Chapter 1

Introduction and Literature Review

1.1. Introduction

Power is indispensable to the human society in this modern world and electrical energy is one of the most important sources of power essential for the industrial and social growth as well as economic development of a country. In India, the demand for electric power has been increasing rapidly and steadily with the population growth and rapid industrialization. Although there are other sources of power such as hydro-electric, solar, wind, nuclear, natural oil and gas, power from thermal energy plays a vital role in the Country's bulk power generation and consumption. Among the thermal power stations, more than 90% are based on coal as the resource. This is because; the coal is abundantly available in the country as a cheap energy resource than other fossil fuel resources. Also the power plants based on coal have a longer working life[1]. Thus coal will dominate as an important source of energy for power generation for many more years to come.

The combustion of pulverized coal in thermal power stations produces different types of Coal Combustion Byproducts (CCBs); such as fly ash, bottom ash, boiler slag and flue gas desulphurization waste. Fly ash constitutes the major portion of CCBs which touches around 85% of the total waste[2]. At present, India generates 130 million tones[3] of fly ash per annum from 84 coal-fired boilers at the thermal power stations in the country. Since considered as a waste material for the thermal power generating industry, the fly ash dumped onto the open space forming huge ponds and heaps creating serious threat to the environment and human health. Nearly 65,000 acres[4] of land has been utilized for disposing such a huge quantity of fly ash in the country. High ash content (30–50%) of coal used in Indian thermal power plants attributes to a very large volume of ash generation[5]. The alarming fact is that the generation of fly ash waste has been projected to be 170 million tons per annum by the year 2012 with the addition of newly commissioned thermal power plants at many places in the country.

Management of fly ash, the bye-product of the thermal power plant as a waste has become an important concern among the Government agencies and policy makers, in view of the environmental pollution it creates on open dumping into the atmosphere. Department of Science and Technology, Government of India, has realized this socioeconomic problem and has ushered in opening a separate unit within the Department to tackle this environmental issue for the safe disposal and utilization of fly ash waste under the program known as "Fly Ash Mission" in 1994. Its objective is to utilize fly ash in bulk and convert this huge waste into a resourceful material in order to prevent pollution and make the environment clean. Since then, the utilization of fly ash has increased many-fold from 22% during 1990s to 46% during the first decade of the 21st century i.e. 2000s. Thus the total utilization of fly ash in various sectors has increased from 1 million tons during 1993–94 to 60 million tons during 2006-07 as against the generation of fly ash from 40 million tons in 1993-94 to 130 million tons in 2006-2007[3].

Although, the fly ash utilization program succeeded partially by increasing the utilization volume of fly ash to 60 millions tons, thus increasing the percentage of utilization up to 46%, however a major portion i.e. 70 million tones of fly ash accounting to 54% of the total produced has still remains unutilized. This waste has created problem of safe disposal and environmental issues[6–10]. Hence various methods of cheap disposal have been envisaged such as for land fill, waste land recovery, dyke raising, mine milling and so on. This has led to various precautionary measures in order to prevent water and air pollution and air borne diseases. In order to prevent airborne diseases from fly ash, the dumping sites are constantly kept wet by sprinkling water on the whole area. To avoid contamination with groundwater and soil, the dumping sites are carefully lined with impermeable materials. On the other hand, dumping lowers soil fertility and contaminates surface and ground water as it can leach into the subsoil. If fly ash gets into the natural draining system, it results in siltation and clogs the system. It also reduces the pH balance and potability of water. In addition, fly ash interferes with the process of photosynthesis of aquatic plants disturbing the food chain. Because of micron-sized particles, fly ash tends to remain airborne for a very long period of time, leading to serious health hazards as the flying ash can enter the body through the nose and affect the lungs[11]. It causes irritation to eyes, skin, nose, throat, and respiratory tract. Repeated inhalation of fly ash dust containing crystalline silica may cause pneumonitis, allergy, asthma, lung fibrosis, bronchitis and lung cancer[12–14]. Since fly ash contains traces of toxic metals[15, 16] (U, Th, Cr, Pb, Hg, Cd etc.), it may have deleterious effect on human health and on flora as well as fauna.

Thus new approaches are in the offing to increase the bulk utilization of fly ash in a way that it can help the humanity physically, physiologically, psychologically, technically and financially. Some of these avenues may be (i) disposal costs are to be minimized; (ii) less area is to be occupied by landfills; (iii) possible financial returns from the sale of byproducts and (iv) can create alternate materials for some of scarce and expensive natural resources. It includes industrial sectors such as cement[17–19] manufacturing, concrete making[20], brick manufacturing[21, 22], tile manufacturing[23, 24], land fills[25], making of roads[26, 27] and embankments[28], reclamation of low lying[29] and waste land for agriculture, back filling of open cast mines[30], stowing in underground mines, soil amendment[31], structural fills[32–34], extraction of valuable trace elements[35, 36] and so on. A smaller fraction of the fly ash is also being utilized in biology and polymer industries[37–39.] The areawise utilization of fly ash as a resource material has been enumerated in Table 1.1.

Table 1.1: Area-wise Break-up For the Utilization of Fly Ash[40]

Area of utilization	**% of utilized fly ash**
Land Development	36.18
Cement and Concrete	35.65
Road/Embankments	8.48
Ash Dyke Raising	12.96
Bricks	0.72
Mine Filling	2.94
Others	3.08

Owing to the remarkable diversity of uses, rubber is inevitable in the modern world. Fillers are used to enhance the technical properties of the rubber which is amorphous in nature and having lower strength properties in its original state. Fillers are also used to cheapen the products. As a result, a number of fillers of different particle size and surface activity are used in the rubber matrices. According to a study by Ceresana research group[41] more than 50 million tones of filler is being utilized in the rubber industry annually and this trend is steadily increasing at an average rate of 3% annually. The use of fly ash as a filler in rubber industry, which has been limited so far, would be the most welcome step viewing from the proximity of this material with other siliceous fillers-such as precipitated silica used to reinforce rubber and because of its availability at no cost. Also being a waste material its bulk utilization would help in disposing the fly ash safely into useful value added products helping the environment free from pollution and making earth greener and cleaner. The use of fly ash as a filler in rubber products based on a wide range of elastomers such as natural rubber[42], styrene butadiene rubber[43], poly isoprene rubber[44], polybutadiene rubber[45] and chloroprene rubber[46] has been reported earlier. Most of the works uses fly ash as such without any modification and reports that the fly ash can be used as a cheapening agent or a replacement for non-reinforcing fillers with the technical properties of rubber composites deteriorating above a critical filler dosage.

