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Preparation of free flowing fly ash granules containing multifunctional molecules

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Abstract

A new approach for the granulation of fly ash powder is studied. The fly ash dispersed in aqueous medium at pH > 10 in the presence of multifunctional molecules such as methylol urea, triethanol amine, glycerol, glucose and pentaerythritol, was centrifugally separated, dried to a moisture content < 0.5 wt.% and then granulated by rotation granulation. Loosely packed powder agglomerates are produced by particle bridging by the multifunctional molecules through hydrogen bonding. The flow property of the powder is remarkably improved by the granulation process. The granules redisperse in aqueous medium, even after heating at 400°C, without any appreciable increase in primary particle size. The heated fly ash granules disintegrate to the primary particles and the particles disperse well in polyester resin by simple stirring.

Keywords: Preparation; Fly ash granules; Multifunctional molecules

1. Introduction

Fly ash is a by product of thermal power stations where coal is used as fuel. Primarily fly ash contains fine silica and alumina along with minor amounts of calcium and magnesium oxides. The ash content varies between 5 and 30 wt.% depending on the sample of coal. The conventional practice of disposal of this waste material poses serious environmental pollution. A number of attempts for safe disposal of this material have been made, some of them being immobilization in cement compositions, wet chemical treatments and vitrification process [1]. Recently, emphasis has been given for making value added products from fly ash. Some of these products are bricks, concrete blocks, vibrated paving slabs and tiles [1–4]. In addition, incorporation of fly ash in a metal matrix results in composite material which has improved properties and reduced cost [5]. Fly ash –polymer composites have been reported to be excellent for roofing and partition applications. Fly ash occurs as fine powders with a particle size in the micron to sub-micron range and, therefore, handling of dry powder becomes difficult. Further, fly ash particles get agglomerated due to moisture in the atmosphere and, therefore, makes it difficult to achieve uniform distribution of the fine powders in the above composites. Hence, treatment of fly ash for obtaining free flowing granules which can be easily redispersed, becomes increasingly important in making use of fly ash efficiently. Kilgour et.al. proposed a granulation process for storage of high calcium fly ash powder for later uses [6].

Granulation is a process generally used in powder processing to make the fine powders free flowing [7–9]. In addition, granulation minimizes physical segregation of the powder in the powder forming process. It also helps to control environmental pollution due to particulate emission during processing [7]. In ceramic powder processing, the particles in each granule must be fully deagglomerated since the origin of the agglomerates present in the powders are often of strength limiting flaws in sintered bodies [10]. The deagglomeration of powders is most effective by milling in aqueous medium. However, reagglomeration of powders is observed during drying of dispersions [11,12]. The granules prepared from these dispersed slurries become hard agglomerates and do not easily deform on further processing, which limits

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the extent of compaction of the powders. Recently, water soluble surface complexing agents such as acetyl acetone, diethanol amine and citric acid were used to prevent the agglomeration of nanoparticles during osmotic consolidation from aqueous medium [13]. These molecules act as hump and prevent the particle–particle contact.

The present work is an attempt for the deagglomeration and granulation of a fly ash powder using multifunctional molecules. Multifunctional molecules are regarded as water soluble molecules with two or more functional groups such as OH and NH groups. The structure of multifunctional molecules used in the present study is given in Fig. 1. These molecules, adsorbed on the surface, would prevent the particle–particle contact in aqueous medium by acting as hump. On the other hand, during drying, they would bridge the fine particles through hydrogen bonding interactions, which would result in loosely packed granules.

2. Experimental

Fly ash used in the present study was supplied by the Materials Department, University of Wisconsin, Milwaukee. The composition of the fly ash is given in Table 1. It has an average particle size of 3.1 μm and surface area 3.2 m^2/g. Other chemicals used were urea (s.d. Fine chemicals India), formaldehyde (37% solution, s.d. Fine chemicals India), triethanol amine (BDH Bomby), glycerol (s.d. Fine chemicals India), glucose (E-Merck India) and pentaerythritol (CDH India). Distilled water was used for the preparation of dispersions. Dilute solutions of reagent grade sodium hydroxide and nitric acid were used for pH adjustment. The fly ash used for the experiments was heated at 600°C for 3 h. The dispersion behaviour of the fly ash in aqueous medium was studied by measuring the viscosity of a 70 wt.% suspension at various pH values in a Brook field viscometer(RVT model, spindle SC4/21).

