

Review article

Preparation and characterization of coal fly ash reinforced polymer composites: An overview

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Abstract. Energy and environmental protection are two major problems that are faced by the current generation. Coal has been utilized traditionally as a source of electricity globally. However, more ash is generated from the combustion of coal which is carried by gases and precipitated into fly ash. The main problem with fly ash is that, if it is not properly disposed it may cause pollution(s) in the water and soil, which in turn disturb ecological cycle and have negative impact on the environment. Based on the above statement(s), more efforts have been done to recycle fly ash or its utilization for advanced applications. One of the preferred methods for recycling fly ash, is to incorporate it in polymer matrices in order to improve the strength of polymer matrices for advanced applications. Fly ash has been utilized as a reinforcing filler for various polymer matrices due to its high strength and low cost. This review paper discusses different fabrication methods for fly ash/polymer matrices composites. The effect of particle size, modification, synergy of fly ash with other fillers reinforced polymer matrices on the mechanical properties are discussed. Furthermore, there is an in-depth discussion about the specific applications of fly ash reinforced with different polymer matrices. There is also a discussion based on the fly ash/fiber/polymer hybrid composites in relation to the preparation method and mechanical properties, since hybrid systems are known for better properties than single fillers.

Keywords: polymer composites, fly ash, coal waste, mechanical properties, hybrid systems

1. Introduction

Coal is regarded as one of the most abundantly used fossil fuels, following oil, globally [1]. According to the World Energy Council (2016) coal remains the second most important fuel, generating approximately 40% of the world's electrical power with China accounting for 60% of the demand. Trends analyzed since 1960 have revealed an exponential increase in coal demand annually and a 64% increase in coal demand was reported from the year 2000 to 2014 [2]. Coal is largely used as the primary raw material in electrical power generation in thermal power plants

as well as in the production of steel, gasification, and liquefaction. The fast-growing demand for coal energy can be attributed to the rapidly growing population as well as industrialization. Fossil fuel has proven to be an essential material(s) in affording people a decent living environment. However, it is also accompanied by a few drawbacks *i.e.* carbon emissions into the atmosphere and the release of fly ash as a waste material. During the process of coal combustion for the purpose of generating electrical power, a by-product referred to as fly ash is produced. Fly ash is made up of incombustible coal particles which are collected

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during the incineration process using electrostatic precipitators, bag houses and other particle filtration mechanism; however, some of these particles settle to the bottom of the boiler by reason of its weight; this is then referred to as bottom ash. Collectively, fly ash and bottom ash are called coal ash. Following collection, the ash is transferred to landfill sites where they are disposed in ash lagoons or slurry dams. As a waste product, fly ash poses a major risk to the environment as it contains toxic heavy metals, such as aluminium oxide (Al_2O_3), calcium oxide (CaO), sulphur oxide (SO_2), potassium oxide (K_2O), magnesium oxide (MgO), iron oxide (Fe_2O_3), and silicon oxide (SiO_2). Coal ash that is disposed in slurry dams becomes a major source of groundwater contamination as these heavy metals permeate the soil and percolate out of the soil into the groundwater [3]. Groundwater sources in areas where fly ash is disposed were discovered to have higher than permissible traces of heavy metals and trace elements such as nickel, lead, and zinc [3]. Furthermore, water containing traces of fly ash may potentially leach into various water sources such as dams, rivers, lakes, and seas polluting such water. Researchers have found that water containing fly ash leachate can be absorbed by freshwater fish through the gills. This induces oxidative stress in the fish [4] as well as causing permanent damage to the outer layer of the fish scales preventing the overall functioning and formation of scales on the fish [5]. Typical fly ash sizes from 0.3–250 μm [6], with the inhalation of smaller fly particles (*viz.*, 2,5 μm) leads to a respiratory infection due to deposition in the lung parenchyma [7] as shown by Figure 1.

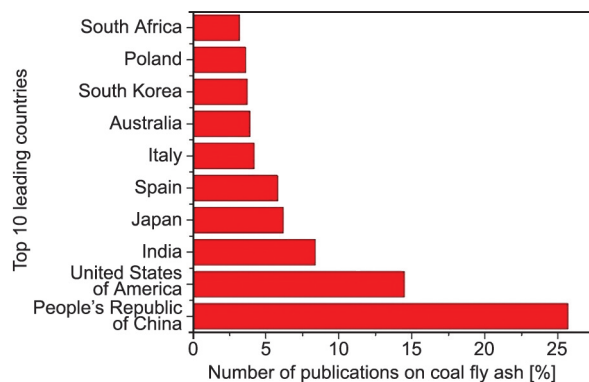


Figure 2. Top 10 leading countries in terms of coal fly ash research (Data captured on the 26/04/2021).

Globally, the People’s Republic of China is the leading country in terms of research based on coal waste, specifically fly ash (Figure 2). This is also correlating with the number of citations obtained globally in the field of fly ash, with the People’s Republic of China being the leading country, followed United States of America (USA) and thirdly Spain (Figure 3).

In an effort to combat this environmental hazard and employ sustainable waste management strategies, scientists have studied the physical, chemical, and mechanical characteristics of fly ash. Based on the statement above, it became very clear that most researchers have put a lot of effort into the research topic of fly ash waste as illustrated by Figure 4, with an increase in the number of publications from 2010 to 2021.

Based on the research works, different methods were suggested for combating the environmental hazard of fly ash. One of the well-known methods is the incorporation of fly ash into polymer matrices in order

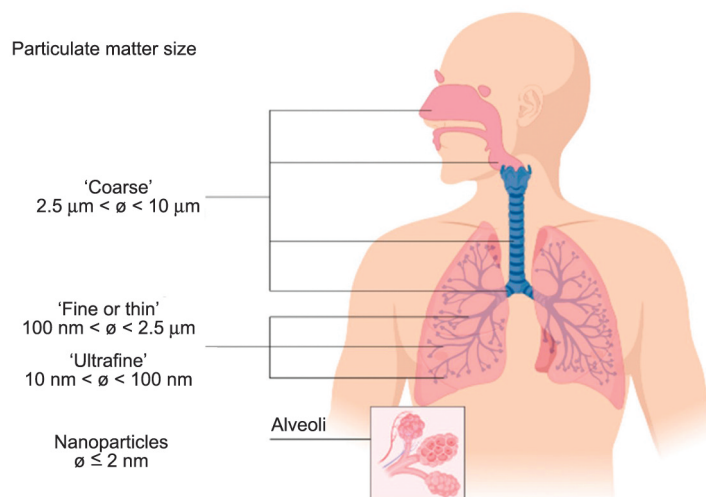


Figure 1. An illustration of the particle size penetration in lungs [8] (MDPI Open access).

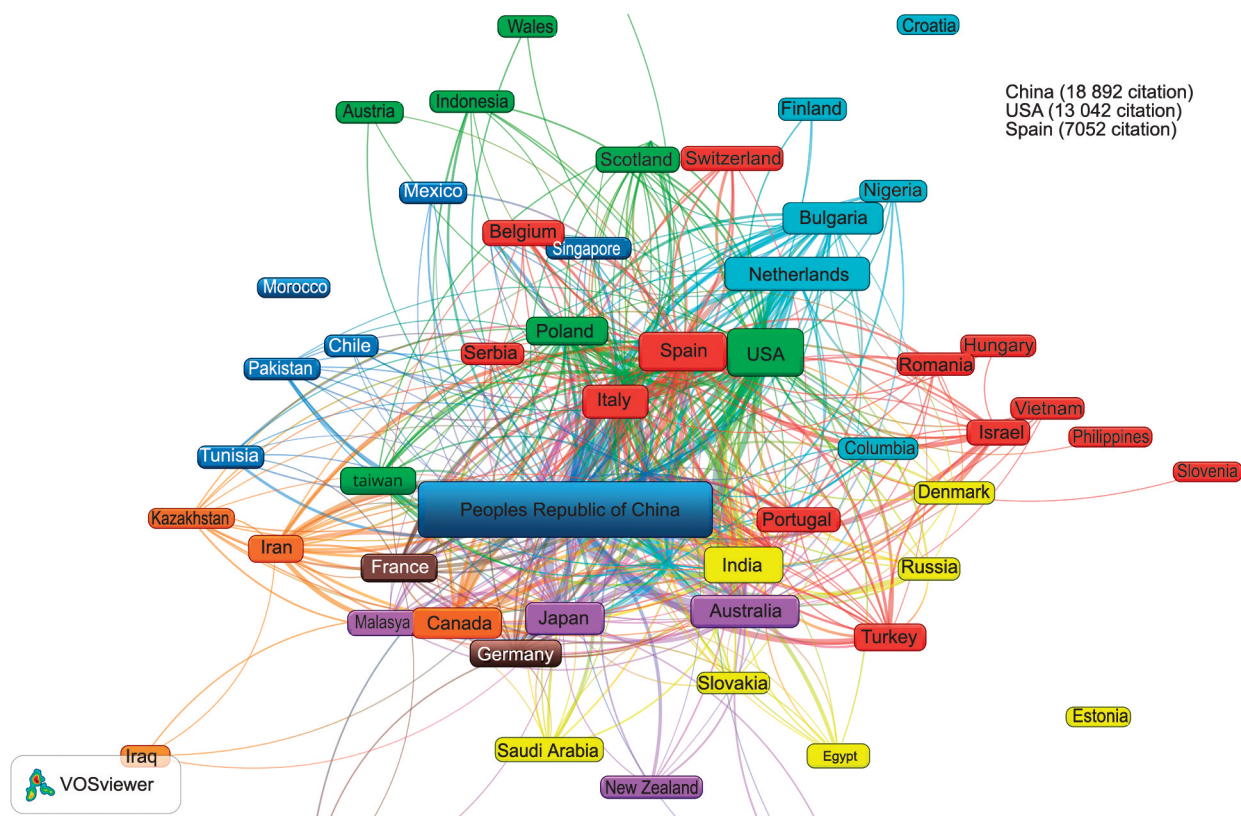


Figure 3. Network visualization of the leading countries in terms of citations (Data captured on the 26/04/2021).

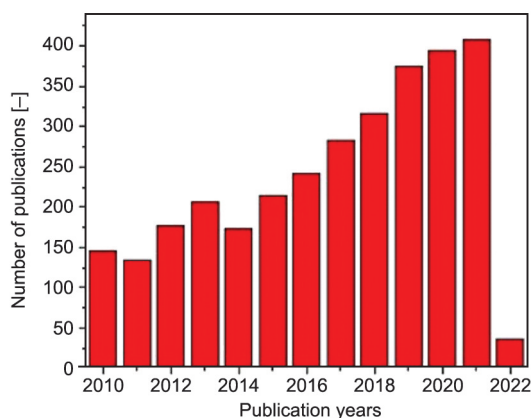


Figure 4. The number of publications on coal fly ash from 2010 to 2022 (Data captured on the 22/03/2022).

to improve the properties of polymer(s), as a result enhancing their widespread applications. This review paper discusses the reinforcing of fly ash and its synergy with different nanoparticles in various polymer matrices for advanced applications.

