Epoxy/Fly ash from Thermal Power Plant/Nanofiller Nanocomposite: Studies on Mechanical and Thermal Properties: A Review

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INTRODUCTION
Fly ash is an industrial waste residue generated by the combustion of pulverized coal in the Thermal power plant. During the combustion of coal in the boiler, the volatile matter and carbon burn off while the impurities like shale, quartz, clays feldspar, become fuse and stay in suspension. These fuse lightweight particles are ejecting out of the boiler of the combustion chamber with flue gases. When flue gas accesses the low-temperature zone, the fused particles solidify rapidly to form spherical particles. Earlier to draining the flue gases, spherical particles of ash are arrested by electrostatic precipitators. These spherical particles are known as fly ash. And the resting particles which aggregate rest down at the bottom of the furnace are called bottom ash [1]. About 90% of the total thermal power generation in India is based on coal. At present scenario in India, there are 167 coals based thermal power plants where 400-550 MT coal is being used every year which discharges 190 MT ashes and out of this 70-80% is fine to fly ash. By the end of the year 2018, about 200 million tons of fly ash was produced by various thermal power plants in India. The production of fly ash expected to increase to 250-300 MT/year by 2019-20. Therefore the stock of fly ash is increasing every year [2,3]. Apart from a small quantity of fly ash is primarily utilized by the cement industry, while an abundant proportion goes to ash ponds and landfills which cause huge environmental problems. In 2012, six million metric tons fly ash was produced by the UK out of which only 50% was utilized by the construction sector, while 50% proportion was gone to landfills. Fly ash also contains toxic metals and traces the concentration of heavy metals such as cadmium, chromium, cobalt, lead, manganese, mercury, molybdenum, and selenium. These heavy metals affect human health like permanent respiratory disorder on inhalation of the presence of toxic metals especially by persons living in the vicinity of disposal sites [4,5]. The toxicity of heavy metals also leached out to underground water. The presence of excess chromium (VI) in fly ash could lead to damage circulatory systems and causes carcinogenic changes due to mutagenic properties associated with its oxidizing activity. Here it becomes obvious to reduce the environmental concern, greenhouse emissions, and disposal issues. So the utilization of fly ash becomes necessary. Fly ash has low-cost effectiveness as compared to other inorganic fillers [6,7]. The article presents the utilization of industrial waste like FA as reinforcement for matrix in

ABSTRACT
A recent development in the field of eco-friendly, lightweight and high-performance nanocomposite and a broad range of their innovative applications attract enormous interest in the field of research. However, the search for lighter materials to replace legacy heavy materials in engineering structures especially in automobile and aerospace industries has made the study of tribological properties of epoxy resin based composites significant. Fly ash, from the thermal power plant, is an industrial by-product that can be utilized as filler in epoxy resin with different wt% owing to its distinctive properties like low density, wide availability, good filler factor, good thermal resistance, and glassy nature instead of dumping into the large area of landfills and ash ponds. This review article presents an expanded literature overview on the utilization of industrial waste fly ash, as reinforcement for matrix in making lightweight, high strength composites. In this investigation broaden literature groundwork also covers the effect of nanoparticles on thermal, morphological and mechanical characteristics such as impact strength, tensile strength and flexural strength of fly ash/epoxy nanocomposites.

Keywords: Fly ash; Nanofiller; Epoxy resin; Nanocomposites; Mechanical properties

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making lightweight, high strength composites. The main objective for the utilization of fly ash in polymer composites has been its surface polarity due to the presence of silanol, aluminol and other types of -OH groups attached to the metal/non-metal atoms of the constituents of fly ash [8]. Generally, the metallic particles are costly so the spherical particles of FA could assist the above objective.

Overall, the polymer matrices are chosen on account of adhesive strength, fatigue resistance, heat resistance, chemical and moisture resistance, etc. For the matrix mechanical strength compatibility with that of the incorporating material is necessary. Therefore for strengthening applications, a structural resin-like thermosetting matrix such as epoxy-based on DGEBA [diglycidyl ether Bisphenol A], needs to be used. Epoxy resin can be widely used to develop composite material due to its superior properties like excellent adhesion to filler, higher thermal stability, easy processing ability, good chemical resistance and low density [9]. However, properties associated with epoxy like undesirable brittleness due to a high degree of cross-linking structure, delamination, low impact strength, and poor cracking resistance made the limited application of epoxy. From a notable time, researchers have been investigating to get rid of these drawbacks of epoxy and observed that the advancement in mechanical and physical properties such as toughness, rigidity, and strengthening can be acquired from the modification of matrix or by reinforcement of various fillers. The filler/epoxy nanocomposites are extensively used in engineering, anti-corrosive coatings, electronic materials, and aerospace industries [10]. So the question arises, “What are nanocomposites”? In nanotechnology, the nanocomposites are classified as advanced heterogeneous solid material having two or more phase where at least one phase has a dimension in nanometer [1 nm to 100 nm], which are regarded as promising alternatives to overcome the drawback of the polymer matrix, micro, and conventional composites. The development of nanotechnology has induced material restructure which changes the properties of the material. It has reported that epoxy resin, reinforced with nanofiller has superior mechanical strength and thermal stability. The nanofillers help to enhance the quality of the product when introduced into the polymer matrix even at very low content (less than 10%). The improvement of mechanical properties and thermal stability is credited to intensely higher surface area and uniform dispersion of nanoparticles with low volume fraction [11]. The nanofillers are incorporated in the form of particles, nanotubes, and whiskers (metallic or nonmetallic single crystal). The performance and characteristics of composites expect the size of reinforcement material, shape, concentration, adaptability with the matrix, the way the filler distributed in matrix, and volume fraction. The interface is also an imperative property of nanocomposite.

In the literature survey, during the fabrication of epoxy nanocomposite, two main challenges i.e., homogeneous dispersion of nanofiller and interfacial nanofiller polymer interaction are encountered. Because nanofiller attributing to a higher ratio of surface to volume, nanoparticles arranged adjacent and form aggregate which restricted homogeneous dispersion of nanoparticles in the polymer matrix [12]. Due to injurious effect of the inorganic nanofillers, there is the strong prospect of agglomeration. Hence, the use of surface modifiers such as silane is used to enhance the dispersion stability of the nanoparticle and evolve the interfacial interactions between inorganic nanofiller and organic matrix is notable. Depoiling and agglomeration of particle are major problem encountered in the fabrication

of polymeric nanocomposites; induce the most problems in nanocomposite research. The results are reported that stirring methods had an indicative effect on dispersion quality because voids exist between nanofiller and matrix reduces the mechanical properties of polymer nanocomposite. Numerous physical stirring methods such as mechanical stirring, high shear mixing, solvent mixing, and ultrasonic bath stirring have been explored to attain a homogeneous dispersion of nanofiller in the matrix. Ultrasonic vibrations make effectiveness in improving the uniform dispersion of nanofillers [13]. Therefore this review article discusses the polymer nanocomposites reinforced with fly ash, epoxy and nanofiller due to their interesting as well as their unique applications. The knowledge of the immense value of nanocomposites will enable the manufacturer to recognize that polymer nanocomposites will herald a new era in material advancement just as polymer composites transformed the face of industry many years ago.

RAW MATERIALS FOR THE FABRICATION OF FLY ASH/EPoxy NANO COMPOSITE

From the literature review it is reported that the development of epoxy/fly ash/nanocomposite is based on epoxy resin, fly ash from the thermal power plant and various types of nanofillers as reinforcing phase.

CHEMICAL AND PHYSICAL CHARACTERISTICS OF FLY ASH

FA is heterogeneous material having various elements such as C, K, Al, Si, Ca present in form of metal oxides like SiO2 (60-70%), Al2O3 (20-25%) and Fe2O3 (2-3%). These oxides lead to positive effects when used as reinforcing material in the polymer matrix [14]. The presence of Al2O3 is due to the existence of clay in fly ash. Besides of these metal oxides, some other chemicals like alkalies, MgO, carbon, and SO3 also present in the fly ash. Ibraheem et al. [15] studied that fly ash has metal oxides that show good effects when embedded in the polymer matrix. SIMS technique has been performed to identify the interfacial distribution of fly ash with 10 wt% and 15 wt%.