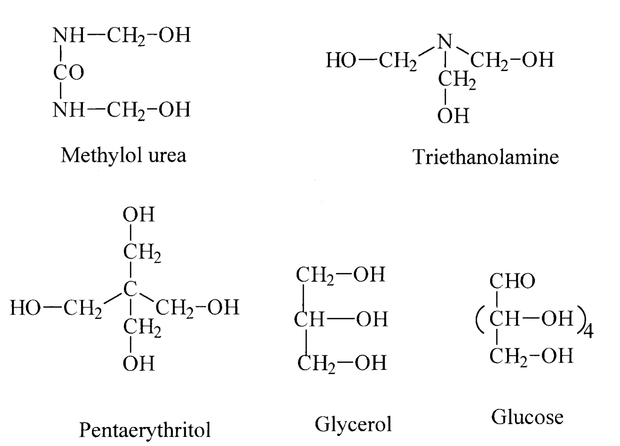

Fig. 1. Structure of the multifunctional molecules.

A 50 wt.% aqueous dispersion of the fly ash is prepared and the pH is adjusted to 10.5. Various amounts of the multifunctional molecules (except methylolurea) are added to the dispersions and ball milled in polyethylene containers using zirconia balls for 6h. The methylol urea is generated in situ from urea and formaldehyde in the ratio 1:2 [14]. The particles are then centrifugally separated and dried at a temperature below 70°C to a moisture content $<0.5\%$. The powder was then granulated by rotation. The granules were separated by sieving through a standard mesh (No. 22). The amount of multifunctional molecules retained after centrifugal separation was estimated from thermogravimetric analysis (thermal analyst 2000). A relative measure of the flow property of as received and granulated powders was obtained as per ASTM by noting the time taken by 50 g of the powders to flow through a funnel [15]. The particle size was measured in a particle size analyzer (Micromeritics sedigraph 5100). The microstructure of the granules was observed under a scanning electron microscope (Jeol JSM-35).

The heat treated granules are dispersed in polyester resin by stirring, using a glass rod, and then the resin was cured at ambient temperature using methyl ethyl ketone peroxide initiator and cobalt naphthanate catalyst. The dispersion of powder in the composite was observed on a polished surface under optical microscope.

3. Results and discussions

Ceramic powders are dispersed in aqueous medium either by adjusting the pH of the medium away from the iso-electric point of the powder or using a suitable dispersing agent [16]. Viscosity measurement is one of the methods commonly used to assess the dispersion of powders such that well dispersed systems show low viscosity values. Fig. 2 shows the viscosity of a 70 wt.% aqueous fly ash dispersion measured at various pH. The dispersion shows minimum viscosity at pH in the range of 10–11. In this pH range, the major components of fly ash such as alumina and silica acquire negative surface

Table 1
Composition of the fly ash

Components	Wt.%
Silica	54.7
Alumina	29.1
Iron oxide	6.7
Titanium oxide	1.6
Calcium oxide	1.1
Magnesium oxide	1
Sodium oxide	0.4
Potassium oxide	2.6
Sulphur trioxide	<0.1
Phosphorous pentoxide	0.3

charge by deprotonation of the surface hydroxyl groups. Therefore, the treatment of fly ash with multifunctional molecules is carried out at 10.5 pH at which the deagglomeration of the powder is most effective.

The multifunctional molecules are expected to get adsorbed on the powder particle surface. During centrifugal separation, the molecules adsorbed on the powder surface is retained and that present in the dispersion medium are removed. The amount of multifunctional molecules retained in the powder is estimated by thermogravimetric analysis and the results are given in Fig.3. There is a remarkable increase in the amount retained in the powder surface up to 3 wt.%. Further

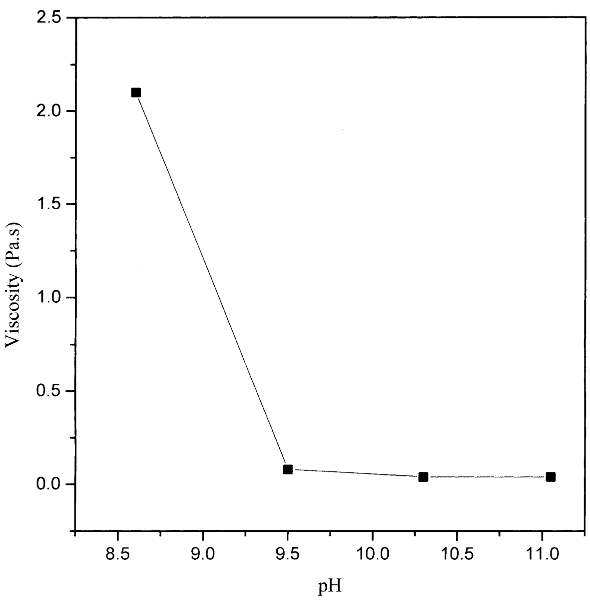

Fig. 2. Viscosity versus pH of the aqueous fly ash dispersions.

