EFFECT OF MICROSILICA IN WOVEN CERAMIC FIBRE/PHENOLIC RESIN COMPOSITES

Balaji.R[1], M.Sasikumar[2], A. Elayaperumal[3]

[1]*Research Scholar, SMBS, VIT University, Chennai Campus*
[2]*Associate Professor, SMBS, VIT University, Chennai Campus*
[3]*Associate Professor, Department of Mechanical Engineering, Anna University, Chennai, India*

Abstract

In this study, phenolic based composite filled with ultra light microsilica is prepared by traditional hand layup method, using ceramic woven fibre as reinforcement. The effect of various percentages of microsilica is investigated on the tensile strength, compression strength, impact resistance and thermal stability of the composite. The result reveals that, up to 15% addition of microsilica enhanced the mechanical properties. However the addition of microsilica beyond 15% decreases the mechanical properties of the composites. This is mainly because, addition of microsilica increases the viscosity of phenolic resin which directly affecting the wettability of fibre. It is found that, the addition of microsilica has great positive influence on the thermal stability of the composite.

Keywords: *Phenolic resin, Ceramic fibre, Microsilica and Thermogravimetric analysis.*

----------***----------

1. INTRODUCTION

Fibre reinforced polymer matrix composite has recently generated immense academic and commercial interest due to their wide application in the field of construction, automobile, aerospace industries etc. Among the various polymer resin system, Phenolic resin retain its position in various industries a century after its introduction because of its good mechanical strength, heat and flame resistance, and also exhibits good chemical resistance against various solvents, acids and water. Phenolic resin exhibits good dimensional stability over a wide range of temperature. Phenolic resin is easy to manufacture and also cost effective when compare to other resin. However Phenolic resin cannot be direct substitutes for epoxies or other thermoset resin because the traditional phenolic resin always suffer from high shaping pressure and brittleness [1].

To improve the properties of the Phenolic resin, many researchers tried out various methods such as usage of binders, nanofillers, thermoplastic resin, unidirectional and bidirectional woven fibre, fillers etc. Carbon fiber reinforced phenolic composite is one of the prime composite for high strength and high temperature application because of the superior properties of both carbon fiber and phenolic resin. Patton et al. [2] used Vapor grown carbon fiber as reinforcement along with phenolic resin and showed improved thermal and mechanical properties, which promises for rocket nozzle application. Pulci et al. [3] used phenolic resin with carbon based graphitic felt and graphitic foam to manufacture ablative material for re-entry space vehicles.

Elaine et al. [4] prepared a composite using tannin–Phenolic modified resin (40 wt% of tannin) reinforced with sisal fiber. The composite showed increase in Izod impact strength and also showed good matrix fiber interface. In another work, Frollini et al. [5] used bark from the Acacia Mimosa tree along with phenol matrix with tannin as a partial substitute. The composites showed high storage modulus and low water absorption, due to the good adhesion at the matrix fiber interface. In a companion paper, Barbosa et al. [6] used coir fiber as reinforcement along with the tannin Phenolic modified matrix. The composites showed intense fiber matrix adhesion and poor impact strength, due to the poor mechanical properties of the coir fiber.

Srikanth et al. [7] and Tani et al. [8] used Zirconium as filler to increase the mechanical properties of the phenolic resin. Bending strength and the barcol hardness of the phenolic composite enhanced with addition of Zirconium metal oxide and also the coefficient of thermal expansion of Zirconium filled phenolic composite decreased. Jonathan et al. [9] used an *in situ* semibatch polymerization process to develop phenolic nanocomposite filled with montmorillonite clay which showed increase in tensile modulus and fracture strength with addition of montmorillonite clay.

The mechanical properties and thermal properties of epoxy resin increased by adding silica particles with the epoxy resin [10-14]. Srikanth et al. [15] manufactured the high ablation resistance carbon phenolic composites using nanosilica as a filler material. Nanosilica filled carbon phenolic composite exhibited higher ablation resistance when compare to neat composite. Addition of silica not only enhanced the mechanical properties but also considerably restricted the thermal degradation of phenolic resin [16, 17]. The focused phenolic resin based composite filled with microsilica as filler were prepared by tradition land layup technique, using ceramic woven fibre as the reinforcement. The mechanical and thermal properties of modified phenolic composite were evaluated, with the effect of microsilica on the tensile properties, compression strength, impact energy and thermal properties to be highlighted.

