MODIFICATION OF ECO-CORE MATERIAL FOR IMPROVED FIRE RESISTANCE AND TOUGHNESS

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ABSTRACT

The constituents and processing of the eco-core were modified to improve the fracture toughness and ignition time. The constituents modifications include eliminating silane treatment of fly ash and adding about 4% of chopped E glass fibers. The process modification involves the surface heat treatment of panels to eliminate solvents. The resulting material has compression strength and modulus of 217 MPa and 1.2 GPa, respectively, fracture toughness of 0.43 MPa·$m^{1/2}$ and did not ignite at 75 kW/m^2 heat flux.

KEY WORDS: Materials-Syntactic Foam, Fire Material Performance, Fly ash

1. INTRODUCTION

Fire has been a major problem for both mobile (mass transit and marine) and immobile (buildings and civil infrastructure) structures. With the wide use of advanced materials such as syntactic fabric, polymers and composites, potential fire problems have increased. Norwegian composite minesweeper fire (Nov. 2002) demonstrated the vulnerability of composite structures against fire. September 11, 2001 twin tower fire and collapse has demonstrated the vulnerability of our unprotected steel skyscrapers. Although fire can not be completely eliminated but it can be mitigated to reduce the loss of life and property.

Extensive research is being conducted to improve fire safety of composite materials for various applications. Some of these results are summarized by Sorathia and Perez (1) for Naval applications. A fly ash based core material (2-3) made by a syntactic process was introduced last year for sandwich constructions. Syntactic foams (4-9) are made by embedding hollow microspheres in a resin matrix. The lightweight hollow microspheres reduce the density of the resin and create a thick mixture that can be applied by hand or sprayed or can be compression molded in a suitable mold. Syntactic foams are used in many applications, such as underwater buoyancy aids, aerospace plug manufacturing and structural components for ship hulls and bulkheads (7-9). The fly ash core called Eco-Core made by Shivakumar et al and others uses a

[1] **The technical views expressed in this paper are the opinions of the contributing authors, and do not represent any official position of the U. S. Navy.**

small quality of high char yield binder with a large percentage of ash. Small percentage of high char binder essentially reduce/eliminate the volatile content thus depriving the fire from fueling. Fly ash is a ceramic hollow micro balloons that can withstand temperature in excess of 1000^{O} C. It has a bulk density range 0.2 to 0.75 gm/cc. In 2004 SAMPE conference the development of eco-core and preliminary results were presented. This paper presents improvements made in processing and composition to enhance fire performances and fracture toughness.

2. MATERIAL MODIFICATION

A class of fly ash known as Cenosphere or Recyclosphere grades CG 100 and SG 300 obtained from Sphere Services Inc. was used in the formulation of the Eco-Core material (3). The binder resin was a phenol-formaldehyde resole resin, Durite SC 1008 supplied by Borden Chemical Co. The fly ash was washed with HCl acid solution to remove the calcium content and then treated with a silane coupling agent, aminoalkyl triethoxysilane, obtained from either Gelest Company or Aldrich Chemicals. The coupling agent is expected to improve the bonding property. Some of the samples used as received and acid washed ashes.

Results obtained in that formulation was found to have good mechanical properties and successfully passed 50kW/m^2 heat flux fire test and did not meet the 75kW/m^2 ignition requirement. Furthermore, the material needed to be tough to meet the handling loads. Therefore, two separate efforts were taken, one to improve the toughness by binder modification and addition of fiber another to improve the ignition time at 75kW/m^2 heat flux by post heat treatment of surfaces to remove excessive volatiles. In addition effect of surface treatment of fly ash was also studied.

The material processed was divided into four groups. Group 1 consists panels made by fly ash as received (AR), acid washed (AW), and silane treated (ST) with and without ATH additive (to suppress the fire). All panels were made in sizes of 152x152x25.4 mm. The Group 2 and 3 panels were made from fiber additives of sizes 2.7μ diameter E-glass fibers supplied by Johns Manville Corp and 10μ chopped E-glass fibers supplied by US composites, respectively. The percentage of fibers was varied from 0.5 to 2% for 2.7μ and 0.5 to 6% for 10μ fibers. The Group 4 panels have different binders and additives and this group was specifically designed for fire resistance. Details of ash treatment, binders, catalyst, additives and post cure of all panels are summarized in Table 1. Details of processing are given in reference 3.

