min. Load and deflection readings were taken using a computer for the entire test duration.

4. TEST RESULTS

Flexural strength (modulus of rupture), strains at the maximum load, modulus of elasticity and density for the various test parameters are presented in Table 2. The test parameters were: fiber type, fiber volume fraction and fabrication technique. The primary response variables were: density, flexural strength, strain at failure and modulus of elasticity. Stress-strain curve for the representative samples made using paper, milled fibers and short fibers are presented in Figures 2, 3 and 4 respectively.

For easy comparison of the performance of various samples, experimentally obtained load-deflection curves were converted to flexural stress versus extreme tension fiber strain curves. This conversion makes it feasible to compare samples of varying thickness. The maximum flexural stress, σ_f , for a given moment, *M*, was computed using:

$$\sigma_f = \frac{6M}{bh^2} \qquad [2.1]$$

Where *b* and *h* are the specimen width and thickness, respectively. The extreme fiber strain, ε_t , was calculated using the following procedure. For the simply supported beam of span length, *L*, with center-point load, *P*, mid-span deflection,

$$\delta = \frac{PL^3}{48EI} \qquad [2.2]$$

or

$$\delta = \frac{ML^2}{12EI} \qquad [2.3]$$

Where *E* is Young's modulus and *I* is the moment of inertia. Since the strain at the extreme tension fiber is the curvature times one-half the thickness of the specimen, the extreme fiber strain becomes:

$$\varepsilon_t = \frac{M}{EI} \times \frac{h}{2} \qquad [2.4]$$

Combining equations [2.3] and [2.4] yields the following relationship between deflection and strain:

$$\varepsilon_t = \frac{6\delta h}{L^2} \qquad [2.5]$$

Since the load-deflection curves were linear up to failure, the aforementioned equations provide accurate values for both stresses and strains. In Table 2 flexural strength is presented as maximum stress and the strain at failure is presented as maximum strain.

Table 2 Test Results

Sample ID	Density (kg/m3)	Maximum		E (GPa)	Fiber Type	Fiber Content (%)	Fabrication Series
		Stress (MPa)	Strain (%)				
P1	1159	16	0.0918	18	Paper	9	I*
P2	1181	17	0.0937	17	Paper	9	I*
P3	1095	15	0.1046	12	Paper	9	I*
P4	1731	30	0.1216	23	Paper	13	I
P5	1772	32	0.1248	25	Paper	13	I
P6	1717	26	0.1037	26	Paper	13	I
M1	2777	62	0.1338	37	Milled	4.4	II
M2	2688	61	0.1348	37	Milled	4.4	II
M3	2748	65	0.1513	30	Milled	4.5	II
M4	2703	60	0.1699	25	Milled	4.5	II
M5	2754	55	0.1511	26	Milled	4.5	II
M6	2654	63	0.1602	26	Milled	6.5	II
M7	2675	64	0.1403	33	Milled	6.5	II
M8	2901	78	0.1522	61	Short Ceramic	6.5	II
M9	2695	91	0.1452	58	Short Ceramic	10.5	II
V1	2573	51	0.1290	46	Milled	9.6	III
V2	2733	75	0.1757	42	Short Ceramic	9.6	III
V3	2735	72	0.1760	43	Short Ceramic	9.6	III
V4	2890	97	0.1889	55	Short Ceramic	11.3	III
V5	2770	93	0.1531	61	Short Ceramic	11.3	III
V6	2856	97	0.1937	52	Short Ceramic	11.3	III

*No pressure applied while curing

5. DISCUSSION

As expected both the strength and the stiffness values are strongly influenced by the density of the samples. All the samples can withstand 1400ºC. Samples heated to 400, 600, 800 and 1050ºC were also tested in flexure. These results are not presented in his paper because of space restriction. Most samples gained strength with exposure to high temperatures. But the increases were not substantial. For clarity, the discussion of the results is presented in three groups. The following are the major observations that cover all the samples.