1.2 Literature Review

1.2.1 Coal Combustion Products (CCP)

Coal contains a substantial range of impurities, including minerals and sulfur. Coal on partial or full combustion, gives rise to huge amounts of heat energy and the mineral matter gets reduced to their respective oxides forming the incombustible residue called 'ash'. The sulfur is converted into sulfur oxides in this process. Power generating plants based on coal produce a large quantity of ash entrained along with the flue gas. This results in increased generation of solid materials referred to as coal combustion products (CCPs). CCPs are categorized into various groups, each based on physical and chemical forms derived from coal combustion methods and emission controls

(a) ***Fly Ash**:* also known as Pulverized Fuel Ash (PFA), is obtained by electrostatic or mechanical precipitation of dust-like particles from the flue gases of coal-fired furnaces at 1200 °C to 1700 °C[47] and is the major component of CCP (more than 75%). Fly ash is a fine powder, which is mainly composed of spherical glassy particles. The inorganic incombustible matter present in the coal[48] melts and solidifies later while suspended in the exhaust gases and collected by electrostatic precipitators or bag house filters. Since the particles solidify while suspended in the exhaust gases, fly ash particles are generally spherical in shape and range in size from 0.5 μm to 100 μm. Fly ashes are generally highly heterogeneous, consisting of a mixture of glassy particles with various identifiable crystalline phases such as quartz, mullite, and various iron oxides. Figure 1.1 shows the

diagram of a thermal power station which shows the recovery of fly ash from exhaust gas.

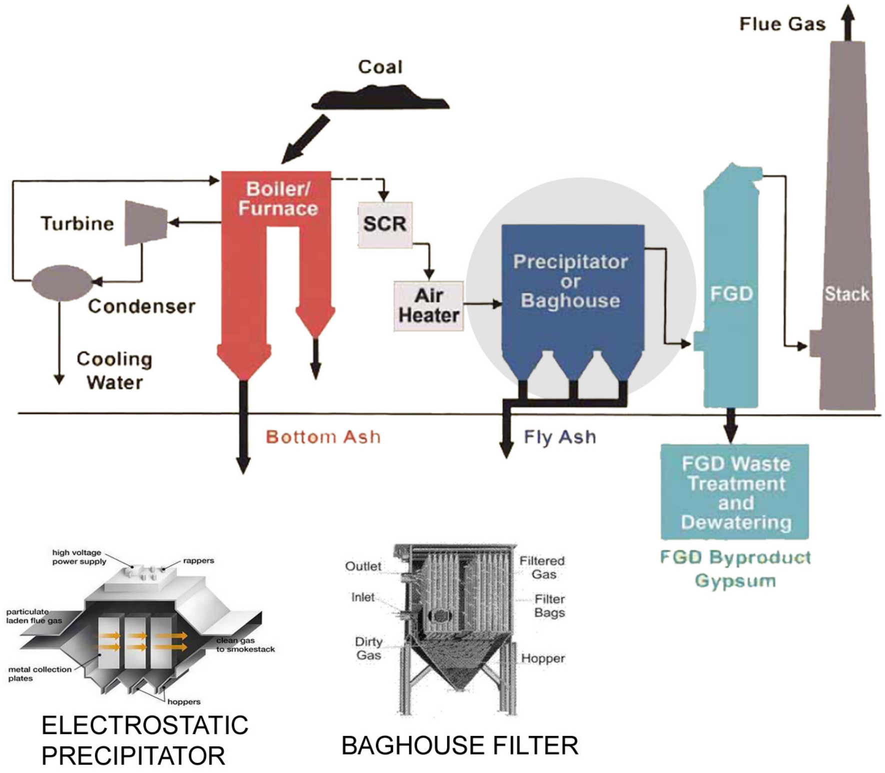

Figure 1.1: Pictorial Representation of Coal-Fired Thermal Power Plant

(b) *Bottom Ash:* is a granular material removed from the bottom of dry boilers, which is much coarser than FA though it formed during the combustion of coal.

(c) *Boiler Slag:* is a vitreous grained material deriving from coal combustion in boilers at temperatures of 1500 °C to 1700 °C, followed by wet ash removal of wet bottom furnaces

(d) *Fluidized Bed Combustion (FBC) Ash*: is produced in fluidized bed combustion boilers. The technique combines coal combustion and flue gas desulphurization in the boiler at temperatures of 800 to 900 °C. FBC ash is rich in lime and sulphur.

(e) *Semi Dry Absorption (SDA) Product*: is a fine grained material resulting from dry flue gas desulphurization with lime acting as the sorbent.

(f) *Flue Gas Desulphurization (FGD) Gypsum*: is natural gypsum like product which is obtained by wet desulphurization of flue gas and special treatment of the adsorbed products.

1.2.2 Classification of fly ash

Fly ash, like volcanic ash, is successfully used as a pozzolanic material for cement, concrete and other related products for more than half century. Vassilev et al. [49–55] have studied extensively the phase mineralogy and chemical structure of the coal combustion products from Bulgarian power stations and published many monograms based on the compositional aspects of fly ash and its relation with the source as well as the combustion technology used. According to them, the composition of the fly ash is primarily dependent on the source and chemical composition of the coal, the precipitation technique, boiler type and plant operating conditions. In 1965, Watt and Throne[56] have carried out compositional studies on various samples of fly ash from Great Britain and concluded that fly ash generally contains 71-88% amorphous glassy phase and 11-17% crystalline phase. Mostly fly ash has a glassy covering with a crystalline core[57]. The crystalline core has different crystalline phases consisting mostly of mullite ($3Al_2O_3.2SiO_2$), quartz (SiO_2), aluminium oxide (Al_2O_3), hematite (Fe_2O_3), lime (CaO) and gypsum ($CaSO_4.2H_2O$)[58], while the glassy phase constitutes alumina and silica as major components with some minor quantities of iron oxide as well as calcium oxide. Oxides of other elements are present in traces[59].

Many researchers have characterized fly ash from different sources. Joshi and Marsh[60] did not find a single parameter which could uniquely be related to the coal type by studying their physical, chemical and mineralogical properties of samples of Canadian fly ash. Kempska[61] classified fly ash according to the type of coal, furnace design and chemical composition. Roy and Griffin[62] proposed a classification system along with nomenclature for coal based fly ash depending on its chemical composition, hydration pH and particle size distribution. Cereda et al.[63] observed that particles of fly ash could be grouped into several classes depending on the matrix as well as trace element composition. Watt[64] studied the characteristic features of different fossil-fuel types of fly ash and observed that the generation of large amounts of clinkers on the fly ash during combustion produced considerable amounts of gypsum and scrubber water in flue gas and the amount of residue depended on the inorganic matter as well as the sulfur content in the coal. McCarthy et al.[65] compiled a database based on chemical, mineralogical and physical characteristics of North American fly ash for utilization and modeling their behaviour for proper disposal. Dudas and Warren[66] presented a submicroscopic model of fly ash particles. Howers et al.[67] studied fly ashes from 21 Kentucky power plant by grouping them according to the sulfur content in the feed coal. De Luxan et al.[68] characterized the fly ash produced by thermoelectric power plants in Spain by physical, chemical and mineralogical properties. Furuya et al.[69] fractionated fly ash samples using nylon sieves and observed that size, density, elemental and morphological distribution gave insight into the softening property of ash, combustibility of coal, and the combustion conditions. Mukai et al.[70] characterized a submicron coal ash chemically after density separation. Lu et al.[71] characterized a chemically modified fly ash by particle size distribution, valence of surface elements, surface topography, dispersion in an organic medium and affinity for water. Kosuge et al.[72] classified fly ash into different groups on the basis of solubility in HCl solution. Rose[73] characterized fly ash with respect to its inorganic ash sphere (IAS) to spheroidal carbonaceous particles (SCP) ratio. Kutchko et al.[74] characterized 12 different types of fly ash samples from nine locations in US using SEM and EDS, and deduced the existence of various mineralogical domains in the surface and bulk of fly ash. Santhakumar et al.[75] classified fly ash according to the different locations in the electrostatic precipitators from where it is being taken out.

