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ACCEPTED MANUSCRIPT

# Towards Sustainable Micro and Nano Composites from Fly Ash and Natural Fibers for Multifunctional Applications

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#### Abstract

Manufacturing of petroleum based synthetic materials, exploitation of timber products from forest reserves, improper management of industrial wastes and natural resources greatly persuade the environmental contaminations and global warming. To find viable solutions and reduce such alarming issues, innovative research work on recycling of unutilized materials such as fly ash and natural cellulosic polymers has been reported in this work to develop advanced sustainable hybrid micro/nano composites. In this study, the use of natural cellulosic sisal fibers with fly ash has enhanced the tensile properties and surface finish of composites. Fly ash particulates acted as fillers, additives, as well as surface-finishing medium and sisal fibers as reinforcing elements in achieving glossy finish sustainable composites. The developed composites have been found to be stronger than wood, plastics and have many opportunities for multifunctional applications.

**Keywords:** Sustainable micro and nano composites; Renewable resources; Mechanical properties; Timber and synthetic wood substitute; Waste particulates

#### **INTRODUCTION**

Recently composites are becoming more fascinating materials and competing with the traditionally available metallic/ ceramic materials and their conventional counterparts due to many significant advantages [1-8]. In particular, natural fiber reinforced polymer matrix composites offers unique features in terms of their inherent advantages such as environmental friendliness, specific strength, low cost, saving energy etc. to name a few [9- 14]. Annually, more than 22 billion tons of wastes particulates are produced and disposed, universally on the earth and in ocean, which leads to many challenges to our environment. Among all other wastes, the quantity of Coal Combustion Residues (CCRs), so called fly ash, produced both in developing and developed countries alone are about 1.5 billion tons. In India and USA alone, during 2014-2015, thermal power stations produced about 240 million tons and 135 million tons of fly ash respectively. Frequently, CCRs comprises of different prime constituents namely pond ash, boiler slag, fly ash, bottom ash, along with some other solid fine particles released during the process of coal combustion [15]. It is apparent that one of the cause for environmental

pollution is due to combustion of coal at high temperature above 1200<sup>o</sup>C for power generation, worldwide, and has become a major challenge to safeguard air, soil, ground water, vegetation, aquatic flora and fauna and human health[16] [17]. Though, fly ash has been used for many applications, maximizing the fly ash consumption and safe management has become a great challenge and issue to the producers, users and researchers[18].

#### Coal Ash: World production and their characteristics

Due to the technological advancement, to meet the demand of energy requirements universally, there has been a considerable increase in power plant every year [19]. Presently, the major producers of coal ash are United States of America (~ 135 MTPA), Russia (~ 155 MTPA), India (~240 MTPA) and China (~520 million tons per annum MTPA) [20]. Different physical properties such as porosity, shape, size, density, water retention capacity etc. has significant influence on the safe disposal and recycling in different appropriate applications [17]. Particle size and other physical properties of Indian coal ash varies widely and specific surface area found to be greater than 0.1038m<sup>2</sup> gm<sup>-1</sup> [18]. It is evident from the work done that chemical constituents in fly ash tend to exist in the finer particles, which are mostly siliceous material. Such materials are used to chemically react with lime (CaO), in water and improve pozzolonic characteristics resulting enhanced mechanical strength in concrete composites [21] [20]. The major mineral phases in fly ash has been found to be hematite, tricalcium aluminate, quartz (SiO<sub>2</sub>), mullite, (3Al<sub>2</sub>.2SiO<sub>2</sub>), and ferrite [20] [21]. Some of the other mineral phases include albite tenorite (CuO), (KalSi<sub>3</sub>O<sub>8</sub>), nepoutite (NiMg) 3Si<sub>2</sub>O<sub>15</sub>(OH) 4, esperite (CaPb) ZnSiO<sub>4</sub>, and mullite (Al<sub>6</sub>Si2Ol3). The geo-technical studies showed that co-efficient of permeability of coal ash varies from 10  $^{-4}$  to 10  $^{-3}$  mm / sec and young's modules of coal ash found to be 13- 126 GPa, which depends on various characteristics of coal ash [22] [23].

#### **Recycling opportunities**

Significant efforts are currently being made to improve the pozzolanic property of ash through grinding and classification to increase the surface area of coal ash particles to increase the reactivity in cement concrete mixtures. High volume use of lignite coal ash (60%) with rice husk ash (25%) and fine aggregates were used to attain 40-50 MPa compressive strength of selfconsolidating concrete [24]. Glass-ceramics were prepared using coal ash for use in wallcovering panels, floors tiles equivalent quality to that of marble and granite [25]. Processed coal ash has many application potential to be used as raw materials in construction sectors such as bricks, cement, concrete, adhesives, road embankment etc., [26] [17] [20]. In some coal ash specimens, the unburned carbon amount has been found to be 10% - 45%, that hinders the use of such ash in cement production, however it helps in broadening its use in waste water treatment as an effective adsorbent [27]. Considerable research has been done universally for effective utilization of coal ash in mine reclamation, composites, paint, agriculture, hazardous waste immobilization, geo-polymeric concrete, waste water treatment and recovery of value added materials [28]. Unfortunately, not much work has been done on the usage of coal ash for the preparation of polymeric composites [29]. Indeed, the coal ash exhibit a very high potential to be used as a low cost reinforcement and an important component in polymer matrix composites (PMC) as well as in other composites systems such as metal /ceramic / cement / concrete matrix composites. Coal ash is potentially a resource materials and can be used as a particulates in composites and its availability become certain till the living system exists. Along with fly ash, sisal fibers represents another important economic biorenewable resource. The usage of these cellulosic sisal fibers have not yet effectively exploited for their use for value added engineering reinforcement. So, in in this work, the properties of the raw materials, process development in fabrication of composites, performance of the composites and possible applications for multifunctional utility have been reported and discussed in detail.

