



Interparticle interactions and lacunarity of mechano-chemically activated fly ash



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ABSTRACT

A class F fly ash was subjected to high-energy ball milling-induced mechano-chemical activation aided by a surfactant. The resultant nanostructured fly ash was characterized by various techniques. X-ray fluorescence results showed that the amount of iron oxide was reduced from 4.39% to 2.75% after pre-treatment of fly ash by magnetic separation. Ethyl acetate as the milling medium, a ball to powder ratio of 12:1 and 2 wt% of surfactant reduced the average particle size of fly ash to 329 nm and led to a specific surface area of 8.73 m²/g. The decrease in crystallite size of mechano-chemically activated fly ash was confirmed from a reduction in peak intensity with a broadened amorphous phase by X-ray diffraction studies. X-ray photoelectron spectroscopic characterization illustrated that peak area of major elements (O, Si and Al) increased after milling. Morphological and FTIR studies revealed that the smooth and inert surface of the fly ash was converted to a rough and more reactive one after mechano-chemical activation. The surface modification of fly ash with the surfactant was determined from FTIR spectroscopy. Also, a fractal approach was used to characterize the lacunarity of the agglomerates in the nanostructured fly ash.

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1. Introduction

Worldwide production of ultrafine particles has undergone a big expansion during the last few years. This significant increase comes from the unique properties of nanoparticles, such as high surface area-to-volume ratio, controlled functionality and greater reactivity [1]. The synthesis of nanostructured particles by different processes, such as mechanical milling, sol-gel synthesis and chemical deposition has provided the means to tailor their physicochemical parameters, such as agglomeration mechanism. With the growing interest in advanced materials using nanoscale building blocks, there is a need to control the sizes and shapes of nanoparticles, as their physical and chemical properties depend on these aspects. The use of nanoparticles as advanced materials in various applications requires them as non-agglomerated, uniform particles with a controlled mean size and a narrow size distribution [2,3]. This strategy offers relevant advantages over traditional materials in numerous industrial applications.

The top-down process of producing nanoparticles by high-energy milling is a versatile alternative to other processing routes. Mechanical milling is a solid-state powder processing technique that involves repeated welding, fracturing and rewelding of powder particles in a high-energy ball mill. The process of ball milling starts by loading the sample into the mill along with the grinding medium. The sample is

then milled for the desired length of time based on the requirements. Thus, the important components of the ball milling process are the raw material(s), the mill, and the process variables [4]. Mechanical activation occurs due to compression, shear (attrition), impact (stroke) and impact (collision) forces acting between two grinding media beads or between grinding media beads and the inner wall of the vial. The ball milling process is greatly affected by a number of factors, such as type of mill, extent of vial filling, milling temperature, type and size of balls, ball-to-powder weight ratio and time of milling [5,6]. The properties of the milled powders, such as the particle size distribution, degree of disorder or amorphisation and the final stoichiometry depend on the abovementioned factors [7,8]. The merit of using mechanical activation for improving bulk and surface reactivity of powders is well accepted by the scientific community. Mechanical activation offers the possibility of altering the reactivity of solids through physicochemical changes in bulk and surface without altering the overall chemistry of the material [9,10].

Fly ash (FA) is a by-product of the combustion of pulverized coal in electric power-generating plants [11]. Upon ignition in the furnace, most of the volatile matter and carbon in the coal are burned off. During combustion, coal's mineral impurities (such as clay, feldspar, quartz and shale) fuse in suspension and are carried away from the combustion chamber by the exhaust gases. Subsequently, the fused material cools and solidifies into spherical glassy particles called FA, which is then collected from the exhaust gases by electrostatic precipitators or bag filters [12]. Particles of FA are often spherical and range in size from 0.5 μm to

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100 μm . It consists of inorganic, incombustible matter, which includes substantial amounts of silicon dioxide (SiO_2), alumina (Al_2O_3) calcium oxide (CaO), iron oxide (Fe_2O_3) and minor amounts of K_2O , Na_2O , P_2O_5 , MgO and ZrO_2 [13]. Worldwide, studies have been carried out towards management of disposal and utilization of FA [14]. Among numerous factors that account for the low level of FA utilization are: poor understanding of the chemistry of FA, absence of standards and specifications for FA products and lack of reliable quality assurance for FA products. FA is often divided into two classes: class F and class C on the basis of iron and calcium levels. The FA that contains more than 70% oxides of silicon, aluminum and iron of the total composition with Fe_2O_3 content higher than that of CaO belongs to class F [15].

In this study, we subjected a class F Indian FA to high-energy ball milling with the objective of producing nanostructured FA, which could be used as value-added reinforcement in polymer matrix composites [15]. The mechano-chemically activated FA (MCA-FA) was characterized by X-ray diffraction (XRD), X-ray photoelectron spectrometry (XPS), Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) to understand the compositional and morphological changes upon high-energy ball milling. Also, a fractal approach by diffusion-limited agglomeration was used to characterize the lacunarity of the agglomerates in the MCA-FA.

2. Materials and methods

2.1. Materials

FA was kindly supplied by Raichur thermal power station, Karnataka, India. The non-ionic surfactant (Triton X-100) procured from Sisco Research Laboratories, Mumbai, India and the solvent ethyl acetate obtained from Nice Chemicals Pvt. Ltd, Cochin, India had a purity of >99% and were used without further purification.