ASTM International classifies fly ash into three categories based on the origin and ASTM C618-03[76] specifies a standard for the coal fly ash and the raw or calcined natural pozzolan.

(i) *Class N*: Raw or calcined natural pozzolans, such as some diatomaceous earths; opaline cherts and shales; tuffs and volcanic ashes or pumicites, calcined or uncalcined; and various materials requiring calcination to induce satisfactory properties, such as some clays and shales.

(ii) *Class F*: Fly ash normally produced from burning anthracite or bituminous coal. This class of fly ash has pozzolanic properties.

(iii) *Class C:* Fly ash normally produced from lignite or sub-bituminous coal. This class of fly ash, in addition to having pozzolanic properties, also has some cementitious properties.

Chemical requirements of each class of fly ash is given in Table 1.2

Table 1.2: Chemical Requirements for Fly Ash Types[76]

	Class N	Class F	Class C
Silicon dioxide (SiO_2) plus aluminium dioxide (Al_2O_3) plus iron oxide (Fe_2O_3), min, %	70.0	70.0	50.0
Sulfur dioxide (SO_3), max, %	4.0	5.0	5.0
Moisture content, max, %	3.0	3.0	3.0
Loss on ignition, max, %	10.0	6.0	6.0

1.2.3 Chemical Composition of Fly Ash

The chemical compositions of fly ash vary widely depending upon the source of the coal, its pretreatment, and the power plant operating conditions. Mainly the nature of the mineral matter and organic constituents present in coal determine the chemical composition of the resulting ash[77, 78]. Chemically, coal is an organic material and constitutes primarily of carbon, hydrogen, nitrogen, oxygen and sulfur. Apart from these, the inorganic constituents associated with the coal include; clay minerals, silica, carbonates, and sulfides. It has been established that the major elements present in fly ash in the order of decreasing abundance are; Si, Al, Fe, Ca, Ng, K, Na, S, Ti, P and Mn[79]. They are mostly present in the core of fly ash hence are relatively stable. The surface layers of the fly ash become embedded with various elements that volatilize during coal combustion, and later condense on the surface of fly ash particles as soon as the temperature of the flu gases reduces. Since the micron-sized particles have larger surface areas, unusually higher concentrations of the trace element oxides are adsorbed on it[80]. These trace element oxides detected on the surface of fly ash are As, Cd, Cr, Cu, Pb, Ni, Zn and B. Since the coal combustion is a never ending process, the fly ash surface also contains trace amounts of unburned carbon.

Berry[77] reported that over 85% of fly ash comprise of chemical compounds and glasses formed from SiO_2, Al_2O_3, Fe_2O_3, CaO and MgO. Amongst these, SiO_2 and Al_2O_3, predominate and together makes up about 45–80% of the total ash. The sub-bituminous and lignite coal ashes have relatively higher proportion of CaO and MgO and lesser proportions of SiO_2, Al_2O_3 and Fe_2O_3 as compared to the bituminous coal ashes[2]. Table 1.3 gives a comparative study of the range of different oxides present in fly ash of different types such as; bituminous coal fly ash, lignite coal fly ash and sub-bituminous coal fly ash. Table 1.3 is in analogy with the ASTM classification of fly ash according to the origin, which has been discussed earlier. The bituminous and sub-bituminous types of fly ash fall into the category of Class F and lignite fly ash in the category of Class C. In class F fly ash, total calcium content range from 1–12%, mostly in the form of calcium hydroxide, calcium sulphate and glassy components, in combination with alumina and silica. In contrast, Class C fly ash is reported to have higher calcium oxide contents up to 30–40%. The other difference between Class F and Class C is that the amount of alkali metals (combined sodium and potassium), present and sulphates (SO_4) are generally higher in the Class C fly ash as compared to the Class F fly ash.

Table 1.3: Normal Range of Chemical Composition for Fly Ash Produced from Different Coal Types[81]

Component (wt. %)	Bituminous	Sub-bituminous	Lignite
SiO_2	20–60	40–60	15–45
Al_2O_3	5–35	20–30	10–25
Fe_2O_3	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO_3	0–4	0–2	0–10
Na_2O	0–4	0–2	0–6
K_2O	0–3	0–4	0–4
Unburnt C	0–15	0–3	0–5

1.2.4 Mineralogy of Fly Ash

The mineralogical composition of fly ash depends on the geological factors related to the formation and deposition of coal and its combustion conditions. Many researchers have identified the mineralogical composition of fly ash by using powder X-Ray Diffraction (XRD) analysis. Fly ash can be mineralogically divided into three major categories[79, 82];

i. Amorphous glass
ii. Mullite ($3Al_2O_3 . 2SiO_2$) – Quartz (SiO_2) and
iii. Magnetic Spinel (includes magnetite (Fe_3SO_4), hematite (Fe_2SO_3), ferrite, and γ-Fe_2O_3

Second and third categories are crystalline phases. Generally, fly ash has 15–45% crystalline structure and the high calcium ashes (Class C) contain larger amounts of crystalline matter ranging between 25 and 45%[83, 84]. According to Watt and Throne[56], the composition has been 71–88% of glassy phase and 11–17% crystalline phase. According to Vassilev and Vassileva[55], major and minor minerals and phases in fly ash in the order of decreasing amounts are; glass, mullite, quartz, char, hematite-magnetite, anhydrite-gypsum, feldspar, lime-portlandite, clay and mica minerals, cristobalite-tridymite, calcite-ankerite, corundum, jarosite and some Ca and Ca-Mg silicates.

Quartz (SiO_2) in the fly ash originates from silt and clay present in the coal. It crystallizes directly from molten ash or by devitrification of the glass after cooling. Their formations require temperatures of above 1000 °C. Mullite is twice as abundant in low-calcium ashes as in high calcium ashes. Ferrite spinel, mahnetite and hematite are the principal iron containing phases in the fly ash[85]. Koukouzas et al.[86] evaluated the XRD patterns of fly ash and confirmed that the major mineral phase present is quartz, while other mineral phases are maghemite, hematite, periclase, rutile, gehlenite and anhydrite. They also observed that almost all ash samples contain quartz, which can be considered as a primary mineral, especially in cases where ash samples originate from fuels such as bituminous coal and lignite, which contain high amounts of silicon dioxide. Formation of iron oxides is partially due to the decomposition of pyrite. Mullite is assumed to form during combustion by the thermal decomposition of the naturally occurring aluminosilicates, such as kaolinite at 1200–1500 °C. Their compositions vary between $Al_2O_3.3SiO_2$ and $Al_2O_3.2SiO_2$ depending on the temperature of formation[48, 58].

