

Research on the Whiteness and Properties of Modified Coal Fly Ash

Guanjie Zhai^{1,3}, Yufen Yang^{2*}, Guosheng Gai², Ping Wu¹, Barry E. Scheetz³ and Della M. Roy³

¹Fly Ash Research Institute, Dezhou University, Shandong, 253023, China;

²Department of Material Science and Engineering, Tsinghua University, Beijing 100084, China; ³Materials Research Institute, The Pennsylvania State University, University Park, PA 16802-6809, USA

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ABSTRACT

In the filling of polymer, coal fly ash has been limited in use by its unlovely grey color. In order to improve the qualities of coal fly ash from Huaneng Power international Incorporation Dezhou Power Plant, its meso-structure and influencing factors on whiteness have been tested and analyzed. Ca(OH)₂-H₂O-CO₂ system to modify the fly ash is conducted. Round coating testify that the system can be achieved under suitable operating parameters. Experimental data show that the method of modification and whitening is available. Compared to raw fly ash, the coated fly ash is of high whiteness with 73.13, high specific surface area with 9.77 m²·g⁻¹ and high coating ratio next to 100%. Filling-test in polymer also show that rough surface of coated fly ash enhances the area of the material contacting as well as improve the matching state between fly ash beads (also contain a small quantity of cenosphere) and polymer granules when they are blended.

1. Introduction

In order to reduce cost of polymer-based composite materials and improve some properties what people hope, kinds of common inorganic mineral fillers such as silicate, carbonate and talcum powder are usually used to fill in polymer^[1].

FA (fly ash) purified would be seem filling in polymer because of lower density and good dispersion and fluidity. However, the use of FA as filler hasn't been widely

generalized in polymer up to now, the following two reasons can explain why. Firstly, interfacial bonding between FA and polymer is weak because of its slippery surface. Secondly, FA presents grey which reduces user's interest and has lower whiteness which is about 30. Although, using coupling agent or surfactant to modify FA can improve in a certain degree the interfacial consistency between FA and polymer, their color can almost not be improved. These restrict the wide use of FA in polymer. So, in order to meet the demands of plastic and rubber industries to tint fillers, to develop a new technology of fly ash surface modification and enhance their whiteness are all through our research keystone.

2 Experiments

2.1 Preparation

Preparation of coated FA was conducted in $\text{Ca}(\text{OH})_2\text{-H}_2\text{O-CO}_2$ system. In order to obtain pure FA sample from minus 300 mesh fly ash sampled from Huaneng Dezhou Power Plant of Shandong Province. Using a magnetic separator with a weak magnetic field to remove magnetic pearls by, and then to clean unburned carbon by a froth flotation in our lab. Mixing slurry of the FA with calcium hydroxide solution, together with some tap water, at 7:1 weight ratio of water/solid and 3:1 of FA/ $\text{Ca}(\text{OH})_2$ weight ratios, was placed into a reactor. The slurry was stirred with a stirrer and heated up with an electric cooker to a temperature 90°C and lasted for a stated time from 1 h to 8h. The temperature was controlled by a temperature director. To the stated time, the electric cooker was took off and the slurry was cooled to $25 \sim 35^\circ\text{C}$. After cooling, CO_2 gas was passed through the reactor to neutralize the redundant $\text{Ca}(\text{OH})_2$ solution. During carbonization, the necessary pulp circulation and last-stirring were performed to boost reaction between CO_2 and $\text{Ca}(\text{OH})_2$. The reaction was judged to be completed when pH value of the slurry reached 7. Then the slurry was filtered and residue left was dried at 110°C in an oven for several hours till it fully was dried. The dried cake was crashed into powder and cased in a plastic-bag.

