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REVIEW A Review on Utilization of Light Weight Fly Ash Cenosphere as Filler in both Polymer and Alloy-Based Composites

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ARTICLE INFO ABSTRACT Fly Ash Cenospheres (FACs) are obtained from the coal power plants in Article history the form of hollow spherical particles by burning the coal. FAC was start-Received: 5 March 2020 ed to use in early 1980-1985 as lightweight filler material in producing Accepted: 19 June 2020 composites of cementitious and at present many researchers are focusing Published Online: 24 June 2020 on use of FAC as filler in polymer and metals. In this paper, the systematic review on research activities and application of FAC in manufacturing Keywords: light weight products are done. The influence of FAC on the physical and mechanical properties of incorporated polymer and alloy-based compos-Fly ash cenosphere ites were summarized. Prospects of future for its use were also suggested Polymer and Alloy composites and summarized in this paper. Mechanical and Physical properties

1. Introduction

The demand for high-performance materials in the latest technical materials is growing day by day. Composites are a mixture of two or more chemically distinct materials which will have improved properties over the individual materials ^[1]. These composites could be synthetic or natural and were flexible in nature because of their important properties like elevated high bending stiffness, modulus, chemical resistance and specific strength for multifunctional applications ^[2,3]. Combining two or more conventional materials can create new high-performance materials. In the current manufacturing industries hybrid materials play a significant role.

Engineering materials are mainly classified as metals and alloys, plastics, ceramics and glasses, and their combinations will form the evolution of composite materials as shown in Figure 1^[4]. The metal filled plastics in which plastic fibers are acting as reinforcement in metal matrix. In metal matrix composites various reinforcement materials were used like fly ash, cenosphere as ceramics. Where as in case of fiber reinforced plastics natural and synthetic fibers are used as reinforcement to get better properties plastic composites. Glass Reinforced Plastics (GRP), Carbon fiber reinforced polymer (CFRP), Polytetrafluoroethylene (PTFE) are various examples of combination of polymer with ceramics and glasses ^[5].

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Figure 1. Classes of engineering materials, showing the evolution of composites

Two Greek words: Kenos (hollow, void) and Sphaera (sphere) coined the term Cenosphere. Cenosphere is a hollow ceramic microsphere contained in fly ash, as it is a natural by-product of coal combustion during electricity generation ^[6]. Cenosphere is recycled from the waste stream as a portion of the fly ash produced in coal combustion. They are consisting of alumina, inert silica, and iron. The cenosphere size ranges from 1 to 500 microns, with an average compressive capacity of 3000+psi. with a white and dark gray colour ^[7,9]. They are stated to as hollow spheres, microspheres, hollow ceramic microspheres, glass beads, or micro balloons.

The actual worldwide use of ash ranges greatly from a minimum of 3% to a maximum of 57%, but the global average is just 16% of total ash^[8]. Throughout India as well as in many other countries, thermal power plants are the primary sources for power generation. India has about 40 major thermal power plants, and they have produced about two thirds of the country's power demands. India generates about 110 million tons of coal ash per year from the annual burning of about 300 million tons of coal for electricity generation. About 73 percent of India's total electricity generation capacity is thermal, 90 percent of it is based on coal ^[10].

1.1 Syntactic Foams

The synthetic foam concept was originally invented in 1955 by the Bakelite Company (New York) for its lightweight composites of hollow phenolic microspheres bonded to a phenolic, epoxy or polyester matrix ^[11]. Syntactic foams are examples of composite particulate materials consisting of hollow spherical fillers in a resin matrix ^[12]. Similar to solid particulate composites and fibre-reinforced composites, these hollow spheres are called micro ballons incorporated in the matrix. The Micro balloons have been used in syntactic foams, can be made of glass, ceramic, steel and aluminium available in different sizes [13,15].