1.2.5 Properties of Fly Ash

The properties of fly ash depend on the source of the coal, its nature, cleaning and pulverization process of the coal, design and operation of the power plant boiler unit, combustion conditions, additives used to assist combustion or to improve precipitation performance, efficiency of the emission control devices, storage and handling of the byproducts and the prevailing climate[87]. Although fly ash production and composition vary with time and place, some generalizations can be obtained for its physical, chemical and mineralogical properties.

1.2.5.1 Physical Properties

(a) Size Distribution: Fly ash is the solid waste residue of combustion of coal which are small enough to be carried away by the flue gases. Martin et al.[88] reported that more than 80 weight % of a fly ash sample passes through a No. 200 sieve, which has 74 µm screen size. Several authors[89, 90] confirm this observation and report that the majority of fly ash particles are in medium to fine size range. Fisher et al.[91] reported three different methods to measure the particle size of fly ash: Count Median Diameter (CMD), Volume Median Diameter (VMD) and Mass Median Diameter (MMD). The sizes of the particles also depend on the concentration of the elements because volatilization of certain elements cause decrease in the particle size[92].

(b) Surface Area: It controls the surface parameters such as water absorpsion capability and surface activity. Schure et al.[93] reported that the surface area is inversely proportional to the particle size and is also related to the particle shape. Several researchers have reported about the surface area range of fly ash particles; which may vary from 0.45 to1.27 m^2/g as per El-Mogazi et al.[79] while Mattigod et al. [16] estimated a wider range of 0.2–3.06 m^2/g. Theis and Gardner[94] have reported an unusually higher surface area ranging from 1 to 9.44 m^2/g owing to the wider range of particle size (0.01–125µm) of the fly ash selected for the study.

(c) Morphology: The particle shape, surface characteristics and inner structure of fly ash depend on the combustion temperature of coal and its grain size[95]. Fisher et al.[91] classified fly ash particles into eleven major categories based on opacity, shape and types of inclusions. According to them, spherically shaped particles which are translucent or transparent predominate (67–95%) in a given sample of fly ash. They also indicated that the chemical composition contributes to the level of opaqueness, whereas the exposure time and temperature of combustion are responsible for its shape characteristics. Apart from solid spherical particles, the existence of thin walled hollow spheres, known as '*Cenospheres*' are also reported, which are formed due to expansion of CO_2 and H_2O vapor evolved from the minerals while the coal is being burnt[96]. Since cenospheres are hollow, they have low bulk density. The percentage of cenospheres increase with the ash content in the coal[97]. Another interesting observation is the occurrence of '*Plerospheres*'

which constitutes of many small spherical particles inside a large hollow glassy sphere[98, 99]. Berry[77] reported the existence of reddish brown particles with high iron content and irregularly shaped porous particles of unburnt carbon in fly ash. Wadge et al.[100] reported a relationship between the pulverization process of coal prior to combustion and the spherical shape of the resulting fly ash and also commented about the dependence of combustion chamber temperature on the fusion of minerals in the coal and its solidification to form spherically shaped particles. Tazeki et al.[80] had a similar observation on the formation of spherical shaped fly ash particles, which they reported that the spherical morphology is acquired during the spontaneous cooling process while being carried along with gaseous combustion products. White and Case[58] reported the agglomerations and clustering of smaller particles thereby the formation of particles with larger size range. Porbaha et al.[101] reported that the fly ash constitutes mostly of glass spheres, along with small crystalline domains and meager amounts of unburnt carbon. Trivedi and Singh[102] observed that coarse ash contain rounded, sub-rounded, spongy and opaque particles. The superfine particles have a tendency to form agglomerates in presence of moisture. Das and Yudhbir[4] reported that the finer fraction of the Indian fly ash is mostly spherical in shape, whereas the coarser fractions of grain size which are more than 75 μm have irregular shape.

(d) Colour: The colour of the fly ash depends on its mineralogical composition and the amount of unburnt carbon present in it. The presence of carbon leads to a grey to black colour of the fly ash, depending on its concentration. Carbon-free ash can range from blue-grey to brown and the colour is generally due to the presence of iron oxides in it. Lee et al.[57] reported that the smaller-sized fly ash particles are brighter than the larger size particles. Liu et al.[78] observed that the fly ash particles are grayish white powders and look like cement.

(e) Specific Gravity: It depends on the morphology, fineness, carbon and iron content and mineralogy of fly ash. Several researchers[102–104] have reported the high specific gravity of fly ash samples that contain iron oxide, like hematite and magnetite. In general specific gravity of coal ash lies in the range of 1–2 g/cm^3. Pandian et al.[104] observed the range of specific gravity varying from 1.46–2.66 g/cm^3 for Indian fly ashes. Bayat[105] reported that the specific gravity of Turkish fly ash range from 1.94–2.94 g/cm^3,

whereas, American fly ash has specific gravity[2] ranging from 2.14 to 2.69 g/cm^3. Existence of various morphologies such as the presence of cenospheres reduces the specific gravity of the fly ash significantly[102, 104]. The dependence of specific gravity on fineness of fly ash particles is also reported by other researchers[57, 105].

1.2.5.2: Chemical Properties

(a) pH: Fly ash may be acidic or basic depending on the source and nature of the coal used. Eastern bituminous coal fly ash is found to have a pH of 4.3–4.9[106], whereas, the western coal fly ash has a higher pH of 8.16–12.4[94]. The literature often does not report the actual pH of the fly ash, but most often the pH of the fly ash media is recorded. El-Mogezi et al.[79] reported that the pH of the fly ash affects the soil media, when it is used in soil amendments. Theis and Wirth[107] commented that the pH of fly ash has very strong effect on aquatic environment as a decrease in pH increases de-sorption of metals from the surface of fly ash. Later, Hollis et al.[108] studied this issue and support this fact.

(b) Solubility: Fly ash constitutes mainly a glassy component, which is insoluble in water. However, the enriched surface elements are soluble in water[62]. The desorption and therefore the solubility of most heavy metals is low in basic environments because these metals are found to be adsorbed onto hydrous iron and aluminium oxides[90, 109]. An acidic pH favors the solubilization of trace cations and a basic pH makes trace anions to solubilize[94]. Solubility largely depends on the extraction procedure, the nature of extractant, ash to-solvent ratio, pH, number of extractions and duration of extraction[89]. Dreesen et al.[110] reported that the metallic nature of the element is vital in its solubility, as they found the most soluble trace elements under alkaline conditions were Mo, F, Se and B. They also found that in acid solutions the highly volatile elements from the combustion process (As, B, Cd, Se and Mo) are most easily extracted.