2.2 Characterizations

Whiteness was mensurated by ZBD type whiteness-meter produced by Wenzhou Ludong Apparatus Factory of Zhejiang Province. Phase identification was performed by X-ray diffraction (XRD, D/max-RB, Rigaku, Japan). SEM, JSM-6301F type produced by Japan JEOL and CSM-950 type produced by Germany OPTON electron microscopes,

were used to observe the morphology of particles before and after coating. X-ray photoelectron spectroscope (XPS, Finder-1000, Beijing Zhongke KeYi Technology Development Co, Ltd, China) was used to analyze elements within 3nm depth of particle surfaces. These devices using to examine mechanical properties of PP-based composites includes $\phi 30 \times 45$ twin screw extruder produced by German W & P, 150ZP type injecting device from Hongkong Zhenxiong Machinery Co., Ltd, RTM-250 type electron tensile testing systems from American Instron and XJZ - 50 type impacting tester produced by Chengteh Testing Machine Co., Ltd in China.

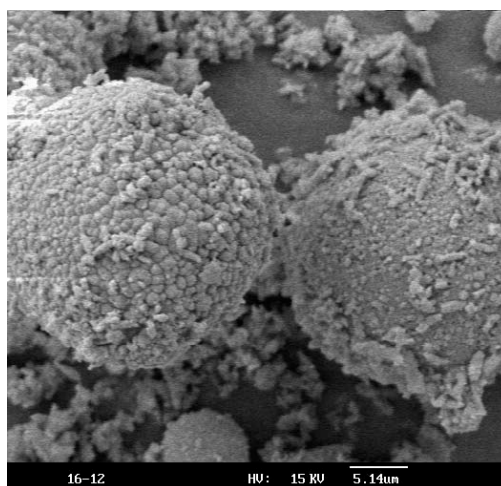
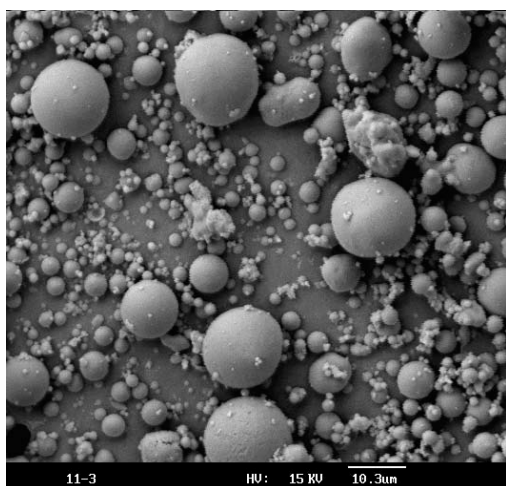
3. Results and discussion

Nearly 100% particles of FA purified are spherical ones(see Fig.1(a)) with good dispersion and fluidity. The main chemical compositions of the FA are SiO_2 and Al_2O_3 which account for near 90%.

SEM morphologies of coated FA are shown in Fig.1(b) and Fig.1(c). One can see from Fig.1(b) and Fig.1(c) that a monolayer coating can be achieved on FA surface. The coating ratio was almost 100% compared with uncoated FA particles in Fig. 1(a). Coated FA has rough surface and high specific surface area increased by 222% from $3.03\text{m}^2/\text{g}$ of the uncoated to $9.77\text{m}^2/\text{g}$ of the coated.

