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STUDIES ON MECHANICAL AND THERMAL PROPERTIES OF EPOXY/FLY ASH/NANOFILLER NANOCOMPOSITE: A REVIEW

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ABSTRACT

A recent development in the field of eco-friendly, lightweight and highperformance 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. 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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HIGHLIGHTS

- Summarized the utilization of industrial pollutant fly ash as filler into the different matrix.
- Summarized general methods of fabrication of epoxy/fly ash nanocomposites.
- Reviewed literature on the effect of fly ash and various nanofillers on thermal, mechanical properties such as Tensile strength, Impact strength, Compressive strength and Hardness of epoxy/fly ash nanocomposites.

1. 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]. It is used as the primary reinforcement material in the composite. The article presents the utilization of industrial waste like FA as reinforcement for matrix in 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]. Overall, the polymer matrices are chosen on account of adhesive strength, fatigue resistance, heat resistance, chemical and moisture resistance, etc. 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, rigidness, 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 [1nm to 100nm], 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 change 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. The nanofillers are used as the secondary reinforcement material in the epoxy/fly ash nanocomposite.

In the literature survey, during the fabrication of epoxy/fly ash 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 adjacently 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. Debonding 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.

2. RAW MATERIALS FOR THE FABRICATION OF EPOXY/FLY ASH NANOCOMPOSITE

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.

3. CHEMICAL AND PHYSICAL CHARACTERISTICS OF FLY ASH

Fly ash 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 the 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 S.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 150µm. 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 S. et al. [20] studied that fly ash is industrial pollutant consists of cenosphere, hollow spherical particles which might be developed highperformance 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.

4. 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].

4.1. 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.

4.2. 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 describes the chemical composition of fly ash[21].

Constituents	Class F Fly ash (Vol %)	Class C Fly ash (Vol %)
Fe ₂ O ₃	8.44	6.86
Al_2O_3	26.56	17.8
SiO ₂	55.85	42.46
MgO	2.4	5.4
CaO	6.59	22.25

Table 1 Chemical composition of fly ash

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

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.



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 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].

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 matrix such as epoxy resin due to its superior properties. Generally, the metallic particles are costly so the spherical particles of fly ash could assist the objective of reinforcement in epoxy matrix [25]. For the matrix mechanical strength compatibility with that of the incorporating material is necessary so epoxy resin is used as matrix for fly ash and nanofillers.

6. 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, polyamides, 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 [28-29].

7. FABRICATION OF EPOXY/FLY ASH COMPOSITES

For the preparation of epoxy/fly ash composites, the following techniques have been reported.

7.1. 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 [30]. Purohit R. et al. [31] 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.

7.2. 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.

7.3. Compo 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 [32].

7.4. 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 [33].

In the literature survey, the various nanofiller have been used as secondary reinforcing material to improve the mechanical and thermal properties of epoxy/fly ash composite has been described.

8. 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 which create a problem in the homogeneous dispersion of nanofillers in the polymer matrix [34-35]. 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 [36]. 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 matrixes with the nanofillers such as calcium carbonate, aluminum oxide, graphene, silica, carbon nanotubes and nanofibers [37].

8.1. Classifications of Nanofillers

Generally, nanofillers can be classified according to their number of dimensions 1D, 2D or 3D in nanocomposites, shape, and morphology [38]. 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 (multiwalled 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 are described as following.

8.2. Nanoclay

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 [39]. 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, hectrite and saponite have also reinforced in polymer nanocomposite

8.3. Carbon Nanotubes

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 [40-41]. In a vacuum, MWCNTs are thermally reliable up to 2800^oC. 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 [42]. 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 [43]. The CNT has wide applications in electronics, thermal and structural industry.

8.4. Metallic Nanoparticles

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 $20-500 \text{ m}^2\text{g}^{-1}$. 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.

8.5. Metal Nano Oxides

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.