#### MATERIALS AND METHODS

In the current study, fly ash was procured from the Electro Static Precipitator and was collected from Satpura Thermal Power Station (STPS), Central India (**Fig. 1a**). The term ash in this work refers to the fly ash. Different Fly ash specimens were dried in an oven at 105  $^{\circ}C\pm 2^{\circ}$  C and were used for physico-chemical characterization as well as conducting experiments for the preparation of polymer composites. Sisal leafs used in this study were harvested from the known source of cultivation at CSIR-AMPRI Bhopal, Central India. Fibers were extracted from the sisal leafs by an instantaneous mechanical process, without affecting its quality, using a Respador machine [30]. Extracted sisal fibers were sun dried at  $36^{\circ}C\pm 2^{\circ}$  for 2-3 hours till these fibers reached the moisture as low as 12 % and were subsequently combed to remove unwanted residues including wax (**Fig. 1b**). Such processed sisal fibers were cut into about 3.5 cm length uniformly and perform mats were fabricated using a motorized rolling screen drum and are shown in **Fig. (1c)** and **Fig. 1(d)** respectively.

#### Test methods adopted for raw materials characterization

Particle size analysis of fly ash particulates was done using Laser Diffraction Particle size analyzer (Model HELOS, Sympatec GMBH, Germany) and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> was used for facile dispersion of Fly ash in water medium. pH and conductivity studies were done using Orion analyser (Model 1260, Orion Research Inc., USA) in a 1:2 solid: water suspension. Fly ash particulates were digested in a microwave digester (QLAB 6000, Canada) and chemical elements were analyzed from the digested extracts using Atomic Absorption Spectrophotometer (Z-5000, Hitachi, Japan) with flame and graphite system. However, the presence of silicon, aluminum, iron, calcium, magnesium, sodium and potassium was estimated by Field Emission Scanning Electron Microscope (FESEM) with Energy Dispersive Spectrometer and Electron back Scattered Diffraction system, Model 1E Synergy 250, Oxford Instrument UK) facility. High purity water distilled from Prima1-3 and Elgastat Maxima, England was used for all chemical analysis. Sisal fiber microstructure was studied using Scanning Electron Microscope (SEM), Model JOEL JSM-5600 Japan. Tensile properties of sisal fibers (ASTM 5526) were studied using Universal Testing Machine (UTM), 5 KN capacity, LRX Plus, Lloyd, UK employing 2.5KN load cell at a rate of speed 5.0 mm/min with a gauge length 50.0 mm. The preload/ stress was 20.0 gf with preload/ stress speed of 2.0 mm/min.

#### **Preparation of composites**

Composite specimens were fabricated using fly ash as a reinforcement in the epoxy polymeric system using hand lay-up process followed by compression molding system. Composites developed in the present study using fly ash with and without sisal fiber in epoxy resin system and neat epoxy are shown **in Fig. 2 (a, b, c, d).** Commercial grade Epoxy resin (Araldite- AY 105) with Hardener (HY-951) at the ratio of 1:0.10 was used for the preparation of composites and different specimens were casted under compression molding system at  $120 \pm 5^{\circ}$ C at a pressure 5PSI for 10 minutes and were cured at  $36 \pm 2^{\circ}$ C for 8 hrs. Similar processing conditions were followed for casting fly ash fortified composites, hybrid composites and sisal fiber reinforced composites. The quantity and concentration of fly ash, fiber volume fraction, composite casting conditions were decided based on various lab experiments performed earlier by the first author as well as work reported elsewhere (13,17). Fly ash particulates fortified epoxy composites (FEC) were fabricated using 1:0.5 fly ash and epoxy resin system (**Fig. 2a**).

Hybrid composites (HBC) were fabricated using fly ash particulates (50%) reinforced with sisal fibers preform mat (15%) in epoxy system (**Fig. 2 b**). Sisal composites (SEC) were fabricated using sisal fiber perform mat alone in 0.4 sisal fiber volume fraction with epoxy resin (**Fig. 2 c**). For comparative performance evaluation, neat epoxy (NE) was also casted (**Fig. 2 d**).

#### Test method adopted for composites characterization

Tensile properties of composites were analyzed as per the ASTM D 638 using UTM, LRX Plus, Lloyd, UK at a crosshead speed of 0.5mm/min. The density of the composites and flexural properties were performed as described in the ASTM D792-91 and ASTM D 790 respectively. FESEM study was done on the fracture surfaces of the hybrid composites using Scanning Electron Microscope.

#### **RESULTS AND DISCUSSIONS**

#### Physico-chemical and radioactive characteristics of fly ash

Particle size of fly ash is an important physical parameter that significantly influences the chemical characteristics of fly ash as well as the mechanical performance of fly ash fortified composites and sustainable hybrid composites. The present study results revealed that fly ash particulates consists of wide range of particles from micrometer to millimeter. **Fig. 3(a)** depicts the particle size distribution curve of fly ash and it has been recorded from the standard mean deviation that 90 % of the particles were below 19.94  $\mu$ m. It has shown almost very fine particles and 10% of fly ash particles were just below 1.36  $\mu$ m and 50% of the particles were 6.48  $\mu$ m and the corresponding shape and microstructure of fly ash particles are shown in **Fig. 3(b)**. The average specific surface area of fly ash particulates was 7117. 67 cm<sup>2</sup>/g. The pH of the fly ash varied from 7.2-7.8 and the electrical conductivity was in the range of 0.522 - 0.614 ds.cm<sup>-1</sup>. It is

evident from the results that density of fly ash varied from 0.99 g/cc - 1.32 g/cc and the corresponding specific gravity was recorded as 2.10-2.31. The other physical properties of fly ash are shown in **Table 1(a)**. The presence of radionuclide present in fly ash is shown in **Table 1** (b). It is imperative to note that the concentration of radionuclide such as Potassium  $\binom{40}{K}$ , Radium  $\binom{226}{Ra}$ , and Actinium  $\binom{228}{Ac}$  in fly ash were found to be almost similar to that of soil of Central India and lower than that of the upper limits recommended for any consumer products.

