

Modification of surface properties of South African coal fly ash for industrial filler applications

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Abstract

Fillers are generally used in polymers and rubber to reduce their production costs and to improve certain physical characteristics of these products. The morphology and particle size of fly ash make it suitable for application as filler in polymers and rubbers, but its application is hindered by the lack of compatibility between the inorganic surface of the ash and the organic matrix of the polymer or rubber. Another concern is the agglomeration between fly ash particles, which has an adverse effect upon its application as filler. In order to meet some of the demands of the coal fly ash, polymer and rubber industries; the chemical and physical properties of the coal fly ash surface need to be chemically modified in order to add functionality to its surface, before its application as filler will be profitable.

In this study, South African coal fly ash was treated under different conditions with an anionic and cationic surfactant, with the aim to modify the surface and physical properties of the ash. Although the overall chemical composition of the SLS and CPC modified coal fly ash investigated in this study was not altered extensively, significant changes could be observed in its physical properties.

Surface and physical properties of the untreated and treated fly ash were studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) in order to determine the extent of interaction between the SLS and fly ash surface. Fourier Transform Infrared spectroscopy (FT-IR) was used to establish if any changes on the fly ash surface has occurred due to the various treatments. .

Keywords: coal fly ash, surface modification, sodium lauryl sulphate, cetyl pyridium chloride

1 Introduction

With the growing concern about pollution and increasing landfill costs, there has been global interest in the utilization of coal fly ash. The great amounts that are not used pose significant environmental and economic threats due to the great need of environmentally safe and economically affordable ways of disposal and handling.

South Africa has a long history regarding the development of new applications for coal fly ash. The country's research and development involving fly ash includes its application into Portland cement, the recovery of alumina, soil amelioration, waste immobilization, refractories and bricks, road stabilization, zeolites, counteracting acid mine drainage, mine backfilling, processing aids and fillers for polymers and functional fillers for rubbers [1].

Recently, Ahmaruzzaman [2] and Blisset [3] published review articles on the utilization of coal fly ash. In these papers, the current and potential applications of coal fly ash, including its utilization in cement and concrete, as adsorbent for the removal of organic compounds, in waste water treatment, light weight aggregates, zeolite synthesis, catalysts, ceramics and glass, agriculture, metal recovery, mine back fill, road construction and CFA separation technologies are discussed. However, no reference is given to the application of fly ash as mineral filler in the polymer manufacturing industry.

Fillers are generally used in polymers and rubber to reduce their production costs and to improve certain physical characteristics of these products. The physical properties of coal fly ash make it a suitable filler for polymers. In particular, the sphericity of coal fly ash particles facilitates dispersity and fluidity within polymeric materials, while the low density and cost of fly ash adds to the list of advantages when compared to conventional fillers. However, the application of coal fly ash in these fields is not common yet. The main reasons are the lack of whiteness and lack of interaction between the fly ash and polymer or rubber, resulting in undesirable properties in the final products. Another concern is the agglomeration between fly ash particles, which has an undesirable effect upon its application as filler.

In order to meet some of the demands of the coal fly ash, polymer and rubber industries; the chemical and physical properties of the coal fly ash surface need to be chemically modified in order to add functionality to its surface, before its application as filler will be profitable. Very little work has been done in this field, and the surface properties of fly ash are little understood. Alkan [4] studied the incorporation of fly ash into polyethylene and Ma [5] studied changes in the properties of fly ash - polypropylene systems after coupling agents were added. In South Africa, fly ash is currently being used as filler in some polymers [6, 7] but its application remains limited.

Surface treatment is one of the principal methods for converting mineral or inorganic fillers into materials bearing covalently bound functional groups, capable of graft formation when used as fillers or reinforcement in rubber or polymers.