- It is feasible to fabricate samples using all three techniques.
- It will be easier to fabricate large samples such as plates, shells or pipes using the paper form of fibers or casting technique using vibration for compaction.
- Irrespective of fiber type and fiber content, strength and stiffness are influenced by the unit weight (density) of the samples.
- The stress-strain behavior is linear up to failure for almost all the samples.
- Flexural strength varies from 15 to 97 MPa where as the modulus of rupture varied from 12 to 61 GPa.
- Failure strain varied from 0.09 to 0.19 percent. Both higher modulus and increase in failure strain capacity contribute to increase in flexural strength. Note that toughness also increases with increase in modulus of elasticity and failure strain.
- As expected short ceramic fibers provided the best results because these fibers had much better mechanical properties and they were easier to disperse. Fibers in paper form had the least strengths. But they also had the lowest density. For applications that require better thermal insulation these formulations have an advantage. Note that these composites can be used as cores to fabricate sandwich beams or plates to satisfy the strength and stiffness requirements.
- Material cost of the composite range from $20 to $75 per kg.

5.1 Samples from Series I

Stress-strain behavior of samples made using alumina paper reinforcement is shown in Figure 2. There is an increase of about fifty percent in the strength when the fiber content was increased from 9% to 13%. This increase is also due to the change in fabrication method. As mentioned previously, the coupons with 9% fiber were not placed under pressure during curing. The stress-strain curves are not perfectly straight, due to some noise picked up by the computer. The authors were not able to identify the source of the noise.

For the samples with 13% fiber content, the density increased by about 60% and the strength increased by about 90% as compared to samples with 9% fibers. The strength increase was contributed by about 60% increase in modulus of elasticity and about 27% increase in failure strain capacity. The increases in modulus and strain capacity are consistent with increase in density.