The microstructure of fly ash particles studied by FESEM revealed that most of the fly ash particles are spherical in nature and very small in size and particle size below 1.36  $\mu$ m can also been seen in the micrograph (**Fig. 3 b**).

Though, all the chemical constituents in fly ash are present in oxide form, in the present study, the chemical properties are estimated in elemental form and the results are shown in **Table 2**. The major chemical constituents in fly ash are oxides of silica, alumina and iron and their concentration has been found to be about 29.07 %, 16.24 %, and 4.23 % respectively. The trace amount of elements in fly ash such as Zn, Cd, Pb, Mo, Ni, As and Se are also present and are an important concern for fly ash disposal as they may contaminate soil and ground water. The total concentration of all these elements as shown in **Table 2** present in fly ash did not show any toxicity are found to be almost similar to that of soil and were also confirmed by earlier researchers [17, 20, 26]. The ultimate impact of these elements would depend on its active state in fly ash and toxicity, mobility and availability in the ecosystem. Interestingly, many of the heavy metals in Indian fly ash found to be in lower concentration than that of in fly ash of Russia, USA and Europe, moreover, leaching of toxic metals in Indian fly ash and pond ash found to be below the USEPA standard and are nonhazardous [18] [8].

#### Physico-chemical and mechanical characteristics of sisal fibers

The mechanical and chemical properties of sisal fibers are shown in Table 3(a) and Table (3b) respectively. Results from this study reveals that diameter of lignocellulosic sisal fiber varied from 253-461µm and the density of sisal fibers ranges from 1.22-1.42 gm / cc. As sisal fibers have been obtained from the plant sources, there was a significant variation in the mechanical properties of lignocellulosic sisal fibers and it depends on cultivation process, age of the sisal plants, agro climatic conditions, sisal fiber extraction and processing method [30]. In the tensile strength of sisal fibers, there has also been a wide variation ranging from as low as 84.6 MPa to and as high as 336.96 MPa in this study. The corresponding tensile modulus was 2.49-10.47 GPa and the elongation at the tensile fracture was 3.37-8.06 %. Due to their better mechanical properties, natural fibers such as sisal fibers can be used as a potential reinforcement in polymer composites, where higher tensile and impact strength is required and was studied by several researchers [31-34]. The microstructure of sisal fiber is shown in **Fig. 3c** depicting many sisal fibrils (below about 25 µm) bonded with in a single sisal fiber having diameter of below 200µm (Fig.3 c). Different constituents that are mainly present in sisal fibers are cellulose; hemicelluloses, lignin and their average concentrations have been found to be ~ 52.1 %, 11.9% and 15.45% respectively. All these constituents has a significant role in improving the mechanical characteristics of the polymer composites (Table 3b). The other substances present in sisal fibers are pectin and wax. The importance of natural cellulosic fibers, macromolecules and their influence on the polymer matrix composites, their applications and opportunities have been reported and discussed in details by many researchers [35-39].

#### Impact of fly ash on the mechanical properties of composites

Fly ash infiltrated composite's tensile test cut specimen and corresponding tensile test stress strain curve is shown in **Fig. 4 (a)**. Fly ash infiltrated / fortified composites developed in the present study in epoxy resin system has shown a very good surface finish (**Fig. 2a**). The density of fly ash infiltrated composites varies from 1.45 to 1.48 gm/cc. The present study revealed that the average tensile strength of fly ash infiltrated and fortified composites was found to be 31.57 MPa and the corresponding average tensile elongation was (0.75%). As compared to neat epoxy (NEC), the tensile elongation of fly ash fortified composites showed almost 72% lower elongation. But, the specific tensile strength of fly ash composite was found to be higher (21.40 $\pm$  1.98 MPa. cc/ g) than the neat epoxy (12.5 MPa. cc/ g). Moreover, the average tensile modulus of fly ash fortified composites was found to be 4.6  $\pm$  0.136 GPa, which is more than 50 % higher than that of neat epoxy.

#### Impact of fly ash and sisal fibers on the performance composites

The mechanical properties of the fly ash fortified with sisal chopped fibers reinforced sustainable hybrid composites (FSEC) are shown in **Table 4a.** Incorporation of sisal fibers with fly ash has shown little increase in the tensile strength  $(33.02 \pm 1.428 \text{ MPa})$  as compared to fly ash composites. But, the density of the hybrid composite was found to be reduced density due to sisal fiber incorporation, and enhanced the tensile elongation about 27% over fly ash composites and reduced the tensile elongation about 54% over neat epoxy. The tensile cut specimens and corresponding stress strain curve for fly ash with sisal fiber reinforced composites is shown in **Fig. 4 (b).** The decrease in density (~17%) and increase in the tensile strength (~36%) and tensile modulus (~78%) of fly ash fortified with sisal fiber reinforcement in the hybrid

composites has shown relatively better performance over fly ash and jute fabric reinforced polyester resin composites as reported [29]. The composites' tensile specimens and corresponding stress strain curve is shown in Fig. 5a. It is interesting to note that the tensile strength of sisal epoxy composites was found to be 71.38±4.65 MPa. The resulting tensile modulus and tensile elongation of SEC were found to be 3.99  $\pm$  0.19 GPa and 2.62  $\pm$  0.12 % respectively. Furthermore the sisal fiber reinforcement in epoxy system has decreased the density (8%) over fly ash fortified composites. Fig. 5(b) shows the neat epoxy tensile test specimen and corresponding stress strain curve (NEC). Though the density of epoxy resin  $(1.24 \pm 0.015 \text{ g/cc})$ is lower but the resulting tensile elongation  $(2.04 \pm 0.184 \%)$  was found to be higher (Table 4b). The average tensile strength of neat epoxy was recorded as 33.72±3.34 MPa, while the tensile modulus (2.28 $\pm$  0.34 GPa) was found to be considerably lower as compared to the fly ash fortified composites as well as fly ash and sisal fibers reinforced hybrid composites. Though randomly oriented short sisal fiber reinforced composites have resulted in higher tensile strength than that of hybrid composites developed using fly ash and sisal fiber, the glossy surface finish could only be achieved using high fly ash particulates incorporation.