(c) Leachability: Potential hydrological impact of fly ash lies in the extent of leaching the toxic contaminants by water medium. Leachate is highly variable as a result of the type of coal and plant process. Strauss[111] performed column leachate tests for fly ash collected from Delaware, which contained high Total Dissolved Solids (TDS) and high levels of arsenic and selenium. Ruane et al.[112] reported that the leachates from fly ash were highly variable, but generally high in TDS, B, Fe, Ca, and Al, and often toxic

enough to contaminate drinking water. The acid ash seems to produce more metals in leachate than alkaline ash. Roy et al.[113] reported that the leachability of certain elements such as P, Fe, Al, B, K and Ca, decreased with ageing of fly ash. It was also concluded that the rate of leaching was affected by the particle size and pH of fly ash and the temperature of water. Liem et al.[82] developed a model to predict the leaching characteristics.

(d) Toxicity: Toxic constituents on fly ash particles are considered to be trace elements like Ni, As, Cr, Pb, Cd etc., polycyclic aromatic hydrocarbons and silica. Depending on their toxicity, chemical properties and its concentration in the air, fly ash particles may pose an inhalation hazard to exposed workers such as fibrosis[114–116] and geno-toxic events[117–119]. As per the extraction procedure by United States Environmental Protection Agency (USEPA), the trace metals should be within the limits put forth by Resource Conservation and Recovery Act (RCRA)[92, 113]. Certain states of elements could be more toxic, mobile and biologically available; such as As(III) oxidation state of arsenic is toxic. Fly ash extracts normally have most of the arsenic in the non-toxic form, As(V)[89]. *In vitro* studies show that coal fly ash exerts cytotoxicity in a number of conventional tests using either animal lung cells, human red blood cells or cell lines such as hamster ovary cells[120]. Fly ash is reported to be less toxic than crystalline silica, which was noted as a human carcinogen by International Agency for Research on Cancer (IARC) in October 1996. In vitro data do not support the importance of silica content in toxicity of fly ash, as in fly ash, crystalline silica domains are less than 10% and are embedded in an aluminosilicate matrix[121, 122]. However, recent reports[123] equate the toxic components in fly ash with those found in rocks and minerals and elaborate that the mere presence of trace elements does not make fly ash toxic; the magnitude and duration of exposure to these constituents must be sufficiently large to cause adverse health effects.

(e) Radioactivity: Fly ash may be considered as radioactive waste if the average ^{226}Ra concentration exceeded 5 picocuries per gram (pCi/g), or if a leachate had 50 picocuries per liter of ^{226}Ra and ^{228}Ra combined[113]. Furr et al.[124] performed gamma emission tests on twenty three fly ash samples. The samples ranged from 3.9–14.4pCi/g above background with an average of 6.4 pCi/g. They also pointed out that the presence of Th and U in the fly ash is directly related to their presence in the earth's crust.

Golden[109] found that the level of radioactivity for both U and Th was 3–5 pCi/g while Torrey[125] reported that the radioactivity concentration ranges from 1.0 to 4.3 pCi/g for ^{226}Ra, ^{228}Ra, $^{228\mathrm{Th}}$ and ^{232}Th individually. Krieger and Jacobs[126] reported that different concentration levels occur as a result of the source of the coal and the differences in mining and coal washing operations. Saxena and Asokan[127] pointed out that the radioactivity level of Indian fly ash is almost similar to that of normal soil. Radioactivity of lignite fly ash is found to be lower than that of bituminous and sub-bituminous fly ash[128] and lower radioactivity is observed with increase in cenosphere content in fly ash[97] which is due to low porosity and presence of bubbles.

1.2.6. Production and Utilization Status of Fly Ash

1.2.6.1. Production and Utilization Status of Fly Ash in the World

Manz[129] has compiled the production and utilization statistics of fly ash in various countries with data collected in 1992 and reported in his communication to *Fuel* in the year 1997. In this report, the total production of fly ash and bottom ash together was estimated to be 459 million tons. The total utilization of fly ash in this period was only 153 million tons (33.3%). Vom Berg[130] updated these statistics in 2001 which reports the total fly ash production figures 480 million tons. According to American Coal Ash Association (ACAA), the total production of fly ash in United States for the year of 2008 is 72 million tons of which, 30 million tons are utilized in various applications at a utilization rate of 41.6%. ECOBA, the European Coal Combustion Products association estimated the total production and utilization of fly ash from 15 countries of European Union (EU) and reported in their annual report of 2007 that 42 million tons of fly ash is being produced in these countries, of which 39 million tons were efficiently utilized at a utilization rate of 91%. Lan and Yuvansheng[131] reported that the estimated fly ash output from China in the year 2006 is around 300 million tons and the country is re-utilizing about 50% this menacing waste in various useful products. Canadian Industries Recycling Coal Ash (CIRCA) reports that the total production and utilization of fly ash in Canada in the year 2004 is 46 million tons and 14 million tons respectively which recorded 31% utilization. The re-utilization plans are scanty in Republic of South Africa, where only 1.4 million tons of the total 27 million tons[132] are converted into various products in the year of 2001. Australia produced 13 million tons of fly ash in 2003; of the total quantity only 2.4 million tons are re-utilized in various industrial sectors. Japan, on the other hand, achieved a utilization rate of above 80% of the total produced fly ash (89 million tones). In the utilization lane, the only country that had achieved triumphant advancement is Israel. Out of 10 million tons[133] of fly ash produced in the year of 2005, Israel had a full utilization record with a situation of more demand over the available supply of fly ash. The total production of fly ash in the world is now exceeds over 600 million tons per year.

1.2.6.2. Production and Utilization Status of Fly Ash in India

Till about a decade back, fly ash had been considered as a 'polluting industrial waste' and a very few utilization areas were explored for it due to the negative perception about fly ash. The focused efforts for the fly ash utilization and safe disposal were started by Department of Science and Technology (DST), Government of India during 1994 as 'Fly Ash Mission'. The main objectives of this mission were; to make fly ash a useful material, to reduce environmental pollution, to reduce land acquired for fly ash disposal and to economize fly ash utilization in various areas.