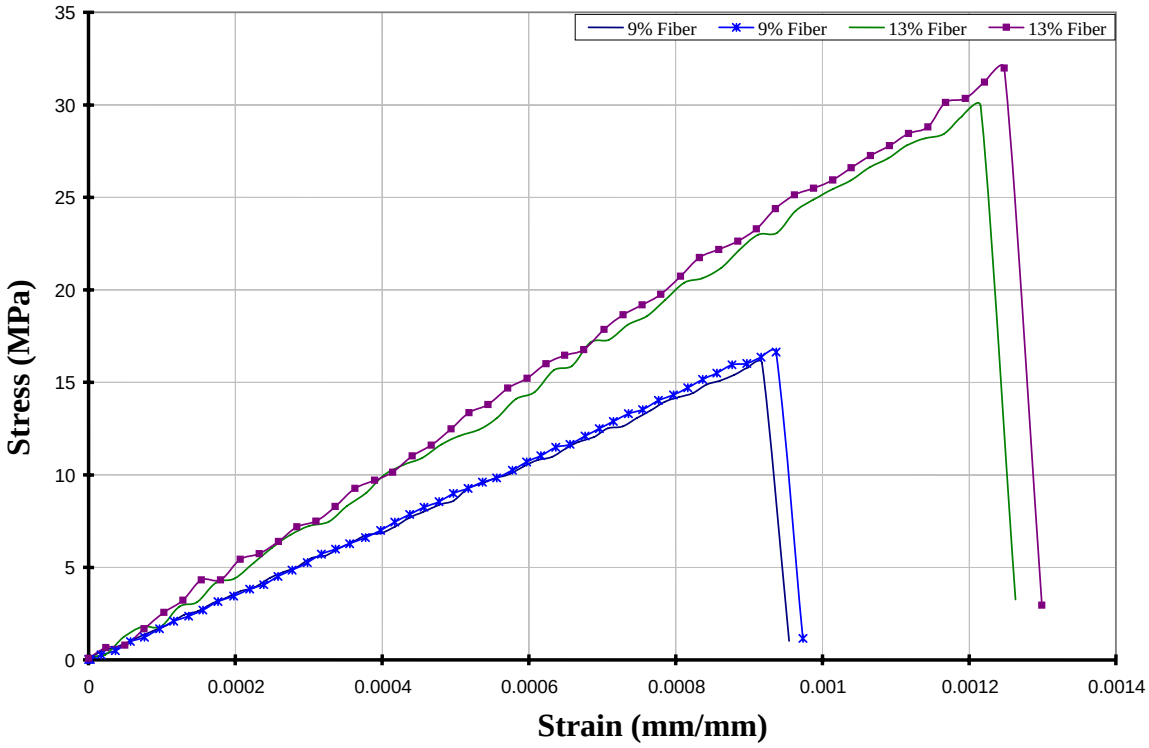

Figure 2 Stress versus Strain Series I

5.2 Samples from Series II

Samples of this series had two different fiber types designated as: milled alumina and short ceramic. From the stress-strain results presented in Figure 3, it can be seen that ceramic fibers provide a better performance. There is considerable increase in modulus of elasticity and strength. In addition there is a slight non-linearity near the peak load for the sample with ceramic fiber, indicating some fiber pull-out. This aspect can be utilized to develop ductile ceramic composites. On the other hand, a different fabrication technique can be used to increase strength but not the ductility. It should also be noted that the cost of ceramic fibers are much higher than the cost of milled alumina fibers.

At a stress level of about 8 MPa and a strain level of 0.00025, there is noticeable strain softening for samples made with milled fibers. A large number of samples show this behavior and hence this is not an experimental error. The authors believe that at these strains, the matrix develop micro cracks and the fibers were not able to compensate the loss of capacity created by this cracking. Absence of this behavior at larger fiber volume fractions supports this hypothesis. Ceramic fibers increases both the stress and strain at which the aforementioned cracking. Similar behavior was also reported by researchers working in fiber reinforced Portland cement composites (4). If there is better bonding due increase in fiber length or more fiber-force contribution due to increase in fiber content, discontinuity in load-deflection behavior at cracking of cement matrix vanishes.

There is also a significant increase in strength between these samples as compared Series I, in spite of lower fiber volume fractions. The change in fabrication technique resulted in a much better compaction, higher densities and possible better anchoring of fibers. There was also considerable increase in modulus of elasticity and failure strain capacity.