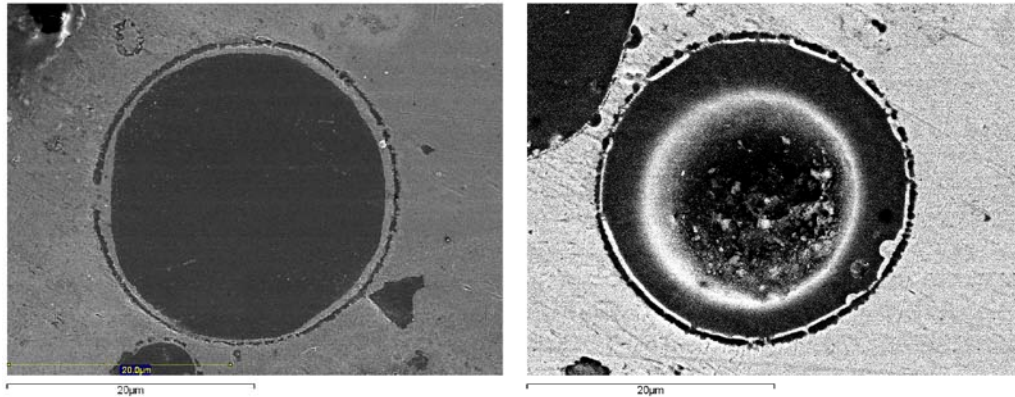
3.1 whiteness

Influencing factors of FA whiteness have many ones, such as the contents of magnetic pearls, unburned carbon and molite content et al. Different samples' code and whiteness are listed in Table1. Sample C is used to prepare coated FA. One can see from Table 1 that the whiteness of sample A is only 29.8. After purification and modification, the whiteness of sample F is enhanced to 66.63, increased by 123.59%. The obvious color difference can be observed by a naked eye for different samples.



(a) uncoated FA

(b) coated FA



(c) section of coated FA

Fig.1 SEM photographs of FA before and after coating**Table 1 Code and whiteness of different samples**

sample	code	whiteness	sample	code	whiteness
Raw FA (minus 300 mesh)	A	29.8	Unburned carbon	D	22.29
FA after removing magnetic pearls	B	33.54	Magnetic pearls	E	9.5
FA after removing magnetic pearls and unburned carbon	C	36.68	Coated FA	F	66.63

3.2 Effect of magnetic pearls on whiteness

Main components of magnetic pearls with a scraggly surface are Fe_3O_4 and magnetic- Fe_2O_3 which were formed by decomposing minerals in coal such as pyrite, magnetite, arsenic-magnetite, et al during combustion in boiler. Its content is 6.73% in raw FA. The magnetic pearls present black and have strong magnetic^[2]. The average grain size is about $20\mu\text{m}$ and whiteness is only 9.5. The content of magnetic pearls has a great influence on whiteness of fly ash. 93% magnetic pearls can be removed from sample A by a small-type magnetic separator with a weak magnetic field in our lab. As can be seen from Table 1, compared to sample A, the whiteness of sample B was increased by 12.55%.

3.3 Effect of unburned carbon on whiteness

Unburned carbon particles with biggish size and anomalistic type mainly concentrating in +300 mesh grain size. The content in sample A is only 2.61%. Although the content is lower, these ultra-fine unburned carbon particles present grey and black color with lower whiteness, 22.29. So, they have bigger effect on whiteness of FA. After unburned carbon being separated from sample B, the whiteness of sample C was increased to 33.68. Erode unburned carbon particles in a single form without conglutination each other, so it is easy to separate them from fly ash by a froth flotation method^[3]. The removing rate of unburned carbon was up to 98% by a small-type flotation separator in our lab.

A great deal of experiments under different conditions had been conducted in order to examine effect of unburned carbon on whiteness of coated FA. Experimental results are shown in Fig.2, in which grey column represents the whiteness after modification of sample B, and blue column indicates the whiteness after modification of sample C. One can see from Fig.2 that the whiteness values, sample C as feedstock, the highest value 73.13, are higher than that, sample B as feedstock, the highest value 60.93. So, the existing of unburned carbon has an obvious effect on quality of coated FA.