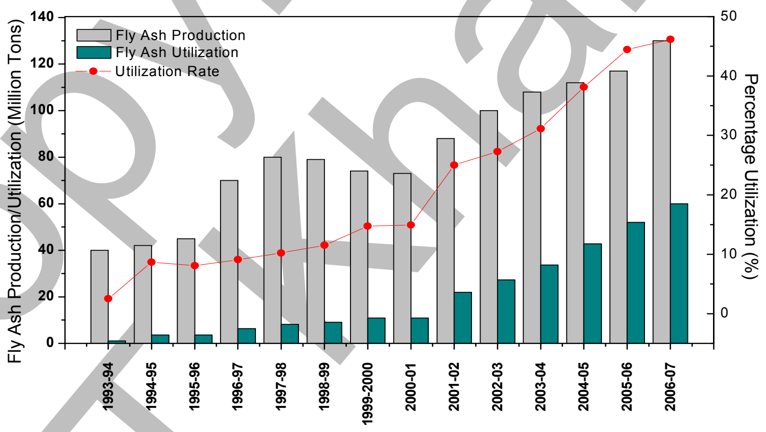

Figure 1.2: Annual Production and Utilization of Fly Ash in India

The concerted efforts during the Mission Mode period (August 1994–March 2002) turned around fly ash from a 'waste material' to a 'resource material' as the utilization increased from one million ton during 1993-94 to 22 million tons during 2001-02. After the Mission period, i.e. after March 2002, the efforts of the Government has continued to search new avenues for fly ash utilization under a new program called ‘Fly Ash Utilization Program (FAUP)’. Orchestrated efforts by DST with other departments such as Ministry of Environment and Forest (MOEF) and Ministry of Power (MOP) has made wonder by increasing the utilization volume of fly ash from 22 million tons of 1993-94 to 60 million tons during 2006-07. Figure 1.2 shows the annual production and utilization of fly ash in India over the years with the utilization rate in percentage.

1.2.7. Utilization of Fly Ash

Fly ash holds certain unique properties that make it suitable candidate for different utilizations. Presently only a fraction of the total generated fly ash is being utilized worldwide in various areas and the remaining residues are rapidly accumulating and are to be disposed off carefully. Therefore an urgent need exists to come up with more utilization options for this lethal solid waste. A brief review on the utilization of fly ash in various industrial fronts is given in the coming sections.

1.2.7.1. Cement and Concrete Products

Fly ash is a pozzolan, a siliceous, or aluminous and siliceous, material which is not cementitious by itself. In finely divided form and in the presence of moisture, it reacts with calcium hydroxide at room temperatures to form cementitious products [134]. There are two approaches to design the concrete mix with fly ash as a component. Fly ash can replace a portion of cement, not exceeding 20% by weight of the cement. These results in sluggish strength gain for concrete and therefore cure time shall be increased[135]. Alternatively, fly ash may be admixed with the concrete mix, to improve the strength properties of the concrete. Fly ash also provides resistance to sulfate reaction with hydrated lime and calcium aluminates, and improve workability which reduces the water requirement resulting in lower bleeding, durable surface, lower permeability, better control of shrinkage, reduced heat of hydration, increased resistance against alkali aggregates and reduced cost[113, 134]. Typically, up to 35% of fly ash can be mixed with concrete. However, high volume fly ash (HVFA) concrete technology allows the use of higher volumes (>35%) of fly ash in concrete and promote resource-efficient construction[136]. Fly ash has also been reported to be used in the manufacture of light weight materials like autoclaved cellular concrete (ACC) with the use of water, cement, aluminium and fly ash up to 70% by weight[137]. ACC provides high insulation value and is fireproof, light weight and cheaper than conventional concrete block.

1.2.7.2. Bricks

Fly ash can be used in making bricks for construction industry and can serve partially in its total demand by enhancing its utilization. Even though, fly ash bricks seem to be costlier than conventional bricks in the first instance, the actual economic benefits can be evaluated in terms of its increased[21, 138–140] strength properties and durability. Fly ash is conventionally used with clays for making clay-fly ash bricks, which has higher porosity, hence can develop better strength and water resistance properties than all-fly ash bricks.

1.2.7.3. Road and Pavement Construction

Fly ash may be used in road construction for (i) stabilizing and constructing the sub-base or base, (ii) in upper layer of pavement and (iii) for filling purposes. Many researchers[141, 142] have reported the use of fly ash as an additive for the base and sub-base layer construction of pavement, as well as for the construction of embankments in compressed soils. Kolias and Karahalios[143] reported that the addition of fly ash reduces the necessary pavement thickness and at the same time reduces the construction cost. Eskiogloru et al.[144] reported that the strength properties are improved by 40%, while the average deflection under the influence of circulating mass decreased by about 35% for sand-gravel paving with fly ash and cement in relation to the natural soil.

1.2.7.4. Land Applications and Soil Amendments

Fly ash, which is presently in abundance, may be used to increase the concentration of certain desirable elements in plants, but at the same time, their concentration beyond the certain range could be harmful to the plant growth. Nevertheless, the role of fly ash in agriculture and reclamation of problematic soils has been well investigated[145–149]. On the other hand, reclamation of fly ash dumps through revegetation is also an important area of research. Fly ash alone is a poor source of nutrients such as nitrogen and phosphorous because all the nitrogen present in the coal has been volatilized during the combustion[150]. Although sufficient phosphorous is present in fly ash, most of it is unavailable. The deleterious effects of fly ash can be improved by modifying with suitable minerals to support the plant growth[151].

1.2.7.5. Recovery of Valuable Metals

Fly ash is the reservoir of trace metals, and the recovery of these trace metals from the fly ash may prove to be beneficial in metal recycling as well as preventing environment from pollution due to heavy metal contamination. The study of treatment of alumina-silica complex containing fly ash by chemical enrichment has been reported[152]. The removal of silica from aluminium-containing raw material with high silica content is based on the property of hydro-aluminium silicates to undergo intra-molecular phase changes by thermal treatment, resulting in the formation of amorphous silica. Leaching of heat treated fly ash with sodium hydroxide solution brings about the dissolution of silica, and recovery of Al_2O_3 can be recovered in the solid state in the form of alpha or gamma alumina. More than 80% of cadmium, copper and zinc, 60% of aluminium, and 30% iron and nickel become solubilized[153]. Apart from these metals, coal ash is known to contain trace metals of relatively higher commercial value.

1.2.7.6. Raw Material for Various Products

Fly ash has been used for the preparation of ferric alum, utensil washing powder, and black board chalks[154]. Further, fly ash used in the preparation of ceramic tableware and artware was found to increase the mechanical strength above that of the original products[155]. Fly ash has also been used in the preparation of ceramic filters suitable for hot gas cleaning[156]. Novel synthetic light weight aggregates have been made by coal fly ash and high density poly ethylene[157] (HDPE). HDPE serves as an excellent protective barrier and has a very good resistance property. The synthesis of zeolites from fly ash for application in the controlled release of fertilizer or absorbents has been reported by researchers[158]. Being a value-added product, it is often capable of overcoming the transport cost barrier than that inhibits many traditional fly ash utilization strategies.