3 MECHANICAL CHARACTERIZATION

3.1 Specimen and Tests

Screening tests were carried out using compression and single edge notched bend fracture tests according to ASTM standards C-365 and E-399, respectively. Specimen configurations used for these tests are shown in Figure 1. The density measurements were carried out on the cored specimens used in compression tests. Both compression and fracture toughness tests were used as quality control tests during this material process development. Panels of size 152x152x25.4 mm were fabricated and four compression samples of diameter 29.2 mm, two indentation specimens of 51x51 mm, and two 3-point bond (SENB) fracture toughness specimens were machined. Figure 2 shows the specimen layout. Compression specimens were represented by

C's, indentation specimens by I's and the two fracture specimens were represented by MC and TC. Out of the two bend-fracture specimens, one had the through-the-thickness crack (TC) and the other one had the mid-plane crack (MC). The two specimens will measure the average and mid-plane toughness of the material. The two tests will verify the material uniformity of the panel.

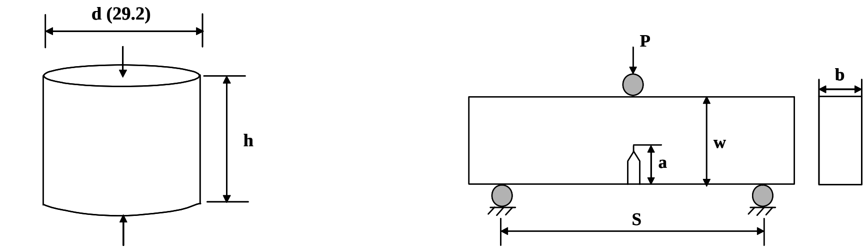
Table 1. Processing parameters and panel ID

	Panel ID	Flyash Treatment	Binder	Catalyst	Additive	Postcure
	SM13	AR				1hr press + 4hr oven at 325шF
Group 1	SM12	AW	SC1008	-	ATH	
	SM01	ST				No
	SM08	ST				
	SM19	ST			0.5% of 2.7 µ glf*	
Group 2	SM18	ST	SC1008	-	1% of 2.7 µ glf	
	SM24	ST			1.5% of 2.7 µ glf	
	SM22	ST			2% of 2.7 µ glf	1hr press + 4hr oven at 325шF
	SM20	ST			0.5% of 10µ cglf**	
	SM16	ST			1% of 10µ cglf	
	SM21	ST			2% of 10µ cglf	
Group 3	SM23	ST	SC1008	-	4% 10µ cglf	
	SM25	ST			6% of 10µ cglf	1hr press + 11hr oven at 325шF
	SM27[1]	AW	Resole Phenolic	CoNap 6% (2g)	805 (20% of binder wt)	No
	SM28[2]	AW	Novalac Solution	Phencat 382 (15%)	ATH (20% of binder wt)	6hr oven at 180ϒF
	SM29[3]	AW	Siloxane 2104	CoNap 6% (1.9g)		No
Group 4	SM30[4]	AW	Novalac solution	Hexamine (10%)		Ramped to 465шF and held for 2hr
	SM31	AW			1.5% of 2.7 µ glf	0.5hr press + 7.5hr oven at 325ϒF, 5hr oven at 375ϒF
	SM32	AW	Resole Phenolic	-	1/4" chopped glass (4%)	
	SM33[5]	AW				
	SM34[6]	AW				

1. Durite resole (dried in 100ϒF vacuum oven for 24hr before mixing)
2. Cellobond liquid phenolic + acid cure
3. Rigid Corning Resin
4. XLC-LL Hi-temp Novalac Resin
5. Fiber sizing oxidized at 600 ϒF
6. Same as SM33 except 4" x 4" 600 ϒF surface contact treatment 2-cycles/6-sides/5-min.ea.side