2.2. Pre-treatment of FA

As-received FA was washed in demineralized water and the carbon that creamed up during washing was removed. It was then dried at 100 °C for 5 h to remove water. This dried FA (called as fresh FA) was sieved using British standard sieves ranging from 150 to 350 meshes. Fresh FA fractions that passed through mesh no. 170, but was retained on mesh no. 200, were collected, as it gave 25% by weight of the total FA taken for sieving. Later, magnetic separation was carried out manually to remove the magnetic impurities. The resultant FA was mechano-chemically activated subsequently.

2.3. Mechano-chemical activation of FA

Mechano-chemical activation of FA was achieved using a high-energy planetary ball mill (Retsch PM 100, Germany). A balls-to-FA weight ratio of 10:1 was used. The milling chamber and balls were made of tungsten carbide; the ball diameter was 10 mm and rotation speed of the planet carrier was 250 rpm. The milling was carried out for 48 h in ethyl acetate medium along with 2 wt% of non-ionic surfactant Triton X-100 to reduce agglomerations of FA particles.

2.4. Characterization of fresh FA and MCA-FA

XRD measurements were carried out to find the crystallite size and lattice strain of fresh FA and MCA-FA, using a goniometer (JEOL DX-GE-2P, Japan) using $\text{CuK}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$) at an accelerating voltage of 30 kV and a current of 20 mA. The samples were scanned at a speed of 1 deg min^{-1} in the 2θ range from 10° to 90°.

Dynamic light scattering (DLS) equipment (Scatteroscope I, Qudix Inc., South Korea) was used to measure the hydrodynamic sizes and size distributions of fresh FA and MCA-FA particles in either aqueous or glycerol media.

The specific surface area of the MCA-FA was measured by a surface area analyzer (Smart Sorb 92/93, Smart Instruments, India). The surface area of MCA-FA was calculated at an accuracy of $\pm 5\%$ for 1 g of sample by Brunauer–Emmett–Teller (BET) method. The sample was first regenerated to remove the adsorbed gases and moisture from the surface by degassing under a vacuum at 350 °C. Surface area was calculated by measuring the volume of N_2 adsorbed using a modified single-point BET equation.

FTIR spectroscopy (Jasco FTIR 4200, Japan) was employed to examine the characteristic structural features of the fresh FA as well as MCA-FA samples in transmission mode by KBr pellet method in the wave number region from 4000 to 400 cm^{-1} at an average of 32 scans with a spectral resolution of 0.5 cm^{-1} .

FESEM (LEO SUPRA55, Carl Zeiss, Germany) and SEM (JEOL-JSM-6380LA, USA) were used to image the texture and morphology of fresh and MCA-FA. The samples for FESEM were prepared by dip-coating of the dispersions of the samples in ethyl acetate on a silicon wafer. For SEM analysis, the samples were sputtered with gold in a sputtering unit (JEOL JFC 1600, auto fine coater, USA) to make their surfaces conductive. The images were taken at suitable accelerating voltages for the best possible resolution using secondary electron imaging. TEM (JEOL JEM-2100, Japan) images were obtained at an accelerating voltage of 120 kV, after dispersing a representative sample of MCA-FA on a 200 mesh carbon-coated copper grid.

The elemental compositions of fresh FA, sieved FA and magnetically separated FA were determined by an X-ray fluorescence (XRF) spectrometer (Axios^{max} PANalytical, Netherlands) using glass discs prepared by fusing the FA sample with lithium tetraborate.

Also, a dynamic contact angle analyzer (FTÅ 200, First Ten Angstroms, USA) was used to determine the wettability of fresh FA and MCA-FA pellets obtained by using a hydraulic press. Test liquid (10 μL of double-distilled water) was dispensed using a micropipette on the surfaces of the fresh FA and MCA-FA pellets. The images of liquid spreading were recorded at specific intervals of time. The captured images were analyzed by FTA software to determine the static contact angles of the droplets on the substrates.

XPS data were obtained using a Thermo Fisher K-alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA) using $\text{Al K}\alpha$ radiation (12 kV, 6 mA). The powder samples were pelletized and mounted with a double-sided adhesive tape onto the probe tip. The working pressure in the spectrometer was 10^{-8} to 10^{-9} Pa and the electron take-off angle was 90°. The area under Si 2p, O 1s, C 1s and Al 2p peaks were divided by the photo-ionization cross-sectional area to calculate the concentration of each element present in the sample.

Table 1
XRF results of fresh FA, sieved FA (−170# + 200#) and magnetic separated FA.

Sample designation	Oxide composition in percentage (%)										
	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	MgO	Na_2O	P_2O_5	TiO_2	W	ZrO_2
Fresh FA	62.68	27.05	3.72	2.46	1.18	0.92	0.08	0.26	1.6	0.02	0.08
Sieved FA	64.17	25.38	4.39	2.6	1.24	0.90	0.08	0.26	1.6	0.02	0.08
Magnetically separated FA	65.24	25.39	2.75	2.64	1.27	0.85	0.08	0.26	1.6	0.02	0.08

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