1.2.7.7. Backfilling of mines

Mine back filling has been demonstrated to be an attractive option for the utilization of fly ash for thermal power plants close to the coal mines. Backfilling of underground mines is technically vulnerable and especially holds good potentials for those areas where sand is scarce. Fly ash grout injection is being used to fill a closed underground mine site, to reduce acid mine drainage[159] (AMD). AMD occurs when sulphide minerals, such as pyrite, found in association with the coal come into contact with oxygen and water during mining. Sulphide mineral undergo bacterially catalyzed oxidation reactions which generate acidity and increase Fe and sulphate concentrations in the adjacent water bodies[160]. The reduction of AMD by fly ash filling can occur by two-approaches; by neutralizing AMD and by preventing contact between water and pyrite material.

1.2.7.8. Waste Water Treatment

Fly ash has the potential in wastewater treatment because of its rich chemical constituents such as alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its porosity, wider particle size distribution and higher surface area. Moreover, the alkaline nature of the fly ash makes it a good neutralizing agent. Fly ash has been reported to be used as the absorbent for treatment for wastewater to remove toxic heavy metals such as chromium[161–164], zinc[165], cadmium[166, 167], copper [168, 169], lead[170], mercury[170, 171] and nickel[172]. Apart from heavy metals, other inorganic contaminants such as phosphorous[173, 174], fluoride[175] and boron[176] are also reported to be removed from wastewater using fly ash as the absorbent.

1.2.8. Fly Ash as Filler in Polymer Matrices

1.2.8.1. Fly ash in Plastic matrices

Uses of fly ash as filler in various plastic matrices have been reported earlier. Srivastava et al.[37] studied the effect of fly ash on the epoxy resin composites to reduce the void formation, thereby enhancing modulus of elasticity and toughness of the cured resin. Wong et al.[177] reported an increase in modulus of polypropylene upon incorporation of 20% fly ash and a further enhancement of properties was observed by using a coupling agent. Sole and Ball[178] compared the abrasive wear behavior of polypropylene filled with various mineral fillers such as calcium carbonate, talc, barium sulfate and fly ash. Sarojadevi et al.[179] demonstrated the use of fly ash as a filler in unsaturated polyester resin. Chand and Khare[180] studied the dielectric properties of fly ash filled PP/LDPE blends and observed that the fly ash loading increased the dielectric constant due to the presence of other metallic oxides and the dissipation factor of the blend shifted towards higher temperature. Chand and Vashishtha[181] attempted to use fly ash in blends of PP/LDPE and PMMA at various loadings to study its melt flow characteristics and reported that fly ash incorporation increased the melt viscosity. Chand and Pandey[182] studied the abrasive wear property of i-PP, PS and blend of i-PP/PS and reported that the abrasive wear rate increased on fly ash incorporation for both i-PP and PS and the increase was found to be more prominent in the blends. Sen and Nugay[183] investigated on the effect of fly ash dosage on the processability characteristics and mechanical properties of uncured and cured unsaturated polyester resins and reported that the composite with 15% fly ash showed property advantages. Guhanathan et al.[184] reported an enhancement in tensile, flexural, compressive and impact strength properties for polyester resins loaded with surface treated fly ash. In another communication, Guhanathan and Sarojadevi[185] reported that the mechanical properties as well as resistance to various environmental stresses were enhanced with loading of surface treated fly ash on to the polyester matrix. Kulkarni and Kishore[186] studied the various aspects of fly ash filled epoxy composites under compressive loading and established the reasons for early failures of the structure. Kishore et al.[187] reported the impact behaviour of epoxy resins containing 10% by volume of surface treated fly ash. Kulkarni and Kishore[188] reported the compressive properties of hybrid epoxy composites filled with fly ash and fibers. Kulkarni and Hore Kis[189] performed the warm water treatment on fly ash-epoxy composites and studied its effect on the compressive strength properties.

Huang et al.[190] studied the effect of fly ash on the properties of polypropylene, LDPE and HDPE and concluded that fly ash filled thermoplastics could be used to produce commercial automotive parts with no difference in injection moldability, dimensional stability and surface smoothness in comparison with the commercially available fillers and their polymer composites. Wang et al.[191] studied the effect of fly ash plerospheres in polypropylene and PVC based composites and found that the incorporation of fly ash improves the tensile as well as rheological properties of the composites. Desai et al.[192] tried to utilize fly ash as a filler in polypropylene matrix. They observed that tensile modulus and flexural strength increases with volume fraction of fly ash up to 5 phr and then decreases at higher doses. Guhanathan et al.[193] prepared the elastomer encapsulated fly ash by the coagulation of emulsified elastomer that contained fly ash and filled the modified fly ash onto the unsaturated polyester matrix to improve the toughness. Kulkarni et al.[194] studied the compression strength properties of saline water-exposed epoxy system containing fly ash particles and reported that moisture ingression and thereby compressive strength decreases with increasing the fly ash content. Ramakrishna et al.[38] compared the performance of fly ash with granite powder as filler in PMMA-toughened epoxy matrix for their tensile and flexural strength properties. Kishore and Santra[39] performed impact strength properties on fly ash filled epoxy composites and compared that with NBR-toughened and CTBN-toughened epoxy systems. Ramakrishna et al.[195] prepared the composites using unsaturated polyester as matrix and fly ash and granite powder as fillers and reported that the tensile and flexural strengths are inferior for fly ash filled composites as compared to those for granite filled composites. In recent communications, they studied on epoxy-fly ash composites, having epoxy toughened with poly methyl methacrylate[196] (PMMA) and with 20% epoxy phenol cashew nut shell liquid [197] as matrix.

Atikler et al.[198] reported that the surface treatment of fly ash by 3-amino propyl triethoxy silane significantly improves the strength properties of High Density Polyethylene (HDPE)-fly ash composites. Narayan et al.[199] prepared the poly aniline/fly ash composites by in-situ polymerization technique and reported that the dc conductivity of the composites is found to be decreasing with fly ash loading. Ray and Gnanamoorthy[200] studied the friction and wear behavior of fly ash filled vinylester resin and reported an improvement in wear resistance with increase in fly ash loading in the matrix. Acharya and Mishra[201] studied the weathering behaviour and flexural strength of composites having fly ash and jute with epoxy as binder. Hashmi et al.[202] studied the thermal and rheological behavior of Low Density Polyethylne (LDPE) filled with ultra fine fly ash. Patnaik et al.[203] developed a mathematical model to estimate the erosion damage caused by solid particle impact on fly ash filled glass fiber reinforced polyester composites. The surface treatment of fly ash cenospheres by organosilane reported to be enhancing the dynamic behaviour and impact resistance of epoxy/cenospheres composites[204]. Deepthi et al.[205] reported that the surface modification of cenospheres followed by compatibilization led to a substantial improvement in mechanical properties and thermal stability of HDPE/Fly ash composites, Keya Das et al.[206] developed recycled polypropylene composites reinforced with fly ash and studied its flexural strength, water absorption and thermal degradation behaviour.