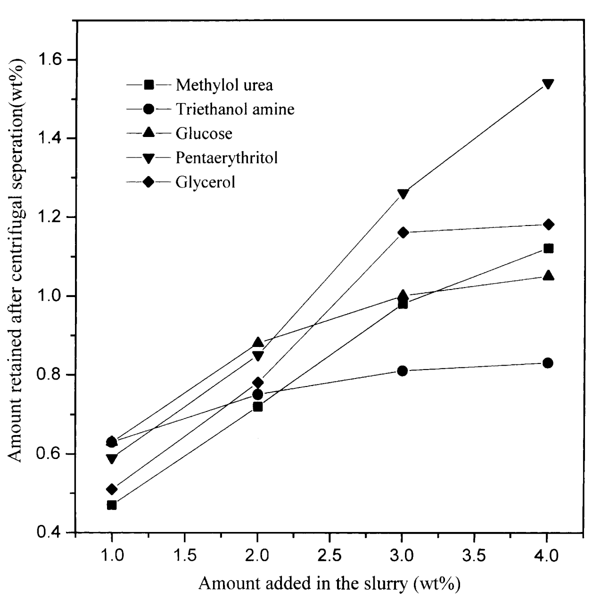

Fig. 3. The amount of multifunctional molecules retained in the powder versus the amount added in the slurry.

increase is marginal, even when a large concentration of the additive is used. The amount retained in the powder is highest for pentaerythritol. In the case of methylol urea, at lower concentrations, the amount retained in the powder is lower than that of triethanol amine and glucose. However, at higher concentration, the amount of methylol urea retained in the powder is higher than that of the other two. At all concentrations, the amount retained in the powder is the lowest for triethanol amine. The difference observed in the amount of multifunctional molecules retained in the powder is due to the difference in the partition of the molecules between water and the powder surface. The highest amount retained in the case of pentaerythritol is due to its relatively lower solubility in cold water.

The powders treated with the multifunctional molecules, after drying, on rotation formed stable granules except that treated with pentaerythritol. However, the powder treated with pentaerythritol formed large agglomerates of a few millimeter size which shows very low handling strength. On the other hand, the powder subjected to the same treatment without multifunctional molecules did not undergo granulation. The minimum amount of different multifunctional molecules required for granulation is given in Table 2. Granulation of fly ash powder is observed at 1 wt.% of multifunctional molecules retained in the powder. The granules produced have near spherical geometry. The morphology of the granules is shown in Fig. 4. The spherical geometry of the granules results in a better flow property of the powder. A relative measure of the flow property of granules prepared with different multifunctional molecules is given in Table 2. The time required by 50 g powder to flow through a funnel is noted as flow time. The as received powder shows a flow time of 13.6 min. The flow time of the powder decreased due to granulation and reached a value as low as 0.83 min. The minimum flow time of 0.83 min is observed for the powder granulated with both glucose and glycerol. The powder granulated with methylol urea and tri-ethanolamine showed more or less same flow time, nearly 1.3 min. However, the powder

Table 2
Minimum amount of various multifunctional molecules required for granulation of the fly ash and the flow time of granules

Sample treated with	Minimum amount of multifunctional molecule required for granulation (wt.%)	Flow time (min/50)	Decrease in flow time (%)
Untreated	–	13.6	–
Triethanol amine	0.81	1.29	0.5
Methylol urea	0.98	1.37	89.9
Glycerol	1.16	0.83	93.9
Penta erythritol	1.26 (Large granules are obtained)	9.1	33
Glucose	0.88	0.83	93.9

treated with pentaerythritol showed high flow time of 9.1 min. The granules are found to be stable after the removal of multifunctional molecules by heating at 400°C for 1 h. The flow time is further improved due to the heat treatment at 400°C except in the case of the powder treated with pentaerythritol. This is due to the decrease in inter-granule adhesion by the removal of the multifunctional molecules from the powder surface. On the other hand, the powder treated with pentaerythritol becomes fluffy on heat treatment, which resulted in the increase of flow time.