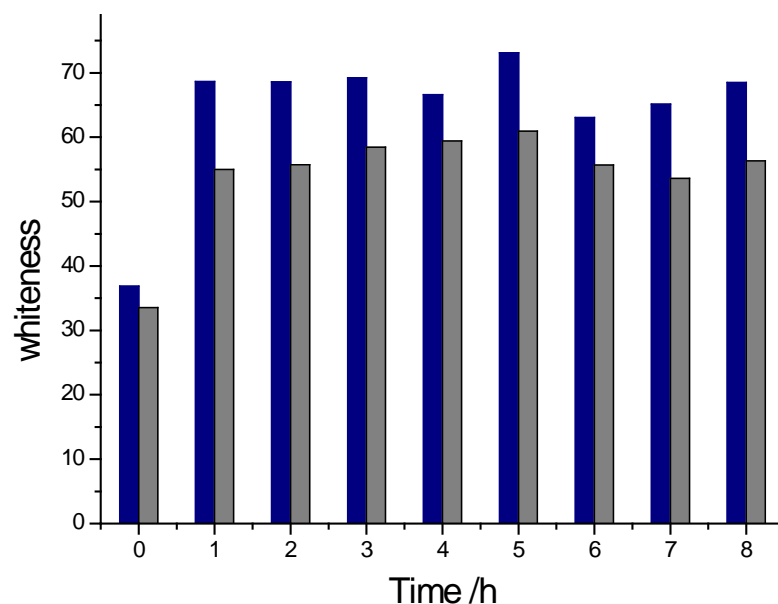


Fig.2 Whiteness comparison of coated FA

3.4 Effect of molite component on whiteness

One can see from X-ray diffraction spectrums of sample C and sample F (shown in Fig.3), the number of diffraction peaks of sample F is more than that of sample C. Strong peaks, middling-strong peaks and weak peaks of molite component are still exist in

sample F. Molite, formed by SiO_2 reacting with Al_2O_3 at high temperature of $1200 \sim 1650^\circ\text{C}$ in a boiler of the power plant, has very stable chemical composition [4]. The preparation of coated FA was conducted below 100°C , so, no change was taken place for molite. In Fig.3, the panes represent calcite formed by CO_2 reacting with $\text{Ca}(\text{OH})_2$ during carbonization and the dots do silicate or aluminate formed by SiO_2 or Al_2O_3 reacting with $\text{Ca}(\text{OH})_2$ before cooling.

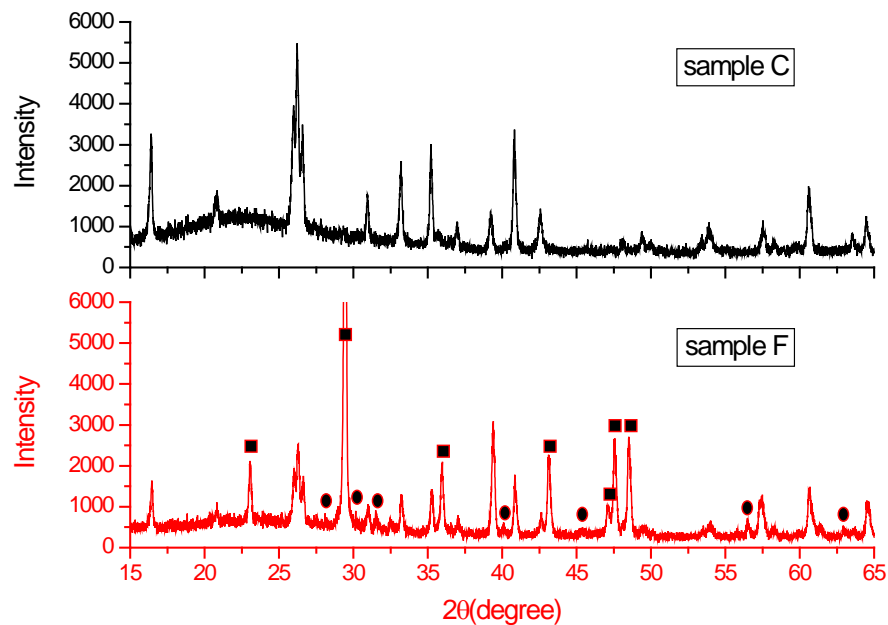


Fig.3 X-ray diffraction spectrum of FA before and after coating

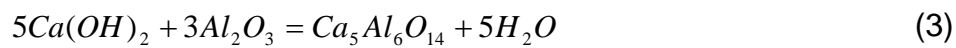
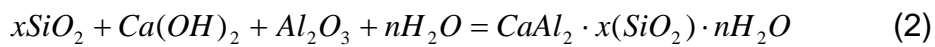
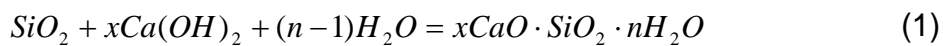
SEM photographs and photoelectric energy spectrums in Fig.4 can also confirm that molite component has stable structure. The obvious phenomena can be observed from Fig.4 that Silicon and Aluminum are main elements on the exposed section and main elements are silicon, Aluminum and Calcium on the coated section.