The quality of fly ash is based on several factors such as type of coal, fineness of coal particles, and content of ash present in coal. The particle size of fly ash varies from 1 to 150 µm. The color of fly ash differ from gray to black depends on the content of carbon present in the ash. Darker the gray to black color of fly ash greater will be chances of the content of suspended unburned carbon in the ash while the brown color typically correlates with the presence of higher content of iron. The light and tan colors of fly ash are attributed to the presence of higher content of lime present in the ash [16]. It is revealed that fly ash is adsorbent for the elimination of numerous by-products. The unburned carbon present in fly ash is involved in adsorption capacity [17]. The pH of fly ash alters from 4.5 to 12 depending upon the particle size as well as the consequent concentration of trace metals [18]. Fly ash consists of both the glassy and crystalline phase; the 60 to 90% of the total mass of fly ash is the glassy phase while remaining is crystalline. The glassy hollow spheres and crystalline phases are dependent on one another and alter in their proportions, which lead to fly ash a complex material to classify and characterize. The glassy phase of fly ash includes solid, hollow spheres called Cenospheres, extent in size from 0.5 to 300 µm, which help in proper binding to fill the intermolecular gap between polymer matrix material layers, which
help in developing high-value-added material. They furnish the benefit of a decrease in weight attributing to their low densities [19]. Nath et al. [20] studied that fly ash is industrial pollutant consists of cenosphere, hollow spherical particles which might be developed high-performance composite material with incorporation into the bio-reinforced composite material.

Generally, the specific gravity of fly ash differs around 1.7-3.1 g/cm³. The variation in specific gravity arises due to chemical composition and shapes of particles. The lower value of specific gravity depends upon several hollow cenospheres. The physical, mineralogical and chemical characteristics of fly ash rely upon the composition and variety of the coal carried out for combustion in the boiler and method of combustion.

CLASSIFICATION OF FLY ASH

Based on the source of coal, their chemistry and the amount of content silica, iron, calcium and alumina, ASTM C618 defines fly ash into two classes: Class C and Class F fly ash [21].

Class F fly ash

This class of fly ash is generated by the combustion of harder and older anthracite and bituminous coal. The amount of lime (CaO) content is less than 7% in class F fly ash. It contains a lower concentration of Fe₂O₃ and the higher concentration of silica about 60%. This is highly pozzolanic so this class of fly ash is utilized in producing cementitious compounds. It has been revealed that as compared to other countries, the low lime Class F fly ash of India has more crystalline nature. In Indian fly ash, the ratio of network formers (SiO₂+Fe₂O₃+Al₂O₃) to network modifiers (Na₂O+K₂O+CaO+MgO) is too high and unbalanced to form high proportions of glass because class F type includes higher fusion temperature for the material. Class F fly ash contains a higher amount of alkali and sulfate.

Class C fly ash

This class of fly ash is generated by the combustion of younger sub-bituminous coal. Class C FA content more than 20% lime (CaO). Generally, the amount of alkali and sulfate contents is less in Class C fly ash. Both types of fly ash consist of 25 to 28% of Al₂O₃ (Table 1).

TRENDS OF FLY ASH PRODUCTION, UTILIZATION, AND PROBLEMS ENCOUNTERED IN DISPOSAL OF FLYASH

Central Electrical Authority of India (CEA) has been reporting the data of generation and utilization of fly ash from all thermal power plants since 1996. CEA has reported that during the year 2010-11, 2011-12, 2012-13, 2013-14, 2014-15, 2015-16, 2016-17 and 2017-18 the production of fly ash was 131.09, 145.42, 163.56, 172.87, 184.15, 176.74, 169.25 and 196.44 million tons whereas the utilization was 73.13, 85.05, 100.37, 99.62, 102.54, 107.77, 107.10 and 131.87 million tons (Figure 1).

The enhancement in the production of fly ash might be due to the establishment of new thermal power plants [22]. During notable decades, there has been a gradual increment in the production of coal ash generated by thermal power plants in the world due to the increasing demand for energy. Therefore the stock of fly ash is increasing tremendously every year. Countries like India and China are exhibiting a rapidly increasing demand for coal. So long the requirement for energy expands more; the generation of fly ash is unavoidable. Researchers have studied compiled data of generation and utilization of fly ash across the world. In the United States, about 37% of total power generation is based on coal resulting in the production of 131 million tons of fly ash every year. The current worldwide scenario production of fly ash is more than 750 million tons. In 1989, the production of fly ash was about 560 million tons, out of which only 92 million tons of this (about 16% of total) was utilized by cement industries. However, the utilization of fly ash is very less still now. In 1989, Germany utilized the largest amount of fly ash about 47% while South Africa utilized the lowest amount of fly ash only 0.8% whereas the amount of utilization of fly ash was in Germany (17.9 million tons) followed by China (16.2 million tons) and USA (16.0 million tons). The worldwide scenario of the utilization of fly ash varies from 3% to 56%. [20]. Less utilization of fly ash always makes a problem for disposal off. On 14 September 1999, the Ministry of Environment and Forests (MoEF) announced a regulation specifying prescriptive levels for gradual utilization for fly ash. As per regulation, it is compulsory for new thermal power plants to prescribed 100% utilization of fly ash within nine years of commencing operation whereas for old thermal power plants it is mandatory to achieve a goal of 100% fly ash utilization within 15 years from the date of the issue of the regulation of governance [23,24]. Different techniques such as XRF (X-ray fluorescence), wavelength dispersive spectroscopy (microprobe WDS), X-ray diffraction (XRD) and X-ray microanalysis (EDS) were carried out for the study the chemical analysis of fly ash. SEM technique was used to examine the surface distribution of fly ash particles in the sample and detection of the surface irregularities.

Table 1: Chemical composition of fly ash.

| Constituents | Class F Fly ash (Vol %) | Class C Fly ash (Vol %) |
|--------------|-------------------------|-------------------------|
| Fe₂O₃        | 8.44                    | 6.86                    |
| Al₂O₃        | 26.56                   | 17.8                    |
| SiO₂         | 55.85                   | 42.46                   |
| MgO          | 2.4                     | 5.4                     |
| CaO          | 6.59                    | 22.25                   |

(Source-Central Electrical Authority of India, annual report on fly ash production and utilization for the period from 2010-11 to 2017-18)

Figure 1: A graph showing fly ash production and utilization (in million tons) for the period from 2010-11 to 2017-18.
However, various authors have studied the possible utilization of fly ash in innovative applications. Fly ash has been widely used as reinforcement material in the various matrix such as epoxy, polypropylene, high-density polyethylene (HDPE) and polybutylene terephthalate (PBT) [25].

**CHARACTERISTICS OF EPOXY RESIN**

In 1936, Dr. Castan of Switzerland and Dr. Greenlee of the USA discovered epoxy resin. The matrix of the composite can be either composed of thermosetting or thermoplastic polymer. Thermoplastics have to mold at elevated temperature, as compared to thermosetting. Thermosetting has a cross-linking, three-dimensional network and highly strong structure. So the main attention is based on the thermosetting polymer such as epoxy resin. The epoxy resin is synthesized by the condensation reaction of epichlorohydrin with bisphenol. In epoxy resins, ECHOCH₂ is a reactive group. Epoxy resin contains more than one epoxide group, oxirane or a glycidyl group. Based on the oxirane ring, the epoxy resins are classified into many categories. The epoxy system contains two parts, one part is resin and the second is hardener (curing agent) [26]. The glycidyl group of epoxy resin reacts with the reactive hydrogen of the curing agents such as aromatic amines, aliphatic amines, polyanides, phenols, and thiols. On the mixing of resin and hardener a chemical reaction proceeds which cures the material. Generally, amines are used as curing agents because amines contain reactive hydrogen, attached with nitrogen which opens the epoxy ring to form a covalent bond. On curing, epoxies have lower shrinkage. The temperature of the curing of epoxy resin is determined by the chemical composition of hardeners. The temperature range varies from 5 to 150°C. As compared to low temperature cured epoxy system, high temperature cured epoxy system show higher glass transition temperature, tensile strength, and stiffness [27]. Many conventional materials are replaced by epoxy resin due to its superior properties. The enhancement in mechanical and physical properties can be obtained from the incorporation of various fillers [28]. Various authors have revealed some interesting studies on epoxy-based nanocomposites with the incorporation of fly ash and various nanofillers.