2. General overview on fly ash

Fly ash can be obtained from various sources including: (i) municipal solid waste, (ii) biomass, (iii) oil and (iv) coal. Due to a rapid increase in the population over a short period of time, more municipal solid waste is generated. Primary waste management

protocols such as disposal in landfills have proven to run short of managing the enormous amount of solid waste produced in homes. As such, incineration of municipal solid waste has been a practiced tradition over many years. A major setback in using incineration as a waste management strategy or a method for obtaining any type of energy, is the production of fly ash and bottom ash [9]. As a result, the use of municipal solid waste fly ash in advanced applications has been introduced. Ferreira *et al.* [10] outline three major factors to be considered when applying municipal solid waste fly ash. These factors are: (i) Physical and chemical characteristics or constituents, (ii) technical applicability and (iii) the presence of toxic trace elements. The author(s) proceeds to outline possible applications for municipal solid waste fly ash which includes geotechnical applications such as concrete, cement, brick, pavements, embankments, ceramic and glass as well as applications in agriculture as soil remediation materials [10]. These applications resemble those of coal fly ash suggesting a possible similarity in terms of physical and chemical constituents. Biomass fly ash, on the other hand, is obtained as a result of combustion of plant and animal organic matter [11]. Biomass can be obtained (i) naturally as remains from forests or plantations,

(ii) residually from wastes obtained because of agricultural activity and (iii) as waste from energy crops including: oil seeds/plants *i.e.*, hempseed, sunflower, coconut, bioethanol producing plants (*viz* sugar cane, starch), and plants containing lignin and cellulose (*i.e.*, wood and grass). Biomass is incinerated for the main purpose of generating electrical power and heat. According to the International Energy Agency in 2012, biomass energy production is expected to increase to 100–300 exajoules (EJ) by the year 2050. Some researchers do not consider biomass combustion as hazardous to the environment but rather neutral in terms of the carbon cycle as it does not temper with the atmospheric carbon concentrations [11, 12]. This phenomenon is illustrated in Figure 5 below.

However, as is the case with any combustion process, by-products in the form of fly ash and bottom ash are obtained. In 2013, the annual production of ash from biomass reached 480 million tons [13]. Agrela *et al.* [11] discussed the properties of biomass fly ash and its potential applications in industry. These applications include geopolymers, thermal and acoustic insulation as well as use as metal absorbents in wastewater treatment processes.

Oil fly ash can be acquired from sources such as oily plants and seeds as stated above. However, combustion of heavy oils and crude oils also results in fly ash residues. Incineration of heavy oil results in approximately 3 kg of fly ash per 1000 liters of oil [14]. Literature and research pertaining to heavy and crude oil fly ash is limited because then it contains lesser amounts of silica making it less desirable in geotechnical applications such as is the case with coal fly ash. Nevertheless, industrial applications for heavy and crude oil fly ash remain a great priority since it is produced in major quantities. Mofarrah and Husain [14] explore ways to utilize heavy oil fly ash as a coloring agent in cement mortar. The researchers collected ash produced from a combination of 2% heavy fuel oil and petroleum choke. The results obtained reveal that no potential environmental harm was detected with the use of 2–5% heavy oil fly ash (HOFA). Overall, no improvements to compressive strength were observed although the color pigmentation was achieved [14]. Dahim [15] investigated the possible use of crude oil fly ash for road pavement applications. The researcher focused on utilizing the surface capacitance sensor to improve asphalt pavement properties, specifically the dielectric properties.

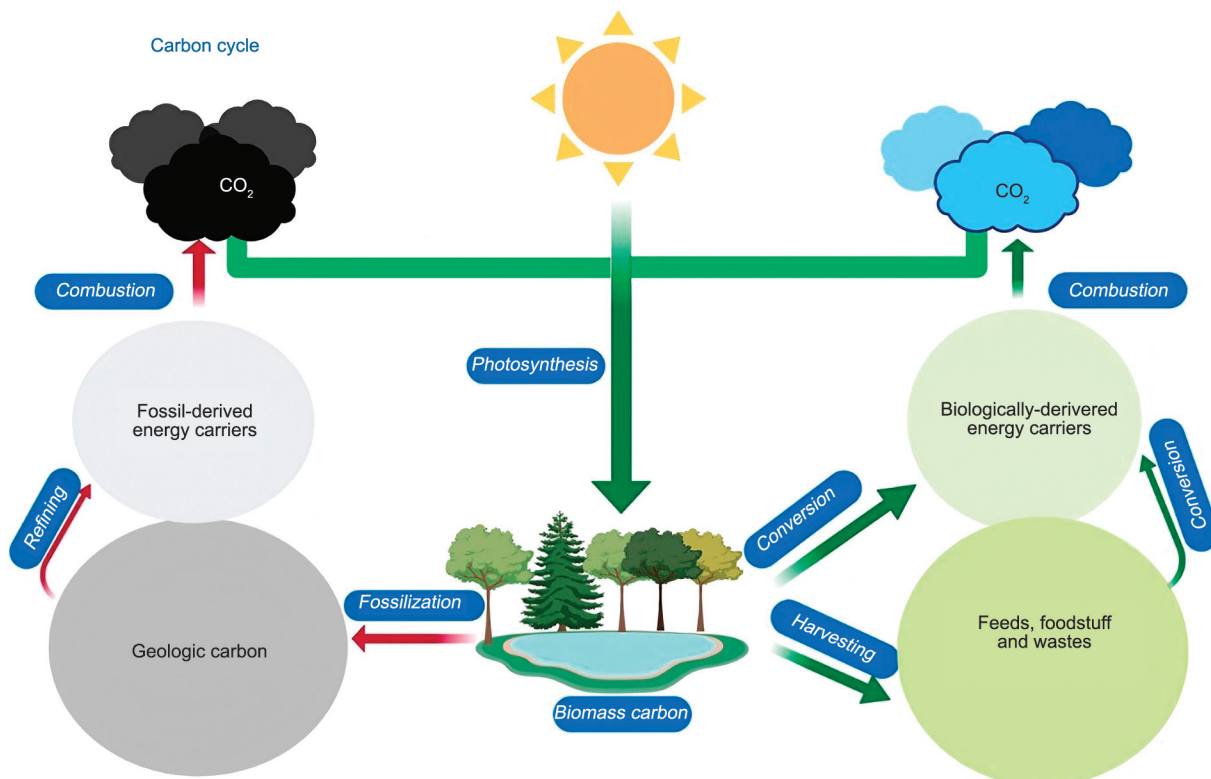


Figure 5. The carbon cycle of biomass [12] (MDPI Open access).

Progressive applications of fly ash from various sources have gained massive attention in the research field. However, the most common and possibly the highest produced type of fly ash globally, is coal fly ash and that will be focused on in this review.

3. A brief history of coal fly ash and its early applications

Throughout its years of existence, fly ash has mostly been used in concrete mixes for the construction industry. However, its use in other fields (*i.e.* use of fly ash as cement extenders, in polymers, in agriculture, in mining and refractories) outside the construction industry emerged later in the 1980s (between 1980 and 1987 to be specific) [16]. The use of fly ash in concrete mixes was a major breakthrough in the use of high volumes of fly ash for commercial purposes. The use of fly ash in concrete mixtures was inspired by the Romans. In 128 A.D., the Romans used high volumes of volcanic ash in cement mixtures to build the Pantheon temple (see Figure 6). Today, after surviving countless storms and earthquakes, the Pantheon still remains in its original form as a result of the quality of concrete materials used to build it. Due to the increasing fly ash waste accumulation, fly ash was later used to replace volcanic ash in concrete

mixtures. This is because it was discovered that fly ash has similar properties to those of volcanic ash [17]. Since, fly ash is a form of a naturally occurring pozzolan, thus it possesses similar properties to volcanic. Pozzolans are a group of materials consisting of silica oxide and aluminum oxide. In their natural state, these materials have little or no cementitious properties. However, in a finely divided form and in the presence of water, these materials chemically react with calcium hydroxide or lime at ambient temperatures to form compounds with cementitious properties [18].

In 1942, the first documentation on the use of fly ash in concrete mixes was carried out by the Bureau of Reclamation in the USA. The documented fly ash concrete mix was used to repair a tunnel spillway for the Hoover dam. Its use in concrete mixtures was later documented between 1948 and 1952 for construction of the Hungry horse dam near Glacier national park in Montana. Till to date, the Hungry horse dam is still rated among the most impressive structures in the USA [17]. In 1983, the USA Environmental Protection Agency endorsed the use of high volumes of coal fly ash in concrete mixes for projects funded by the federal government. As a result, the Washington D.C. area metro subway system was built using high volumes of fly ash-based concrete. The

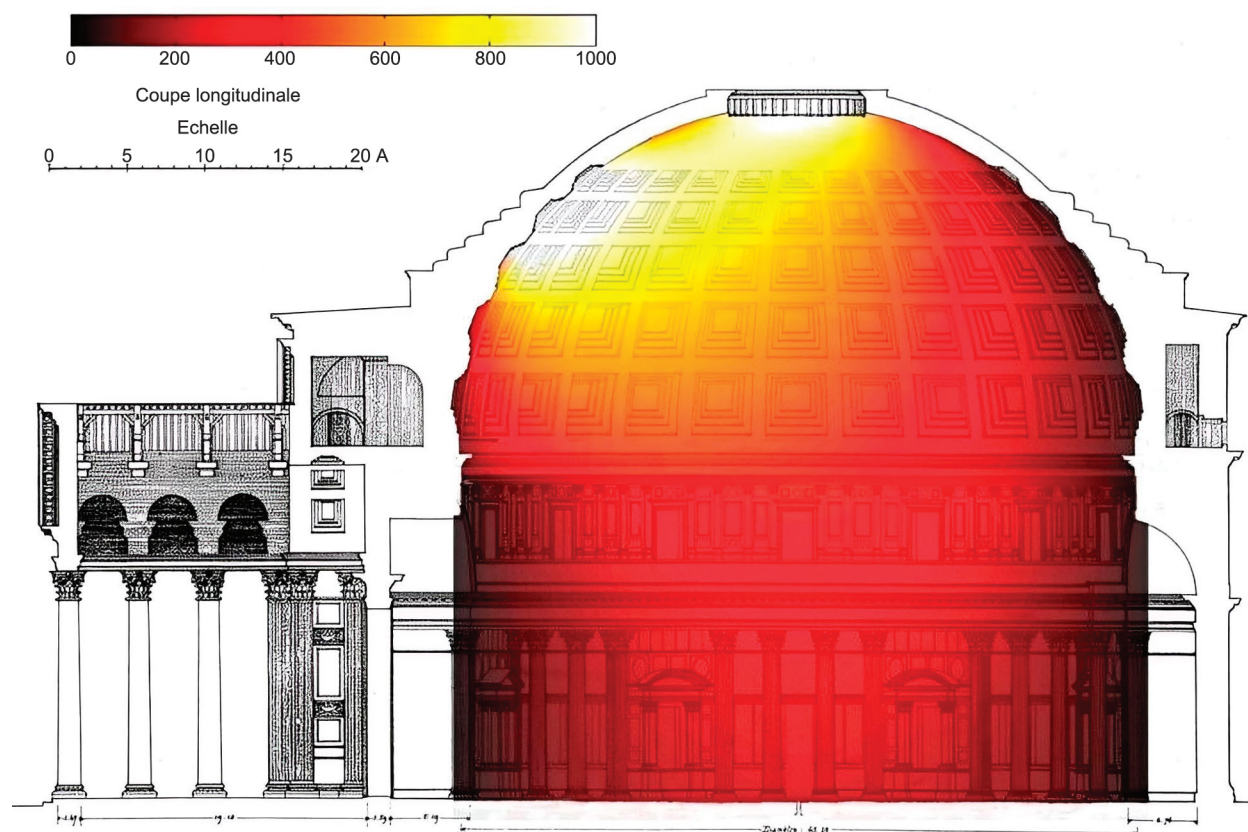


Figure 6. Lighting simulation of the Pantheon as done and validated by Almodovar-Melendo *et al.* [19] (MDPI Open access).

endorsement also led to the construction of the massive 85 000-seat stadium in Atlanta for the 1996 summer Olympics [17]. This shows that coal fly ash has a rich history in the construction industry. However, in order to expand its application scope, it has been reported that coal fly ash can be used for other non-conventional applications outside the construction industry. The use of fly ash in polymers is one such application [16] and this application was first discovered in the 1980s. In polymers, fly ash is used in the place of functional fillers like limestone, talc and other inorganic fillers just to mention a few. The advantage of using fly ash in polymers as compared to other fillers is to improve the polymer processing and compounding. The spherical shape of the fly ash particles, as shown in Figure 7 below, improves the flow properties of materials during extrusion and casting. This imparts physical properties to the resultant fly ash-based polymer materials. However, for optimum properties, strong compatibility between the fly ash filler and host polymeric matrix is essential. Today, a majority of the commercially available polymer-based materials in South Africa consist of fly ash as filler. These materials include garden hoses, electrical conduits, water pipes and shoe soles [16].