3.5 Coating Mechanism

By the principle of chemically-activated FA[], reactants formed during heating deposit and grow on FA particle surface. X-ray diffraction spectrums in Fig.3 show that silicate and aluminate compositions such as $\text{Ca}_3\text{Si}_3\text{O}_9 \cdot \text{H}_2\text{O}$ (No.190250) ,

$\text{CaAl}_2(\text{SiO}_3)_4 \cdot 2\text{H}_2\text{O}$ (No. 70326 or 70327) , $\text{Ca}_5\text{Al}_6\text{O}_{14}$ (No.110357) exist in coated FA, which would be reactants between $\text{Ca}(\text{OH})_2$ with active SiO_2 or Al_2O_3 . These reactants coating on FA particle surface not only alter the surface morphology of FA but also enhance the whiteness value of coated FA.

The conceivable chemical reactions in system during heating are the following [5]:



The chemical reactions in system during carbonization after cooling is the following:



CaCO_3 as filler was widely used in polymer all over the world, so, the reactant CaCO_3 mixing with coated FA is beneficial to filling in PP.

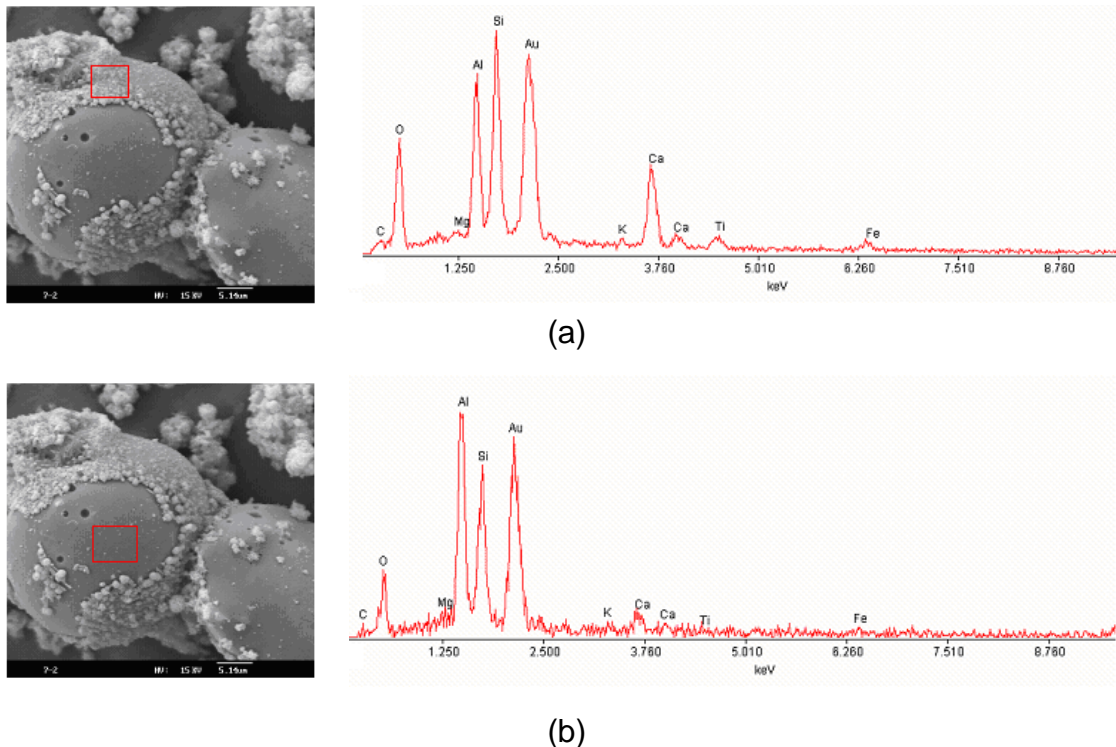


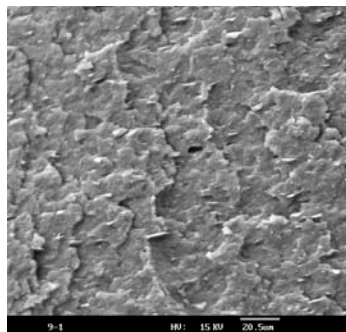
Fig.4 SEM photographs and corresponding energy spectrum of coated FA

4. Filling test

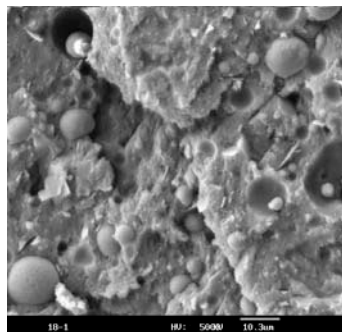
Sample F has been compared with sample C as fillers to PP with 25% filling ratio by our partner, Institute of Plastics Processing and Application of Light Industry as cooperative effort toward practical applications. The mechanical performance tests of the PP-composite materials were performed under the Chinese national standards of GB1040-92 and GB1043-93. Experimental results are shown in Table 2. SEM photographs of composites PP fracture face broken at low temperature cooled by liquid nitrogen are shown in Fig. 5.

Table 2 Mechanical properties of filling sample C and sample F in PP (MPa)

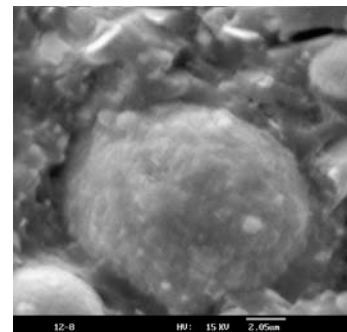
sample	Tensile strength	Fracture strength	Elastic modulus	Impact strength(10KJ/m ²)