Little work has been reported on the development of composites using fly ash and jute fiber in polyester system and their practical applications are still being explored [29]. One initial study has reported on the tensile strength property of E-glass fiber (20%) reinforced composites employing cenosphere ash (10%), however the other primary mechanical characteristics were not reported in this study[40]. Earlier researchers reported on the usage of sisal fibers in chopped / short fiber forms with polymer, but, no work has recorded the tensile strength and its corresponding modulus, density and elongation as well as on use of fly ash with sisal fibers reinforcement [29] [41] [42]. The traditional glass/ carbon fiber reinforced plastics, and other polymeric composites are the highly competitive materials in today's word. But the fibers used as reinforcing materials in all such composites are non-environmental friendly and involve highly energy consuming process. In addition, the handling of these materials also causes serious health concerns. Due to these reasons, the use of natural cellulosic fibers has received greater attention of researchers, environmentalists and technocrats[43]. Hence, the work performed in the present study seeks to address to the multiple issues on different aspects with multifunctional solution.

Mechanical properties of particulates infiltrated polymer composites has been reported to depend on particle size, particle concentration and particulates- matrix interface [44]. In the present study, silica and alumina rich inorganic fly ash particulates' particle size ranging from 1.36 - 19.94 µm with about 50 % loading of reinforcement in epoxy resin system enhanced the tensile modulus and reduced the elongation in composites. In the present study, presence of alumina and silica in fly ash, though have not much influenced the tensile strength, but the overall performance in terms of modulus, surface finish and bonding between matrix and fibers has been found to be considerably improved. The effect of particle size on the modulus of epoxy- silica composites was also studied and the results demonstrated that the modulus remains constant with increment in particle size [45]. Table 5 shows the comparison of mechanical properties of fly ash fortified sisal composites, fly ash with sisal fibers reinforced hybrid composites over neat epoxy, fly ash polyester composite, teak wood and synthetic wood. It is summarized from the present study that the density of fly ash infiltrated composites was relatively higher in comparison to the fly ash and sisal fiber reinforced hybrid composites as well as those of conventional materials such as wood and synthetic wood (Fig. 6a). The mechanical properties of composites developed in the present study over neat epoxy and conventional

materials have been also compared (**Fig. 6b**) and the results revealed that there was significant materials performance in terms of tensile strength, modulus and elongation as compared to the other studied materials. It is evident from the findings of present study that the fly ash composites as well as fly ash and sisal fiber reinforced hybrid composites have shown increased tensile strength, modulus and reduced elongation over neat epoxy. The sisal fiber epoxy composites have demonstrated the highest tensile strength as compared to related materials. However, the excellent surface finish could only be achieved with addition of fly ash particulates. In fly ash fortified composites, presence of chemical constituents in fly ash such as oxides of silica, alumina and titanium enhanced the tensile modulus and improved surface finish over synthetic wood and teak wood. Furthermore, these research findings are also expected to create opportunity in bringing a new classes of sustainable hybrid composites using inorganic fly ash particulates as a filler, binder and surface finishing catalyst and utilizing renewable sisal fibers as a reinforcing materials for the development of sustainable hybrid composites and create new industrial opportunities.

### Microscopic and thermal degradation study of fly ash and sisal fibers composites

The FESEM technique employed in the present study to characterize different composites microstructure revealed that there is a good reinforcement with uniform dispersion of fly ash particulates and also confirmed the local failure in the fractured composites. The microstructure of tensile fracture surface of casted neat epoxy, fly ash particulates infiltrated composite, hybrid composites and sisal fibers reinforced composites in epoxy resin system under different magnifications using FESEM is shown **Fig. 7 (a, b, c & d)**. It is evident from the microstructure of the composites that there is a very good bonding of fly ash particulates in epoxy resin

consisting different spherical shaped sizes from  $2 \mu m - 30 \mu m$ . As can be shown in Fig. 7(b), the surface of fly ash particulates have been well bonded with epoxy resin and even after the tensile pullout test, the particulates are well resistant in the polymeric system. The FESEM micrograph reveals that there is very good interfacial bonding between epoxy resin and fly ash particulates. Fig. 7 (c) shows the FESEM microstructure of fly ash particulates and short sisal fibers reinforced composites in epoxy resin system studied under 5000 magnification showing fiber and fly ash particulates. Fly ash particulates of spherical shaped as well as short sisal fibers (rod shaped) can be seen with very good bonding between particulates and fibers with matrix in the tensile fracture surface of composite. Fig. 7c shows the fractured fibers broken down during the tensile stress. Fig. 7(d) shows the FESEM image of sisal fibers reinforced epoxy composites studied under 5000 magnification and the sisal fibril as well as fiber diameter of 2.72 - 19.74 µm can be seen with good bonding in matrix in the tensile fracture surface of composite. It is understood that presence of silica, alumina, titanium and other light metals in fly ash particulates and cellulose content in sisal fibers acted as reinforcement to increase the strength of hybrid composites and enhanced the interfacial adhesion between particulates, fibers and resin system. Earlier study performed on the interface analysis of Nickel particle-reinforced Aluminum-Silicon (AlSi) having spherical powder (with maximum particle of diameter of 45 µm ) in the composites showed reasonable dispersion of Ni particulates in the studied composites [46]. But, in the fly ash particulates reinforced composites and HBC composites, a very good interfacial bonding could be seen in the micrograph as shown in Fig. 7b and 7c. Also the spherical fly ash particles were strongly bonded with rod shaped sisal short fibers and could be easily seen in the polymer matrix composites successfully confirming the adhesion between fiber and particulates in matrix system.