2. MANUFACTURING

2.1. Materials

A resole type phenolic resin is selected as matrix material because of its high thermal stability and the good oxidation resistance [18]. The resole type phenolic resin is produced by the reaction of phenol with formaldehyde in an alkaline medium. Due to the presence of their reactive methyl groups, the resole type will starts to crosslink by exposure to heat. Phenolic resin was supplied by Linear Polymer Pvt Ltd, Chennai. The properties of the phenolic resin are listed in table 1. Ceramic woven fibre is used as reinforcement was supplied by Dail Electricals Pvt. Ltd, Mumbai. The properties of ceramic woven bidirectional fibre are tabulated in the table 1. Ultra light micro silica was used as filler which supplied by the Astrra Chemicals, Chennai. Silica fume, also known as microsilica, is an amorphous made up of silicon dioxide. It is an ultrafine powder collected as a by-product of the ferrosilicon and silicon alloy production. The properties of microsilica are listed in the table 1.

Table: 1. Properties of Ceramic Woven Fibre, Phenolic resin and Microsilica

Reinforcement: **Ceramic Woven Fibre**	Matrix : **Phenolic Resin**	Filler : **Microsilica**
Density : 2.7 g/cc GSM : 200gsm Thickness: 0.6mm Constituents: Alumina (<99%) Color : White	Density : 1.2 g/cc Constituents: Phenol and Formaldehyde Color : Dark red Curing Temperature : 160˚C	Density : 0.81g/cc Specific gravity: 2.2 Constituents: Silica (<95%) Particle Size: 5 µm(avg) Color: White

2.2 Specimen Preparation

The composite specimens are manufactured from bi-directional woven ceramic fibre and ultra light micro silica filled Phenolic resin using traditional hand layup method. The percentage of weight of ultra light micro silica varied from 5% to 20 % in the phenolic resin. Initially, microsilica is mixed with pre calculated phenolic resin. Then this mixture was stirred slowly and thoroughly for about 30 minutes by using handheld electrical stirrer. The composite specimens were prepared consists of 7 layer of bi-directional woven ceramic fibre. Then curing is done by place this specimen in hot air oven for about 1 hour at the temperature of 160˚C at very slow rate of heating (2˚C per minute). Again post curing is done at 210˚C for about 2 hours in hot air oven.

The ASTM standard based samples for tensile, compression, impact testing and thermo gravimetric analysis were cut from the specimens. Samples for impact testing were notch cut before testing.

3. CHARACTERIZATION AND TESTING

3.1. Mechanical Properties

The mechanical testing is performed to quantify the effect of the microsilica on the mechanical performance of the microsilica filled composite. Tensile strength and Compression strength were measured at ambient condition using a universal testing machine (Shimadzu's Autograph AG-X Plus 50K Universal testing machine), according to ASTM procedures D638 and D695 respectively; at a crosshead speed of 3 mm per minute for tensile testing and 1mm per minute for compression testing. The tensile strength and compressive strength of the composites filled with various percentage of microsilica are showed in table 2.

Table: 2 Tensile strength, Compressive strength and Impact energy absorbed by the composites

Percentage of Filler	Tensile		Compression		Energy Absorbed during Impact load (Charpy) (J)
	Tensile Strength (N/mm^2)	Load at Peak (kN)	Compressive strength (N/mm^2)	Load at peak (kN)	
0% (Neat Composite)	49.87	7.48	17.47	2.62	4.5
5%	62.58	9.37	21.94	3.29	5.75
10%	66.93	10.04	24.01	3.60	6.5
15%	69.82	10.48	25.85	3.88	7
20%	68.31	10.24	24.90	3.735	6.75

Notched Charpy impact strength was determined at ambient condition according to ASTM D256 standard, using Charpy impact tester (Impact Testing Machine AIT-300N). Energy absorbed by the composites filled with various percentage of microsilica is showed in the table 2.