Pure PP	18.64	15.10	417.7	19.34
Sample C	14.19	12.08	250.6	4.29
Sample F	17.30	15.07	384.5	6.35



(a) pure PP



(b) uncoated FA filled in PP



(c) coated FA filled in PP

Fig.5 SEM photographs of composites PP fracture face

It can be seen from Table 2 that, compared to uncoated FA as filler, all tested values of mechanical performances of the composites filled coated FA in PP are increased. Impact strength of the PP materials was increased by 48.02%. One can distinctly see from Fig.5(c) that there is close binding and better consistency between the FA and polymer. However, relaxing link and obvious groove and gap exist between the original FA particles and polymer(see Fig.5(b)). The matching effect of coated FA as filler in PP is better than that of original FA as filler in the same PP. Such improvement can mainly be attributable to the changes in surface morphology of coated FA. The coating of ultra-fine

silicate particles on FA surface has allowed the formations of rough surface and larger surface areas. This increases contacting opportunities between the powders and polymer and improve the matching state between them when coated FA are blended with PP polymer. Coarseness of surface may improve interfacial coalescent between inorganic materials and polymer.

5. Conclusions

(1) After classification and purification and modification, Whiteness value of FA are enhanced a greater range from 29.8 to 66.63.

(2) The modification results in an evident change in surface morphology of FA obtaining a rough surface and high specific surface area which was increased by twice above compared with the uncoated FA. This increases contacting opportunities between coated FA and polymer and improve the matching state between them when they are blended with PP polymer.

Acknowledgement

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* **corresponding author:** yangyufen@mail.tsinghua.edu.cn