Surfactants are used in coatings for a number of reasons, some of which include emulsion polymerization, wetting and dispersion. Nath [8] have shown how the surface of fly ash can be modified by the anionic surfactant sodium lauryl sulphate (SLS), and the resulting fly ash be used in manufacture of composite films with polyvinyl alcohol (PVA). They have compared the properties of unmodified and modified fly ash using a range of analytical methods. The PVA composite films reinforced with SLS modified fly ash showed an increase in strength compared to those of unmodified fly ash filled films. The enhancement of tensile strength was attributed to increased physical bonding

between SLS–FA and PVA surfaces. Ma [5] modified silica nanoparticles by a cationic surfactant - CTAB. Optimal conditions were discussed, and the results of FT-IR, TGA and BET confirmed that there exist interactions between the cationic surfactant and anionic surface of the silica. They have shown that the agglomeration in the silica nanoparticles was reduced and that the better dispersal state of CTAB-modified silica nanoparticles will be advantageous to be used as the filler in polymeric materials.

The abovementioned studies have therefore indicated that surface modification of coal fly ash can strengthen the positive morphological properties of fly ash, by creating new functional groups on the fly ash surface that can actively interact with another matrix, for example a polymer.

In a recent study, I have reported on an initial study on the characterization of SLS modified South African coal fly ash, using the method described by Nath [9]. In that study, it was reported that although the overall chemical composition of the SLS modified coal fly ash was not altered extensively, significant changes could be observed in its physical properties. In this paper, the feasibility of altering the characteristics and surface reactivity of South African coal fly ash by both a cationic and anionic surfactant is investigated. Sodium lauryl sulphate (SLS) is again used as anionic surfactant, and the optimised results are shown here. Cetyl pyridium chloride (CPC) was used as cationic surfactant. No other references could be found where South African coal fly ash was chemically modified by surfactants.

2 Materials and coal fly ash modification

The coal fly ash utilized in this study was obtained from the Ash resources Pty Ltd Ash beneficiation site at the Lethabo Thermal Power station located at Lethabo, South Africa. This material is marketed under the name *SuperPozz*[®], and currently finds application in mainly the construction but also the rubber and polymer industries. This fly ash sample is classified, with 95% of its particles having a diameter of < 5 µm. Sodium Lauryl Sulphate (SLS) with a purity of 98% was obtained from Merck, Cetyl Pyridium Chloride (CPC) was obtained from Sigma-Aldrich.

The chemical composition of the fly ash used in this study is presented in Table 1. The composition is typical of a Class F coal fly ash, and the low loss on ignition value is an indication that the ash contains a very low percentage moisture, carbonates and hydroxides.

The qualitative and quantitative results obtained from XRD analysis are presented in Table 2. The amorphous content of the ash was determined to be 62.0 % by weight, while the major crystalline phases observed were quartz (SiO₂), mullite (Al_{4.56}Si_{1.44}O_{9.72}), and small amounts of calcite (CaCO₃) and magnetite. No significant difference was observed in the quantitative analysis of the untreated and SLS modified fly ash.

For the chemical modification experiments, 20 g of fly ash was mixed with 200 ml of a 4% (by weight) SLS or CPC solution. The fly ash-surfactant mixtures were treated in a shaking waterbath at while shaking continuously at 130 revolutions per minute for 6 hours. The reaction temperatures were 60 °C of the CPC mixture and 80 °C for the SLS mixture. The pH of the CPC mixture was kept at around 9. The pH of the SLS mixture was not controlled. Thereafter, the samples were filtered, washed and dried for 2 days at 50 °C in a laboratory oven.

3 Morphology of untreated and surface modified fly ash

To study the morphology of the untreated and treated fly ash samples, they were mounted on a double-sided carbon tape by dipping carbon stubs into the samples. Excess material was removed by gentle blowing with compressed nitrogen. The samples were then coated with gold using a Sputter-coater (Emitech K550X, Ashford, England). A JEOL JSM 840 Scanning Electron Microscope (SEM), operated at 5kV, was used to view the samples. Images were collected with the aid of a flame-grabber (Orion Version 6).

The morphologies of the untreated and a surfactant modified coal fly ash are presented in Figures 1 - 4. The studied untreated coal fly ash samples have good sphericity, but agglomeration of the glass spheres (Figure 1) might introduce problems with workability upon compaction of this type of fly ash into polymeric materials. Comparing the untreated and surfactant modified fly ash samples at similar magnification (Figures 2 - 4); it seems that the degree of agglomeration was reduced significantly in the modified samples. Distinct agglomerates were observed on the surface of both surfactant modified fly ash samples. Not all SLS and CPC modified fly ash particles were covered with agglomerates to the same degree, and it seemed that the fly ash modified by CPC were covered by much finer agglomerates than the SLS modified ash.