In 1988, Srivastava et al. [29] studied that flyash powder is an industrial waste that helps to capture the crack path, thus enhance the mechanical properties of fiber-reinforced plastic (FRP) composites. The ultrasonic technique was performed to determined qualities like toughness, fracture surface energy of epoxy/fly ash, epoxy/carbon fiber/fly-ash, epoxy/glass fiber, and epoxy/glass fiber/fly ash composites. They further studied that properties like fracture toughness and surface fracture energy of continuously coated, uncoated fly-ash filled unidirectional glass fiber reinforced epoxy resin can be enhanced by a continuous coating of fiber tows with the epoxy resin before slashing into molding pellet [30]. Ibraheem et al. [31] investigated to utilize fly ash, an industrial by-product into developing significant green composite. Fly ash is a waste product can be recycled into low-cost effectiveness and better quality composite as a potential lightweight structure material instead of dumping into the large area of landfills. Different types of fillers like carbon nanotubes, fly ash and milled carbon fiber with different wt% were reinforced into the matrix to evaluate the mechanical, chemical and morphological properties of composites. They revealed that the reinforcement of CNT nanofillers having a high surface area of bonding enhances the mechanical properties of composites. The effect of epoxy resin to filler proportion on physical and mechanical characteristics of epoxy resin hybrid composites incorporated with fly ash and sawdust were determined by Krishna et al. [32]. The density and compressive behavior of composites were also explored. The results indicated that the increment in the filler quantity lowered the cost of the composite along with enhanced its durability. Barpanda et al. [33] compared the sliding wear behavior of neat epoxy with the epoxy-containing different volume fraction of fly ash. Obtain results showed the different magnitudes of wear loss for neat epoxy and epoxy/fly ash composite. RamaKrishna et al. [34] studied the utilization of fly ash as reinforcement material in the epoxy/PBT blend matrix. The mechanical properties of PBT (%) epoxy blend matrices such as tensile, impact, flexural compression, chemical resistance, and water absorption properties were found better as approached to epoxy/fly ash composite. The size of fly ash as a filler also affects the mechanical properties of a composite. Raja et al. [35] prepared the fly ash/epoxy composite with reinforcement of 10 wt% of different particle sizes of fly ash (50 μm, 480 nm, 350 nm, and 300 nm) and studied the impact strength and hardness of the composite. The ball milling technique analyzed the reduction in size. The characteristics of fly ash was carried out with a Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS). The strength was found improved with size reduction of fly ash particle.

In 2002, Kishore [36] evaluated the impact factor of the epoxy/fly ash system. The larger size of particles of fly ash serves as crack initiating points which deteriorate the impact strength of the material. SEM technique demonstrated that fly ash particles affect the crack at all stages. They further [37] studied the mechanical characteristics such as impact, flexural strengths, and flexural modulus of Fly ash Censpheres/epoxy composite. The impact and flexural modulus of the epoxy composite was found enhanced with increasing the wt% of FAC’s and reached the highest values at 15 wt% of FAC. Epoxy resin is a thick viscous liquid, so manually mixing of fly ash is quite difficult. So mechanical stirring followed by ultrasonicator was reported. Liu et al. [38] studied an epoxy-based carbon nanomaterial’s nanocomposite. Carbon nanomaterials are drawing an enormous interest in nanotechnology due to its incredible properties such as superior flame retardancy, electrical conductivity, and excellent mechanical characteristics. The performance development in mechanical, electrical and thermal conductivity and flame retardancy of carbon nanomaterial/epoxy composite, challenges, and opportunities in epoxy-based nanocomposite material were also discussed. Verma et al. [39] studied the reinforcement of industrial pollutants, fly ash and synthetic fibers like E-glass in different ratio into epoxy resin. The mechanical properties of polymer composite like tensile, flexural and compressive strength were studied. The results revealed that compressive strength, tensile strength, and flexural strength were enhanced by 231.97 MPa, 48 MPa, and 114 MPa with the incorporation of 5 wt% fly ash. SEM technique was analyzed to check the particle size of fly ash and uniform distribution of fly ash and E-glass fiber into epoxy resin.

**FABRICATION OF EPOXY/FLY ASH COMPOSITES**

For the preparation of Fly ash composites, the following techniques have been reported.

**Hand lay-up technique**

The Hand lay-up technique is the uncomplicated method of
processing of composite. This technique is economically favorable. This technique is the oldest, simple and prevalent method for the production both of small and large fiber incorporated products.

It includes simple processing steps. Firstly, a lubricant is sprayed uniformly on the surface of the mold to prevent the sticking of polymer into the mold surface. To attain the excellent finishing of the surface of composite, the thin sheets are kept at the top of the mold. The strand mats are cut as per the block size of the mold and placed at the surface of the mold. Later the dough of thermosetting polymer with a convenient ratio of specified curing agent poured into the mold cavity. The mixture is uniformly spread with the help of a brush. After curing the mold is opened and the specimen of the composite is cut out from the sample sheet for different processed. Further, the second layer of the mat is kept on the surface of the polymer and a roller is lifted with moderate pressure to dismiss the air bubbles along with the presence of extra polymer. Some lubricant is drizzled on the inner surface of the mold further placed on stacked layers and pressure is adapted [40]. Purohit et al. [41] prepared fiber glass-epoxy-fly ash composites by using a hand lay-up technique with the addition of fly ash and glass fiber into epoxy resin. The fly ash was reinforced in epoxy resin with different wt% differ from 4-10 wt% in steps of 2 wt%. The main objective of this study was to observe the effect of fillers on the properties of composite such as micro structural properties and mechanical properties such as tensile strength, impact strength, and flexural strength.

Stir casting method

In the stir casting method, the dispersion of the dispersed phase into the molten matrix is performed by mechanical stirrer. Usually, in stir casting graphite stirrer is carried out due to tending to bear higher temperatures as compared to matrix. The stir casting method is convenient for the fabrication of the composites incorporated with 30% of reinforced material [42].

Comp casting

The Campo casting process is based on the liquid state in which particles are reinforced to solidifying melt although being actively moved. It has been observed that primary solid particles previously create in the semisolid slurry can mechanically capture the incorporating particles, resulting in improved dispersion of particles in the matrix [42].

In-situ deposition technique

In situ deposition technique, the addition of the reinforcing phase into polymer matrix carried out by disciplined metallurgical reactions so this process needs to screen carefully. Frequently one of the reacting elements is matrix while another may be fine powders. This type of reinforcement has attractive characteristics. It is highly systematic with a matrix and has fine particle size and homogeneous dispersion [43].

The literature survey, the incorporation of a various number of nanofillers in the matrix has been described.

CHARACTERISTICS OF NANOFILLERS

Nanofillers are those additives which enhance the properties of the material. Due to having a higher surface area, the nanoparticles show a tendency to form aggregates, resulting in micron-sized filler clusters. A major problem creates in the homogeneous dispersion of nanofillers in the polymer matrix [44,45]. The interfacial interaction between nanofiller and matrix material plays an important role. Certainly, the overall material properties adapt by the diversity in the macromolecular state region around the nanoparticles due to the high surface area of nanoparticles [46]. A well-dispersed system generally yields the most desirable properties. The dispersion of nanoparticles was characterized by the nano and micro scale. Carbon nanotubes and Graphenes draw enormous interest due to their unique structure and excellent properties. Various authors have developed the polymer nanocomposites based on various polymer matrices with the nanofillers such as calcium carbonate, aluminum oxide, graphene, silica, carbon nanotubes and nanofibers [47].

Classifications of nanofillers

Generally, nanofillers can be classified according to their number of dimensions 1D, 2D or 3D in nanocomposites, shape, and morphology [48]. The nanofillers are usually incorporated in the form of particles, nanotubes, fibers, and whiskers. The three types of nanofiller are given the following.