3.2. Thermal Properties

Thermo Gravimetric Analysis (TGA) is done to evaluate the effect of microsilica on the thermal behavior of the composite. Themogravimetric analysis is performed by a NETZSCH STA 409PC/PG thermal system. The analysis is performed at a heating rate of 10˚C/min under nitrogen atmosphere under the temperature ranges from room temperature to 1400˚C. This analysis is performed to evaluate the weight loss of the composite under various temperatures. Thermogravimetric analysis curves for composite filled with various percentage of microsilica are shown in figure 1.

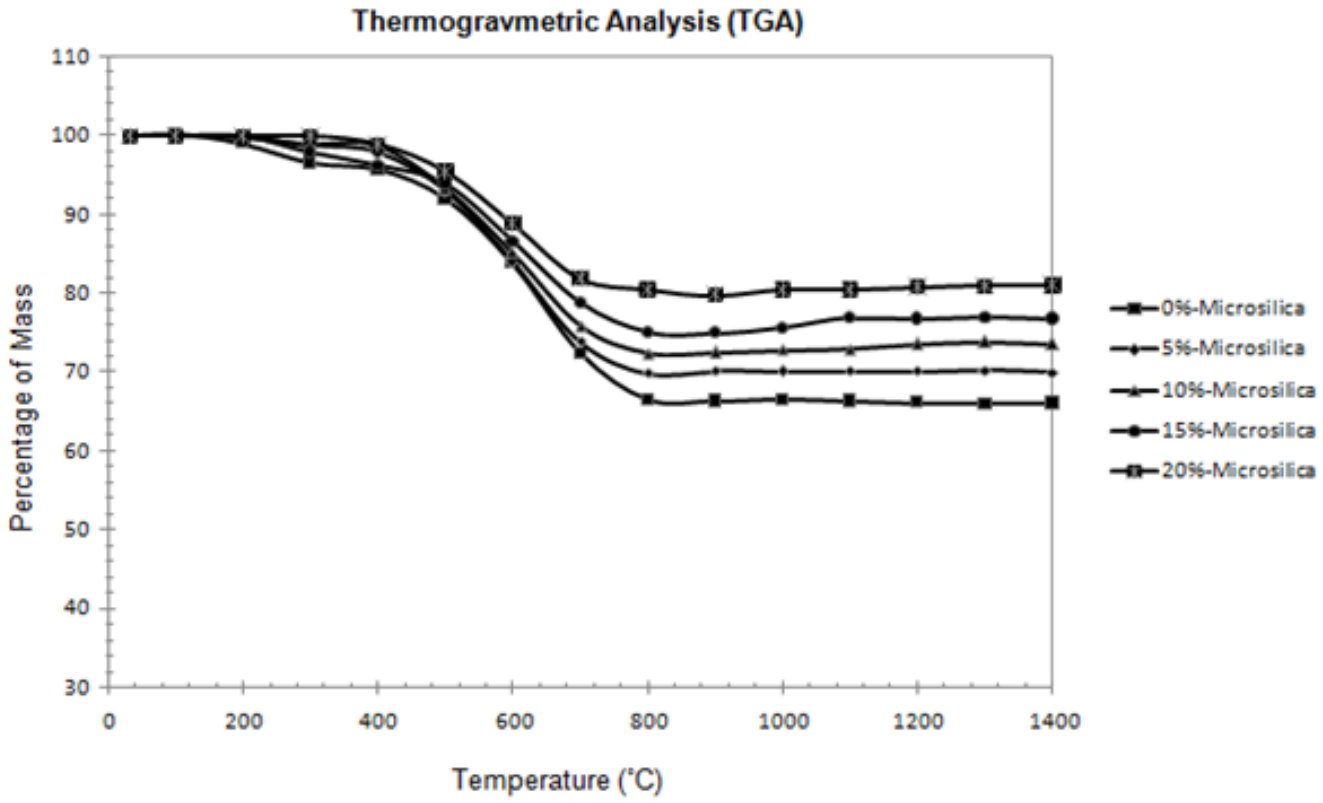

Fig: 1 TGA curve of composites filled with various percentage of microsilica.