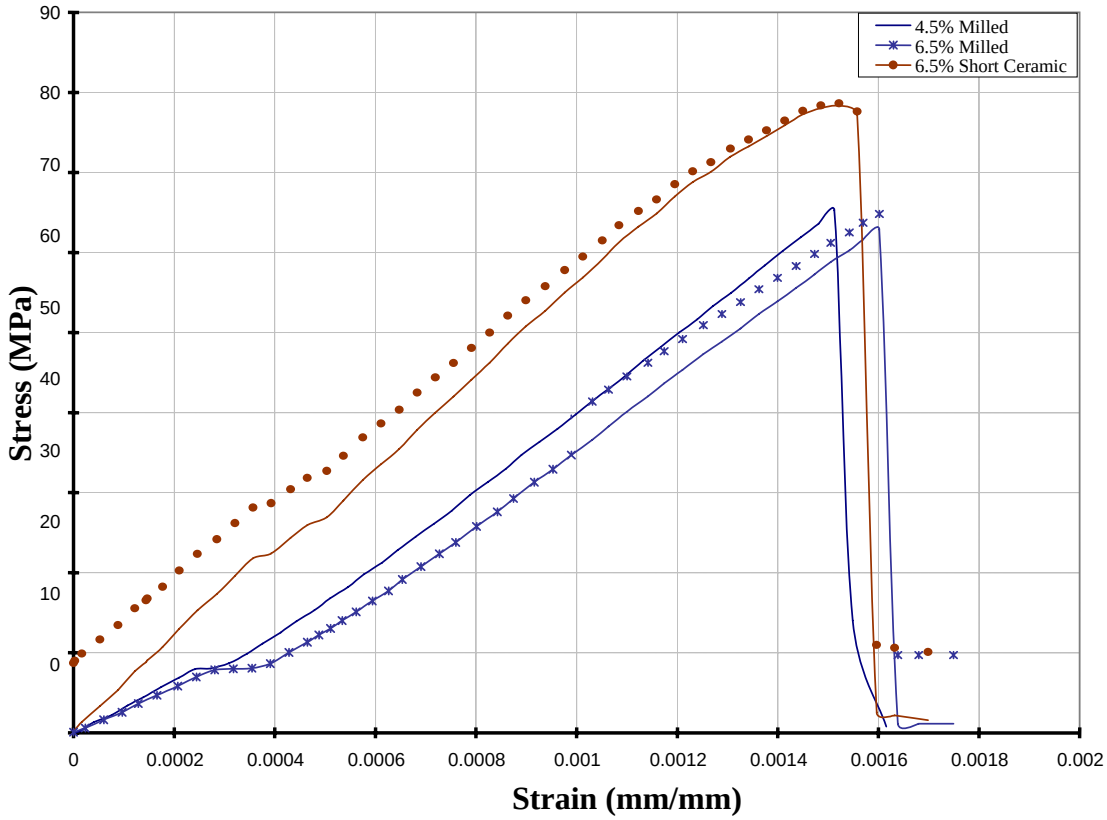

Figure 3 Stress versus Strain Series II

5.3 Samples from Series III

Stress-strain curves for this series are presented in Figure 4. Vacuum bagging technique provided the sample with the highest flexural strength. But the performance was not consistently better as compared to samples of Series II. Note that the fiber contents for this series were: 9.6% to 11.3% as compared to fiber contents of 4.4 to 8.5% for Series II. A careful review of results from Series II and III lead to the following observations.

- At fiber contents of 9.6 and11.3% and vacuum bagging fabrication, the discontinuity at lower stress level disappears for the sample with ceramic fiber. However, the sample with milled fiber still experiences strain softening around a stress level of 11 MPa. Note that this stress level is higher than the level for samples with lower fiber contents of Series II.
- Vacuum bagging combined with heated pressure typically provides a higher density but the fiber content plays a stronger role. For example samples with lower fiber contents of series II have higher densities and higher strengths. As in the case of Portland cement fiber composites, higher fiber contents result in more entrapped air and reduced

compaction and density. Vacuum bagging was not able to remove these air voids. However it might be possible to remove these air voids using higher compaction pressure. The authors chose not to increase the compaction pressure because it will be very difficult and expensive to increase compaction pressure for fabrication of large and complex shaped samples.

- Samples with ceramic fibers show a slight non-linearity at the maximum loads.