The first type of nanofiller is described by one dimension in the nanometer scale like needle-shaped material, laminas and/or shells. In this category, the filler consists of sheets of 1 to a few nm thicknesses and hundreds to thousands nanometer long. For example: nanoclay, nanosheets, nanoplatelets, and nanorods, etc.

The second type is characterized by one large and two-dimension in nanometer range forming elongated structure. In this group nanofiber, nanotubes or whiskers are studied. The nanotubes are generally classified into three main categories (1) SWNT (single-walled nanotubes) (2) DWNT (double-walled nanotubes) (3) MWNT (multivalled nanotubes).

The third type of reinforcement consists of all three dimensions in the nanometre range. In this group, spherical silica, metal particles, semiconductor nanoclusters, and nanogranules are studied. Metal-based nanomaterials are those nanomaterials which can be obtained from the metals including quantum dots, nanogold, nanosilver and metal oxides, such as aluminum oxide, titanium oxide. Nanofillers are reinforced into the matrix at very low content from 1% to 10% (in weight).

Nanofillers are also reinforced in inclusion to other fillers like fly ash, sawdust, and additives, and ultimately incorporated with some fibers such as carbon, E-glass, etc. The various nanofillers based nanocomposites are described as following.

Nanoclay (clay-modified epoxy nanocomposites)

The organoclay nanoparticles of layered silica are known as nanoclay. The classification of nanoclay is based on the morphology of particles, crystalline structure, and chemical composition. Montmorillonite is most commonly nanoclay which is reinforced in polymer nanocomposite. And many material applications have revealed an enhancement in properties. Phyllosilicates consist of a shell-shaped structure with thickness in the nanometer range and their crystal lattice is made up of 2-D layers. The natural availability of clay and high form factor plays an important role in developing nanoclay based nanocomposites which create enhancement in physical performances. Nanoclay has a tendency of hydrophilic nature which creates difficulties in homogeneous dispersion
within polymer matrixes [49]. Further, the better dispersion of a large amount of nanoclay within polymer matrixes can be acquired with hydrophobic surfactants by the exchange of metal ions with alkylammonium ions. The enhancement in chemical compatibility (interaction of nanoclay with matrix, resulting in good dispersion) may be attributed to the alkylammonium ions constituting the surface functionalities on nanoclays. Recently the related clays like kaolinite, hecgrite and saponite have also reinforced in polymer nanocomposite [50]. In 2012, Azeel et al. [51] studied the applications of nanocomposites. Due to high intercalation chemistry and high aspect proportion nanoclay, perform an important role with incorporation in the epoxy matrix. These epoxy/clay nanocomposites have widely used in various applications like aerospace, defence, and automobile industries. Wang et al. [52] developed epoxy/clay nanocomposites exhibiting exfoliated morphology. TEM and optical microscopy were carried out to characterize the nanocomposites. Young's modulus and fracture toughness were enhanced with reinforcement of 2.5 wt% nanoclay. Nanosized clays have commonly used in the advancement of nanocomposites with improved mechanical, thermal, and flame retardant properties grazing from automobile parts to packaging materials.

Carbon nanotubes (properties and carbon tubes-modified epoxy nanocomposites)

Carbon nanotubes (CNT) were discovered in 1991 and gave an interesting approach to the modification of nanocomposites. The main aim of incorporation of CNT is based on the achievement of maximum dispersion into the polymer matrix. CNT is thin, carbon-containing long tubes including unique size and shape show superior mechanical and physical properties. CNT is a special type of fullerene thus the walls of CNT consists of hexagonal graphite structure. Generally, the three types of CNT are examined i.e. single-walled CNT (SWCNT), Double-wall carbon nanotubes (DWCNT) and multi-walled CNT (MWCNT). SWCNT exhibits a hollow structure procured by covalent bonding of carbon atom. The diameter of a SWCNT exists in the range of 0.6-2 nm, the diameter of DWCNT lies between 2 and 4 nm, while the inner diameter of MWCNT in the 1.5-15 nm and the outer diameter of 2.5-50 nm [53,54]. In a vacuum, MWCNTs are thermally reliable up to 2800°C. CNT exhibits superior electrical conduction similar to copper. CNT possesses 1/6 of the density of steel and shows 100 times better tensile strength than steel [55]. CNT also has excellent thermal stability than the purest diamond. The heat conductivity of CNT is 3000 W·m⁻¹K⁻¹, electric conductivity of 10⁷ S·m⁻¹. These unique properties of CNT make them compelling material for nanotechnology [56]. The CNT has wide applications in electronics, thermal and structural industry. In 2012, Prolongo [57] considered the water absorption behavior of neat epoxy resin and epoxy resin with a distinct proportion of CNTs and carbon nanofibres. During the hydrothermal ageing, a noticeable change in mechanical properties took place due to the effect of water absorption. Initially, the mechanical strength decreases but later it is renewed. Recently, Marriam et al. [58] studied that the extension of carbon nanotubes thin films (CNTi) in a polymer such as epoxy resin, significantly enhanced the properties like strain sensing, conductivity and thermal properties of various composites. The poor bonding of CNTi with polymers reduces the properties of composites, to get rid of this problem, first the polymer modified with CNT with different wt% and then CNTi introduced to modified polymer solution which demonstrated a new CNT to CNT interphase and interlocking interactions which results in enhancement in tensile strength by 164.76% and peeling strength by 74.38% as compared to unmodified CNT/epoxy composites.

Tao et al. [59] examined that at lower temperatures the thermal deterioration of epoxy composites induced due to the inclusion of CNT. SEM technique investigated the better interfacial dispersion of CNT with the epoxy matrix. Allauqi et al. [60] determined the electrical and mechanical characteristics of epoxy/Multiwalled carbon nanotube nanocomposite. MWCNT were reinforced with different wt%. They observed that incorporation of MWCNT by 1 wt% and 4 wt% make, double and quadruple improvement in Young’s modulus and yield strength. The insulator to conductor transition occurs with MWCNT conc. between 0.5 and 1 wt%. Whereas, Meeuw et al. [61] studied the morphological characteristic of MWCNT/epoxy nanocomposite with different aspect ratio and content of filler. The strain sensing capabilities were improved by the alignment of particles in load direction. Yuen et al. [62] developed Multiwalled carbon nanotube (MWCNT)/epoxy composites by reinforcement of 0.5 wt% MWCNT into epoxy resin. The morphological properties and characteristics were studied. The glass transition temperature enhances from 167°C for neat epoxy to 189°C for 0.5 wt% CNT/epoxy. However, the bulk resistivity and surface resistivity were reduced from the addition of MWCNT. The bulk resistivity was reduced from 21.1 × 10⁶ Ω cm for neat epoxy to 6.72 × 10⁸ Ω cm for 1 wt% MWCNT/epoxy. The surface resistivity of CNT/epoxy composites also reduces from 4.92 × 10¹² Ω for neat epoxy to 3.03 × 10⁹. The dielectric constant was found improved from 3.5 for neat epoxy to 5.5 for 1 wt% MWCNT/epoxy. Tanabi and Erdal [63] prepared CNT/epoxy nanocomposite under different dispersion conditions. They determined that the dispersion process and concentration of CNT also affect the mechanical, electrical and strain sensing properties of CNT/epoxy nanocomposite. Based on the results, two reversion models were carried out to conclude the electric conductivity and the tensile strength of the CNT/epoxy nanocomposites. Implementing verification tests were performed to certify the robustness and efficiency of the models. The obtained results revealed that the fabrication of nanocomposite by dispersion of a lesser amount of CNT with high mixing speeds and long mixing times had enhanced the sensory properties that were much convenient for strain sensing applications.