These matrix materials have more influence on the tensile properties. The tensile strength could be enhanced by a chemical surface treatment of the particles, such as silanisation, which allows for the creation of strong bonds between glass particles and epoxy matrix. Including fibrous materials often improves tensile strength. Syntactic foams are typically structuring of two phases, namely matrix and micro-balloons. Due to the presence of porosity inside the micro-balloons these foams are known as closed porous foams. Nevertheless, air, or voids can be entrapped inside the matrix during the manufacture of syntactic foams. The presence of air or voids within the matrix is called open cell porosity and thus gives syntactic foams a three-phase structure ^[14].

The main contribution of syntactic foams to enhancing composite performance relies primarily on nature's buoyancy and insulation.

Buoyancy characteristics- including high strength, low density and low water absorption make the material suitable for applications with sub-surface buoyancy.

Current syntactic foam applications include the buoyancy modules for Remote operation of underwater vessels / Autonomous underwater exploration of underwater vessels / Ship hulls / Helicopter and aircraft parts.

Insulation characteristics - Syntactic foam has a low thermal conductivity coefficient which gives it superior properties, especially under highly compressive loads. It can be used for Liquefied Natural Gas (LNG) and industrial applications in underwater plumbing, load bearing insulation, subsea and insulation. The material's strength enables it to be used as a light weight, load carrying structure for marine, military and acoustic applications ^[16].

Many syntactic foam applications include: Deep-sea buoyancy foams, Thermoforming plug aids, Radar transparent materials, acoustically attenuating materials, Blast reducing materials, Sports goods such as tennis rackets and soccer balls, Drilling devices, Riser buoyancy, Upstream SURF ancillary gear, Mooring buoyancy, Deepwater buoyancy, Subsea buoyancy, Defense / oceanographic buoyancy.

1.2 Cenosphere

The cenosphere (spherical shape) improves the flow capacity in most applications and provides an even distribution of the composite matrix filler material. Cenospheres are 75 percent lighter than other commonly used minerals as fillers or extender. It is possible to use them in dry or wet slurry form due to the natural properties of the cenosphere ^[17]. Cenosphere is easy to manage because of its inert properties and has a low surface area-to-volume ratio and is not influenced by liquids, solvents, alkalis or acids etc.

These hollow spheres used as an extender for plastic compounds and are compatible with thermoplastics, latex, polyesters, plastisol's, epoxies, phenolic resins and ure-thanes ^[18]. Synthetic cenosphere foams have shown superior mechanical properties compared to those fabricated with microspheres ^[19]. Due to lower production costs of cenospheres often replace mined materials. the cenosphere will support the finished product properties by increasing electrical insulation, durability and better sound proofing ^[18]. Cenosphere compatibility, especially in cements and other building materials, such as wall coatings and composites, and also used in a wide range of other items, including sports equipment, insulation, vehicles, marine crafts, paints, and fire and heat protection devices ^[20].

Currently, the manufacturers have begun filling the cenospheres in metals and polymers in order to make light-weight composite materials with higher strength, when compared with the other types of foam materials.

 Table.1 Chemical composition of fly ash cenosphere

Sl.No	Element	% of composition
1	Silicon Oxide (Sio ₂)	93.28
2	Aluminium Oxide (Al ₂ O ₃)	0.33
3	Ferric Oxide (Fe ₂ O ₃)	0.57
4	Calcium Oxide (CaO)	0.63
5	Loss On Ignition	4.80
6	Magnesium Oxide (MgO)	0.34

2. Literature Review

A few inquiries were recorded concerning the physical and mechanical properties of polymer and alloy composites reinforced by fly ash cenosphere.

2.1 Cenosphere Reinforced Polymer Composites

Das A and Satapathy BK^[21] prepared composite by adding cenosphere and Polypropylene and to study their structural and mechanical properties such as flexural and tensile. Morphological properties of the composite were studied using Wide-angle X-ray diffraction (WAXD) and scanning electron microscopy and they found that increase in tensile and flexural properties increased with 30% of reinforcement.