*- glf - Insulation Glass fiber supplied by Johns Manville

**- cglf - Chopped glass fiber



a) Compression Test: ASTM C 365

b) Fracture Test: ASTM E 399

Figure 1 Specimen configurations

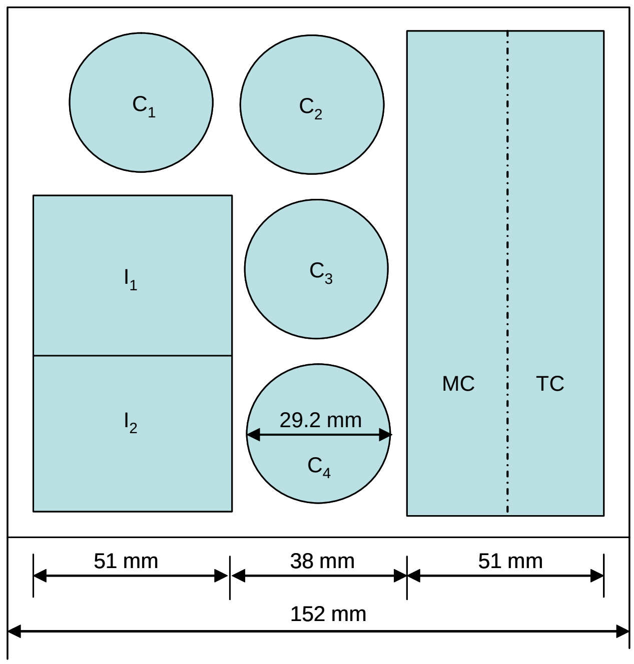


Figure 2 Compression and fracture toughness specimen layout

3.2. Results and Discussion

3.2.1 Fly ash treatment

Table 2 summarizes density, compression modulus and strength, and fracture toughness of all 21 panels. The density ranged from 0.50 to 0.58 g/cc but the majority of the panels has 0.54 g/cc. Among Group 1, the panel SM01 was not post cured that had the lowest modulus and strength compared to the panels with post cure. Different Ash treatments practically had no effect on the compression properties. However, the fracture toughness of the panels with acid wash and acid wash followed by silane treatment had more than 20% increased toughness than as received ash data. Therefore, a simple acid wash, which eliminates the calcium carbonate contamination in the ash is essential. The acid washed fly ash can produce a core material of compression modulus and strength of about 1.2 GPa and 21.7 MPa, respectively and fracture toughness of 0.42 MPa·m$^{1/2}$. Figure 3 shows the compression failure modes of the Eco-Core with and without glass fiber (10μ) additives.

Table 2 Compression properties and fracture toughness

	Panel ID	Density g/cc	Compression		Fracture Toughness MPa.m $^{1/2}$	
			Modulus GPa	Strength MPa	Through thickness (TC)	Mid thickness (MC)
Group 1	SM13	0.582	1.15	20.25	0.346	0.362
	SM12	0.542	1.17	21.66	0.417	0.434
	SM01	0.540	0.92	19.73	0.429	0.399
	SM08	0.579	1.22	21.88	0.418	0.461
Group 2	SM18	0.537	1.13	20.69	0.455	0.457
	SM19	0.539	1.09	15.49	0.403	0.387
	SM22	0.532	0.88	15.84	0.392	0.460
	SM24	0.547	1.13	22.68	0.453	0.478
Group 3	SM20	0.540	1.21	15.81	0.415	0.385
	SM16	0.541	1.20	20.49	0.441	0.424
	SM21	0.541	1.23	16.87	0.454	0.468
	SM23	0.553	1.23	21.46	0.613	0.566
	SM25	0.572	1.15	20.33	0.576	0.651
Group 4	SM27	0.528	1.14	11.14	0.196	
	SM28	0.502	1.13	14.43	0.208	
	SM29	0.511	0.71	12.00	0.180	
	SM30	0.506	1.14	12.99	0.216	
	SM31	0.542	1.34	20.80	0.339	
	SM32	0.540	1.26	18.16	0.448	
	SM33	0.538	1.28	20.91	0.406	
	SM34	0.528	1.19	17.46	0.342	

(a) Panel SM01, no fiber (b) Panel SM21, with 2% 10µ fibers

Figure 3 Compression failure of Eco-Core without and with fiber additives

3.2.2 Fiber addition

Table 2 summarizes the compression and fracture toughness data for Group 2 and 3 panels having different amounts of 2.7µ residential insulating glass and 8 mm long 10µ chopped glass fiber. Dispersion of 2.7µ fiber in resole phenolic was a problem, especially at higher loads. Therefore the properties of 1% (SM18) and 1.5% (SM24) 2.7µ glass content was superior to 0.5

and 2%. Furthermore properties improvement with 2.7μ fiber was not substantial. However, 10μ glass fiber data had 23% and 47% increased mid-thickness and through-the-thickness fracture toughness, respectively, for 4% loading. The optimum value maybe around 4% for 10μ glass fiber. Fiber content was expressed as a percent of ash + binder weight.