Metallic nanoparticles (metallic nanoparticles-modified epoxy nanocomposites)

Since 1990, the metallic nanoparticles are in existence in the research field. The particle size of nanoparticles gravely relies upon the production approach of nanoparticles. Metallic nanoparticles correlate to spherical crystal shape of metals such as Ag, Au, and Fe. The main objective of the reinforcement of this type of nanoparticle into the polymer matrix is based on the enhancement of the electrical conductivity of composites. The examples of Metallic nanoparticles are nanogold, nano zinc, nanosilver, nanodiamond, and quantum dots. These nanoparticles show catalytic property which creates antibacterial effects at the surface. Metallic nanoparticles consist of the dimension of particles in the range of 20 to 300 nm with surface areas of 20–500 m²g⁻¹. In comparison to their bulk counterparts, metallic nanoparticles possess different physical and chemical characteristics to have an enormous attraction to industrial applications. The property of high surface area to volume ratio makes metallic nanoparticles unique.
In 2016, Arbaoui et al. [64] developed epoxy/different nanoparticle composites with reinforcement of different nanoparticles such as alumina, spinel, and graphite with different wt% into the epoxy matrix. They studied the mechanical and thermal properties of these nanocomposites and revealed that with an increment of nanoparticle concentration into the matrix, the nanocomposite gradually reduces their plasticity and embrace a brittle behavior.

**Metal nano oxides-based modified epoxy nanocomposites**

The objective with nano-oxides is to obtain a maximized exfoliation and full dispersion into the matrix. The main aim of reinforcement of nano-oxide is to achieve homogeneous distribution and maximum exfoliation into the polymer matrix. Metal nano oxides are also used in commercial applications. In general, the examples of metal oxides are ZnO, CuO, SiO2, TiO2, Fe2O3, and Al2O3.

**Nanosilica-based nanocomposites:** Nanosilica particles are used as reinforcement material in a broad range of sizes, from 20 nm to micrometer. Alumina particles have made up of spherical crystal particles of alumina. In 2011, Fu et al. [65] evaluated the effect of nano Al2O3 particles on structure, mechanical characteristics, thermal conductivity, bulk resistivity and thermal stability of Hyper branched [HTTE]/DGEBA analyze the impact properties of these nanocomposites. SEM technique analyzed the impact properties of nanocomposites. The results revealed that the toughness of epoxy composite embellished by the addition of Al2O3 nanoparticles and HTTE epoxy due to the distribution of nanoparticles in the epoxy matrix and clarify the hindrance of single filler reinforced epoxy nanocomposite.

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**Nano titanium oxide-based nanocomposites:** In 2010, Al-Turaiﬁ H.A. [67] fabricated TiO2/epoxy nanocomposite by the reinforcement of two different particle sizes of nano TiO2 (17 nm and 50 nm) into epoxy resin. The nanoparticle of both different particle sizes was reinforced with different wt% (1%, 3%, 5%, and 10%) into the matrix. The characterization of the fracture surface was carried out by the SEM technique while X-ray photoelectron spectroscopy was carried out for the characterization of tensile, flexural, pull-off and abrasion tests. The results revealed the maximum improvement in flexural properties at the addition of TiO2 of 1 wt%. The highest value of tensile stress was observed at the incorporation of 3 wt.% for 17 nm and 50 nm particle size of TiO2. They analyzed that the addition of higher TiO2 fraction and larger size of TiO2 lead to reduction in the mechanical properties of nanocomposites. The reduction in mechanical properties leads to the property of developing agglomeration associated with nano TiO2. Thind et al. [68] studied the epoxy hybrid nanocomposite. The nano TiO2 was reinforced varying from 1 wt% to 4 wt% in epoxy resin. The results showed that the mechanical properties and wear properties enhanced with 2 wt% of nano TiO2 material. The tensile and scratch tests for nano TiO2/epoxy nanocomposite were determined by Ng [69]. They also compared the scratch resistance and strain to failure with a 10% loading of nano TiO2 and micron size TiO2. Maheshaa et al. [70] studied the mechanical and tribological wear behavior of Basalt fabric-Epoxy (BE) composites. Nano TiO2 was reinforced alone and in combination with nanoclay. The results revealed that by an increment of filler, tensile strength and dimensional stability of the nanocomposites were enhanced. Bezy [71] revealed the effect of reinforcement of nano TiO2 on the mechanical properties of the epoxy nanocomposite. The XRD technique was carried out for the characterization of the nanocomposite. The variation in mechanical properties was observed due to the different distribution of nano TiO2 particles in the epoxy matrix. Laarej studied [72] epoxy/TiO2 nanocomposite. The TiO2 nanoparticles having the dimension of diameter in 21 nm with different wt% at 0.5, 1, 5, and 20 wt% were ultrasonically dispersed for different time 5, 30, and 60 min into epoxy matrix. The hardness and Young’s modulus for 5 wt% reinforced epoxy resin were found improved as compared to neat epoxy resin. Carballeira et al. [73] studied the incorporation of different wt% of titanium dioxide (TiO2) nanoparticles into epoxy resin. SEM, TEM and electronic microscopy techniques were performed to check the distribution of nano TiO2 into epoxy resin. Stiffness and toughness of nano TiO2/epoxy nanocomposites were found enhanced as compared to neat epoxy resin.

**Various nano oxide-based nanocomposites:** Han and Cho [74] performed the single notched bending 9(SENB) test to determine the fracture toughness of epoxy/nanoclay nanocomposite for a broad range of temperatures. The nano-silica arrests the crack path to move interface between micro-silica particles and thus improve fracture toughness. The results revealed that the fracture toughness of an epoxy molding compound promoted by the incorporation of nano-silica with very low volume fraction. Chan et al. [75] compared the electrical, thermal and mechanical characteristics of nanocomposites loading with 20 nm CuNPs (copper nanoparticle) with 5 vol% and with 20 nm silver nanoparticles (AgNPs) with 5 vol%. The obtained results revealed that there was a slight similarity in electrical conductivities of 0.01 and 0.02 s/cm of both nanocomposites. Salehi et al. [76] examined the mechanical and viscoelastic characteristics of hybrid glass/epoxy nanocomposites, prepared from the incorporation of RIO3 nanoparticle with different wt% (0.25, 0.5 and 1). The obtained results revealed that strength and stiffness of composite were enhanced by 20-30% and 10-20%. The creep resistance was also found improved. Zhenga et al. [77] prepared nano SiO2/epoxy nanocomposite. The nanoparticle was ultrasonically and mechanically dispersed in epoxy resin. TEM technique was carried out for the characterization of nanocomposites. Mohan AC. and Renjanadevi [78] investigated the behavior of nano ZnO reinforced epoxy nanocomposites. The particle size of ZnO nanoparticle was commenced to be 25 nm. The effect of reinforcement of ZnO nanoparticle and curing agent on curing kinetics, mechanical and morphological characteristics of epoxy resin were also studied. The mechanical properties were found enhanced with 2 wt% of ZnO nanoparticle reinforced epoxy nanocomposite as compared to neat epoxy resin.

**Nano calciumcarbonate-based nanocomposites:** Wang et al. [79] prepared polyethersulphone/nano CaCO3 with the incorporation of nano CaCO3 varying from 1–2 wt% into polyethersulphone. They also studied the mechanical properties of the nanocomposite.
The obtained results revealed that there was an enhancement of 47%, 51% and 32% in compressive strength, the maximum compressive modulus, and the flexural modulus as compared to the neat thermoplastic resin.

**In-situ polymerization**

*In-situ* word is derived from a Latin phrase that translates literally to "on-site" or "in position. In this method, nanoparticles are dispersed in monomer as well as in monomer solution. Further, this homogeneous mixture was initiated either by radiation or heat, relevant initiator or catalyst [89,90]. The main approach of *in-situ* polymerization must be the desirable dispersion of nanofiller in the monomer. However, the difficulty arises due to the control of intragallery polymerization that makes limited applications. Al-Harthi [91] prepared PET/MWCNT nanocomposite by *in-situ* polymerization with the use of metallocene catalyst (Cp2ZrCl2). Ever *in-situ* polymerization gives an impressive way to the synthesis of various polymer/nanoclay composites [92]. Cardoso et al. [93] fabricated PP/MMT composites by *in-situ* polymerization. An enhancement in mechanical characteristics was observed. Korivi [94] also prepared PET/MWCNT nanocomposite by *in-situ* polymerization.