4. RESULTS AND DISCUSSION

4.1. Mechanical Properties

From the experimental result of tensile test, it is observed that the addition of microsilica with phenolic resin upto 15%, increases the tensile strength of the composite is shown in figure 2.When compare to neat composite, addition of filler from 5 to 15%, tensile strength of the composite increased from 30 % to 55% of the tensile strength of composite filled with no filler respectively. It is also observed that the further addition of microsilica with phenolic resin for about 20% decreases the tensile strength of the composite. The reduction in tensile strength of the composite filled with more than 15% of microsilica may be due to addition of microsilica increases the viscosity of the phenolic resin. The increase of viscosity of the modified phenolic resin decreases the impregnation ability of the phenolic resin. Hence increase of modified phenolic resin's viscosity decreases the wettability of the ceramic woven fibre, which in turn directly affects the tensile strength of the composite.

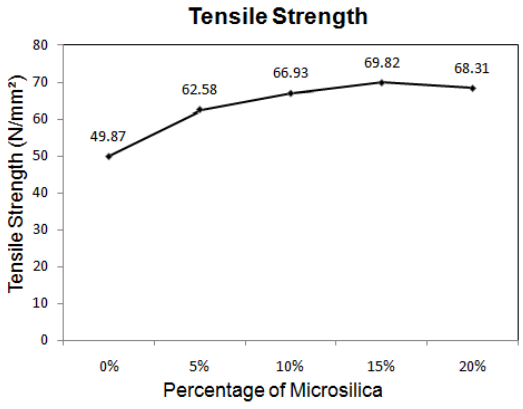

Fig: 2 Influence of microsilica on the tensile strength of the composites

It is found that the compressive strength of composite filled with microsilica increases upto 15% addition of microsilica and beyond the transition limit of 15%, further addition of microsilica decreases the compressive strength of the composites. The compressive strength of the composites filled with various percentage of microsilica is shown in

figure 3. Specifically compared to the composite with no filler, compressive strength of 15% and 20% filled composite increased and decreased by 45% and 30% respectively.

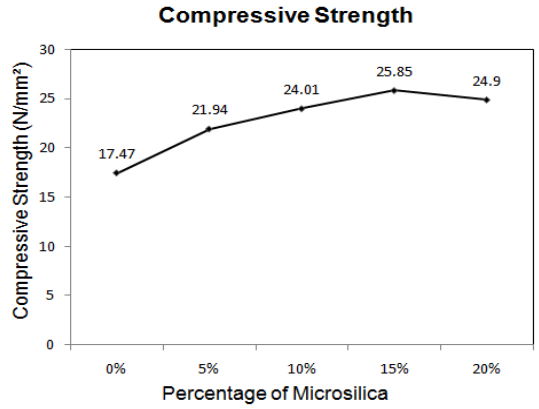

Fig: 3 Influence of microsilica on the compressive strength of the composites

Energy absorbed by the composite filled with various percentage of silica during impact loading (Charpy) is shown in figure 4. Composite filled with 5% of silica absorbed 27% more than the composite filled with no silica. Similarly, the composite with 10% and 15% of silica absorbed 43% and 55% more energy than the composite filled with no silica respectively. This result indicated that the addition of silica with phenolic resin increases the energy absorbing nature of composite when subject to high rate of loading. However, composite filled with 20% of silica, shows decrease in energy absorbing capacity, when to compare to composite filled with 15% of silica. Hence the addition of microsilica beyond the transition limit of 15%, inversely affect the impact resistance of the composite.