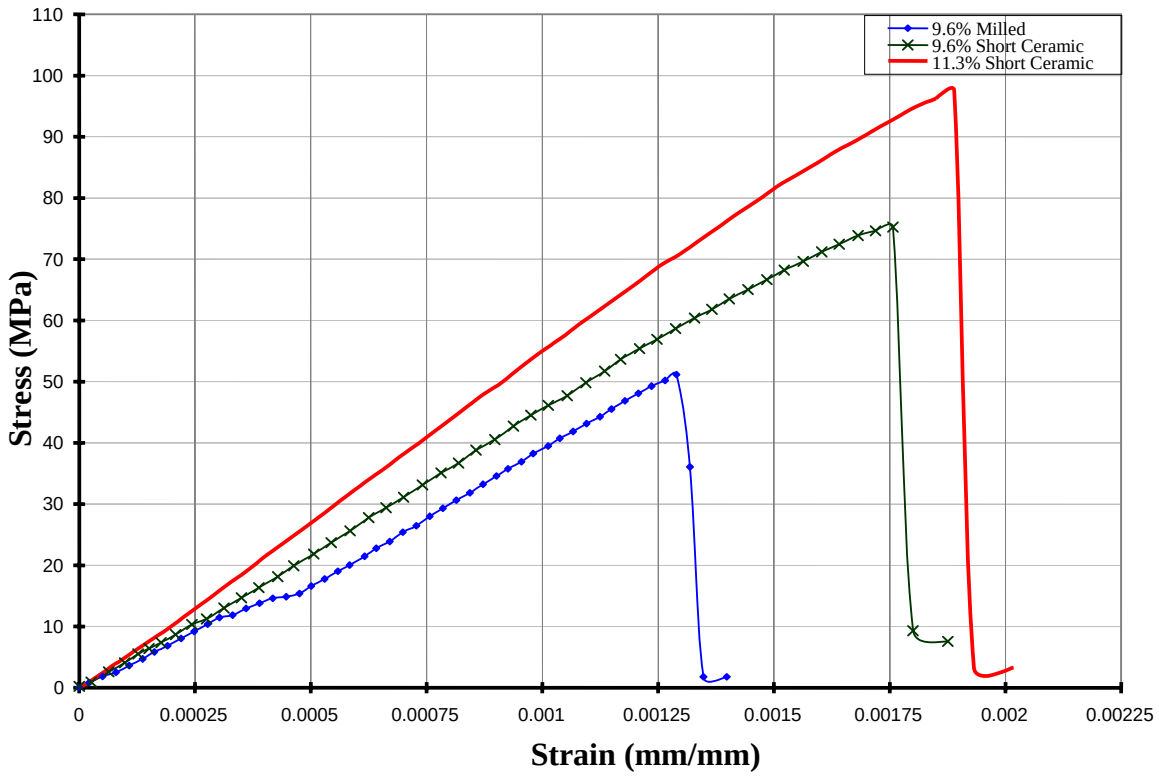

Figure 4 Stress versus Strain Series III

5.4 Influence of Unit Weight (Density) and Fiber Content

The density of the samples reported in this paper varies form 1095 to 2901 kg/m^3. In general a three fold increase in density provides a six fold increase in strength. Corresponding increase in modulus of elasticity and failure strain are about 300 and 200% respectively. The density versus the maximum flexural strength is plotted in Figure 5. This plot includes all of the data represented in Table 2 as well as additional experimental data not presented in this paper. In general, increase in density provides exponential increase in strength. Although the density shows to have an affect on the flexural properties, the amount of fiber also plays a role. The fiber content is plotted versus the maximum flexural strength, failure strain, and modulus of elasticity in Figures 6, 7and 8 respectively. Note the samples designated as M5 and V1 from Table 2 have been eliminated from these figures. The matrix used for these coupons had less powder and more water, which led to the lower stiffness. More water was added to aid compaction but not produce the desired results, Table 2.

- Even though the density has a strong influence on the mechanical properties, its influence is also affected by the type and volume fraction of fibers and fabrication technique.
- For the same density, ceramic fibers provide better mechanical properties. This should be expected because these fibers were more uniform in diameter and length and were easier to work with.
- For the same density, higher fiber volume fraction provides better performance.
- For different fiber contents, increase in strength is more consistent than increase in failure strains or modulus.
- It might be possible to obtain more than 100 MPa with 12 or 13% fiber content. Tests are in progress to verify this possibility.