**Melt-intercalation method**

This method is employed for polymer nanocomposite which consists of layered silicates such as montmorillonite and silica. In this method, nanocomposite fabricated with a uniform dispersion of plate-like inorganic nanofillers intercalated to exfoliation of layered silicate. Shen et al. [95] studied Poly (ethylene oxide)/Na-montmorillonite and PEO/organo modified bentonite nanocomposite by using the intercalation method. FTIR shows no variation in the spectrum of these nanocomposites. Melt Intercalation methods are environmentally well dispose of but not compatible with industrial polymer processes [96].

**Sol-gel method**

This method is a tangled combination of *in situ* polymerization process and *in situ* formation of nanofiller as reinforcing phase. Halder S.et al. [97] studied the effect of polyvinyl alcohol ZnO nanoparticles on the thermal and mechanical properties of epoxy/ZnO nanocomposites. The sol-gel method was used to synthesize the modified ZnO nanoparticles. The enhancement in tensile strength, tensile modulus, compressive strength, flexural strength and flexural modulus by 24, 47, 48, 44 and 77% respectively as compared to the neat epoxy system is reported.

**Template method**

This method is performed to form particular shapes such as layered, hexagonal shape to nanocomposite materials. The formation of layers exhibits due to the presence of soluble polymer as a template. Mesoporous materials are widely synthesized by the template method but still lacking development of layered silicates. [99].

**Direct mixing of matrix and nanoparticles**

In the direction polymerization method, the reinforcement between nanoparticles as the reinforcing phase and in polymerization...
takes place simultaneously. A catalyst or radical initiator starts the polymerization. The approach of direct mixing is based on the disruption of the agglomeration of fillers during the process of mixing [100]. Generally, the mixing of polymer and nanofiller followed in two ways. The first way is based on the mixing of polymer and nanofiller, in the absence of solvent whereas the second, the mixing of nanofiller and polymer matrix as in a solution is.

The above attempts were made to the uniform dispersion of nanofillers by using different methods for the fabrication of the surface of nanofillers. But the production of nanocomposite on an industrial scale, by these fabrication techniques, not suitable because these techniques required complicated chemical reactions. So the Direct melt-compounding method, a conventional method was developed because in this method the surface modification of nanofillers is not required.

Although, the prosperous applications of above various techniques for fabrication of polymer nanocomposites have been reported but the report on several factors is still deficient like the approach of convenient and lower cost process-based method for fabrication of high content nanofiller reinforced polymer nanocomposite to provide optimum property combinations.

**METHODS FOR DISPERSION OF VARIOUS NANOFLILERS IN MATRIX**

During the fabrication of epoxy nanocomposite, two main greatest challenges endure i.e. homogeneous dispersion of nanofiller and interfacial nanofiller polymer interaction. Therefore, all the properties of nanocomposite are affected by better dispersibility of nanofiller, which provides maximum surface area for neighboring polymeric chains. Owing to an extremely higher ratio of surface to volume of nanofiller, the nanoparticles arrange adjacently and form micron-sized filler clusters aggregate which restricted homogeneous dispersion of nanoparticles in a polymer matrix. That attracts researchers to develop a preferred way of homogeneous dispersion and de-agglomeration of nanofillers [44,45]. This agglomeration of nanoparticle takes place due to a difference in the density of reinforced material and polymer matrix. This arises as an absence of needed force to breakdown it. By stirring at higher speed, the shearing force is enforced on polymer matrix resulting in transition for the reinforced phase to motion inside over the vortex produced by stirring. The higher speed of stirrer is capable to distribute the reinforced phase which creates homogeneous dispersion of incorporated phase into the polymer matrix. Consequently, the processing techniques affect the dispersion of nanofiller for any matrixes. Because of this issue, the numerous physical stirring methods such as mechanical stirring, high shear mixing, solvent mixing, and ultrasonic bath stirring were attempted. These methods have been explored to obtain a homogeneous dispersion of nanofiller in the matrix. The results showed that stirring methods had a significant effect on dispersion quality, as the inclusion of voids between nanofiller and matrix reduces the mechanical properties of polymer nanocomposite [47,48]. The appropriate dispersion of reinforcing material into the polymer matrix is also impressed by the pouring rate, pouring temperature and gating systems. The dispersion of reinforcement material is affected during various stages along with (a) dispersion in the matrix as a result of mixing, (b) dispersion in the matrix after mixing, but before curing and (c) redistribution as a result of curing. Some parameters such as relative density, wetting condition of material and settling velocity also affect the distribution of dispersed phase.

**Ultrasonic oscillations**

Among various mechanical stirring methods, the ultrasonic vibrations were found more impressive in improving the homogeneous distribution of nanofillers both in solution and melt polymers as compared to other methods. Ultrasonic vibration supply ultrasound waves of higher energy which are capable to break C-C bonds resulting in the generation of a large number of radicals that form chemical bonds on the clay surface of nanocomposite and interrupt physical and chemical interactions [101]. Therefore this technique has been extensively reported for crushing, emulsifying and dispersing the particles, Xia et al. [102] carried out the ultrasonication method to diminish the agglomeration of nanosilica particles. In aqueous phases, a redispersion of nanoclay was also ascertained. In 2016, Pattanaika [103] examined the epoxy/fly ash composite by using Ultrasonic Technique. TOPSIS, a multi-criteria decision method was performed to optimize the composite, whereas ANOVA help in enhancing the dry sliding wear of epoxy/fly ash composite.

**LIMITATIONS AND PROCESS OF IMPROVEMENTS**

Due to improper and insufficient dispersion of nanoparticles, the processing of nanocomposites is one of a major challenge. The nanoparticles exhibit extremely higher surface area and volume effect which causes agglomeration. The improvement in various properties of nanocomposite is strongly associated with the microstructure of nanocomposite.

**CHARACTERIZATION OF POLYMER NANO-COMPOSITES**

To install the structure-property relationships for nanocomposite, the characterization of morphology is important. Various techniques such as Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), Infrared spectroscopy (IR) or Atomic force microscopy (AFM) have been reported for characterization of the surface of nanocomposites. Bhuiyan et al. [104,105] carried out Atomic force microscopy (AFM) to evaluating the morphological variations of the areas around the particle surface. Among these techniques, TEM is the most appropriate method to analyze the state of dispersion of nanoparticles, filler size, local crystallinity, size and shape of void. The only drawback of TEM is that only a small area of material could be analyzed. Wetzal [106] carried out the TEM technique to investigate the scattering aspect of nanoparticles. They revealed the homogeneous dispersion of nanoparticles with few cramped aggregates in the polymer matrix. Further, the SEM technique has been carried out for analysis of the cross-sectional area as well as the dispersibility of nanofiller in the matrix. In the SEM technique, a beam of electrons is carried out, which scans the sample and generates images of the samples at various magnifications. X-ray diffraction (XRD) is also an appropriate technique to analyze the space between clay layers. The thermal stability of nanocomposite can be examined by TGA (thermogravimetric analyzer).

**EFFECT OF NANOFILLERS ON MECHANICAL, MORPHOLOGICAL, AND THERMAL PROPERTIES OF POLYMER NANO-COMPOSITES**

In the literature survey, the enhancement in mechanical properties
such as Tensile strength, Yield strength, Compressive strength, Hardness, resistance, wear-resistance, and thermal properties are taken into consideration for study the effect of reinforcement of nanofiller with different wt% into the polymer matrix. The mechanical, optical, rheological, flame retardancy and dielectric properties of polymer nanocomposites have been extensively studied.