Group 4 panels were specially designed for fire test. The surface heat treatment reduced the compression strength and fracture toughness to nearly one-half for some of the panels while the compression modulus remained nearly the same. Among the different binders experimented, the resole phenolic with no additive is the best choice and 4% chopped glass fiber will have at least the properties that are equivalent to the core material without fiber and no heat treatment.

4. FIRE CHARACTERIZATION

Fire resistance of the eco-core was determined at the NSWC Carderock Division laboratories using a cone calorimeter (ASTM E1354). A cone calorimeter is used to determine the ignitability, heat release rate and combustion product generation rate of a material exposed to a specified irradiance level. A 100 mm by 100 mm sample was placed beneath the conical shaped heater that provides a uniform irradiance on the sample surface (see Figure 4).

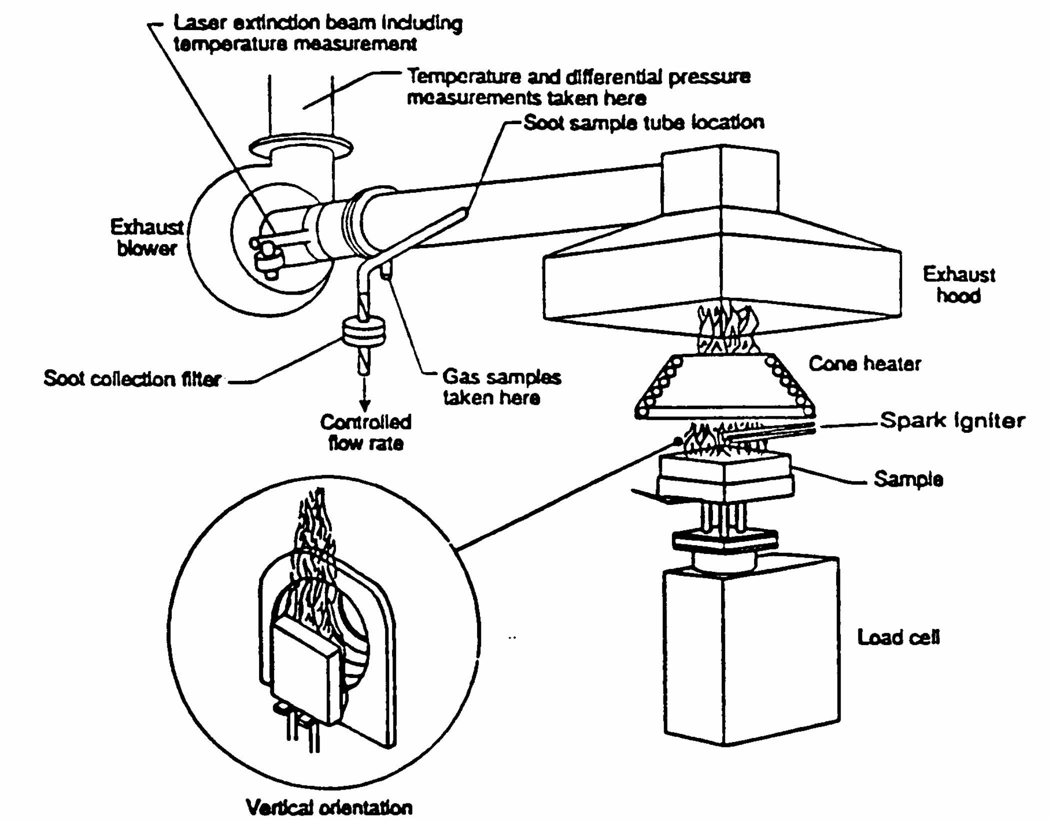


Figure 4 ASTM E1354 Cone calorimeter test apparatus

The sample mass was constantly monitored using a load cell, and the effluent from the sample was collected in the exhaust hood above the heater. In the duct downstream of the hood, the flow rate, smoke obscuration, and O_2, CO_2 and CO concentrations were continuously measured. A spark igniter 12.5mm from the sample surface was used to initiate the burning of any combustible gas mixture produced by the sample. Once the sample ignites, the burning of the sample causes a reduction in the oxygen concentration within the effluent collected by the hood. This reduction in oxygen concentration was shown to correlate with the heat release rate of the material, 13.1 MJ/kg of O_2 consumed. This was known as the oxygen consumption principle. Using this principle, the heat release rate per unit area of the sample was determined with time using measurements made within the duct. The fly ash foam samples were tested at irradiance levels of 50 and 75 kW/m^2 to evaluate their performance when exposed to different heat loads.