The powder particles in the granules are loosely packed. Fig. 5 shows the scanning electron micrograph of the granules. The granules prepared with all multifunctional molecules spontaneously dispersed when added to water and the particle size analysis of the dispersions shows no increase in particle size. When heated at 400°C and then redispersed in water, the granules dispersed well except that prepared using glucose. Fig. 6 shows the particle size distribution of the dispersion prepared in aqueous medium from fly ash as received and granules prepared with triethanol amine and glucose, after the heat treatment. The dispersions obtained from the granules prepared with methylol urea, glycerol and pentaerythritol showed more or less similar particle size distribution as that of the granules prepared with triethanol amine. The study suggests that the dispersion and granulation of fly ash powder with multifunctional molecules did not produce hard agglomerates during drying and heat treatment up to 400°C. The dispersion obtained from the granules prepared with glucose show remarkable increase in particle size. This may be due to the particle bridging by carbon residue produced by the pyrolysis of glucose.

In the dispersion state itself, the multifunctional molecules expected to interact with the powder surface by the OH or NH groups through hydrogen bonding which would promote the powder dispersion due to steric repulsion. While drying the powder obtained by centrifugal separation of the dispersions, the multifunctional molecules bridge the particles through weak hydrogen bonding. The possible ways of interaction between particles through the multifunctional molecules is given in Fig. 7. These weak interactions between particles through the multifunctional molecules makes the granulation possible and prevent the direct particle–particle contact and formation of hard agglomerates during drying.

The fly ash granules, after heat treatment at 400°C, can be easily blended with polyester resin and thus get dispersed very uniformly after getting disintegrated to primary particles. Fig. 8 shows the microstructure of

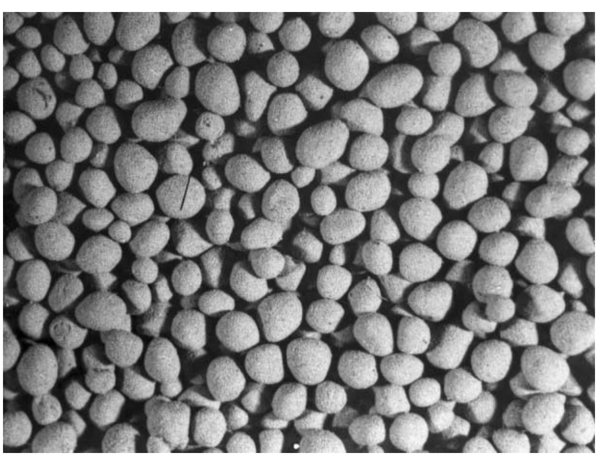

Fig. 4. Optical micrograph showing morphology of the fly ash granules (×10).

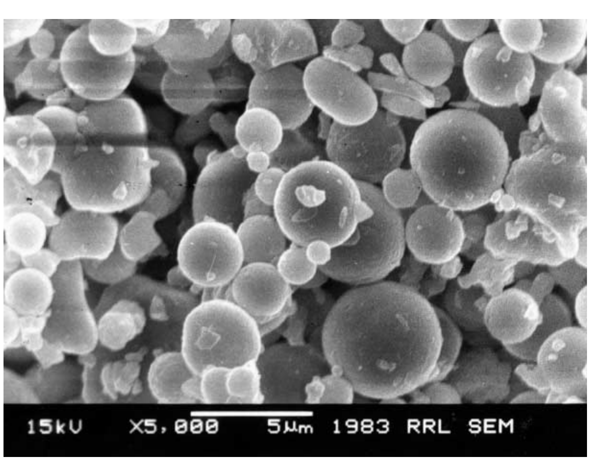

Fig. 5. Scanning electron micrograph showing loose particle packing in the fly ash granules.

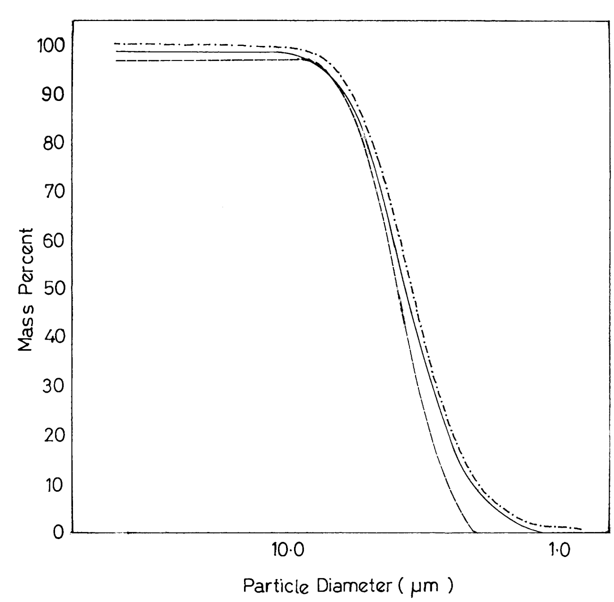

Fig. 6. Particle size distribution of fly ash powder dispersed in aqueous medium (– · – as received powder, — heated treated granules prepared using tri ethanolamine, - - - - heat treated granules prepared using glucose).