In 2006, Tjong et al. [107] studied the structure-property relationship of polymer composite reinforced with layered silicates, ceramic nanoparticles, and carbon nanotubes. The CaCO₃ and silica nanoparticles were arranged on a nanometer scale with large surface areas and revealed the enhancement in mechanical properties when introduced into a matrix. The desired mechanical and physical properties can be acquired from a uniform and homogeneous distribution of nanofillers in the polymer matrix. In 2013, He et al. [108] evaluated that matrix modification is an effective way to improve the properties of the composite. An interfacial modifier KH550 was introduced to improve the interfacial interactions. There was an appropriate enhancement of 13.5%, 6.1%, 42.5% and 106.3% in compressive strength, elastic modulus, displacement, and the total fracture work of epoxy resin cast filled with 4 wt% nano-CaCO₃, as compared to neat epoxy resin. It indicated that the modification of nano CaCO₃ leads to improving in enhancement in compressive properties. Chatterjee et al. [109] studied the incorporation of two different dimensions of (GnP) Graphene nanoplates with flake size of the 5 micro meter and 25 micrometer and various mixture proportions of carbon nanotubes with GnP into epoxy matrix. In GnP reinforced composites, larger flakes of GnP Help to vigorously dominate the failure mechanisms in composites. The fracture toughness was improved with 76% in the mixture sample having the highest CNT content (9:1).

He et al. [110] observed that thermal stability and mechanical strength of epoxy resin enhanced by surface modification of nano CaCO₃ particles. The mechanical and TGA tests were carried out to investigating the effect of nano CaCO₃ on the thermal and mechanical properties of epoxy resin. Interfacial modifier as silane coupling agent KH550 was introduced into nanocomposite to improve interfacial interaction between epoxy and nano CaCO₃. Khashaba et al. [111] modified the Epocast epoxy resin with different nanofillers’ immersion. The nanofillers with different wt% were ultrasonically dispersed in epoxy resin. The shear strength of these nanocomposites was enhanced by 5.5%, 4.9% and 6.3% and shear moduli enhanced by 10.3%, 16%, and 8.1%. Gurusidewar [112] evaluated the effect of nanoclay on tensile modulus of neat epoxy and glass/epoxy composites at low strain rates. The ultrasonication technique disperses the nanofiller in epoxy resin by different wt% (1.5, 3, and 5%). SEM, TEM and XRD technique characterized the nanoclay. They observed that longitudinal strength and stiffness increases just as clay loading increases. As the content of clay increases, the tensile modulus enhances both epoxy and epoxy/glass nanocomposite. Saba et al. [113] studied mechanical and morphological hybrid nanocomposites, by dispersion of nanofiller (nano OPEFB, MMT, OMMT) by 3% loading with the help of wet-hand lay-up technique. Mechanical and morphological characteristics were found improved. Oszoy et al. [114] investigated and compared the tribological and mechanical performance of nano and micro epoxy composite nanofillers such as Al₂O₃, TiO₂ and clay and micro fillers like Al₂O₃, TiO₂ and fly ash. On pin-on-disc arrangement, wear test was examined under dry atmospheric conditions values 5, 10,15 N, Sliding speed 0.8 m/s and sliding distance by 2000 m. They concluded that the tribological and mechanical performance of micro filler epoxy composite was found better than nanofiller epoxy composite. Shimpi et al. [115] studied the effect of mineral nanofiller on the thermal and morphological properties of the epoxy composite. The ultrasonic cavitation technique was performed to disperse (2 to10%) nano CaCO₃. The noticeable change in cross-linking density was found by reinforcing the nanoparticles. Thermal properties of epoxy nanocomposites were found to be enhanced as compared to neat epoxy resin. Ultrasonic synthesis technique help in the formation of long term stable polymerization which consists of polymer/inorganic nanoparticle composite. Kavitha et al. [116] observed the effect of nanofillers like CaCO₃, TiO₂, Al₂O₃ and layered silicate on dielectric strength and partial discharge resistance of the epoxy matrix. The result showed that the improvement in dielectric strength and partial discharge resistance depend on the percentage loading and type of nanofiller. Majeed et al. [117] investigated the significant mechanical behavior of epoxy nanocomposites reinforced with nano carbon black particles (N220). Ultrasonic Wave bath Machine was performed to disperse the nanofiller with (1 to 10%). They observed that properties like tensile strength, the tensile modulus of elasticity, flexural strength and impact strength were enhanced by (24.02%, 7.93%, 17.3%, and 6%) respectively at 2 wt% of nanofiller. The hardness and compressive strength were enhanced by (44.4%, 12%) at 4 wt% of nanofiller. Wang et al. [118] evaluated that nitrogen-doped carbon nanotubes epoxy nanocomposites show better mechanical properties as compared Carbon nanotubes/epoxy nanocomposites because NCNT has a relatively low viscosity which favors for subsequent applications as compared to Carbon nanotubes epoxy nanocomposite. The reinforcement of nitrogen-doped Carbon nanotubes was proposed for the development of lightweight and high-performance composite. Eskizyebek et al. [119] studied the static and dynamic properties of CaCO₃ modified epoxy/carbon fiber. The nano CaCO₃ with different wt% was dispersed into the epoxy matrix. Vacuum-assisted resin infusion method (VARIM) was used to impregnation of carbon fabrics into epoxy. The tensile, bending and low-velocity impact loadings test was carried out for these prepared nanocomposites. The tensile strength, flexural strength was improved by about 48% and 47% with 2 wt% reinforcement of nano CaCO₃. By low-velocity impact tests, they observed that nano CaCO₃ reinforced CF/epoxy having higher impact performances as compared to neat CF/epoxy composites. Zeng et al. [120] developed montmorillonite-multiwalled carbon nanotube (Mt-MWCNT) as reinforcing nanofiller for epoxy-based composites. They observed that Mt restrict the micro crack path and thus arrest thermal transfer while MWCNTs attached to Mt nanosheets could smooth the stress and heat transfers and extend the mechanical interlocking with epoxy matrix. The tensile strength and modulus of epoxy-based composites enhanced by 42% and 20.3% with reinforcement of 0.5 wt% Mt-MWCNT (Mt:MWCNT=10:1) as compared to pure epoxy. The storage modulus in the glassy region was also improved by 21.2%. Zeorge and Ishida [121] studied the mechanical, electrical gas barrier and flame retarding properties and various novel techniques for the fabrication of high filler-content nanocomposites. However, for many years the reinforcement of inorganic filler content was surpassed only 10 vol%. He et al. [122] studied the effect of nano CaCO₃ on the moisture absorption and diffusion properties of epoxy-based composites. The moisture absorption capacity was found reduced with the addition of nano CaCO₃ with 2 wt% and
4 wt%. As compared to dry nanocomposites the flexural strength of epoxy/nano CaCO₃ impaired. Silvestre et al. [123] studied the effect of different reinforcement materials at nano-scale like CNT, nanoclay, graphene, nano-silica to the polymer matrix and the results indicate the enhancement in mechanical characteristics of polymer composites. From a noticeable period, the Polymer nanocomposites (PMC’s) have been extensively studied due to their appropriate mechanical, thermal and durable properties. Asiri et al. [124] investigated the epoxy nanocomposite which was prepared from reinforcement of Ni-La-Fe-O nanoparticles with different wt% (0, 0.5, 1, 1.5 and 2) into the epoxy resin by Ultrasonic technique. FTIR, XRD, DSC, TGA, SEM characterized the nanocomposite. The compressive coating properties, coating, ionic charge transfer resistance were enhanced by the dispersion of Ni-La-Fe-O nanoparticles.

In the literature survey, it was revealed that the mostly mechanical properties dramatically reduce with further excessive addition of fly ash and nanofillers. Because fly ash particles are a type of rigid particle help to deliver a part of the load to assure the epoxy matrix form. But the excessive addition of fly ash creates agglomeration of fly ash as stress concentration points which posses’ physical defects, resulting in damage from these points. Mishra [125] investigated the mechanical properties and water absorption capacity of fly ash/epoxy/coconut shell dust (CSP). Tensile strength was enhanced by 15% by an increment of CSP although dramatically reduces with 20 wt% of CSP. Recently, Chen et al. [126] studied the mechanical properties like impact strength, flexural strength and flexural modulus of Fly ash Cenospheres/EP composites. Fly ash Cenospheres (FAC) is an industrial waste was utilized as a filler to enhance the properties of the epoxy matrix. With the incorporation of increasing weight fraction of FAC with epoxy matrix, the mechanical properties were found better. Higher values were obtained when the weight fraction of FAC’s exceeding to 15 wt%. However the further increment in FAC content reduced the mechanical properties of FACs/EP composites.