Labella M et al ^[22] prepared the composite by adding Vinyl ester filled with fly ash cenospheres. By adding the cenosphere the flexural strength decreased by 73% while the flexural modulus increased by 47% at 60 vol. % cenospheres. They also found that coefficient of thermal expansion decrease by reinforcing the composite with the cenosphere.

Chand N et al ^[23] studied how cenosphere could be used as a filler to improve the mechanical properties of the polymer matrices. Due to the homogeneous dispersion of cenospheres in polymer matrix it also exhibits improved wear resistance of high density poly ethylene composites.

Takuya Morimoto et al ^[24] have investigated porous particles filled phenolic composites. They found that the fracture toughness and the wear rate decreased as the volume fraction of hollow particles increased.

Gupta N et al ^[25] have done the work on syntactic foams. The mechanical properties and density of the syntactic foam could be changed by using different inner radius but cenospheres of same outer radius in the matrix.

Chauhan SR and Thakur S^[26] were prepared the specimens with varying particle size cenosphere reinforced vinyl ester composite It was found that cenosphere particles of submicron size as fillers contributed to the improvement of the specific wear rate and the mechanical properties significantly, for all the vinyl ester composites it decreases with sliding distance and after certain duration attains approximately a steady state value.

Sampathkumaran P et al^[27] have carried work on fly ash cenosphere reinforced different polymer composites, and they found that improved properties of both physical and mechanical properties with respect high density poly ethylene (HDPE) and low density poly ethylene (LDPE) polymer composites.

Divya VC et al ^[28] have carried out work on the composite, with a high density polyethylene, cenosphere and multiwall carbon nanotubes (MWCNT), and they found that these composites showed better mechanical properties than the composites without cenosphere and MWCNT. The addition of cenosphere and MWCNT increase the flammability property of the composite.

Jalageri HB et al^[29] have prepared the cenosphere/multi wall carbon nano tubes reinforced polymer composites, and they found that the composite with 0.5 wt. % exhibits higher impact strength, and for 0.1 to 0.2 wt. % of MWCNT were found good flexural and tensile properties.

Ren S et al ^[30] were demonstrated that Fly ash Cenospheres-hollow glass microspheres / borosilicate glass composites (FACs-HGMs / BG) have outstanding mechanical properties both at room and high temperatures can be used in the near future as potential candidates for structural materials or temperature-resistant buoyant material.

Balaji R et al^[31] prepared phenolic composites filled with Cenosphere, and studied their thermo-oxidation,

properties and its characteristics. They found that decrease in the thermal degradation occurred due to composite filled with the cenosphere.

Wang MR et al ^[32] prepared the geopolymeric based composites by adding metakaolin and fly ash cenosphere based geopolymeric slurry. They found that by the transmission electron microscopy and scanning electron microscope in alkaline condition fly ash cenosphere did not dissolve. 40 vol. % of this composite gives promising material for intermediate-temperature thermal insulation.

Bora PJ et al ^[33] were prepared the composites by solution-processing of Polyvinylbutyral (PVB)-FAC, PVB-CoOx-FAC and PVB-NiO-FAC. Such composites are suitable for applications focused on microwave absorption such as robotic engineering, radar, electromagnetic gasket, military, aircraft and unmanned vehicles.

Balaji R and Sasikumar M^[34] were prepared the composite of cenosphere filled phenolic of ceramic woven. The oxyacetylene ablation test and Thermogravimetric Analysis were used to study the ablative properties and thermal properties. They found that thermal degradation of cenosphere filled composites increases with the increase in concentration of cenosphere.

Sambyal P et al ^[35] have studied the advanced poly (aniline-co-toluidine)/flyash corrosion resistance properties on mild steel substrates using powder coating techniques, and noble potential for epoxy with copolymer-coated steel coated specimens relative to epoxy-coated steel. They noticed even low corrosion current for 2.0 and 3.0 wt coatings. Copolymer composite loading per cent at 3.5 wt. % NaCl solution.