1.2.8.2. Fly Ash in Rubber Matrices

Capp and Makovsky[207] in 1972 tried sintered fly ash in rubber formulations in view of increasing the skid and wear resistance, but failed to get positive results. Kruger et al.[208] studied the effect of loading fly ash on the processability characteristics and mechanical properties of the natural rubber (NR) composites. They reported that the spherical shape of fly ash aided easy processing by reducing the NR compound viscosity. Garde et al.[44] studied the effect of surface treated fly ash as a reinforcing filler on the technical properties of polyisoprene rubber composites and reported that only limited reinforcement could be achieved with surface treatment attributed to the lack of bound rubber formation. Hundiwale et al.[209] reported that the mechanical properties of fly ash filled natural rubber composites are superior to those with calcium carbonate filled NR composites. They also reported the use of fly ash as the filler in Styrene Butadiene Rubber[42] and in polybutadiene rubber[43]. In both the cases, untreated fly ash gave marginal improvement in technical properties, but showed better performance after silane treatment. Cokca and Yilmaz[210] reported the use of powdered rubber and bentonite mixed with fly ash as a liner material for construction industry. Alkadasi et al.[211] reported an improvement in tensile strength by 50% and modulus by 400% for polybutadiene-fly ash composites, by using titanate coupling agent treated fly ash as filler. In another communication[46], they reported the use of fly ash treated with silane and titanate coupling agents in chloroprene rubber.

Sompatsompop and his coworkers had done extensive research on the use of fly ash in elastomer applications. They compared untreated fly ash and silica for their reinforcing capabilities in NR and SBR[43], and concluded that the silica excels over fly ash in its technical performance. They found out in a later study that the optimized dose[212] of silane coupling agent is 2 to 4% for fly ash to achieve good technical properties in NR composites. The use of NaOH[213] as a surface modifier for fly ash was reported in their laboratory recently. Their research group explored the possibility of using silica from the fly ash as a reinforcing filler in NR/SBR blend system[214]. They carried out an in-depth study on the thermal ageing characteristics of these blend system with Si69 treated fly ash[215]. The use of fly ash silica as filler yielded better elastic response[216] than those with precipitated silica in natural rubber compounds. Studies on viscosity, cure characteristics and viscoelastic properties[217] were also carried out by Sombatsompop's research group and reported that NR composites with fly ash as filler had shown lower viscosity and thereby higher processability than those with precipitated silica. Recently, they compared the cure characteristics, mechanical properties and oil resistance of fly ash-acrylonitrile butadiene rubber (NBR) composites[218] with those of NBR composites containing precipitated silica as filler. Effect of fly ash loading on the viscoelastic properties[219] of fly ash-NR composites have been reported in their recent research publication. Kantala[220] of Sompatsompop's research lab, used fly ash as reinforcement for compatibilized blends of NR/NBR and compared its performance with precipitated silica filled NR/NBR blends. Thongpin et al.[221] reported that the use of fly ash as a second filler in Si69 treated precipitated silica/NR composite to improve the tensile strength and modulus, but experienced a decrease in elongation at break. Their study on cellular NR/SBR vulcanizates[222] reported that the fly ash filled composites show superior elastic recovery in comparison with the composites containing carbon black and silica as fillers.

Mishra et al.[223] compared the mechanical and flame retarding properties of polybutadiene rubber filled with nanoparticles and fly ash. Alkadasi et al. studied separately the effect of titanate coupling agent on the mechanical properties of fly ash filled SBR[224] and chloroprene rubber[225]. Hossain[226] studied the effect of titanate coupling agent on the rheological properties of fly ash-isoprene rubber composites. Menon et al.[227] put forth another approach to modify the fly ash surface by treating with cardanol derivatives. Improvement in mechanical properties was obtained for cardanol treated fly ash-NR composites. Mishra and Shimpi[228] compared fly ash with nano-sized $CaCO_3$ as well as conventional $CaCO_3$ by using them as filler in polybutadiene rubber and studied the mechanical, thermal, and flame retarding properties of the composites. They reported that fly ash shows inferior performance as compared to nano-sized $CaCO_3$. Wu and

Chen[229] recognized fly ash as an excellent filler that can be used as replacement for silica for reclaimed rubber-fly ash composites. Ismail and Kheong[230] studied the effect of Si69 on the tensile properties, swelling behaviour and morphological characteristics of recycled poly (vinyl chloride)/ NBR/fly ash composites. Sridhar et al.[231] used fly ash as a reinforcement in thermoplastic elastomers prepared from waste tire powder and reported that the fly ash particles show more affinity towards rubbery phase rather than plastic phase.

1.3. Scope of the Present Work

The major obstacle in using fly ash as a filler in polymer and rubber industries is its lack of reinforcing ability in these matrices, which may be attributed to the following reasons as presented below

(i) Larger particle size (varying from 60µm to 250µm),
(ii) Presence of smooth and spherical surface finish,
(iii) Presence of crystalline structures (11–18%) and
(iv) inactive surface

Not much research has been reported on tackling these issues in the literature. An approach of modifying the fly ash surface physically or chemically, in view of improving the rubber-filler interactions have never been addressed by the researchers. There is a tremendous scope in addressing these issues scientifically to make this waste fly ash as a resourceful material in the polymer and rubber industries. In this thesis the concept of ‘nano’ has been introduced for the first time for fly ash and attempts have been made to develop ‘nanomaterials’ from fly ash. Mechanical activation is taken as a tool to reduce the particle size from micron to nano scale by adapting the ‘top-down’ process popularly practiced in nanomaterial development. Through this process, the crystallinity could be reduced drastically and the morphology of the fly ash particles could be changed significantly. Mechanical activation by ball milling technique leads to nanomaterial development which is inexpensive, adaptable and can be scaled up for large quantity production in fuure. The resulting nanostructured fly ash (NFA) may act as a reinforcing filler in rubber opening up a new era in the utilization of fly ash as a cheap reinforcing filler in comparison with conventional reinforcing fillers in rubber and polymer industries. As per the composition of the fly ash, it closely tally with the silica filler, where silica is the major constituent in it and the minor constituent being alumina, which can also be used as a reinforcing filler. Further modification of the surface of NFA may be done as and when required to enhance the rubber-filler interaction between inorganic fly ash and organic hydrocarbon chains, thereby improving the technical properties of the rubber composites.

1.4. Objectives of the Current Research

i. To convert the micron-sized Fresh Fly Ash (FFA) particles into Nanostructured Fly Ash (NFA) by mechanical activation, a top-down process usually applied in nanotechnology in the preparation of nanomaterials.

ii. To characterize the NFA for its particle size, surface area, surface energy, surface activity and crystallinity as well as surface morphology after mechanical activation.

iii. To study the effect of NFA as a reinforcing nano-filler in Styrene Butadiene Rubber (SBR) and to compare the NFA-SBR composites with those containing conventional reinforcing fillers such as HAF black and precipitated silica for its physico-mechanical and technical properties.

iv. To modify the surface of NFA by physical and chemical means for improving the bonding with the rubber matrix.

v. To investigate the performance of the surface modified NFA in SBR composites vis-à-vis unmodified NFA-SBR composites at equivalent doses.