4. Fly ash waste management protocols, challenges, and regulations for disposal

4.1. Fly ash waste management protocols

The process of waste management with reference to fly ash disposal starts when ash is transferred from

dust filtration systems into various storage systems depending on the intended use, application, and type of fly ash. The handling and storage thereof may vary as follows: (1) Dry fly ash (stored in silos and domes); (2) Conditioned fly ash (mixed with small amounts of water and stored in stockpiles); (3) Ash slurry (mixed with higher volumes of water and stored in slurry dams and dikes) [21]. Fly ash is regarded as a hazardous waste substance in many countries and thus the disposal therefore is regulated. According to He *et al.* [22], in The People's Republic of China, the 'Standard for Pollution Control on the Storage and Disposal Site for General Industrial Solid Wastes' outlines mandatory measures for the storage location and measures of fly ash in order to avoid leachate, run-off and fugitive dust. However, stockpiling fly ash at disposal sites takes up large amounts of land space due to the high quantities of fly ash being produced; and although these disposal sites were engineered to protect the environment, it cannot entirely prevent leachate, run-off, or fugitive dust [22]. Moreover, in India the Ministry of Environment and Forestry endeavoured to regulate fly ash utilization in 1999 by proposing that all coal-fired power plants utilize 100% of all produced fly ash within prescribed times. New coal-fired power plants are required to utilize 100% of all produced fly ash within 9 years of operation and existing coal-fired power plants are expected to utilize 100% of all produced fly ash within 15 years of the commencement of the regulation. The regulation also permitted fly ash be utilized in

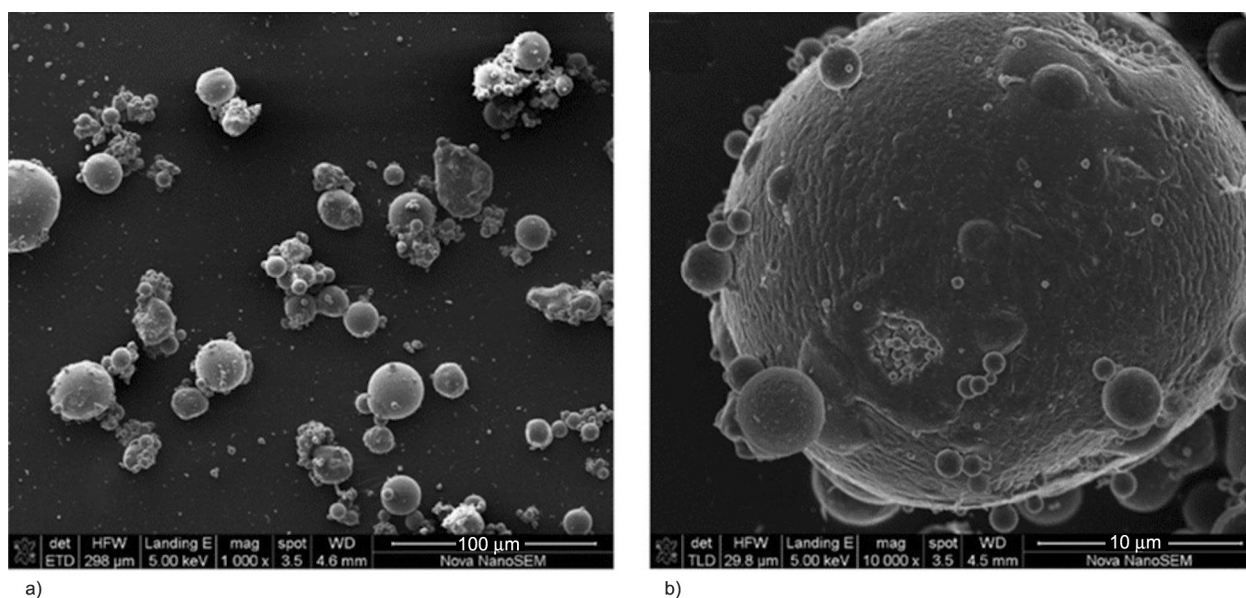


Figure 7. (a) 1000× and (b) 10 000× magnifications of coal fly ash as shown by scanning electron microscope images [20] (MDPI Open access).

construction and agriculture and be provided to potential users within 300 km radius free of charge [23]. However, in the United States of America Coal Combustion Residuals (CCR) are not considered ‘hazardous waste’ and storage as well as disposal thereof was never regulated until 2015 following the collapse of a dike resulting in major coal spills in Tennessee, New York, Eden and Kingston. The Environmental Protection Agency (EPA) introduced the CCR rule which would regulate the disposal of fly ash in order to minimize pollution and potential adverse health effects [23]. The toxic nature of fly ash makes it imperial to regulate its waste management systems as improper disposal may lead to adverse health and ecological outcomes.

4.2. Challenges regarding improper fly ash storage

Due to high volumes of fly ash production in the developing countries, improper fly ash disposal has become a nation-wide challenge. Poor planning of disposal protocols and an increase in demands for thermal power through coal plants leads to an inevitable socio-medical and environmental problems leading to air pollution, water pollution and soil pollution. The range in sizes of fly ash particles means that they may undoubtedly become airborne when disposed in landfills; these airborne particles can lead to pneumoconiosis when inhaled [24]. Hagemeyer *et al.* [25], demonstrated this by examining the respiratory health of adults exposed to coal ash by living near coal storage sites. The results indicated that individuals who had been exposed to coal ash, experience greater respiratory illnesses than those who were not exposed to the coal ash thus suggesting that coal ash particles may be present in the ambient air in areas surrounding coal ash storage sites. Fly ash polluted water has an adverse effect on aquatic and plant life. Toxic heavy metals contained in the ash contaminate watercourses may have negative effect on the supply of water intended for potable use. Ankita *et al.* [26] express this as a dual stress which is exerted on the biological communities as well as aquatic communities present in watercourses. Additionally, the normal pH of fly ash ranges between 7 and 12 [27] rendering it a medium to strong alkaline. When fly ash residues settle on the soil surface, they are able to alter the soil pH levels, thus interfering with the metabolic activity of plants influencing the types of animals that are able to thrive in the particular

habitat, subsequently affecting the ecosystem of the region [24]. Tiwari *et al.* [28] outlines the leachate pollution caused by coal ash and slag as well as the environmental implications thereof. Some present-day health diseases such as anemia and hemochromatosis may be linked to groundwater pollution and soil pollution caused by industrial leachate resulting in access amounts of iron and chromium evident in groundwater.

4.3. Fly ash waste management strategies

There has been a lot of effort to promote waste utilization of fly ash rather than ash aimless disposal, which includes: horticulture as a long-term waste management option [29], influence the pH levels of in-vessel compost systems to increase the growth rate of mesophilic and thermophilic microorganisms [30], incorporation in concrete for building applications [31], synthesis of zeolites for water purification [32] and most recently the incorporation of fly in polymer matrices for advanced applications. The incorporation of fly ash into polymer matrices is the preferred method of waste management of fly ash, since the fabricated composites has a potential to be applied in various applications.

5. Morphology

5.1. Fly ash/polymer and other nanoparticles hybrid composites

Polymer-filler composites have been an ever-advancing topic amongst researchers for many decades. The demand for polymer composites with advanced performance has given rise to many innovative ideas, including the use of waste products such as fly ash as fillers in polymer composites. When introducing a filler into a polymer matrix, factors such the mixing and blending processes have a direct influence on whether the desired outcome is achieved. For an effective compounding, a uniform and optimum dispersion of the particles is of utmost importance. This determines the level of interaction between the filler and the host polymer. The morphology of the fly ash reinforced polymer composites was reported to be affected by factors such as (i) preparation method (ii) particle size of the fly ash, (iii) content of the fly ash, (iv) surface modification, (v) type of the polymer and (vi) its synergy with other fillers [33–44]. Morphological studies are conducted using a scanning electron microscope (SEM), transmission electron microscope (TEM) and polarized optical microscopy

(POM) in order to indicate the filler dispersion into the polymer matrix. Alghamdi [33] reported on the effect of fly ash particle size reinforced high-density polyethylene (HDPE) composites. The particle sizes of fly ash utilized were 50–90 μm denoted FA1, 90–150 μm which was symbolized as FA2 and finally 150–250 μm which was denoted FA3 (Figure 9). The three types of fly ash, *i.e.* 10 wt%, were incorporated into the HDPE matrix using a melt mixer at 220 °C for 30 minutes [33], as schematically represented

in Figure 8. Furthermore, the freshly fabricated samples were recycled by utilizing an extrusion and recycling process four times and the samples were ‘termed’ the recycled samples. From SEM images, it was reported that fresh samples showed high interfacial adhesion between the composite’s components (Figure 9). It was noticed that, after the first recycling there was a high delamination of the fly ash in the composites. The lowest debonding was obtained at FA1/HDPE composite after the first recycling

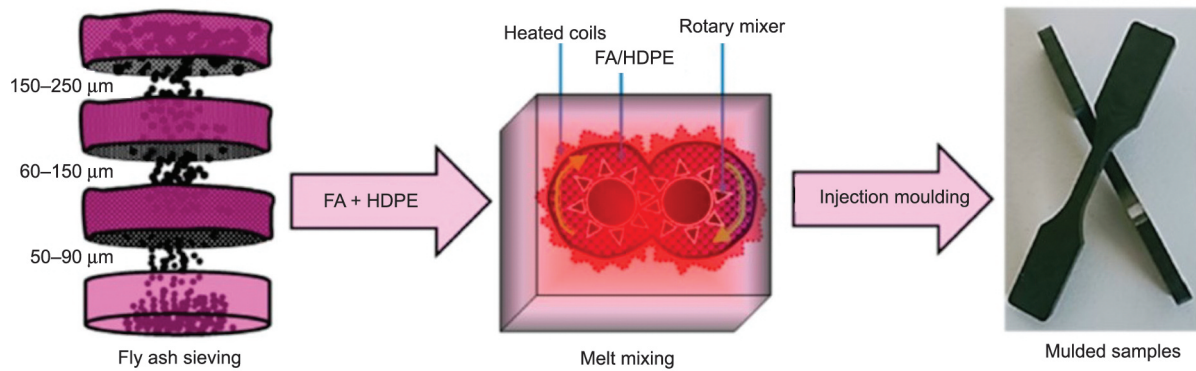


Figure 8. Preparation method for HDPE/fly ash composites consisting of various fly ash particle sizes [33] (MDPI Open access).