Dong et al. [127] studied nanocomposites, Zinc oxide nanoparticles, alumina nanoparticles and nanoclays with 1, 3, 5 and 8 wt% were dispersed by ultrasonically and mechanical stirring. The results show that composite modulus enhanced by 27% with the incorporation of alumina microparticles for 8 wt%. Flexural modulus was also found quite improved. Saleem et al. [128] studied the effect of graphene in the bettering of mechanical, thermal and electrical properties of polymer nanocomposite. They also observed the enhancement in properties of commercially relevant thermosetting materials. Shokrieh et al. [129] studied the effect of graphene nanoplatelets(GPLs) and graphene nanosheets (GNs) on the fracture toughness and tensile strength of epoxy resin. The incorporation of 0.5 wt% GPLs enhances the fracture toughness of nanocomposite by 39% and 16% for 0.5 wt% GPs. Sonawane, et al. [130] studied the polyamide CaCO₃ nanocomposite, which was fabricated by melt intercalation on the twin-screw extruder. In situ deposition technique synthesized CaCO₃ of particle sizes (23, 17 and 11 nm). Nano CaCO₃ was reinforced with 1 to 4 wt% 9 in polyamide. The results indicate that tensile strength, elongation, hardness and flame retardancy were enhanced for polyamide CaCO₃ nanocomposite as compared to commercial CaCO₃ nanocomposite. Polyamide CaCO₃ nanocomposite shows enhancement in Young’s modulus by 3 fold contrast to commercial CaCO₃ and 4.7 folds to neat polyamide. Zhou et al. [131] evaluated the tensile fatigue and fracture test of epoxy/Carbon nanofibre (CNF) nanocomposite. CNF with different (1, 2, and 3) wt% were dispersed by the high-intensity ultrasonic liquid processor. The result showed that tensile and flexural strength were enhanced by 11 wt% and 22.3 Wt% with the incorporation of CNF by 2 wt%. The reinforcement of 2 wt% CNF showed superior enhancement in strength. Gikas et al. [132] analyzed the reinforcement of MWCNT into the epoxy matrix to improve the thermo-mechanical and toughness characteristics of the nanocomposite. The dispersion of CNT with 0.5 and 1 wt% ultrasonically in polymer matrix enhances the modulus and glass transition temperature. Saw [133] prepared nanocomposite based on natural coir fiber, organically modified montmorillonite [ommt] with the different weight ratio of blends of novolac (ENR) and (DGEB) resin. Ustuna et al. [134] evaluated the experimental results of epoxy nanocomposite reinforced with carbon nanotubes and for boron nitride nanoplastes (BNPs). The Burst and Hoop strengths were enhanced by up to 17 wt% and 31.7% with reinforcement of nanofiller. Chaowasakoo et al. [135] have determined or evaluated the effect of conventional thermal and microwave curing methods on the morphological and mechanical properties of fly ash/epoxy composite. The conventional thermal curing was achieved at 70°C for 80 min. while the microwave curing was performed at 240 W for 18 min to attain the optimum cure of the composite. The results reveal that the tensile, flexural moduli of the fly ash/epoxy composite improved with the increase in the fly ash content while the mechanical strength (tensile, flexural and impact strength) continuously reduced with an increase in fly ash content. The enhancement in mechanical properties could be achieved with the addition of 0.5 wt% coupling agent. Kumar et al. [136] prepared TiO₂/epoxy nanocomposites, by addition of nano TiO₂ with different wt% 5, 10 and 15 into epoxy resin. The mixing was performed by the ultrasonic dual mixing process (UDM) process. The effect of nano TiO₂ on the thermal and mechanical properties of these nanocomposites was studied. The distribution of nanoparticle in the matrix was analyzed by field emission scanning electron microscopy (FESEM) while analysis of thermal stability of nanocomposite was performed by TGA. Prabu et al. [137] studied for utilization of industrial pollutant such as sawdust, rice husk, fly ash and red mud as reinforcing material such as epoxy and polyester for developing high-performance composite. The fillers were incorporated in different wt% of 2, 4, 6, 8, 10, 20, 30, 40, and 50. Hand-layup technique was performed for the fabrication of composites and tensile strength, impact strength and hardness were studied. The tensile strength of sawdust and rice husk reinforced composites was enhanced by 14 and 18% and impact strength by 61 and 142%. SEM technique was analyzed to study the failure mechanism of composites. The tensile and impact strength of fly ash/epoxy composite was improved by 63% and 42% due to the good mechanical performance of fly ash in a polyester matrix. Baheti et al. [138] prepared the fly ash/epoxy composite by ball milling technique. Three-layered laminated composite of glass fabrics was prepared with reinforcement of nanofiller into the epoxy matrix. The obtained results indicate that with the incorporation of activated fly ash with different weight 1, 3, 5 and 10 wt% at 200°C, the storage modulus of the nanocomposite was improved by 85.71, 38.09, 104.76 and 80.95% as compared to neat composites.

**APPLICATIONS OF FLY ASH/EPoxy/NANOCOMPOSITES**

The Fly ash/epoxy/nanocomposite is a multiphase system with...
excellent properties and eco-friendly. Therefore, the applications of nanocomposite propose new opportunities for several sectors of aerospace, automotive and electronics applications. However, no single application establish 100% utilization of fly ash thus a large number of skilful application is needed for assisting and bettering the utilization of fly ash. The innovative applications of fly ash offer opportunities to further enhance the utilization.

RESEARCH GAP WHERE THE WORK IS AIMED

The literature review was revealed that work on composite based on fly ash, epoxy resin and nanofiller has hardly done in the past. In the literature survey, it has also reported that the mostly mechanical properties dramatically reduce with further excessive addition of fly ash and nanofillers. Therefore, for a particular application, the optimum level should be analyzed. So, an idea of developing high-performance composite matrices by utilization of waste material fly ash, nanofiller, and epoxy resin has emerged into mind based on literature survey. A lot of efforts have been required to utilize the industrial waste fly ash. With the incorporation of inorganic and nanoparticles, nucleation of crystallization can appear. The nucleation of crystallization developed with the reinforcement of inorganic and nanoparticles. Therefore at the nanoscale, the nanoparticle can change for deficiency of primary nuclei emulating with trapped crystallization. At higher content of nanofiller, lower crystallization kinetics is achieved due to higher viscosity. At low concentrations, the nucleation of crystallization was monitored by the Onset temperature of crystallization (Tc) and crystallization halftime. Slightly an interruption in the rate of crystallization has been observed at higher concentrations. This was alike observed in specific composites, where nucleation viewed at low concentrations [139-145].

CONCLUSION

In this context, nanocomposites are suitable materials to meet the emerging demands arising from scientific and technologic advances. They are generally more advantageous composites because the enhancement in properties of nanocomposite can be acquired from the addition of the small amount of nano-sized filler content having a high aspect ratio. The review article covers the effect of nanoparticles on mechanical characteristics including impact strength, flexural strength and tensile strength of fly ash/epoxy composite and fly ash/epoxy nanocomposites. It has concluded that the reinforcement of nanofiller even in small content enhances the mechanical properties of fly ash/epoxy composite. Because the homogeneous dispersion of nanofillers reduces the defects between fillers and polymer interface, resulting in improvement in the mechanical properties of filler/fly ash/epoxy nanocomposites. Finally, the review core provides a few awareness of safety and predictability features that would impact the market comeback for new nanocomposites. The increment in the progressive rate of utilization of fly ash also depends upon the government directives. The utilization of fly ash will sustain the natural raw material and diminished the disposal cost. While keeping safe the environment, fly ash will also bring out the business opportunities at the same time. To develop the epoxy nanocomposites with enhanced mechanical properties is associated with (a) The modification of nanofillers with functionalities to enhance the dispersion quality of the nanofillers (b) To improve the interfacial interaction between the nanofillers and the polymer matrix is mandatorily required. Hence, to explore the new functionalities of filler/fly ash/epoxy nanocomposites is the main effort for researchers in the future.

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