#### Conclusions

In this work, silica rich fly ash was used as the reinforcement as well as finishing agent in the epoxy resin for preparation of polymer composites. Chopped cellulosic sisal fiber preform mat was also used to explore additional reinforcement in the prepared composites. It has been demonstrated in this study that the presence of cellulosic content in biofiber and silica and alumina in fly ash particulates influences the quality of hybrid composites. The resultant composites have high potential to use in architectural interiors in building construction industries, and transportation system. Commercialization of this research finding is expected to substantiate as an alternative to traditional wood/plastic/ GRP materials. Effective use of fly ash and sisal fibers would lead to reduction in the consumption of non-renewable resources and introduce a new class of hybrid composite materials to the composite industry.

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#### References

- [1] I. Hölken, M. Hoppe, Y.K. Mishra, S.N. Gorb, R. Adelung, M.J. Baum, Complex shaped ZnO nano- and microstructure based polymer composites: mechanically stable and environmentally friendly coatings for potential antifouling applications, Phys. Chem. Chem. Phys. 18 (2016) 7114–7123. doi:10.1039/C5CP07451G.
- [2] V.K. Thakur, D. Vennerberg, S. A. Madbouly, M. R. Kessler, Bio-inspired green surface functionalization of PMMA for multifunctional capacitors, RSC Adv. 4 (2014) 6677–6684. doi:10.1039/C3RA46592F.
- [3] N. Kumar, K. Biswas, R.K. Gupta, Green synthesis of Ag nanoparticles in large quantity by cryomilling, RSC Adv. 6 (2016) 111380–111388. doi:10.1039/C6RA23120A.
- [4] K.M. Tripathi, A. Tyagi, M. Ashfaq, R.K. Gupta, Temperature dependent, shape variant synthesis of photoluminescent and biocompatible carbon nanostructures from almond husk for applications in dye removal, RSC Adv. 6 (2016) 29545–29553. doi:10.1039/C5RA27432J.
- [5] S. Garlof, M. Mecklenburg, D. Smazna, Y.K. Mishra, R. Adelung, K. Schulte, B. Fiedler, 3D carbon networks and their polymer composites: Fabrication and electromechanical investigations of neat Aerographite and Aerographite-based PNCs under compressive load, Carbon. 111 (2017) 103–112. doi:10.1016/j.carbon.2016.09.046.
- [6] S. Garlof, T. Fukuda, M. Mecklenburg, D. Smazna, Y.K. Mishra, R. Adelung, K. Schulte, B. Fiedler, Electro-mechanical piezoresistive properties of three dimensionally interconnected carbon aerogel (Aerographite)-epoxy composites, Compos. Sci. Technol. 134 (2016) 226–233. doi:10.1016/j.compscitech.2016.08.019.
- [7] A.S. Singha, V.K. Thakur, Synthesis and Characterization of Grewia Optiva Fiberreinforced PF-based Composites, Int. J. Polym. Mater. Polym. Biomater. 57 (2008) 1059– 1074. doi:10.1080/00914030802257800.
- [8] A.S. Singha, V.K. Thakur, Fabrication and study of lignocellulosic hibiscus sabdariffa fiber reinforced polymer composites, BioResources. 3 (2008) 1173–1186.
- [9] V.K. Thakur, A.S. Singha, M.K. Thakur, Green composites from natural fibers: Mechanical and chemical aging properties, Int. J. Polym. Anal. Charact. 17 (2012) 401–407.
- [10] A.S. Singha, V.K. Thakur, STUDY OF MECHANICAL PROPERTIES OF UREA-FORMALDEHYDE THERMOSETS REINFORCED BY PINE NEEDLE POWDER, BioResources. 4 (2009) 292–308. doi:10.15376/biores.4.1.292-308.
- [11] V.K. Thakur, A.S. Singha, M.K. Thakur, Surface modification of natural polymers to impart low water absorbency, Int. J. Polym. Anal. Charact. 17 (2012) 133–143.
- [12] A.S. Singha, V.K. Thakur, Mechanical, Thermal and Morphological Properties of Grewia Optiva Fiber/Polymer Matrix Composites, Polym.-Plast. Technol. Eng. 48 (2009) 201–208. doi:10.1080/03602550802634550.
- [13] P. Asokan, M. Firdoous, W. Sonal, Properties and Potential of Bio Fibres, Bio Binders, and Bio Composites, Rev. Adv. Mater. Sci. 30 (2012) 254–261.
- [14] V.K. Thakur, A.S. Singha, M.K. Thakur, In-air graft copolymerization of ethyl acrylate onto natural cellulosic polymers, Int. J. Polym. Anal. Charact. 17 (2012) 48–60.
- [15] P. Asokan, M. Saxena, S.R. Asolekar, Coal combustion residues—environmental implications and recycling potentials, Resour. Conserv. Recycl. 43 (2005) 239–262. doi:10.1016/j.resconrec.2004.06.003.