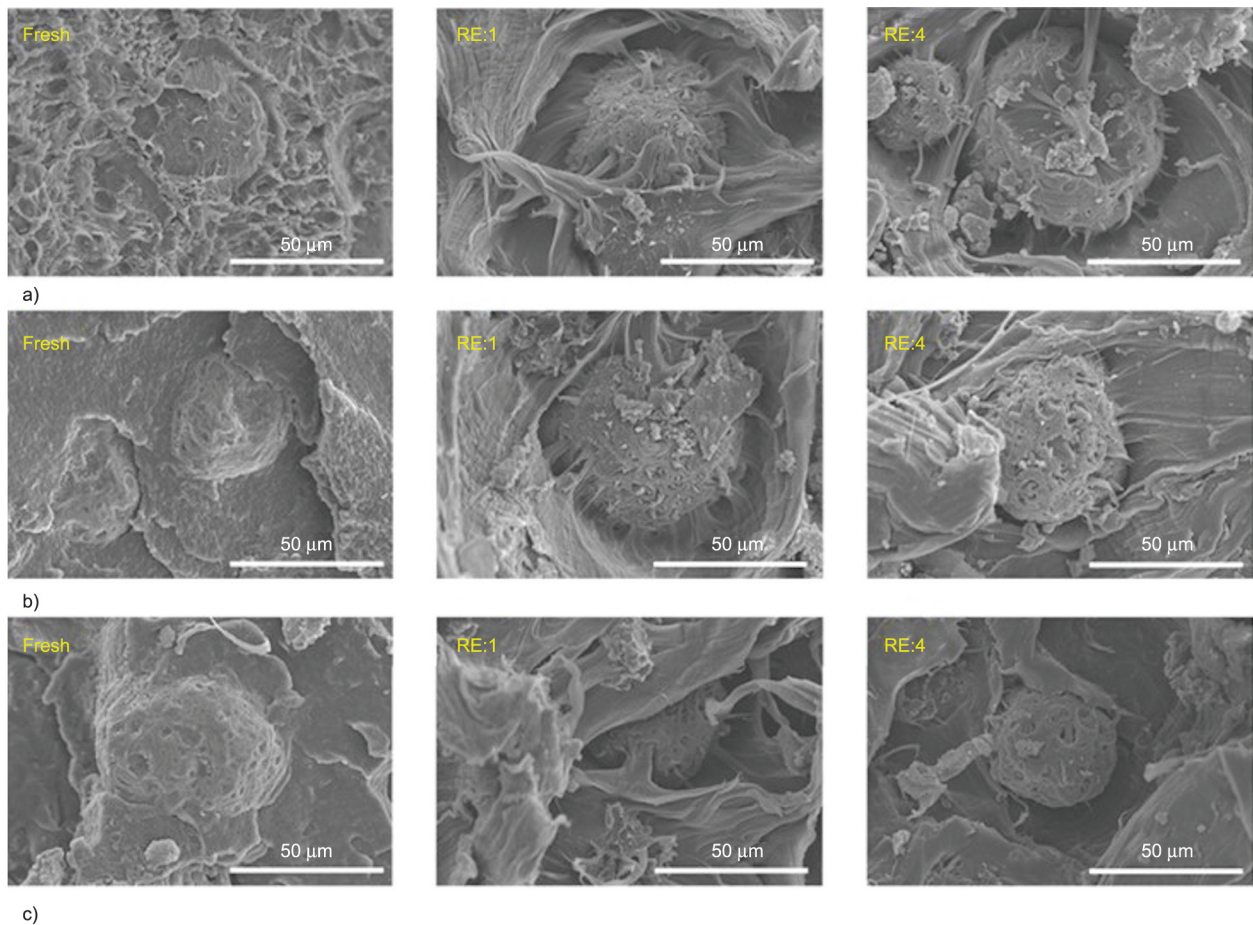


Figure 9. Cryogenically fractured fresh and recycled SEM images of: (a) FA1/HDPE, (b) FA2/HDPE, and (c) FA3/HDPE composites [33] (MDPI Open access).

(Figure 9). Fly ash particles of similar sizes kept consistency in terms of the adhesion between the filler/matrix system. It was further concluded that, after the fourth re-cycle, there were no changes in the interfacial adhesion between the components (Figure 9) [33].

The effect of the fly ash content on the morphology of the fly ash/polymer composites was reported by Sim *et al.* [34]. The authors reported that the fly ash/epoxy composites with 10 vol% fly ash with a size less than 53 μm showed debonding between the matrix and fly ash due to poor interfacial adhesion between the polymer and fly ash. Furthermore, when the content of fly ash was more than 50 vol%, there was a significant debonding between the epoxy matrix and fly ash. Several researchers [35–43] have reported on the morphology of polymer reinforced with fly ash together with other fillers. Various particles such mica, carbon nanotubes, calcium carbonate and clays have been incorporated with fly ash into polymer matrices, as a result different morphologies were obtained when compared with single fly ash/polymer composites. The synergy of calcium carbonate (CaCO_3) and fly ash were incorporated into the epoxy matrix, with the composites fabricated by mixing the epoxy, polyamine (curing agent), fly ash (10 wt%) and various content of calcium carbonate (1, 3 and 5 wt% by ultra-sonication for a duration of 30 minutes [35]. There was strong interaction between the epoxy matrix and the nanoparticles, with fewer agglomerates in the nanocomposites. However, the inclusion of the second nanoparticles into the system still requires more of surface treatment and coating technologies in order to enhance interfacial adhesion, and thus improve the overall properties [36]. Different modifications such as silanization, alkalization, and addition of compatibilizers were employed into the fly ash/polymer systems in order to enhance the adhesion between fly ash and polymer matrices. Parvaiz *et al.* [37] enhanced the interaction between fly ash and polyetheretherketone (PEEK) through chemical modification by utilizing calcium hydroxide. The unmodified fly ash/PEEK composites showed poor filler/polymer interaction, emphasizing a debonding at the interface between the fly ash and PEEK matrix. On contrary, calcium hydroxide modified fly ash/PEEK composites showed an enhanced interfacial adhesion between composite' components. This was due to the formation of calcium hydroxide coatings on the surface of fly ash,

which enhanced fly ash interaction with the PEEK matrix.

Numerous researchers [44–46] have reported on the utilization silane coupling agents for improving the dispersion of fly ash into the organic polymer matrices. Silane as a coupling agent has the amphiphilic functional groups *i.e.*, silane is able to react with the polymer matrices and inorganic fillers by forming chemical bridges in the polymer/filler composites, as a result improves the adhesion between the two phases. Qin *et al.* [44] reported on the silane treatment of mesoscopic fly ash (MFA) reinforced polyurethane composites. In this study, 3-glycidoxypropyltrimethoxysilane (GPTMS) was grafted on the surface of MFA to form modified fly ash and the modified fly ash was mixed polyurethane (PU), as illustrated in Figure 10. It reported that GPTMS was successfully grafted on the surface on fly ash, with the optimum concentration of GPS/FA being 2.5 wt%. When compared with neat PU (Figure 11a), the SEM images of the unmodified PU/MFA showed voids at the interface between the fly ash and PU, which is an indication that there was no crosslinking between the two phases (Figure 11b, 11c). The incorporation of 2.5 wt% of GPTMS into the PU/MFA was observed to eliminate the gaps between the polymer matrix and fly ash filler (Figure 11e, 11d). The mechanism of chemical crosslinking of PU/MFA in the presence of GPTMS is explained as follows from the literature: It is suggested that the alkoxy groups are hydrolyzed into the silanol with the incorporation of silane coupling agent, with the silanol forming a membrane coating on the surface of the mesoscale fly ash particles. Furthermore, it was suggested that the silanol is dehydrated and undergoes condensation with the hydroxy groups which are present in the MFA, as result there is a fabrication of chemical crosslinking. Figures 12a shows the dispersion of modified MFA into the PU matrix and the chemical crosslinking mechanism of the silane coupling in the PU/MFA composite (Figure 12b), respectively [44]. In general, the incorporation of the fly ash *i.e.*, 40% and above, have a negative effect on the resulting properties, such as mechanical strength and dielectric properties [45]. Based on the above statement, one of the most effective methods that was utilized in order to enhance the overall properties of the polymer/fly ash composites is the incorporation of the second filler [35, 37, 39, 41, 43, 47]. This method is the preferred method because of the improvement in

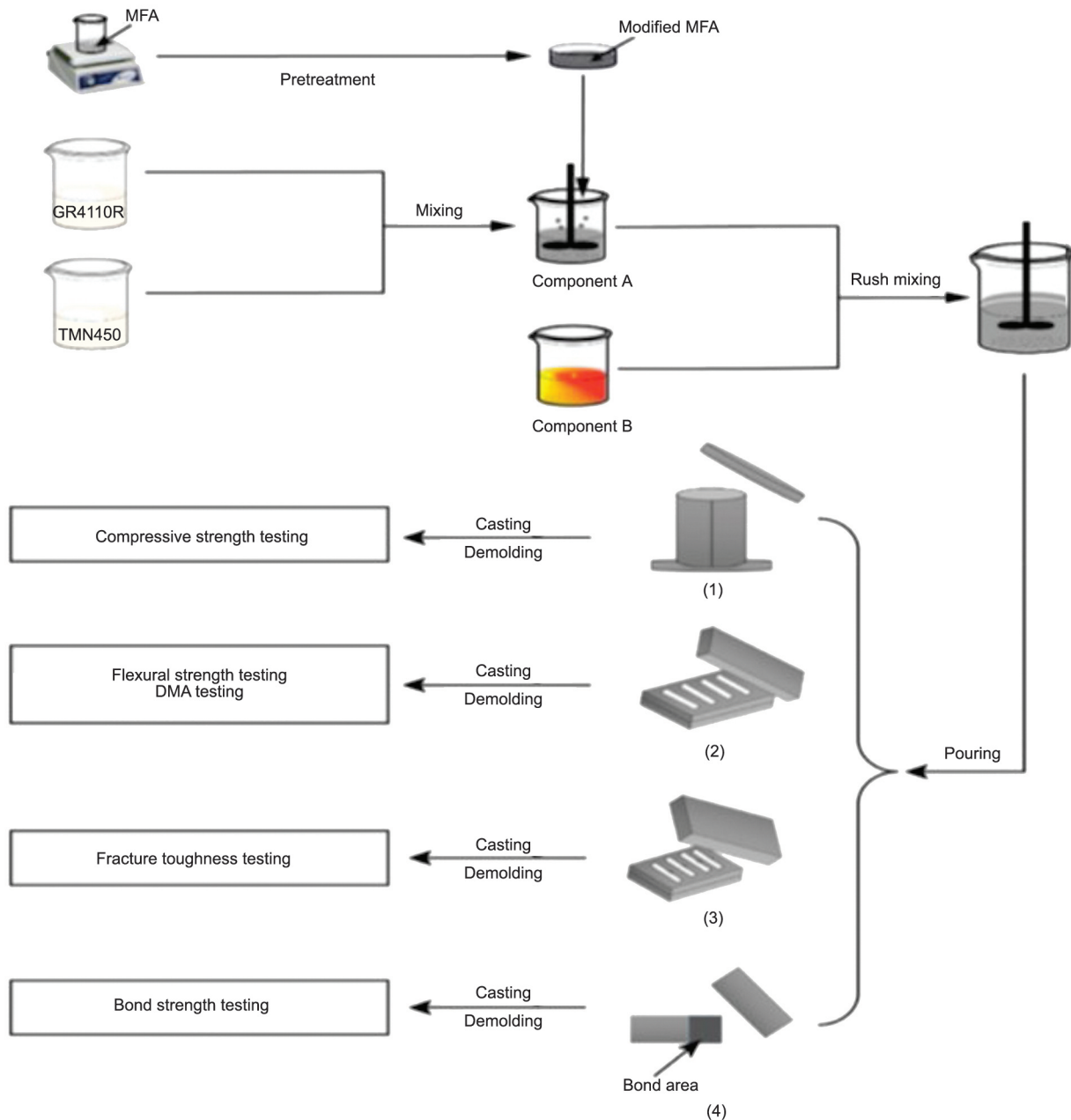


Figure 10. An illustration of the preparation method for mesoscopic fly ash/polyurethane composites [44] (MDPI Open access).