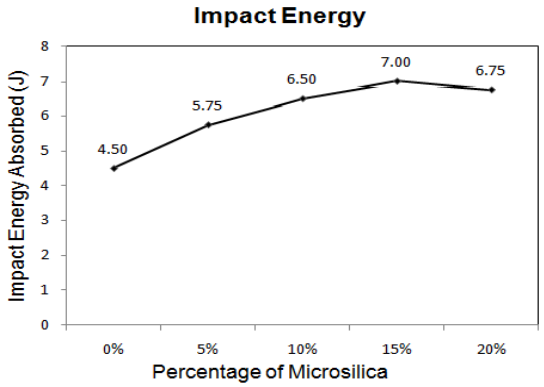

Fig: 4 Influence of microsilica on the Impact resistance of the composites

4.2. Thermal Properties

Thermogravimetric analysis (TGA) is performed to evaluate the physical phenomena such as vaporization, sublimation etc and chemical phenomena such as dehydration, decomposition, etc as a function of increasing in temperature. It is commonly used to measure the variation in mass of the materials when subjected to heating. Thermogravimetric analysis (TGA) curve of the specimens are shown in figure 1. The thermal degradation of the neat composite and filled composite occurred in three stages: a) a low temperature stage, below 200˚C, b) an intermediate temperature stage, 200˚C to 500˚C and c) a high temperature stage, above 500˚C [19]. At the low temperature stage, the phenolic composite with and without silica, were stable relatively in nitrogen atmosphere. However a small amount of weight loss (1 to 2%) were happened because of the evolution of gaseous trapped in the matrix material during the curing process. At the intermediate temperature stage, the most of significant changes observed in the Phenolic composite. The gaseous components such as carbon dioxide, water vapor, methane etc are released in this stage. The presences of microsilica slightly shift the weight loss curve above when compare to the neat composite weight loss curve. At the high temperature stage, TGA curve for all studied materials are almost flat. At 700˚C, the residual mass of neat composite is 72%, and residual mass of composite filled with 5%, 10%, 15% and 20% of silica were 74%, 76%, 79% and 82% respectively. The percentage of weight loss of ceramic phenolic composite filled with various percentage of microsilica at 300˚C, 600˚C, 900˚C and 1200˚C are in shown in figure 5. Hence, it is found that the addition of microsilica on phenolic ceramic composite has great influence on the thermal stability of the composite.

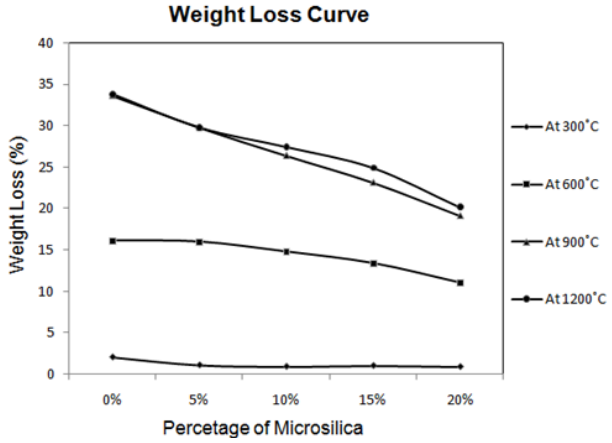

Fig: 5 Weight loss (%) of composite filled with microsilica (%) at various temperature

5. CONCLUSION

The addition of microsilica up to 15% with the phenolic resin as filler in the Woven ceramic fibre/phenolic resin composite increases the tensile strength, compressive strength and impact resistance of the composite. However, the addition of microsilica beyond 15% reduces the tensile strength, compressive strength and impact resistance of the composite due to poor wettability of the fibre. It is also observed that the addition of microsilica with phenolic resin increases the thermal stability of the composite filled with the various percentage of microsilica.

REFERENCES

[1]. Zhiyang Bu, Jijiang Hu, Bogeng Li, "Novel silicon-modified phenolic novolac resins: Non-isothermal curing kinetics, and mechanical and thermal properties of their biofiber-reinforced composites," Thermochimica Acta. 575 (2014) 244–253.

[2]. R.D. Patton, C.U. Pittman Jr, L. Wang, J.R. Hill and A.Day, "Ablation, mechanical and thermal conductivity properties of Vapour Grown Carbon Fibre/Phenolic matrix composites", Composites: Part A. 33 (2002) 243-251.