4 Topography of the untreated and surface modified fly ash

A JEOL JEM 2100F TEM was used to study the topography of the fly ash. The samples were dispersed in 100% ethanol with sonication. A drop of the diluted suspension was poured onto a copper grid which was then placed into the sample injection holder for analysis.

The results obtained from TEM measurements are shown in figures 5 - 7. Most of the TEM images show agglomerates on the surface of the fly ash spheres. However, there is a distinct difference between the morphology of these agglomerates on the untreated, SLS and CPC modified fly ash. The needle-like shape of the agglomerates on the SLS modified fly ash was different from that of the agglomerates observed on the CPC modified ash, which were finer and less ordered in shape. The thickness of the agglomerate layer on the SLS modified fly ash was much higher than that of the CPC modified ash, confirming the results obtained by the SEM measurements.

5 Comparison between the FT-IR results obtained for the fly ash samples

Mid-infrared spectra were recorded with a Brüker Vertex 70v Fourier transform infrared (FTIR) spectrometer, by placing the finely grounded samples in a diamond ATR (attenuated total reflection) cell. The sample chamber was evacuated to eliminate contributions from CO₂ and water vapour in the atmosphere, the resolution was 2 cm⁻¹ and 32 scans were signal-averaged in each interferogram.

The spectra of the treated samples were compared to that of the original fly ash to determine if any modification on the surface of the fly ash particles could be observed. The mid-infrared spectrum of the sample treated with SLS (the anionic surfactant) is shown in Figure 8 (b) and for comparison purposes the spectrum of pure SLS (8d) and the untreated fly ash (8a) is included in the figure.

The most prominent peaks (600-1100 cm⁻¹) in both spectra 8a and 8b are attributed to Si-O and Al-O stretch vibrations as both samples consist of 60% silica aluminium glass. The peaks are quite broad

and no evidence of other crystalline phases could be observed in the spectra as both quartz and mullite (Table 2) have peaks in the same region as the glass. In Figure 8b small sharp peaks at the exact positions of the SLS bands are clearly visible in the spectrum of the modified fly ash, which is not observed in the spectrum of the untreated fly ash (8a). In Figure 8c the spectrum of the untreated fly ash was subtracted from the SLS treated spectrum resulting in spectrum 8c, which enhances the intensity of the peaks. A closer look shows that the peaks at 1248 and 1217 cm^{-1} , assigned to S-O stretch vibrations, have shifted slightly towards lower wavenumbers, which is an indication that there might be interaction between the SLS and the fly ash surface. As the shift is quite small this could be attributed to electrostatic interaction. As the peaks in the C-H stretch region do not display a shift it points to interaction through the sulphate anion implying that the hydrocarbon chain is aligned outwards from the fly ash kernel. This is in line with the shape of the protrusions observed in the TEM photographs. It should be noted that this was not observed in all of the spectra recorded for this sample which suggests that the particles are not evenly coated with SLS, which is in accordance with the results obtained from the TEM micrographs. In some of the spectra recorded on other modified samples the same peaks were observed, but with lower intensities.

In contrast to the anionic surfactant the infrared spectra of samples treated with the cationic surfactant appeared exactly the same as the spectrum of the untreated fly ash. The technique is therefore not sensitive enough to pick up the modifications seen in the SEM and TEM micrographs.

6 Conclusions

These results indicate that surface modification of South African coal fly ash by both a cationic and anionic surfactant is feasible. The SEM results indicate good coverage of the fly ash spheres by both types of surfactants, and TEM indicate differences in the structure of the surface agglomerates.

The FTIR results of the anionic surfactant showed the presence of SLS on the samples, as well as a small shift in bands associated with S-O vibrations, which indicates an interaction through the sulphate anion. FTIR spectroscopy was not sensitive enough to detect the surface changes that took place during treatment with the cationic surfactant.