properties, *i.e.*, mechanical, flame retardancy and dielectric properties at lower content of the fly ash [42, 48]. Nguyen *et al.* [45] fabricated a hybrid composites consisting of the fly ash and nano clay nanoparticles incorporated into the epoxy matrix. In order to find the best possible combinations between the two nanoparticles, various contents of fly ash (*viz.*, 10, 20, 30, 40 and 50%) and nano clay (*i.e.*, 1, 3, and 5%) were fabricated by dispersing the fillers into the epoxy matrix and stirring the mixture for 8 hours at 3000 rpm. Furthermore, the nanoclays were sonicated for 6 hours in order to break their bundles and improve its dispersion. It was reported that the optimum

ratio of the fly ash: nano clay was 40:3, which was evident by a better dispersion of both fillers within the epoxy matrix at this ratio. The same polymer matrix, in the form of epoxy was incorporated with both fly ash and carbon nanotubes in order to fabricate an eco-friendly composite with an enhanced flame retardancy and mechanical properties [45]. Various concentrations of fly ash (*viz.*, 30, 40 and 50 wt%) together with carbon nanotubes (CNTs) at different contents (0.03, 0.04, and 0.05 wt%) were dispersed into the epoxy matrix for 8 hours at 3000 rpm. Similar to the previous study on clays, the carbon nanotubes in the form of multi-walled carbon nanotubes

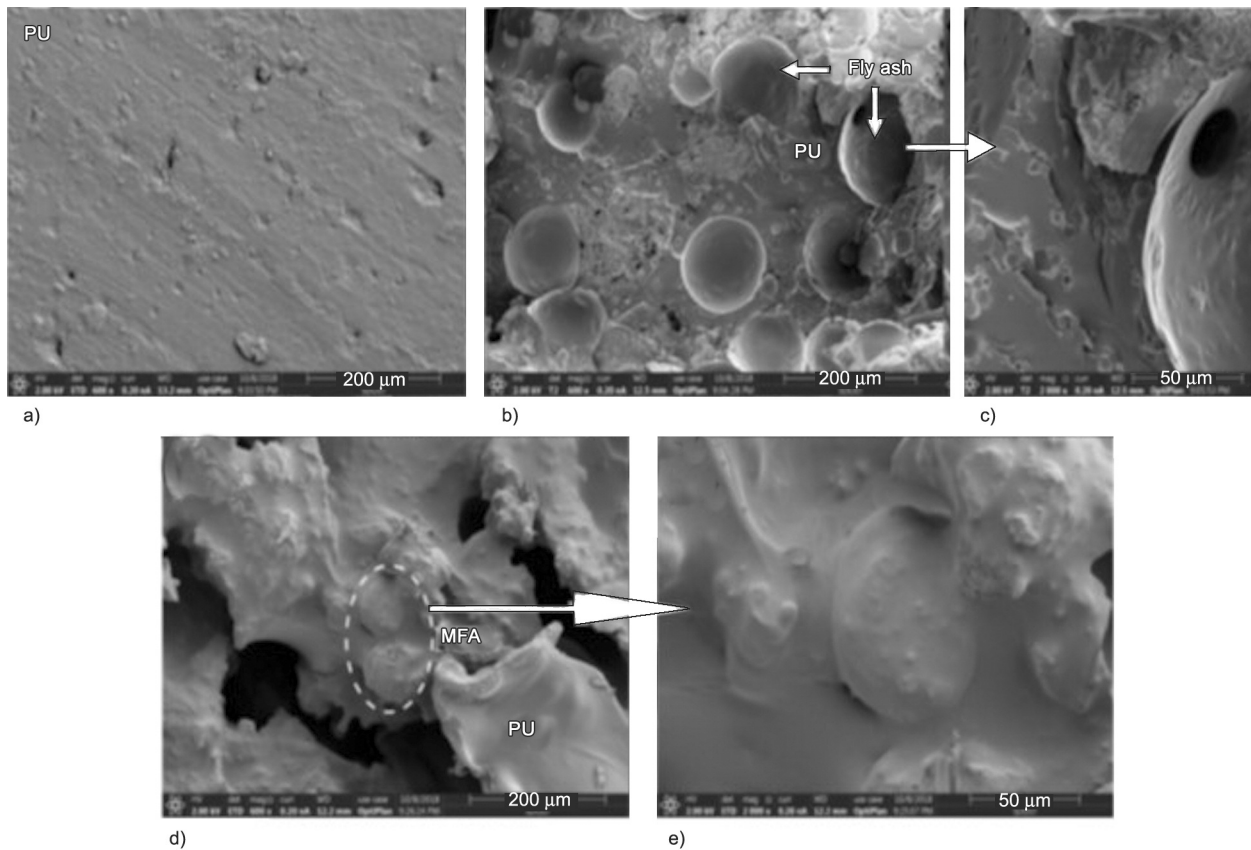


Figure 11. SEM images of: (a) neat PU, (b) and (c) PU-reinforced with MFA, (d) and (e) PU/MFA-2.5 wt% fractured surfaces [44] (MDPI Open access).

(MWCNTs) were dispersed by an ultrasonication for a period of 6 hours at a temperature of 65 °C. The morphology of the mechanically stirred composites revealed better compatibility of the two nanoparticles (MWCNTs-fly ash) into the epoxy matrix with no visible clusters or agglomerates. Table 1 summarizes different studies based on the preparation and morphology of fly ash and its synergy with other nanoparticles.

5.2. Fly ash/fiber/polymer hybrid composites

Researchers [49–53] have reported on the hybrid composites based on the fibers/fly-ash/polymer composites in order to enhance the properties of the resultant hybrid composite. Sathishkumar *et al.* [49] fabricated a jute fiber/lignite fly ash /epoxy hybrid composite by hand layup process followed by compression molding. The hybrid composites were prepared with various fly ash contents (0.5, 1.0, 1.5, 2.0 and 2.5 wt%) while the content of the jute fiber was kept constant at 10 wt%. The jute fiber was modified by utilizing acetic and sodium hydroxide which happens to have resulted in roughness in the surface of the composites which enhanced the bonding of jute

fiber with both fly ash and polymer matrix. It was reported that the small size of the lignite fly ash (LFA) allowed it to easily penetrate the polymer network and as a result filled up the voids [49]. Biswas *et al.* [50] fabricated a hybrid composite system based on alkali treated fibers (*viz.*, jute and sisal)/silanized fly ash incorporated in polyester matrix by compression molding. There was a better dispersion as well as compatibility of the silane treated FA and treated fibers with the polyester matrix when compared with untreated composites [50]. Maurya *et al.* [53] produced a hybrid composite system consisting of mechano-chemically activated fly-ash/sisal fiber/PP. The polymer matrix was made of 85 wt% PP, 10 wt% of SEBS and 5 wt% of SEBS-*g*-MA, which was termed the base matrix. In order to enhance its dispersion and reduce agglomeration, fly ash was modified with 2, 4, and 6 wt% modifier in the form of cetyltrimethylammonium bromide (CTAB). It was further noted that the activation of the fly ash was undertaken by using planetary ball milling. The hybrid composites were fabricated by Rheomix and extruded at the temperature of 190 °C at the speed of 50 rpm. The SEM images of the fracture tensile specimen of

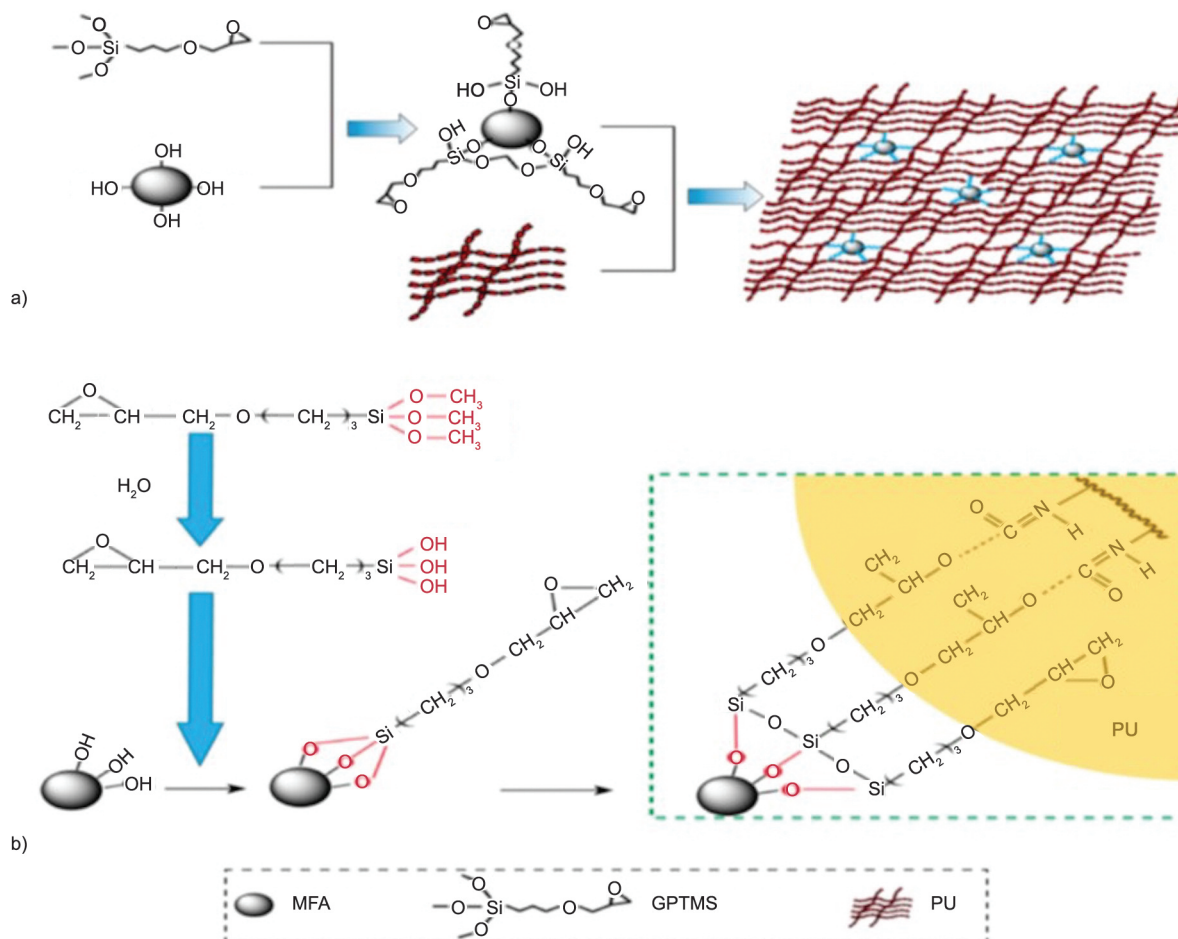


Figure 12. Possible mechanism for chemical crosslinking of PU/MFA in the presence of silane coupling agent a) mechanism of the PU/MFA synthesis, b) the mechanism by which modified MFA is crosslinked by 3-glycidypropylmethoxysilane (GPTMS) and PU matrix [44] (MDPI Open access).

the hybrid composite showed that the sisal fibers as well as the FA were embedded in the matrix, with the fibers well covered and wetted into the base matrix [53]. Besides the utilization of natural fibers as second fillers for fabrication of polymer hybrid composites, other authors [54] have reported also on the preparation of glass fibers for production of such hybrid system. Raghavendra *et al.* [54] used the hand lay-up method for preparation of the jute/glass woven fabric/epoxy hybrid composites reinforced with fly ash. The addition of glass fiber alone into the epoxy matrix revealed a fiber bending, while minor bending was observed in the presence of jute in the epoxy matrix. The incorporation of fly ash in both systems resulted in a decrease in bending in both systems.