Sharma J et al ^[36] have carried out work on effect of fly ash cenosphere on dielectric properties of low-density polyethylene (LDPE) and found that the variation of the relative dielectric constant with frequency indicates the presence of material interface polarization processes at low frequency. They also found that there is little variance in alternative current conductivity with rising cenosphere concentration.

GU J et al ^[37] characterize filler/matrix and hollow structure characteristic (porosity). They have investigated damping properties of the composites in the temperature range of 40 to 150 0C and they found better damping properties than matrix.

Angadi SB et al^[38] have prepared epoxy composite reinforced with cenosphere. They have carried out experimental investigation on drilling characteristics of prepared composite. They have considered drilling aspects, such as hole, thrust and drilled hole surface roughness. They have prepared specimens at different wt. % of cenosphere in epoxy resin as the composite matrix, and found that the reduced thrust forces of lower diameter drill bit, whereas greater surface roughness were found for lower diameter drilled hole. Cenosphere addition of 60% shows a significant reduction in surface roughness and thrust force.

2.2 Cenosphere Reinforced Alloy Composites

Chandel V et al ^[39] Identified potential applications of Al 7075 alloy as matrix and cenosphere as reinforcement in the aircraft and space industries due to lower weight to strength ratio, creep resistance and high wear resistance. They suggested that composites are likely to overcome the cost barrier as well as the various physical and mechanical properties for use worldwide today and serve a wide range of applications.

Vikrant C and Onkar SB^[40] found that cenosphere as reinforcement in Al 7075 alloy as matrix have been used widely in various applications because of their lower weight to strength ratio, wear resistance and creep resistance such as aircraft and space industries.

Goel MD et al^[41] studied the compressive deformation by varying densities and cenosphere sizes at different strain rates (from 0.01/s to 10/s) of aluminum cenosphere syntactic foams. It was found that relative density will not affect the densification strain, strain rate and cenosphere size. But, relative density and cenosphere size affect the plateau stress and energy absorption of syntactic foams.

Birla S et al ^[42] using casting technique and CaH2 as a foaming agent prepared the Al-Si-Cu-Mg-cenosphere hybrid foams (HFs) of varying relative densities. They have found that the addition of cenospheres up to 30 vol. % improved the yield strength, plastic collapse stress, and plateau stress. Hybrid foam energy absorption is increasing with cenosphere size decrease and relative density increase. It was also discovered that densification strain is almost invariant with cenosphere size.

Rohatgi PK et al ^[43] studied the mechanical behavior and microstructure f die casting AZ91D magnesium alloy -fly ash cenosphere composites. The presence of fly ash cenospheres in AZ91D has been reported to result in significant refinement of the surrounding matrix alloy, which becomes more intense with the increasing weight percentage of fly ash. They also investigated that the hardness of the composites based on AZ91D was improved by the introduction of fly ash, the composite toughness was a maximum where 5 wt. % fly ash was added and becomes slightly lower with the addition of 10 and 15 wt. % fly ash.

Kumarasamy SP et al^[44] carried out work on the Hybrid Aluminum Metal Matrix Composites (HAMMC) by reinforcing constant quantities of fly ash cenosphere (10%) and varying quantities of graphite (2%, 4% and 6%), cenosphere, hardness and tensile strength were found to increase and vice versa for graphite addition. Owing to reinforcement particles, the improved tensile strength of the Aluminum matrix from 178 N/mm² to 213 N/mm² as for the composite is concerned. The wear resistance improves considerably with the addition of cenosphere and but there is a wear rate decreases with graphite addition due to its self-lubricating nature. They found that minimizing the surface roughness of developed composite, the cutting speed and % of graphite addition have the major contribution.