[3]. G. Pulci, J. Tirillo, F, Fossati et al, "Carbon-phenolic ablative materials for re-entry space vehicles: Manufacturing and Properties", Composites: Part A. 41 (2010) 1483-1490.

[4]. Elaine C. Ramires and Elisabete Frollini, "Tannin Phenolic resin: Synthesis, characterization, and application as matrix in bio based composites reinforced with sisal fibers," Composites Part B: Engineering. 43 (7) (2012) 2851–2860.

[5]. Frollini E, Oliveira FB, Ramires EC, Barbosa Jr., "Composites based on tannins: production, process and uses," Brazil Patent. (2008) Patent BRPI0801091.

[6]. V. Barbosa Jr, E.C. Ramires, I.A.T. Razera, E. Frollini, Biobased composites from tannin-phenolic polymers reinforced with coir fibers, Industrial Crops and Products. 32 (3) (2010) 305–312.

[7]. I. Srikanth, N. Padmavathi, Suresh Kumar, P. Ghosal, Anil Kumar and Ch. Subrahmanyam, "Mechanical, thermal and ablative properties of zirconia, CNT modified carbon/phenolic composites," Composites Science and Technology. 80 (2013) 1–7.

[8]. Jun-ichi Tani, Hajime Kimura, Ken Hirota and Hiroyasu Kido, "Thermal expansion and mechanical properties of phenolic resin/ZrW2O8composites" Journal of Applied Polymer Science. 106 (5) (2007) 3343–3347.

[9]. Jonathan Pappas, Kandarp Patel and E. B. Nauman, "Structure and properties of phenolic resin/nanoclay composites synthesized by in situ polymerization", Journal of Applied Polymer Science. 95 (5) (2005) 1169–1174.

[10]. Chenggang Chen, Ryan S. Justice, Dale W. Schaefer and Jeffery W. Baur, "Highly dispersed nanosilica–epoxy resins with enhanced mechanical Properties", Polymer. 49 (2008) 3805-3815.

[11]. Peerapan Dittanet and Raymond A. Pearson, "Effect of silica nanoparticle size on toughening mechanisms of filled epoxy", Polymer. l53 (2012) 1890-1905.

[12]. T.H. Hsieh, A.J. Kinloch, K. Masania, A.C. Taylor and S. Sprenger, "The mechanisms and mechanics of the toughening of epoxy polymers modified with silica nanoparticles", Polymer. 51 (2010) 6284-6294.

[13]. J. Tarrı Saavedra, J. Lo pez-Beceiro, S. Naya and R. Artiaga, "Effect of silica content on thermal stability of fumed silica/epoxy composites", Polymer Degradation and Stability. 93 (2008) 2133–2137.

[14]. Michele Preghenella , Alessandro Pegoretti and Claudio Migliaresi, "Thermo-mechanical characterization of fumed silica-epoxy nanocomposites", Polymer. 46 (2005) 12065–12072.

[15]. Srikanth.I, Alex Daniel, Suresh kumer, etal., " Nanosilica modified carbon-phenolic composites for enhanced ablation resistace", Scripta Materialia. 63 (2012) 200-203.

[16]. K. Haraguchi, Y. Usami and Y. Ono, "The Preparation and characterization of hybrid materials composed of phenolic resin and silica," Journal of Materials Science. 33 (1998) 3337-3344.

[17]. Jia-Min Lin and Chen-Chi, "Thermal degradation of phenolic/silica hybrid creamers, Polymer Degradation and Stability. 69 (2000) 229-235.

[18]. Donghwan Cho and Byung Il Yoon, "Microstructural interpretation of the effect of various matrices on the ablation properties of carbon-fiber-reinforced composites", Composites Science and Technology. 61 (2), (2001) 271–280.

[19]. Knop A and Pilato L.A., "Phenolic resins: chemistry, applications and performance", Springer-Verlag Berlin Heidelberg 1985: ISBN 978-3-662-02431-7.

[20]. Jigang Wang, Haiyun Jiang and Nan Jiang, "Study on the pyrolysis of phenol-formaldehyde (PF) resin and modified PF resin," Thermochimica Acta. 496 (1–2) (2009) 136–142.