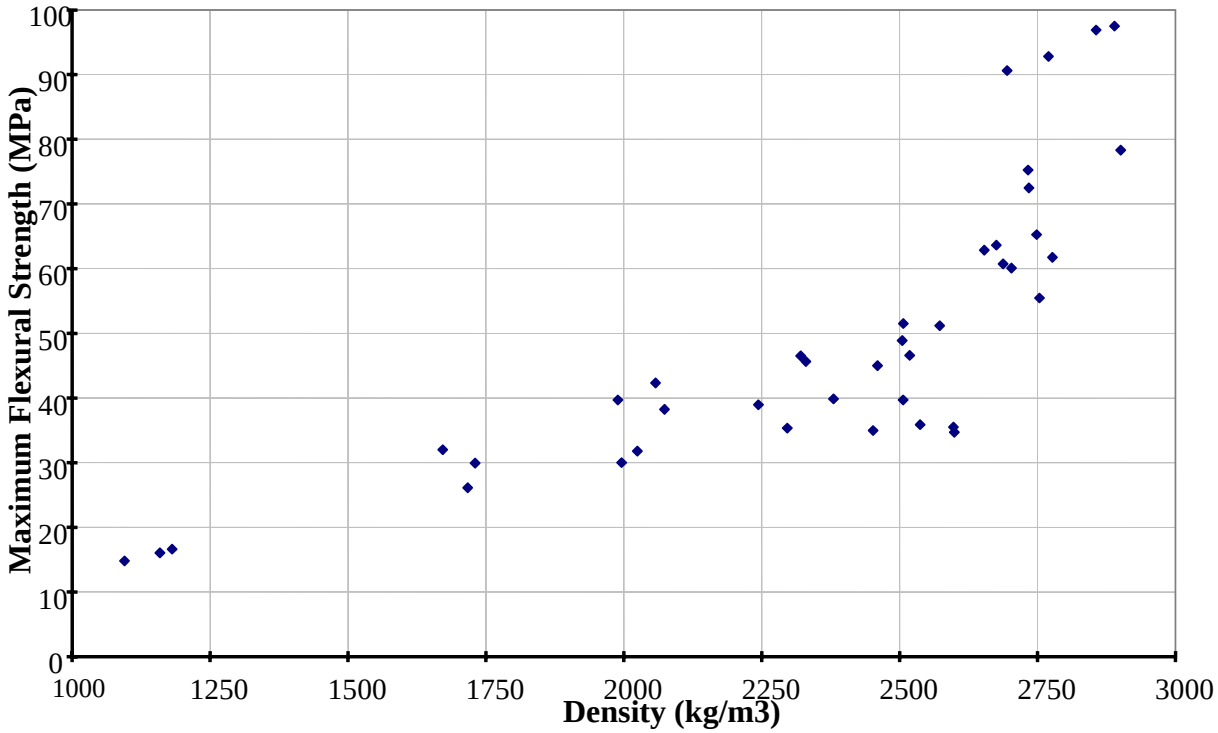

Figure 5 Flexural Strength versus Density

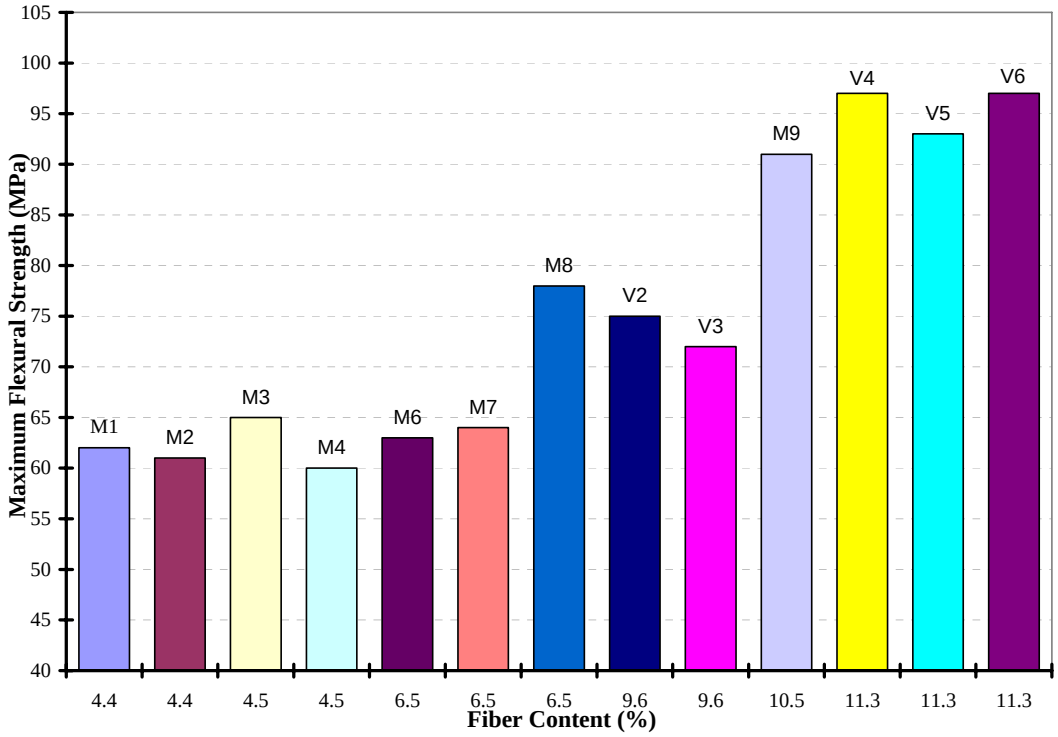

Figure 6 Flexural Strength versus Fiber Content

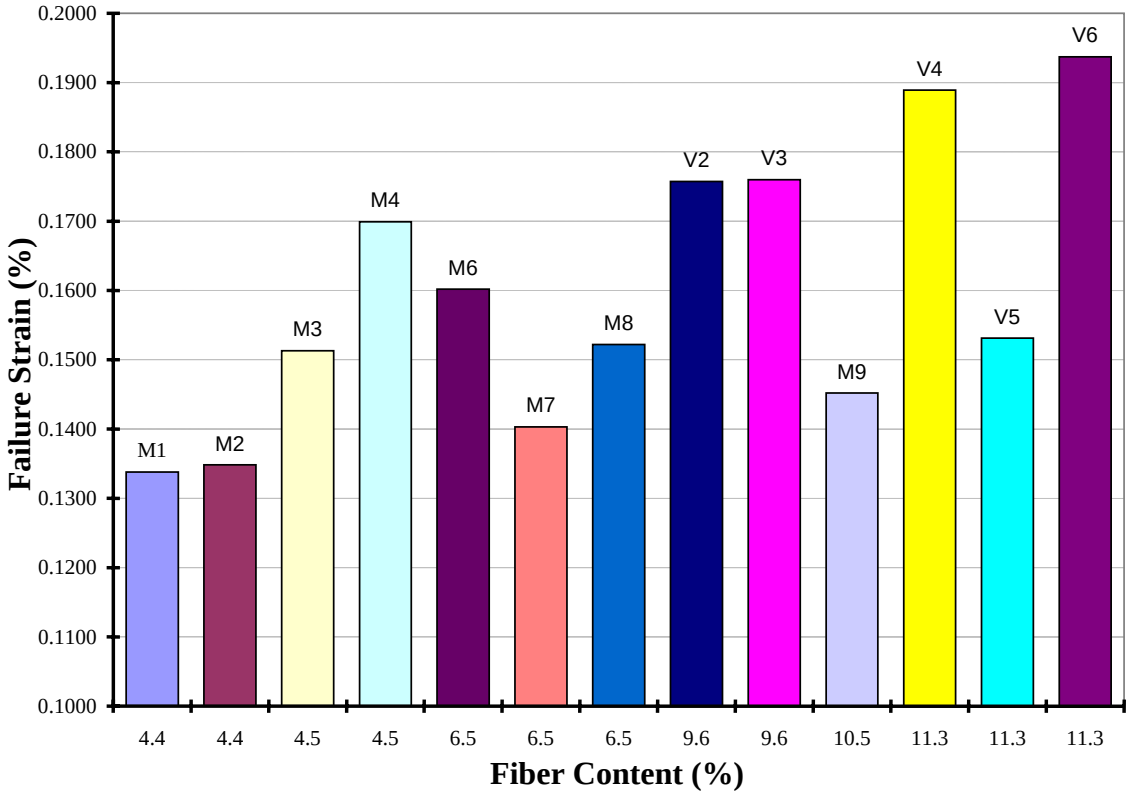

Figure 7 Failure Strain versus Fiber Content

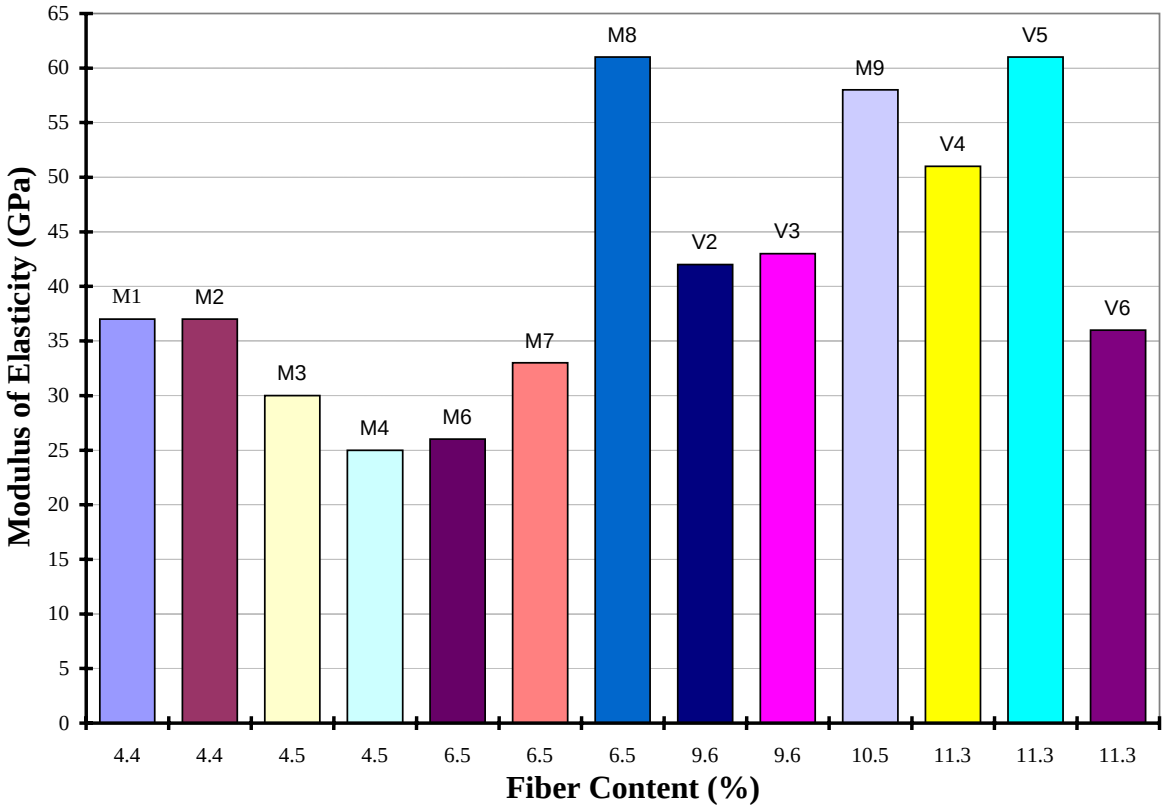

Figure 8 Modulus of Elasticity versus Fiber Content

6. CONCLUSIONS

The following conclusions can be drawn based on the observations made during casting and testing and the results presented in this paper.

- It is feasible to use all three fabrication methods. The first method is conducive for fabricating large samples with lower densities.
- Vacuum bagging technique provided the highest strength. However, these samples also had the highest fiber contents.
- Although more expensive, the short ceramic fibers provide better workability and increased flexural strength irrespective of the fabrication technique.
- An increase in fiber content results in higher failure strain capacity and strength even if there is no increase in density.
- If all the variables are kept constant, higher density provides better mechanical properties.

7. ACKNOWLEGEMENTS

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8. REFERENCES

1. J. Giancaspro, (2004). "Influence of Reinforcement Type on the Mechanical Behavior and Fire Response of Hybrid Composites and Sandwich Structures." Ph.D. Thesis, Rutgers University, 513 pp.
2. P.N. Balaguru, (2003). "High Strength Composites for Infrastructure: Current and Future Directions of Research," *The Thirteenth International Offshore and Polar Engineering Conference*, Honolulu, Hawaii, May 25–30, 2003.
3. American Society for Testing and Materials (1999). "Standard Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials," ASTM Test Method D790, Annual Book of ASTM Standards, Vol. 8.01, pp. 269-278.
4. Balaguru, P. and Shah, S.P., Fiber Reinforced Cement Composites,
McGraw-Hill, New York Publisher 1992, 535 pages.