The degree of agglomeration between fly ash spheres seemed to be reduced in the surfactant modified fly ash samples. Future work will include an investigation into the stability of the surfactant agglomerates on the fly ash surface, and possible interaction of the surface modified fly ash with different types of polymers. Since the fly ash surface is reactive to both cationic and anionic surfactants, other types of surfactants will also be investigated, with the aim of enhancing interaction between the surfactant and polymer.

7 Acknowledgements

This project is supported financially by Ash Resources Pty Ltd and the South African National Research Foundation, NRF THRIP Grant number TP2009062900014. Any opinions, findings and recommendations expressed in this material are those of the authors and therefore the NRF does not accept any liability in regard thereto.

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Table 1 Chemical composition of Lethabo fly ash (Class F), as determined by XRF analysis. All values are reported as weight percentages; only major elements are reported.

Compound	Concentration
SiO ₂	49.30
TiO ₂	2.01
Al ₂ O ₃	33.97
Fe ₂ O ₃	5.78
MnO	0.05
MgO	0.99
CaO	5.06
Na ₂ O	<0.01
K ₂ O	0.87
P ₂ O ₅	0.59
Cr ₂ O ₃	0.07
NiO	0.05
V ₂ O ₅	0.04
ZrO ₂	0.08
Loss on Ignition	0.52
TOTAL	99.39

Table 2 XRD quantitative results of Lethabo fly ash

Content	Weight %
Amorphous (glass)	62.0
Mullite	31.8
Quartz	6.2

Fig. 1 Surface morphology of the untreated coal fly ash sample, showing the degree of agglomeration in the untreated ash

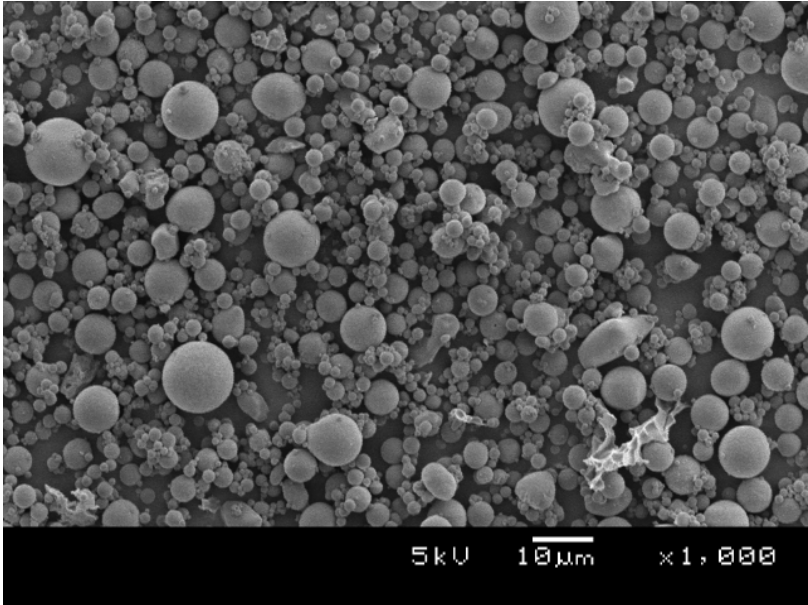


Fig. 2 Surface morphology of the untreated coal fly ash sample, at higher magnification, showing the smooth surface of the untreated ash