9. GENERAL METHODS OF FABRICATION OF EPOXY/FLY ASH NANOCOMPOSITES

The surface modification for every type of nanofillers is achievable. The reinforcement of various types of nanofillers in any type of matrix has to need pre-treatment to enhance the interaction between matrix and nanofiller [44]. Based on various parameters the fabrication methods of polymer-based nanocomposites are classified. The process which occurs at the surface of material resulting in different physical and chemical behavior from one originally exhibit on the surface of the material is known as a surface modification. The different techniques such as the sol-gel process, in-situ polymerization, and solution mixing process, melt mixing process and in-situ intercalative polymerization were used for the fabrication of nanocomposites. The following techniques have been reported to modify the nanofillers and reinforced within the polymer to form a nanocomposite.

9.1. 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 [45-46]. 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.

9.2. 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. Melt Intercalation methods are environmentally well dispose of but not compatible with industrial polymer processes [47].

9.3. Sol-Gel Method

This method is a tangled combination of in situ polymerization process and in situ formation of nanofiller as reinforcing phase.

9.4. Intercalation Method

The approach of this method is based on the reducement of fillers into nano dimensions. In this method, the exfoliation of layered silicates acts as inorganic filler exhibits by intercalating an organic compound into the interlayer space of silicate, resulting in a uniform and homogeneous dispersion of plate-like nanofillers [48].

9.5. 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. [49].

9.6. 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 [50]. 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.

10. METHOD FOR DISPERSION OF FLY ASH AND NANOFILLERS IN MATRIX

During the fabrication of epoxy/fly ash 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 [34-35]. 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 [37-38]. 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.

10.1. 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 [51]. Therefore this technique has been extensively reported for crushing, emulsifying and dispersing the particles. Xia H.S. et al [52] carried out the ultrasonication method to diminish the agglomeration of nano-silica particles. In 2016, Pattanaika A. [53] examined the epoxy/fly ash composite by using Ultrasonic Technique.

11. 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.

12. CHARACTERIZATION OF POLYMER NANOCOMPOSITES

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 M.A. et al. [54-55] 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. Wetzel B. [56] 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 (thermal gravimetric analyzer).

13. EFFECT OF FLY ASH AND NANOFILLERS ON MECHANICAL, MORPHOLOGICAL, AND THERMAL PROPERTIES OF FLY ASH/EPOXY NANOCOMPOSITES

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 fly ash and nanofiller with different wt% into the polymer matrix. The mechanical, optical, rheological, flame retardancy and dielectric properties of polymer nanocomposites have been extensively studied. Various authors have revealed some interesting studies on epoxy-based nanocomposites with the incorporation of fly ash and various nanofillers.

In 1988, Srivastava V.K. et al. [57] studied that fly-ash 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[58]. Ibraheem S. et al. [59] 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 M.P. et al. [60]. 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 P. et al. [61] 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 H.V. et al. [62] studied the utilization of fly ash as reinforcement material in the epoxy/PBT blend matrix. The mechanical properties of PBT (2%)/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 R.S. et al. [63] prepared the fly ash/epoxy composite with reinforcement of 10 wt% of different particle sizes of fly ash (50 μ m, 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 characterization 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 S.M. [64] 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 [65] studied the mechanical characteristics such as impact, flexural strengths, and flexural modulus of Fly ash Cenospheres/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 15wt% 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 S. et al. [66] studied an epoxy-based carbon nanomaterial's nanocomposite. Verma D. et al. [67] 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 231.97MPa, 48MPa, and 114MPa 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 Eglass fiber into epoxy resin.

Ozsoy I. et al. [68] 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, 10,15N, Sliding speed 0.8m/s and sliding distance by 2000m. They concluded that the tribological and mechanical performance of micro filler epoxy composite was found better than nanofiller epoxy composite. Ultrasonic

synthesis technique help in the formation of long term stable polymerization which consists of polymer/inorganic nanoparticle composite. 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 A. [69] 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 reduced with 20 wt% of CSP. Recently, Chen P. et al. [70] studied the mechanical properties like impact strength, flexural strength and flexural modulus of Fly ash Cenospheres/EP composites. Fly ash Cenosheres (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.

Chaowasakoo T. et al. [71] 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. Prabu V.A. et al. [72] 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 V. et al. [73] 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.

14. APPLICATIONS OF EPOXY/ FLY ASH NANOCOMPOSITES

The epoxy/fly ash nanocomposite is a multiphase system with excellent properties and ecofriendly. 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 skillful 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.

15. 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 half-time. 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 [74-80].

16. 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 reduced 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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