- [16] C.-C. Hung, Y.-F. Su, Medium-term self-healing evaluation of Engineered Cementitious Composites with varying amounts of fly ash and exposure durations, Constr. Build. Mater. 118 (2016) 194–203. doi:10.1016/j.conbuildmat.2016.05.021.
- [17] A. Dey, K.M. Pandey, Characterization of Fly Ash and Its Reinforcement Effect on Metal Matrix Composites: A Review, Rev. Adv. Mater. Sci. 44 (2016) 168–181.
- [18] P. Asokan, M. Saxena, A. Aparna, S.R. Asolekar, S.R. Asoletar, Characteristics variation of coal combustion residues in an Indian ash pond, Waste Manag. Res. J. Int. Solid Wastes Public Clean. Assoc. ISWA. 22 (2004) 265–275.
- [19] P. Asokan, M. Saxena, S.R. Asolekar, Recycling hazardous jarosite waste using coal combustion residues, Mater. Charact. 61 (2010) 1342–1355. doi:10.1016/j.matchar.2010.09.005.
- [20] E.A. Azimi, M.M.A.B. Abdullah, L.Y. Ming, H.C. Yong, K. Hussin, I.H. Aziz, Processing and Properties of Geopolymers as Thermal Insulating Materials: A Review, Rev. Adv. Mater. Sci. 44 (2016) 273–285.
- [21] A. Pappu, M. Saxena, S.R. Asolekar, Solid wastes generation in India and their recycling potential in building materials, Build. Environ. 42 (2007) 2311–2320. doi:10.1016/j.buildenv.2006.04.015.
- [22] S. Ghosal, S.A. Self, Particle size-density relation and cenosphere content of coal fly ash, Fuel. 74 (1995) 522–529. doi:10.1016/0016-2361(95)98354-H.
- [23] T. Matsunaga, J.K. Kim, S. Hardcastle, P.K. Rohatgi, Crystallinity and selected properties of fly ash particles, Mater. Sci. Eng. A. 325 (2002) 333–343. doi:10.1016/S0921-5093(01)01466-6.
- [24] G. Sua-iam, N. Makul, Utilization of high volumes of unprocessed lignite-coal fly ash and rice husk ash in self-consolidating concrete, J. Clean. Prod. 78 (2014) 184–194. doi:10.1016/j.jclepro.2014.04.060.
- [25] T.W. Cheng, M.Z. Huang, C.C. Tzeng, K.B. Cheng, T.H. Ueng, Production of coloured glass-ceramics from incinerator ash using thermal plasma technology, Chemosphere. 68 (2007) 1937–1945. doi:10.1016/j.chemosphere.2007.02.046.
- [26] R. Ahmad, M.M.A.B. Abdullah, K. Hussin, A.V. Sandu, M. Binhussain, N.A. Jaya, Processing and Properties of Polymer Filled Geopolymer Ceramics Fabricated Via Powder Metallurgy Method: A Review, Rev. Adv. Mater. Sci. 44 (2016) 26–32.
- [27] L. Bartoňová, Unburned carbon from coal combustion ash: An overview, Fuel Process. Technol. 134 (2015) 136–158. doi:10.1016/j.fuproc.2015.01.028.
- [28] Z.T. Yao, X.S. Ji, P.K. Sarker, J.H. Tang, L.Q. Ge, M.S. Xia, Y.Q. Xi, A comprehensive review on the applications of coal fly ash, Earth-Sci. Rev. 141 (2015) 105–121. doi:10.1016/j.earscirev.2014.11.016.
- [29] M. Saxena, R.K. Morchhale, P. Asokan, B.K. Prasad, Plant Fiber Industrial Waste Reinforced Polymer Composites as a Potential Wood Substitute Material, J. Compos. Mater. 42 (2008) 367–384. doi:10.1177/0021998307087014.
- [30] A. Pappu, M. Saxena, V.K. Thakur, A. Sharma, R. Haque, Facile extraction, processing and characterization of biorenewable sisal fibers for multifunctional applications, J. Macromol. Sci. Part A. 53 (2016) 424–432. doi:10.1080/10601325.2016.1176443.
- [31] A. Pappu, V. Patil, S. Jain, A. Mahindrakar, R. Haque, V.K. Thakur, Advances in industrial prospective of cellulosic macromolecules enriched banana biofibre resources: A review, Int. J. Biol. Macromol. 79 (2015) 449–458. doi:10.1016/j.ijbiomac.2015.05.013.