6. Mechanical properties

6.1. Fly ash/polymer composites and its nanoparticles hybrid composites

The employment of fly ash in polymer matrices has been suggested to improve the mechanical and

tribological properties of polymer materials [60]. Same as the morphology, the (i) preparation method, (ii) concentration and particle size of the filler (iii) surface modification, (iv) viscosity of fly ash composite, and (v) synergy with other fillers and/or fibres have a direct impact on the mechanical properties of the final composite. Sim *et al.* [34] reported on the mechanical properties of fly ash/epoxy composites. The tensile strength of the composite improved with the addition of fly ash into the polymer matrix. However, 30% of fly ash was found to be an optimum concentration whereby enhanced mechanical properties (*viz.*, tensile strength) were obtained (Figure 13). In addition, larger fly ash particles (>50 μm) resulted in hollow pores being present in the matrix, significantly weakening the mechanical properties of the composite [34]. Kumar *et al.* [61] studied the effect of fly ash particle size(s) and content on the mechanical properties of polyester-based composites. In the study, varying sizes of class F fly ash (75 and 150 μm) and the filler content ranging

Table 1. Selective studies on the preparation of fly ash/polymer composites and its hybrid composites.

Fly ash/polymer system(s)	Preparation method	Modification(s)	Summary of results	References
Fly ash/nylon 6	Twin-screw extruder		<ul style="list-style-type: none"> SEM images showed that there was less encapsulation of the fly ash by polymer at 30 wt%. 	[55]
Fly ash/polypropylene	Internal mixer at 200 °C at 35 rpm	Three silane coupling agents with different functional groups <i>i.e.</i> , vinyl, amine, and vinyl-benzylamine.	<ul style="list-style-type: none"> SEM images showed that untreated fly ash as well as specimens treated with vinyl-benzylamine exhibited poor adhesion behavior. Whereas fly ash treated with amine and vinyl exhibited better adhesion and effective interaction between the filler and the matrix. 	[56]
Fly ash/epoxy	Thermal and microwave curing	<i>N</i> -2(aminoethyl)-3-aminopropyltrimethoxysilane (KBM603)	<ul style="list-style-type: none"> SEM analysis revealed that samples cured using microwave curing were coarse and ductile. Samples cured by conventional cure were smoother in texture and more uniform. 	[57]
Recycled poly(vinyl chloride) resin (<i>r</i> -PVC)/fly ash	Melt mixing followed by compression molding.		<ul style="list-style-type: none"> SEM showed dewetting of fly ash particles with <i>r</i>-PVC polymer matrix at 10 wt%. Stronger adhesion and uniformity at 20 wt% fly ash with <i>r</i>-PVC. 40–50 wt% fly ash resulted in agglomeration of fly ash particles in the <i>r</i>-PVC matrix. 	[58]
Fly ash/recycled poly(ethylene terephthalate)	Samples were Melt blended using a twin-screw extruder		<ul style="list-style-type: none"> SEM images revealed uniform dispersion of filler in the polymer matrix. Smaller filler particles (below 43 μm) demonstrated an enhanced interaction with PET matrix. 20 wt% concentration of fly ash resulted in agglomeration and poor filler/matrix adhesion 	[59]
Fly ash cenospheres/multi-walled carbon nanotubes/epoxy	FA and MWCNTs were added into epoxy matrix solution and mixed for 15 min.	Silane coupling agent (KH550)	<ul style="list-style-type: none"> Flexural fracture of 20 wt% FAC-0.5 wt% MWCNTs/EP displayed the agglomeration of fillers into the matrix. 	[38]
High density polyethylene/ultrafine fly ash/MWCNT	Melt mixing using Brabender followed by compression moulding.	<ul style="list-style-type: none"> Acid functionalized multiwalled carbon nanotubes (MWCNTs). Ultrafine fly ash (UFFA) was modified with aminosilane coupling agent. Epoxy functionalized HDPE 	<ul style="list-style-type: none"> TEM revealed that at higher loading of MWCNTs (<i>viz.</i> 0.4%) in combination with UFFA, there was a clustering of particles and uniform dispersion in the matrix. 	[39]

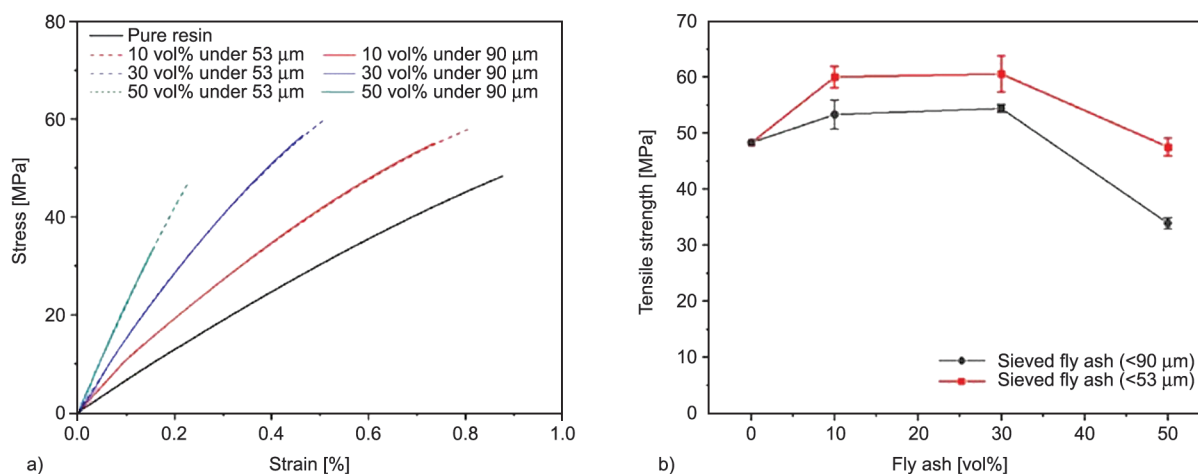


Figure 13. (a) Stress-strain curves of fly ash/epoxy composites reinforced with less than 90, and 53 μm fly ash particles and (b) tensile strength graphs of the fly ash/epoxy composites [34] (MDPI Open access).

from 10–30 wt% was investigated. The authors employed a basic hand lay-up technique in order to prepare the samples. The results suggested that an increase in filler content led to a reduction in tensile strength irrespective of the fly ash particles' size. The decrease in tensile strength with increasing in filler content was due to weak interfacial adhesion between the two phases (*i.e.*, filler and polymer matrix). However, the flexural strength increased with an increase in filler content with the smaller particle size fly ash (*viz.* 75 μm) displaying a slight increase when compared with larger particle size (*i.e.*, 150 μm) with 30 wt% of fly ash. The compressive strength increased with increasing in filler content with the 30 wt% of fly ash (75 μm) displaying a maximum value of 91.8 MPa when compared with 72 MPa of neat polyester matrix [61]. Alghamdi [33] reported on the effect of fly ash particle size on the recyclability of fly ash/HDPE composites by comparing the mechanical properties of the three-particle incorporated into the HDPE matrix. The fly ash samples collected had the following sizes: sample 1 (50–90 μm), sample 2 (90–150 μm) and sample 3 (150–250 μm). The smaller particle size fly ash (50–90 μm) based HDPE composites displayed a higher Young's modulus than the neat HDPE, fly ash (90–150 μm)/HDPE and fly ash (150–250 μm)/HDPE composites. However, both the large fly ash particles-based composites had a higher Young's modulus when compared with neat HDPE matrix. This behaviour was ascribed to a uniform dispersion of fly ash within the polymer matrix with limited agglomerates. The authors further compared the mechanical properties of the recycled system with the unrecycled HDPE/fly ash system. Similarly, with the unrecycled fly ash/HDPE composites, the recycled fly ash/HDPE system with lower particle size (90–150 μm) returned higher mechanical properties (Young's modulus and tensile strength at yield) when compared with large fly ash particles (90–150 μm and 150–250 μm)/HDPE based composites. This behaviour was attributed to a weak filler/polymer interfacial interaction in the presence of large particle sizes [33]. Surface treatment is continuously employed when fabricating a filler/polymer composites with the aim of enhancing interaction between the two phases, in order to have a positive effect on the morphology and mechanical properties [36]. The main aim of surface treatment of fly ash with silane and/or surfactants is to introduce functional groups on the surface

of the inorganic filler, as a result it enhances its interaction with the polymer matrices. Dharmalingam *et al.* [62] treated fly ash with silane coupling agent and surfactant in the form of sodium lauryl sulfate (SLS). Epoxy matrix was modified with the amine consisting of the liquid silicone (ACS). It was reported that the flexural strength decreased with the increasing in fly ash content *i.e.*, from 10 to 40%, irrespective of the modification method employed. Despite the fact that the addition of fly ash reduced the flexural strength, the silane treated samples displayed higher flexural strength when compared with SLS. It was further reported that the highest flexural modulus was attained for 10% fly ash-based composites (*viz.*, 20, 30 and 40%). The decrease in flexural modulus at higher contents was attributed to a poor interaction between the fly ash and polymer matrix [62]. The effect of two types of silane in the form of vinyl silane as well as aminosilane on the fly ash reinforced waste poly(ethylene terephthalate) (WPET) was also reported [63]. There was an enhancement in mechanical properties (*viz.*, tensile strength) for both silane functionalization fly ash, with the optimum concentration of aminosilane treated system being 1%. The vinyl silane treated samples displayed different trends. At 0.5% of the coupling agent there was an increase in tensile strength, however above it there was not much of improvement in the tensile strength. It was found that the impact strength increased in the presence silane coupling agents. It was further emphasized that 1% of amino silane was the optimum concentration to obtain the highest impact strength, which was 280% enhancement when compared with untreated composites [63]. Similar observation was reported by Gohatre *et al.* [47] who investigated the effect of silane treated fly ash reinforced recycled poly(vinyl chloride) composites. The authors showed that the silane treatment at higher concentration (*viz.*, 5%) had a negative impact on the mechanical properties, with the lower silane content (*i.e.*, 1%) revealing higher tensile strength. Besides the utilization of the silanization as a modifier, other authors [64] employed stearic acid for surface modification of fly ash. There was an enhancement in the mechanical properties (see Figure 14) of the epoxy reinforced with stearic acid treated fly ash. Generally, the modification of fly ash improves the overall mechanical properties. Such improvements in mechanical properties results from strong interfacial adhesion between the polymer matrix and fly ash, which enable