As a first effort three samples A, B, and C were tested for fire resistance properties. Samples A and B were 25.4 mm thick whereas sample C was 12.7 mm thick. The test data are summarized in Table 3. Sample B was heaviest with a density of 0.53 kg/cc while A and C had densities of 0.34 and 0.39 kg/cc, respectively. All three samples at an irradiating heat flux of 50 kW/m^2 exhibited no ignition, which is very encouraging. These samples did not emit any of the known toxic gas except for carbon monoxide (less than 200 ppm), which is about 1/18th of the acceptable limit. At 75 kW/m^2 heat flux, the samples did ignite after exposure for 26, 35 and 59 seconds for samples A, B and C, respectively.

Table 3 Cone calorimetry data on fly ash foam samples

Material/ Thickness (mm)	Heat Flux	Time To Ignition	Peak Heat Release Rate	5 MIN Average Heat Release Rate	Average Heat of Combustion	Average CO Yield	Total Heat Released
	kW/m^2	sec	kW/m^2	kW/m^2	MJ/kg	kg/kg	MJ/m^2
Panel-A/ 25.4	50	NI	53	6	13	0.28	4
Panel-B/ 25.4		NI	31	13	14	0.18	10
Panel-C/ 25.4		NI	8	14	5	0.43	8
Panel-A/ 25.4	75	26	47	6	5	0.35	3
Panel-B/ 25.4		35	33	18	10	0.24	6
Panel-C/ 25.4		59	59	36	26	0.12	16
NI- No Ignition							

The cone calorimetry test results for the modified panels SM27 through SM34 are summarized in Table 4. In this panel SM28 (made form cellobond J2027L binder) and SM31 through SM34 (Resole binder) did not ignite over the complete test duration and all other parameters such as heat release, mass loss, and effective heat of combustion are very well within the limits of acceptability. Therefore, Eco-Core material made from acid washed ash, resole phenolic binder (about 6% by weight), and 10μ glass fiber (4%) filler with surface heat treatment offers a superior compression as well as fire resistant properties.

Table 4 75kW/m^2 cone calorimetry test results of modified eco-core

Sample		SM27	SM28	SM29	SM30	SM31	SM32	SM33	SM34
Ignition time, s		34.2	NO	61.1	44.1	NO	NO	NO	NO
Flameout time, s		85.0		164.0	180.0				
Total test duration, s		408	777	450	359	670	638	662	658
Peak heat Release	Rate, kW/m^2	16.3	24.6	44.3	29.9	26.8	26.3	2.2	24.7
	@ time, s	46.0	76.0	76.0	56.0	66.0	56.0	66.0	86.0
Average Heat Release Rate, kW/m^2	Total	-2.9	11.5	23.1	20.5	15.1	14.6	-9.1	15.0
	T60	11.3	9.2	37.7	26.1	11.8	11.4	-11.9	13.9
	T180	3.5	16.2	29.4	23.6	19.1	18.7	-5.4	18.8
	T300	-1.0	15.3	25.2	20.9	18.1	17.4	-7.1	17.9
Total Heat Released, MJ/m^2		0.9	9.0	9.0	6.8	10.1	9.4	0.0	10.0
Average Effective HOC, MJ/kg		-1.8	8.2	31.5	12.3	13.2	11.7	-7.6	13.1
Average Specific Extinction Area, m^2/kg		18.3	51.1	-102.3	123.0	-22.1	552.7	94.0	-16.2
Average Mass Loss Rate, g/sm^2		2.4	1.7	0.8	2.0	1.4	1.5	1.4	1.3

5. CONCLUSIONS

1. A process for low-cost syntactic foam from fly ash, a waste product of coal combustion from thermal power plants, has been developed using a resole phenolic resin as well as similar high char yield binders at a low volume percentage of about 6%. This core material is named as Eco-Core.
2. The original formulation of Eco-Core was modified by different fillers to enhance toughness and surface heat treated to improve fire resistant properties.
3. Fracture toughness increased by 47% by 4% addition of 10µ 8mm shopped glass fibers.
4. The surface treatment expels solvents thus increases the ignition time. The material successfully passed 50 and 75 kW/m^2 heat flux cone calorimeter test without ignition and very low heat release.

6. ACKNOWLEDGEMENTS

The authors wish to thank the Office of Naval Research for the financial support through grant N00014-01-1-1033 and Dr. Yapa Rajapakse, program manager for ship structures, for his continuing interest in this work.

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