- [32] V.K. Thakur, A.S. Singha, M.K. Thakur, Ecofriendly Biocomposites from Natural fibers: Mechanical and Weathering study, Int. J. Polym. Anal. Charact. 18 (2013) 64–72. doi:10.1080/1023666X.2013.747246.
- [33] V.K. Thakur, A.S. Singha, Rapid Synthesis, Characterization, and Physicochemical Analysis of Biopolymer-Based Graft Copolymers, Int. J. Polym. Anal. Charact. 16 (2011) 153–164. doi:10.1080/1023666X.2011.564726.
- [34] V.K. Thakur, M.K. Thakur, R.K. Gupta, Synthesis of lignocellulosic polymer with improved chemical resistance through free radical polymerization, Int. J. Biol. Macromol. 61 (2013) 121–126. doi:10.1016/j.ijbiomac.2013.06.045.
- [35] A.S. Singha, V.K. Thakur, Physical, Chemical and Mechanical Properties of Hibiscus sabdariffa Fiber/Polymer Composite, Int. J. Polym. Mater. Polym. Biomater. 58 (2009) 217–228. doi:10.1080/00914030802639999.
- [36] A.S. Singha, V.K. Thakur, Synthesis, Characterization and Study of Pine Needles Reinforced Polymer Matrix Based Composites, J. Reinf. Plast. Compos. 29 (2010) 700– 709. doi:10.1177/0731684408100354.
- [37] A.S. Singha, V.K. Thakur, Fabrication and characterization of S-cilliare fibre reinforced polymer composites, Bull. Mater. Sci. 32 (2009) 49–58. doi:10.1007/s12034-009-0008-x.
- [38] A.S. Singha, V.K. Thakur, Fabrication of Hibiscus sabdariffa fibre reinforced polymer composites, Iran. Polym. J. 17 (2008) 541–553.
- [39] A.S. Singha, V.K. Thakur, Grewia optiva fiber reinforced novel, low cost polymer composites, J. Chem. 6 (2009) 71–76.
- [40] M. Idicula, N.R. Neelakantan, Z. Oommen, K. Joseph, S. Thomas, A study of the mechanical properties of randomly oriented short banana and sisal hybrid fiber reinforced polyester composites, J. Appl. Polym. Sci. 96 (2005) 1699–1709. doi:10.1002/app.21636.
- [41] A. Athijayamani, M. Thiruchitrambalam, U. Natarajan, B. Pazhanivel, Effect of moisture absorption on the mechanical properties of randomly oriented natural fibers/polyester hybrid composite, Mater. Sci. Eng. A. 517 (2009) 344–353. doi:10.1016/j.msea.2009.04.027.
- [42] O. Faruk, A.K. Bledzki, H.-P. Fink, M. Sain, Biocomposites reinforced with natural fibers: 2000–2010, Prog. Polym. Sci. 37 (2012) 1552–1596. doi:10.1016/j.progpolymsci.2012.04.003.
- [43] V.K. Thakur, A.S. Singha, M.K. Thakur, Biopolymers Based Green Composites: Mechanical, Thermal and Physico-chemical Characterization, J. Polym. Environ. 20 (2012) 412–421. doi:10.1007/s10924-011-0389-y.
- [44] S.-Y. Fu, X.-Q. Feng, B. Lauke, Y.-W. Mai, Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate-polymer composites, Compos. Part B Eng. 39 (2008) 933–961. doi:10.1016/j.compositesb.2008.01.002.
- [45] Y. Nakamura, M. Yamaguchi, M. Okubo, T. Matsumoto, Effect of Particle-Size on Mechanical-Properties of Epoxy-Resin Filled with Angular-Shaped Silica, J. Appl. Polym. Sci. 44 (1992) 151–158. doi:10.1002/app.1992.070440116.
- [46] G. Miranda, M. Buciumeanu, O. Carvalho, D. Soares, F.S. Silva, Interface analysis and wear behavior of Ni particulate reinforced aluminum–silicon composites produced by PM, Compos. Part B Eng. 69 (2015) 101–110. doi:10.1016/j.compositesb.2014.09.017.

S. No.	Properties	Values
1.	рН	7.20 - 7.80
2	Bulk density(gm.cm <sup>-3</sup> )	0.98-1.32
3.	Particle density	2.10 - 2.31
4.	Porosity (%)	46.5 - 49.00
5.	Electrical conductivity [ds.cm <sup>-1</sup> ]	0.522 - 0.614
6	Water holding capacity	48.6-64.75
7	Specific surface area[cm <sup>2</sup> .gm <sup>-1</sup> ]	7117.67
8	Particle Size (D <sub>90</sub> ) µm	19.94
9	Particle Size (D <sub>950</sub> ) µm	6.48
10	Particle Size (D <sub>10</sub> ) µm	1.36

Table 1 (a) Physical properties of fly ash

## Table 1 (b) Radionuclide in fly ash

Radionuclide (Bq/kg)	Fly ash	Soil in Central	Upper Limit
		India	
<sup>40</sup> K (β Emitters)	254.6 - 314.0	242.3-261.7	925
Ra ( $\alpha$ Emitters)	62.9 - 67.20	39.2-46.1	370
$Ac (\alpha \text{ Emitters})$	66.0 - 77.27	51.2-65.9	259

S. No.	Elemental composition	Concentration
1.	Si (%)	27.22 - 30.92
2.	Al (%)	15.38- 17.10
3.	Fe (%)	3.64 - 4.82
4.	Ca (%)	0.076 - 0.921
5.	Mg (%)	0.048 - 0.644
6.	Na (%)	0.098 - 1.24
7.	K (%)	0.0.08- 1.60
8.	P (%)	0.040-0.068
9.	S (%)	0.002-0.007
10.	Cu (ppm)	732 - 86.1
11.	Zn (ppm)	36.6 - 42.8
12.	Pb (ppm)	20.9 - 41.6
13.	Cr (ppm)	69.4 - 88.4
14.	Cd (ppm)	30.0 - 39.1
15.	Co (ppm)	29.0 - 58.3
16.	Ni (ppm)	99.2 - 120.7
17.	Mn (ppm)	420 - 540
18.	As (ppm)	5.6 -12.6
19.	Se (ppm)	2.8 -6.5
20.	Mo (ppm)	3.5 -7.8

## Table 2 Chemical characteristics of fly ash

S. No.	Diameter (µm)	Tensile Strength (MPa)	Young's Modulus (MPa)	Percentage total elongation at fracture (%)
1	378	152.75	4298.8	5.02
2	437	110.45	2844.2	5.32
3	448	154.27	3592.9	6.69
4	275	272.55	6417.0	8.06
5	440	106.59	3621.6	5.10
6	294	198.49	6546.1	4.22
7	462	138.56	2955.8	6.52
8	293	159.43	5303.5	3.37
9	278	230.67	6545.5	4.49
10	475	160.91	3468.7	10.86
11	283	224.53	6861.1	4.43
12	253	336.96	10472.0	5.39
13	325	226.11	5559.5	7.17
14	287	214.72	7723.3	4.4
15	430	119.78	3835.1	4.39
16	461	84.60	2795.5	4.59
17	370	143.48	3830.8	5.32
18	288	149.03	6214.6	3.66
19	312	197.87	5506.4	4.89
20	451	121.05	2592.3	5.29
21	432	136.36	3258.7	5.73
22	458	169.80	4348.8	24.52
23	424	177.96	4719.6	5.31
24	427	176.67	3762.0	6.10
25	457	104.87	2494.4	6.84
Mean	377.52	170.73	478.28	6.84
SD	78.21	57.69	192.39	4.10