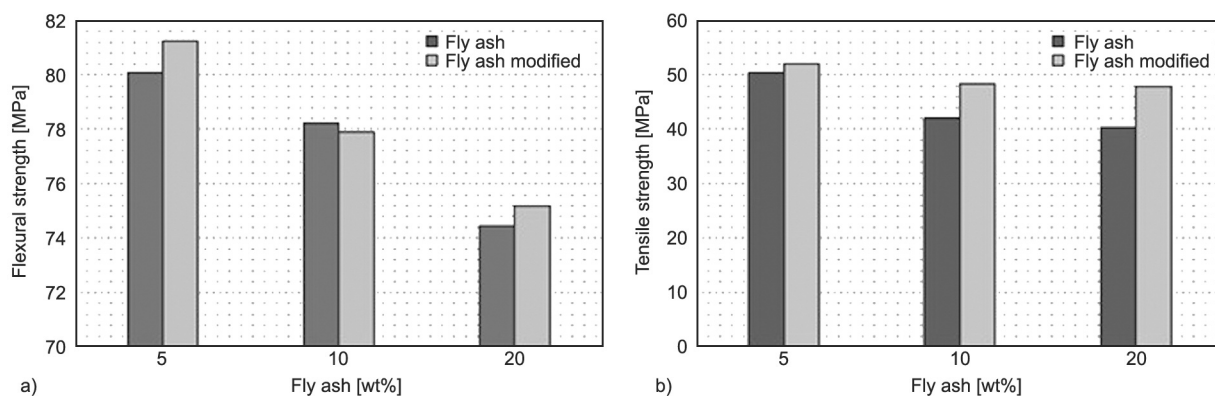


Figure 14. Mechanical properties of unmodified and modified fly ash/epoxy composites [64]. (a) Flexural strength [MPa] and (b) tensile strength [MPa] of unmodified and modified fly ash/epoxy composites (Hindawi Open access).

and facilitates stress transfer between the two phases. It is worth mentioning that there is optimal concentration of the coupling agent in order to achieve preferable mechanical properties.

Mechanical properties of fly ash with other nanoparticles were reported by various researchers, and it became apparent that the synergy between the two nanoparticles showed higher mechanical properties when compared single fly ash reinforced polymer composites. For example, Li *et al.* [65] reported that hybrid composites (GO-FAC/EP) exhibited higher tensile strength values when compared with composites reinforced with GO alone. The optimum filler content in both the GO and GO-FAC hybrid systems was ~0.5 wt% to achieve superior mechanical performance [65]. Chaturvedi *et al.* [66] reinforced epoxy with both the carbon nanotubes and fly ash through ball milling and compression molding method. Carbon nanotubes and fly ash were mixed at various concentrations *i.e.*, 5, 10, 15, and 20 vol%. Flexural strength was observed to increase with the addition of the carbon nanotubes irrespective of the content when compared with neat polymer, which was attributed to a better dispersion within the epoxy matrix. However, it was reported that the optimum concentration was 5 vol%, and above this the flexural strength was found to decline [66]. Tiwari *et al.* [35] reported that the addition of calcium carbonate into the fly ash reinforced epoxy matrix enhanced the overall mechanical properties. The influence of CaCO₃ on the mechanical properties of the fly ash/epoxy was proven by an enhancement in the tensile strength, with 5 wt% resulting in 52.41% improvement in tensile strength. The impact strength and flexural strength were enhanced by 43.24% as well as 42.36% with 3 wt% of CaCO₃, respectively when compared with fly ash/epoxy composites [35].

6.2. Fly ash/fibers/polymer hybrid composites

Several authors [40, 41, 49, 67–69] have reported on the mechanical properties of the fly ash/fiber reinforced polymer composites. The reason for incorporating fly ash into fiber(s) based polymer composites was to enhance the mechanical properties of the resultant hybrid composites. It is well-known that the incorporation of the fly ash/fiber synergy as reinforcements for plastics is an attractive method for development of materials for advanced applications. Sathishkumar *et al.* [40] reported on the mechanical properties of the sisal fiber/lignite fly ash/epoxy hybrid composites fabricated by hand layup process. The fabricated epoxy hybrid composite consisted of a constant 20 wt% of sisal fiber (SF) together with lignite fly ash (LFA), with the content of LFA varying between 0 to 10 wt%. The incorporation of 2.5, 5.0, 7.5 and 10 wt% of the fly ash into the epoxy/sisal fiber composite was found to enhance the tensile strength by 29.54, 29.88, 30.01, and 31.09 MPa, correspondingly when compared with neat epoxy (*viz.* 13.01 MPa) and EP/SF 80/20 (*i.e.*, 26.28). This behaviour was attributed to a uniform distribution of the fly ash within the epoxy matrix, as a result enhanced the mechanical properties. According to the SEM, it was reported that the spherical fly ash particles were found within the cracks and voids in the hybrid composites, which enhanced the mechanical properties. Similar results were reported by Sathishkumar *et al.* [49], whereby lignite fly ash was incorporated into the epoxy/jute fiber composites. In this study, mechanical strength which includes tensile strength, compressive strength, impact energy and flexural strength were found to improve with the addition of the 2 wt% fly ash content in the epoxy matrix. It became apparent that the addition of the fly ash beyond 2 wt% in other components of the mechanical

properties (*viz.*, compressive strength, barcol hardness and impact strength) revealed no significant influence. Jayamani *et al.* [67] reported on the mechanical properties fly ash/sugarcane fiber reinforced epoxy matrix. The sugarcane fiber was varied between 0 to 10 wt%, with the fly ash incorporated with 2 wt% into the epoxy/sugarcane fiber system. The optimum content of fly ash and sugarcane fiber was reported to be 2 and 4 wt%, respectively. This was proved by high mechanical properties at this ratio of the synergy, with samples at 4 wt% sugarcane fiber and 2 wt% fly ash displaying the highest tensile strength. It was noted that the fly ash filled voids in the composites with minimum agglomerates. The addition sugarcane fibers at higher content *i.e.*, 6, 8, and 10 wt%, showed a reduction in mechanical properties which was ascribed to an inappropriate wetting of the fiber. It was emphasized that the reduction may also be due to a non-uniform distribution of the fly ash at this fiber contents, which may have resulted voids, and dry spots, which hindered an improvement in mechanical properties [67]. The effect of fiber aspect ratio together with fly ash on the compressive properties of epoxy was investigated in the literature [68]. Generally, there was a reduction in the strengths at higher fiber loading (*viz.*, 15 to 25 vol%) in the absence of fly ash. The behaviour was ascribed to the bunching of glass fibers together with improper wetting between the fibers and epoxy matrix. Therefore, the addition of fly ash into the fiber/epoxy composites resulted in better strength at higher range of the fibers content. Furthermore, the addition of fly ash was also found to have a positive impact in the modulus with a noticeable enhancement in the modulus. Generally, the improvement and/or reduction in the mechanical properties (compressive strength and modulus) was explained by few factors *i.e.*, bunching of fibers took place in the absence of fly ash (*viz.*, lower mechanical properties), and in the presence of smaller fly ash particles there was a better wettability which gave rise to enhanced properties initial, with debonding observed in the presence of larger fly ash particles which may account for reduction in mechanical properties [68]. Kavya *et al.* [69] investigated the impact of fly ash and TiC nanoparticles on the mechanical properties of the coir fiber/ epoxy-based hybrid composites. The tensile strength and modulus of epoxy + 5 wt% coir fibers + 5 wt% fly ash (CFE), epoxy + 5 wt% coir fibers + 5 wt% TiC (CTE), and epoxy + 3 wt% coir + 3 wt% TiC + 4 wt% fly ash

(CFTE) enhanced with the addition TiC nanoparticles, fly and a combination of TiC + fly ash synergy. It is well-known that the reinforcement of inorganic ceramic fillers with higher modulus than polymers have the ability to enhance both modulus and tensile strength. Furthermore, the addition of either filler or a combination of fillers in epoxy enhanced both the flexural modulus and strength, with a reduction in strain to break. Besides the enhancement in flexural characteristics, the CFTE system showed lower values when compared with CTE system. The improvement in flexural parameters was ascribed to a stronger bond between the epoxy matrix and the fillers. Furthermore, a good distribution of fillers in the polymer matrix also played a key role in enhancement of the flexural properties [69]. Table 2 shows the fly ash content used to achieve optimum mechanical and tribological properties.

7. Applications of coal fly ash/polymer composites

Due to the increasing worldwide environmental concern on coal fly ash waste accumulation, numerous efforts have been made to find new ways of using it for various applications [83]. Currently, the production rate of coal fly ash waste stands at five million tons per annum. Out of these five million tons, 16% is recycled whilst the remaining 84% is buried in landfills and lagoons [83]. This is not good for the surrounding population and ecosystem. As a result, over the past few decades, researchers have been effortlessly trying to find new applications for coal fly ash waste. The most common use of coal fly ash to date is in building materials as an additive in cement and concrete [83–86]. Nowadays, coal fly ash is also used in adsorbents for the removal of heavy metals as well as organic and inorganic compounds from aqueous media [87–90]. For example, Darmayanti *et al.* [91] prepared a fly ash based adsorbent for the removal of copper(II) ions from an aqueous solution. Results showed that the adsorption of copper(II) ions by the fly ash-based adsorbents improved with increasing adsorbent dosage, even when two kinds of fly ash (fly ash 1 and fly ash 2) were used. According to their explanation, the improvement in adsorption was due to an increase in surface area and adsorption sites with increasing fly ash content. Malek *et al.* [92] prepared a new magnetic Schiff's base-chitosan-glyoxal/fly ash/Fe₃O₄ (Chi-Gly/FA/Fe₃O₄) biocomposite for the removal of an anionic azo dye. The biocomposite was

Table 2. A summary of the mechanical and tribological properties of fly ash/polymer composites.