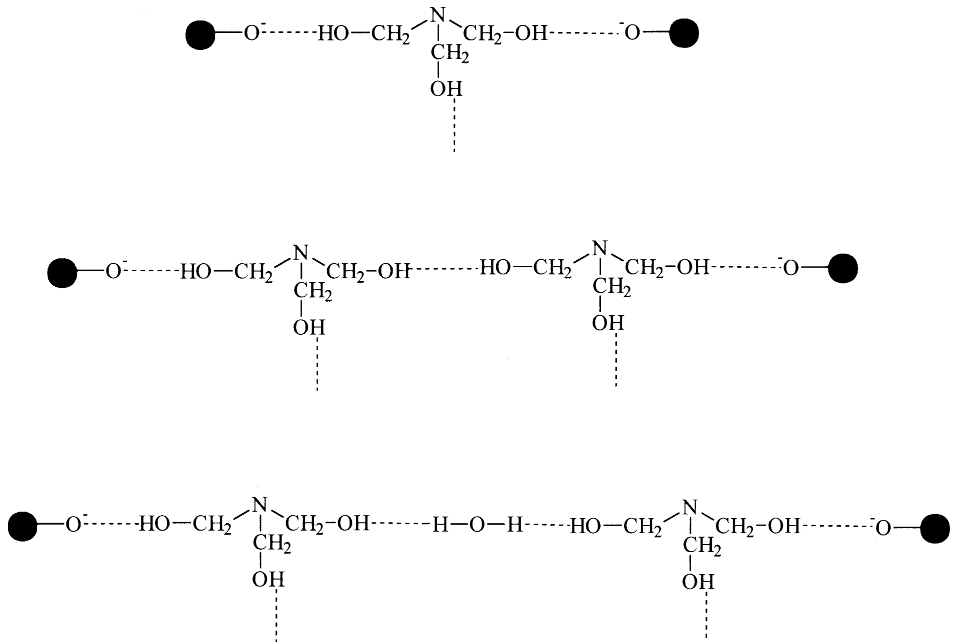

Fig. 7. Possible interactions between fly ash particles through multifunctional molecules (●: fly ash).

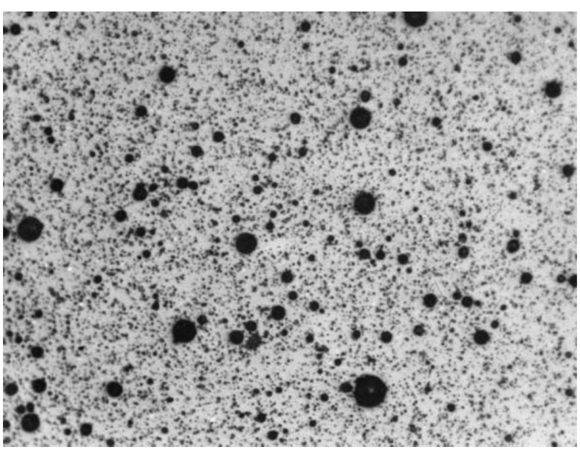

Fig. 8. Optical micrograph showing excellent dispersion of the treated fly ash powder in polyester matrix (×50).

polyester–20 vol.% fly ash composite showing excellent dispersion of the powder in the matrix.

4. Summary and conclusions

A new approach for the granulation of fly ash powder is studied. Multifunctional molecules such as methylol urea, triethanol amine, glycerol and glucose bridge the fly ash particles through hydrogen bonding interactions which resulted in the formation of loosely packed, free flowing granules. The multifunctional molecules prevent the formation of hard agglomerates during drying of the aqueous powder dispersions. The granules retain their spherical shape and showed further improvement in flow property after the removal of the multifunctional molecules by heating at 400°C. The granules when subjected to heat treatment at 400° C, redisperse in aqueous medium without appreciable increase in primary particle size. Excellent dispersion of the fly ash in polyester matrix was obtained by simply stirring the heat treated granules with the resin.

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