Huang Z and Yu S^[45] were carried out work on 5 wt. % and 100 microns of fly ash cenosphere particles integrated in the AZ91DMg alloy to manufacture in situ Mg2Si and MgO strengthened AZ91D / Flyash composites using compo casting technique. They observed that the cenosphere particles were distributed homogenously in the alloy matrix, and filled with the alloy matrix on most of the cenosphere particles.

Vishwakarma A et al ^[46] carried out the study on analysis of various cenosphere sizes at different applied pressures and sliding speeds for dry sliding aluminum alloy (LM13) cenosphere syntactic foam behaviour. They have found that the coefficient of friction, frictional heating and the wear rate decreases with the decrease in cenosphere depth. They also found that the yield strength of syntactic foam increases with the decrease in cenosphere size, the wear rate also decreases with the decrease in cenosphere size and the increased strength often leads to increased wear resistance by decreasing the size of the cenosphere.

Uju WA and Oguocha INA^[47] prepared the composite of Al-Mg alloy A535 reinforced with a mixture of 5 wt. % silicon carbide and 5 wt. % fly ash with varying wt. % fly ash particles. They found that by adding fly ash and silicon carbide, the coefficient of thermal expansion of A535 goes on decreasing.

Saravanan V et al ^[48] found that 10 vol. Cenosphere percent reinforced aluminum alloy (AA) 6063 composite as the most suitable material for brake disks instead of more costly particles of aluminum oxide (Al_2O_3) or silicon carbide (SiC).

Luong DD et al ^[49] found that energy-absorption potential of A4032 / fly ash cenosphere composites were higher at higher strain levels.

3. Conclusion

The role of density, hardness, wear resistance, co-efficient of friction, slide wear and strength properties of cenosphere reinforced polymers and alloy composites were clearly identified and summarized. The density value drops when the thermoplastic polymers is filled in with the fly ash cenospheres. With the addition of cenosphere filler, the hardness value of thermoplastic polymers had improved. With the introduction of FAC fillers, the compression and impact strengths decrease, and the variance in the compression strength value was least for LDPE.

It was found that slide wear resistance of cenosphere filled composites showed better results when compared with the un-filled composites. Further, the wear loss also increases with the increase in load of both un-filled and filled composite specimens.

Cenosphere reinforced polymer samples coefficient of friction values were slightly lower than those of unfilled counterparts. Filling cenospheres in polymer and alloys has made a significant contribution to reducing friction, and increases wear resistance.

The investigation of the polymer materials has been confirmed as the best option for wear resistance applications, particularly HDPE. Owing to its improved slide wear properties, lower friction coefficient, lower percentage reduction in compression strength and impact energy compared to other polymer materials.

It was observed that with the addition of weight percentage of fly ash in both the polymer and alloy composites, there was an improvement in tensile strength, compressive strength as well as hardness. Whereas in the case of both polymer and alloy composites the ductility decreases with the percentage weight percentage of fly ash. It is also concluded that with an increase in particle size of fly ash cenosphere reinforced alloy composites the tensile strength, compressive strength & hardness decreases.

In case of alloy composites, it was found that fly ash cenosphere was mainly added in aluminium alloy when compared with the other alloys. FAC reinforced alloy composites have shown a vital applications in the aerospace industries because of their light weight, high tensile strength and hardness.

As fly ash cenosphere is made with hollow spheres, it was observed that the distribution of FAC at molecular level in polymer and alloy composites matrix were not much uniform and also the chances of getting blow holes due to its porous nature. To overcome this problem and getting the newer techniques for the preparation of FAC composites, becomes challengeable in the current scenario.

From the above literature review, it has been concluded that the fly ash cenosphere reinforced polymer and alloy composites had played an important role in the structural applications, aerospace industries and naval applications because of their light weight, wear resistant, anti-corrosion and buoyancy in nature. In the current scenario the production of composites with low environmental impact and strong commercial viability has become a big trend. Thus, the use of FAC in polymer and metal matrix composites also plays an significant role in greenhouse emissions by avoiding the other widely used mineral fillers.

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