Fly ash/polymer system	Preparation method	Fly ash content	Achieved mechanical properties	References
Fly ash/polymer composite	casting	10 vol% (paraffin oil modified fly ash particles)	Modulus = 58.8%, compressive strength = 55%	[70]
Fly ash/epoxy composite	casting	10 vol% (silane modified)	Modulus = 100%, compressive strength = 43.3%	[70]
Fly ash/epoxy composite	casting	6.5 vol%	Toughness = 56.2%, tensile strength = 8.3%	[71]
Fly ash/aramid fiber/phenolic hybrid composite	Sequential mixing then curing and post curing	70 vol%	Coefficient of friction = 0.12, wear depth = 0.25 mm	[72]
Fiber glass/epoxy/fly ash hybrid composite	Hand lay up	10 wt%	Impact strength = -26.4, tensile stress = -24%	[73]
Fly ash/E-glass fabric/polyester hybrid composites	Hand lay up and vacuum bagging techniques	5 wt%	Impact strength = 186.9 kJ/m ² , tensile strength = 275 MPa, flexural strength = ~369 MPa, hardness = 84.9, roughness = 0.33 μm	[74]
Fly ash/carbon fiber/phenolic hybrid composite	Casting on a glass mold	30% fly ash and 4 laminates of carbon fiber	Flexural strength = 91.42 N/mm	[75]
Fly ash/polyester composite	Curing of liquid polyester resin consisting of fly ash cenospheres	4.9 vol%	Compressive yield strength = 12%	[76]
Fly ash/polyester composite	Curing of liquid polyester resin consisting of fly ash cenospheres	29.5 vol%	Compressive yield strength = -19%	[76]
Fly ash/vinyl ester composite	Sequential mixing then casting in aluminium molds then curing and post curing	60 vol%	Flexural strength = -73%, flexural modulus = 47%, coefficient of thermal expansion = - 67%	[77]
Fly ash/vinyl ester composite	Sequential mixing then casting in aluminium molds then curing and post curing	40 vol%	Compressive strength = -25%, compressive modulus = 45%	[77]
Functionally graded fly ash cenosphere/epoxy resin syntactic foams	Mixing then casting in aluminium molds then curing and post curing	16 wt%	Compressive modulus = 68%	[78]
Fly ash/epoxy cast slabs	Casting then curing and post curing	10 vol%	Modulus = 23.5%	[79]
Fly ash/epoxy composites	Compression molding	10 wt%	Flexural strength = -12.37%, tensile strength = -38%	[80]
Fly ash/geopolymer composite	Solution mixing	48.2 wt%	Compressive strength = 63%	[81]
Fly ash/epoxy composite	Film casting	20 wt%	Tensile strength = 33.3%	[82]

prepared by using a direct combination of magnetic chitosan and fly ash powder particles followed by a crosslinking reaction of glyoxal with Schiff's base formation. The biocomposite was used to specifically remove the reactive orange 16 (RO16) dye. The surface morphology of the Chi-Gly/FA/Fe₃O₄ biocomposite before RO16 adsorption was rough, porous, consisted of crevices and cracks. The surface morphology of the Chi-Gly/FA/Fe₃O₄ biocomposite after RO16 dye adsorption showed void of crevices, indicating that the RO16 dye molecules were successfully adsorbed onto the Chi-Gly/FA/Fe₃O₄ biocomposite. EDX analysis of the biocomposite after RO16 dye adsorption confirmed the presence of the S element which belonged to the RO16 dye. This

was further proof that the RO16 dye was adsorbed by the Chi-Gly/FA/Fe₃O₄ biocomposite [92].

Fly ash is also used in other diverse applications such as in zeolite synthesis [93] and in carbon dioxide adsorbents [94, 95]. Amongst all the uses of fly ash, its use as a filler in polymer composites is gaining much more attention. Fly ash is used to improve the thermal and mechanical properties of polymers. Furthermore, due to its flame retardant properties, fly ash has also been used to improve the flame retardant properties of polymers. Flame retardant fillers like fly ash are essential for use in applications such as construction, electrical and electronic industries as well as in transportation [96]. The fly ash flame-retardant filler is composed of ceramics such as silica, alumina

and calcium oxide and is therefore considered to be inert to fire [48, 52, 97–99]. Furthermore, fly ash does not emit any toxic gases and smoke and its use serves as a potential way of fostering economic savings by reusing waste materials [100, 101]. For instance, fly ash has been used by several researchers

Table 3. Summary of fly ash/polymer properties and their applications.

Fly ash/polymer composite	Preparation method	Achieved properties	Applications	References
Fly ash (FA)/recycled polypropylene composites	Twin-screw extrusion	<ul style="list-style-type: none"> Composites filled with fly ash exhibited a higher ductility compared with composites filled talc. Composites with a talc and fly ash hybrid filler system exhibited a higher ductility and a lower impact strength when compared with talc filled composites. 	Automotive applications	[107]
Coal fly ash derived mesoporous silica/polysulfone mixed matrix membranes	Solution mixing and solution casting	<ul style="list-style-type: none"> Permeability tests confirmed that the membranes can be used to remove CO₂ from CH₄. This was due to unnoticeable differences between real and ideal selectivity. Membranes exhibited high resistance to CO₂ plasticization. This was due to a decrease in permeability even at a high feed pressure (up to 16 bar). 	CO ₂ /CH ₄ separation	[108]
Cationic fly ash/polyepichlorohydrin-dimethylamine adsorbent	Immobilization of poly-epichlorohydrin-dimethylamine (PED) onto raw fly ash	<ul style="list-style-type: none"> Immobilization of PED changed the zeta potential of fly ash from negative to positive within a pH range of 3 to 11. The crystal structure of the fly ash was not altered in the process. Static adsorption results showed that the dye was adsorbed spontaneously, and that the adsorption process was endothermic. The cationic fly ash dye adsorption capability was 1.5 times higher than that of activated commercial carbon. The synthesized cationic fly ash adsorbent can be reused repeatedly. To avoid secondary pollution, the disabled cationic fly ash adsorbent can be used in polymer concretes as a functional filler. 	Dye wastewater treatment	[109]
Carbonated fly ash/silicon rubber (SR) composites	Mixing of fly ash and silicon rubber using a twin-roll mill followed by hot press molding.	<ul style="list-style-type: none"> Fire resistance of the composites was studied using the gas torch method. The gas torch method confirmed that the carbonation of fly ash increased the penetration time of the composites by 11%. Penetration time of carbonated fly ash /silicon rubber composites was 2–3 times higher than that of composites filled with other commercially available fillers. 	Fire-proofing applications	[83]
Fly ash and aramid fiber reinforced phenolic hybrid polymer matrix composites	Samples were prepared by following a predefined sequential mixing schedule followed by curing and then compression molding and then post curing in a standard oven.	<ul style="list-style-type: none"> Friction-fade behaviour followed a consistent decrease with decreasing fly ash content. The friction fluctuations ($\mu_{\max} - \mu_{\min}$) decreased with increasing fly ash content. A higher friction-recovery response was observed at a fly ash content of 80 wt%. Material integrity and temperature increase of the disc determined the wear behaviour. Friction braking applications 		[72]
Sulfonated poly(ether ether ketone) (SPEEK)/single walled carbon nanotubes (SWCNTs)/fly ash polymer electrolyte nanocomposite membranes	Solution casting	<ul style="list-style-type: none"> SPEEK/SWCNTs/fly ash membranes exhibited proton conductivity values of up to 0.02 S·cm⁻¹ at 30 °C and 0.034 S·cm⁻¹ at 90 °C whilst pristine SPEEK membranes exhibited proton conductivity values of up to 0.019 S·cm⁻¹ at 30 °C and 0.031 S·cm⁻¹ at 90 °C. SPEEK/SWCNTs/fly ash membranes also exhibited excellent thermal and mechanical stability when compared to pristine SPEEK membranes. 	Electrolyte membranes in fuel cell applications	[110]

Table 3. Continued.

Fly ash/polymer composite	Preparation method	Achieved properties	Applications	References
Magnetic chitosan-polyvinyl alcohol (m-Cs-PVA)/fly ash (FA) biocomposite blend	Incorporation of fly ash microparticles into a magnetic chitosan-polyvinyl alcohol polymeric matrix	<ul style="list-style-type: none"> – The highest removal of RO16 dye was found to be 90.3% at a m-Cs-PVA/FA dosage of 0.06 g, solution pH of 4, working temperature of 30 °C and contact time of 17.5 min. 	Removing reactive orange 16 (RO16) textile dye from aquatic environments	[111]
Crosslinked sulfonated poly (vinyl alcohol) (SPVA)/ fly ash (FA) composite membranes	Solution casting	<ul style="list-style-type: none"> – SPVA/FA composite membranes consisting of 20 wt% fly ash exhibited an ionic conductivity of 0.016 S·cm⁻¹ whilst pristine SPVA membrane exhibited an ionic conductivity of 0.008 S·cm⁻¹. 	Polymer electrolyte membrane for fuel cell applications	[112]
Fly ash/ <i>in situ</i> reduced graphene oxide (rGO) geopolymeric composites	Solution mixing of fly ash and <i>in situ</i> reduced graphene oxide	<ul style="list-style-type: none"> – rGO increased the electrical conductivity of fly ash/rGO geopolymeric composites from 0.77 S·cm⁻¹ at 0.00 wt% to 2.38 S·cm⁻¹ at 0.35 wt%. – rGO also increased the gauge factor of the geopolymeric composites by 112 and 103% for samples subjected to tension and compression. 	Self-sensing structural materials for civil engineering applications	[113]
Fly ash/octadecane shape-stabilized composite phase change materials (PCMs)	Preparation of fly ash/ <i>n</i> -octadecane composites using the vacuum impregnation process followed by doping the composites with carbon nanotubes, carbon nanofibers and graphene for enhanced thermal conductivity	<ul style="list-style-type: none"> – Differential scanning calorimetry results showed that the shape-stabilized composite phase change materials exhibited acceptable phase change temperatures (25.01–26.43 °C) and reasonable latent heat storage capacities (60.50–64.47 J/g) for solar thermal energy storage operations in building applications. – The thermal conductivities of the phase change materials were enhanced by 187.09, 135.48 and 203.22% with the addition of 8 wt% of carbon nanotubes, carbon nanofibers and graphene. 	Thermal energy storage in buildings	[114]
Ultra-lightweight fly ash-based cement (ULFC) foams consisting of ethylene-vinyl acetate (EVA) emulsion and waste-derived calcium silicate hydrate (C–S–H) seeds	Introduction of EVA emulsion into ULFC slurry and addition of A-3 lab-made hardening acceleration and waste-derived C–S–H seeds.	<ul style="list-style-type: none"> – The dry density, compressive strength and heat conductivity of ULFC after 28 days was 154.7 kg/m³, 0.57 MPa and 0.0514 W/(m·K). – The EVA film solidified at the gas-solid interface and well-interwined with hardened cement stone in order to improve the compressive strength when the specimens were cured at a relative humidity of 60–65%. – The foam stability of ULFC was improved by enhanced bubble confinement force with increasing the EVA content. 	Ultra-lightweight cement foams in construction applications	[115]

to improve the flame retardant properties of polymers such as polycarbonate or polyurethane [97, 102], epoxy resins [98, 99], polybutadiene rubber [103, 104], ethylene-propylene-diene rubber [105] and polymer foams such as styrene and urethane foams [99, 106]. Table 3 shows more applications and properties of fly ash-based polymer composites.

8. Conclusions

Generally, the global energy resource is currently commanded by coal. Coal is employed in many countries as the primary fuel, contributing 36% of the overall fuel utilization in the production of global electricity. During the combustion of coal for production of electricity, a byproduct in the form of fly

ash is produced, which is regarded as a waste material. More research works have been done on the utilization of fly ash reinforced polymer matrices for advanced applications. Fly ash reinforced polymer was found to improve various properties of polymer matrices. However, different factors were found to affect the properties of fly ash/polymer composites such as functionalization of the fly ash, its synergy with other fillers, and the particle size of the fly ash. Generally, it can be concluded that the treated fly ash polymer composites showed better properties than the untreated polymer composites. Furthermore, the synergy of fly ash with other fillers was found to enhance the properties of the composites more than fly ash reinforced polymer composites alone. The smaller

particle sized fly ash fillers were more dominant than larger particles in terms of improving the properties of the overall composites. Based on the improvements in the polymer composites with the incorporation of fly ash, the fly ash polymer composites have been utilized in various applications such as construction, self-sensing structural materials for civil engineering, automotive, fuel cell, dye wastewater treatment and friction braking applications. It is realized from the literature that fly ash has been utilized as a reinforcing filler for polymers such nylon, polypropylene, epoxy, polysulfone etc., with limited utilization of the biopolymers. There is a need for fabrication of fly ash with biopolymers, since the biopolymers are compatible with the environment.

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