## Table 3 (a) Mechanical properties of single sisal fibres

Sl. No.	Chemical Constituents	Sisal fiber
1	Cellulose (%)	41.6-62.6
2	Hemi cellulose (%)	9.2 -14.6
3	Lignin (%)	11.4 -19.5
Mechani	ical characteristics (Range Minimum	n and Maximum)
1	Single fibre diameter (µm)	253-461
2	Density (g/cm <sup>3</sup> )	1.22-1.42
2	Tensile strength (MPa)	84.6-336.96
3	Tensile Modulus (GPa)	2.49-10.47
4	Elongation (%)	3.37-8.06

1

Table 3 (b) Chemical composition and mechanical properties (range) of sisal fiber

 Table 4a Mechanical properties of fly ash with sisal fiber reinforced hybrid green

 composites

Sample ID	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)	Density (g/cc)	Specific Tensile strength (MPa.cc/gm)
FSEC_R1	32.07	4.13	0.97	1.48	21.71
FSEC_R2	31.78	4.03	0.88	1.39	22.80
FSEC_R3	35.26	3.38	1.02	1.39	25.42
FSEC_R4	32.40	3.46	1.16	1.37	23.70
FSEC_R5	33.58	3.44	1.15	1.43	23.48
Mean	33.02	3.69	1.04	1.41	23.42
SD	1.428	0.361	0.120	0.043	1.359

FSEC- Fly ash Sisal fibres reinforced epoxy composites

Table 4b Mechanical properties	of neat epoxy composites (NEC)

Sample ID	Tensile Strength (MPa)	Tensile Modulus (GPa)	Elongation (%)	Density (g/cc)	Specific Tensile strength (MPa.cc/gm)
NEC_R1	35.46	2.24	2.53	1.24	28.55
NEC_R2	30.38	2.03	2.02	1.25	24.38
NECs_R3	29.90	2.20	1.82	1.25	23.90
NEC_R4	37.19	1.93	2.51	1.26	29.52
NEC_R5	35.67	1.80	2.54	1.22	29.24
Mean	33.72	2.04	2.28	1.24	27.12
SD	3.340	0.184	0.340	0.015	2.745

NEC-Neat Epoxy

 Table 5 Comparison of mechanical properties of different composites over neat epoxy, teak

 wood and synthetic wood

Sample .No.	Tensile	Tensile	Elongation	Density	Specific Tensile
	Strength	Modulus	(%)	(g/cc)	strength
	(MPa)	(GPa)			(MPa.cc/gm)
FEC	31.57	4.6	0.75	1.46	21.62
FSEC	33.02	3.69	1.04	1.41	23.42
SEC	71.38	3.99	2.62	1.35	52.80
NEC	33.72	2.04	2.28	1.24	27.12
FPC	21.26	0.80	2.67	1.70	12.50
Teak Wood and	l Synthetic	Wood availd	able in the loca	l market	
Teak Wood	4.0	Æ	<u> </u>	0.8	5.0
MDF	0.65	Q- 7	-	0.63	1.0
Particle Board	0.425	· · · · ·	-	0.7	0.6
Rice Husk	0 405			0.7	0.15
Board	0.403	-	-	0.7	0.15

The tensile modulus and elongation of conventional materials such as teak wood, particle board, rice husk board is not reported



Fig. 1(a) Fly ash of STPC, Sarni, Madhya Pradesh, India (b) Processed sisal fibres from CSIR-AMPRI Bhopal, India (c) Processed sisal fibres cut into about 3.5 cm length 3-4 cm (d) Perform mats fabricated out of sisal fibres



Fig. 2 Photographic images of (a) Fly ash fortified epoxy composite (FEC) (b) Hybrid green composites made out of fly ash and sisal fibres (HBC) (c) Sisal chopped fibers perform mat reinforced epoxy composites (SEC) (d) Neat epoxy (NE)



Fig. 3 (a) Particle size distribution curve of fly ash samples (b) Microstructure of fly ash particles studied by FESEM (c) SEM view of cross section of sisal fibres after tensile fracture



Fig. 4 (a) Tensile stress strain curve of fly ash infiltrated epoxy composites and photographic image of tensile test cut specimens of fly ash infiltrated epoxy composites (inset).



Fig. 4 (b) Tensile stress strain curve of sustainable hybrid composite made out of fly ash and sisal fibre and photographic image of tensile test cut specimens of sustainable hybrid composite made out of fly ash and sisal fibre (inset).



Fig. 5 (a) Tensile stress strain curve of sisal fibers perform mat reinforced composites and photographic image of tensile test cut specimens of sisal fibers perform mat reinforced composites (inset).



Fig. 5 (b) Tensile stress strain curve of Neat epoxy and photographic image of tensile test cut specimens of Neat epoxy (inset).







Fig. 6(b) Comparison of Tensile strength of fly ash and sisal fibers reinforced composites vs conventional materials



Fig. 7. (a) FESEM microstructure of Neat Epoxy (b) FESEM microstructure of fly ash particulates fortified composites in epoxy resin system (c) FESEM microstructure of fly ash particulates and short sisal fibres reinforced composites in epoxy resin (d) FESEM microstructure of sisal fibres reinforced epoxy composites

### Highlights

High importance of proper selection of sustainable materials and design was demonstrated Environmental and economic benefits of sustainable hybrid materials were demonstrated Developed sustainable materials from fly ash and natural fibres exhibited outstanding performance compared to their traditional counterparts

New advanced green production routes from waste to wealth

CHR HAN