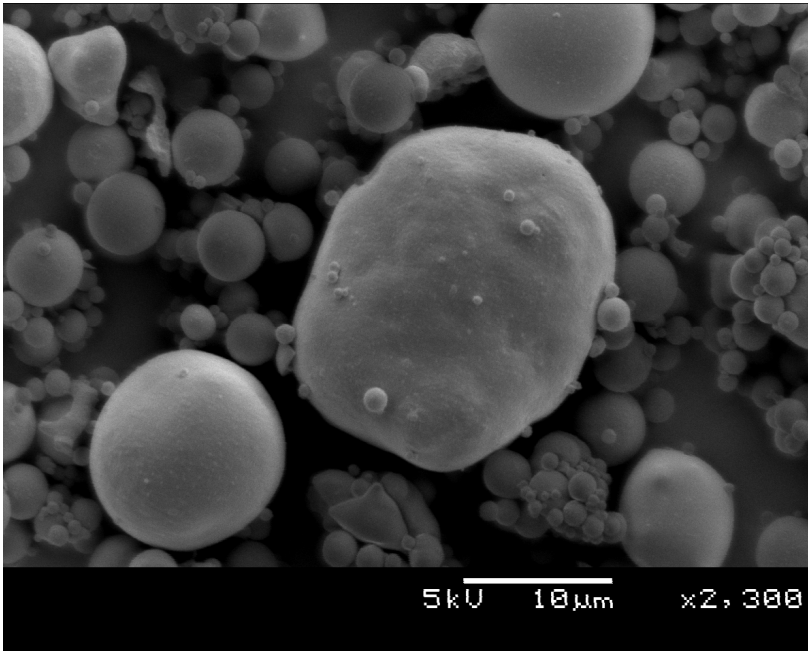


Fig. 3 SEM result of the SLS modified fly ash

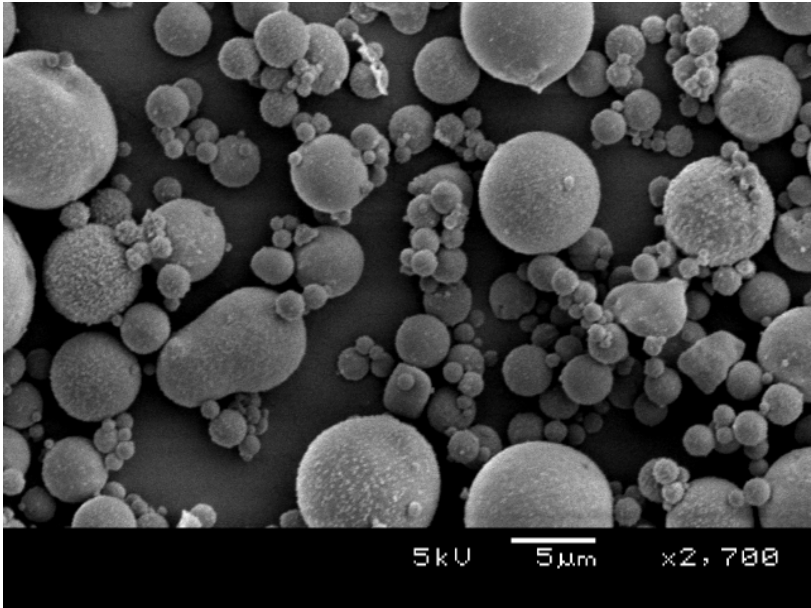


Fig. 4 SEM result of the CPC modified fly ash

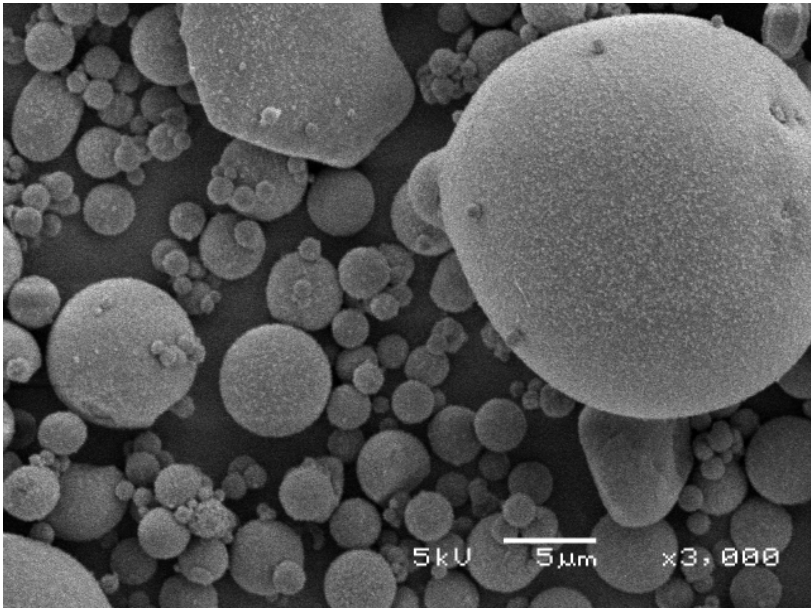


Fig. 5 Surface topography of the untreated coal fly ash sample

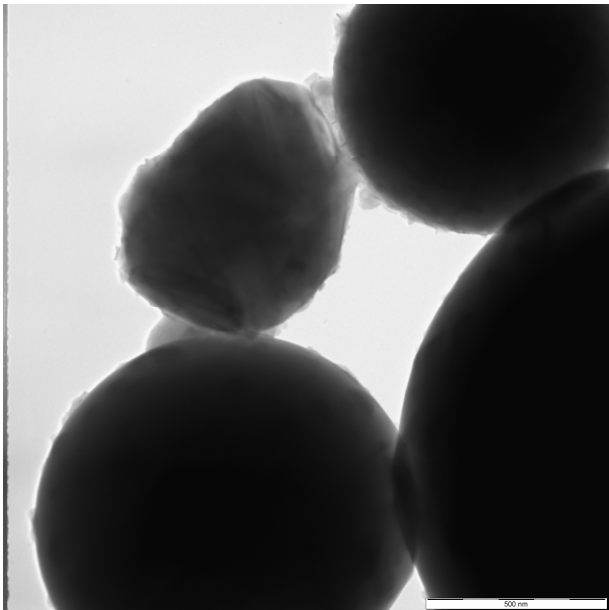


Fig. 6 TEM result of the SLS modified fly ash

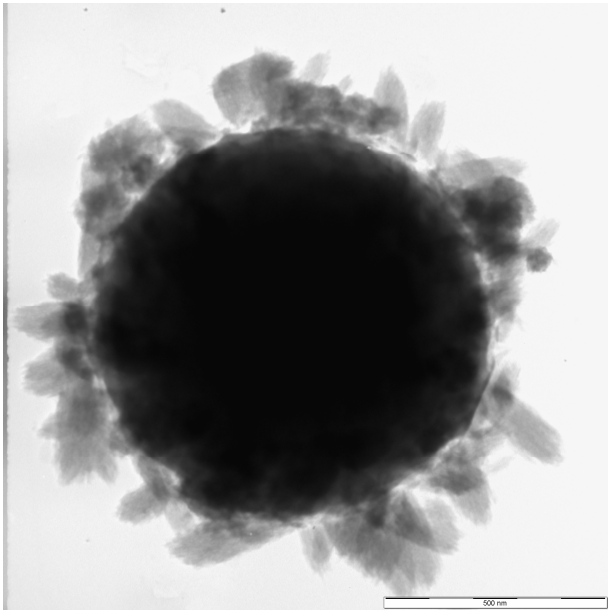


Fig. 7 TEM result of the CPC modified fly ash

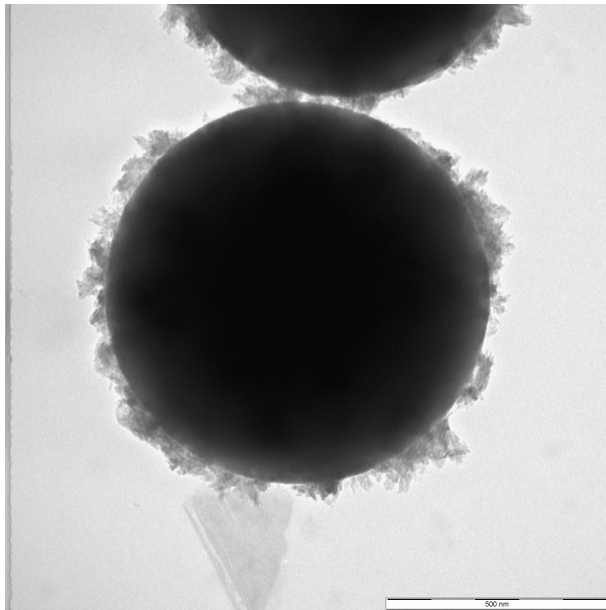


Fig. 8: (a) untreated fly ash (b) fly ash treated with SLS (c) curve b – curve a (d) pure SLS

